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The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments

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Abstract

Research over the past ten years has created a more detailed and coherent view of the relation between O_3 and its major anthropogenic precursors, volatile organic compounds (VOC) and oxides of nitrogen (NO_x). This article presents a review of insights derived from photochemical models and field measurements. The ozone–precursor relationship can be understood in terms of a fundamental split into a NO_x-senstive and VOC-sensitive (or NO_x-saturated) chemical regimes. These regimes are associated with the chemistry of odd hydrogen radicals and appear in different forms in studies of urbanized regions, power plant plumes and the remote troposphere. Factors that affect the split into NO_x-sensitive and VOC-sensitive chemistry include: VOC/NO_x ratios, VOC reactivity, biogenic hydrocarbons, photochemical aging, and rates of meteorological dispersion. Analyses of ozone–NO_x–VOC sensitivity from 3D photochemical models show a consistent pattern, but predictions for the impact of reduced NO_x and VOC in indivdual locations are often very uncertain. This uncertainty can be identified by comparing predictions from different model scenarios that reflect uncertainties in meteorology, anthropogenic and biogenic emissions. Several observation-based approaches have been proposed that seek to evaluate ozone–NO_x–VOC sensitivity directly from ambient measurements (including ambient VOC, reactive nitrogen, and peroxides). Observation-based approaches have also been used to evaluate emission rates, ozone production efficiency, and removal rates of chemically active species. Use of these methods in combination with models can significantly reduce the uncertainty associated with model predictions. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ozone; Hydrocarbons; Nitrogen oxides; Photochemical production

1. Introduction

The relation between ozone and its two main precursors, NO_x ($= NO + NO_2$) and volatile organic compounds (VOC), represents one of the major scientific challenges associated with urban air pollution. It is generally known that for some conditions the process of ozone formation is controlled almost entirely by NO_x and is largely independent of VOC, while for other conditions ozone production increases with increasing VOC and does not increase (or sometimes even decreases) with increasing NO_x. However it has been difficult to determine whether ozone production during specific events is associated with NO_x-sensitive chemistry or VOC-sensitive chemistry. Particulates and other secondary air pollutants also show a complex dependence on NO_x and VOC (Meng et al., 1997). There is also an analogous split into NO_x-sensitive and NO_x-saturated chemistry in the

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remote troposphere. The relation between ozone, NO_x and VOC is especially important as a basis for environmental policy. Ozone is a major environmental concern because of its adverse impacts on human health (Lippman, 1993; Bascomb et al., 1996) and also because of its impact on crops and forest ecosystems (NRC, 1991). Most major metropolitan areas in the US have continually violated government health standards for ozone continually since the passage of the first Clean Air Act in 1970. Throughout this period policy plans to have been developed for lowering ambient ozone and bringing cities into compliance with the law. These plans have had only modest success (Fiore et al., 1998). Elevated ozone has also been observed in Europe since the 1970s (e.g. Guicherit and van Dop, 1977) and is especially bad in Athens and other cities of southern Europe (e.g. Moussiopoulos et al., 1995; Giovannoni and Russell, 1995; Prevot et al., 1997). Elevated ozone has also been observed in urban areas in Canada, Japan, China, India and, most notably, Mexico City (MARI, 1994). Because ozone forms most rapidly in conditions with warm temperatures and sunshine, cities with warm climates (including cities in developing nations) are especially likely to experience high ozone. In each of these locations it is necessary to understand how ozone depends on NO_x and VOC in order to develop an effective policy response.

In addition to its importance for policy, the relation between ozone, NO_x and VOC is worthy of attention as a purely scientific problem. The process of ozone formation provides a case study of the interaction between nonlinear chemistry and dynamics in the earth sciences, and frequently calls for sophisticated mathematical and analytical treatment. The nonlinear ozone chemistry extends into rural and remote areas as well, where it has important implications for global photochemical equilibria in the atmosphere. Interpretation of ozone chemistry also raises questions about the use of models and the nature of scientific proof in the environmental sciences.

In recent years there have been major advances in understanding the process of ozone formation, based in part on the development and use of 3D models for atmospheric processes and in part on interpretation of field measurement campaigns. This has resulted in a more sophisticated understanding of ozone–NO_x– VOC sensitivity relative to the last major review (NRC, 1991). Sections 2 and 3 below summarize the current understanding. Section 2 presents an overview of ozone–NO_x–VOC sensitivity. Section 3 describes the pattern that has emerged from recent investigations of ozone–NO_x–VOC sensitivity, including the factors that tend to produce NO_x-sensitive and VOC-sensitive chemistry in models, geographical variations and sources of model uncertainty. These sections are also intended to provide an overview for readers whose primary expertise lies in other fields or in policy. Section 4 presents the chemistry that drives the relation between ozone, NO_x and VOC in greater detail, including the role of odd hydrogen radicals (OH, HO_2, etc.), ozone production efficiency and comparisons with the chemistry of the remote troposphere. Section 5 describes some of the recent innovative attempts to evaluate ozone–NO_x–VOC chemistry based on interpretation of field measurements rather than the more traditional model-based evaluations. This section also includes a brief overview of methods to evaluate other features of ozone chemistry (ozone production efficiency, NO_x removal rates, and emission rates) based on measurements. Although these methods have been developed and applied primarily in the US it is likely that they will be applicable to events in other locations as well.

A central theme throughout this paper is the uncertain nature of predictions concerning the response of ozone to reductions in NO_x and VOC emissions, and the difficulty of obtaining scientifically valid evidence. Most evaluations of ozone–NO_x–VOC sensitivity are based on predictions from 3D Eulerian models which contain representations of emission rates, dynamics and photochemistry. The predicted response to reduced emissions is derived by repeating the model base case with reduced NO_x or VOC. These models are useful for identifying general features of ozone–NO_x–VOC chemistry, but predictions for specific events and specific urban areas are uncertain. There is also no direct way to test whether these NO_x–VOC predictions are accurate. In recent years considerable skepticism has been expressed about the use of models as the basis for environmental policy (Oreskes et al., 1994). The viewpoint in this paper is that model predictions for ozone–NO_x–VOC sensitivity should be accepted as scientifically valid only when there is extensive measurement-based evidence to show that the specific model prediction is true. The description of observation-based methods and interpretations of field campaigns illustrate some recent approaches to this difficult task.

2. Overview of ozone–NO_x–VOC sensitivity

The central features of the relation between ozone, NO_x and VOC can be illustrated by ozone isopleth plots, a form of which is shown in Fig. 1. This plot shows the rate of ozone production (ppb h^{-1}, where ppb is parts per billion) as a function of NO_x and VOC concentrations. A more familiar form of this plot (e.g. NRC, 1991, see also Fig. 4 below) shows ozone concentrations as a function of NO_x and VOC emission rates or initial concentrations. The isopleth plot with ozone production rates is used here because it provides a representation of instantaneous ozone chemistry that would apply to a broad range of atmospheric conditions and is less dependent on (though not totally independent of) assumptions of the individual calculation.

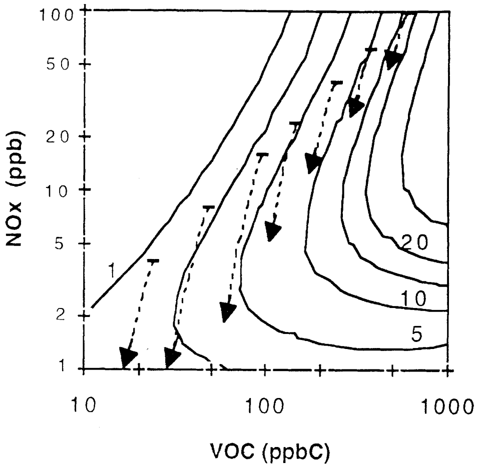

Fig. 1. Isopleths giving net rate of ozone production (ppb/h, solid lines) as a function of VOC (ppbC) and NO_x (ppb) for mean summer daytime meteorology and clear skies. The solid lines represent production rates of 1, 2.5, 5, 10, 15, 20 and 30 ppb/h. The dashed lines and arrows show the calculated evolution of VOC and NO_x concentrations in a series of air parcels over an 8 h period (9 am–5 pm), each with initial $VOC/NO_x = 6$ and speciation typical of urban centers in the US, based on calculations shown in Milford et al. (1994).

The isopleth plot shows that ozone formation is a highly nonlinear process in relation to NO_x and VOC. When NO_x is low the rate of ozone formation increases with increasing NO_x in a near-linear fashion. As NO_x increases the rate of increase in ozone formation slows and eventually reaches a local maximum. At higher NO_x concentrations the rate of ozone formation would decrease with increasing NO_x. The line representing the local maxima for the rate of ozone formation (the "ridge line") can be thought of as a dividing line separating two different photochemical regimes. In the *NO_x-sensitive* regime below the ridge line, ozone increases with increasing NO_x and shows relatively little change in response to increased VOC. In the *VOC-sensitive* (or *NO_x-saturated*) regime, ozone increases with increasing VOC and decreases with increasing NO_x. The contrast between NO_x-sensitive and VOC-sensitive regimes in Fig. 1 (see also Fig. 13) illustrates the difficulties involved in developing policies to reduce ozone in polluted regions. Ambient ozone can be reduced only by reducing emissions of its precursors, NO_x and VOC (and CO). Reductions in VOC will only be effective in reducing ozone if VOC-sensitive chemistry predominates. Reductions in NO_x will be effective only if NO_x-sensitive chemistry predominates and may actually increase ozone in VOC-sensitive regions.

The "ridge line" that divides NO_x-sensitive and VOC-sensitive regimes generally follows a line of constant VOC/NO_x ratio, with high VOC/NO_x ratios corresponding to NO_x-sensitive chemistry and low VOC/NO_x ratios corresponding to VOC-sensitive chemistry. It should be noted that the actual split between NO_x-sensitive and VOC-sensitive chemistry includes a broad transitional region rather than a sharp dividing line. There are also ambiguities associated with the definition of terms such as "NO_x-sensitive", "VOC-sensitive" and "NO_x-saturated". The divide between the two regimes is sometimes defined relative to the maxima for ozone formation as a function of NO_x and VOC, so that the NO_x-saturated regime refers specifically to conditions in which increased NO_x would result in lower O_3. This is the most broadly useful definition because it applies equally to regions in the remote troposphere and to power plants, where concepts from urban chemistry such as "VOC-sensitive" are not applicable. In the context of urban chemistry the divide is sometimes defined based on the relative impact of a given percent reduction in NO_x relative to VOC. In this definition the VOC-sensitive regime refers to situations in which a percent reduction in anthropogenic VOC would result in a significantly greater decrease in O_3 relative to the same percent reduction in NO_x. The NO_x-sensitive regime refers to situations in which a percent reduction in NO_x results in a significantly greater decrease in O_3 relative to the same percent reduction in anthropogenic VOC. This definition contains a number of ambiguities (e.g. in relation to the role of biogenic hydrocarbons or to power plants with little anthropogenic VOC) but it has a number of advantages for describing urban chemistry. In this paper the latter definition for the terms "NO_x-sensitive" and "VOC-sensitive" will be used in general, although it is recognized that the former definition and use of the term "NO_x-saturated" (rather than VOC-sensitive) is more broadly applicable to the troposphere as a whole. The term "NO_x-saturated" will be used in reference to the remote troposphere and power plant plumes where the term "VOC-sensitive" does not apply.

The isopleth plot (Fig. 1) illustrates many important features of ozone–NO_x–VOC sensitivity but it does not provide a complete understanding. The most important feature in addition to the isopleth plot is the pattern of evolution of an air mass as it moves downwind from emission sources. Typically (though not always) freshly emitted pollutants are characterized by VOC-sensitive chemistry and evolve towards NO_x-sensitive chemistry as the air mass ages. This process is illustrated by the air mass trajectories superimposed on the isopleth plot in Fig. 1 (from Milford et al., 1994). These trajectories illustrate the change in VOC and NO_x concentrations calculated for air parcels that were initialized with a fixed concentration of VOC and NO_x (with a 6 : 1 ratio) and allowed to react chemically for an 8 h period. As the air parcels age the VOC/NO_x ratios increase and the chemistry changes from the VOC-sensitive to the NO_x-sensitive regime. The speed of conversion from VOC-sensitive to NO_x-sensitive depends on how rapidly the NO_x in the air parcel reacts away. For real-world conditions this upwind–downwind pattern would be modified by the complex geography of emissions. However the split between VOC-sensitive conditions near urban centers and NO_x-sensitive conditions further downwind also appears in 3D models (Milford et al., 1989, 1994; Sillman et al., 1990). In general, NO_x emissions within an urban area determine the total amount of ozone that is formed after the air moves downwind and chemistry has run to completion, while VOC emissions control the rate of the initial buildup of O_3.

The pattern of downwind evolution is also related to a fundamental feature of ozone chemistry: the NO_x-saturated regime is associated with lack of sunlight to fuel the ozone formation process. The split between the NO_x-sensitive and NO_x-saturated regimes is related to the relative supply of NO_x (from emissions) in comparison with the supply of radicals generated by sunlight (Kleinman, 1991, 1994). In a freshly emitted plume of polluted air the initial NO_x supply greatly exceeds the supply of radicals. As the air mass ages the total amount of radicals created during the process of photochemical evolution catches up with and eventually surpasses the initial NO_x source, causing a switch from NO_x-saturated to NO_x-sensitive conditions. The chemistry of odd hydrogen radicals in connection with the ozone–NO_x–VOC system is described in detail in Section 4.

The above description of O_3–NO_x–VOC sensitivity refers only to the process of ozone production in association with NO_x and VOC emissions. There is also an important process of ozone removal associated with directly emitted NO. This process, referred to as *NO_x titration*, occurs because freshly emitted NO (typically, 90% or more of total NO_x emitted) reacts rapidly with O_3 to produce NO_2. In situations with significant ozone production (including most urban and polluted rural areas during meteorological conditions favorable to ozone formation) this removal of O_3 is small compared to the rate of ozone production. The process of NO_x titration can only remove at most one O_3 per emitted NO (up to 1.5 O_3 per NO_x at night), wheras the process of ozone formation typically produces four or more O_3 per emitted NO_x (Lin et al., 1988; Liu et al., 1987; Trainer et al., 1993; Sillman et al., 1998; see Section 4). However, the process of NO_x titration has a large impact in three situations: night time, winter and large power plants. At night there is no ozone formation and loss through NO_x titration becomes the dominant process. O_3 at night in urban centers is often lower than in the surrounding rural area for this reason. Similarly, in cold-weather climates during winter the process of ozone formation is very slow and polluted plumes can be characterized by net loss of ozone for a long distance downwind (Parrish et al., 1991).

Power plants are characterized by very large emissions of NO_x (with emissions from a single plant often exceeding total NO_x emissions in many urban centers) and very low emissions of VOC and CO. NO_x concentrations in power plant plumes are often high enough to prevent any ozone production near the plume source and to cause significant loss of ozone through NO_x titration. As shown in Fig. 2, power plants are often associated with

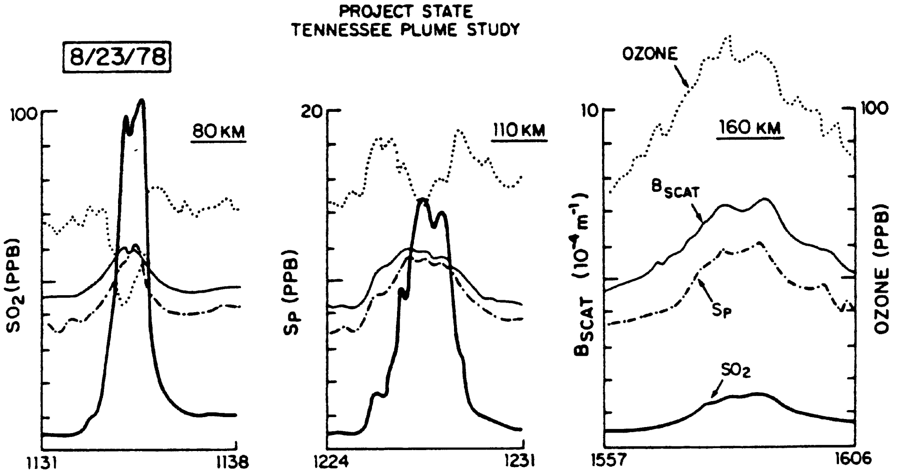

Fig. 2. Stages in the chemical development of a power plant plume. The three sets of profiles show measurements of SO_2 (surrogate for NO_x, heavy solid line), ozone (dotted line), particulate sulfur (S_p, line-dot-line), all in ppb; and the light scattering coefficient (B_{scat}, 10^{-4} m, light solid line) made during crosswind aircraft traverses through the plume of the Cumberland power plant in NW Tennessee on 23 August 1978. The traverses at 80, 110 and 160 km downwind distances illustrate the "early", the "intermediate" and the "mature" stages of chemical development of the plume, respectively. From Gillani et al. (1996).

decreased O_3 within 80 km of the plume source. As the plume moves further downwind NO_x concentrations are reduced by dilution and chemistry and production of ozone in the plume replaces the initial loss of O_3. During meteorological conditions that favor ozone formation (high sunlight and warm temperatures) ozone in the downwind plume can be higher than in the surrounding rural area by as much as 50 ppb (Miller et al., 1978; White et al., 1983; Gillani and Pleim, 1996). The early stage of a power plant plume represents an extreme case of NO_x-saturated chemistry, but the loss of ozone through NO_x titration should not be confused with the NO_x-saturated or VOC-sensitive chemistry discussed above. VOC-sensitive chemistry occurs in regions characterized by net production of ozone, and the tendency for ozone to decrease with increasing NO_x is due to the chemistry of ozone production (see Section 4) rather than to NO_x titration.

3. The relation between ozone, NO_x and VOC in photochemical models

The development and expansion of 3D Eulerian models for ozone photochemistry and transport has lead to extensive use of these models to predict the response of ozone to reductions in NO_x and VOC. These types of predictions, if accurate, are very useful for evaluating the benefits of pollution control policies. It must be emphasized that NO_x–VOC predictions for specific events are subject to large uncertainties and that all models include assumptions that can cause predictions for the relative impact of NO_x vs. VOC to be biased in one direction or another. However, model NO_x–VOC results provide an excellent basis for identifying the causal factors that distinguish NO_x-sensitive and VOC-sensitive cases. Model-based studies are especially useful for identifying the way NO_x–VOC predictions depend on model assumptions.

This section contains a summary of: (a) factors that affect model predictions for NO_x–vs.–VOC sensitivity; (b) geographical variations in NO_x–VOC sensitivity; and (c) sources of uncertainty in model NO_x–VOC predictions. Throughout this section an attempt is made to distinguish between speculative or uncertain NO_x–VOC predictions as opposed to predictions that have some level of support through interpretation of field measurements or model-measurement comparisons. Section 5 below describes methods for evaluating the accuracy of NO_x–VOC predictions.

3.1. Factors that affect NO_x–VOC sensitivity

NO_x–VOC chemistry in models is affected by five major factors: the VOC/NO_x ratio; the reactivity of the VOC mix; the role of biogenic hydrocarbons; the extent of photochemical aging; and the severity of the air pollution event. These factors are described here.

3.1.1. VOC/NO_x ratio

The impact of VOC/NO_x ratios on ozone–NO_x–VOC chemistry was first identified by Haagen-Smit (1954) as part of the earliest investigations into the ozone formation process. Since then, the impact of VOC–NO_x ratios has been demonstrated in model calculations and in smog chamber experiments (see summary in NRC, 1991). The isopleth plot (Fig. 1) discussed in the previous section illustrates this impact.

In the 1980s analyses of NO_x–VOC chemistry were frequently made with a Lagrangian model (EKMA) that calculated the evolution of a specific VOC/NO_x mixture (representing morning VOC and NO_x concentrations in an urban center) through the course of a day (see summary in NRC, 1991). Based on these analyses a simple rule was developed in which morning VOC/NO_x ratios lower than 10 were equated with VOC-sensitive peak ozone and morning VOC/NO_x ratios greater than 20 correspond to NO_x-sensitive peak ozone. This rule does not account for the impact of VOC reactivity, biogenic hydrocarbons, geographic variations or the severity of the event, all discussed later. It has also been repeatedly shown to fail in more sophisticated photochemical models (Chameides et al., 1988; Milford et al., 1989, 1994). Despite these failings, the morning VOC/NO_x rule is still used to justify NO_x–VOC predictions and policies (e.g. Hanna et al., 1996).

3.1.2. VOC reactivity

Although the impact of VOC on ozone chemistry is frequently expressed in terms of VOC/NO_x ratios, the true impact of VOC is related more closely to the reactivity of the VOC species with respect to OH rather than to the total amount of VOC. Locations with highly reactive VOC, e.g. xylenes or isoprene, are more likely to have NO_x-sensitive chemistry than locations with similar total VOC but lower reactivity. The impact of VOC reactivity is especially important with regard to biogenic hydrocarbons, which typically have relatively low ambient concentrations but high reactivity. The importance of VOC reactivity has also been highlighted by studies that show uncertainties in the emission rates of some of the more reactive anthropogenic hydrocarbons (Fujita et al., 1992). In general, model evaluations based on measured total VOC have the potential to be misleading because total VOC concentrations are dominated by relatively less reactive alkanes.

Chameides et al. (1992) developed the concept of “propylene-equivalent carbon” as a simple method for quantifying the impact of VOC reactivity. This represents a weighted sum of VOC in which each VOC species is weighted by its reaction rate with OH divided by the reaction rate of propene (i.e. so that the weighting factor for propene is one); and then multiplied by the number of carbon atoms it contains (with 0.7 for CO). The number of carbon atoms is used to approximate the impact of relatively short-lived intermediate hydrocarbons (e.g. aldehydes) that are generated following reaction of the primary VOC with OH. Carter (1994, 1995) and earlier works by Carter and Atkinson developed a more sophisticated method for estimating the contribution of individual VOC species. His method is based on incremental reactivity, defined as the relative impact of changes in individual VOC concentrations on calculated rates of ozone formation. Either of these formulations can be used to generate a reactivity-weighted sum of VOC species, which in theory should represent the impact of VOC on ozone formation more accurately than the total concentration of VOC. However it should be emphasized that no simple rule has been established that would relate reactivity-weighted VOC/NO_x ratios with predicted NO_x–VOC sensitivity. Section 5 describes recent attempts to derive a rule of this type.

3.1.3. Biogenic hydrocarbons

Biogenic hydrocarbons, emitted primarily by deciduous trees, have a major impact on ozone formation (Trainer et al., 1987; Chameides et al., 1988). Within the US emission of biogenic hydrocarbons during summer is estimated to equal or exceed the total emission of anthropogenic hydrocarbons (Lamb et al., 1985; Geron et al., 1994). Since the initial study by Chameides et al. (1988) it has been recognized that biogenic hydrocarbons, especially isoprene (C_5H_8) have a large impact on ozone formation in urban areas as well.

Two properties of biogenic hydrocarbons tend to lead to errors in interpreting their role in urban ozone chemistry. First, emission rates for isoprene shows a strong diurnal signal with zero emissions at night and maximum emissions between noon and 4 pm local time. Evaluations of ozone chemistry based on measured VOC concentrations during the morning hours do not account for the impact of biogenics (Chameides et al., 1992). As illustrated in Fig. 3 for a suburban site near Los Angeles, biogenic VOC form a negligible component of measured reactivity-weighted VOC at 8–12 am but account for 25% of reactivity-weighted VOC at 12–4 pm. Second, biogenic VOC species are extremely reactive relative to most anthropogenic VOC. Consequently the impact of biogenic VOC is large relative to their ambient concentrations. For the 12–4 pm measurements shown in Fig. 3 the average isoprene concentration was just 1.5 ppb, representing less than 1% of total VOC, but it accounts for 25% of VOC reactivity (Chameides et al., 1992).

The role of biogenic VOC deserves special emphasis because it has often been ignored or underestimated. The most recent inventories in the US (BEIS2, Geron et al., 1994) (see also Geron et al., 1995; Guenther et al., 1995) have emission rates for isoprene, the most important biogenic hydrocarbon, that are 3–5 times larger than previous estimates. Many published analyses of NO_x–VOC sensitivity are based on older inventories with underestimated biogenic emissions (e.g. Roselle and Schere, 1995) or ignore biogenic emissions entirely (Hanna et al., 1996). An underestimate of the magnitude identified by Geron et al. (1994) is likely to have a large impact on model NO_x–VOC predictions in the US. Unpublished model applications developed for the Ozone Transport Assessment Group (1996) showed that the predicted chemistry for peak ozone in most major urban areas in the eastern US would shift from VOC-sensitive to NO_x-sensitive if the older emission estimates were replaced by BEIS2. Similar results were reported by Sillman et al. (1995a) for Atlanta. Thus, the choice of biogenic emission inventories is possibly the most important science issue associated with NO_x–VOC policy in the US.

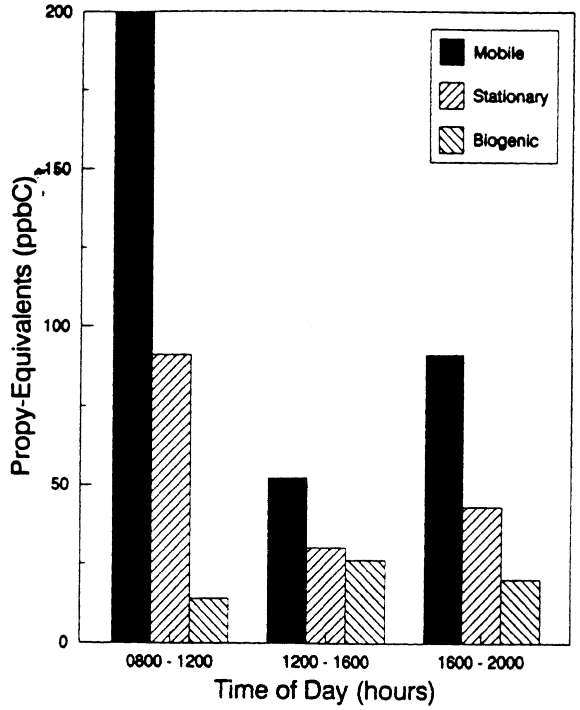

Fig. 3. Reactivity weighted as propylene equivalents (ppbC) observed at Glendora, CA (near Los Angeles) as a function of time of day and apportioned by source category. Sampling period was from 8–20 August 1986, a period of extremely high temperatures. From Chameides et al. (1992).

It is unclear whether biogenic hydrocarbons have a similar impact on NO_x–VOC chemistry in Europe. Simpson et al. (1996) reported that biogenic emissions had little impact on model NO_x–VOC predictions throughout Europe. Vogel et al. (1995) found that biogenic hydrocarbons affect ozone formation rates in Karlsruhe, Germany, although they did not analyze the impact on NO_x–VOC sensitivity. Biogenic emissions are generally smaller in Europe than in the eastern US, due in part to smaller forest cover and in part to the types of trees. The same considerations may limit the role of isoprene elsewhere. Terpenes (emitted by conifers) also tend to be relatively more important in Europe.

3.1.4. Photochemical aging

The impact of photochemical aging on VOC–NO_x chemistry is approximately equal in importance to the impact of VOC/NO_x ratios. A polluted air mass is most likely to have VOC-sensitive chemistry when it is close to its emission sources. As the air mass ages, chemistry tends to shift to NO_x-sensitive chemistry. The impact of photochemical aging was first demonstrated in peer-reviewed literature by Milford et al. (1989). Milford et al. showed that models for Los Angeles generate VOC-sensitive chemistry close to downtown and NO_x-sensitive chemistry in downwind locations. Johnson (1984, 1990) and Hess et al. (1992) showed a similar effect in smog chamber experiments. They described a situation in which the initial rate of ozone formation associated with a given VOC–NO_x mixture is controlled by VOC, but the total amount of ozone produced at the end of the aging process is controlled by NO_x. The shift between a VOC-sensitive downtown and NO_x-sensitive downwind is often accelerated by the higher rate of biogenic emissions in downwind locations.

In addition to the difference between downtown and downwind, the process of photochemical aging can create differences in predicted NO_x–VOC sensitivity between events dominated by local photochemistry in a single city and events characterized by multi-day transport. Transport events are common in regions that are characterized by a high overall emissions density and numerous cities in close proximity to each other. Multi-day transport can also be associated with "recirculation" of air within a single metropolitan area, as has been hypothesized for Los Angeles (Jacobson et al., 1996; Lu and Turco, 1996) and in Spain (Millan et al., 1996) and Israel (Tov et al., 1997). Multiday transport involves photochemically aged air which is more likely to have NO_x-sensitive chemistry. Models that evaluate NO_x–VOC sensitivity relative to region-wide VOC and NO_x reductions during multiday events with significant transport or recirculation tend to predict greater sensitivity to NO_x then models for a single city without recirculation (Sillman et al., 1990; Winner et al., 1995).

3.1.5. Severity of the event

A combination of theoretical analyses and results from photochemical models have suggested that events with higher overall concentrations of ozone precursors are more likely to have peak ozone sensitive to VOC-sensitive chemistry, while events with lower precursors are more likely to have peak ozone sensitive to NO_x. Higher precursor concentrations are associated with either higher emissions densities (i.e. larger cities) or events with more stagnant meteorology (i.e. light winds and lower daytime vertical mixing).

This effect is demonstrated by the air parcel trajectories in Fig. 1, as analyzed by Milford et al. (1994). The series of air parcels in Fig. 1 were all initiated with the same VOC/NO_x ratio and VOC speciation but with different VOC and NO_x concentrations. At the end of an 8 h calculation the air parcels with lower initial VOC and NO_x had NO_x-sensitive chemistry while the air parcels with higher initial VOC and NO_x still had VOC-sensitive chemistry. The effect can be explained using the theoretical description of NO_x-sensitive and NO_x-saturated chemistry from Kleinman (1991, 1994), discussed in the previous section. NO_x-saturated chemistry occurs so long as the NO_x source exceeds the accumulated source of radicals. When the NO_x source per unit volume is high (after accounting for dilution through daytime vertical mixing) it takes more time for the accumulated source of radicals to catch up with and surpass the NO_x source, so that NO_x-saturated conditions persist for a longer time. When the NO_x source is low then the accumulated radical source exceeds the NO_x source after a short period of photochemical aging and the situation shifts to NO_x-sensitive conditions.

Milford et al. (1994) found that a shift occurs in NO_x–VOC chemistry in box model calculations with low and high precursor concentrations even with identical VOC/NO_x emission ratios. Milford et al. also found that VOC-sensitive chemistry in 3D models can be correlated with high total reactive nitrogen (NO_y), which is indicative of high precursor concentrations. A similar finding was reported by Simpson et al. (1995). Roselle and Schere (1995) found in a 3D simulation for the eastern US that VOC-sensitive chemistry was associated both with the largest metropolitan areas (New York and Chicago) and with the most severe events. Their evaluation ranked events in each geographic region based on peak O_3 and found that events with the highest O_3 were more likely to have VOC-sensitive chemistry (Fig. 4). The studies by Milford et al. and Roselle both used older emission estimates for biogenic hydrocarbons and are therefore likely to overestimate the extent of VOC-sensitive chemistry, but the tendency towards greater sensitivity to VOC in large cities and during more severe events is likely to remain in models with corrected biogenic emissions. More recently Sistla et al. (1996) showed that wind speeds and mixing heights had a comparable effect on NO_x–VOC predictions in simulations for New York. Their scenarios with lighter winds and lower mixing heights generated higher peak O_3 and VOC-sensitive chemistry while the scenarios with more vigorous mixing generated NO_x-sensitive chemistry.

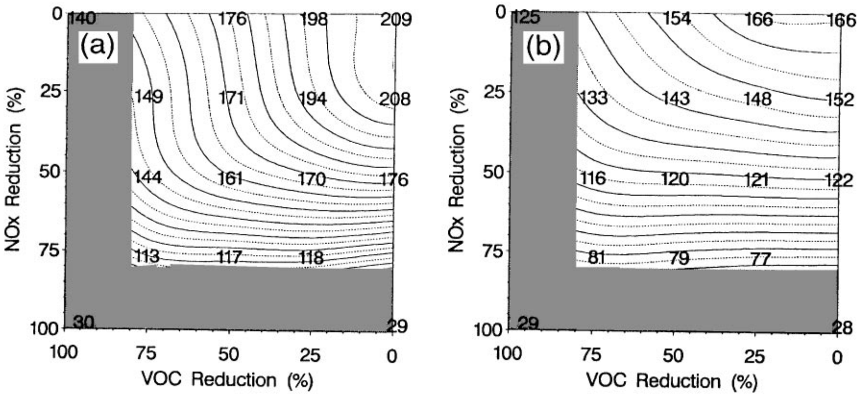

Fig. 4. Simulated response of O_3 (ppb) to reductions in VOC and NO_x emissions ranging from 0% (base case) to 100% (zero emissions) in the northeast corridor of the US on 9 July 1988. Results are shown for (a) peak O_3 and (b) 99th percentile O_3 in the region. Results for (a) show greater sensitivity to VOC for emission reductions lower than 50% and greater sensitivity to NO_x for higher emission reductions. Results for (b) show greater sensitivity to NO_x for all levels of emission reductions. From Roselle and Scbere (1995).

There is one important caveat for this effect. The results described here all refer to NO_x–VOC sensitivity associated with peak ozone during an event. They may not apply to individual locations within a metropolitan area. A. Russell (Georgia Institute of Technology, private communication, 1998) pointed out that light winds would allow air to undergo photochemical aging for a longer period of time before being advected out of a metropolitan area while strong winds would advect emissions away from a metropolitan area before there has been significant photochemical aging. This would counteract the tendency towards VOC-sensitive chemistry during stagnant events and NO_x-sensitive chemistry during events with more rapid dispersion. Future research may clarify this issue.

3.1.6. Other factors

Sunlight, cloud cover and water vapor concentration are all expected to impact NO_x–VOC chemistry. Decreasing sunlight, increased cloud cover and decreased water vapor all cause a reduction in the source of radicals Following Kleinman (1991), these can all be expected to cause a shift towards VOC-sensitive chemistry. These factors are also expected to reduce O_3. None of these factors have been studied explicitly in 3D models, but Jacob et al. (1995) (see also Hirsch et al., 1996) identified a seasonal transition between NO_x-sensitive chemistry during summer and VOC-sensitive chemistry during autumn in rural Virginia, partly associated with reduced sunlight during the autumn. This finding may be especially relevant for studies in Europe, where models have shown a greater tendency towards VOC-sensitive chemistry in northern locations (Simpson, 1995; Simpson et al., 1996). Walcek et al. (1997) and Matthijsen et al. (1997) found that aqueous chemistry significantly reduced rates of ozone formation in urban areas, but did not discuss implications for NO_x–VOC chemistry.

Temperature is expected to have no direct effect on NO_x–VOC chemistry. Lower temperatures are associated with lower O_3. Cardelino et al. (1990) and Sillman et al. (1995b) both attributed the reduced rates of ozone formation to the increased photochemical lifetime of peroxyacetyl nitrate (PAN) at lower temperatures, and PAN acts as a sink for both NO_x and radicals. Since NO_x–VOC chemistry is associated with the relative amounts of NO_x and radicals the increased rate of formation of PAN should have little impact. However lower temperature has several indirect effects on NO_x–VOC chemistry. Lower temperature usually coincides with decreased sunlight, decreased water vapor and sharply lower biogenic emissions, all of which favor VOC-sensitive chemistry.

A final NO_x–VOC factor relates to the definitions used to identify NO_x- and VOC-sensitive conditions. The above discussion presumes that NO_x- and VOC-sensitive chemistry is defined based on model responses to moderate reductions (25–50%) in VOC and NO_x concentrations; so that VOC-sensitive chemistry occurs when a 25 or 50% reduction in VOC is more effective in reducing O_3 than a corresponding percent reduction in NO_x. If VOC–NO_x chemistry were defined based on larger percentage reductions in VOC and NO_x, reduced NO_x is likely to be more effective relative to reduced VOC. Simulations with 100% reductions in anthropogenic VOC in the eastern US predict 80 ppb O_3, but simulations with 100% reductions in NO_x predict that ozone concentrations reduce to background values (30–40 ppb) (Roselle and Schere, 1995). In other words, ozone chemistry is always "NO_x-sensitive" when analyzed based on 100% reductions in NO_x or VOC. The impact of 100%

reductions predicted by Roselle and Schere are also consistent with observed O_3 in power plants (with high NO_x but little anthropogenic VOC) in contrast to sites in Brazil (with high biogenic VOC but little NO_x, e.g. Chameides et al., 1992). Alternately, VOC–NO_x analyses based on very small percent decreases or on percent increases in NO_x and VOC emissions are more likely to show VOC-sensitive chemistry then the definition used here (see Fig. 4).

3.2. Geographical variation in NO_x–VOC chemistry

Results from Roselle and Schere (1995) and other 3D models (Sillman et al., 1990, 1993; Milford et al., 1989, 1994; McKeen et al., 1991, Simpson et al., 1996) have generated the following picture of the geography of NO_x–VOC chemistry.

Rural areas appear to be predominantly NO_x-sensitive. Ozone formation in rural areas of the eastern US has been studied in great detail, including both model and measurement-based studies (Trainer et al., 1987, 1993; Sillman et al., 1990, 1993; McKeen et al., 1991; Jacob et al., 1993, 1995; Kleinman et al., 1994; Olszyna et al., 1994; Buhr et al., 1995; Roselle and Schere, 1995). It has long been recognized that elevated ozone in eastern North America and western Europe frequently extends over 500 km or more (e.g. Vukovich et al., 1977; Samson and Ragland, 1977; Guicherit and van Dop, 1977; Logan, 1989). These regional events are characterized by near-uniform high ozone (80–100 ppb) in rural locations and intermittent higher ozone associated with urban plumes. The uniform nature of elevated ozone concentrations during these events and their role in regional transport was demonstrated in aircraft measurements by Clark and Ching (1983). This type of regional ozone results from a mixture of widely distributed small emission sources and urban and power plant plumes that have been aged for more than 24 h (Sillman et al., 1990). Multiday transport during these events also contributes significantly to elevated ozone in cities within the region. Similar events have been studied in Europe (e.g. Guicherit and van Dop, 1977; Vogel et al., 1995; Simpson et al., 1996).

Studies of this type of background rural ozone have almost always found evidence of NO_x-sensitive chemistry, but there are some exceptions. Jacob et al. (1995) reported a seasonal transition between NO_x-sensitive conditions during summer and VOC-sensitive conditions in autumn. VOC-sensitive chemistry is also possible in rural locations that are directly impacted by large urban plumes (e.g. Sillman et al., 1993; Hanna et al., 1996), and NO_x-saturated chemistry occurs in the early stages of power plant plumes. Results from Simpson et al. (1996) suggest that rural areas in densely populated parts of northern Europe may have VOC-sensitive chemistry, although Simpson et al. (1995) and others (e.g. Dommen et al., 1996, 1998; Prevot et al., 1997; Kuebler et al., 1996) found evidence of NO_x-sensitive rural chemistry elsewhere in Europe.

VOC-sensitive chemistry is most likely to occur in central locations in large cities. Urban chemistry has been studied most extensively in the city of Los Angeles, including model-based studies (Milford et al., 1989; Harley et al., 1993; Kumar et al., 1994, 1996; Winner et al., 1995; Reynolds et al., 1996; Jacobson et al., 1996; Lu and Turco, 1996), field measurements (Lawson, 1990; Drummond et al., 1989; Williams and Grosjean, 1990; Sakugawa and Kaplan, 1989; Sillman et al., 1997) and evaluation of emission inventories (Fujita et al., 1992). These studies have found strong evidence for VOC-sensitive chemistry in downtown Los Angeles and possibly in much of the metropolitan region. NO_x-sensitive chemistry is possible in outlying regions (Milford et al., 1989). Even in Los Angeles there is significant uncertainty based on the possibility of "recirculation" of air exported from Los Angeles back into the city center on subsequent days, as a result of the complex ocean and mountain circulation in the region (Jacobson et al., 1996; Lu and Turco, 1996). The impact of recirculation on NO_x–VOC chemistry has not been reported, but transported air is more likely to have NO_x-sensitive chemistry (Winner et al., 1995). Nonetheless, most evidence suggests that the urban center in Los Angeles has VOC-sensitive chemistry. VOC-sensitive chemistry has also been reported in urban centers in New York (Sistla et al., 1996), Chicago (Hanna et al., 1996) and Milan (Prevot et al., 1996), although the evidence is less clear than in Los Angeles. In each of these cases it may also be possible to find NO_x-sensitive chemistry at downwind locations (e.g. Sillman et al., 1993; Prevot et al., 1996).

This split between NO_x-sensitive rural areas and VOC-sensitive urban centers has inspired an unofficial debate on policy. Advocates of VOC controls emphasize the impact of VOC in locations with the highest population density. Advocates of NO_x controls, including environmental groups, emphasize the fact that VOC controls have little impact on the eventual total ozone produced, but merely delay the process of ozone formation until the air has moved further downwind. Evaluations of ozone policy that weigh impacts based on population exposure are more likely to favor VOC controls. By contrast, evaluations that include the impact of ozone concentrations at levels below the current US ambient standard (125 ppb), possibly including the recently proposed switch from a 1 h to an 8 h standard, are more likely to favor NO_x controls.

The highest ozone concentrations are typically found in urban plumes as they move downwind of the city center. Peak O_3 usually occurs 50–100 km from the city center but in some instances the peak occurs much further downwind, especially in coastal environments (e.g. Maine, Lake Michigan). Peak O_3 often represents an intermediate point, both geographically and chemically, between VOC-sensitive urban centers and NO_x-sensitive rural areas. Peak O_3 is also associated with the greatest uncertainties in NO_x–VOC predictions. It is frequently possible to generate both NO_x-sensitive and VOC-sensitive model scenarios for these locations by making reasonable variations in model assumptions (e.g. Sillman et al., 1995a; Reynolds et al., 1996) (see Section 3.3). Model predictions for NO_x–VOC chemistry associated with peak ozone are the most important results in terms of policy, but they are also the results that should be viewed with the greatest skepticism.

3.3. Uncertainties in photochemical models

This paper has repeatedly emphasized the uncertain nature of model VOC–NO_x predictions. Sources of uncertainty will be summarized here.

3.3.1. Emission rates

Emission rates are probably the largest source of uncertainty in NO_x–VOC predictions. The uncertainty associated with emission of biogenic hydrocarbons and its impact on NO_x–VOC chemistry has already been discussed. Similar uncertainties are associated with emission inventories for anthropogenic VOC. Fujita et al. (1992) identified possible underestimates in anthropogenic VOC inventories of a factor of two or more, associated with auto emissions, in southern California. Evaluations of photochemical models tend to confirm this (Harley et al., 1993; Jacobson et al., 1996; Lu and Turco, 1996; Sillman et al., 1997). Fujita et al. (1992) also found underestimates in the reactivity of the anthropogenic VOC mix. By contrast, recent studies in Atlanta (Cardelino et al., 1994) and Baltimore (Pierson et al., 1996) found no evidence of underestimated VOC emissions. NO_x emissions are generally regarded as more accurate than VOC emissions. These estimates of uncertainty associated with emissions apply only to the US.

3.3.2. Meteorology

Meteorology especially wind speed is frequently the largest source of uncertainty in individual model applications. Most modelers are familiar with model applications with large underestimates or overestimates in ozone concentrations, with errors in the location of the ozone peak, both of which are attributed to errors in wind speed. High-ozone events are frequently associated with very low wind speeds (<2 m/s). In these situations the uncertainty in wind speeds is frequently has the same magnitude as the wind speed itself (Kumar and Russell, 1996; Sistla et al., 1996; Al-Wali et al., 1996). Uncertainties are generated by imprecision in measurements, the stochastic nature of wind and the need for interpolation based on measurements separated by 200 km or more, especially in prognostic models. Uncertainties in the height of the convective mixed layer (Marsik et al., 1995) also contribute to errors in model ozone.

It is important to recognize that uncertainties in emission rates and in wind speed have very different impacts on model performance. Uncertain emission rates (especially VOC/NO_x ratios, VOC reactivity and biogenics) have a direct impact on model NO_x–VOC chemistry but may have less impact on model ozone concentrations. By contrast, uncertainties in wind speeds or mixing heights have a direct impact on ozone formation but only a secondary impact on NO_x–VOC chemistry. Thus, model performance evaluations based on measured ozone do not provide evidence for the accuracy of model VOC–NO_x predictions.

3.3.3. Chemistry

Chemistry as a source of uncertainty was analyzed by Gao et al. (1996). Gao found that known uncertainties in reaction rates and stoichiometries caused a 20% uncertainty in simulated concentrations of ozone and most other species (40% for H_2O_2). Gao et al. (1996) did not report impacts of uncertain chemistry on NO_x–VOC predictions.

3.3.4. Evaluating the uncertainties

Few studies have attempted to derive a quantitative estimate for the uncertainty associated with model predictions for the impact of reduced NO_x and VOC on ozone. Sillman et al. (1995a) examined the impact of changed model assumptions on NO_x–VOC predictions in Atlanta. They found that the size of the reduction in peak O_3 resulting from reduced VOC varied by a factor of two or more in model scenarios with 25% changes in anthropogenic emissions, wind speeds and mixing heights (see Fig. 5, results for 10 August 1990). Even

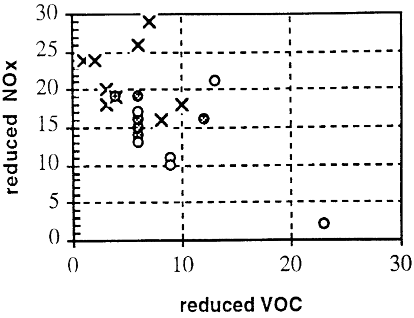

Fig. 5. Predicted reduction in peak O_3 (ppb) resulting from either a 35% reduction in anthropogenic VOC or a 35% reduction in NO_x, from different model scenarios for Atlanta. The closed and open circles represent scenarios for 8 October 1992. Closed circles represented scenarios that were in agreement with measured O_3/NO_y; open circles represented scenarios that differed from measured O_3/NO_y. The X's represent scenarios for 8 November 92.

larger changes were found if uncertainties associated with biogenic VOC were included. The size of the reduction in peak O_3 resulting from reduced NO_x varied by up to a factor of ten. Uncertainties in model NO_x–VOC predictions were also reported for Los Angeles, based on uncertain emissions and transport (Winner et al., 1995), and for New York, based on model representation of vertical mixing (Sistla et al., 1996).

To some extent the format of Fig. 5 exaggerates the uncertainty associated with model NO_x–VOC predicions. The level of uncertainty is assoiated specifically with the split between NO_x-sensitive and VOC-sensitive chemistry. If models were evaluated relative to the predicted response to simultaneous reductions in both VOC and NO_x, the variation among different scenarios would have been much smaller. Uncertainties are also much smaller in models for events with strongly NO_x-sensitive or strongly VOC-sensitive chemistry. During a second event in Atlanta with strongly NO_x-sensitive chemistry (11 August 1998 in Fig. 5) the predicted reduction resulting from reduced NO_x varied by less than 30% and variations in the predicted response to reduced VOC were all small in magnitude. These results demonstrate central importance of the NO_x–VOC split as a source of uncertainty. The biggest concern associated with model performance is the possibility of bias in predictions for the impact of NO_x vs. VOC.

The uncertainty in model predictions can also be greatly reduced if model predictions are evaluated based on comparisons with ambient measurements for species other than ozone. In the Atlanta event shown in Fig. 5, it was possible to reject several model scenarios based on discrepancies between model and measured reactive nitrogen. If the rejected scenarios were excluded, then the uncertainty in predicted reductions in peak O_3 among the remaining model scenarios would be $\pm 30\%$. Observation-based methods for determining O_3–NO_x–VOC sensitivity and evaluating model predictions will be discussed further in Section 5.

4. Chemistry of ozone, NO_x and VOC

This section describes the chemical factors that create the split between NO_x-sensitive and VOC-sensitive regimes for ozone, which were presented in general terms in Section 2. It also presents urban NO_x–VOC chemistry in a broader context, linked to photochemical processes in the remote troposphere. Several common analytical terms (odd hydrogen radicals, odd oxygen, and ozone production efficiency) are also presented and defined here.

Ozone is produced directly by photolysis of NO_2

$$NO_2 + h\nu \rightarrow NO + O \qquad (R1)$$

where the oxygen atom (O) rapidly recombines with molecular oxygen (O_2) to produce ozone (O_3). Normally, this reaction is counterbalanced by the reaction of NO with ozone:

$$NO + O_3 \rightarrow NO_2. \qquad (R2)$$

Taken together, reactions (R1) and (R2) produce no net change in ozone. Each of these reactions occurs rapidly, on a time scale of 200 s or less. Typically, the two major components of NO_x (NO and NO_2) adjust to establish a near-steady state between reacions (R1) and (R2). However there are two distinct situations in which these reactions result in a net change in ozone concentration: removal of ozone via reaction (R2) at nighttime or in the vicinity of large NO_x sources (sometimes referred to as NO_x titration) and ozone production associated with daytime NO_x–VOC–CO chemistry. Removal of ozone occurs when $O_3 + NO \rightarrow NO_2$ (i.e. reaction (R2)) dominates over $NO_2 + h\nu \rightarrow NO + O$ (i.e. reacton (R1)). There is always net removal of ozone at nighttime since photolysis rates are zero. Surface O_3 is normally low at night (<30 ppb) and high NO emissions are associated with lowest nighttime O_3. During the daytime significant removal of ozone via reaction (R2) occurs in the vicinity of large NO emission sources, especially large point sources. In these situations ambient NO_x concentrations reach 50 ppb or higher, equal to or greater than ambient O_3. Since ambient NO_x originates mostly from emission of NO, the rapid interconversion of O_3, NO and NO_2 via reactions (R1) and (R2) results in a photochemical equilibrium with significant loss of O_3. This process, sometimes referred to as NO_x titration, results in reduced O_3 in the vicinity of large emission sources of NO, especially in power plant plumes. Analyses of ozone chemistry often use the concept of odd oxygen, $O_x = O_3 + O + NO_2$ (Logan et al., 1981) as a way to separate the process of NO_x titration from the processes of ozone formation and removal that occur on longer time scales. Odd oxygen is unaffected by reactions (R1) and (R2) and remains constant in situations dominated by NO_x titration, such as the early states of a power plant plume. Production of odd oxygen occurs only through NO_x–VOC–CO chemistry, and loss of odd oxygen occurs through conversion of NO_2 to PAN and HNO_3 or through slower ozone loss reactions (e.g. reaction (R7) below), rather than through the more rapid back-and-forth reactions (R1) and (R2). The chemical lifetime of odd oxygen relative to these losses is typically 2–3 d in the lower troposphere. This lifetime is often more useful for describing atmospheric processes associated with ozone then the chemical lifetime of ozone relative to reaction (R2).

The chemical process of ozone formation occurs through reaction sequences involving VOC, CO and NO_x, which result in the conversion of NO to NO_2 through processes other than reaction (R2). The NO-to-NO_2 conversion is followed by $NO_2 + h\nu \rightarrow NO + O$ (i.e. reaction (R1)) and results in additional O_3. These reaction sequences are almost always initiated by reactions of hydrocarbons (RH) or CO with OH:

$$\mathrm{RH} + \mathrm{OH} \xrightarrow{[\mathrm{O_2}]} \mathrm{RO_2} + \mathrm{H_2O}, \quad (\mathrm{R3})$$

$$\mathrm{CO} + \mathrm{OH} \xrightarrow{[\mathrm{O_2}]} \mathrm{HO_2} + \mathrm{CO_2}, \quad (\mathrm{R4})$$

followed by reactions of RO_2 and HO_2 radicals with NO

$$\mathrm{RO_2} + \mathrm{NO} \xrightarrow{[\mathrm{O_2}]} \mathrm{R'CHO} + \mathrm{HO_2} + \mathrm{NO_2}, \quad (\mathrm{R5})$$

$$\mathrm{HO_2} + \mathrm{NO} \xrightarrow{[\mathrm{O_2}]} \mathrm{OH} + \mathrm{NO_2}. \quad (\mathrm{R6})$$

Reactions (R5) and (R6) convert NO to NO_2 and result in the formation of ozone when followed by reaction (R2). R′CHO represents intermediate organic species, typically including aldehydes and ketones. The directly emitted hydrocarbons and intermediate organics are collectively referred to as volatile organic compounds (VOC). Since these reactions also affect the ratio NO_2/NO, measured values of this ratio can be used (especially in the remote troposphere) to identify the process of ozone formation. When the ratio NO_2/NO is higher than it would be if determined solely by reactions (R1) and (R2), it provides evidence for ozone formation (e.g. Ridley et al., 1992). Reactions (R1), (R2), (R5) and (R6) can be combined to derive the summed concentration of HO_2 and RO_2 radicals from measured O_3, NO, NO_2 and solar radiation (e.g. Duderstadt et al., 1998).

For $NO_x > 0.5$ ppb (typical of urban and polluted rural sites in the eastern US and Europe) reactions (R5) and (R6) represent the dominant reaction pathways for HO_2 and RO_2 radicals. In this case the rate of ozone production is controlled by the availability of odd hydrogen radicals (defined by Kleinman (1986) as the sum of OH, HO_2 and RO_2) and in particular by the OH radical in connection with the rate-limiting reactions with CO and hydrocarbons reactions (R3) and (R4). The split into NO_x-sensitive and VOC-sensitive regimes is closely associated with sources and sinks of radicals.

Odd hydrogen radicals are produced by photolysis of ozone, formaldehyde and other intermediate organics:

$$\mathrm{O_3} + h\nu \xrightarrow{[\mathrm{H_2O}]} 2\mathrm{OH}, \quad (\mathrm{R7})$$

$$\mathrm{HCHO} + h\nu \xrightarrow{[\mathrm{O_2}]} \mathrm{HO_2} + \mathrm{CO}. \quad (\mathrm{R8})$$

They are removed by reactions that produce peroxides and nitric acid:

$$\mathrm{HO_2} + \mathrm{HO_2} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2}, \quad (\mathrm{R9})$$

$$\mathrm{RO_2} + \mathrm{HO_2} \rightarrow \mathrm{ROOH} + \mathrm{O_2}, \quad (\mathrm{R10})$$

$$\mathrm{OH} + \mathrm{NO_2} \rightarrow \mathrm{HNO_3}. \quad (\mathrm{R11})$$

Formation of peroxyacetyl nitrate (PAN) is also a significant sink for odd hydrogen. The split into NO_x-sensitive and VOC-sensitive regimes is determined by the size of the peroxide- and nitric-acid-forming reactions (Sillman et al., 1990; Kleinman, 1991). When nitric acid represents the dominant sink for odd hydrogen, then the concentration of OH is determined by the equilibrium between reactions (R7) and (R11). In this case OH decreases with increasing NO_x and either remains constant or increases (due to the impact of reaction (R8) with increasing VOC. The rate of ozone formation is controlled by the hydrocarbon–OH reactions (R5) and increases with increasing VOC and decreases with increasing NO_x. This is the VOC-sensitive regime. When peroxides represent the dominant sink for odd hydrogen, then the sum $HO_2 + RO_2$ is relatively insensitive to changes in NO_x or VOC. The rate of ozone formation, approximately equal to the rate of reactions (R5) and (R6), increases with increasing NO_x and is largely unaffected by VOC. This is the NO_x-sensitive regime. These patterns can be seen in Figs. 6 and 7, which show OH and $HO_2 + RO_2$ as a function of NO_x and VOC for conditions corresponding to the isopleths in Fig. 1. The "ridge line" in Fig. 1 that separates NO_x-sensitive and VOC-sensitive chemistry corresponds to high OH, while $HO_2 + RO_2$ is highest in the region corresponding to NO_x-sensitive chemistry. OH is lowest for conditions with either very high NO_x (due to removal of OH through formation of nitric acid, reaction R5) or very low NO_x (due to the slow rate of conversion from HO_2 to OH through reaction (R6)).

Fig. 8 shows the ratio of the rate of formation of peroxides (reactions (R5) and (R6)) divided by the rate of

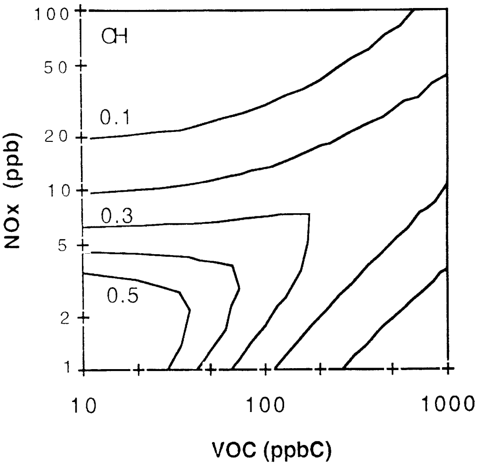

Fig. 6. Isopleths showing the concentration of OH (ppt) as a function of VOC (ppbC) and NO_x (ppb) for mean summer daytime meteorology and clear skies, based on 0D calculations shown in Milford et al. (1994) and in Fig. 1. The isopleths represent 0.1, 0.2, 0.3, 0.4 and 0.5 ppt.

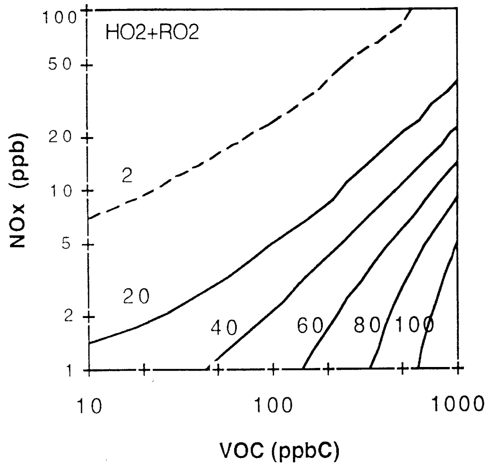

Fig. 7. Isopleths showing the concentration of $HO_2 + RO_2$ (ppt) as a function of VOC (ppbC) and NO_x (ppb) for mean summer daytime meteorology and clear skies, based on 0D calculations shown in Milford et al. (1994) and in Fig. 1. The isopleths represent 2 ppt (dashed line) and 20, 40, 60, 80 and 100 ppt (solid lines).

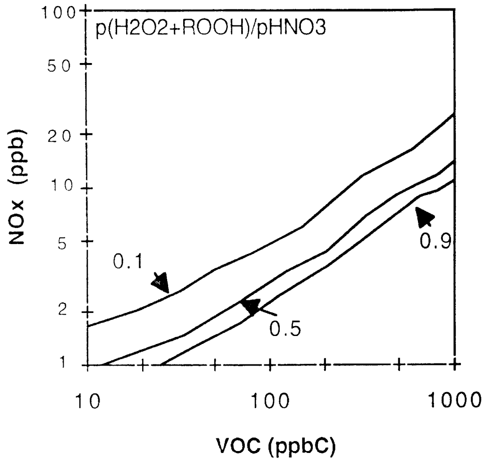

Fig. 8. Isopleths showing the rate of production of peroxides (including H_2O_2 and organics) divided by the rate of production of HNO_3 as a function of VOC (ppbC) and NO_x (ppb) for mean summer daytime meteorology and clear skies, based on 0D calculations shown in Milford et al. (1994) and in Fig. 1. The isopleths represent ratios of 0.1, 0.5 and 0.9.

formation of HNO_3 (based on Kleinman et al., 1997; Sillman et al., 1990). A comparison with Fig. 1 shows that this ratio is closely associated with the split between NO_x- and VOC-sensitive regimes. The ratio is typically 0.9 or higher for NO_x-sensitive conditions, where peroxides dominate over HNO_3 as a sink for odd hydrogen, and 0.1 or less for VOC-sensitive conditions, where HNO_3. The "ridge line" that separates NO_x-sensitive and VOC-sensitive chemistry corresponds to a ratio of 0.5 (Sillman, 1995; Kleinman et al., 1997). This result provides the basis for using peroxides and nitric acid as "indicators" for NO_x–VOC chemistry, described in Section 5.

Kleinman (1991, 1994a) found that NO_x–VOC chemistry is related to the relative size of the sources of odd hydrogen radicals (from reactions (R7) and (R8)) and NO_x (determined by emissions and/or transport). If the source of radicals exceeds the source of NO_x, then peroxides become the dominant sink for odd hydrogen and NO_x-sensitive conditions apply. If the source of NO_x exceeds the source of radicals, then the supply of OH to initiate the ozone-forming reaction sequence is limited by NO_x. Nitric acid becomes the dominant sink for radicals and NO_x-saturated conditions apply. This analysis has been used in Sections 2 and 3 as a basis for understanding NO_x–VOC chemistry.

Another central concept for NO_x–VOC chemistry is the ozone production efficiency (Liu et al., 1987; Lin et al., 1988; Trainer et al., 1993). Ozone production efficiency represents the ratio of production of odd oxygen to removal of $NO_x (= P(O_3 + NO_2)/L(NO_x))$. Liu et al. (1987) and Lin et al. (1988) found that production efficiencies are highest at low NO_x concentrations, even when VOC is assumed to increase with increasing NO_x. Lin et al. (1988) also found that production efficiencies increase with VOC. In theory, ozone production efficiencies are given by the ratio between reactions (R3 + R4) and (R11), i.e. by the ratio of the sum of reactivity-weighted VOC and CO to NO_x, although they are also influenced by the rate of formation of organic nitrates. An updated analysis (Fig. 9, adapted from unpublished work by Greg Frost, NOAA Aeronomy lab) showed the same pattern but with lower values than initially reported by Liu and Lin. Ozone production efficiencies in polluted regions are likely to be even lower than shown in Fig. 9 because these calculations typically do not include removal of ozone (even though removal of NO_x is directly linked to removal of ozone through the reaction sequence (R2) followed by (R11), and also do not count net formation of PAN or nighttime formation of HNO_3 in the sum of NO_x losses. Recent studies (e.g. Sillman et al., 1998; Ryerson et al., 1998; Nunnermacker et al., 1998; Trainer et al., 1995; NARSTO review, in preparation) estimated an ozone production efficiency of 3–5 during pollution events.

The characteristics of the NO_x-saturated regime can be explained in part by the chemistry of odd hydrogen radicals and in part by the ozone production efficiency. In the NO_x-saturated regime the rate of removal of NO_x is limited by the availability of radicals, so that the rate of chemical processing of NO_x does not increase with increasing NO_x. At the same time, increased NO_x is associated with lower ozone production efficiency. These two factors in combination result in a lower rate of ozone production as NO_x increases. In the NO_x-sensitive

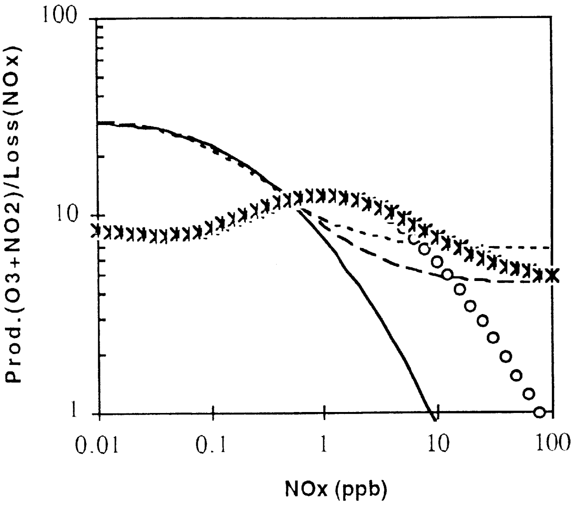

Fig. 9. Ozone production efficiency, expressed as the rate of production of odd oxygen ($O_3 + NO_2$) divided by the loss of NO_x, from steady state calculations. The calculations assume: (i) CO and CH_4 only (solid line); (ii) anthropogenic VOC with $VOC/NO_x = 10$ (dashed line); (iii) anthropogenic VOC with $VOC/NO_x = 20$ (short dashed line); (iv) CH, CH_4 and 1 ppb isoprene (circles); and (v) anthropogenic $VOC/NO_x = 10$ and 1 ppb isoprene (asterisks). Calculations use chemistry described in Sillman et al. (1998), with PAN at steady state, and are based on similar unpublished analyses by Greg Frost (NOAA Aeronomy lab).

regime an increase in NO_x concentrations is always associated with a higher absolute rate of removal of NO_x, and consequently with increased ozone production. The rate of ozone production is determined by the rate of NO_x removal and the ozone production efficiency.

Jaegle et al. (1998) has described a similar split between NO_x-sensitive and NO_x-saturated photochemical regimes in the remote troposphere. This split is associated with the relative rates of formation of peroxides and nitric acid and the relative source strength for radicals vs. NO_x, as described by Sillman and Kleinman for the polluted troposphere. The source of radicals greatly exceeds the source of NO_x for the troposphere as a whole, so that the oxidizing capacity of the troposphere is more than sufficient to process the burden of NO_x imposed by human activities. For this reason most of the troposphere is in a NO_x-sensitive rather than a NO_x-saturated state. However model calculations suggest that ozone increases with increasing VOC even in the NO_x-sensitive remote troposphere (e.g. Jaegle et al., 1998; Kanakidou et al., 1991), apparently because the reaction sequence initiated by hydrocarbons (R1) leads to greater ozone formation per OH then the reaction sequence initiated by CO (R2) which otherwise dominates in the remote troposphere. Ozone increases with increasing VOC in both the NO_x-sensitive and NO_x-saturated regimes in the remote troposphere. NO_x-saturated chemistry occurs at lower NO_x concentrations in the remote troposphere than in polluted regions (1 ppb or higher in the remote troposphere, 5–10 ppb or higher in polluted regions) because the radical source (driven by lower H_2O in reaction (R7)) is lower.

5. Observation-based methods for evaluating ozone–NO_x–VOC chemistry

Observation-based methods refer to a number of techniques that may be used to derive features of ozone–NO_x–VOC chemistry directly from ambient measurements. In recent years there has been interest in developing methods for determining the sensitivity of ozone to NO_x and VOC from measurements (e.g. Chameides et al., 1992). This interest in observation-based methods has been motivated by the high level of uncertainty associated with O_3–NO_x–VOC predictions from models, discussed in Section 3. Observation-based methods have been used more broadly in the field of atmospheric chemistry to identify important features of ozone chemistry other than O_3–NO_x–VOC sensitivity. These include observation-based estimates of emission rates, ozone production efficiency and removal rates for NO_x. This section presents a brief description of the recent attempts to develop observation-based methods.

It has occasionally been suggested that NO_x–VOC predictions from observation-based methods might be used by themselves as a replacement for model-based predictions (Chameides et al., 1992; Cardelino et al., 1995; Sillman, 1995). This use of observation-based NO_x–VOC predictions would require enormous confidence in the method and an extensive measurement network. A more realistic goal for the observation-based methods would be to provide a basis for evaluating the accuracy of model NO_x–VOC predictions. As discussed in Section 3, model NO_x–VOC predictions are often critically dependent on assumptions in the individual model scenario, and would change significantly if different assumptions were used. Observation-based methods can be used to establish limits on the uncertainty associated with model assumptions, or to evaluate the accuracy of NO_x–VOC predictions from individual model scenarios. This could significantly reduce the level of uncertainty associated with model NO_x–VOC predictions.

Models for urban ozone have always been subject to evaluation based on ambient measurements, chiefly O_3. The US EPA has recommended an extensive set of criteria for model performance vs. ambient O_3, which must be passed before the model can be used for policy-making purposes (NRC, 1991). However, measured O_3 provides little basis for confidence in model NO_x–VOC predictions. Sillman et al. (1995a) and Reynolds et al. (1996) have both shown that alternative model base cases can generate similar O_3 along with very different predictions for NO_x–VOC sensitivity. In recent years, model results have been evaluated against a more complete set of ambient measurements (e.g. Harley et al. 1993, 1995; Giovanoni and Russell, 1995; Jacobson et al., 1996), although these evaluations have been limited to a small number of cities (mostly, Los Angeles) during specific events. The observation-based approaches provide a basis for a different type of model evaluation which would be targeted specifically at the accuracy of model NO_x–VOC predictions.

Observation-based methods can be divided into two broad categories: methods based on ambient VOC, NO_x and CO; and methods based on secondary reaction products, usually involving reactive nitrogen and peroxides. These methods will be briefly reviewed here. More detailed descriptions will be included in articles associated with the current NARSTO critical review series (Sillman, 1998; Kleinman, 1998; Trainer, 1998; Cardelino, 1998).

5.1. Evaluations based on ambient VOC, NO_x and CO

Ambient VOC and NO_x probably represent the most important single factor that determines the predicted response of O_3 to reduced emissions in models. For this reason attempts to evaluate NO_x–VOC sensitivity have always emphasized the need to include measured VOC and NO_x as part of the analysis. Comparisons between model and measured VOC and NO_x have been used as part of general model evaluations and to evaluate the accuracy of emission inventories (e.g. Harley et al., 1993, 1995; Giovannoni and Russell, 1995; Jacobson et al., 1996). Chameides et al. (1992) proposed that the ratio of reactivity-weighted VOC/NO_x can be used directly to obtain information about NO_x–VOC sensitivity. Rappengluck et al. (1998) also used reactivity-weighted VOC/NO_x ratios to evaluate VOC–NO_x sensitivity in Athens.

Cardelino et al. (1995, 1998) developed a more detailed observation-based model that would calculate the dependence of ozone on NO_x and VOC based on a network of measured ambient O_3, NO_x and VOC. In this method, emission inventories are regarded as the largest source of uncertainty in VOC–NO_x predictions from Eulerian models ("emission-based models"). The observation-based model concept seeks to use ambient measurements for NO_x and VOC as a replacement for the emission inventory in a calculation of ozone chemistry. A series of 0-dimensional photochemical calculations are performed at each measurement site in which measured NO_x and VOC are used to calculate concentrations of unmeasured secondary species (intermediate VOC, PAN, etc.) and production rates for ozone. The impact of reduced VOC or NO_x emissions on ozone production is identified by repeating the calculation with assumed lower ambient concentrations of VOC or NO_x.

There are two types of problems associated with this and other attempts to calculate O_3–NO_x–VOC sensitivity directly from measured VOC and NO_x. First, measured VOC and NO_x are associated with the instantaneous rate of production of O_3 (see Fig. 1), but do not provide a basis for evaluating long-term ozone chemistry and transport. Ozone concentrations at individual locations are the result of photochemical production that has occurred over several hours (or sometimes 2–3 d) in a moving air mass. NO_x has a photochemical lifetime of 2–4 h, and some important hydrocarbons (e.g. isoprene) have an even shorter lifetime. Ambient VOC and NO_x represent immediate local conditions rather than the history of ozone production in the air mass. Chameides et al. (1992), Tonnesen and Dennis (1998) and Sillman (1998) found that the ratio of reactivity-weighted VOC to NO_x was strongly correlated with the NO_x–VOC dependence associated with instantaneous rates of ozone production. However Sillman (1998) failed to find a similar correlation between VOC/NO_x ratios and NO_x–VOC sensitivity associated with ozone concentrations in 3D models.

Because ambient VOC and NO_x are correlated with instantaneous rather than long-term ozone chemistry, attempts to use ambient VOC and NO_x to evaluate the sensitivity of ozone concentrations to NO_x and VOC often implicitly assume a specific pattern of emissions and transport history. For example, the old rule that used morning VOC/NO_x ratios to identify NO_x-sensitive vs. VOC-sensitive conditions, described in Section 3, was based on an assumed pattern of transport and diffusion of air as it left an urban center, including zero downwind emissions and zero biogenics. The method developed by Cardelino et al. is more sophisticated, but the method of aggregating the total response to reduced NO_x and VOC may be dependent on assumed patterns of transport and geography. The method has been tested against results from a 3D Eulerian model only for a single event in Atlanta.

A second problem associated with NO_x–VOC sensitivity evaluations based on ambient NO_x and VOC concerns the impact of vertical mixing and surface emissions. Measured VOC and NO_x are typically available only at sites near the ground, and measured concentrations are influenced by near-surface emissions and the rate of vertical diffusion away from the surface. By contrast, the process of ozone formation typically takes place in a convective mixed layer which extends 500 m above the surface in Los Angeles and 1000–2000 m above the surface in most continental cities in the US and Europe. During conditions associated with elevated O_3 (that is, sunny afternoons) there is typically little variation in the concentration of ozone vs. height, but primary NO_x and VOC may have significantly higher concentrations near the surface than throughout the convective mixed layer.

The variation in species concentrations with height within the convective mixed layer has been studied most

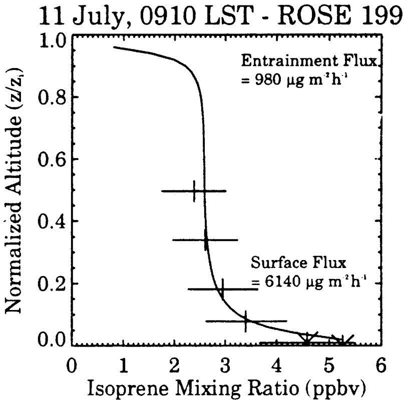

Fig. 10. Observed isoprene mixing ratio (ppb) vs. altitude (crosses and asterisks) and fitted theoretical vertical profile based on flux-gradient calculations. Error bars represent theoretical variances. Altitude (vertical axis) is expressed relative to z_i, the daytime convective mixing height, which is typically 500–2000 m. From Davis et al. (1994).

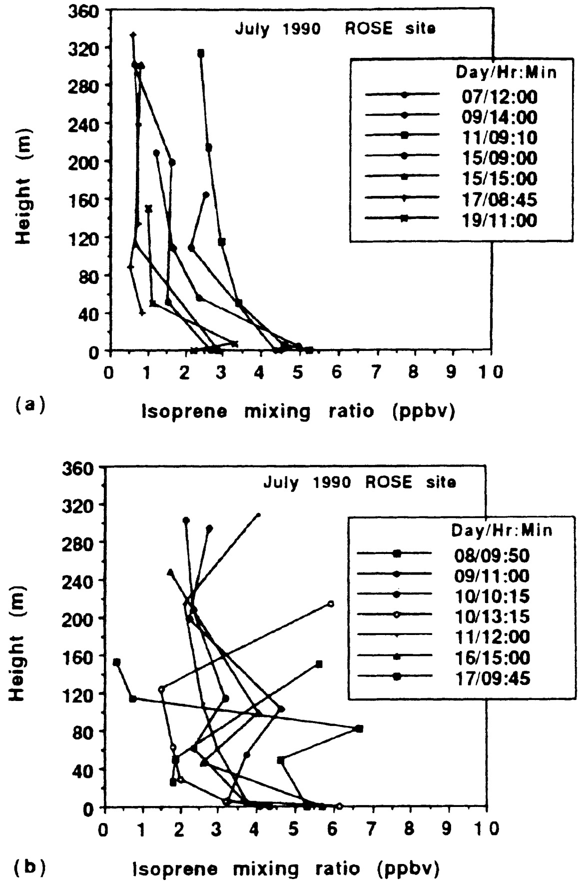

Fig. 11. Variations in the observed vertical profile of isoprene (ppb) vs. height (m): (a) profiles with relatively simple patterns, (b) more complex patterns. The times denote the hour and minute of the start of each air sampling segment. Measurements were made at Rose, AL, in July 1990. From Andronache et al. (1994).

intensely for isoprene at rural locations (Davis et al., 1994; Andronache et al., 1994; Guenther et al., 1996a, b). Davis et al. (1994) and Guenther et al. (1996a) have both found that the rate of decrease of isoprene with height during convective conditions can be approximated by using a mixed layer gradient and other mesoscale models to represent the rate of near-surface mixing (see Fig. 10). However, Andronache et al. (1994) found considerable day-to-day variation in observed vertical profiles for isoprene and also found some cases with maximum isoprene at 100 m rather than near the surface (see Fig. 11). Guenther et al. (1996a, b) report that mixed-layer average concentration for isoprene is 38–58% lower than the near-surface (0–150 m) concentration. These ratios, along with the pattern shown in Fig. 11, might be used as a basis for estimating mixed-layer average concentrations of isoprene when only surface measurements are available. Typically, mixed-layer average values must be used when ambient VOC and NO_x are used to evaluate NO_x–VOC chemistry. There have been few studies that would identify vertical profiles for anthropogenic VOC in urban areas, but Sillman et al. (1995a) reported that the xylenes vary with height in a way similar to isoprene.

Apart from the attempts to evaluate NO_x–VOC chemistry, ambient NO_x and VOC are widely used as a basis for evaluating the accuracy of emission inventories and for evaluating 3D ozone models. The most direct way to evaluate emission inventories is to compare measured NO_x and VOC with model results (e.g. Harley et al., 1993, 1995; Jacobson et al., 1996). Chang et al. (1997) also developed a series of calculations in which the emission inventory used in a 3D model were modified to obtain the closest possible agreement with ambient measurements. The method described by Chang et al. (1997) implicitly assumes that emission inventories are uncertain and derives emission rates from model analyses of ambient measurements. In all the model-measurement comparisons for VOC and NO_x, it is often uncertain whether differences between models and measurements are due to errors in the emission inventory or other factors (rates of vertical mixing, horizontal transport, impact of direct emission sources near the measurement site, etc.).

A variety of methods have been developed for evaluating emission inventories directly from measured VOC and NO_x, often based on measured ratios between species. The morning VOC/NO_x ratio in urban centers has frequently been used to evaluate emissions ratios (e.g. Fujita et al., 1992). Early morning measurements are used

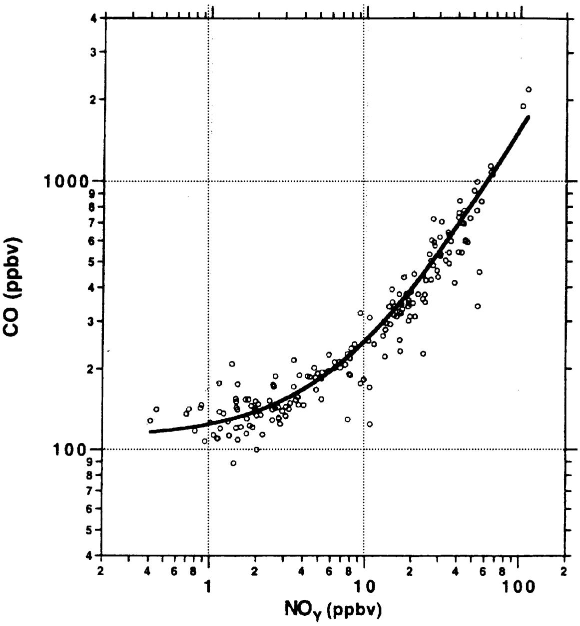

Fig. 12. Observed mixing ratio of CO vs. NO_y (both in ppb) plotted on logarithmic scales. The line represents a linear fit, $[CO] = 110 + 14.4\ NO_y$. Measurements are from February 1991 in Boulder, CO. From Goldan et al. (1995).

for this purpose because chemical losses are relatively small at that time and ambient concentrations reflect the ratio of directly emitted species. Profiles of speciated VOC have also been used along with the general techniques of chemical mass balance and receptor modeling to identify emission sources of VOC (Henry et al., 1984). Parrish et al. (1991) used ambient CO/NO_y ratios at rural sites (where NO_y represents the sum of reactive nitrogen species, including NO_x, HNO_3, PAN and other organic nitrates) as a basis for evaluating the CO/NO_x emissions ratio. Goldan et al. (1995) used CO/NO_y, speciated VOC/NO_y and VOC/VOC ratios for individual VOC species to evaluate urban emissions ratios. McKeen et al. (1996) extended the techniques for interpreting ambient VOC/VOC ratios in remote locations, accounting for photochemical losses and dilution as emission sources move downwind. Buhr et al. (1995) was able to derive information about emission inventories and NO_x–VOC sensitivity by performing a principal component analysis on a set of measured VOC, NO_x, NO_y and CO. These evaluations based on ambient species ratios (especially the comprehensive evaluation in Goldan et al., 1995) provide an excellent basis for evaluating urban emission inventories (see Fig. 12). In the case of isoprene and other biogenic hydrocarbons, Guenther et al. (1996b) also developed methods for deriving surface fluxes based on measured vertical profiles.

5.2. Evaluations based on secondary reaction products: reactive nitrogen and peroxides

Methods for evaluating ozone chemistry based on secondary reaction products fall into two broad categories: methods to evaluate the ozone production efficiency (e.g. Trainer et al., 1993) and methods to evaluate O_3–NO_x–VOC sensitivity directly (e.g. Sillman, 1995).

Trainer et al. (1993) found that in rural areas during periods of photochemical activity, a strong correlation is found between measured ozone and the sum of NO_x reaction products (NO_y–NO_x, or NO_z). Sillman et al. (1990) and Trainer et al. (1993) tried to use the positive correlation between O_3 and NO_y and between O_3 and NO_z as evidence for NO_x-sensitive chemistry. However, the main use of the O_3–NO_z correlation, proposed by Trainer et al. (1993), has been to estimate the ozone production efficiency. Because NO_z represents the sum of species produced by the removal of NO_x, the notion that ozone production efficiency is associated with the O_3–NO_z slope follows directly from the definition of ozone production efficiency (Section 4).

Since the initial work by Trainer et al. (1993) there have been extensive measurement and analysis of the correlation between O_3 and NO_z at rural sites in the US and in a few urban areas in the US and Europe (Olszyna et al., 1994; Kleinman et al., 1994; Jacob et al., 1995; Trainer et al., 1995; Daum et al., 1996; Hirsch et al., 1996; Prevot et al., 1997; Ridley et al., 1998; Staffelbach et al., 1998; Dommen et al., 1998). Slopes between O_3 and NO_z during periods of photochemical activity typically range from 5 to 10. Several authors (e.g. Chin et al., 1994; Jacob et al., 1995) expressed concern that the true ozone production efficiency is lower than the observed O_3–NO_z slope because NO_z species (chiefly HNO_3) are removed from the atmosphere more rapidly than ozone. Ridley et al. (1994, 1998), Atherton et al. (1996) and Roberts et al. (1996) also found that the O_3–NO_z slope is higher in air that is several days downwind from emission sources, presumably due to removal of NO_z as the air travels downwind. Recently Nunnermacker et al. (1998), Ryerson et al. (1998) and Sillman et al. (1998) estimated that ozone production efficiencies in the eastern US were approximately 3, significantly lower than the observed O_3–NO_z slope. Chin et al. (1994) and Hirsch et al. (1996) also derived ozone production efficiencies based on the observed slope between O_3 and CO ($\Delta O_3/\Delta CO = 0.3$), using an assumed emissions ratio for CO/NO_x. A more extensive review of this subject is found in Trainer et al. (1998).

The concept of evaluating ozone–NO_x–VOC sensitivity directly from measured reactive nitrogen and other secondary reaction products was developed by Milford et al. (1994), Sillman (1995, 1998) and Sillman et al. (1997, 1998). They found that NO_x-sensitive conditions in 3D models for ozone nearly always coincided with predicted high values for certain species ratios, and that VOC-sensitive conditions in models nearly always coincided with low values for the same ratios. They proposed that ratios with this type of behavior might be regarded as "indicators" for ozone–NO_x–VOC sensitivity. Ambient measurements of the indicator ratios would be interpreted as evidence for NO_x-sensitive or VOC-sensitive conditions if the measurements corresponded to values that were associated with NO_x-sensitive or VOC-sensitive conditions in models. The indicator ratios identified by Sillman et al. (1997) were O_3/NO_y, O_3/NO_z, H_2O_2/HNO_3, and other similar ratios involving ozone, reactive nitrogen and peroxides. The ratio H_2O_2/HNO_3 in particular is closely related to the chemical factors that create the split between NO_x-sensitive and VOC-sensitive conditions (Section 4). In contrast with VOC–NO_x ratios (Fig. 1) or with production rates of nitric acid and peroxides (Fig. 8), the proposed indicators represent relatively long-lived species (12 h or more during daytime) and are associated with the long-term process of ozone formation rather than instantaneous ozone chemistry.

The indicator concept is illustrated in Fig. 13, which shows the predicted reduction in O_3 in response to reduced NO_x and reduced anthropogenic VOC in 3D Eulerian models for the Chicago/Lake Michigan region and for the northeast corridor (New York to Boston) in the US. This figure also serves to illustrate the sharply divergent responses to reduced NO_x and VOC associated with the NO_x-sensitive and VOC-sensitive regimes. The model for Lake Michigan includes a large VOC-sensitive region in which reduced VOC would cause a large reduction in O_3, while reduced NO_x would cause either little change or an increase in O_3. The model for the northeast corridor includes a large NO_x-sensitive region in which reduced NO_x would cause a large reduction in O_3 and reduced VOC would cause little change in O_3. In both models the locations with predicted VOC-sensitive conditions also have low values (<8) for the ratio O_3/NO_z, while the locations with predicted NO_x-sensitive conditions have high values (>10) for O_3/NO_z. This result suggests that the model NO_x–VOC predictions could be confirmed if measured indicator ratios showed low values in predicted VOC-sensitive locations and high values in predicted NO_x-sensitive locations. Conversely, measured indicator ratios that contrast with model predictions (NO_x-sensitive indicator values vs. VOC-sensitive model prediction, or vice versa) would provide evidence for erroneous NO_x–VOC predictions. In contrast with Trainer et al. (1993), this interpretation is based on the ratio O_3/NO_z rather than the slope of the correlation between O_3 and NO_z.

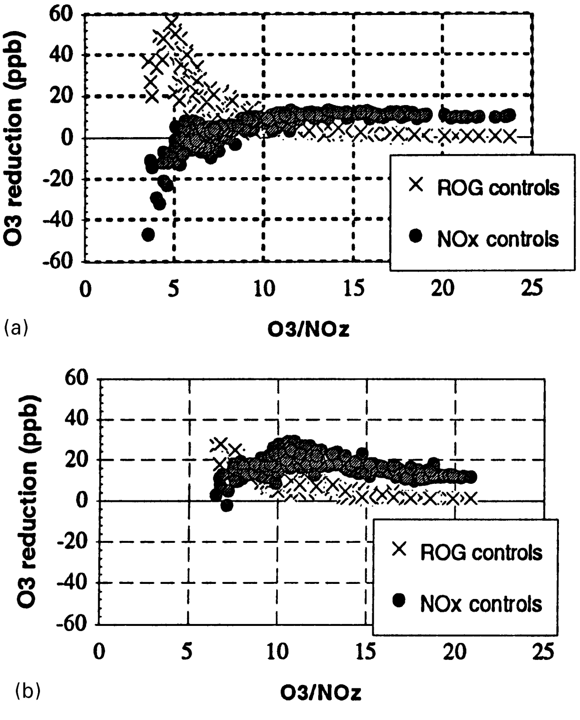

Fig. 13. Predicted reduction in peak O_3 (ppb) resulting from a 35% reduction in the emission rate for anthropogenic VOC (crosses) and from a 35% reduction in the emission rate for NO_x (circles), plotted against predicted O_3/NO_z concurrent with the ozone peak, in simulations for (a) Chicago/Lake Michigan and (b) New York/northeast corridor. From Sillman (1995) based on models described in Sillman et al. (1993).

Ambient measurements show that the proposed indicator ratios vary in a way that is consistent with the hypothesized difference between NO_x-sensitive and VOC-sensitive locations. High values for several indicator ratios were observed at rural sites in Colorado (Watkins et al., 1995) and in the eastern US (Jacob et al., 1995; Daum et al., 1996; Sillman et al., 1998) and in Atlanta (Sillman et al., 1995a, 1997), consistent with expected NO_x-sensitive conditions in those locations. Low values for the indicator ratios were observed in Los Angeles (Sillman, 1995; Sillman et al., 1997), consistent with expected VOC-sensitive conditions there. Measurements in the urban plume from Milan, Italy, showed values consistent with VOC-sensitive chemistry 1–3 h downwind of Milan, transitional or NO_x-sensitive chemistry further downwind in the Milan plume, NO_x-sensitive chemistry in the surrounding rural region (Prevot et al., 1997; Staffelbach et al., 1997). Dommen et al. (1995, 1998), (see also Kuebler et al., 1996) also found indicator values suggestive of NO_x-sensitive chemistry over most of the Swiss plateau. Jacob et al. (1995) also reported a large shift in measured values of the ratios O_3/NO_z and H_2O_2/NO_z between summer and autumn at a rural site in Virginia, consistent with a hypothesized seasonal transition from NO_x-sensitive chemistry in summer to VOC-sensitive chemistry in autumn.

In a case study for Atlanta, measured O_3 and NO_y was used as a basis for evaluating NO_x–VOC predictions from a series of model scenarios. As illustrated in Fig. 5 and discussed in Section 3, predictions for the impact of reduced NO_x and VOC in Atlanta varied greatly among model scenarios with different assumptions about emissions and meteorology. As reported in Sillman et al. (1995a, 1997), the model scenarios with predicted NO_x-sensitive chemistry showed good agreement with measured O_3 and NO_y. The scenario with predicted VOC-sensitive chemistry showed good agreement with measured O_3 but seriously underestimated the indicator ratio O_3/NO_y (measured $O_3/NO_y = 14$, model $O_3/NO_y = 6$). If the model scenarios with erroneous O_3/NO_y were rejected, the remaining model scenarios would show much less variation in their NO_x–VOC predictions. Thus, the use of measured indicator ratios has the potential to reduce the uncertainty associated with model NO_x–VOC predictions.

Deposition and other removal processes represent a major problem for the proposed NO_x–VOC indicators. The indicator ratios all involve species (HNO_3, H_2O_2) that are rapidly removed by wet deposition. They also have relatively rapid dry deposition rates and may be subject to removal through interaction with aerosols. It is possible that the indicator–NO_x–VOC correlations may change with time of day or with aging as an air mass moves downwind. The indicator ratios may also be affected by uncertain peroxide chemistry. Lu and Chang (1998) reported a case in which the correlation between NO_x–VOC predictions and indicator ratios was significantly different from the results reported by Sillman. A more complete description of these issues is presented in Sillman (1998).

Because removal of NO_y is a critical uncertainty for both the ozone production efficiency and for the NO_x–VOC indicators, several efforts have been made to estimate this removal rate. Munger et al. (1996, 1998) used eddy covariance methods to derive removal rates for NO_y from field measurements. Hall and Claiborn (1997) also measured deposition of H_2O_2. Ryerson et al. (1998) and Nunnermacker et al. (1998) both derived removal rates for NO_x by evaluating changes in the ratios CO/NO_x and SO_2/NO_x in urban and power plant plumes. In each case, increases in the ratio as the plume moved downwind was interpreted as evidence for the removal of NO_x. These methods are expected to be used and refined in future research.

The ratio $O_3/(NO_z + 2H_2O_2)$ has been proposed as a critical test for the proposed NO_x–VOC indicators. Sillman (1995) and Sillman et al. (1998) found that this ratio assumed a near-constant value ($= 6$–7) in photochemical models for conditions with high ozone (that is, sunny, warm afternoons). This ratio is related to radical chemistry, since O_3 represents the major source or radicals and NO_z and H_2O_2 represent major sinks. Unlike the proposed indicator ratios, the ratio $O_3/(NO_z + 2H_2O_2)$ does not appear to change when model conditions vary from NO_x-sensitive to VOC-sensitive. However, the ratio $O_3/(NO_z + 2H_2O_2)$ is sensitive to removal rates and peroxide chemistry, both of which represent major uncertainties for the indicator ratios. If measured values for $O_3/(NO_z + 2H_2O_2)$ differ from the model values in Sillman et al. (1998), it would suggest that the indicator ratios O_3/NO_z and H_2O_2/NO_z are affected by processes that were not accurately represented in the models used to derive the indicator interpretation, and their use would be suspect.

The relation between ozone, reactive nitrogen and peroxides is conveniently summed up in Fig. 14, which shows correlations in a polluted air mass from the eastern US as it travels over the nearby Atlantic Ocean (Daum et al., 1996). Ozone increases with NO_z throughout the air mass, but the O_3–NO_z slope decreases as O_3 and NO_z get higher. This pattern of decreasing O_3–NO_z slope appears in some but not all sets of measurements. Following Trainer et al. (1993), the O_3–NO_z slope

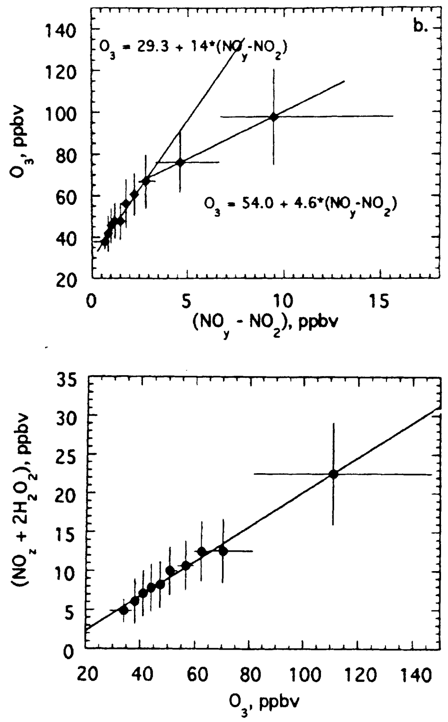

Fig. 14. Measured O_3 as a function of (NO_y–NO_2) (a, upper panel), and the sum ($NO_z + 2H_2O_2$) as a function of O_3 (b, lower panel), all in ppb. Measurements were made the North Atlantic Ocean downwind from the northeast corridor of the US. Measurements are presented as bins in which the original data set was ordered based on the abcissa and then divided into ten intervals. Horizontal bars represent the range of abcissa values; vertical bars represent the standard deviation of the variable on the vertical axis for each interval. Linear fits with slopes and intercepts were calculated from the individual data points. From Daum et al. (1996).

would be interpreted as evidence for the ozone production efficiency in the air mass. The decrease in slope might suggest that ozone production efficiency is lower in highly polluted regions. However the decrease in slope might also be caused by a higher removal rate of NO_z in the regions with lower O_3 and NO_z (presumably because these regions are further from emission sources) rather than by differences in ozone production efficiency. Following Sillman (1995), the ratios O_3/NO_z and H_2O_2/NO_z (not the O_3–NO_z slope) would be interpreted as indicators for NO_x–VOC sensitivity. In this view the split between NO_x-sensitive and VOC-sensitive regimes is caused by differences in radical chemistry (as evidenced by changes in the indicator ratios) and not by differences in the ozone production efficiency. The high O_3/NO_z and H_2O_2/NO_z in the region with lower O_3 would be indicative of NO_x-sensitive chemistry while the lower values ($O_3/NO_z = 10$, $H_2O_2/NO_z = 0.3$) in the more polluted region would suggest conditions that are closer to the transition between NO_x-sensitive and VOC-sensitive chemistry. This interpretation is also dependent on assumptions about removal rates for NO_z and H_2O_2. The linear correlation between O_3 and the sum $NO_z + 2H_2O_2$ with near-constant ratio ($= 5$) would be interpreted as evidence that the NO_x–VOC interpretation of the indicator ratios is valid in this case.

6. Conclusions

This review of ozone–NO_x–VOC sensitivity has emphasized three themes.

(1) The relation between ozone, NO_x and VOC can be understood in terms of a few theoretical concepts. These include: the split into VOC-sensitive (or NO_x-saturated) and NO_x-sensitive photochemical regimes; the evolution from VOC-sensitive to NO_x-sensitive chemistry as a plume moves downwind; the role of odd hydrogen radicals and the supply of radicals relative to NO_x; and the ozone production efficiency.

(2) Predictions for the impact of reduced NO_x and VOC on ozone derived from 3D Eulerian photochemical models have large uncertainties. The uncertainty in model predictions is associated specifically with the difference between the NO_x-sensitive and VOC-sensitive regimes, and can be quantified by comparing NO_x–VOC predictions from different model scenarios that reflect uncertainties in emission rates and meteorology.

(3) The uncertainties associated with NO_x–VOC predictions can be significantly reduced if investigations place greater emphasis on ambient measurements rather than just models. Observation-based techniques have been developed that seek to identify NO_x-sensitive or VOC-sensitive chemistry and also to evaluate emission inventories, ozone production efficiency and removal rates for chemically active species.

Measurement-based studies have traditionally received heavy emphasis as part of investigations into the chemistry of the remote troposphere and at rural sites. Rural and remote sites have been the subject of frequent measurement intensives (e.g. Hoell et al., 1996; Fehsenfeld et al., 1996) or long-term monitoring of chemically active species (e.g. Trainer et al., 1993). By contrast, investigations of urban chemistry, especially in the US, has emphasized the development and use of photochemical models. These model-based studies are often closely associated with specific issues of regulatory policy (e.g. Hanna et al., 1996). Consequently, the question of ozone–NO_x–VOC sensitivity is sometimes viewed as primarily a question of policy rather than a subject for scientific investigation. The view presented here is that model predictions for ozone–NO_x–VOC sensitivity should be regarded as scientific hypotheses, and their validity must be established by comparison with ambient measurements. These model-measurement comparisons should be designed specifically to evaluate the accuracy of model NO_x–VOC predictions or to evaluate critical model assumptions and results (e.g. emission inventories, ozone production efficiencies), and should involve species other than just O_3. They should also be combined with measurement-based investigations that are comparable to recent efforts at rural and remote sites.

Investigation of ozone–NO_x–VOC sensitivity has been given impetus by its close connection to regulatory policy, but this can also be a disadvantage. Research in this field has been influenced by political considerations to a much greater extent than normally occurs in the geophysical sciences. This review article has sought to demonstrate that the issue of ozone–NO_x–VOC chemistry can and should be addressed as a purely scientific issue, which is separate from questions of policy.

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