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Photochemical production of ozone and control strategy for Southern Taiwan

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Abstract

An observation-based method (OBM) is developed to evaluate the ozone (O_3) production efficiency (O_3 molecules produced per NO_x molecule consumed) and O_3 production rate ($P(O_3)$) during a field campaign in southern Taiwan. The method can also provide an estimate of the concentration of OH. A key step in the method is to use observed concentrations of two aromatic hydrocarbons, namely ethylbenzene and *m,p*-xylene, to estimate the degree of photochemical processing and amounts of photochemically consumed NO_x and NMHCs by OH. In addition, total oxidant ($O_3 + NO_2$) instead of O_3 itself turns out to be very useful for representing ozone production in the OBM approach. The average O_3 production efficiency during the field campaign in Fall (2003) is found to be about 10.2 ± 3.9 . The relationship of $P(O_3)$ with NO_x is examined and compared with a one-dimensional (1D) photochemical model. Values of $P(O_3)$ derived from the OBM are slightly lower than those calculated in the 1D model. However, OH concentrations estimated by the OBM are about a factor of 2 lower than the 1D model. Fresh emissions, which affect the degree of photochemical processing appear to be a major cause of the underestimate. We have developed a three-dimensional (3D) OBM O_3 production diagram that resembles the EKMA ozone isopleth diagram to study the relationship of the total oxidant versus O_3 precursors. The 3D OBM O_3 production diagram suggests that reducing emissions of NMHCs are more effective in controlling O_3 than reducing NO_x . However, significant uncertainties remain in the OBM, and considerable more work is required to minimize these uncertainties before a definitive control strategy can be reached. The observation-based approach provides a good alternative to measuring peroxy radicals for evaluating the production of O_3 and formulating O_3 control strategy in urban and suburban environments.

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1. Introduction

Increases of tropospheric ozone (O_3) are a serious environmental concern because of their adverse impacts on human health, vegetation as well as their green house effect. Elevated O_3 concentrations

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ranging from local to regional scales have been reported extensively (e.g., Lee et al., 1998; Oltmans et al., 1998; Jacob et al., 1999; Lin et al., 2000; Bronnimann et al., 2002; Akimoto, 2003; Lelieveld et al., 2004; Parrish et al., 2004; Jonson et al., 2005). For example, there is evidence of regional increase of O_3 over East Asia in the range of 7–10 ppbv from 1970s to 1980s (Lee et al., 1998). In addition, the increase in Asian continental outflows was suggested to account for an increase of O_3 in northern Pacific Ocean region (Parrish et al., 2004). Jacob et al. (1999) suggested that tripling Asian anthropogenic emissions from 1985 to 2010 would lead to an increase in monthly mean O_3 concentration by 2–6 ppbv in the western United States and by 1–3 ppbv in the eastern US. Akimoto (2003) discussed that intercontinental transport of O_3 and hemispheric O_3 pollution would jeopardize agriculture and ecosystems worldwide and have a strong effect on climate. Both studies emphasize that international initiatives to mitigate global air pollution from both developed and developing countries are necessary.

Taiwan is located in the southern part of East Asia where the background O_3 is influenced strongly by the outflow from Asian Continent in winter and spring. Taiwan itself also has had an extraordinary rapid economic development in the last few decades. Local photochemical production of O_3 due to the large emissions of precursors plays a controlling role in the O_3 distribution. According to Chou et al. (2006), the O_3 concentration over Taiwan has increased consistently in the last 13 years, while other pollutants such as SO_2 , NO_x and PM_{10} have decreased. Their analysis suggested that the reduction in the titration effect of NO played an important role in the increase of O_3 in urban areas. In addition, trends in photochemical production/loss due to changes in local emission of O_3 precursors as well as long-range transport also contribute to the trends of O_3 . The relationship between O_3 and its precursors is important but complex. It affects trends of O_3 , more importantly, it is critical to the formulation of O_3 control strategies. This work will focus on understanding the relationship between the production rate of O_3 and its precursors.

Several approaches have been suggested for estimating the O_3 production rate (Trainer et al., 2000). The most direct approach is to have measurements of concentrations of peroxy radicals, i.e. HO_2 , R_iO_2 and NO (Cantrell et al., 1996;

Mihelcic et al., 2003) and then apply the following equation to estimate gross production rate of O_3 (Levy et al., 1985; Trainer et al., 1991), i.e.

$$P_g(O_x) = [NO] \left(\bar{k}_i \sum_i [R_iO_2] + k_3 [HO_2] \right), \quad (1)$$

where $P_g(O_x)$ denotes gross O_x production rate, R_iO_2 are alkyl peroxy radicals, $\bar{k}_i$ represents the average reaction rate constant for the reactions of NO with R_iO_2 , and k_3 is the reaction rate constant for the reaction of NO with HO_2 . Other approaches estimate the peroxy radical concentration either from photo-stationary state assumption (Cantrell et al., 1993; Parrish et al., 1986) or from photochemical budget calculation (Kleinman, 1986; Kleinman et al., 2002a) and then use measured NO concentrations to derive $P_g(O_3)$. Still other approaches are based on photochemical model simulations that use the measured concentration of NO_x and VOCs to calculate the peroxy radical concentration (McKeen et al., 1997; Frost et al., 1998). It is important to note that a straightforward photochemical representation of the production terms of O_3 does not yield the simple expression in (1). To obtain Eq. (1), a “total oxidant” needs to be defined as suggested by Liu (1977) and Levy et al. (1985). There are various ways to define the total oxidant. A convenient and practical way is $O_x = O_3 + NO_2$, which is frequently used to study the O_3 chemistry in local, regional and global scales (Logan, 1989; Sillman, 1999; Jacob, 1999; Finlayson-Pitts and Pitts, 2000; Molina and Molina, 2002; Kleinman et al., 2002b). A major advantage of this definition is that its production and loss are independent of the rapid photochemical reactions, which convert O_3 to NO_2 and vice versa. Since these reactions are fast in the urban and suburban atmosphere, bypassing them enable $P_g(O_x)$ to represent the real photochemical production of O_3 better than $P_g(O_3)$.

In this study, two intensive field measurements in southern Taiwan are used in the OBM approach (Cardelino and Chameides, 2000) to estimate the production rate of O_3 . The major advantage of OBM is that it uses observations to constrain the model or the analysis, thus reducing some of the uncertainties in the model/analysis. We will also adopt the concept of O_3 production efficiency suggested by Liu et al. (1987) and Trainer et al. (1993). It will become apparent later that our OBM approach consists primarily of observation-based

analyses. The only modeling is a simple Lagrangian trajectory approach that is used to calculate photochemical oxidation rates of VOC and NO_x by OH. Results of the OBM approach will be compared with previous studies as well as those simulated by a one-dimensional (1D) photochemical model. Actually, although to a much lesser extent, the 1D model is also an OBM because its emission rates of NO_x and VOC are constrained by fitting observed concentrations of NO_x and VOC in the surface layer. Detailed description of the measurements, methodology and the model is given in Section 2.

We will show that our OBM approach can provide valuable information for formulating O_3 control strategies. It can also be used to estimate the concentration of OH. Finally, because the approach is process-oriented, it is not location sensitive and thus can be readily applied to other regions.

2. Measurements

Two intensive field experiments were conducted by the Research Center for Environmental Changes (RCEC) of Academia Sinica in the Kaohsiung-Pingtung (KaoPing) area in southern Taiwan during 26–29 September and 23–28 October 2003 (hereafter referred to as RCEC 2003 Experiment). Non-

methane hydrocarbons (NMHCs) were collected daily with stainless canisters side by side with the air quality instruments at 12 Taiwan EPA (TEPA) air quality monitoring stations (as shown in Fig. 1) in two periods, namely 9–10 and 11–12 am, during the 10-day field campaign. The measurements between 11 and 12 am were intended to examine the NMHCs composition just before the peak of O_3 , which usually occurs between 12 and 1 pm. Measurements between 9 and 10 am were designed to study the composition of NMHCs near the start of the daily photochemical cycle to get a measure of their O_3 production potential for that day. The EPA monitoring stations have routine hourly measurements of O_3 , CO, NO_x , SO_2 , PM10 and meteorological parameters. Detailed sampling strategy and geographical information can be found in Chang et al. (2005).

Southern Taiwan centered around Kaohsiung urban center is a multi-town “mega-city” spanning over $30 \text{ km} \times 50 \text{ km}$ with more than six million inhabitants. Oxidants such as O_3 and peroxyacetyl-nitrate (PAN) have become a serious environmental problem. In addition to large vehicle emissions, there are significant emission sources from four industrial parks nearby. During autumn and winter seasons when high-pressure conditions prevail, severe deteriorations of air quality with O_3 over 120 ppbv frequently occur in this region.

Fig. 1. Measurement stations of the intensive field experiments in southern Taiwan, East Asia. Solid circles represent the twelve Taiwan EPA air quality monitoring stations in Kaohsiung and Pingtung counties and the rectangles denote the four industrial parks in this region.

O₃ is measured using an ultra-violet photometric instrument with a precision of 1 ppbv. The oxides of nitrogen (NO and NO₂) are measured using a chemiluminescence instrument. The manufacturer suggested value of precision is 0.4 ppbv. However, our independent evaluation of the accuracy showed that the signal to noise level was about one at 3 ppbv for NO, significantly worse than the manufacture suggested value (Chou et al., 2006). Similar accuracy was found for NO₂. This can cause serious problem for NO measurements as NO values frequently dip below 5 ppbv during photochemically active hours. It is not a serious problem for NO₂ because its values are usually greater than 10 ppbv. On the other hands, it is well known that the catalytic converter converting NO₂ to NO suffers interference from none-NO₂ compounds such as PAN and even HNO₃. This problem will be elaborated later. A total of 56 C₂–C₁₀ non-methane hydrocarbons were analyzed by a GC/MS system. It

is estimated that species not resolved by the GC/MS system are about 30–60% of the 56 NMHCs in terms of reactivity toward OH (Chang et al., 2003). Detailed description regarding the accuracy of the GC/MS instrument can be found in Chang et al. (2003).

2.1. Meteorological conditions

Meteorological parameters observed by the Central Weather Bureau station in Kaohsiung during the RCEC 2003 Experiment are shown in Fig. 2. Generally speaking, the weather was fair during the two field experiments and there was a typical land–sea breeze with westerly to northwesterly winds in the daytime and easterly to northeasterly winds at night. The diurnal variation of wind speed was consistent with the influence of land–sea breeze. The daytime maximum temperature during the 1st periods of experiment (26–29 September 2003) was

Fig. 2. Meteorological parameters observed during the 10-day intensive field experiments. The vertical dashed line in the figure is intended for separating the two periods of experiments (26–29 September and 23–28 October 2003).

around 32 °C, and 28 °C the 2nd period (23–28 October 2003). The atmospheric moisture contents of 2nd period were lower than those of 1st period.

2.2. Air quality during RCEC 2003 experiment

Hourly time series of concentrations of O₃, NO, NO₂, CO and PM10 for three EPA stations are shown in Fig. 3. Two urban stations, i.e. Lernwu and Zhaoin are located in the Kaohsiung city, while Chaochou is a suburban station in Pingtung County. The day-to-day variations of O₃ for different stations show a similar pattern, but the primary pollutants like CO, NO and NO₂ distributions change greatly from station to station. Concentrations of NO, NO₂ and CO of Chaochou station are usually smaller than those of Lernwu

and Zhaoin because of low industrial activities and smaller population density.

2.3. Ozone production rate

As mentioned earlier the derivation of O₃ production efficiency follows the approach developed by Liu et al. (1987) and Trainer et al. (2000). The production rate of O₃, $P(O_x)$, can be expressed as

$$P(O_x) = \frac{d[O_x]}{d[NO_x]} \frac{d[NO_x]}{dt} \approx \frac{\Delta[O_x]}{\Delta[NO_x]} \frac{\Delta[NO_x]}{\Delta t} = \varepsilon \frac{\Delta[NO_x]}{\Delta t}, \quad (2)$$

where $P(O_x)$ is net O_x production, which is different from the gross O_x production $P_g(O_x)$ in Eq. (1).

Fig. 3. Hourly time series of O₃, NO, NO₂, CO and PM10 for the two experiments are shown in three different colors for three stations: Lernwu, Zhaoin and Chaochou.

The net O_x production derived from observation of $\Delta[O_x]$ is equal to the gross O_x production minus the gross photochemical loss, deposition and dispersion of O_x .

$$\varepsilon = \Delta[O_x]/\Delta[NO_x] \quad (3)$$

is the O_3 production efficiency. It is the number of O_3 molecules produced per molecule of NO_x consumed photochemically (Liu et al., 1987; Trainer et al., 2000). Typical values of ε over United States are in the range 1–20 mol mol⁻¹ (Jacob, 1999). In the following, we use the data from field measurements to derive the O_3 production efficiency, consumed NO_x (i.e. $\Delta[NO_x]$) and $P(O_x)$.

In the daytime, the major removal process of NO_x is the oxidation of NO_2 by OH that produces HNO_3 . HNO_3 is readily scavenged by gas-to-particle conversions, wash out or dry deposition. A minor sink of NO_x is the formation of PAN. However, PAN can undergo rapid thermal decomposition and regenerate NO_x at the prevailing temperature during the experiments. Nighttime reactions of NO_3 and N_2O_5 are significant but neglected because the region studied in this work has substantial fresh emissions in the morning and we are mainly dealing with the production of O_3 a few hours after the emissions of O_3 precursors. Therefore, we consider reaction of NO_2 with OH as the only removal process for NO_x and assume the removal of NO_x is pseudo-first order as shown below. In this case, following a Lagrangian trajectory, we have

$$[NO_x] = [NO_x]_0 \exp(-k \int_0^t [OH] dt), \quad (4)$$

where k is the reaction rate constant of NO_x with OH. The reaction rate constant for NO_2 with OH is $1.04 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 25 °C and 1 atm pressure (Sander et al., 2002). Since NO_2 is part of NO_x , the value of k should be scaled down by the ratio NO_2/NO_x . The average of NO_2/NO_x ratio is about 0.6, thus k for NO_x is prescribed at $6.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

The ratio of two hydrocarbons that have same emission sources but different reactivities with OH can be used as a measure of photochemical oxidation by OH (Calvert, 1976; Singh, 1977; Robert et al., 1984; Parrish et al., 1992; McKeen and Liu, 1993; Kramp and Volz-Thomas, 1997). We choose a pair of aromatic hydrocarbons, ethylbenzene and *m,p*-xylene, for this purpose (Chang et al., 2007). Again following the Lagrangian trajectory,

we have

$$E/X = (E_0/X_0) \exp\left(-\int_0^t (k_e - k_x)[OH] dt\right), \quad (5)$$

where E and X represent concentrations of ethylbenzene and *m,p*-xylene at time t , respectively. E_0 and X_0 are their corresponding initial concentrations, k_x and k_e their reaction rate constants with OH, k_x and k_e equal to 2.17×10^{-11} and $7.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively (Atkinson, 1990). The value of ratio E_0/X_0 is about 0.4 for the emission sources in southern Taiwan. This value is usually observed in the early morning around 7–8 am. In fact even around 9–10 am when we collect the first daily VOCs samples, the E/X ratios were fairly close to 0.4 because the photochemical activities are relatively weak before 9–10 am. Using the observed value of E/X at 11–12 am, $\int_0^t [OH] dt$ between early morning and 11–12 am can be calculated from Eq. (5). Then using observed values of NO_x at 11–12 am, initial values of NO_x in the early morning (along the backward Lagrangian trajectory) can be calculated from Eq. (4), and the photochemically consumed values can be obtained from the difference between initial values and the values at 11–12 am. Similarly, NMHCs consumed by OH and initial values can be calculated from Eq. (6) (Chang et al., 2007).

$$[NMHCs] = [NMHCs]_0 \exp\left(-k_i \int_0^t [OH] dt\right), \quad (6)$$

where k_i is the reaction rate constant of the individual NMHC reaction with OH. It is important to note that any NMHCs derived from Eq. (6) along the backward Lagrangian trajectory, e.g. initial NMHCs and consumed NMHCs, are a sum of OH reactivity-weighted NMHCs, not a straight sum of NMHCs.

It should be noted that values calculated from Eqs. (4)–(6) so far do not need to know the time interval of $\int_0^t [OH] dt$. If one wants to derive the OH concentration, the time interval of the integration needs to be determined.

2.4. 1D photochemical model

The model is an updated version of the 1D photochemical model developed by Trainer et al. (1987, 1991). Photochemical mechanisms and reaction rate constants are updated following those in Wang et al. (2000). The vertical resolution of the model decreases from 2 m near the surface to 1 km

at 12 km altitude. Species with a photochemical lifetime shorter than 10 min are calculated by neglecting the transport. The time step for model integration for transport and chemistry is 30 s. Initial vertical distributions of trace species are prescribed by assuming constant mixing ratios equal to observed values in the mixed layer. The initial values of short-lived species in the mixed layer are not important to the model results because emissions and photochemistry quickly redefine the concentrations after a few days of model simulations. Above the mixed layer, mixing ratios of trace gases are assumed to be negligible except for CO and O₃, which are assumed to be their observed seasonal average values. The value of eddy diffusion coefficient (K_z) in the surface layer is calculated from the similarity theory (Trainer et al., 1987). The value of K_z above the surface layer is specified to be 60 m s^{-2} . Dry deposition and heterogeneous removal processes are included in the same way as Trainer et al. (1987). The surface resistance is set at 2 s cm^{-1} for O₃ and peroxides, 0.1 s cm^{-1} for HNO₃, and 3.3 s cm^{-1} for carbonyls and organic nitrates. Lifetimes of heterogeneous losses of soluble gases HNO₃, H₂O₂, ROOH, CH₃OOH, CH₂O, HCOOH, CH₃COOH, SO₂, SO₄ and CRESOL are assumed to be 5 days (Logan et al., 1981). Results of the layer of 16 m height at which most surface measurements were made are used to compare with measurements at surface stations and the OBM results.

The emission rates of O₃ precursors are based on the Taiwan Emission Data System (TEDS 5.0, version of year 2000) published by the TEPA (<http://www.aqmc.org.tw/>). Area and line sources in the KaoPing area are averaged to obtain the average emission rates. The emission rates of NO_x, CO and SO₂ are assumed to be 3.4×10^{16} , 5.0×10^{16} , and 3.0×10^{15} molecules $\text{m}^{-2} \text{ s}^{-1}$, respectively. The emission rates of ethane, propane, butane, ethane, propene and toluene were assumed to be 3.4×10^{15} , 2.5×10^{15} , 2.7×10^{15} , 5.9×10^{15} , 8.4×10^{15} and 2.6×10^{15} molecules $\text{m}^{-2} \text{ s}^{-1}$, respectively. Emission rates of NO_x and NMHCs are then tuned into the diurnal emission rates by multiplying a diurnal variation factor (from 6 to 5 am: 1.0, 1.3, 2.8, 1.2, 0.9, 0.8, 0.7, 0.7, 0.7, 0.7, 0.6, 0.6, 0.6, 0.6, 0.5, 0.5, 0.5, 0.5, 0.5, 0.6, 0.8). Isoprene emission rate is fixed at 3.6×10^{15} molecules $\text{m}^{-2} \text{ s}^{-1}$. The solar zenith angle is set to be that of 30 September 2003 for 22.5°N. The photo-dissociation rate constants are generated by Tropospheric Ultra-Violet (TUV) Radiation model (TUV 4.2;

Madronich and Flocke, 1998). The climatological values of total O₃ observed by Brewer ozone-meter at Chengkung station (121.3°E, 23.1°N, close to the latitude of northern Kaohsiung county) and aerosol optical depth of 0.4 at 550 nm are used. The model calculation is carried out for 3 days to reach a quasi-steady-state condition. Atmospheric concentrations at 11–12 am of day 4 simulation are used to compare with the OBM results.

3. Results and discussion

3.1. Ozone production efficiency

$\Delta[\text{O}_x]$ in Eq. (3) for calculating the O₃ production efficiency can be calculated from observed O₃ + NO₂ at 11–12 am minus the concentration of O₃ + NO₂ observed at 9–10 am. This assumes that the increase in O_x from 9–10 to 11–12 am is equal to the photochemical production of O_x. In reality, we know that part of the increase in O₃ is the result of downward transport of O₃ above the inversion layer, which is O₃ leftover from the previous day. We estimate that the downward transport is insignificant after 10 am and is compensated in part by the loss and dispersion of O_x near 12 am when peak O_x is approached. Dilution effect of O_x due to the growth of the mixed layer is also a concern. A major reason the late morning is chosen to make the OBM study is to avoid the dilution effect. Diurnal variations of trace species such as CO and long-lived NMHCs in the morning can give a good measure of the dilution effect. Decreases of CO and long-lived NMHCs between 8 and 10 am range from 30% to 50%, but only 15% to 25% between 10 and 12 am. Surely dilution of short-lived species like NO_x should be higher than CO because the air above the mixed layer contains negligible NO_x. Observed decreases of NO_x is about a factor of 1.3 greater than the decrease of CO, but part of that is due to greater photochemical loss of NO_x between 10 to 12 am.

ΔNO_x in Eq. (3) should be the NO_x consumed by OH between 9–10 and 11–12 am at each station. The NO_x consumed between 11 and 12 am and early morning can be calculated from Eq. (4), using $\int_0^t [\text{OH}] dt$ from Eq. (5), similarly for the NO_x consumed between 9 and 10 am and sunrise. However, ΔNO_x does not equal to the difference between the above two values, because the consumed NO_x at a station between a time and sunrise is a quantity calculated along the Lagrangian

trajectory, which does not necessarily pass over the same station at an earlier time. Instead we calculate ΔNO_x by assuming the consumed NO_x at different time interval is proportional to the UV dosage in each interval, i.e. we multiply the NO_x consumed between 11 and 12 am and sunrise by the fraction of solar UV radiation between 9–10 and 11–12 am. ΔNO_x calculated this way is plotted against ΔO_x calculated in Fig. 4.

Each data points in Fig. 4 can yield a value for $\Delta\text{O}_x/\Delta\text{NO}_x$, i.e. the O_3 production efficiency (ε). Because the data are from 12 stations, the scattered distribution of Fig. 4 is expected. Values calculated from the 1D model is shown by the solid line. The agreement with the linear fit line is reasonably good. The equivalent plot for NMHCs can be seen in Fig. 5. ΔNMHC of the figure is calculated individually from Eq. (6), i.e. each of the 56 identified NMHCs is treated the same way as NO_x in calculating ΔNO_x . If the consumption of CO and CH_4 were also added to the consumption of NMHCs, the R^2 for ΔO_x vs. $\Delta\text{NMHCs} + \Delta\text{CO} + \Delta\text{CH}_4$ would be improved a little more ($R^2 = 0.68$, not shown). It is interesting to note that the R^2 of ΔO_3 vs. ΔNMHCs is greater than that for ΔO_3 vs. ΔNO_x , suggesting that O_3 production in KaoPing area is more closely related with the consumed NMHCs than the consumed NO_x . Nevertheless we

Fig. 4. $\Delta[\text{O}_3 + \text{NO}_2]$, i.e. difference between $[\text{O}_3 + \text{NO}_2]$ at 11–12am and that at 9–10am, is plotted as a function of the NO_x consumed by OH between 9–10 and 11–12 am, i.e. ΔNO_x . The dashed line is the linear regression line for all points, and R^2 is the coefficient of determination. Values simulated by the 1D model are shown in solid line.

Fig. 5. Same as Fig. 4 except the horizontal axis is changed to ΔNMHCs .

note that NO_x is also correlated with NMHCs as the two O_3 precursors share a major common source, namely the vehicular emissions. This means that NMHCs and NO_x cannot be treated as independent variables and the correlations shown in Figs. 4 and 5 need to be interpreted with caution.

We examined the corresponding plots of Figs. 4 and 5 for each station in KaoPing area and found that 9 out of 12 stations have $R^2 > 0.5$ and up to 0.9 for ΔO_x versus ΔNO_x (not shown). Furthermore, R^2 for ΔO_x versus consumed NMHCs usually are higher than those of ΔO_x versus consumed NO_x (not shown). After inspecting the diurnal variation of NO_x , CO and O_3 of the 12 stations, we found that the three stations with exceptional low R^2 values are mostly affected by significant fresh emissions at 11–12 am. Fresh emissions also contribute significantly to many points that have very low values of consumed NO_x . Strictly speaking, all surface stations are affected to certain degree by fresh emissions. The fresh emissions can be detected by large ratio of isobutene to ethane because the former has relatively short lifetime compared with that of ethane. Significant fresh emissions at 11–12 am can introduce a significant error in Eq. (5) and result in under-estimating the photochemical activity. The error can result in an unreasonably large value of ε because of an erroneous small consumed NO_x in the denominator. In order to screen out the bias due to significant fresh emissions, we exclude the points with ratio of

isobutene to ethane greater than 0.2. Values of ε calculated this way are shown in open circles in Fig. 6 as a function of the observed NO_x .

An independent method to estimate the O_3 production efficiency was given in a simple analytical formula by Jacob (1999):

$$\varepsilon = \frac{P_g(\text{O}_x)}{L(\text{NO}_x)} \approx \frac{\sum_i 2k_i[\text{RH}_i]}{k[\text{NO}_2]}, \quad (7)$$

where $L(\text{NO}_x)$ is the loss rate of NO_x , $P_g(\text{O}_x)$ the gross O_x production, $[\text{RH}_i]$ is the concentration of i th hydrocarbon and k_i are the corresponding reaction rate constants for reacting of RH_i with OH, and the “ k ” in $k[\text{NO}_2]$ is the reaction rate

constant for $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$. According to the 1D model, $P_g(\text{O}_x)$ is about 20% greater than the net O_x production $P(\text{O}_x)$ at 10–12 am. The gross O_x loss is about 15% of $P_g(\text{O}_x)$, while dry deposition and dispersion of O_x is estimated to be about 5% of $P_g(\text{O}_x)$.

Consumed NO_x and NMHCs between 10 and 12 am, which are consistent with Jacob's formulation are used in calculating Eq. (7). Also, an adjustment factor 1.5 is multiplied to the 56 NMHCs to account for the unresolved NMHCs. Eq. (7) is similar to the O_3 production efficiency derived by Kleinman et al. (2002b) except that an O_3 yield resulting from the production of peroxy radicals are simplified to a constant i.e. 2. The values of ε as a function of NO_x derived for the 12 stations in KaoPing area for 11–12 am are shown in solid circles in Fig. 6a. The distribution of ε as a function of NO_x and the regression line for 9–10 am (not shown here) are similar with those for 11–12 am. One can see that the OBM method and the Jacob equation are in good agreement, albeit the OBM values have rather large scattering. The median and 75 percentile of the OBM values are $23.5 \pm 7.3 \text{ mol mol}^{-1}$ at $\text{NO}_x \leq 10 \text{ ppbv}$, and converges to 8.6 ± 3.5 for $\text{NO}_x \geq 20 \text{ ppbv}$ (Fig. 6b). The median and 75 percentile of values from the Jacob method are $12.5 \pm 6.1 \text{ mol/mol}$ at $\text{NO}_x \leq 10 \text{ ppbv}$, and converges to 6.4 ± 1.3 for $\text{NO}_x \geq 20 \text{ ppbv}$ (Fig. 6b). The values of ε from the 1D model are slightly smaller than both OBM and Jacob method for NO_x greater than 10 ppbv. But at lower NO_x the OBM values are about two times higher than the 1D model.

Both methods show that ε increases with decreasing NO_x . This implies that the O_3 production efficiency is greater when O_3 precursors are diluted and diffused. E.g. ε tends to be greater in rural and suburban conditions than the highly polluted urban conditions. This is consistent with earlier works (Liu et al., 1987; Kleinman et al., 2002b; Zaveri et al., 2003). ε approaches a constant average value of about 5–8 (as shown by the regression curves) when NO_x is higher than 10 ppbv. Sillman et al. (1998), Nunnermacker et al. (1998), Ryerson et al. (1998) and Daum et al. (2000) all found ε values from 3 to 5 at NO_x concentrations of urban level, derived from both models and measurements. Others (Chin et al., 1994; Olszyna et al., 1994; Trainer et al., 1995) estimates about 1.5–10 for rural and regional environments. These values are about a factor of two to three less than our values. An obvious reason

Fig. 6. (a) Total oxidant production efficiency calculated from Eq. (7) (solid circles) and from the OBM or Eq. (2) (open circles) are plotted as a function of NO_x concentration. Also shown is the total oxidant production efficiency simulated by the 1D model (solid line). (b) Similar to (a) but data are shown in median values (dotted and dashed lines) and 75 percentile (vertical bars), dotted line is from Eq. (7) and dashed line is from the OBM or Eq. (2).

for our over-estimate of ε is that our estimate is derived in the ambient environment near noontime, i.e. around peak O_3 production time. Since the nighttime loss of NO_x through NO_3 and N_2O_5 can contribute up to 40% of the total loss of NO_x , our ε value should be about 60% higher than diurnal average values for this reason alone. Possible loss of NO_x through PAN, other organic nitrates, and even HONO, which are not included in our calculation of ε can also contribute significantly to the over-estimate.

3.2. Ozone production rate

Values of the O_3 production rate, $P(O_x)$, derived from Eq. (2) are shown as a function of NO_x

Fig. 7. (a) Median values and 75 percentile of total oxidant production rate derived from Eq. (7) (dotted line and bars) and from the OBM or Eq. (2) (dashed line and bars) are plotted as a function of the NO_x concentration. Also shown is ozone production rate calculated by the 1D model (solid line). (b) Same as (a) but plotted as a function of ΔNO_x .

concentration in Fig. 7. OBM-based $P(O_x)$ in KaoPing area can range from a few to 10 ppbv h^{-1} when NO_x concentration is less than 10 ppbv . When NO_x concentration is increased to 30 ppbv , $P(O_x)$ can be as large as 30 ppbv h^{-1} . Because the data for OBM are from 12 different sites in KaoPing area that include upwind, urban center and downwind sites, the scattered distribution of $P(O_x)$ vs. NO_x is expected. $P(O_x)$ can also be calculated from the Jacob equation. Values of $P(O_x)$ from this method agree very well with those of OBM approach. There are some outliers estimated by the OBM with low values less than 2 ppbv h^{-1} . As discussed earlier, they are likely the result of fresh emissions.

Also shown in Fig. 7a are the model simulated $P(O_x)$ versus NO_x . The median values of $P(O_x)$ obtained by OBM and the Jacob equation are about 60% and 40% smaller than model simulated values, respectively.

We have compared our values of $P(O_x)$ from OBM with those derived by Frost et al. (1998). Unfortunately our values are at much higher concentrations of NO_x than Frost et al. (1998) as theirs are aircraft measurements while ours are from surface stations in urban and suburban areas in the morning between 9–10 and 11–12 am. It is well known that the top of the mixed layer usually grows in the morning and does not reach the top of the boundary layer of the previous day ($\sim 1.5 \text{ km}$) until about noontime. As a result, surface stations tend to be influenced by fresh emissions significantly in the morning. This is evident by the observed decreasing concentrations of CO, NO_x and NMHCs in the morning at nearly all stations. Part of the decreases of NO_x and NMHCs is due to photochemical consumption, the decrease of CO is due to the dilution of fresh emissions when the mixed layer grows in thickness.

$P(O_x)$ simulated by our 1D model is very similar to that of Frost et al. (1998) below a few ppbv of NO_x . Above a few ppbv of NO_x , $P(O_x)$ in the model of Frost et al. (1998) levels off and starts to decrease, while $P(O_x)$ in our model continue to increase with NO_x (Fig. 7a). One reason for the difference is that their NMHC mix has significant higher isoprene, which does not increase with NO_x . Another reason is probably because we have a more reactive mix of NMHCs. In this context, we note that Kleinman et al. (2002a) compared $P(O_x)$ vs. NO_x in 5 urban areas in the United States and found that the peak $P(O_x)$ occurred at NO_x concentration of about few to 20 ppbv for those

cities. In very polluted site, the $P(O_x)$ was larger than 30 ppbv h^{-1} and the decreasing values of $P(O_x)$ with increasing NO_x was not observed, consistent with results of our 1D model and the OBM.

From the discussion on the O_3 production efficiency, it is clear that $P(O_x)$ should be related to the consumed NO_x better than NO_x itself. In Fig. 7b, $P(O_x)$ is plotted against ΔNO_x , the consumed NO_x between 9–10 and 11–12 am. As expected the correlation of $P(O_x)$ with ΔNO_x improved significantly because ΔNO_x is a better measure of the photochemical activity. Values of $P(O_x)$ from the OBM agree well with those from the 1D model at $\Delta NO_x > 3 \text{ ppbv}$. Below 3 ppbv of ΔNO_x , values of $P(O_x)$ from OBM are about 50% lower. Consider the uncertainties involved in all three methods, the discrepancies are surprisingly small. In fact, the good agreement between the 1D model and Jacob's approach is likely to be fortuitous as the latter is the gross photochemical production of O_x , while the former is the net O_x photochemical production. The OBM values are expected to be less than the other two approaches because OBM also include loss of O_x due to processes such as heterogeneous loss, dispersion and surface deposition of O_3 and NO_2 . The effect of these processes is expected to be more significant at low production rate of O_x , consistent with the feature in Fig. 7b that $P(O_x)$ from OBM starts to become lower than the other two approaches at about 5 ppbv of ΔNO_x .

The agreement of $P(O_x)$ from Eq. (7) with the 1D model is even better. Given the independent nature of the three methods in evaluating $P(O_x)$, the good agreement among them provides a strong support for the validity of all three methods. In this context, we need to qualify that the validation applies only to the evaluation of $P(O_x)$ as a function of consumed NO_x . The validation does not necessarily extend to other applications of the three methods.

3.3. Derivation of OH concentration

OH can be derived from Eq. (5) if the reaction time is known. This OBM-derived OH can be compared with the model simulated OH. The reaction time is 2 h (from 9–10 to 11–12 am). Fig. 8a depicts values of OH derived from the OBM as a function of the average NO_x between 9–10 and 11–12 am, and compared with the OH from 1D model. Values of OH by our 1D model are in good agreement with those calculated by

Fig. 8. Similar to Fig. 7 except for OH concentrations.

McKeen et al. (1997), despite rather different ambient conditions. The OBM-derived OH concentrations are smaller than model simulated values by a factor of about 2 at NO_x less than 30 ppbv. This is similar to the finding of McKeen et al. (1997). Using ΔNO_x instead of average NO_x does not improve the discrepancy (Fig. 8b). We have looked into the corresponding distributions of each data points in Fig. 8b and found that those OBM-derived OH values closed to the 1D model curve are mainly from the downwind stations where there are less fresh emissions. Lower values of OBM-derived OH are from stations located in the Kaohsiung urban center, suggesting that fresh emissions can affect E/X ratio at urban sites (or upwind sites) and lead to the underestimate of OH values by the OBM.

3.4. Implications for ozone control strategy

The results above can be applied to formulating O_3 pollution control strategies. Fig. 9 shows

Fig. 9. Total oxidant production rate, i.e. $\Delta[\text{O}_3 + \text{NO}_2]$ between 10 and 12 am (black dots), are plotted in a three dimensional space as a function of initial concentrations of NO_x and NMHCs. The shaded plane is a linear surface fit to the black dots. The equation listed represents the surface as a function of initial NO_x and NMHCs. R^2 is the correlation coefficient of the fitting. Lines between the black dots and the plane denote the deviation from the fitting plane.

$\Delta[\text{O}_3 + \text{NO}_2]$, or O_x production rate, as a function of initial NO_x and initial NMHCs concentrations. $\Delta[\text{O}_3 + \text{NO}_2]$ is calculated from $[\text{O}_3 + \text{NO}_2]$ at 11–12 am minus the values at 10–11 and 9–10 am. Similar to the earlier calculation, the initial concentration of NO_x at each site is derived from the consumed NO_x plus the concentration of NO_x observed at 11–12 am. Initial NMHCs are calculated similarly. Consumed CO, CH_4 and isoprene are also taken into account. Also, effects of NMHCs not resolved in the GC are included by multiplying the 56 NMHCs by a factor of 1.5.

Fig. 9 is similar to the concept of the empirical kinetic modeling approach (EKMA) or O_3 isopleth diagrams (e.g. Milford et al., 1989; Gery and Crouse, 1990; Altshuler et al., 1995; Seinfeld and Pandis, 1998), which are intended to relate daily peak O_3 levels to initial concentrations of O_3 precursors. In fact, Fig. 9 is equivalent to a three-dimensional (3D) OBM O_3 production rate isopleth diagram as a function of initial concentrations of O_3 precursors. Initial concentrations are used because they are directly proportional to the emissions of O_3 precursors.

In order to obtain a simple relationship between the O_x production rate and the precursors of O_3 , we

have made a flat surface (linear) fit to data points of RCEC 2003. Multivariate statistical regression is used to evaluate whether the correlations versus initial NO_x and NMHCs have statistical significance as separate entities and uncertainty ranges associated with the slopes versus initial NO_x and NMHCs. The correlation coefficient (R^2) for the surface fit is 0.62. The slopes of $\Delta[\text{O}_3 + \text{NO}_2]$ versus initial NO_x and NMHCs are 0.097 ± 0.069 and 0.158 ± 0.027 , respectively. The statistical result of F test shows that the regression surface is statistically significant and the value of the slope is significant against initial NMHCs but not significant against initial NO_x . This lack of significance can weaken the conclusions in the following interpretation of Fig. 9.

The slightly greater slope against NMHCs suggests that NMHCs are slightly more effective than NO_x in controlling the production rate of the total oxidant. Moreover, because NO_2 is a part of the total oxidant O_x , reducing NO_x emissions will reduce the titration of O_3 and thus increase O_3 . For example, a 20 ppbv reduction in the initial concentration of NO would reduce the titration of O_3 by 20 ppbv, which can be converted to about 5 ppbv h^{-1} of O_3 production rate over the morning hours ($\sim 4 \text{ h}$). In comparison the reduction of O_x

production rate for the 20 ppbv reduction in the initial concentration of NO is about $0.11 \times 20 = 2.2 \text{ ppbv h}^{-1}$. This means that the production rate of O_3 (not O_x) will increase by 2.8 ppbv h^{-1} , i.e. O_3 concentration will increase when the NO_x initial value is decreased. The effect of titration on O_3 in KaoPing is substantiated by an independent study (Chou et al., 2006) on the trends of urban O_3 levels in three major metropolitan centers in Taiwan in 1993–2003. They showed that urban O_3 levels in Taiwan increased significantly between 1993 and 2003 due to reduced titration by NO when NO_x emissions were reduced. Fig. 10 illustrates this point for KaoPing area. One can see that nearly 90% of the increase of O_3 in 1993–2003 can be accounted for by the reduction in NO_2 , i.e. by the reduction of titration. We also use the 1D model to generate a similar surface as the diagram of Fig. 9 (not shown). The slope of O_x against initial NMHCs is more than a factor of three greater than the slope against initial NO_x , consistent with the OBM result.

The efficacy of each NMHC for KaoPing area can be found in Chang et al. (2005). Their study suggested that the NMHCs with top 10 O_3 formation potentials are toluene, ethene, xylene, propene, 1,2,4-trimethylbenzene, styrene, isopentane, isoprene, isobutene and 1-butene.

The balance of evidence suggests that O_3 production rate is likely to be NMHCs-sensitive and controlling NMHCs is more efficient than controlling NO_x in reducing urban O_3 production. How-

ever, significant uncertainties remain in the OBM, and considerable more work is required to minimize these uncertainties before a definitive control strategy can be reached.

3.5. Uncertainty of OBM

In this section, we summarize processes and factors that can contribute to the uncertainties or even compromise the conclusions derived by the OBM. The largest source of uncertainty should be fresh emissions, which have been discussed many times above. Fresh emissions exist everywhere all the time. They affect the OBM in various ways, including biasing the E/X toward a smaller value, biasing NO_x , NMHCs and CO toward higher values, but affecting O_x very little. The effect of fresh emissions can become so large that some data have to be filtered out. For example, when the ratio of isobutene to ethane is greater than 0.2, which indicates fresh emissions, the data points are screened out to reduce the associated bias.

A second source of uncertainty is that ΔO_x can be affected significantly by entrainment (including advection, dispersion and dilution). The entrainment problem is a major reason we choose to calculate ΔO_x near the peak O_3 production time. As mentioned above, ΔO_x in the early morning is well known to contain significant O_x entrained from altitude above the mixed layer where high levels of O_x from the previous day often reside. Near peak O_x time both photochemical production and the concentration of O_x are high, thus tend to be less affected by entrainment. On the other hand, entrainment can also dilute O_x or decrease ΔO_x when the concentration of O_x in the mixed layer is high. Entrainment of other key species such as NO_x , NMHCs and CO can also add to the uncertainty.

Missing NMHCs, i.e. those NMHCs not identified in the measurements, are another source of uncertainty. Although we tried to alleviate the problem as in Fig. 9 by adding to the NMHCs an estimated missing component, the lack of information on the reactivity of the missing NMHCs prevents an accurate estimate of their effect. In addition, oxygenated NMHCs are also not accounted for.

As mentioned in the discussion of Fig. 9, the limited number of measurements contributes significantly to the uncertainty. More measurements can increase the statistic significance and robustness. Moreover, since all the data from 12 stations

Fig. 10. Trends in the annual average daytime (0900–1800) mixing ratios of $[\text{O}_3 + \text{NO}_2]$, $[\text{O}_3]$, and $[\text{NO}_2]$ of eight stations in Kaohsiung from 1994 to 2003. Slopes of $[\text{O}_3 + \text{NO}_2]$, $[\text{O}_3]$, and $[\text{NO}_2]$ are 0.15, 1.02 and $-0.88 \text{ ppbv yr}^{-1}$, respectively.

are included in Fig. 9, the OBM cannot distinguish geographic variation, upwind–downwind differences or multi-day O_3 production. Lumping data from 12 stations with different ambient environments together certainly add to the scattering of the data and thus the uncertainty. In fact, it is known that a rural downwind station is more likely to be NO_x limited in the O_3 production than an urban station (e.g. Blanchard et al., 1999). In this context, more measurements would allow the generation of Fig. 9 for upwind and downwind stations separately and even for individual station, thus reduce the uncertainty of the OBM.

Uncertainties in the measurements of trace species can contribute significantly to the uncertainty of the OBM. In particular, the high detection limit of about 3 ppbv for NO_2 (Chou et al., 2006) is of concern, as mixing ratios of NO_2 at downwind suburban stations Chaochou and Maynon frequently stay around 5 ppbv in late morning.

Finally, as noted above, NO_x is correlated with NMHCs as the two O_3 precursors share a major common source, namely the vehicular emissions. This means that NMHCs and NO_x are not two independent variables, thus tends to weaken the conclusions drawn from Fig. 9.

4. Summary and conclusions

An observation-based method (OBM) is developed in this work to study the relationship between the ozone (O_3) production rate and the precursors of O_3 in southern Taiwan. We use the method to estimate the O_3 production efficiency and the production rate of O_3 . A key step in this approach is to use a pair of hydrocarbons, which have a common emission source but different reaction rate constants with OH, namely ethylbenzene and *m,p*-xylene, to study the degree of photochemical activity of O_3 production. Another key step in the method is to use the total oxidant ($O_3 + NO_2$) instead of O_3 itself to examine the O_3 production because the former has the advantage of staying invariant during the titration process of O_3 by NO and photo-dissociation of NO_2 , hence the ($O_3 + NO_2$) concentration responds better than the O_3 concentration to the real photochemical production rate of O_3 . In addition, a one-dimensional (1D) photochemical model has been developed to evaluate the performance of the OBM.

Average O_3 production efficiency (ϵ) derived by the OBM approach is about 23.5 with 75 percentile

of 7.3 mol mol^{-1} at $NO_x \leq 10 \text{ ppbv}$. It converges to $8.6 \pm 3.5 \text{ mol mol}^{-1}$ at $NO_x \gg 20 \text{ ppbv}$. These values are in good agreement with the O_3 production efficiency calculated from a simple formula developed by Jacob (1999). Values of ϵ from the 1D model are slightly smaller than both OBM and Jacob method for NO_x greater than 10 ppbv. But at lower NO_x the OBM values are about two times higher than the 1D model. Results from the three methods imply ϵ tends to be greater in rural and suburban conditions than the highly polluted urban conditions, consistent with Liu et al. (1987).

OBM-derived total oxidant production rate, $P(O_x)$, in KaoPing area ranges from a few to 10 ppbv h^{-1} when NO_x concentration is less than 10 ppbv, and when NO_x concentration is near 30 ppbv, $P(O_x)$ can be as large as 30 ppbv h^{-1} . Values of $P(O_x)$ from the OBM agree well with those from the 1D model at ΔNO_x greater than 3 ppbv. Below 3 ppbv of ΔNO_x , values of $P(O_x)$ from OBM are about 50% lower. There are a few points with very low values of $P(O_x)$ from the OBM, which are mainly due to the influence of fresh emissions. The agreement of $P(O_x)$ from the Jacob approach with the 1D model is even better. The good agreement among the three independent methods lends a strong support for the validity of our OBM approach. On the other hand, OBM-derived concentrations of OH are smaller than values calculated by the 1D model by about a factor of 2.

We have developed a three-dimensional (3D) OBM oxidant production rate isopleth diagram that mimics the concept of the EKMA O_3 isopleth diagram. The 3D OBM oxidant production rate isopleth diagram (Fig. 9) turns out to be extremely useful for formulating the O_3 pollution control strategy. The 3D OBM O_3 production diagram suggests that reducing emissions of NMHCs are more effective in controlling O_3 than reducing NO_x . However, significant uncertainties remain in the OBM, and considerable more work is required to minimize these uncertainties before a definitive control strategy can be reached.

It is clear that the OBM approach developed in this work is an effective method for studying the relationship between production rate of O_3 and its precursors and a powerful tool for formulating control strategies for urban and regional O_3 pollution. Finally, the OBM approach is process-oriented, it is not location sensitive and can be readily applied to other regions.

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References

- Akimoto, H., 2003. Global air quality and pollution. *Science* 302, 1716–1719.
- Altshuler, S.L., Arcado, T.D., Lawson, D.R., 1995. Weekday vs. weekend ambient ozone concentrations: discussion and hypotheses with focus on northern California. *Journal of the Air & Waste Management Association* 45 (12), 967–972.
- Atkinson, R., 1990. Gas-phase tropospheric chemistry of organic compounds: a review. *Atmospheric Environment* 24A, 1–42.
- Blanchard, C.L., Lurmann, F.W., Roth, P.M., Jeffries, H.E., Korc, M., 1999. The use of ambient data to corroborate analyses of ozone control strategies. *Atmospheric Environment* 33 (3), 369–381.
- Bronnimann, S., Buchmann, B., Wanner, H., 2002. Trends in near-surface ozone concentration in Switzerland: the 1990s. *Atmospheric Environment* 36 (17), 2841–2852.
- Calvert, J.G., 1976. Hydrocarbon involvement in photochemical smog formation in Los Angeles atmosphere. *Environmental Science & Technology* 10, 256–262.
- Cantrell, C.A., Shetter, R.E., Calvert, J.G., Parrish, D.D., Fehsenfeld, F.C., Goldan, P.D., Kuster, W., Williams, E.J., Westberg, H.H., Allwine, G., Martin, R., 1993. Peroxy radicals as measured in ROSE and estimated from photostationary state deviations. *Journal of Geophysical Research* 98 (D10), 18355–18366.
- Cantrell, C.A., Shetter, R.E., Gilpin, T.M., Calvert, J.G., Eisele, F.L., Tanner, D.J., 1996. Peroxy radical concentrations measured and calculated from trace gas measurements in the Mauna Loa observatory photochemical experiment 2. *Journal of Geophysical Research* 101, 14653–14664.
- Cardelino, C.A., Chameides, W.L., 2000. The application of data from photochemical assessment monitoring stations to the observation-based model. *Atmospheric Environment* 34, 2325–2332.
- Chang, C.-C., Lo, S.-J., Lo, J.-G., Wang, J.-L., 2003. Analysis of methyl tert-butyl ether (MTBE) in the atmosphere and implications as an exclusive indicator of automobile exhaust. *Atmospheric Environment* 37, 4747–4755.
- Chang, C.-C., Chen, T.-Y., Lin, C.-Y., Yuan, C.-S., Liu, S.C., 2005. Effects of reactive hydrocarbons on ozone formation in southern Taiwan. *Atmospheric Environment* 39, 2867–2878.
- Chang, C.-C., Liu, S.C., Shiu, C.-J., Lai, C.-J., Wang, J.-L., 2007. A concept for estimating consumption of ozone precursors and assessing correlation between oxidant and precursors, submitted for publication.
- Chin, M., Jacob, D.J., Munger, J.W., Parrish, D.D., Doddridge, B.G., 1994. Relationship of ozone and carbon monoxide over North America. *Journal of Geophysical Research* 99 (D7), 14565–14573.
- Chou, C.C.-K., Liu, S.C., Lin, C.-Y., Shiu, C.-J., Chang, K.-H., 2006. Trends of ozone and its precursors in Taiwan: implications for ozone control strategies. *Atmospheric Environment* 40, 3898–3908.
- Daum, P.H., Kleinman, D.G., Nunnermacker, Y.-N., Lee, Springston, S.R., Newman, L., Weinstein-Lloyd, J., 2000. Analysis of the processing of Nashville urban emissions on July 3 and July 18, 1995. *Journal of Geophysical Research* 105 (D7), 9155–9164.
- Finlayson-Pitts, B., Pitts, J.N. (Eds.), 2000. *Chemistry of the Upper and Lower Atmosphere*. Elsevier, New York.
- Frost, G.J., et al., 1998. Photochemical ozone production in the rural southeastern United States during the 1990 Rural Oxidants in the Southern Environment (ROSE) program. *Journal of Geophysical Research* 103, 22,491–22,508.
- Gery, M., Crouse, R., 1990. User's Guide for Executing OZIPR, Order No. 9D2196NASA, US Environmental Protection Agency, Research Triangle Park, NC.
- Jacob, D.J., 1999. *Introduction to Atmospheric Chemistry*. Princeton University Press, Princeton, NJ, 266pp.
- Jacob, D.J., Logan, J.A., Murti, P.P., 1999. Effect of rising Asian emissions on surface ozone in the United States. *Geophysical Research Letters* 26, 2175–2178.
- Jonson, J.E., Simpson, D., Fagerli, H., Solberg, S., 2005. Can we explain the trends in European ozone levels? *Atmospheric Chemistry and Physics Discussions* 5, 5957–5985.
- Kleinman, L.I., 1986. Photochemical formation of peroxides in the boundary layer. *Journal of Geophysical Research* 91 (D10), 10889–10904.
- Kleinman, L.I., Daum, P.H., Imre, D., Lee, Y.-N., Nunnermacker, L.J., Springston, S.R., Weinstein-Lloyd, J., Rudolph, J., 2002a. Ozone production rate and hydrocarbon reactivity in 5 urban areas: a case of high ozone concentration in Houston. *Geophysical Research Letters* 29 (10), 1467.
- Kleinman, L.I., Daum, P.H., Lee, Y.-N., Nunnermacker, L.J., Springston, S.R., Weinstein-Lloyd, J., Rudolph, J., 2002b. Ozone production efficiency in an urban area. *Journal of Geophysical Research* 107 (D23), 4733.
- Kramp, F., Volz-Thomas, A., 1997. On the budget of OH radicals and ozone in an urban plume from the decay of C5–C8 hydrocarbons and NO_x. *Journal of Atmospheric Chemistry* 28, 263–282.
- Lee, S.H., Akimoto, H., Nakane, H., Kurnosenko, S., Kinjo, Y., 1998. Lower tropospheric ozone trend observed in 1989–1997 at Okinawa, Japan. *Geophysical Research Letters* 25 (10), 1637–1640.
- Lelieveld, J., van Aardenne, J., Fischer, H., de Reus, M., Williams, J., Winkler, P., 2004. Increasing ozone over the Atlantic Ocean. *Science* 304, 1483–1487.
- Levy II, H., Mahlman, J.D., Moxim, W.J., Liu, S.C., 1985. Tropospheric ozone: the role of transport. *Journal of Geophysical Research* 90 (D2), 3753–3772.

- Lin, C.-Y.C., Jacob, D.J., Munger, J.W., Fiore, A.M., 2000. Increasing background ozone in surface air over the United States. *Geophysical Research Letters* 27, 3465–3468.
- Liu, S.C., 1977. Possible effects on tropospheric O₃ and OH due to NO emission. *Geophysical Research Letters* 4, 325–328.
- Liu, S.C., Trainer, M., Fehsenfeld, F.C., Parrish, D.D., Williams, E.J., Fahey, D.W., Hukbler, G., Murphy, P.C., 1987. Ozone production in the rural troposphere and the implications for regional and global ozone distributions. *Journal of Geophysical Research* 92 (D4), 4191–4207.
- Logan, J.A., 1989. Ozone in rural areas of the United States. *Journal of Geophysical Research* 94, 8511–8532.
- Logan, J.A., Prather, M.J., Wofsy, S.C., Mcelroy, M.B., 1981. Tropospheric chemistry—a global perspective. *Journal of Geophysical Research* (D86), 7210–7254.
- Madronich, S., Flocke, S., 1998. The role of solar radiation in atmospheric chemistry. In: Boule, P. (Ed.), *Handbook of Environmental Chemistry*. Springer, Heidelberg, pp. 1–26.
- McKeen, S.A., Liu, S.C., 1993. Hydrocarbon ratios and photochemical history of air masses. *Geophysical Research Letter* 20, 2363–2366.
- Mckeen, S.A., Mount, G., Eisele, F., Williams, E., Harder, J., Goldan, P., Kuster, W., Liu, S.C., Baumann, K., Tanner, D., Fried, S., Sewell, C., Cantrell, C., Shetter, R., 1997. Photochemical modeling of hydroxyl and its relationship to other species during the tropospheric OH photochemistry experiment. *Journal of Geophysical Research* 102, 6467–6493.
- Mihelcic, D., et al., 2003. Peroxy radicals during Berlioz at Pabstthum: measurements, radical budgets and ozone production. *Journal of Geophysical Research* 108 (D4), 8254.
- Milford, J.B., Russell, A.G., McRae, G.J., 1989. A new approach to photochemical pollution control: implications of spatial patterns in pollutant responses to reductions in nitrogen oxides and reactive organic gas emissions. *Environmental Science & Technology* 23, 1290–1301.
- Molina, M.J., Molina, L.T. (Eds.), 2002. *Air Quality in the Mexico Megacity: An Integrated Assessment*. Springer, New York.
- Nunnermacker, L.J., Imre, D., Daum, P.H., Kleinman, L., Lee, Y.-N., Lee, J.H., Springston, S.R., Newman, L., Weinstein-Lloyd, J., Luke, W.T., Banta, R., Alvarez, R., Senff, C., Sillman, S., Holdren, M., Keigley, G.W., Zhou, X., 1998. Characterization of the Nashville urban plume on July 3 and July 18, 1995. *Journal of Geophysical Research* 103 (D21), 28129–28148.
- Olszyna, J.K., Bailey, E.M., Simonaitis, R., Meagher, J.F., 1994. O₃ and NO_y relationship at a rural site. *Journal of Geophysical Research* 99 (D7), 14557–14563.
- Oltmans, S.J., Lefohn, A.S., Scheel, H.E., Harris, J.M., Levy II, H., Galbally, I.E., Brunke, E.-G., Meyer, C.P., Lathrop, J.A., Johnson, B.J., Shadwick, D.S., Cuevas, E., Schmidlin, F.J., Tarasick, D.W., Claude, H., Kerr, J.B., Uchino, O., Mohnen, V., 1998. Trends of ozone in the troposphere. *Geophysical Research Letters* 25 (2), 139–142.
- Parrish, D.D., Trainer, M., Williams, E.J., Fahey, D.W., Hukbler, G., Eubank, C.S., Liu, S.C., Murphy, P.C., Albritton, D.L., Fehsenfeld, F.C., 1986. Measurements of the NO_x–O₃ photostationary state at Niwot Ridge, Colorado. *Journal of Geophysical Research* 91, 5361–5370.
- Parrish, D.D., Hahn, C.J., Williams, E.J., Norton, R.B., Fehsenfeld, F.C., Singh, H.B., Shetter, J.D., Gandrud, B.W., Ridley, B.A., 1992. Indications of photochemical histories of Pacific air masses from measurements of atmospheric trace species at Point Arena, California. *Journal of Geophysical Research* 97, 15833–15901.
- Parrish, D.D., et al., 2004. Changes in the photochemical environment of the temperate North Pacific troposphere in response to increased Asian emissions. *Journal of Geophysical Research* 109, D23S18.
- Robert, J.M., Fehsenfeld, F.C., Liu, S.C., Bollinger, M.J., Hahn, C., Albritton, D.L., Sievers, R.E., 1984. Measurements of aromatic hydrocarbon ratios and NO_x concentrations in the rural troposphere: observation of air mass photochemical aging and NO_x removal. *Atmospheric Environment* 18 (11), 2421–2432.
- Ryerson, T.B., Buhr, M.P., Frost, G.J., Goldan, P.D., Holloway, J.S., Hübler, G., Jobson, B.T., Kuster, W.C., Mckeen, S.A., Parrish, D.D., Roberts, J.M., Sueper, D.T., Trainer, M., Williams, J., Fehsenfeld, F.C., 1998. Emissions lifetimes and ozone formation in power plant plumes. *Journal of Geophysical Research* 103 (D17), 22569–22583.
- Sander, S.P., Friedl, R.R., Ravishankara, A.R., Golden, D.M., Kolb, C.E., Kurylo, M.J., Huie, R.E., Orkin, V.L., Molina, M.J., Moortgat, G.K., Finlayson-Pitts, B.J., 2002. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 14*, JPL Publication 02-25.
- Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric Chemistry and Physics from Air Pollution to Climate Change*. Wiley, New York, 1326pp.
- Sillman, S., 1999. The relation between ozone, NO_x, and hydrocarbons in urban and polluted rural environments. *Atmospheric Environment* 33, 1821–1845.
- Sillman, S., He, D., Pippin, M., Daum, P., Kleinman, L., Lee, J.H., Weinstein-Lloyd, J., 1998. Model correlations for ozone, reactive nitrogen and peroxides for Nashville in comparison with measurements: implications for O₃–NO_x–hydrocarbon chemistry. *Journal of Geophysical Research* 103 (D17), 22629–22644.
- Singh, H.B., 1977. Atmospheric halocarbons: evidence in favor of reduced average hydroxyl radical concentration in the troposphere. *Geophysical Research Letters* 4, 101–104.
- Trainer, M., Hsie, E.Y., Mckeen, S.A., Tallamaju, R., Parrish, D.D., Fehsenfeld, F.C., Liu, S.C., 1987. Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site. *Journal of Geophysical Research* 92 (D10), 11879–11894.
- Trainer, M., et al., 1991. Observations and modeling of the reactive nitrogen photochemistry at a rural site. *Journal of Geophysical Research* 96, 3045–3063.
- Trainer, M., Parrish, D.D., Buhr, M.P., Norton, R.B., Fehsenfeld, F.C., Anlauf, K.G., Bottenheim, J.W., Tang, Y.Z., Weibe, H.A., Roberts, J.M., Tanner, R.L., Newman, L., Bowersox, V.C., Meagher, J.T., Olszyna, K.J., Rodgers, M.O., Wang, T., Berresheim, H., Demerjian, K.L., Roychowdhury, U.K., 1993. Correlation of ozone with NO_y in photochemically aged air. *Journal of Geophysical Research* 98 (D2), 2917–2925.
- Trainer, M., Ridley, B.A., Buhr, M.P., Kok, G., Walega, J., Hübler, G., Parrish, D.D., Fehsenfeld, F.C., 1995. Regional ozone and urban plumes in the southeastern United States: Birmingham, a case study. *Journal of Geophysical Research* 100 (D9), 18823–18834.
- Trainer, M., Parrish, D.D., Goldan, P.D., Roberts, J., Fehsenfeld, F.C., 2000. Review of observation-based analysis of the

- regional factors influencing ozone concentrations. *Atmospheric Environment* 34, 2045–2061.
- Wang, Y.-H., Liu, S.C., Yu, H.-B., Sandholm, S.T., Chen, T.Y., Blake, D.R., 2000. Influence of convection and biomass burning outflow on tropospheric chemistry over the tropical Pacific. *Journal of Geophysical Research* 105 (D7), 9321–9333.
- Zaveri, R.A., Berkowitz, C.M., Kleinman, L., Springston, S.R., Doskey, P.V., Lonneman, W.A., Spicer, C.W., 2003. Ozone production efficiency and NO_x depletion in an urban plume: Interpretation of field observations and implications for evaluating O_3 – NO_x –VOC sensitivity. *Journal of Geophysical Research* 108 (D14), 4436.