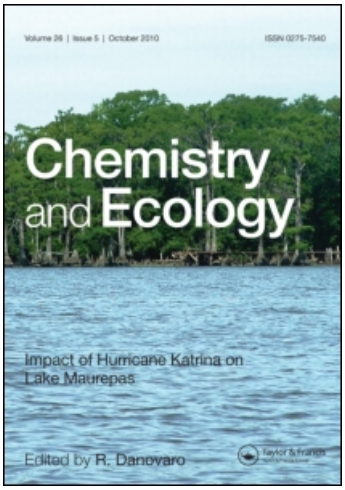

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Sensitivity of Ozone Production to the Nmhc Composition, Aerosol Back-Scattering and High Chimney Emission

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SENSITIVITY OF OZONE PRODUCTION TO THE NMHC COMPOSITION, AEROSOL BACK-SCATTERING AND HIGH CHIMNEY EMISSION

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In this paper, three sensitivity studies are designed to analyze the effect of the NMHC (Non-Methane HydroCarbon) composition, the aerosol back-scattering and the high chimney NO_x emission to the photochemical prodution of ozone by using a one-dimensional photochemistry-diffusion model under a favourable meteorological condition. Measurements of the NMHC composition in Taipei indicated that the percentage of iso-butene, cis-2-butene, trans-2-butene and benzene in a unit volume was much higher than of those observed in other major cities. The high ratio of benzene was directly linked to its high percentage in gasoline. As to the unusually high amount of iso-butene, cis-2-butene and trans-2-butene, more researches are needed to identify their source. Concerns are raised as to how productive is NMHC composition is to the photochemical production of the surface ozone. A rough estimate shows that the total reactivity of the Taipei NMHC composition is about 1.21×10^{-9} cm^3 s^{-1} which is 1.6 times that of the Los Angeles (LA) NMHC composition, while the simulated noon peak will be different by 28 ppbv, i.e. 18% more than that simulated with a LA composition.

Meanwhile, high aerosol loading is a serious problem in Taipei. The attenuation of the UV radiation by aerosols cannot be ignored. A numerical simulation shows that the noon ozone level will decrease from 178 to 141ppbv, i. e. about 21% reduction, with deterioration of the visual range from 85 to 5 km.

In the southern Taiwan, industry parks are mixed with the populated Kaohsiung city, hence the large emission of NO_x from high chimneys cannot be ignored. In this study, NO_x is assumed to be emitted in the layer between 235–460 m high with an emission rate of 0.05 or 0.145 ppbv/sec. The results show that the NO_x emitted from the elevated stack lead to a considerable reduction of surface ozone. Such conclusion is obtained due to the fact that a one-dimensional model is used in this paper. Whereas, if a three-dimensional regional model was used, then a higher productivity of ozone downstream would be simulated.

KEY WORDS: Ozone modeling, sensitivity studies, NMHC composition, aerosol effect, high chimney effect (NO_x).

1. INTRODUCTION

High oxidant pollution is a well known phenomenon in Taiwan. Liu (1989) and Liu *et al.* (1990) discussed the ozone diurnal variation in Taipei and pointed out that in each summer there was 60% probability to observe high ozone episodes. The diurnal variation was marked with a low ozone level before 8 am, a steep increase to a peak before 2 pm, and then a steady decrease. In order to study the meteorological

environment associated with the ozone episodes, an observation experiment was conducted in Taipei during the summer of 1989 (Liu, 1990a). Liu *et al.* (1994a) summarized the findings and concluded that there were seven favourable synoptic conditions to an efficient photochemical production and accumulation of ozone. Under those conditions, the local diurnal circulation, which was triggered by the land-sea breeze, the mountain-valley breeze and the urban heat-island effect, dominated over the prevailing flow. Stagnant air associated with low cloud amount and strong sunshine occurred during 8–11 am, was crucial to the occurrence of an ozone episode.

In addition, Liu (1990b, 1991, 1992a) and Liu and Young (1994) analyzed the ozone data collected by the 19 air-quality stations in Taiwan, which were operated by the Environmental Protection Administration (EPA) of the Republic of China during 1988–1993. These stations were mostly in the urban area and near the ground where pollutants emitted by moving vehicles were high, and had clearly recorded an increasing trend of CO and NO_x. Frequent episodes of ozone marked with the hourly ozone level exceeding 120 ppbv were noted not only in Taipei, but also in middle and southern Taiwan.

Since July 1993, a total of 66 air-quality stations have been installed all over Taiwan to replace the outdated stations (Lee and Liu, 1994). These stations are in general 15–25 m above the ground and 20–40 m away from the traffic. Hence, the data collected are more representative of the ambient air-quality conditions. In particular, the ozone level correlates very well with the NO_2/NO ratio, which indicates that sufficient photochemical reactions have taken place before the air was sampled. Young and Liu (1995) have analyzed about one and half years of the new dataset and found that the new stations have much higher ozone levels than those observed in the past. As a result, the frequency of ozone episodes in Taiwan has been increased considerably. It is now not only in the urban area, but also in the suburban and rural areas, and sometimes even at remote clean sites, that ozone episodes can be detected.

The major emission source of NO_x and NMHC (Non-Methane HydroCarbon) in Taiwan is due to moving vehicles, with the number of motorcycles are twice that of automobiles. Insufficient combustion processes associated with the two-cycle engines used by motorcycles result in increased hydrocarbon emissions and a higher $NMHC/NO_x$ ratio and more reactive hydrocarbons. Liu and Lu (1991) used the information in 1986 to estimate that the $NMHC/NO_x$ ratio was about 15 (ppbc/ppbv) in comparison to the 5.45 ratio based only on the automobile emission data, and suggested that reducing the number of motorcycles is a control strategy for ozone. Based on a box model simulation, Liu and Lu pointed out that by lowering the $NMHC/NO_x$ ratio from 15 to 5.45 could result in a reduction of the noon ozone amount by about 50%.

In this paper, three sensitivity studies are designed to analyze the effect of the NMHC composition, the aerosol back-scattering and the high chimney NO_x emission to the photochemical production of ozone by using a one-dimensional photochemistry-diffusion model under a favourable meteorological condition. These key factors are important to a successful development of a numerical model suitable for Taiwan.

2. MEASUREMENT AND ANALYSIS OF THE NMHC COMPOSITION IN TAIPEI

During 1990–1991, Tso *et al.* (1991) sampled and analyzed the air at a number of different locations in Taipei during early morning hours. These air samples were analyzed to determine a mean composition of NMHC. The results were used by Liu *et al.* (1994b) to produce a lumped hydrocarbon composition (Tab. I) to be used as a box model (Atkinson *et al.*, 1982). The technique and equipment that used to sample and to measure the C_2-C_{12} NMHC have been discussed in detail by Liaw *et al.* (1994) and Lo *et al.* (1994). In short, the C_2-C_5 species were determined by a HP 5890 gas chromatography with FID (Flame Ionization Detector) to analyze the air samplers collected by canisters. The C_6-C_{12} species were distinguished by a Shimadzu GC-9a gas chromatography with FID to analyze samplers collected by glass tubes stuffed with Tenax-TA.

Liu *et al.* (1994b) compared the ratios of different NMHC species to C_2H_2 (in ppbc/ppbc units) and the ratios of C_6-C_{12} species to benzene (in ppb/ppb units), with those measured in New York (Rasmussen, 1976; Altwicker *et al.*, 1980), Los Angeles (Butcher and Charlson, 1972; Roberts *et al.*, 1984), other US major cities (Sexton and Westberg, 1984; Roberts *et al.*, 1984), Sydney (Nelson and Quigley, 1982), Toronto (Pilar and Graydon, 1973), Tokyo (Uno *et al.*, 1985), New York, Lincoln Tunnel (Lonneman *et al.*, 1974, 1986), Houston (Siddiqi and Worley, 1977), Johannesburg (Louw *et al.*, 1977), Leningrad (Isidorov *et al.*, 1983), Hague (Burghart and Jeltes, 1975). The ethene/acetylene ratio was 2.63 in Taipei, which was close to measurements in the Lincoln Tunnel by Lonneman *et al.* (1986) and indicated that the major emission sources were moving vehicles. Meanwhile, the ratios of *n*-butane, *n*-pentane and

Table I The lumped structure of the Taipei NMHC composition (Liu *et al.*, 1994b), in along with the Los Angeles NMHC composition (Leone and Seinfeld, 1985) and the reaction rate of each hydrocarbon with OH, K_{OH}.

% in carbon	*Taipei (this study)*	*Los Angeles (LA) (Leone and Seinfeld, 1985)*	K_{OH} ($x10^{-11}$ cm^3 s^{-1})
ethane	7.82	7.25	0.0281
propane	3.02	2.4	0.115
butane	35.43	31.33	0.26
ethene	8.69	4.08	0.792
propene	6.18	1.50	0.251
trans-2-butene	6.68	0.13	6.86
benzene	–	0.45	0.12
toluene	10.15	5.55	0.6
2, 3-dimethyl-butane	–	27.63	0.58
m-xylene	20.46	16	2.4
formaldehyde	1.32	1.79	1
acetaldehyde	0.25	1.89	1.9

n-hexane to acetylene were close to those measured in the major cities, but different from those in the tunnels, which indicated that emission sources such as gasoline stations, leakage of liquid propane and gas from either the major selling points or the connecting pipes, could not be ignored. Also, it was noted that the ratios of isobutene, cis-2-butene, and trans-2-butene to acetylene were 1.12, 0.42 and 0.48, respectively, and were all higher than those observed elsewhere, and would certainly enhance the productivity of ozone as the reaction rate of these species with OH was quite high. More researches are needed to identify the sources of these species.

The ratio of benzene to acetylene was 4.51, about 1.6–5.5 times those measured in other major cities and could be directly linked to the higher percentage of benzene in the local gasoline. For the same reason, the ratio of toluene to acetylene, which was 8.5, was also higher than those measured in other cities, except Tokyo (Uno *et al.*, 1985). Meanwhile, the ratios of toluene, ethyl-benzene, *m*, *p*-xylene, *o*-xylene, 1,2,4-trimethyl-benzene to benzene were all close to that measured elsewhere. Hence, even though benzene itself has a low reactivity with OH and is negligible in photochemical reactions in the urban atmosphere, the higher portion of other aromatic compounds, e. g. such as toluene, *m*-xylenes, would enhance significantly the productivity of ozone.

There were no measurements of ethane in Taiwan which usually contributed to a large portion in the total NMHC, so Liu *et al.* (1994b) decided to lump the hydrocarbons identified by Tso *et al.* (1991) through the following approach:

(1) The percentage of total alkanes, alkenes, aromatics and acetylene in a unit volume were the same as those measured by Lonneman *et al.* (1986) in the Lincoln Tunnel, i.e. 39.1%, 21.8%, 35.4% and 3.7%, respectively.
(2) Toluene and mono-alkyl-benzenes were grouped into toluene.
(3) Di- and tri-alkyl-benzenes were grouped into *m*-xylene.
(4) Alkenes with carbon number larger than three were assumed to have the reactivity of propene and trans-2-butene.
(5) Alkanes with carbon number larger than four were assumed to have the reactivity of butane.
(6) Acetylene and benzene were assumed to have the reactivity of ethane.

The resultant lumped NMHC composition is listed in Table I. For comparison, the equivalent composition for Los Angeles (LA) is also shown (Leone and Seinfeld, 1985). Following Lin *et al.* (1988), a measure of the total reactivity of the NMHC can be calculated by summing over the reaction rate coefficient of each NMHC with OH and weighted by the percentage of each NMHC in carbon number. The total reactivity for Taipei NMHC calculated this way is 1.21×10^{-9} cm^{-3} s^{-1} and is about 1.6 times that of LA.

3. ONE-DIMENSIONAL PHOTOCHEMISTRY-DIFFUSION MODEL

A one-dimensional (1-D) photochemistry-diffusion model is used in this paper to study the sensitivity of the NMHC composition, the aerosol back-scattering and the high chimney NO_x emission to the photochemical production of ozone. This 1-D

model was originally developed by Trainer *et al.* (1987) and has been modified to include the chemical reactions involving toluene and *m*-xylene. The three major modules: the planetary boundary layer (PBL) module, the photolysis rate module, and the chemistry module, were described in detail by Liu *et al.* (1990), Liu (1992b, 1993) and Tsay (1993). The flow chart is plotted in Figure 1. In short, the sounding data at 8 pm of the previous day is used as the input for the 1-D PBL module to estimate the temporal and vertical variation of the diffusion coefficient, temperature, relative humidity and wind field below 6 km high. In total, 71 levels are used to resolve the vertical structure. In the surface layer, i.e. below 80 m high, 12 levels are designated. Meanwhile, the photolysis rate module provides the temporal variation of the photolysis rates of 15 species, under a clear and undisturbed condition. Only the information of data and location are required for this module. Finally, the 1-D photochemistry-diffusion module will simulate the temporal and vertical variation of 44 long-lived and 40 short-lived chemical species. A total of 133 gas-phase reactions are handled in this module. The information of NMHC composition, NO_x and NMHC emission rate and a diurnal emission pattern are required.

Two high ozone episodes, one for the city Taipei, and one for Kaohsiung, are simulated. On September 25, 1989, an ozone peak of 160ppbv was observed in Taipei. The simulated evolution of the temperature profile from 4 am to 4 am of the

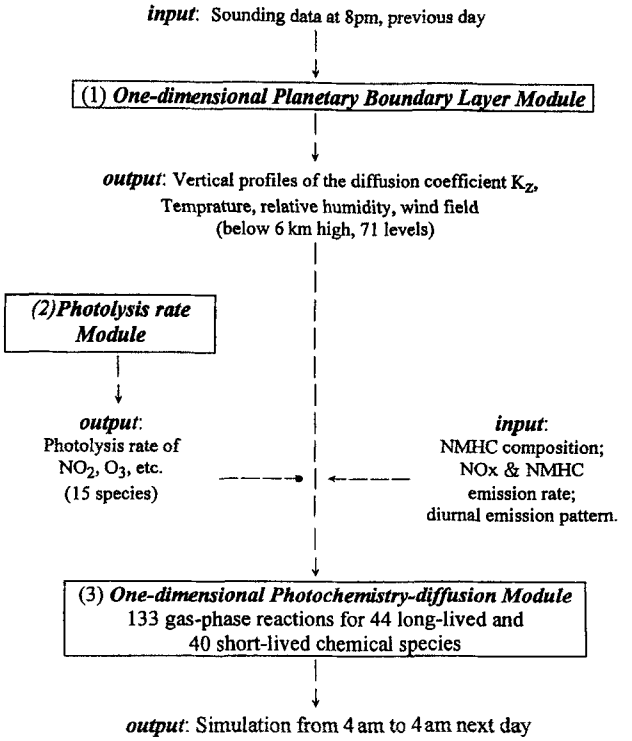

Figure 1 Flow chart of the one-dimensional planetary-diffusion model.

next day is shown in Figure 2a. Because the model does not handle the horizontal advection, while the vertical diffusion is weak above the mixing layer, there is little variation of the temperature field above 2.5 km high. Also, the lack of horizontal advection has caused the temperature between the 2.5 km high and the top of the nocturnal radiative-inversion layer to stay nearly constant, after the occurrence of the noon maximum. The air temperature at 5 m high compares well with that observed in the central Taipei (Fig. 1b), except that the simulated temperature is about 2.5 degrees higher after 2 pm. For studying the ozone field, it is adequate to take only the output up to noon and ignore the evolution in the afternoon.

In the Kaohsiung case, a similar model calculation run has been performed (Figs. 2c and d). The ozone episode simulated is for November 7, 1989, when a peak of 172 ppbv was observed. Kaohsiung is located in southern Taiwan. It is the second largest city with about two million habitants. The simulated air temperature at 5 m

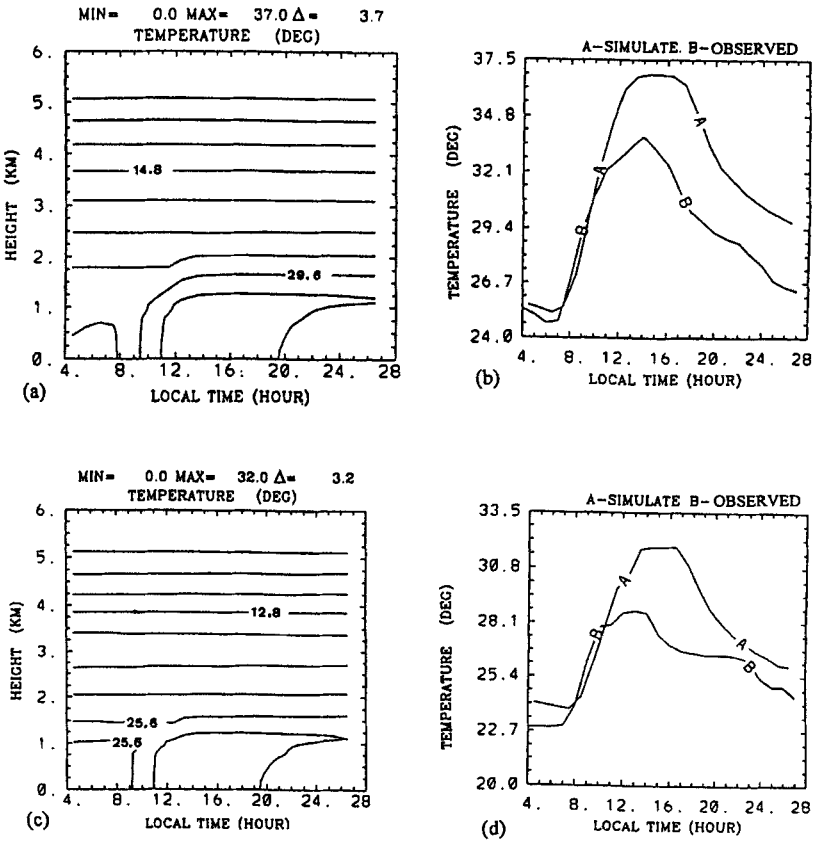

Figure 2 One-dimensional photochemistry-diffusion model simulated (a) temporal-vertical profile of temperature in Taipei from 4 am to 4 am next day on September 25, 1989; (b) the comparison of the simulated temperature at 5 m high with that observed in the central Taipei. (c) model-simulated temporal-vertical profile of temperature in Kaohsiung from 4 am to 4 am next day on November 7, 1989; (d) the comparison of the simulated temperature at 5 m high with that observed in Kaohsiung.

(Fig. 2d) compares also quite well with that observed in Kaohsiung, except for a higher degree after 10 am.

The daily emission of NO_x from moving vehicles is estimated to be about 2.33×10^{16} m^{-2} in Taipei and 2.25×10^{16} m^{-2} in Kaohsiung. The daily emission of NMHC is about 1.69×10^{17} m^{-2} in Taipei, 2.15×10^{17} m^{-2} in Kaohsiung. Thus the emission ratio of NMHC/NO_x is about 7.25 in Taipei and 9.56 in Kaohsiung. The emission by other sources are ignored, except in the third sensitivity study. The diurnal emission pattern is obtained from the inventory study by EPA (1992).

4. SENSITIVITY OF OZONE PRODUCTION TO NMHC COMPOSITION

By using the NMHC composition of Taipei and that of LA (Tab. I) as the initial composition in the 1-D model, we can study the dependence of ozone production on the NMHC composition. Figures 3a and b show the simulated ozone amount at 5 m, 235 m, 460 m, 1060 m and 2560 m high for the Taipei simulation case. Due to

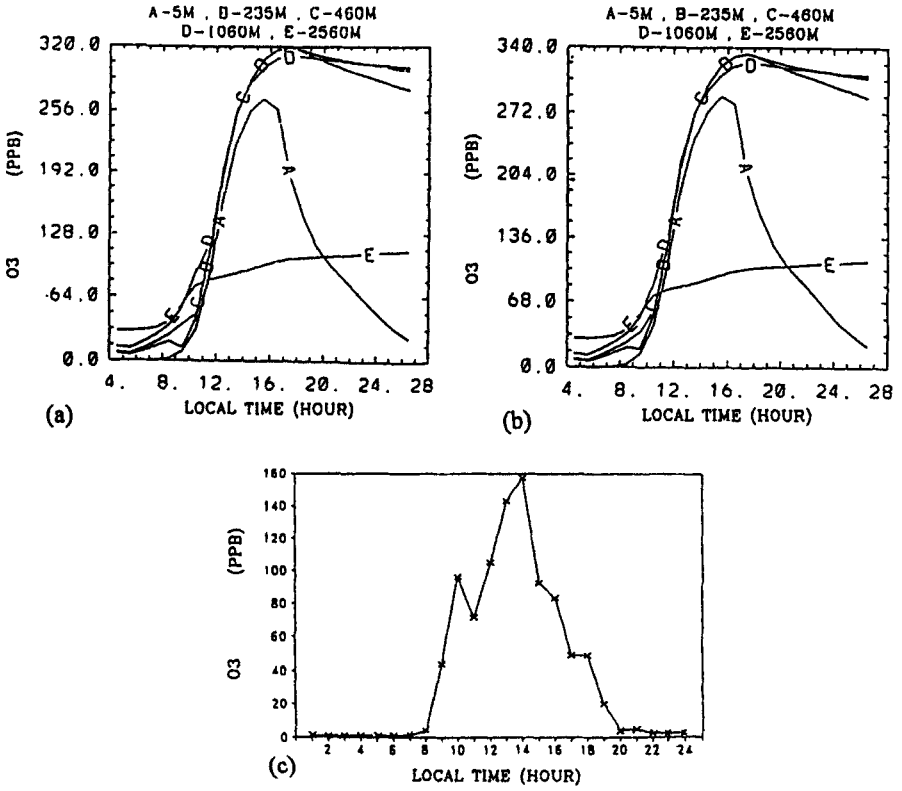

Figure 3 Temporal varition of the model-simulated ozone at 5 m, 235 m, 460 m, 1060 m and 2560 m high for the Taipei case with (a) LA and (b) Taipei NMHC initial composition. (c) The observed ozone level at Panchiao, Taipei, on September 25, 1989.

the lack of horizontal advection associated with the local diurnal circulation, ozone tends to accumulate until sunset. After sunset, only in the nocturnal radiative-inversion layer that a steady decrease of ozone amount occurs due to surface deposition; the ozone level varies little in all other layers. Hence, it is reasonable to just take the noon result to be compared with the observed peak ozone amount. Figure 3c shows the hourly variation of the ozone level observed at Panchiao, which is located in the southwestern corner of Taipei and is considered to be in the downstream region. The highest level of 160 ppbv occurred at 2 pm. After 2 pm, a significant convergence of air flow and a strong sea-breeze act to dilute the surface ozone level very efficiently (Liu *et al.*, 1994a). The current 1-D model cannot simulate the afternoon event.

The case with the LA composition will result in the noon ozone level to be about 135–154 ppbv in the mixing layer (Fig. 3a), i.e. below 1 km high, whereas the run with the Taipei composition results in a 163–182 ppbv noon level (Fig. 3b). The differences between the simulated ozone fields have a maximum at noon which is about 28 ppbv in the mixing layer (Figs. 4a and b), i.e. 18–21% increase. Obviously, the higher reactivity of the Taipei composition has resulted in a higher noon ozone level.

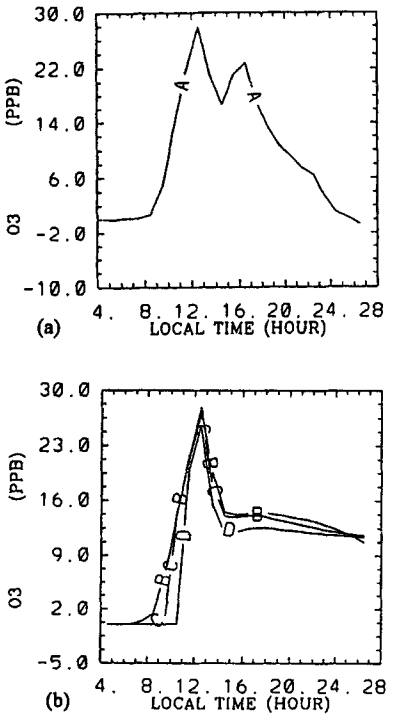

Figure 4 Temporal variation of the difference of ozone level between the run with the Taipei NMHC composition and the one with the LA composition for the Taipei episode, (a) at 5 m high (marked as A), (b) at 235 m (marked as B), 460 m (marked as C) and 1060 m (marked as D) high.

Similar calculations have also been done for the Kaohsiung case. The highest noon ozone level of 172 ppbv was observed at Chishen, which is in the middle of the Kaohsiung city. The afternoon sea-breeze played a crucial role to dilute the surface ozone after 12 am (Young and Liu, 1995). The case with the LA composition will result in the noon ozone level to be about 118–130 ppbv in the mixing layer, whereas the run with the Taipei composition is with a noon level of 146–170 ppbv. A change of the NMHC composition contributes to an enhancement of 38–40 ppbv at noon, i.e. 24–32% increase. Since most of the parameters used in both the Taipei and Kaohsiung cases are similar, it is because the higher emission amount of NMHC in Kaohsiung has magnified the reactivity effect of the Taipei composition.

5. SENSITIVITY OF OZONE PRODUCTION TO THE AEROSOL BACK-SCATTERING EFFECT

Aerosols from anthropogenic sources scatters significantly the solar radiation (Ball and Robinson, 1982). In the past, most of the studies focused on relating the aerosol pollution to the visibility problem (Trijonis *et al.*, 1990). Liu *et al.* (1991) estimated that the amount of biologically active solar radiation (UVB, 280 to 315 nm) reaching the surface over non-urban areas of the industrialized countries has decreased by 5–18% since the industrial revolution, primarily due to aerosols formed from emissions of sulphur dioxide (SO_2), which could have offset partly or fully the UVB increases associated with the depletion of stratospheric ozone. For the same reason, high loading of aerosols in metropolitan areas can efficiently scatter the ultra-violet (UV) radiation and weaken the photodissociation processes of NO_2, O_3, and lead to a weaker production of surface ozone.

In Taiwan, besides photochemical pollution, aerosol loading is also a serious pollution problem (Liu, 1990b, 1991, 1992a). Liu *et al.* (1995) recently analyzed the visibility data in Taiwan, and just 30 km north of Kaohsiung, and noted that the level of PM10, i.e. aerosols with size smaller than 10 μm, was negatively correlated with the visual range. Such relationship was most clear during September–April when the prevailing northeasterly winds were strong and carried little moisture to southern Taiwan. A visual range as low as 4 km occurred when the daily-mean PM10 level reached 230 $\mu g\, m^{-3}$. Actually, throughout Taiwan the national standard of 125 $\mu g\, m^{-3}$ of the daily-mean PM10 level was frequently exceeded.

In Taipei, the visual range was about 5 km on a clear sunny day. The back-scattering of UV radiation by aerosols can never be ignored. In this paper, we have assumed that the aerosol extinction coefficient at 550 nm, b_{550}, in the boundary layer, is related to the visual range (or visibility), *vis*, through the following relationship (Middleton, 1963)

$$b_{550} = 3.91/vis,$$

by which we may change the visual range to estimate the change of aerosol scattering effect. Meanwhile, the aerosol model developed by Shettle and Fenn (1979), with optical constants corresponding to a bimodal aerosol size distribution composed of

70% water soluble, a 30% dustlike material at 70% relative humidity, is adopted. My calculations for this aerosol model give a net single scattering albedo of 0.94 approximately, independent of wavelength, an asymmetry factor of 0.66 at 550 nm and 0.69 at 310 nm, and an attenuation coefficient (for 25 km visual range) of 0.15 km^{-1} at 550 nm and 0.25 km^{-1} at 310 nm. The angular distribution of the scat- tering was represented with a Henyey-Greenstein phase function. Furthermore, the aerosols are assumed to be well mixed in the mixing layer. These aerosol properties are inputted into a discrete ordinate radiative transfer model (Stamnes *et al.*, 1988) to calculate the irradiance at ground level as a function of wavelength, which are then used in the photolysis-rate module to estimate the photolysis rate of different chemical species.

By changing the visual range from a clear condition of 85 km to the smoky condition of 5 km, we may analyze the change of the aerosol optical depth at 500 nm (Fig. 5a), the photolysis rate of NO_2 and formaldehyde (Figs. 5b, c), and the noon ozone level (Fig. 5c). The optical depth increases from the top of the radiative transfer model to the surface, and has a most dramatic change below 3 km. At surface, the aerosol optical depth can differ from 0.18 to 2.21, as the aerosol loading increases. Meanwhile, the photolysis rates of NO_2 and formaldehyde at surface tend to decrease with both the zenith angle and the deterioration of the visual range. The latter causes the photolysis rate of NO_2 to decrease by 45–50% with a change of visibility from 85 to 5 km. The photodissociation of NO_2 is one of the key reactions leading to the production of ozone. The decrease of the HCHO photolysis rate is

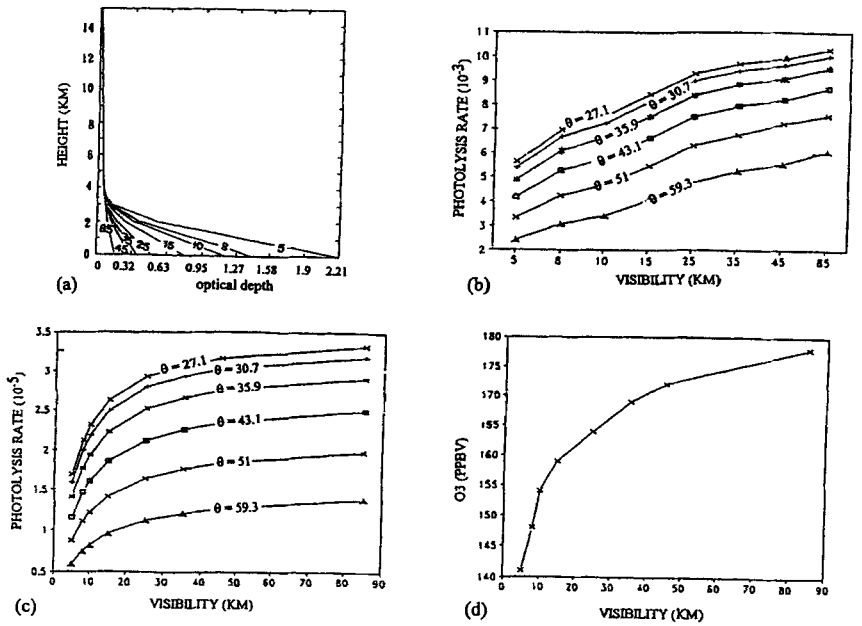

Figure 5 (a) The vertical profile of aerosol optical depth as a function of visibity, which changes from 85 to 5 km; the photolysis rate of (b) NO_2 and (c) formaldehyde as a function of visibility and zenith angle; (d) the model-simulated noontime ozone level as a function of visibility.

much more dramatic at smaller zenith angle with a shorter visibility, and can decrease by 50–60% with a change of visibility from 85 to 5 km. The photodissociation of formaldehyde is one of the major sources of OH, and the amount of OH determines the level of reactivity of the gas-phase reactions.

The simulated noon ozone level at 5 m high decreases significantly with the deterioration of the visual range (Fig. 5c). The simulation case is the Taipei episode with the Taipei NMHC composition. In the previous section, a visibility of 25 km was used. Based on Figure 5c, a change of visibility from 85 to 5 km can lead to a decrease of the noon ozone level from 178 to 141 ppbv, i.e. 21% reduction. Similar analyses on the noon OH level show that the amount of OH at 5 m high is reduced by 50%. The reduced ozone and OH production is most significant when the visibility is lower than 10 km, which strongly suggests that a more realistic aerosol model is needed when a simulation of a polluted region is performed.

6. SENSITIVITY OF OZONE PRODUCTION TO THE STACK-EMITTED NO_x

Surrounding Kaohsiung, many industry plants with elevated chimneys are mixed with the populated areas. It is expected that NO_x emitted from these stacks will enhance the ozone production downstream, but how will these elevated NO_x effects change the local ozone level? In this section, we assume that NO_x is being emitted in the layer between 235–460 m high. The emission rate is either 0.05 or 0.145 ppbv/sec.

By running the Kaohsiung episode case with the Taipei NMHC composition, we may compare the differences in the ozone field between the run with the stack-emitted NO_x and the control run (Figs. 6a, b, c). Obviously, the titration effect due to enhanced NO_x emission has caused the ozone level below 1060 m high, i.e. in the mixing layer, to decrease steadily. At surface (Fig. 6a), a peak reduction about 17 and 45 ppbv occurs at noon with 0.05, and 0.145 ppbv/sec emission of NO_x i.e. about 12 and 31% reduction. Similar reduced amount is also noted at levels below 1060 m high (Figs. 6b, c).

This demonstrate the importance of chimney emission on affecting the ozone production in Kaohsiung region. Since the current model is not a three-dimensional regional model, we are unable to check the sensitivity of ozone production downstream.

7. DISCUSSIONS ON THE CONTROL STRATEGIES TO THE PHOTOCHEMICAL POLLUTION IN TAIWAN

How can the oxidant pollution be controlled? NRC (1991) has debated this issue after many years of experiments in the United States. The most reasonable approach is to reduce moving vehicles, but this has been impossible in Taiwan, Motorcycles use deteriorated the quality of living standard. Hence, even though the Taiwan EPA has the most strict motorcycle emission, the net amount of pollutants from motorcycles is still incredibly high. Currently, Taiwan EPA has kept upgrading the

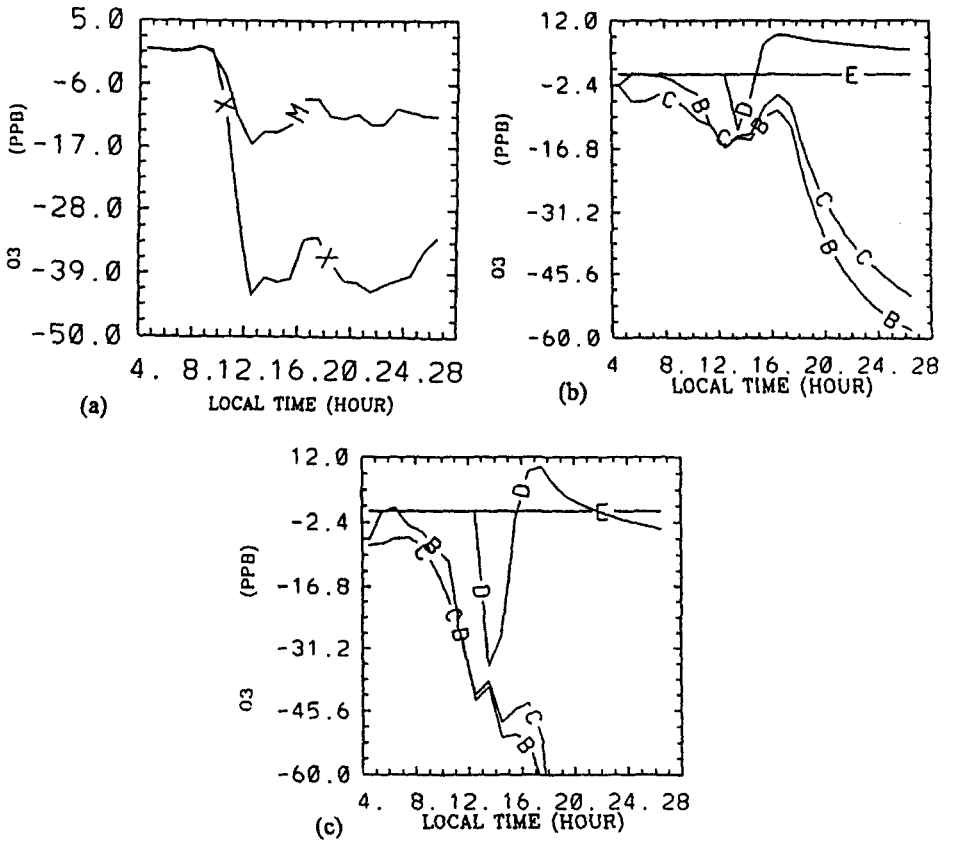

Figure 6 Temporal variation of the difference of ozone level between the run simulated with and the one without the inclusion of stack-emitted NO_x in the 235–460 m layer in Kaohsiung, (a) at 5 m high for the emission rate of 0.05 ppbv/sec (marked as M) and 0.145 ppbv/sec (marked as X), (b) at 235 m (marked as B), 460 m (marked as C) and 1060 m (marked as D) high for the emission rate of 0.05 ppbv/sec; (c) same as (b), but for the emission rate of 0.145 ppbv/sec.

emission standard for all moving vehicles. However, the effect of a tougher emission standard is still unable to cope with a continuous growth of moving vehicles.

Another useful approach is to change the type or composition of the fuel (Russell *et al.*, 1995). In Section 2, we have pointed out that the NMHC composition in Taipei contains a large proportion of iso-butene, cis-2-butene, trans-2-butene and benzene. More researches are needed to pin down their sources, and because of their high reactivity with OH. Meanwhile, the high percentage of benzene is directly linked to its higher portion in gasoline. Hence, even though benzene itself has a low reactivity with OH, it is negligible in photochemical reactions in urban atmosphere. The higher portion of other aromatic compounds, such as toluene, *m*-xylene cannot be ignored, for their high reactivity with OH. To lower the percentage of benzene in gasoline would be the most direct approach. Recently, Taiwan EPA has approved a plan to use liquid propane as fuel for cars. It will be operational in 1995–1996.

Another interesting phenomenon that has been noted in the recent air-quality data is the occurrence of ozone episodes in mountain and even coastal clean sites (Young and Liu, 1995). This certainly results from the long-range transport of ozone precursors. Meanwhile, the reduction on ozone production caused by the aerosols back-scattering of UV radiation and the stack-emitted NO_x, as shown in this paper, have stressed a point that the ozone level near the urban and industrial areas must be lower than those in the downstream suburban and rural areas. Since ozone can cause a direct damage on vegetables and plants, more ozone monitors are needed in suburban and rural areas. The current set-up of the 66 air-quality stations in Taiwan (Young and Liu, 1995) is to fit the spatial distribution of population. Such design is useful to monitor primary pollutants such as PM-10, CO, SO_2, but needs to be modified to monitor the oxidant pollution. This concept should be implemented into the future air-quality monitoring stations.

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References

Altwicker, E. R., Whitby, R. A. and Lioy, P. J. (1980) Specific non-methane hydrocarbons and their relationship to ozone in an eastern metropolitan area, Manhattan. *J. Geophys. Res.*, **85**: 7475–7487.

Atkinson, R. A., Loyd, C. and Winges, L. (1982) An updated chemical mechanism for hydrocarbon/NO_x/SO_2 photoxidations suitable for inclusion in the atmosphere simulation models. *Atmos. Environ.*, **16**: 1341–1355.

Ball, R. J. and Robinson, G. D. (1982) The origin of haze in the central United States and its effect on solar radiation. *J. Applied Meteor.*, **21**: 171–189.

Burghardt, E. and Jeltes, R. (1975) Gas chromatographic determination of aromatic hydrocarbons in air using a semi-automatic pre-concentration method. *Atmos. Environ.*, **9**: 935–940.

Butcher, S. S. and Charlson, R. J. (1972) *An Introduction to Air Chemistry*. Academic Press, N.Y, pp.

Dodge, M. C. (1984) Combined effects of organic reactivity and NMHC/NO_x ratio on photochemical oxidant formation – A modelling study. *Atmos. Environ.*, **18**: 1657–1665.

Environmental Protection Administration (EPA) (1992) *The Emission Inventory of Air Pollutants and Planning for Reduction at Northern, Middle, Southern and Kaoshoung Areas.* EPA, R.O.C. (in Chinese) pp.

Isidorov, V. A., Zenkevich, I. G. and Ioffe, B. V. (1983) Methods and results of gas chromatographic/mass spectrometric determination of volatile organic substances in an urban atmosphere. *Atmos. Environ.*, **17**: 535–549.

Lee, C.-S. and Liu, C.-M. (1993) *Air Quality Monitoring and Prediction.* EPA-82-007-03-04, EPA, R.O.C. (in Chinese) pp.

Leone, J. A. and Seinfeld, J. H. (1985) Comparative analysis of chemical reaction mechanisms for photochemical smog. *Atmos. Environ.*, **19**: 437–464.

Liaw, S.-J., Tso, T.-L. and Lo J. G. (1994) Measurement of C_2-C_6 nonmenthane hydrocarbons (NMHCs) in the background atmosphere of Taiwan by using the canister-gas chromatography method. *Analytical Sciences*, **10**: pp.

Lin, X., Trainer, M. and Liu, S. C. (1988) On the nonlinearity of the troposphere ozone production. *J. Geophys. Sci.*, **93**: 15897–15888.

Liu, C.-M. (1989) *A Study of the Surface Ozone Characteristics during Summer and Winter in the Taipei Basin.*, EPA-78-002-10-069, EPA, R.O.C. (in Chinese) pp.

Liu, C.-M. (1990a) *An Extensive Observation Program for Studying the Photochemical Pollution in the Taipei Basin.*, EPA-79-002-01-007, EPA, R.O.C. (in Chinese) pp.
Liu, C.-M. (1990b) *A Study of the Daily Air-Quality Trend and Prediction.*, EPA-79-007-01-161, EPA, R.O.C. (in Chinese) pp.
Liu, C.-M. (1991) *A Study of the Daily Air-Quality Trend and Prediction.*, EPA-80-E3L1-09-04, EPA, R.O.C. (in Chinese) pp.
Liu, C.-M. (1992a) *The Application of the Air-Quality Data: (2) A Study of the Daily Air-Quality Trend.*, EPA-81-E3L1-02, EPA, R.O.C (in Chinese) pp.
Liu, C.-M. (1992b) A development of 1-D photochemcial model. *Atmos. Sci.*, **20**: 119–134.
Liu, C.-M. (1993) The effect of horizontal transport on the ozone production in Taipei. *Atmos. Sci.*, **21**: 1–22.
Liu, C.-M. and Lu, K.-S. (1991) A preliminary development, verification and application of a box photochemical model. *Atmos. Sci.*, **19**: 33–65 (in Chinese) pp.
Liu, C.-M. and Young C.-Y. (1994) An analysis of Taiwan surface ozone (1988–1993). *J. Environ. Protection Society of R.O.C.*, **18**: 15–30.
Liu, C.-M., Huang, C.-Y., Shieh, S.-L. and Wu C.-C. (1994a) Important meteorological parameters for ozone episodes experienced in Taipei basin. *Atmos. Environ.*, **28a**: 159–173.
Liu, C.-M., Liu, S.-C. and Shen, S. H. (1990) A study of Taipei ozone pollution. *Atmos. Environ.*, **24A**: 1461–1472.
Liu, S.-C., McKeen, S. A. and Madronich, S. (1991) Effect of anthropogenic aerosols on biologically active ultraviolet radiation. *Geophys. Res. Lett.*, **18**: 2265–2268.
Liu, C.-M., Sheen, K. C. and Young, C.-Y. (1995) A preliminary study on the effect of aerosols on the surface visibility in Tainan. *Meteorol. Bulletin*, (accepted for publication).
Liu, C.-M., Tsay, Y.-W., Tso, T.-L., Lo, J.-G. and Liu, S.-C. (1994b) The relationship between the hydrocarbon composition and the surface ozone production. *Atmos. Sci.*, **22**: 431–453.
Lo, J.-G., Chen, T.-Y. and Tso, T.-L. (1994) Improved resolution and determination of ambient C_5-C_{12} hydrocarbons by GC-coupled refocussing system. *J. Chromatog.*, **38**: 151.
Lonneman, W. A., Kopczynski, S. L., Darley, P. E. and Sutterfield F. D. (1974) Hydrocarbon composition of urban air pollution. *Environ. Sci. Technol.*, **8**: 229–236.
Lonneman, W. A., Sella, R. L. and Meeks, S. A. (1986) Non-methane organic composition in the Lincoln Tunnel. *Environ. Sci. Technol.* **20**: 790–796.
Louw, C. W., Richards, J. F. and Faure, P. K. (1977) The determination of volatile organic compounds in city air by gas chromatography combined with standard addition, advective subtraction, infrared spectrometry and mass spectrometry. *Atmos. Environ.*, **11**: 703–717.
Middleton, W. E. K. (1963) *Vision through the Atmosphere.* University of Toronto Press, Toronto, Canada
National Research Council (1991) *Rethinking the Ozone Problem in Urban and Regional Air Pollution.* US NRC, 489 pp.
Nelson, P. F. and Quigley S. M. (1982) Non-methane hydrocarbons in the atmosphere of Sydney, Australia. *Environ. Sci. Technol.* **16**: 650–655.
Pilar, S. and Graydon, W. F. (1973) Benzene and toluene in Toronto atmosphere.. *Envir. Sci. Technol.*, **7**: 628–631.
Rasmussen, R. A. (1976) What do hydrocarbons from trees contribute to air pollution? *J. Air Pollut. Control., Ass.*, **22**: 537–543.
Roberts, J. M., Fehsenseld, F. C., Liu, S. C., Bollinger, M. J., Hahn, C., Albriton, D. L. and Sievers, R. E. (1984) Measurements of aromatic hydrocarbon ratios and NO_x concentration in the rural troposphere: Observation of air mass photochemical aging and NO_x removal. *Atmos. Environ.*, **18**: 1125–1132.
Russell, A., Milfoed, J., Bergin, M. S., McBride, S., McNair, L., Yang, Y., Stockwell, W. R. and Croes, B. (1995) Urban ozone control and atmospheric reactivity of organic gases. *Science*, **269**: 491–495.
Sexton, K. and Westberg, H. (1984) Nonmethane hydrocarbon composition of urban and rural atmosphere. *Atmos. Environ.*, **18**: 1125–1132.
Shettle, E. P. and Fenn, R. W. (1979) *Models for Aerosols of the Lower Atmosphere and the Effects of Humidity Variations on their Optical Properties.* AFGL-TR-79-0214. Air Force Geophysics Laboratory, Hanscom AFB, Massachusettes, USA.
Siddiqi, A. A. and Worley, F. L. (1977) Urban and industrial air pollution in Houston, Texas. I. Hydrocarbon. *Atmos. Environ.*, **11**: 131–143.
Stamnes, K., Tsay, S., Wiscombe, W. and Jayaweera, K. (1988) Numerical stable algorithm for discrete-ordinate-method radiative transfer in multiple scattering and emitting layered media. *Applied Optics*, **27**: 2502–2508.
Trainer, M., Hsie, E. Y., McKeen, S. A., Tallamraju, R., Parrish, D. D., Fehsenfeld, F. C. and Liu, S. C. (1987) Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site. *J. Geophys. Res.*, **92**: 11879–11894.

Trijonis, J. C., Malm, W. C., Pitchfold, M. and White, W. H. (1990) *Visibility in Existing and Historical Conditions-Causes and Effects.* NAPAP (National Acid Precipitation Assessment Program), report 24–200 pp.

Tsay, Y.-W. (1993) *Important Factors Affecting The Photochemical Production of The Surface Ozone in Taipei and Kaoshoung.* M. S. Thesis, Department of Atmospheric Sciences, National Taiwan University, Taipei, Taiwan, R. O. C. (in Chinese).

Tso, T.-L., Lo, J.-G. and Liu, C.-M. (1991) *Development of Reactive Air Quality Model: Study of Plume Model.* EPA-81-F102-09-04, EPA, R.O.C. (in Chinese).

Uno, I., Wakamatsu, S., Wadden, R. A., Konno, S. and Koshio, H. (1985) Evaluation of hydrocarbon reactivity in urban air. *Atmos. Environ.*, **19**: 1283–1293.

Young, C.-Y. and Liu, C.-M. (1995) Analyses of several ozone episodes in Taiwan (1993–1994). (submitted to *J. Environ. Protection Society of R.O.C.*).