Diagnostic Modeling of PAMS VOC Observation

SHENG-PO CHEN,† TSUN-HSIEN LIU,† TU-FU CHEN,‡ CHANG-FENG OU YANG,‡ JIA-LIN WANG,† AND JULIUS S. CHANG*†

Institute of Atmospheric Physics and Department of Chemistry, National Central University, Taiwan

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Although a number of gas-phase chemical mechanisms, such as CBM-IV, RADM2, and SAPRC have been successful in studying gas-phase atmospheric chemical processes, they all used different combinations of lumped organic species to describe the role of organics in gas-phase chemical processes. Photochemical Assessment Monitoring Stations (PAMS) have been in use for over a decade and yet it is not clear how the detailed organic species measured by PAMS compare to the lumped modeled species. By developing a detailed mechanism specifically for the PAMS organics and embedding this diagnostic model within a regional-scale transport and chemistry model, one can then directly compare PAMS observation with regional-scale model simulations. By means of this comparison one can perhaps better evaluate model performance. The Taiwan Air Quality Model (TAQM) was modified by adding a submodel with transport processes and chemical mechanism for interactions of the 56 species observed by PAMS. It is assumed that TAQM can simulate the overall regional-scale environment including time evolution of oxidants and radicals; these results are then used to simulate the evolution of PAMS organics with species-specific source functions, meteorological transport, and chemical interactions. Model simulations of each PAMS organic were compared with PAMS hourly surface measurements. A case study with data collected at three sites in central Taiwan showed that when meteorological simulations were comparable with observations, diurnal patterns of most organics performed well with PAMS data after emissions were corrected. It is found emissions of over half of the PAMS species require correction, some by surprisingly large factors. With such correlation, simulated time evolution of ratios of ethylbenzene/m,p-xylenes and ethane/n-butane showed similar behaviors as shown by observation data. From the results of PAMS organics diurnal variations as well as indicator ratios, one can conclude that PAMS Air Quality Model (PAMS-AQM) has been successfully developed and can be applied to the study of evolution of PAMS organics in regional and urban environments. Further, one finds that an existing VOC emissions estimation procedure heavily dependent on U.S.-data based emissions speciation factors is suspect in application in Taiwan and perhaps in other countries as well. A protocol, using PAMS-AQM for testing consistency between detailed VOC emissions and PAMS observations, has been developed and demonstrated.

1. Introduction

In regional-scale or urban-scale air pollution, ozone formation by photochemical interactions from its precursors, NOx (NO + NOy) and volatile organic compounds (VOCs), has been well-documented (1–4). A number of useful models have been developed for various applications from research to regulatory use (5–8). Evaluation of model performance involves comparison of model simulated species mixing ratios with corresponding observations. NOx observations are direct and comparison of model simulation with observation is straightforward although not always simple. Uncertainties in measurement (such as nitrate interference of NO2 measurement) and model resolution (thickness of the lowest vertical levels and inability to resolve source-rich urban locations) all lead to complications in using grid model simulation. But validation of simulated VOCs with observation has been far behind that of NOx for a long time.

For many years, there have not been enough data of atmospheric organics due to thousands of compounds emitted to the atmosphere; only a small number have been investigated by comparing observations and model simulations at a few sites for a limited time (9–12). Only the lumped total amounts of organics (nonmethane hydrocarbons, NMHC) have been monitored at air quality stations regularly over extended period. Using NMHC data for VOC validation is not sufficiently sensitive if one is to understand the details of oxidant formation. Urban- and regional-scale chemical transport models, to save computing resources, use tens of grouped species to stand for hundreds of organics in the environment in their chemical mechanism (13–17). But very few of them can be compared directly with any of the limited observations.

Since 1990, Photochemical Assessment Monitoring Stations (PAMS) for ozone and its precursors, especially for VOCs, have been developed. Since then relatively large number of organics compounds have been systematically monitored in the U.S. (18). In Taiwan, PAMS have been in use since 2001. Even though more data are collected, there are still only 56 species (list of species can be found in the Supporting Information), and these species cannot be grouped together to be comparable with any individual grouped species in the most often used gas-phase chemical mechanisms (13–17). For example, the second generation Regional Acid Deposition Model (RADM2) chemical mechanism (13) has 37 grouped VOC species. HC3 is one such grouped organics representing slow reactivity alkanes (other than methane and ethane) and alcohols. For PAMS observed organics, there are only five species that can be included in HC3: acetylene, propane, isobutane, n-butane, and 2,2-dimethylbutane, and other species such as methanol, et al., are not included in PAMS species. These five species constitute, by emission weighting (w/w), approximately 4%, 3%, 6%, 30%, and 1% of HC3, respectively, based on emissions data for Taiwan, adding to a total fraction of 44%. Therefore the correspondence of HC3 with PAMS measurement is rather tenuous; no direct comparison is possible. In all, the PAMS observed 56 organics are only parts of 10 lumped VOCs in RADM2 mechanism. Similar situations are true for CBM-IV and SAPRC mechanisms and the newer CBM-V and RACM2 mechanisms.

At present most research related to PAMS observations is on monitoring technique (19, 20) or data analyses (21–23).
Harley and Cass (24) conducted the first study with limited canister data (compared to PAMS data) collected over selected days in southern California. They expanded the Lurmann mechanism to include 53 resolved VOCs and lumped the rest. Based on data from 4–10 data points over two days for the 53 species showed gross errors of 37–90% in comparison. For most species a normalized bias of less than ±50% was achieved for one of the days. Biswas et al. (25) used CBM-IV mechanism to model the variations of four PAMS species that correspond best to simulated species. But they focused more on the intermodel differences and relative importance of different control processes within the models. No direct comparison of PAMS observation with model simulations was shown or discussed. Seigneur et al. (26) modified the existing CBM-IV mechanism within CMAQ to study specifically atmospheric benzene and the role of diesel emissions and particulates. This study did include direct comparisons of model-simulated surface benzene time series at several PAMS sites. Their focus was on diesel particulates and not on the implication of the comparison of benzene results. Doraiswamy et al. (27) summarized PAMS organic observations corresponding to their CBM-IV groups and compared with lumped VOCs simulations individually. But their comparison protocol is heavily dependent on the assumed relative weighting of individual species within each lumped group not a direct comparison of individual species. Further, present study showed that, at least for Taiwan, many weighting factors based on existing emissions estimates are very much in error.

The objective of this study is to design one chemical mechanism (PAMS diagnostic chemical mechanism) suitable for diagnostic study of PAMS observed organics and embed it into a regional-scale chemical transport model. This PAMS Air Quality Model (PAMS-AQM) is then used to interpret and analyze PAMS observations and improve air quality modeling of volatile organics in the atmosphere.

2. Research Procedure and Simulation Designs

2.1. PAMS-AQM Development. To simulate the distribution and time evolution of PAMS organics in a regional-scale chemical transport model, one needs to develop a new gas-phase chemical mechanism or alternatively modify existing mechanisms appropriately. Both approaches will take considerable effort and require verification of the new mechanism with a large set of environmental chamber data (13, 28, 29). Because all existing gas-phase mechanisms use lumping of selected volatile organic compounds to varying degrees, very few PAMS organics are explicitly represented in any widely used mechanisms. For example, RADM2 mechanism has only three individually represented species (ethane, isoprene, and ethylene) among all PAMS measured organics. All the other species of PAMS organics can be grouped into 7 RADM2 lumped VOC species (30, 31). Unfortunately, for all these, PAMS measured species represented only portions of each lumped VOCs. Each RADM2 lumped VOCs includes many other species. Therefore both approaches to developing a new gas-phase mechanism suitable for analysis of PAMS measurements are tedious and perhaps unnecessarily complicated.

A third approach can be developed. In so far as RADM2 chemical mechanism has been verified by comparison with many smog chamber experiments and its use in regional-scale chemistry and transport model has also been found useful through many comparisons with atmospheric observations of oxidants and even radicals (13, 28, 29, 32–34), one can use it to simulate atmospheric oxidants and radicals. The oxidation reactions of PAMS VOCs can be used in parallel to calculate the depletion of those VOCs. This will leave the original mechanism and emission inventory unchanged and no products from the PAMS VOCs are needed since they are already treated in the original mechanism in a surrogate manner. This specialized PAMS submechanism can then describe the chemical transformation of PAMS organics and by adding the influence of other physical processes such as transport, mixing, and dry deposition one then has a diagnostic submodel for tracking the evolution of PAMS organics in the atmosphere (see Supporting Information for details of PAMS diagnostic chemical mechanism and PAMS-AQM model development).

2.2. Experimental Design. PAMS has been in use in Taiwan since 2001. Initially a sequence of three stations was set up in central Taiwan (see Figure 1). The first site, Chonglun, is located at the center of a major city (Taichung) as an upwind site sitting among urban sources, and the other sites, Tsaotun and Jhushan, are downwind transition site and maximum ozone mixing ratio site, respectively. The distance from Chonglun to Jhushan is about 40 km. All PAMS sites are either close to regular air quality stations with hourly trace gases and meteorological measurements by Taiwan EPA (Jhongming site neighbors Chonglun site within the same city park, and Nantou site neighbors Tsaotun site within the same urban area about 8 km away) or colocated with a regular air quality station (Jhushan). Hereafter these stations will be identified by the names of the PAMS stations to minimize
confusion. PAMS data from the first year and operational details were reported by Yang et al. (23). A well-used time period, April–May of 2003, is used as a first test for PAMS-AQM; Chiang et al. (35) analyzed the influence of Asian continental outflow on northern Taiwan air quality. The 5-day period of May 20–24, 2003 is used to assess the performance of PAMS-AQM. During this period there is a general upwind–downwind relationship among the three PAMS sites.

This 5-day period was in early summer season with a high-pressure system on the Asian continent moving easterly to the Pacific Ocean. Diurnal variations of temperature at three sites were similar, with the highest temperature about 33.7 °C and the lowest temperature about 22.3 °C, namely a photochemically active, hot, and cloudless period. Wind speeds at Chonglun and Tsaotun are familiar species such as benzene, toluene, and m,p-xylene. Triangles are observation data and solid lines are the corresponding simulation results. The date makers (e.g., 23 May) are at local time 8 a.m. of the day so indicated. The vertical scale shows the mixing ratios of all species in ppbC unit. Clearly, there are diurnal changes and day-to-day variations in all observations. Diurnal changes are due to photochemistry and daily emission patterns. The multiday variations in each species are probably due to variations in meteorological transport.

After sunset, HO radical had disappeared and soon after that O₃ also reached a daily minimum that means nearly all photochemical reactions for PAMS organics had ceased. With steady emissions and stable boundary layer, surface mixing ratios should show a nearly linear growth as is seen in all the figures for the evening hours for most the days and especially clearly for the first day (nearly linear increase after sunset of May 20). This nearly linear growth is clear for the source region. For a remote site such as Jhushan it will not be so obvious unless there are strong local sources for some specific organics. This growth pattern would also be different if wind direction changed from the normal patterns such as on the night of May 22 at Chonglun and one can see clearly the difference in time evolutions of many of the observed mixing ratios for the short period from midnight May 22 to the morning of May 23 at Chonglun. This change in observed time pattern in PAMS organics associated with distinct wind direction is a clear signal that needs to be duplicated by model simulation. It will be a true challenge for the model to simulate these detailed changes in observations.

Figure 2 shows that benzene and toluene are simulated well for the whole 5-day period, capturing the after-sunset build up of each species and the impact of one night having different wind direction variations on May 22. But the other two species shown in Figure 2 are grossly underestimated. Figure 3a shows comparison of corresponding time series of four species at Chonglun. It illustrates the four possible outcomes of this type of comparison—comparable, under-estimated, overestimated, and no comparison (no emissions estimate in the database). For this case study, time series of 17 of the 55 species simulated at Chonglun are found to be comparable to observations; 26 species are underestimated; 10 species are overestimated; and 2 have no source functions in the original emissions database. 2-Methyl-1-pentene was not observed by PAMS in this area, hence only 55 species are available for comparison. As was discussed earlier, for the initial period after sunset on May 20 all species build-ups are due to emissions only. Differences shown in Figure 3a indicated strong errors in model emissions for at least 36 species. Of course, this is for certain only for this particular time period. With this in mind one can suitably rescale the underestimated and overestimated time series from PAMS-AQM simulation (note the scale changes on the right side of Figure 3b). Figure 3b shows that with this rescaling, diurnal and multiday variations for both underestimated and overestimated species are now comparable to observations. This
further supports the conjecture that emissions derived from TEDS for most of the PAMS species are in error. To quantify this error and correct it, calculated correlations of observation and PAMS-AQM simulation for each species at Chonglun were analyzed as this site is most clearly a source site. The slope of the linear best-fit curve of each correlation, made by Pearson product–moment correlation, comparison was used as the correction coefficient for that species. Table S4 in Supporting Information shows all the correction coefficients. Correction factors ranged from 0.06 to 34. For the two species with no emissions data the source function of their isomers were used as one expects them to be from the same industrial processes.

3.2. Evaluation of PAMS Species Emissions. Figure 4 shows the comparison as in Figure 3a where the green curves are the time series derived with modified emissions and red curves are original simulation results. It is clear that significant improvement has been achieved. Recalculation of the scaling coefficients showed a range of 0.93–1.18, except for five species including the two with emissions estimated from their isomers. For these because the original emissions appear to be very uncertain, scaling of emissions only adds to the uncertainty. Since Chonglun is the site where emissions modification were derived one can expect improved simulations but one must consider the changes at other two stations. Here and in all following discussions while comparisons of all individual species are not shown, the selected comparisons do cover the overwhelming majority of the comparison findings. One exception to this general conclusion is isoprene comparison. Chonglun site is in the middle of a city park, i.e., in a sea of semitropical plants emitting isoprene. But the isoprene emissions estimate is for an average city environment. Therefore it is not possible for PAMS-AQM to simulate isoprene observation at Chonglun. For the other two sites, comparison of model simulation and observations of isoprene followed the general pattern of the other species. Figure 5a shows time evolutions of m,p-xylene at all three PAMS sites. Although PAMS species emissions were modified according to data only at the one source site, model simulations at Tsao-tun and Jhushan sites also had better performance with observations (green curves in contrast to the red ones). Figure 5b shows similar comparison of a previously overestimated species, cyclohexane, at all three sites. The significant improvement at Chonglun is as expected. The improvement at the remote site, Jhushan, is very notable. But at the intermediate site Tsao-tun, the original simulation appears to be much better than the new simulation results. This means that at this site the balance among point, line, and area sources is different from that at Chonglun. In fact a closer examination reveals that at Tsao-tun line sources (traffic sources) dominate, contribute over 75% of cyclohexane emission, and is mostly from diesel trucks while at Chonglun over 53% of the emissions are from area sources. Table S5 in Supporting Information shows the relative contributions of source function types of representative species. One sees that indeed there are strong local differences. Therefore there are no “universal” corrections suitable for large areas. Ideally, one must go back to the original data and reassess the complete VOC emissions database. The correction method used here merely serves to prove that general corrections are needed and emissions errors are the most critical factors in diagnostic interpretation of PAMS observations.

Sometimes the source of error can be ascertained easily. Propane emission is one such example. A close examination of TEDS emissions estimation procedure reveals that TEDS uses speciation factors from U.S. EPA compilation of air pollution emission factors (AP-42). In the U.S., home fuel use was almost all methane, therefore the emissions factor associated with home fuel use is 90% methane. But in Taiwan, a majority of household fuel is propane, therefore fuel use source function should be mostly propane. If one makes this correction to area source of propane then at Chonglun the overall correction factor should be 4.83 and at Tsao-tun should be 4.68. Both are close to the value of 4.84 used in the modified simulation. At Jhushan the overall correction factor is estimated to be 4.07. Indeed the comparison with measurements...
at Jhushan showed considerable overestimate. This likely is due to overestimation of area sources in the original data.

### 3.3. Evaluation of Diurnal Averages of PAMS Species

If one averages the diurnal variations of each PAMS species one can obtain a rough estimate of the influence of atmospheric transport on PAMS species mixing ratios. The diurnal averaged mixing ratios are equivalent to nonreactive tracers in the simulation. Correlation coefficients ($R^2$) of the
full set of individual daily averaged values of model and observation are 0.96, 0.91, and 0.92 at Chonglun, Tsaotun, and Jhushan sites, respectively. It reveals that PAMS-AQM simulation correlated well with observations although there are some slight differences among these stations. At the three sites the five-day average of the total PAMS VOCs are 245, 200, and 37 ppbC, respectively. The corresponding PAMS-AQM simulated values are 198, 109, and 54 ppbC. The single largest contributor to these differences is the error in toluene emissions. At all three sites errors in toluene alone contributed to 40–50% of the total uncertainty. From Figure S1 of the Supporting Information one can see that when wind directions are consistent for extended periods then simulation results are in good agreement with observations (at Chonglun site) but when the observed winds fluctuate on an hourly basis then simulations become very difficult (mostly at the other two sites). For the sake of completeness Table S6 in Supporting Information shows the standard statistical measures of comparisons. All averages are within ±45% of the corresponding averages of observations, with Chonglun site showing the best agreement of better than 80%. It is clear that away from urban sites, estimations of emissions are indeed very uncertain. Ongoing study with observations at other newer PAMS sites in Taiwan and for more diverse time periods is expected to shed some new light.

3.4. Comparisons of Indicators for the Relative Age of Air Mass. Another independent test of model performance is to compare certain ratios of species mixing ratios derived from observation and simulation results. As was pointed out (39–42), if two atmospheric chemical species were released at the same location into the same air mass then their ratio within this air mass will change only according to their relative rate of chemical transformation and not be affected by atmospheric mixing and transport. Of course this assumes that there is no significant encounter with new sources along the path of this air mass. For the present, among the 56 PAMS species, ratios of ethylbenzene and m,p-xylenes as well as ethane and n-butane are two such indicator ratios (39, 43). One can compare the time evolution of these indicator ratios at the three observation sites. This is a rather stiff challenge as one must have the correct reaction mechanism and transport and mixing history to have comparable time series of ratios at the three sites. The agreement in the time evolution of the indicator ratio values between measured and simulated results is a strong indication that the changing contributions of various physical and chemical processes were correctly modeled.

The atmospheric chemical lifetimes of m,p-xylenes, ethylbenzene, n-butane, and ethane are about 0.5 day, 2 days, 6 days, and 2 months, respectively. When the ratios of ethylbenzene/m,p-xylenes and ethane/n-butane are low then the air mass is relatively fresh and conversely when they are high then the air mass is aged unless there are fresh local emissions for the species in the numerator of the ratio in discussion. Figure 6 shows the five-day time series of the indicator ratios of ethylbenzene/m,p-xylenes and ethane/n-butane at the three PAMS sites in central Taiwan. Because there were many hour-to-hour fluctuations, the cause(s) of which are unlikely to be included in any model, three-hour running averages were used in this comparison. For ethylbenzene/m,p-xylenes indicator ratio, original and modified PAMS-AQM results had similar magnitudes and day-to-day variations with observations except for a few short time periods. Averages of the modeled ethylbenzene/m,p-xylenes ratio at three sites were about 0.33, 0.54, and 0.73, comparable to the corresponding ratios of about 0.39, 0.57, and 0.53. As is clear from Figure 6a, at Jhushan the difference of 0.73 and 0.53 in simulated and observed ratios is due to the difference of the baseline, i.e., probably due to an error in the relative source strengths of ethylbenzene/m,p-xylenes. Ethylbenzene/m,p-xylenes ratios of PAMS-AQM simulations with modified emissions were almost equal to the original simulations because emissions for these two species were modified about the same. Note that during the daylight hours this ratio was
consistently underestimated by the model but at nighttime the agreement between model and observation was excellent at Chonglun and Tsaotun. As the relative contributions of line sources at these sites were much smaller during the night, one can conclude that the overall fraction of line sources of these two species was not correct from TEDS data file.

For ethane/\(n\)-butane, PAMS-AQM results with modified emissions are in much better agreement with observation.
FIGURE 6. Diurnal patterns of (a) ethylbenzene/m,p-xylene and (b) ethane/n-butane three-hour running averages at three PAMS sites (labeled at LT 8:00, black lines with triangles are observations, red and green lines are original simulations and simulations with modified emissions, respectively).
than the simulation with original emissions. Figure 6b shows the original simulations (red curves) are at least a factor of 5 off the ratio derived from observations. After emissions were modified, PAMS-AQM gave ratios (green curves) of ethane/n-butane that are in good agreement at Chonglun and reasonable agreement at Jhushan. The overestimate at Tsaotun is probably due to errors in the original emission as the modification did not change the relative contribution of different sources only the overall strength. This significant change in comparison of ratios at Chonglun and Jhushan not only demonstrated the necessity for modifying emissions but also the power of PAMS-AQM in estimating regional behaviors of PAMS organics. In addition, each of these species was modeled accurately showing that the agreement in ratios was derived for correct reason.

The performance at Tsaotun site is also understandable. As airmass moves away from the source site this ratio will increase unless it encounters new sources. One sees that the observed average ratios at the three sites are 1.05, 0.73, and 1.51 going from Chonglun to Tsaotun and then to Jhushan. It is generally accepted that Chonglun is a source region and Jhushan is a rural location. The ethane/n-butane ratio of 0.73 strongly suggests Tsaotun is an even stronger source region than Chonglun. If this is so and given that the ratio was underestimated one expects stronger sources of n-butane at Tsaotun. An examination of the location of Tsaotun site showed that it is near the juncture of two very busy national expressways. With wind coming from any direction but the southeast observations will be strongly influenced by the traffic on these expressways. Emissions database has only the area average regional emissions not the near source real-time emissions. Therefore the underestimate of this ratio at Tsaotun is understandable.

3.5. Discussion of Findings. A major and very significant finding of this study is that detailed emissions of VOCs in the existing emissions database are often in error. With the new PAMS-AQM and PAMS observations one can assess the extent of these errors and make corrections. Although results from this study only strictly reflect the situation in Taiwan, but as the emissions estimation procedure used in Taiwan follows that of many other countries and all are, to differing degree, based on a procedure and database developed in the U.S., it does raise certain doubts on equivalent emissions data used in the U.S. and other countries. Because differences in societal development may leads to differences in VOC emissions pattern in a number of localities, the findings of this study, at the minimum, suggest the need for immediate re-examination of estimation procedures for VOC emissions for almost all countries using U.S.-developed protocols. In so far as no study of U.S. PAMS observations similar to the present study has been carried out, it is possible that diagnostic study using PAMS-AQM and PAMS observations in the U.S. may yield important results. It is to be noted that this is not suggesting that overall VOC (NMHC) is in error, because past successes of regional- and urban-scale AQMs in studying urban and regional oxidant variations have already proved the overall value of these models and the data they have used. It is the detail in speciation of VOCs and the use of PAMS observations for model validation that needs to be carefully conducted.

Supporting Information Available
Details of PAMS diagnostic chemical mechanism, PAMS-AQM model development, tables of comparison of daytime averages of selected chemical species, correlation coefficients of PAMS-AQM simulations with PAMS observations, comparison of relative contributions of source function types to emissions of selected species, statistic analyses of hourly averaged total PAMS observed species, and the figure of the comparison of wind field observations with simulation results. This material is available for free charge via the Internet at http://pubs.acs.org.

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