

Volatile Organic Compounds (VOCs) Emitted from Petroleum and their Influence on Photochemical Smog Formation in the Atmosphere

Hai Guo*

Air Quality Studies, Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hong Kong

Petroleum contains a wide variety of volatile organic compounds (VOCs). Due to their low boiling points, VOCs can be emitted to the atmosphere and immediately contaminate the air. More critically, it is well documented that VOCs are key ozone (O_3) precursors [1]. The main anthropogenic VOC sources include fuel used for motor vehicles, consumer products, various industrial processes, fossil fuel combustion and solvent usage. Most of the sources use products generated from petroleum.

Photochemical smog, characterized by high concentrations of O_3 and fine particles, is of great concern in many cities around the world. Although VOCs and NO_x have been confirmed as the key precursors of O_3 , the development of an effective strategy for reducing O_3 pollution in megacities is still problematic due to the non-linear dependency of O_3 formation on NO_x and VOCs [1,2]. VOCs as a group include many hundreds of species, and each one reacts at different rate and with a different reaction mechanism. Furthermore, they are also emitted into the atmosphere at different mass emission rates, depending on the local and regional industries, land-use and biogenic sources. Hence, it is important to figure out which VOC species have the highest influence on the O_3 formation. Without this knowledge we will not be able to formulate proper O_3 reduction strategy, i.e. which target pollutants need to be controlled.

As stated above, O_3 is produced by a series of complicated chemical reactions. In conjunction with this chemical production, O_3 concentration is also influenced by different physical processes such as advection, diffusion, deposition, emission processes and so on. It is not easy to obtain the inner relations among these processes and to identify which precursors dominate the O_3 formation solely by observation studies, due to the limited number of measurements available. Mathematical models are necessary and capable of integrating as many as environmental variables and pollutant species, to look at the potential mechanisms of O_3 formation, and give clue to identify the process mostly responsible for the O_3 formation. A variety of air quality simulation (AQS) models are available nowadays to study the O_3 formation from box models to three-dimensional chemistry and transport models, such as Weather Research and Forecasting-Chemistry model (WRF-Chem), the U.S. Environmental Protection Agency's Community Multi-scale Air Quality (CMAQ), observation-based model (OBM), and photochemical trajectory model (PTM).

One of the most important components in the AQS models is the chemical mechanisms that describe the formation of O_3 from VOCs and NO_x . The chemical mechanisms used in the WRF-chem include CBMZ, CBM4, RACM, and RADM2. The chemical mechanisms used in the CMAQ include CBM4, CB05, and SAPRC-99. All the chemical mechanisms mentioned above are condensed mechanisms, which use parameterizations to describe the general features of O_3 formation, and their sensitivity to emission controls. The aforementioned condensed mechanisms cannot provide information on the roles of individual

VOCs in the formation of O_3 and other secondary oxidants and aerosols. Nevertheless, the roles of individual VOCs in O_3 formation are quite important for VOC control strategy formulation, which is currently a big challenge for many cities. Therefore, other approaches need to be developed to describe the complex photochemistry of VOCs as explicitly as possible, leading to a vast number of VOC species and chemical reactions taken into account.

The widely used Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism describing the detailed degradation of a large number of emitted organic compounds and the resulting generation of O_3 and other secondary pollutants under conditions appropriate to the atmospheric boundary layer [3]. The MCM v3.1 describes the oxidation of 139 non-methane VOCs, which contains around 13,500 reactions involving 5,900 chemical species. Recently, a photochemical trajectory model (PTM) incorporated with the MCM mechanism for Europe, America and south China has been successfully developed. The PTM model can identify the contributions of individual VOC species and each source category to O_3 formation. This model has been applied to an intensive measurement dataset in south China for validation [4]. The results indicated the simulated diurnal variations and concentrations of O_3 were in good agreement with observed data ($R^2=0.78$, $P<0.05$) in the region, and alkanes and oxygenated organic compounds had relatively low reactivity, while alkenes and aromatics presented high reactivity in this region.

In addition to the PTM model, the O_3 formation was also simulated using an observation-based model (OBM) and validated the modeling results with measurement data. The OBM model, using measurements of ambient concentrations of O_3 and its precursors as input, is a helpful tool to compare and validate the results of PTM model. Furthermore, a comprehensive air quality model system (WRF-CMAQ) was also used to simulate an O_3 pollution event in many cities, which is also beneficial to the comparison of PTM model. The results of various models on the simulation of the two-month long dataset generally showed good agreement for O_3 variations. However, discrepancy between modeled and observed values for other air pollutants such as NO_x , CO and VOCs still exists, though the degree of discrepancy may be different from different models.

*Corresponding author: Hai GUO, Air Quality Studies, Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hong Kong, E-mail: ceguohai@polyu.edu.hk

Received December 28, 2011; Accepted January 11, 2012; Published January 13, 2012

Citation: Guo H (2012) Volatile Organic Compounds (VOCs) Emitted from Petroleum and their Influence on Photochemical Smog Formation in the Atmosphere. J Pet Environ Biotechnol 3:e104. doi:10.4172/2157-7463.1000e104

Copyright: © 2012 Guo H. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

As noted earlier, one reason for the discrepancy is probably the low resolution of the emission inventory of air pollutants used in the models. For instance, most previous modelling studies used the emission inventory developed by Street et al. [5]. The emission inventories used included TRACE-P 2001, INTEX-B 2006, and the PATH emission inventory. These inventories are either low resolved or out of date. Recently, highly resolved spatiotemporal emission inventories for some regions such as the Pearl River Delta of south China and Hong Kong have been developed by Zheng et al. [6,7] and Hong Kong Environmental Protection Department, respectively, which makes it possible to compare and validate the modeling results of different photochemical and transport models.

Therefore, in order to better identify the ozone-precursor relationships, and determine the VOC species and emission source categories which mostly contribute to regional scale O₃ formation, PTM model incorporating with explicit chemical mechanisms (MCM) and updated regional emission inventories should be used to compare and validate the existing long-term online measurement data and the simulation results of observation based OBM model. The results of the PTM and OBM models should be of help to the understanding of individual VOC species in photochemical smog formation and to the development of effective control strategies to the O₃ formation in many regions.

References

1. Cardelino CA, Chameides WL (1995) An Observation-Based Model for Analyzing Ozone Precursor Relationships in the Urban Atmosphere. *J Air Waste Manag Assoc* 45: 161-180.
2. Sillman S (1999) The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmospheric Environment* 33: 1821-1845.
3. Jenkin ME, Saunders SM, Pilling MJ (1997) The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmospheric Environment* 31: 81-104.
4. Cheng HR, Guo H, Saunders SM, Lam SHM, Jiang F, et al. (2010) Photochemical ozone formation in the Pearl River Delta assessed by a photochemical trajectory model. *Atmospheric Environment* 44: 4199-4208.
5. Streets DG, Bond TC, Carmichael GR, Fernandes SD, Fu Q, et al. (2003) An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. *Journal of Geophysical Research* 108: 8809.
6. Zheng JY, Shao M, Che W, Zhang L, Zhong L, et al. (2009a) Speciated VOC Emission Inventory and Spatial Patterns of Ozone Formation Potential in the Pearl River Delta, China. *Environ Sci Technol* 43: 8580-8586.
7. Zheng J, Zhang L, Che W, Zheng Z, Yin S (2009b) A highly resolved temporal and spatial air pollutant emission inventory for the Pearl River Delta region, China and its uncertainty assessment. *Atmospheric Environment* 43: 5112-5122.