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Application of photochemical indicators to evaluate ozone nonlinear chemistry and pollution control countermeasure in China

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HIGHLIGHTS

- O_3 sensitivity in China was studied using WRF-CALGRID.
- The transition values of H_2O_2/HNO_3 (0.16–0.40) and H_2O_2/NO_z (0.14–0.28) were calculated.
- *Ra* was defined, with the transition value of 1 to evaluate O_3 sensitivity.
- A new approach to quantify the transition values of indicators by *Ra* was proposed.
- NO_x- and VOC-sensitive regions in China were located.

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ABSTRACT

Ozone sensitivity in China was investigated by using a comprehensive three-dimensional air quality model system WRF-CALGRID. A real case and two cases with 35% emission reduction for either NO_x or VOC were conducted for the period of March in 2010. The simulation results of O_3 agreed fairly well with the observation data. Based on the meaning of O_3 sensitivity, the ratio *Ra* was defined, with the transition value of 1 to distinguish NO_x-sensitive region from VOC-sensitive region. With the aid of *Ra*, VOC- and NO_x-sensitive regions in China were preliminary located. The transition ranges for some photochemical indicators were quantified. Only those of H_2O_2/NO_z and H_2O_2/HNO_3 met the requirement that the 95th percentile VOC-sensitive value should be equal to or lower than the 5th percentile NO_x-sensitive value. 0.16–0.40 for H_2O_2/HNO_3 and 0.14–0.28 for H_2O_2/NO_z were adopted to distinguish different O_3 sensitivity in China. The results showed that the VOC-sensitive regions are primarily distributed over the urban centers and the developed industrial areas in eastern and southern China, while the NO_x-sensitive regions are mainly located in the remote areas of northern and western China. High correlation between *Ra* and indicators was found, and a new approach to quantify the transition values of indicators was proposed. These indicators can play an important role in the air complex pollution control of urban clusters over East Asia.

1. Introduction

Over the past decades, along with the rapid economic development and accelerated urbanization process, many areas of China are suffering from high levels of ozone (O_3) and fine particles ($PM_{2.5}$) pollution (Chan and Yao, 2008; Zhang, 2009; Ma et al., 2012). O_3 is the key species in atmospheric chemistry, and plays a significant role in the oxidation of many primary pollutants (Seinfeld and Pandis, 2006). In China, the photochemical smog with high level of O_3 pollution was first reported in Xigu petrochemical industrial zone of Lanzhou in 1970s (Tang et al., 1989). Nowadays, due to the industrial boom and the rapid increase of cars, photochemical smogs frequently deteriorate the atmospheric environment in the Beijing-Tianjin area, Yangtze River Delta (YRD) region

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and Pearl River Delta (PRD) region, especially in non-haze days. Consequently, the formation mechanism and the integrated prevention of regional O_3 pollution have become the popular topics of the environmental sciences (Wang et al., 2006; Tu et al., 2007; Chan and Yao, 2008; Guo et al., 2009; Ma et al., 2012; Ding et al., 2013).

In troposphere, O_3 formation is initiated by the photolysis of NO_2 at wavelengths less than 424 nm

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

$$O + O_2 + M \rightarrow O_3 + M. \quad (R2)$$

Reactions (R1) and (R2) are normally counterbalanced by the following reaction

$$O_3 + NO \rightarrow O_2 + NO_2. \quad (R3)$$

Consequently there is a photostationary state, and O_3 would not accumulate if no other species existed. As a matter of fact, HO_2 and RO_2 radicals from reactions of VOCs (volatile organic compounds) with OH can lead to the conversion of NO to NO_2 instead of O_3

$$RO_2 + NO + O_2 \rightarrow R'CHO + HO_2 + NO_2 \quad (R4)$$

$$HO_2 + NO \rightarrow OH + NO_2, \quad (R5)$$

where R′CHO represents the intermediate organic species. The aforementioned reaction sequences involving NO_x ($NO + NO_2$) and VOCs finally result in net O_3 production. Hence NO_x and VOCs are usually regarded as the major precursors of O_3, and to control O_3 pollution is to reduce their anthropogenic emissions (Sillman, 1999; Atkinson, 2000; Jenkin and Clemitshaw, 2000; Seinfeld and Pandis, 2006).

The relation between O_3 and its precursors is driven by complex nonlinear photochemistry. Therefore, the first step to make abatement strategies for O_3 is to confirm which reduced species may result in more O_3 loss. In the past, the model EKMA was applied to output the ozone isopleth plots, which illustrate peak O_3 during the afternoon as a function of NO_x and VOC mixing ratios, to identify two regimes with different O_3 sensitivity (NO_x- and VOC-sensitive regime) (Sillman, 1999). Nevertheless, the exact dependence of O_3 on NO_x and VOCs in isopleth plots varies greatly relying on modeling assumptions and conditions. Furthermore, the impact of VOC reactivity, the actual emissions and the complex meteorological fields are not taken into account in this approach. Consequently, it was used unsuccessfully in some studies (Chameides et al., 1988; Milford et al., 1989, 1994; Sillman, 1999).

In recent years, an increasing number of researchers have investigated O_3 sensitivity with the aid of some indicators, which were usually defined as the ratios of certain secondary photochemical products, including H_2O_2/HNO_3 (Sillman, 1995; Lu and Chang, 1998; Hammer et al., 2002; Sillman and He, 2002; Lam et al., 2005; Chen and Chang, 2006; Zhang et al., 2009b; Liu et al., 2010; Peng et al., 2011), $HCHO/NO_y$ (Sillman, 1995; Lu and Chang, 1998; Zhang et al., 2009b; Liu et al., 2010), O_3/NO_z (Sillman, 1995; Lu and Chang, 1998; Sillman et al., 1998; Sillman and He, 2002; Chen and Chang, 2006), H_2O_2/NO_z (Sillman et al., 1998; Chen and Chang, 2006), NO_z/NO_y (Lu and Chang, 1998), O_3/NO_y (Sillman and He, 2002; Stein et al., 2005; Liu et al., 2010; Peng et al., 2011; Miñarro et al., 2012), O_3/HNO_3 (Sillman and He, 2002; Chen and Chang, 2006; Peng et al., 2011), $H_2O_2/(O_3 + NO_2)$ (Zhang et al., 2009b; Liu et al., 2010), $HCHO/NO_z$ (Zhang et al., 2009b), and NO_y (Milford et al., 1994; Sillman, 1995; Lu and Chang, 1998; Vogel et al., 1999; Zhang et al., 2009b; Liu et al., 2010) etc. Based on atmospheric chemistry theory and chemical kinetics analysis, it is not difficult to prove that those species ratios have different values for NO_x- and VOC-sensitive regime (Sillman, 1995; Sillman and He, 2002). In addition, the involved species such as O_3, HNO_3, NO_y and H_2O_2 can be readily measured under the condition of current technology. It is feasible to study O_3 sensitivity by using the ratios of their observation values. Generally, the transition value of a certain indicator is firstly determined by models. Secondly, the observation values of the indicator are calculated from in-situ monitoring data. Finally, by comparing the observation values with the predicted transition value, NO_x- or VOC-sensitive O_3 chemistry is determined. The transition value only needs to be computed once. In the previous studies, both zero-dimensional (0-D) (Vogel et al., 1999; Hammer et al., 2002; Sillman and He, 2002) and three-dimensional (3-D) (Milford et al., 1994; Sillman, 1995; Lu and Chang, 1998; Sillman et al., 1998; Hammer et al., 2002; Sillman and He, 2002; Stein et al., 2005; Chen and Chang, 2006; Peng et al., 2011) models were applied. 3-D models exhaustively describe the emission, 3-D transport and diffusion, atmospheric chemical reactions, and deposition processes in the air. Their results are closer to reality and more acceptable. In China, works have seldom been done about the application of photochemical indicators to evaluate O_3-NO_x-VOC sensitivity. Lam et al. (2005) reported that the transition range for H_2O_2/HNO_3 could be 0.8–1 in Hong Kong. Running CAMx for four O_3 episodes in southern Taiwan, Peng et al. (2011) simulated the transition ranges of H_2O_2/HNO_3 (0.5–0.8), O_3/HNO_3 (10.3–16.2) and O_3/NO_y (5.7–10.8). Liu et al. (2010) assessed the O_3 sensitivity over China with the modified transition values of indicators only based on the previous studies.

In this work, 3-D air quality model system WRF-CALGRID was applied to simulate the concentrations of O_3 and relevant pollutants over East Asia for the period of March in 2010. A base case and two reduction cases with 35% abatement for either NO_x or VOC emissions were conducted. The transition values of H_2O_2/HNO_3 and H_2O_2/NO_z were calculated. Then, modeled values of H_2O_2/HNO_3 or H_2O_2/NO_z in each model grid were compared with the transition value to evaluate which precursor controlled O_3 production. Meanwhile, ratio of impacts from different precursors (*Ra*) was introduced to confirm the results from indicator analysis. A new approach to quantify the transition values of indicators was proposed. The results may help to make efficient emission reduction strategy to improve regional air quality.

2. Methodology

2.1. Model introduction

The 3-D air quality model system used in this study consists of WRF and CALGRID (WRF-CALGRID). WRF is a new generation of medium-scale weather forecast model and assimilation system. Lots of applications have indicated that it has a good performance in all kinds of weather forecasts, and has broad application prospects (Jiang et al., 2008). WRF provides off-line meteorological fields for the chemical transport model CALGRID. The original version of CALGRID(1.6b), which only contains gaseous chemistry, was constructed by the California Air Resources Board (Yamartino et al., 1992). The CALGRID used here was improved by us, and was incorporated with a thermodynamic equilibrium model ISORROPIA for inorganic aerosols (Nenes et al., 1998), a secondary organic aerosol model SORGAM (Schell et al., 2001), a natural emission model for O_3 precursors (Xie et al., 2007), and a simple aqueous-phase chemical mechanism. So far, the improved CALGRID has most characteristics of the third generation air quality model, and has successfully been applied in the research of regional air pollution (Xie et al., 2007, 2009).