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Exploring ozone pollution in Chengdu, southwestern China: A case study from radical chemistry to O_3-VOC-NO_x sensitivity

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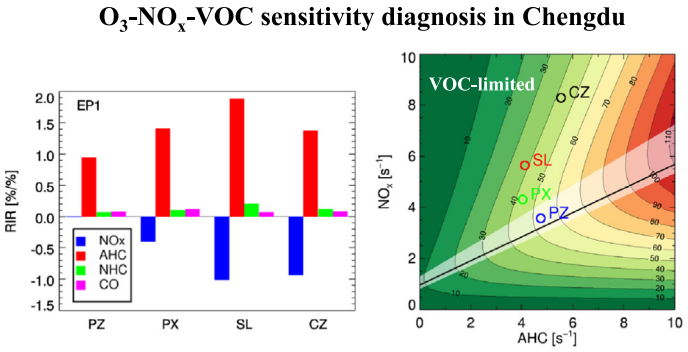
HIGHLIGHTS

- Ozone pollution is analyzed in Chengdu, southwestern China.
- High ozone concentrations were observed in early autumn.
- Fast ozone production is a result of favorable emission and solar radiation.
- VOC emission mitigation, especially alkenes, is of importance for ozone control.

GRAPHICAL ABSTRACT



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ABSTRACT

We present the in-situ measurements in Chengdu, a major city in south west of China, in September 2016. The concentrations of ozone and its precursor were measured at four sites. Although the campaign was conducted in early autumn, up to 100 ppbv (parts per billion by volume) daily maximum ozone was often observed at all sites. The observed ozone concentrations showed good agreement at all sites, which implied that ozone pollution is a regional issue in Chengdu. To better understand the ozone formation in Chengdu, an observation based model is used in this study to calculate the RO_x radical concentrations ($RO_x = OH + HO_2 + RO_2$) and ozone production rate ($P(O_3)$). The model predicts OH daily maximum is in the range of 4–8 × 10^6 molecules cm^{-3}, and HO_2 and RO_2 are in the range of 3–6 × 10^8 molecules cm^{-3}. The modelled radical concentrations show a distinct difference between ozone pollution and attainment period. The relative incremental reactivity (RIR) results demonstrate that anthropogenic VOCs reduction is the most efficient way to mitigate ozone pollution at all sites, of which alkenes dominate >50% of the ozone production. Empirical kinetic modelling approach shows that three out of four sites are under the VOC-limited regime, while Pengzhou is in a transition regime due to the local petrochemical industry. The ozone budget analysis showed that the local ozone production driven by the photochemical process is important to the accumulation of ozone concentrations.

1. Introduction

In the troposphere, ozone is a hazardous gas that can do harm to human skin, eyes and respiratory system and also to animals and plants,

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which was first discovered by Haagen-Smit and then accepted as the major cause of air pollution in Los Angeles Basin. Since then, photochemical smog has been widely observed in the megacities and petrochemical industrial regions in the United States, Europe, and Eastern Asia (Hidy, 2000; Kleinman et al., 2000; NRC, 1991). In recent years, air pollution events happened more frequently in China, which has attracted public attention. Fine particle is of most concern recently, especially during winter. However, ozone is becoming another critical air pollution issue. In fact, the primary pollution has been reduced by stronger emission mitigation but ozone concentrations still increased. The increasing trend for ozone regardless of the reduction in precursors highlights the difficulty in secondary pollution control (Wang et al., 2017; Yue et al., 2017). A field study performed in North China found that summertime ozone concentrations increased by about 2 ppbv/yr from 2003 to 2015, even given the reduction of NO_x emissions since 2012 (Sun et al., 2016). Recent studies show that ozone is becoming a critical air pollutant in megacities, where a large population is located. In Beijing, the summer ozone concentrations increased from 1982 to 2011 (Shao et al., 2006; Zhang et al., 2014). The mean ozone concentrations in Pearl River Delta were determined to be increased by 0.9 ppbv per year from 2006 to 2011 (Li et al., 2014) and >200 ppbv ozone were also reported frequently (Lu et al., 2010; Xue et al., 2016; Zhang et al., 2007; Zhang et al., 2008). The reduction of NO_x is believed to be of importance to control fine particle pollution because nitrate has become the dominant contributor to the fine particle (Guo et al., 2014; Huang et al., 2014). Given the strong reduction in NO_x to control particle pollution in the future, ozone pollution in the four large city clusters in China (e.g. Jiang et al., 2018) could arise at the beginning of the NO_x control because of the drawback of NO_x reduction. Many studies have been performed to investigate the O_3-VOC-NO_x sensitivity in the eastern part of China (An et al., 2015; Cheng et al., 2010; Geng et al., 2008; Ou et al., 2016; Pan et al., 2015; Shao et al., 2009; Xue et al., 2014; Zhang et al., 2014). To our knowledge, only a few studies reported in two cities in the west part of China (Su et al., 2018; Xue et al., 2014). Ozone pollution was as serious as in the cities in eastern China, because of similar fast economic growth and urbanization.

We present the in-situ measurements in Chengdu in September 2016. Chengdu is the capital of Sichuan province and is one of the largest cities in the southwest of China. Chengdu is located in Sichuan Basin which is separated by the Longquan Mountains into two parts, namely west and east parts. Chengdu is fenced by the Longmen Mountains to the east side and surrounded by mountainous terrain to the south and north. Therefore, slow wind and even stagnant meteorological conditions are frequently observed in Chengdu, which lead to accumulation of air pollutants and even severe air pollution events at the regional scale. Only little analysis has been performed to analyze the ozone pollution in the Chengdu. The early studies focused on the concentrations levels (Yuan et al., 2003) and meteorological role in pollution formation (Yang, 2004). Recently, the temporal and spatial distribution of ozone is studied based on observational data set, which reveals the serious ozone pollution in the urban area. Also, the relation between ozone and its precursors was analyzed preliminarily (Qian et al., 2011). Although high temperature and strong solar radiation in summertime are both favors to ozone production, it is also the rainy season in Chengdu, which suppresses the pollutants accumulation by raindrop washout effect. However, the ozone pollution in autumn is more serious because it is a dry season and meteorological conditions still favor to photochemical reactions, while nearly few studies reported during this period.

In this study, measurements of ozone and its precursors are presented at four different field sites in Chengdu in autumn. The temporal and spatial distributions are discussed based on observational data. Furthermore, an observation based model is used to study the relation between ozone and precursors from the perspective of OH-HO_2-RO_2 radical chemistry. The controlling factors of ozone pollution are discussed. Finally, the ozone pollution control strategy is proposed for the near future.

2. Methods

2.1. Field sites and instrumentations

This study presents the results from a filed campaign in Chengdu in 2016 (from 3 September to 2 October). Four stations were set up along the dominant wind direction with comprehensive instruments to capture the chemical and meteorological conditions. As shown in Fig. 1, Pengzhou (PZ) and Pixian (PX) are upwind areas of city center, while Shuangliu (SL) is located in the downwind area of city center. An urban site (Chengzhong, CZ) was set up to represent the urban condition. Pengzhou is characterized by industry region with a petrochemical complex, although located in the upwind of downtown. Because Chengdu is in the southwest part of China (104°E), the local solar time is about one hour later than Chinese National Standard Time (CNST). The CNST is used in this study. The sunrise and sunset were at 07:30 and 20:30 CNST, respectively.

In all sites, similar instrumentations were deployed. Table 1 summaries the measured trace gas compounds and measurement principles. Ozone was measured by UV absorption method using the Thermo O_3 analyzer (Model 49i). The NO_2 measurement was performed by the chemiluminescence after chemical conversion to NO. The Molybdenum catalyst was used to convert NO_2 to NO, which is well known to be interfered by other NO_z species. CO was measured by the Infrared absorption using Thermo instrument (Model 20). All Thermo instruments were maintained carefully and calibrated at 01:00 every day. Speciated VOC measurement was performed by the GC–MS/FID. The instruments were calibrated using the full set of standards before and after the campaign, which showed stable sensitivity deviated in the range of 10% to 20% for all measured species (Table S1). The VOCs instruments were also daily calibrated for a few important VOC species (Bromochloromethane, 1,4-Dichlorobenzene, Chlorobenzene, and Fluorobromobenzene) to ensure the stability of the instrument.

The photolysis frequencies were calculated by the TUV model, which is corrected for clouds based on satellite data provided by European Centre for Medium-Range Weather Forecasts (ECMWF). Because all stations are located within 30 km, less than the resolution of the ECMWF data, the same correction is applied to all stations. We performed sensitivity tests the impact of aerosol on photolysis frequencies due to light extinction. The AOD data measured by Aeronet were used to as an input for the TUV model, the reduction in photolysis frequencies was only 4%.

2.2. The model

An observation based box model is used in this study to simulate the formation of ozone. The model is based on Regional Atmospheric Chemical Mechanisms version 2 (RACM2) updated with detailed isoprene oxidation mechanism. Detail can be found in Tan et al. (2017) and the reference therein. The model runs were constrained by O_3, NO_2, CO, VOCs (VOC species and assignment to RACM2 were listed in Table S1), photolysis frequencies, ambient temperature, RH, and pressure, which were averaged or interpolated (only VOCs) to a time resolution of 5 min for the model constraints. The modelled uncertainty is about 40%, including the uncertainties in the measurements used as model constraints and reaction rate constants. A series of tests based on Monte Carlo simulations show that the uncertainty of the model calculations is approximately 40%. The ozone budget is analyzed using the box model. Furthermore, relative incremental reactivity and empirical kinetic modelling approach are performed to elucidate the controlling factor of ozone production in Chengdu.

2.2.1. Local ozone production

In the troposphere, ozone is produced in the reaction between VOCs and NO_x under sunlight. In the atmosphere, it is a low temperature "combustion", which is driven by the atmospheric radicals (RO_x = OH