Surface O_3 photochemistry over the South China Sea: Application of a near-explicit chemical mechanism box model[☆]

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ABSTRACT

A systematic field measurement was conducted at an island site (Wanshan Island, WSI) over the South China Sea (SCS) in autumn 2013. It was observed that mixing ratios of O_3 and its precursors (such as volatile organic compounds (VOCs), nitrogen oxides ($NO_x = NO + NO_2$) and carbon monoxide (CO)) showed significant differences on non-episode days and episode days. Additional knowledge was gained when a photochemical box model incorporating the Master Chemical Mechanism (PBM-MCM) was applied to further investigate the differences/similarities of O_3 photochemistry between non-episode and episode days, in terms of O_3-precursor relationship, atmospheric photochemical reactivity and O_3 production. The simulation results revealed that, from non-O_3 episode days to episode days, 1) O_3 production changed from both VOC and NO_x-limited (transition regime) to VOC-limited; 2) OH radicals increased and photochemical reaction cycling processes accelerated; and 3) both O_3 production and destruction rates increased significantly, resulting in an elevated net O_3 production over the SCS. The findings indicate the complexity of O_3 pollution over the SCS.

1. Introduction

Tropospheric ozone (O_3), a major constituent of photochemical smog, is of great impact on atmospheric chemistry, human health and climate change (NRC, 1991; NARSTO, 2000; Seinfeld and Pandis, 2006). Ozone pollution is a complex phenomenon since it involves precursor emissions, photochemical formation and dynamic transport on different scales (Jacob, 1999; Guo et al., 2017). With the rapid urbanization and industrialization, the Pearl River Delta (PRD) region has been experiencing severe O_3 pollution over the past decades (Chan et al., 1998a, b; Ding et al., 2004; Zhang et al., 2007). The maximum hourly O_3 mixing ratio frequently exceeds national air quality standard (100 ppbv), mainly attributed to the elevated emissions of local precursors and regional/super-regional transport of O_3 and its precursors from other parts of China (Wang et al., 2003; Guo et al., 2009, 2013). Previous studies found that O_3 precursors such as volatile organic compounds (VOCs) and nitrogen oxides ($NO_x = NO + NO_2$) emitted in urban areas can travel to the downwind rural areas or oceanic areas, enhancing the photochemical O_3 formation in these areas (Finlayson-Pitts and Pitts, 1993; Solberg et al., 2004). Ozone photochemistry in the PRD region has been documented, including VOC speciation and abundance (Lee et al., 2002; Guo et al., 2006, 2007, 2011; Liu et al., 2008; Ou et al., 2015), in-situ photochemical O_3 production (Zhang et al., 2007; Lyu et al., 2016a; Wang et al., 2017a), process analysis of regional O_3 formation (Wang et al., 2003, 2010; Zhang et al., 2008; Guo et al., 2009; Jiang et al., 2010; Cheng et al., 2010a), atmospheric oxidative capacity (Xue et al., 2016; Wang et al., 2017b) and radical chemistry (Lou et al., 2010; Lu et al., 2012, 2014; Ling et al., 2014; Lyu et al., 2016b), while limited studies on O_3 formation were undertaken over the South China Sea (SCS, Wang et al., 2005; Ou Yang et al., 2013). Since interaction between continental and maritime air sometimes forms weak circulation cells in which pollutants become entrained,

resulting in increased concentrations, it is essential to investigate the chemical characteristics of O_3 formation over the SCS.

Although the coastline of mainland China covers approximately 14500 km, studies of the characteristics of O_3 pollution in coastal areas are limited. Han et al. (2015) reported the variation of surface O_3 over the East China Sea (ECS) and found that Chinese outflows brought higher O_3 concentrations to the ECS. Ou Yang et al. (2013) investigated regional background O_3 level at Dongsha Island, which is located between Taiwan and the Philippines in the northern SCS. They revealed that during winter Asian monsoon, polluted air masses were delivered from the northern continent to Dongsha Island by strong northeastern winds, resulting in O_3 mixing ratios of ca. 60 ppbv. With the O_3 transport from the continent, O_3 precursors can also be transferred to the maritime atmosphere and contribute to photochemical O_3 production. However, limited studies have been carried out to improve our knowledge of photochemical O_3 formation above the ocean. One of the reasons was the lack of comprehensive precursor emissions data, especially VOC data, which hinders the investigation of mechanism of O_3 production in maritime environments. Although Wang et al. (2005) reported comprehensive observations of O_3 and its precursors at Tai O, a coastal site in Hong Kong, and established seasonal profiles of background air pollutants over the SCS and regional pollution of PRD, the photochemical O_3 formation in the region was not fully elaborated.

To fill the gap, continuous measurements of air pollutants, including O_3 and its precursors, were conducted at a remote island site (Wanshan Island, WSI) in the SCS from August to November 2013. A photochemical box model incorporating the Master Chemical Mechanism (v3.2) was applied to simulate the photochemical processes of local O_3 production. The scientific objectives of this study are (1) to investigate the causes of high O_3 episodes over the SCS; (2) to understand the regime and O_3 production conditions over the SCS in order to inform policy decisions; and (3) to explore the impact of VOCs on O_3 formation pathways over the SCS.

2. Methodology

2.1. Sampling site

Real-time field measurements of trace gases were carried out at the WSI site in the SCS (Fig. S1). The WSI site (21.93° N, 113.73° E) is about 34 km south from the coast, and is bounded to the north by the Pearl River Estuary. The distance from WSI to the urban center of Hong Kong, Macau and Zhuhai is about 64 km, 35 km and 40 km, respectively. The island has an area of 8.1 km^2 and a population of about 3000. The island has a subtropical maritime climate and is a downwind location of the PRD region in autumn and winter, when the Asian winter monsoon dominates. The measurement facilities were established on the rooftop of the National Marine Environmental Monitoring Station on Wanshan Island with a height of about 65 m above sea level and ~10 m above ground level.

2.2. Measurement methods

2.2.1. On-line measurements of O_3, CO, SO_2 and NO_x

Sampling equipment was installed in an air-conditioned room at the top floor of the National Marine Environmental Monitoring Station. A 5 m long perfluoroalkoxy (PFA) Teflon tube, with inner diameter of 9.6 mm and outer diameter of 12.7 mm, was used as a sampling tube. The inlet of the sampling tube was 2 m above the rooftop of the building, while the other end was coupled to a PFA manifold which linked together all the gas analyzers in the room. A bypass pump connected to the manifold drew ambient air at a rate

of 5 L min^{-1} into the intakes of the gas analyzers.

Trace gases including O_3, NO_x, CO and SO_2 were simultaneously monitored during the sampling period (11 August—22 November 2013). Briefly, the target pollutants were measured with commercial analyzers developed by Advanced Pollution Instrumentation (API) Inc. A UV photometric analyzer (API model 400E with a detection limit of 0.6 ppbv) was used to monitor O_3, while NO-NO_2-NO_x was measured with a chemiluminescence analyzer (API model 200E with a lower detectable limit of 0.4 ppbv) equipped with a replaceable molybdenum-converter cartridge. A gas filter correlation trace level CO analyzer (API model 300EU with a detection limit of 0.02 ppmv) with a heated, platinum CO scrubber to correct its baseline was utilized to measure CO, and SO_2 was detected with a pulsed UV fluorescence monitor (API model 100E with a detection limit of 0.4 ppbv). In addition, meteorological parameters (solar radiation, temperature, relative humidity, wind speed and wind direction) were continuously measured by a weather station (Vantage Pro 2, Davis Inc).

For quality control, a transfer standard (Thermo Environmental Instruments (TEI), 49 PS) was used to calibrate the O_3 analyzer. For CO, SO_2 and NO, NIST (National Institute of Standards and Technology)-traceable standard (Scott-Marrin, Inc.) was diluted using a dynamic calibrator (Environics, Inc., Model 6100). The standard contained 156.5 ppm CO (±2%), 15.64 ppm SO_2 (±2%), and 15.55 ppm NO (±2%). Through injecting scrubbed ambient air (TEI, Model 111) and a span gas mixture, these analyzers were calibrated. In addition, a data logger (Environmental Systems Corporation, Model 8832) was used for calibration control and data collection, with a time resolution of 1 min intervals (Guo et al., 2013).

2.2.2. VOCs sampling and analysis

Intermittent whole-air canister samples for VOCs and carbonyl cartridge samples for aldehyldes were obtained at WSI for 8 O_3 episode days and 13 non-O_3 episode days. The O_3 episode days were defined as the days with maximum hourly average O_3 value exceeding 100 ppbv (China's Grade II Standard). Specifically, the 13 non-O_3 episode days included 11—12, 18, 26 September, 9—10, 17, and 30—31 October, and 18—21 November 2013, while the 8 O_3 episode days were 2—4 and 22—25 October, and 15 November 2013. The whole-air samples were collected using evacuated 2-L electro-polished stainless steel canisters. The canisters were cleaned, conditioned and evacuated before sampling. A flow-restrictor was used to collect air samples over 1-h integration. Seven 1-h VOC samples (every 2 h from 7:00—19:00 LT inclusive) were collected on each of the 13 non-O_3 episode days and the 8 O_3 episode days at the site with additional samples collected at 01:00, 03:00, 05:00 and 21:00 on episode days. The speciation and abundance of individual VOCs in the canisters were determined by gas chromatography (GC) with flame ionization detection (FID), and GC with electron capture detection (ECD) and mass spectrometer detection (MSD). 59 C_2-C_{11} hydrocarbon species were quantified. The detection limits of VOCs ranged from 3 to 57 pptv with a measurement precision of 2—5%, and a measurement accuracy of 5%. Detailed descriptions of the analysis system, quality control and quality assurance for VOC samples are provided elsewhere (Simpson et al., 2010; Zhang et al., 2012).

Furthermore, 2-h carbonyl cartridge samples were simultaneously collected every 2 h during 07:00—19:00 using acidified 2,4-dinitrophenylhydrazine (DNPH) silica cartridges at a flow rate of 0.4—0.6 L min^{-1}. The procedures including the pretreatment, the configuration of the analysis system, and the methods of the quality control and quality assurance for carbonyl samples can be found in detail elsewhere (Guo et al., 2009). Briefly, the carbonyl samples were analyzed using high performance liquid chromatography (HPLC) with an auto-sampler. The identification and quantification