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## Observations of air quality on the outskirts of an urban agglomeration during the implementation of pollution reduction measures

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#### ABSTRACT

Based on observations at Heshan, a boundary area in the city agglomeration of the Pearl River Delta region in China, atmospheric pollutants such as  $PM_{2.5}$ ,  $O_3$ , CO,  $SO_2$ ,  $NO_2$ ,  $NO_2$  and NO were monitored between the  $12^{th}$  and  $29^{th}$  November, 2010. Meteorological parameters, including temperature, humidity, dew point, air pressure, ultraviolet light, wind direction, and wind speed were also measured. By combining the meteorological parameters with the atmospheric pollutant data, we performed Positive Matrix Factorization (PMF) and ozone production efficiency (OPE) analysis to objectively understand the interrelations among the pollutants, as well as between the pollutants and the meteorological factors. During the observation period, there were various meteorological changes such as rainfall, cold air transit, and sunshine that created conditions for the formation or dispersal of pollutants. The study period coincided with the  $16^{th}$  Asian Games, during which time the government adopted strict measures to reduce the discharge of pollutants around the Pearl River Delta area. However, we still observed serious pollution of PM<sub>2.5</sub> and  $O_3$ , of which the highest value of PM<sub>2.5</sub> was 210  $\mu$ g m<sup>-3</sup> and the highest value of  $O_3$  reached 117 ppb. At the same time, the high concentrations of CO, NO, NO<sub>2</sub>, NO<sub>2</sub>, and SO<sub>2</sub> could not be cleared away with rainfall in such a short period of time. On the basis of PMF analysis, we found that three factors influence the air quality of this region: local biomass burning, secondary pollutants of regional transport, and high industrial pollutant emissions. According to OPE analysis, the  $O_3$  pollution was mostly found to be VOC–sensitive but occasionally NO<sub>x</sub>–sensitive for OPE values greater than 10.

Keywords: Ozone, PM2.5, PMF, NOz, OPE

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#### 1. Introduction

Poor air quality is a topical issue in China due to the rapid increase in industry, vehicle numbers, and pollutant transport. The Pearl River Delta region (PRD) is one of the most seriously polluted areas, and its air quality problems are characterized historically by high concentrations of primary pollutants, such as sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NOx) (Xiao et al., 2006; Chan and Yao, 2008). In recent years, due to poor air quality and visibility, secondary air pollutants, such as fine particles as well as ozone pollution, have drawn increasing attention (Lam et al., 2005; Hagler et al., 2006; Zhang et al., 2007; Cheng et al., 2008; Zheng et al., 2010; Huang et al., 2012; Liu et al., 2013). Levels of SO<sub>2</sub>, total reactive nitrogen ( $NO_Y$ ), carbon monoxide (CO) and volatile organic compounds (VOCs) all contribute to the formation of fine particulate matter (PM<sub>2.5</sub>) and ozone (O<sub>3</sub>) (Hidy, 2000; Zaveri et al., 2003; Pathak et al., 2011; Lamsal et al., 2013). The NO and NO<sub>2</sub> emissions from fossil fuel combustion will exist for less than one day before being oxidized by air to become NO<sub>z</sub> (NO<sub>z</sub>=NO<sub>Y</sub>-NOx), HNO<sub>3</sub>, PAN (peroxyacetyl nitrate) and other reactive oxidized nitrogen species (Berkowitz et al., 2001; Jiang and Fast, 2004; Volz-Thomas et al., 2005; Horii et al., 2006; Raivonen et al., 2009). Previous studies have shown that PM2.5 contains high concentrations of NOz (He et al., 2001; Pathak et al., 2004; Pathak and Chan, 2005; Pandey et al., 2006; Sillanpaa et al., 2006; Lee et al., 2008; Pathak et al., 2011).



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Therefore, a part of PM<sub>2.5</sub> will be generated during the formation of  $O_3$  in the photochemical reaction of  $NO_X$  and VOCs (Seigneur, 2001), which has not been analyzed in previous studies in the PRD. In the present study, observations were made in Heshan, the boundary area of the PRD city agglomeration, of atmospheric pollutants including PM<sub>2.5</sub>, O<sub>3</sub>, CO, SO<sub>2</sub>, NO<sub>2</sub>, NO<sub>2</sub> and NO between the 12<sup>th</sup> and 29<sup>th</sup> November 2010. NO<sub>z</sub> concentrations were obtained by subtracting NO and NO<sub>2</sub> from observed NO<sub>Y</sub>. Meteorological parameters, such as temperature, humidity, dew point, air pressure, ultraviolet light, wind direction and wind speed were also measured. A series of analyses regarding the whole set of meteorological and air quality data were performed, including Positive Matrix Factorization (PMF) and ozone production efficiency (OPE) analysis, so as to understand the changes and interrelations among the pollutants, as well as between the pollutants and meteorological parameters, when strict controls on pollutant discharges were imposed in this region.

These controls were introduced because, during the observation period, the 16<sup>th</sup> Asian Games were being held in Guangzhou, the largest city in the PRD region, 30 km away from the observation station. The Guangzhou Asian Games provided us with a unique opportunity to investigate the potential for pollution reduction in the PRD. The occurrence of this major sporting event condensed a comprehensive air quality management plan into a short–term aggressive abatement, revealing the possible improvements in air quality that can be made against a background of comprehensive environmental control measures (Liu et al., 2013).

#### 2. Methods

The research site is located at the Heshan National Field Research Station in the forest ecosystem of the Chinese Academy of Sciences, which lies in the central region of Guangdong Province (112°53'E, 22°40'N). This experimental area features many low, gentle hills and a mild climate with an average annual temperature of 21.7 °C and maximum and minimum temperatures of 29.2 °C and 12.6 °C, respectively. The height of the sampling point was approximately 45 m above sea level, and located 34 km southwest of Guangzhou and 20 km and 30 km away from Foshan and Jiangmen, respectively (see the Supporting Material, SM, Figure S1). The predominant wind direction in the fall is from the northeast (see the SM, Figure S7). Because a high concentration zone tends to form approximately 30 to 80 km from an emission source by remote transmission and evolution of atmospheric photochemical pollutants, Heshan is in a good location to observe the pollutant levels in an atmospheric smoke plume from surrounding cities.

The  $O_3$  and  $NO_Y$  analyzers were Model 49i and Model 42Y (Thermo Environmental Instruments Inc., USA); while for NO and  $NO_2$ , Model CLD 88 and Model PLC 860 (ECO PHYSICS AG, Switzerland) were used. All analyzers were calibrated before the field campaign according to the standards of the Chinese Environmental Protection Bureau. The SO<sub>2</sub> and CO analyzers were Model

43i and Model 48i (Thermo Environmental Instruments Inc., USA) while the PM<sub>2.5</sub> mass concentrations over the station was measured using a Tapered-Element Oscillating Microbalance (TEOM) instrument with quartz filter (Pallflex TX40) and one record every two seconds and with an accuracy of  $\pm 1.5 \,\mu g \,m^{-3}$  for hourly averages, although it can underestimate PM<sub>2.5</sub> mass concentration owing to volatilization of ammonium nitrate and organic carbon (Gupta and Christopher, 2009). For the meteorological variables, the Milos520 (Vaisala, Finland) was used, which is an automatic, meteorological observation tower located at Heshan Station, and its observation parameters include air temperature, relative humidity, sea level pressure, and wind (Hu et al., 2010). The location of the present observation point complied with China Ambient Air Quality Standards II which requires 24-hourly average concentration limits of  $SO_2$ ,  $NO_2$ , CO, and  $PM_{2.5}$  respectively to be below 150 m<sup>-3</sup>, 80  $\mu g$  m<sup>-3</sup>, 4 mg m<sup>-3</sup>, 75  $\mu g$  m<sup>-3</sup> and 1–hourly average concentration of  $O_3$  below 200 µg m<sup>-3</sup>

#### 3. Results

#### 3.1. Pollutants time series analysis

The mixing ratio curves of  $PM_{2.5}$ ,  $O_3$ , CO,  $SO_2$ ,  $NO_2$ ,  $NO_2$  and NO are plotted as time series in Figure 1, while Figure S2 (see the SM) shows wind speed, temperature, relative humidity, dew, ultraviolet radiation, and air pressure for the observed period.



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