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# Trends of ambient fine particles and major chemical components in the Pearl River Delta region: Observation at a regional background site in fall and winter

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## HIGHLIGHTS

- The annual reduction trend of $PM_{2.5}$ was 8.58 μg $m^{-3}$ in fall and winter of 2007 to 2011.
- The reduction rate of sulfate ($SO_4^{2-}$) was 1.72 μg $m^{-3}$ $yr^{-1}$.
- Nitrate ($NO^{3-}$) presented a growth trend with a rate of 0.79 μg $m^{-3}$ $yr^{-1}$.

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## ABSTRACT

In the fall and winter of 2007 to 2011, 167 24-h quartz filter-based fine particle ($PM_{2.5}$) samples were collected at a regional background site in the central Pearl River Delta. The $PM_{2.5}$ showed an annual reduction trend with a rate of 8.58 μg $m^{-3}$ ($p < 0.01$). The OC component of the $PM_{2.5}$ reduced by 1.10 μg $m^{-3}$ $yr^{-1}$ ($p < 0.01$), while the reduction rates of sulfur dioxide ($SO_2$) and sulfate ($SO_4^{2-}$) were 10.2 μg $m^{-3}$ $yr^{-1}$ ($p < 0.01$) and 1.72 μg $m^{-3}$ $yr^{-1}$ ($p < 0.01$), respectively. In contrast, nitrogen oxides ($NO_x$) and nitrate ($NO^{3-}$) presented growth trends with rates of 6.73 μg $m^{-3}$ $yr^{-1}$ ($p < 0.05$) and 0.79 μg $m^{-3}$ $yr^{-1}$ ($p < 0.05$), respectively. The $PM_{2.5}$ reduction was mainly related to the decrease of primary OC and $SO_4^{2-}$, and the enhanced conversion efficiency of $SO_2$ to $SO_4^{2-}$ was related to an increase in the atmospheric oxidizing capacity and a decrease in aerosol acidity. The discrepancy between the annual trends of $NO_x$ and $NO_3^-$ was attributable to the small proportion of $NO_3^-$ in the total nitrogen budget.

*Capsule abstract:* Understanding annual variations of $PM_{2.5}$ and its chemical composition is crucial in enabling policymakers to formulate and implement control strategies on particulate pollution.



## 1. Introduction

Many cities in China currently suffer severe air pollution problems, in particular haze caused by fine particles ($PM_{2.5}$), resulting in visibility degradation and adverse health effects (Zhang et al., 2012a). Numerous heavy haze episodes have been observed in megacities such as Beijing, Shanghai, and Guangzhou in recent years (Wu et al., 2005; Sun et al., 2006; Fu et al., 2008; Chang et al., 2009). During these episodes, ambient 24-h average $PM_{2.5}$ levels up to 175 μg $m^{-3}$ have been recorded, well over the World Health Organization (WHO) daily Air Quality Guidelines of 25 μg $m^{-3}$. High $PM_{2.5}$ levels are closely associated with long- and short-term health problems (Tie et al., 2009; van Donkelaar et al., 2010; Chen R.J. et al., 2012; Shang et al., 2013). In an attempt to reduce particulate pollution, the Chinese government has recently implemented new national ambient air quality standards, which for the first time include $PM_{2.5}$. Moreover, the government has emphasized the control of particulate pollution at a regional scale, with the main focus on the three economically relevant and densely populated city clusters; the North China Plain (NCP), the Yangtze River Delta (YRD) region, and the Pearl River Delta (PRD) region.

The PRD region in southern China makes up less than 0.5% of China's total land area but contributes about 10% of the nation's GDP, and is home to around 10% of its population. The ambient annual mean $PM_{2.5}$ level in this highly urbanized and industrialized region exceeded 100 μg $m^{-3}$ in 2004 (Andreae et al., 2008). However, in recent years, the number of hazy days recorded a large drop from over 120 days in 2005 to less than 60 days in 2011 (http://www.gzepb.gov.cn/). Despite this reduction, average annual $PM_{2.5}$ levels in the PRD still exceed the daily

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and annual guidelines of the WHO. A systematic, long-term investigation into the variations in the main components of $PM_{2.5}$ and its mass concentrations will provide important information on sources and formation mechanisms, which will be useful in the formulating and implementing of particulate pollution control measures in the region, and also of value to other Chinese city clusters.

Over the last decade, studies have been conducted at different locations in the region on $PM_{2.5}$ mass concentrations and their major components, such as water soluble ions and carbonaceous aerosols (e.g. Lai et al., 2007; Hu et al., 2008; Tan et al., 2009a,2009b; Yang et al., 2011), and on the aerosols' light extinction and visibility impairment (Andreae et al., 2008; Jung et al., 2009; Tao et al., 2012). However, the measurements were mainly carried out over short periods. Thus, the long-term variations in $PM_{2.5}$ mass concentrations and compositions were not determined. In this study, $PM_{2.5}$ filter samples were systematically collected from a background site in the region in fall and winter from 2007 and 2011 so that the annual trends of the mass concentrations and chemical components of $PM_{2.5}$ could be obtained.

## 2. Experimental

### 2.1. Field sampling

The PRD region has a typical Asian monsoon climate — hot and humid in the summer, with prevailing southwesterly monsoon winds from the sea, and relatively cool and dry in the fall and winter, when northeasterly monsoon winds from northern China dominate (Ding and Chan, 2005). The region is often under the influence of high pressure ridges in the fall and winter, causing long periods of sunny days, with a low boundary layer and a high frequency of inversion. This stable meteorological condition facilitates the accumulation of pollutants and a resulting deterioration of air quality. As a result, high levels of air pollutants usually occur in fall and winter (Simpson et al., 2006; Fan et al., 2008; Liu et al., 2008; Cheng et al., 2010). Field measurements were thus collected in those two seasons each year.

The sampling site, Wanqingsha (WQS: 22.42° N, 113.32° E), was located in a small town south of Guangzhou, in the center of the PRD (Fig. 1). The town was surrounded by farmland, has little traffic, and very few textile and clothing workshops. The local anthropogenic emissions were thus not significant, with most air pollutants originating from the surrounding cities. The site was 50 km southeast of Guangzhou center, 40 km southwest of Dongguan, 50 km northwest of Shenzhen, and 25 km northeast of Zhongshan, making it a good regional station to characterize the air pollution of the inner PRD (Guo et al., 2009). The $PM_{2.5}$ high-volume samplers (Tisch Environmental Inc., USA) were placed on the rooftop of a building, about 30 m above the ground. Gas-phase pollutants, including $SO_2$ and $NO_x$, were also monitored.

The 24-h $PM_{2.5}$ samples were collected by drawing air through an 8 × 10 inch quartz filter (QMA, Whatman, UK) at a rate of 1.1 $m^3\ min^{-1}$. The filters were pre-baked at 450 °C for 4 h, wrapped in aluminum foil, zipped in Teflon bags, and stored at −20 °C before sampling. They were again stored in this way after sample collection. In 2007, 2008, 2009, 2010, and 2011, 32, 29, 25, 53, and 28 samples were collected, respectively. The meteorological parameters were measured by a mini weather station (Vantage Pro2TM, Davis Instruments Corp., USA) with wind speed/direction, relative humidity (RH), and temperature recorded every minute.

### 2.2. Chemical analysis

The $PM_{2.5}$ filters were weighed before and after field sampling, after 24-h equilibrium, at a temperature of 20–23 °C and with a RH between 35 and 45%. The organic carbon (OC) and elemental carbon (EC) in the $PM_{2.5}$ were determined by the thermo-optical transmittance (TOT) method (NIOSH, 1999) using an OC/EC analyzer (Sunset Laboratory Inc., USA), with a punch (1.5 × 1.0 cm) of the sampled filters. For the water-soluble inorganic ions, a punch (5.06 $cm^2$) of the filters was extracted twice with 10 ml ultrapure Milli-Q water (18.2 MΩ·cm/25 °C) each for 15 min using an ultrasonic ice-water bath. The total water extracts (20 ml) were filtered through a 0.22 μm pore size filter and then stored in a pre-cleaned HDPE bottle. The cations (i.e. $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$) and anions (i.e. $Cl^-$, $NO_3^-$, and $SO_4^{2-}$) were analyzed with an ion-chromatography system (Metrohm, 883 Basic IC plus). Cations were measured using a Metrohm Metrosep C4-100 column with 2 mmol $L^{-1}$ sulfuric acid as the eluent. Anions were measured using a Metrohm Metrosep A sup5-150 column equipped with a suppressor. The anion eluent was a solution of 3.2 mmol $L^{-1}$ $Na_2CO_3$ and 1.0 mmol $L^{-1}$ $NaHCO_3$.

### 2.3. Quality assurance/quality control (QA/QC)

Field and laboratory blank samples were analyzed in the same way as field samples. All the OC/EC and cation/anion data were corrected using the field blanks. The method detection limits (MDLs) were 0.01–0.05 μg $m^{-3}$ for the OC, EC, cations, and anions. Ions balance was used as a quality control check in the cation/anion analysis. Nano-equivalents

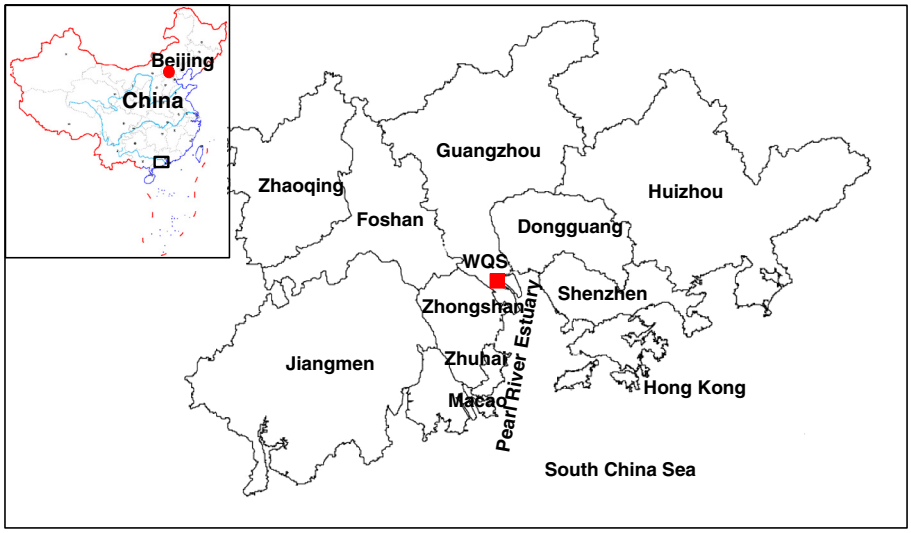


**Fig. 1.** Location of the sampling site Wanqingsha (WQS) and its surrounding environments.