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Characteristics and formation mechanism of regional haze episodes in the Pearl River Delta of China

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ABSTRACT

To investigate the characteristics and the specific mechanism of continuous haze, comprehensive measurements were conducted from 15 October to 19 November in the Atmospheric Environment Monitoring Super-Station in Heshan of Guangdong province. Five haze episodes occurred in October and November 2014 in the Pearl River Delta (PRD) region. The meteorological parameters, gas data, chemical compositions, and optical parameters of the aerosols were obtained. Among these events, the second haze episode, with the highest concentration of $PM_{2.5}$ of 187.51 μg/m^3, was the most severe. NO_3^- was always higher than SO_4^{2-}, which indicated that motor vehicles played an important role in the haze, even though the oxidation rate from SO_2 to SO_4^{2-} was faster than that of NO_X to NO_3^-. The difference between the hourly averages of Na^+ and K^+ during the haze episode and clean days was small, implying that straw combustion and sea salt had no significant effect on the occurrence of haze, and the backward trajectories of the air masses also conformed with this result. The air pollutants were difficult to disperse because of the significant decrease in the planetary boundary layer (PBL) height. Relative humidity played a crucial role in the formation of haze by leading to hygroscopic growth of the diameter of aerosols.

Introduction

During the past 30 years, many cities in China have suffered from air pollution and haze episodes caused by the rapid economic and social development. The definition of haze can be described as follows: a condition in which the horizontal visibility is less than 10 km and the atmospheric relative humidity (RH) is less than 90% (Wu et al., 2007; Liu et al., 2013b). Because of their close relationship with human disease, haze events have attracted increased attention (Miller et al., 2007; Araujo et al., 2008).

The Pearl River Delta (PRD) region is one of the most important manufacturing centers of South China (Chan and Yao, 2008). High population density and rapid mobilization, urbanization, and industrialization have led to a rapid increase in primary emissions of airborne pollutants (Hu et al., 2008). In the PRD region, the degree of complexity of the air pollution has caused extensive concern among scholars and

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the government. A large number of studies have shown that PM pollution in this region remains problematic, and many studies have been carried out to research the characteristics of the air pollution in the PRD region (Zhang et al., 2008). Previous studies found that water soluble inorganic ions (WSII) (*e.g.*, SO_4^{2-}, NO_3^-, NH_4^+) and secondary organic aerosol (SOA) were always at high levels; NO_3^- and SO_4^{2-} in particulate matter equal to or less than (PM_{10}) existed in the forms of $(NH_4)_2SO_4$, NH_4NO_3 and $NaNO_3$. Moreover, the hygroscopic properties had a good positive correlation with the WSF (water-soluble mass fraction) and SSF (sea-salt aerosol mass fraction), but a negative correlation with the TCF (total carbon mass fraction). Because the difference in physical and chemical properties of atmospheric aerosols between clean and haze days was so striking, research in the PRD region has focused mainly on these physical and chemical properties (Tan et al., 2009; Zhang et al., 2013; Han et al., 2013; Liu et al., 2008).

Although many studies have been conducted to understand the characteristics of haze episodes in the PRD region, the acidity of ions in particulate matter equal to or less than ($PM_{2.5}$), gas-to-particle transformation, and the source of airflow during haze episodes have scarcely been investigated. In order to obtain an improved understanding of the characteristics of the haze episodes in the PRD region, this study aimed to analyze the particulate, gaseous and meteorological conditions to study the characteristics of the haze episodes and the acid–base properties by analyzing ions, and also to examine the formation mechanism of haze episodes in the PRD region.

1. Experimental

1.1. Experiment site

Heshan is located in the hinterland of the PRD region. At the end of 2013, the resident population was 0.5 million, of which immigrants accounted for one-fourth, and the density of the population was 320 people per km^2 (the 2014 Statistical Yearbook of Jiangmen Province). A comprehensive field measurement from 15 October to 19 November, 2014, was performed at the Atmospheric Environment Monitoring Super-Station (22.7279° N, 112.9290° E) in Heshan of Guangdong province. The site is located at a hill named Huaguo, which is 80 km from Guangzhou City, at an altitude of 60 m above ground level, and is surrounded by trees, fishponds, and farmhouses.

1.2. Measurements and methods

The instruments used in this study are listed in Table 1. The $PM_{2.5}$ mass concentration was measured by a tapered element oscillating microbalance (TEOM, RP1400A, USA). The visibility was measured by a visibility sensor (Belfort 6000, USA), which consisted of a transmitter, a receiver, and a controller, and had a range of 10 m to 80 km. The wind direction (WD), wind speed (WS), and RH were monitored by a meteorological station (Vaisala, Finland). An organic carbon/elemental carbon (OC/EC) analyzer (Sunset Laboratories, USA) was used to detect the concentration of OC/EC and calibration was done once a week. Ozone (O_3) was detected by an O_3 analyzer. Gaseous pollutants (HF, HCl, SO_2, NH_3, *etc.*) and aerosol components (F^-, Cl^-, K^+, Ca^{2+}, Mg^{2+}, *etc.*) were detected by a gas and aerosol collector (GAC).

2. Results and discussion

2.1. Overall description of the haze episodes

Five haze episodes occurred during the comprehensive observation. The peak value of $PM_{2.5}$ was 187.51 μg/m^3. The particulate matter equal to or less than (PM_1)/$PM_{2.5}$ ratio had a negative correlation with the concentration of $PM_{2.5}$. [H^+] showed a positive correlation with [SO_4^{2-}]. The daily average [NO_3^-]/[SO_4^{2-}] ratio showed a positive correlation with the concentration of $PM_{2.5}$.

2.1.1. Meteorological conditions

Fig. 1a shows the measured variations of RH and visibility during the field measurement. According to the definition of haze, there were five haze episodes during the field measurement, which occurred during 15 to 17 October, 23 to 28 October, 30 October to 2 November, 5 to 8 November, and 13 to 16 November, respectively. As Sun et al. (2013) reported, variations in RH can influence the composition of aerosol. The RH in the campaign varied from 40% to 90%, with a mean value of 66.6%, resulting in large differences in the composition of aerosol in different periods. The visibility decreased when a haze episode occurred. Particularly, on 25 October, the visibility was reduced to the minimum value of 1.0 km, which

Table 1 – Overview of the instruments used in this study.

Instrument	Model	Parameters	Temporal resolution
TEOM	TEOM 1400A	$PM_{2.5}$	1 min
Visibility sensor	Belfort 6000	Visibility	1 min
Meteorology	Vaisala	Wind speed, wind direction, relative humidity, pressure, temperature	1 min
Sunset Lab. OC/EC analyzer	/	OC/EC	1 hr
O_3 analyzer	49i	O_3	1 min
GAC	TH-PKU303	Gaseous pollutants, aerosol components	30 min

TEOM: tapered element oscillating microbalance; PM: particulate matter; OC/EC: organic carbon/elemental carbon; GAC: gas and aerosol collector.

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