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Characterizing ionic species in $PM_{2.5}$ and PM_{10} in four Pearl River Delta cities, South China

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Abstract

$PM_{2.5}$ and PM_{10} samples were collected at four major cities in the Pearl River Delta (PRD), South China, during winter and summer in 2002. Six water-soluble ions, Na^+, NH_4^+, K^+, Cl^-, NO_3^- and SO_4^{2-} were measured using ion chromatography. On average, ionic species accounted for 53.3% and 40.5% for $PM_{2.5}$ and PM_{10}, respectively in winter and 39.4% and 35.2%, respectively in summer. Secondary ions such as sulfate, nitrate and ammonium accounted for the major part of the total ionic species. Sulfate was the most abundant species followed by nitrate. Overall, a regional pollution tendency was shown that there were higher concentrations of sulfate, nitrate and ammonium in Guangzhou City than those in the other PRD cities. Significant seasonal variations were also observed with higher levels of species in winter but lower in summer. The Asian monsoon system was favorable for removal and diffusion of air pollutants in PRD in summer while highly loading of local industrial emissions tended to deteriorate the air quality as well. NO_3^-/SO_4^{2-} ratio indicated that mobile sources have considerably contribution to the urban aerosol, and stationary sources should not be neglected. Besides the primary emissions, complex atmospheric reactions under favorable weather conditions should be paid more attention for the control of primary emission in the PRD region.

Key words: water-soluble ions; seasonal and spatial variations; Pearl River Delta

Introduction

Over the last decade, there has been intense interest concerning the role of aerosols in climate and atmospheric chemistry (Andreae and Crutzen, 1997). A typical chemical composition for fine aerosol in the lower troposphere is mainly composed of water-soluble inorganic ions, insoluble mineral dust, and carbonaceous material (Heintzenberg, 1989). Water-soluble inorganic ions are the major components of atmospheric aerosols and can comprise up to large fraction of particulate matter (PM) (Ali-Mohamed, 1991; Yao *et al*, 2002; Xiu *et al.*, 2004; Wang *et al*, 2005). Sulfate aerosols and carbonaceous aerosols are of competitive importance in urban aerosols. Sulfate, nitrate and ammonium dominate the identifiable components within both fine and coarse fractions. They are the most common components of secondary particles. The investigations of chemical transformation and equilibrium processes, ionic species and their relationships measured in the air were usually regarded as the indicator to estimate the pollution situation (Wexler and Seinfeld, 1991; Watson *et al.*, 1994; Hu *et al.*, 2002; Lin, 2002a; Yao *et al.*, 2002).

The Pearl River Delta (PRD) is located in Guangdong Province in southern China and is one of the most developing areas in China. Population of the PRD is about 38.7 millions covering a land area of 42794 km^2. The cities within the region are distributed like satellite cities around two centers–Hong Kong and Guangzhou. Increasing anthropogenic activities caused serious air pollution in this region in recent years (Cao *et al.*, 2003, 2004; Ansmann *et al.*, 2005; Hagler *et al.*, 2006). Numerous anthropogenic pollution sources are centralized in main cities like Guangzhou, Hong Kong and Shenzhen. Guangdong Province consists of 17 cities, about 63% area is divided as acid rain control zones by Chinese government and the pH values of rain in about 70% cities are less than 5.6 in 2003 (Shi, 2005). Concerning about the air quality of this region has come to front recently. Chemical species, including water-soluble ions in atmospheric aerosols, have been investigated in Hong Kong, Guangzhou and Shenzhen (Ho *et al.*, 2003; Yao *et al.*, 2003; Zhuang *et al.*, 1999; Wai and Tanner, 2005; Hagler *et al.*, 2006; Niu *et al.*, 2006; Wu *et al.*, 2006). Previous studies indicated that ionic species especially secondary ions such as sulfate, nitrate and ammonium accounted for the major part of aerosol in this

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area, and their concentration levels as well as variations closely related to local emission and influenced by the Asian monsoon system. Nevertheless, the fast developing economics bloom the urbanization in this area with more new-built cities coming forth. Furthermore, due to close relationship in geographical location, the mutual influences of air pollutants among these cities in PRD should be taken into account. A multi-city-campaign becomes necessary to investigate the situation and variation of urban aerosol simultaneously and to estimate the sources, which might provide further knowledge of airborne aerosol in this area and to give more cues for control strategies. In this study, eight sites in four major cities in PRD and two typical periods of winter and summer were chosen for sampling. The objective of this study was to investigate the levels, spatial and seasonal variations of water-soluble ions in the airborne particles at the four major PRD cities. Moreover, detailed characterizations of ionic species will provide unique information on sources and atmospheric chemistry that will be served as part of the database for region acid rain and atmospheric haze studies.

1 Experiment

1.1 Sampling sites

A total of eight sampling sites among four cities were selected, including three sites in Hong Kong, three in Guangzhou, one in Shenzhen, and one in Zhuhai. The description of these sampling sites is as follows:

Polytechnic University (PU) in Hong Kong (HK): It is an urban road site in Hong Kong with about 6 m above ground level, and about 8 m away from the main traffic road that leads to the Cross Harbor Tunnel. The traffic volume on this road is extremely high with about 170000 vehicles per day.

Baptist University (BU) in Hong Kong: It represents a residential and commercial environment of urban area with 30 m above ground on the roof of a building at Baptist University.

Hok Tsui (HT) in Hong Kong: It situates at the southern tip of Hong Kong Island where the least anthropogenic pollution is expected nearby and can be considered as a background monitoring station.

Sun Yat-sen University (SU) in Guangzhou (GZ): It locates on a 15-m high rooftop of campus building and represents an urban environment.

Huangpu District (HP) in Guangzhou: It locates in an industrial region with chemical and metallurgy factories and power plants around the site and it is about 20 m above ground level.

Longgui (LG) in Guangzhou: It is 25 km away from downtown Guangzhou and can be regarded as a suburban site, which was on the roof (10 m) of a building.

Luohu (LH) in Shenzhen (SZ): It locates in Honghu Park with 10 m above ground, which is one of the urban monitoring stations operated by SZ Environmental Protection Bureau.

Xiangzhou (XZ) in Zhuhai (ZH): It locates in First Middle School of Zhuhai with 20 m above ground, which is one of the urban monitoring stations operated by ZH Environmental Protection Bureau.

1.2 Sample collection

$PM_{2.5}$ and PM_{10} samples were collected simultaneously at a flow-rate of 5 L/min using portable mini-volume samplers (Airmetrics, USA) loaded with 47 mm in diameter Whatman quartz microfiber filters (QM/A) during winter (January to February, 2002) and summer (June to July, 2002). Prior to sampling, all the samplers were checked and calibrated carefully. $PM_{2.5}$ and PM_{10} impactors were installed on top of the pre-separator assemblies to collect 24-h PM samples simultaneously at eight sites. A total of 103 pairs of $PM_{2.5}$ and PM_{10} samples were collected and used in this study.

1.3 Ionic species analyses

A quarter of the filtered sample was put into an ultrasonotor with 20 ml of ultra-pure water for 15 min. Six major ionic species (Na^+, NH_4^+, K^+, Cl^-, NO_3^-, and SO_4^{2-}) were measured by ion chromatography (Dionex, DX600). A CS12 and AS14 column (both 250 mm 4 mm) were used for the determinations of cations and anions, respectively. Field blanks were used to correct the concentrations of ionic species. The detection limits of Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, and K^+ were 5, 15, 20, 15, 15, and 15 μg/L, respectively. Replicate checks were performed each 10 samples. Relative standard deviations (RSD) of replicate analyses were 0.5%–2.1% for Cl^-, 0.6%–2.5% for NO_3^-, 0.1%–2.3% for SO_4^{2-}, 0.7%–3.2% for Na^+, 1.4%–1.8% for NH_4^+, and 2.3%–3.6% for K^+.

1.4 Meteorological data and air mass trajectories

Meteorological data including temperature, sunshine hours, atmospheric pressure, precipitation, wind speed and wind direction during the sampling periods were obtained from the Guangdong Meteorological Bureau. Air mass trajectories were calculated by HYSPLIT 4 model of the Air Resources Laboratory of NOAA in each sampling day

Table 1 Air mass back trajectories classification

Season	Type	Time	Description
Winter	1 Marine air mass	Jan. 12–18	Originated from the east (Pacific Ocean)
	2 Continental air mass	Jan. 20–23	From north China
	3 Continental marine mixed air mass	Jan. 8–11; Jan. 24–26; Jan. 28–30; Feb. 1/Feb. 3–6	Originated from north China but affected by the marine air mass when they approached sampling area
Summer	4 Marine air mass	Jun. 25–Jul. 8; Jul. 10; Jul. 13–25	Almost all air mass originated from southeast Asia; only in Jul. 10 air mass from the east
	5 Continental air mass	Jul. 11–12	From northeast China

(Table 1). Back trajectory was computed at 0:00 h UTC and at 500 m above the starting point. FNL Meteorological data were chosen as the input. Five kinds of air mass types were classified (Table 1). According to meteorological data in 2002, evident variation of weather conditions were found between winter and summer in PRD, which shows the highest temperature, relatively humidity, sunshine hours, rainfall amount and frequencies was in June and/or July and the lowest ones were in January and/or February. Back trajectories also confirmed that PRD were dominantly affected by continental air mass in winter and by marine air mass in summer.

2 Results and discussion

2.1 Ionic species in $PM_{2.5}$ and PM_{10}

2.1.1 Concentration levels

The ionic concentrations of $PM_{2.5}$ and PM_{10} in winter and summer are summarized in Tables 2 and 3, respectively. The calculated results from the data in Tables 2 and 3 showed that ions accounted for 34.7%–73.6% of $PM_{2.5}$ and 25.6%–58.7% of PM_{10} in winter, and 29.2%–51.9% of $PM_{2.5}$ and 22.6%–49.6% of PM_{10} in summer. This indicates that ionic species were the major fraction of the atmospheric aerosols in PRD. Low levels of sea salt fraction (Na^+ and Cl^-) and high levels of sulfate and nitrate were observed at all the sites.

At present, anthropogenic emissions account for about 75% of total sulfur emission in Northern Hemisphere (Seinfeld and Pandis, 1998). In urban area, most of the sulfate is formed by oxidation of sulfur dioxide, which is mainly produced by fossil fuel combustion, and some biogenic gases (Wang and Shooter, 2001). In this work, sulfate was the most abundant ionic specie either in winter or in summer. Data issued by Guangdong Environment Protection Bureau showed that emission amount of SO_2 was 1.07×10^6 t in 2003 in Guangdong Province. The emission from thermo power plants accounted to 0.65×10^6 t, ranking as the largest contributor (Shi, 2005). There-

Table 2 Ion concentrations (μg/m³) of the $PM_{2.5}$ and PM_{10} samples in winter at eight sits in Pearl River Delta[a]

City	Site	n[b]	PM	Na^+	NH_4^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
$PM_{2.5}$									
Hong Kong	PU	14	60.4±22.9	4.2±1.4	2.8±1.3	0.9±0.3	1.4±0.7	6.1±3.6	10.7±4.2
	BU	5	48.5±24.7	4.8±0.4	1.5±0.7	1.2±0.4	1.8±0.9	4.2±2.5	8.1±4.1
	HT	4	41.3±20.0	4.5±1.0	2.1±2.1	1.1±0.5	1.4±0.6	3.5±1.2	11.8±2.6
Guangzhou	SU	10	90.5±41.0	4.6±1.2	3.9±2.9	1.9±1.2	2.7±1.4	10.2±2.3	15.0±6.0
	HP	5	104.0±77.8	4.5±1.4	1.9±1.7	2.5±1.0	5.3±2.1	4.7±3.8	12.9±5.4
	LG	5	138.6±111.6	5.3±0.8	7.4±7.0	2.2±0.7	6.3±5.6	11.2±9.7	17.3±6.7
Shenzhen	LH	10	60.8±18.0	4.4±0.4	2.0±1.7	1.4±0.7	2.1±0.6	4.4±1.8	13.0±3.0
Zhuhai	XZ	9	59.3±23.7	5.0±1.5	4.5±2.0	1.6±0.6	2.1±0.5	8.6±2.5	17.1±4.8
PM_{10}									
Hong Kong	PU	6	78.4±34.1	5.1±0.7	3.3±2.2	1.2±0.4	2.1±1.6	6.3±2.6	11.2±3.9
	BU	3	55.7±19.3	5.4±0.4	1.7±1.4	1.3±0.1	2.1±1.1	5.1±2.9	9.0±3.0
	HT	3	82.9±17.9	7.9±0.7	3.1±2.0	1.4±0.3	6.1±1.3	7.4±1.0	14.6±2.1
Guangzhou	SU	10	138.2±70.1	5.4±1.1	5.4±3.1	2.5±1.0	3.4±2.1	12.3±5.9	19.1±6.5
	HP	5	167.0±146.1	6.0±0.9	2.8±2.7	4.1±1.4	5.5±2.0	6.2±3.4	14.9±5.7
	LG	5	203.4±161.7	5.4±1.0	8.8±8.6	2.7±1.0	7.4±6.6	15.9±13.2	22.1±11.4
Shenzhen	LH	10	83.7±27.4	5.5±0.8	3.0±2.0	1.7±1.0	2.6±0.9	6.3±1.9	13.7±3.7
Zhuhai	XZ	7	84.1±31.6	5.9±1.3	7.1±3.0	2.1±0.7	2.5±0.3	10.9±3.2	17.5±3.6

[a] Values represent average ± standard deviation; [b] numbers of samples.

Table 3 Ion concentrations (μg/m³) of the $PM_{2.5}$ and PM_{10} samples in summer at eight sits in Pearl River Delta

City	Site	n	PM	Na^+	NH_4^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
$PM_{2.5}$									
Hong Kong	PU	5	40.1±19.7	3.6±0.9	1.8±1.9	0.4±0.2	0.5±0.2	1.7±1.1	9.1±3.7
	BU	6	30.8±7.6	3.1±0.5	0.1±0.0	0.2±0.1	0.4±0.1	1.5±0.5	5.7±2.2
	HT	6	15.8±2.4	2.1±0.2	0.1±0.1	0.1±0.0	0.8±0.5	0.6±0.1	3.2±1.2
Guangzhou	SU	10	66.3±18.9	3.5±0.5	0.6±0.7	1.9±1.1	0.8±0.5	2.9±1.3	15.7±6.4
	HP	5	101.7±11.4	3.8±0.1	2.7±1.9	3.8±1.6	2.5±1.9	4.7±1.7	22.4±3.0
	LG	5	78.2±46.9	3.7±0.6	2.0±3.2	1.9±0.9	1.2±0.5	4.6±3.5	13.6±7.2
Shenzhen	LH	9	47.1±16.7	3.6±0.9	0.4±0.4	0.3±0.2	1.0±0.4	2.5±1.7	8.7±2.8
Zhuhai	XZ	9	31.0±20.0	1.7±0.5	1.0±1.5	0.3±0.3	0.5±0.3	1.4±1.2	11.2±7.4
PM_{10}									
Hong Kong	PU	5	40.8±15.6	3.7±0.5	2.2±1.8	0.4±0.1	1.2±0.6	3.8±0.9	9.2±3.1
	BU	6	38.6±12.8	4.9±0.8	0.4±0.2	0.5±0.4	1.0±0.5	2.5±0.4	7.6±2.1
	HT	6	31.9±4.9	6.7±0.9	0.2±0.2	0.5±0.2	2.3±0.6	2.9±1.0	5.1±1.4
Guangzhou	SU	10	102.7±32.5	5.3±1.9	1.2±1.4	2.5±1.7	2.5±2.2	6.0±2.4	19.0±6.3
	HP	5	164.2±17.4	4.0±0.3	3.0±2.3	4.3±1.8	2.8±1.8	6.8±2.8	24.5±3.6
	LG	5	129.5±93.5	7.2±4.2	10.9±13	3.4±1.8	2.5±1.4	7.3±8.3	22.6±14
Shenzhen	LH	9	75.1±23.0	5.5±3.6	0.6±0.7	0.5±0.2	2.7±1.3	3.6±2.0	10.8±3.0
Zhuhai	XZ	8	44.0±24.8	2.1±0.4	1.2±1.7	0.4±0.3	1.5±1.1	2.8±1.7	11.3±7.1

fore, high SO_4^{2-} was associated with high emission of SO_2 in these flourishing cities. At HT, the seashore site, high percentage of sulfate was also observed and was shown that it related mainly to the non-sea-salt sources although sulfate may come from the natural sources such as oceanic emissions (see Section 2.3.2). The second highest ionic species was nitrate. Particulate-related nitrate is mainly formed by oxidation of nitrogen oxides (NO_x) to nitric acid, which then forms particles through the reactions with sodium chloride or with ammonia (Clase and Gysels, 1998). NO_x mainly comes from the anthropogenic emissions such as vehicular emissions, industrial emissions etc. in urban area. The high concentrations of nitrate at each city imply a large contribution of motor vehicular emissions is not neglected. The significant contribution of vehicular emissions on urban aerosol in PRD has been observed in previous studies by using indicator from carbonaceous aerosol (Cao *et al*., 2003, 2004). Sulfate, nitrate and ammonium that are suggested as secondary composition were the dominant ions among the species measured in this work. They accounted for 59.3%–77.7% and 59.3%–77.1% of total ionic species measured for $PM_{2.5}$ and PM_{10} in winter and accounts for 56.5%–84.5% and 46.3%–79.2% of the total ionic species of $PM_{2.5}$ and PM_{10} in summer.

Potassium levels in the 3 sites in Guangzhou were higher than the other sites in other cities, which possibly imply that the contribution biomass burning around Guangzhou area is obvious. The influence of biomass burning in Hong Kong was detected in previous report (Louie *et al*., 2005; Zheng *et al*., 2006). There were relatively low levels of sodium and chloride observed at all sites except HT site that is close to seashore.

The concentrations of sea-salt components (Na^+ and Cl^-) in $PM_{2.5}$ and PM_{10} in this study are in relatively high level compared to the other cities except Cl^- in $PM_{2.5}$ in Beijing (Wang *et al*., 2005) and in PM_{10} in Kaohsiung (Lin, 2002b) (Table 4). The close vicinity to the ocean in Kaohsiung leads to the considerable influence of sea salts (Lin, 2002b). The highest K^+ concentration has been found in Nanjing (Wang *et al*., 2003) then followed by Guangzhou whereas other cities have much lower K^+ concentrations. NO_3^- in Guangzhou and Zhuhai are comparable to that in Beijing (Wang *et al*., 2005) and Nanjing (Wang *et al*., 2003). Guangzhou has the highest sulfate concentration among the listed cities (Table 4), which may be due to the high amount emission of SO_2 from coal-related industrial combustion (Cao *et al*., 2003). Ammonium concentrations in the PRD cities were similar to those in Hong Kong measured by Ho *et al*. (2003), and much lower than in the other cities, especially in summer period. Relative high concentrations of Cl^- and NO_3^- suggested that the heterogeneous reactions of NH_4NO_3 and NH_4Cl occurred in PRD atmosphere. In addition, higher temperature in Guangzhou compared to other cities especially in summer may result in the loss of these salts during sampling periods.

2.1.2 Spatial variation

The concentrations of Na^+ and Cl^- in $PM_{2.5}$ have slight differences among the three sites in Hong Kong, but significant variations were found in PM_{10}. HT, a seaside site, had higher concentrations of Na^+ and Cl^- in PM_{10} than those at the other two sites, indicating that sea salt might mainly concentrate in PM_{10}. The percentages of sodium were always shown as the sequence of HT > BU > PU in Hong Kong, and sulfate and nitrate concentrations at HT during winter period were higher than those at urban sites (PU and BU). It indicates air pollutants transported from Mainland

Table 4 Concentrations (μg/m^3) of ionic species of PM in several Chinese cities

Sites	Sampling periods	Size	Na^+	NH_4^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	Remark
Hong Kong	Jan.–Feb. 2002	$PM_{2.5}$	4.5	2.1	1.1	1.5	4.6	10.2	This study
	Jun.–Jul. 2002	$PM_{2.5}$	2.9	0.7	0.2	0.6	1.2	6.0	This study
Guangzhou	Jan.–Feb. 2002	$PM_{2.5}$	4.8	4.4	2.2	4.8	8.7	15.0	This study
	Jun.–Jul. 2002	$PM_{2.5}$	3.8	1.8	2.5	1.5	4.1	17.2	This study
Shenzhen	Jan.–Feb. 2002	$PM_{2.5}$	4.4	2.0	1.4	2.1	4.4	13.0	This study
	Jun.–Jul. 2002	$PM_{2.5}$	3.6	0.4	0.3	1.0	2.5	8.7	This study
Zhuhai	Jan.–Feb. 2002	$PM_{2.5}$	5.0	4.5	1.6	2.1	8.6	17.1	This study
	Jun.–Jul. 2002	$PM_{2.5}$	1.7	1.0	0.3	0.5	1.4	11.2	This study
Kaohsiung	Nov.1998–Apr.1999	$PM_{2.5}$	1.8	7.9	NA	2.1	11.3	14.3	Lin, 2002b
Hong Kong	Nov. 2000–Feb.2001	$PM_{2.5}$	NA	3.0	NA	0.5	2.5	15.3	Ho *et al*., 2003
Beijing	2001–2003	$PM_{2.5}$	0.6	8.7	1.5	3.1	11.6	16.5	Wang *et al*., 2005
Shanghai	Sep. 2003–Jan. 2005	$PM_{2.5}$	0.6	3.8	0.6	3.0	6.2	10.39	Wang *et al*., 2006
Nanjing	Feb.2001–Dec.2001	$PM_{2.5}$	2.4	9.5	3.3	1.1	7.5	16.3	Wang *et al*., 2006
Hong Kong	Jan.–Feb. 2002	PM_{10}	6.1	2.7	1.3	3.4	6.3	11.6	This study
	Jun.–Jul. 2002	PM_{10}	5.1	1.0	0.4	1.5	3.1	7.3	This study
Guangzhou	Jan.–Feb. 2002	PM_{10}	5.6	5.7	3.1	5.4	11.4	18.7	This study
	Jun.–Jul. 2002	PM_{10}	5.5	5.0	3.4	2.6	6.7	22.0	This study
Shenzhen	Jan.– Feb. 2002	PM_{10}	5.5	3.0	1.7	2.6	6.3	13.7	This study
	Jun.– Jul. 2002	PM_{10}	5.5	0.6	0.5	2.7	3.6	10.8	This study
Zhuhai	Jan.– Feb. 2002	PM_{10}	5.9	7.1	2.1	2.5	10.9	17.5	This study
	Jun.– Jul. 2002	PM_{10}	2.1	1.2	0.4	1.5	2.8	11.3	This study
Kaohsiung	Nov.1998–Apr.1999	PM_{10}	3.5	11.8	NA	3.7	15.3	18.7	Lin, 2002b
Hong Kong	Nov. 2000–Feb.2001	PM_{10}	NA	3.1	NA	1.5	4.9	15.8	Ho *et al*., 2003
Nanjing	Feb.2001–Dec.2001	PM_{10}	3.8	10.8	3.4	1.5	9.2	18.1	Wang *et al*., 2003

NA. data are not available at the site.

China has impact on Hong Kong atmosphere, which can be confirmed by the back trajectories (Table 1). Ammonium observed at PU was higher than those at BU and HT (Tables 2 and 3). Particulate ammonium is formed by the neutralization between ammonia gas and acidic species (H_2SO_4, HNO_3, HCl), so the emission of NH_3 from large amount of running vehicles and foot passengers can lead to the increasing formation of NH_4^+ in PU roadside site.

The highest SO_4^{2-} was found at LG, a suburban site with 25 km north from Guangzhou downtown, among eight sites for both $PM_{2.5}$ and PM_{10} in winter, which can be attributed to the high emission of SO_2 in Guangzhou and long residence time for atmospheric reaction. The highest SO_4^{2-} was found at HP, an industrial site, among eight sites for both $PM_{2.5}$ and PM_{10} in summer, which can be viewed as the mixture contribution of high emission of SO_2 around this site and short reaction time in the atmosphere since the weather conditions like high temperature, long sunshine hours, and no rainfall were in favor of the photochemical reactions especially in July. Niu *et al.* (2006) also found that serious secondary pollution was displayed during the high temperature period in summer time in Shenzhen, a PRD city near Guangzhou. The highest NH_4^+ was also observed at LG among eight sites for $PM_{2.5}$ and PM_{10} in hot and cold seasons except the second highest in $PM_{2.5}$ in summer (Tables 2 and 3), which can be ascribed to many agricultural farmlands and activities around LG. Ammonium associates with ammonia vaporization from animal farming, fertilizers and organic decomposition. Usually, ammonia is not transported at very long distances as it is rapidly converted into ammonium aerosols at a rate 30%/h (Asman and van Jaarsveld, 1991).

2.1.3 Seasonal variations

Most of the ionic species had higher concentrations in winter than in summer with the exception of higher potassium and sulfate measured during the summer in Guangzhou (Tables 2 and 3). The PRD is a delta close to the South China Sea and its climate is affected by the shifting of Asian Monsoon system, which causes the significant seasonal differences of meteorological conditions. In summer, the subtropical high pressures, typhoon, heavy monsoon rain, and the monsoon blowing from the Pacific Ocean can help the removal and dispersion of air pollutants. By contraries, pollutants transported from the China inland, plus the strong temperature inversion, low air pressure and humidity in winter are favorable for the accumulation of particulate matters and can deteriorate the air quality. The back trajectories of air parcel show a clear picture in the two sampling periods (Table 1). Higher summer levels for sulfate in Guangzhou were probably strongly affected by the increasing emission of industrial activities such as chemical, metallurgy, and petrochemical factories locating near the Pearl River estuary as well as several coal burned power plants among and around Guangzhou (Xie and Chen, 2003). For example, high electronic demand in summer associated with air conditions will result in more SO_2 emission from firepower plants.

2.2 Cation and anion balance and ammonium balance

2.2.1 Cation and anion balance

The calculations of the equivalence of cation and anion are obtained by following equations.

$$\text{Cation equivalence} = \frac{Na^+}{23.0} + \frac{K^+}{39.098} + \frac{NH_4^+}{18.04} \quad (1)$$

$$\text{Anion equivalence} = \frac{Cl^-}{35.453} + \frac{NO_3^-}{62.005} + \frac{SO_4^{2-}}{48.03} \quad (2)$$

The correlations between the calculated equivalence of cation and anion are shown in Fig.1. Good correlations ($R > 0.7$) between the cation and anion concentrations measured at all sites were found indicating the measured cations (Na^+, NH_4^+, K^+) and anions (Cl^-, NO_3^-, SO_4^{2-}) kept quite constant relationship in neutralization during two seasons. The slopes are larger than 1 except at LH site in Shenzhen implying an acidic tendency of aerosol samples in PRD atmosphere. In 2004, 19 cities occurred acid rain in Guangdong Province and the average pH values reached to 4.71. The occurrence of acid rain increased to 54.5% compared with the 42.5% in 2003 (Zhong, 2005).

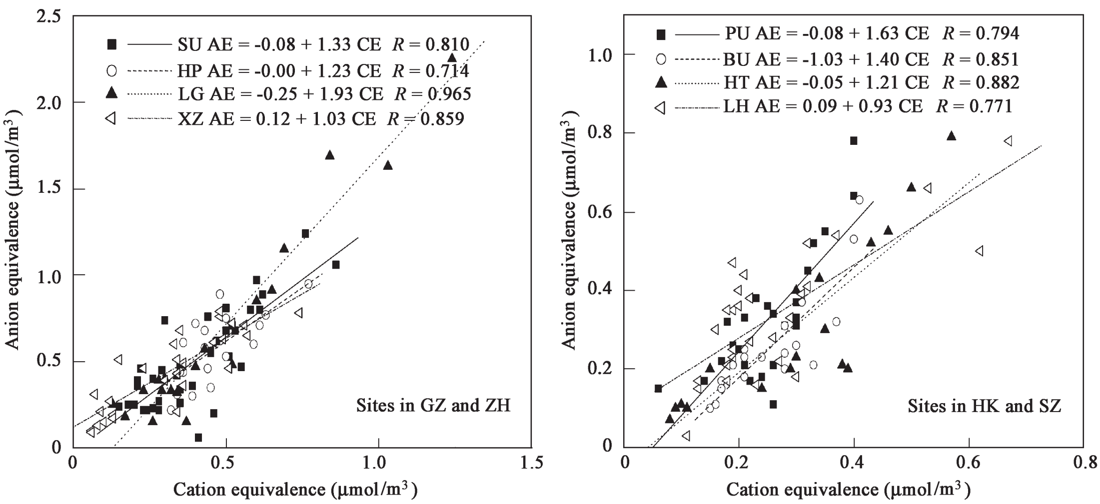

Fig. 1 Cation and anion balance for four PRD cities.

2.2.2 Ammonium balance

Ammonia reacts with acidic gases such as sulfuric, nitric, and hydrochloride acid. However, much ammonium exists in the air as the form of ammonium sulfate (Zhuang *et al*., 1999) due to its stability and low volatile compared to ammonium chloride. Although the reaction balance between ammonia and nitric acid can be affected by temperature and relative humidity, and ammonium nitrate is not as stable as ammonium sulfate, it is still one of the main forms of nitrate in the air. NH_4^+ can be calculated based on the stoichiometric ratios of the different compounds and compared with that which was measured. Correlation between calculated and measured concentrations of ammonium was made. Equation (3) is applied to calculate the concentration of ammonium based on NH_4NO_3 and NH_4HSO_4. Equation (4) is used to calculate the concentration of ammonium based on NH_4NO_3 and $(NH_4)_2SO_4$.

$$C_{cal(1)(NH_4^+)} = 0.29C_{NO_3^-} + 0.192C_{SO_4^{2-}} \quad (3)$$

$$C_{cal(2)(NH_4^+)} = 0.29C_{NO_3^-} + 0.38C_{SO_4^{2-}} \quad (4)$$

Good correlations (R>0.88) were found between measured ammonia and calculated ammonium based on NH_4NO_3 and $(NH_4)_2SO_4$ or based on NH_4NO_3 and NH_4HSO_4 (Fig.2). However, all intercepts are not close to 0, which indicates that sulfate and nitrate were not fully neutralized by ammonia and also relate to other cations such as Na^+, Mg^+, Ca^{2+}. In winter, the slopes were 0.80 and 0.94 in $PM_{2.5}$ and PM_{10} assuming $(NH_4)_2SO_4$ while they are 0.58 and 0.68 in $PM_{2.5}$ and PM_{10} assuming NH_4HSO_4 in winter. It implies that more sulfate were neutralized by ammonium with the form of $(NH_4)_2SO_4$. On the contrary, the slope in summer was 0.86 assuming NH_4HSO_4 compared with 1.45 assuming $(NH_4)_2SO_4$ in $PM_{2.5}$ whereas there were 0.95 compared to 1.50 in PM_{10}. It suggests that more sulfate existed as NH_4HSO_4 in summer during the sampling period.

2.3 Sources identification

2.3.1 NO_3^-/SO_4^{2-} ratio

The mass ratio of NO_3^-/SO_4^{2-} has been used as an indicator of the relative importance of stationary vs. mobile sources of sulfur and nitrogen in the atmosphere (Arimoto *et al*., 1996; Yao *et al*., 2002; Wang *et al*., 2006). Gasoline, diesel fuel and coal are the major fossil fuel used in mobile and stationary sources. In China, gasoline and diesel fuel contain 0.12% and 0.2% sulfur (by weight), respectively (Kato, 1996). The estimated ratios of NO_x to SO_x from the emission of gasoline and diesel fuel burning are 13:1 and 8:1, respectively (Wang *et al*., 2006). The sulfur content in coal is 1% and the estimated ratio of NO_x to SO_x is 1:2 from coal burning (Yao *et al*., 2002). In this study, NO_3^-/SO_4^{2-} ratios at 8 sites were in the range of 0.37–0.68 in $PM_{2.5}$ and 0.36–0.62 in PM_{10} in winter (Fig.3). In summer, lower NO_3^-/SO_4^{2-} ratios were found in all sites with the range of 0.17–0.40 in $PM_{2.5}$ and 0.26–0.42 in PM_{10}. The ratios in winter were a little lower than in other metropolises in China: Beijing

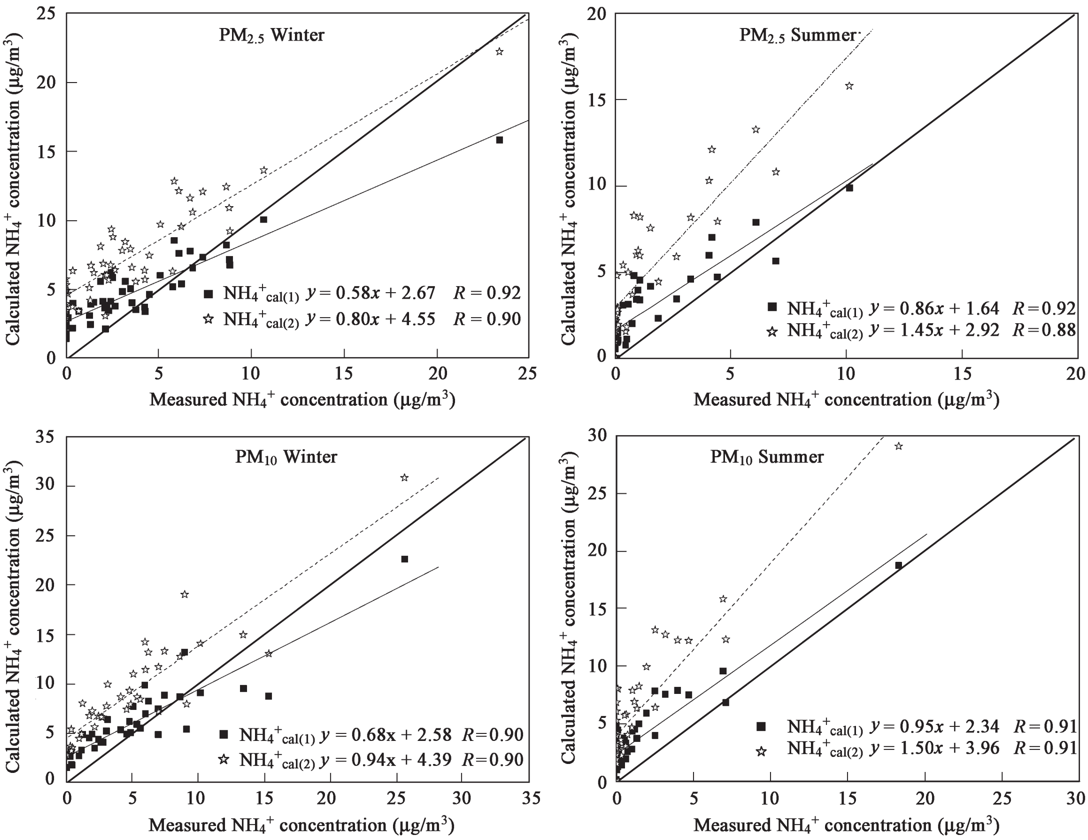

Fig. 2 Ammonia balance in $PM_{2.5}$ and PM_{10} during winter and summer.

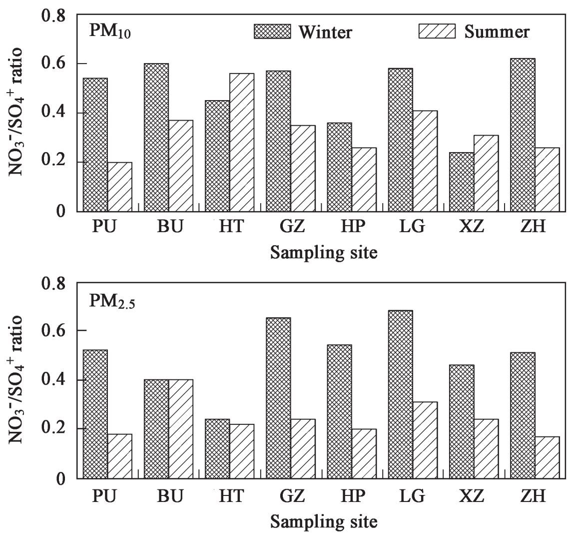

Fig. 3 NO_3^-/SO_4^{2-} ratio at eight sites in PRD.

(0.71) and Shanghai (0.64) (Wang *et al*., 2005, 2006), but higher than that in Qingdao (0.35) (Hu *et al*., 2002) and Taiwan (0.20) (Fang *et al*., 2002). The increasing amount of vehicle population in PRD is considered as one of the important reasons for relatively higher NO_3^-/SO_4^{2-} ratios. The numbers of new vehicles are increased about 300/d in Guangzhou and 500/d in Shengzhen (Zhong, 2005). Obvious seasonal variations have been found in the study, i.e., higher NO_3^-/SO_4^{2-} ratios were found in winter except NO_3^-/SO_4^{2-} in $PM_{2.5}$ at BU site and in PM_{10} at HT and LU sites. It indicates vehicular emissions have more contribution to atmospheric aerosol in winter than in summer. Furthermore, all the NO_3^-/SO_4^{2-} ratios are lower than 1.0 also shows that the stationary sources like the power plants and other industrial emissions were still important and should not be neglected in this fast-developing area.

2.3.2 Non-sea-salt sulfate and potassium

Since sea salts is one of the main contributors to ionic species in PRD (Tables 2 and 3), the contributions from other sources excluding sea salts can be estimated for sulfate and potassium using the concentrations of non-sea-salt sulfate (nss-SO_4^{2-}) and potassium (nss-K^+), as expressed in Eqs.(5) and (6). The soluble sodium in PM was assumed to be only from sea salts (Morales *et al*., 1998).

$$C_{\text{nss-SO}_4^{2-}} = C_{\text{SO}_4^{2-}} - 0.2455 C_{\text{Na}^+} \quad (5)$$

$$C_{\text{nss-K}^+} = C_{K^+} - 0.0355 C_{\text{Na}^+} \quad (6)$$

The nss-SO_4^{2-} and nss-K^+ concentrations at different sites during the sampling are summarized in Table 5. There were very high ratios of nss-SO_4^{2-} to SO_4^{2-} (82.7%–95.8%) at all sites during two seasons, except PM_{10} at seaside HT during summer (64.3%). This suggests that sea salt was not the main carrier of particulate sulfate among the four cities. Particularly, in Guangzhou, only 10% or much less particulate sulfate was from sea-salt sources. Non-sea-salt has much greater contribution to potassium in PM_{10} than that in $PM_{2.5}$ indicating that potassium from sea salts is much related to coarse mode ($PM_{2.5-10}$) or PM_{10} fraction. The nss-K^+ concentrations at the three sites in Hong Kong were much lower than those at the other sites. Especially at HT, the seashore site, the nss-K^+ accounted for only 36.0% for $PM_{2.5}$ and 47.5% for PM_{10} in summer. Lower nss-K^+ concentrations during summer were also found at the other sites except HP and LG sites, which indicate that the sea salts source from South China Sea exerts a clear influence on PRD atmosphere during summer period. The nss-K^+ concentrations at the three sites in Guangzhou were extremely high compared with that in the other sites (nss-K^+/K^+ ratio > 90%). This is consistent with particulate potassium in Guangzhou being associated with other emissions such as biomass burning instead of sea salt

Table 5 Summary of nss-K^+ and nss-SO_4^{2-} concentrations (μg/m^3) and mass distributions of nss-K^+ and nss-SO_4^{2-} (%) for $PM_{2.5}$ and PM_{10} in winter and summer periods

City	Site	$PM_{2.5}$				PM_{10}			
		$C_{\text{nss-K}^+}$	$C_{\text{nss-K}^+}/C_{\text{K}^+}$	$C_{\text{nss-SO}_4^{2-}}$	$C_{\text{nss-SO}_4^{2-}}/C_{\text{SO}_4^{2-}}$	$C_{\text{nss-K}^+}$	$C_{\text{nss-K}^+}/C_{\text{K}^+}$	$C_{\text{nss-SO}_4^{2-}}$	$C_{\text{nss-SO}_4^{2-}}/C_{\text{SO}_4^{2-}}$
Winter									
Hong Kong	PU	0.7	64.2%	8.7	88.0%	1.1	92.6%	11.3	95.4%
	BU	1.1	83.2%	6.3	89.6%	1.1	84.7%	7.6	83.0%
	HT	0.9	79.8%	13.3	90.8%	1.1	78.4%	15.7	88.0%
Guangzhou	SU	1.7	88.0%	12.1	90.8%	1.9	89.6%	15.4	92.9%
	HP	2.3	93.3%	11.7	89.4%	4.0	95.1%	12.0	90.6%
	LG	2.0	89.2%	15.9	90.9%	2.5	91.9%	20.7	92.6%
Shenzhen	LH	1.3	84.0%	11.5	89.8%	1.3	85.9%	12.6	91.5%
Zhuhai	XZ	1.4	85.2%	13.9	92.1%	1.9	88.3%	16.0	90.8%
Summer									
Hong Kong	PU	0.3	63.0%	8.7	85.6%	0.3	67.7%	9.0	88.0%
	BU	0.1	38.9%	5.0	84.2%	0.3	74.9%	6.4	82.7%
	HT	0.03	36.0%	2.7	80.4%	0.2	47.5%	3.4	64.3%
Guangzhou	SU	1.7	83.0%	14.1	90.6%	2.0	86.4%	17.8	92.9%
	HP	3.6	95.1%	21.4	95.6%	4.2	95.6%	23.5	95.8%
	LG	1.7	91.1%	12.7	90.4%	3.1	90.4%	20.8	89.1%
Shenzhen	LH	0.2	43.1%	8.6	88.1%	0.3	51.9%	9.5	87.1%
Zhuhai	XZ	0.3	57.9%	10.8	84.5%	0.4	62.7%	10.8	92.8%

contribution.

3 Conclusions

Ionic composition in $PM_{2.5}$ and PM_{10} has been investigated at eight sites in four cities in Pearl River Delta during 2002 winter and summer. The concentrations followed an order of SO_4^{2-} > NO_3^- > Na^+ > NH_4^+ > Cl^- > K^+ in winter, and SO_4^{2-} > NO_3^-, Na^+ > NH_4^+, Cl^- > K^+ in summer for both $PM_{2.5}$ and PM_{10}. More than 60% of ionic species were found in $PM_{2.5}$ except chloride (41.8%) and nitrate (54.3%) in summer. The good correlations between measured NH_4^+ and calculated NH_4^+ as well as the different slopes imply that NH_4^+ exist mainly in the form of $(NH_4)_2SO_4$ and NH_4NO_3 in winter instead of NH_4HSO_4 and NH_4NO_3 in summer. In most cases, evident seasonal variations have been found in the six ions with higher concentrations in winter and lower concentrations in summer, which related closely to the influence of the Asian Monsoon system. Although the PRD is adjacent to the seashore, the four cities were dominantly influenced by non-sea-salt sources. The estimations of non-sea-salt sulfate and potassium imply that anthropogenic sources are the main sources of ionic species. NO_3^-/SO_4^{2-} ratios in four cities pointed to vehicular emissions in this fast-developing area become more important but stationary emissions are still necessary to be taken into account. Besides the primary emissions, complex atmospheric reactions under favorable weather conditions should be paid more attention, especially when considering the coupling reactions between higher concentrations of inorganic ionic species and secondary organic matter (Cao *et al.*, 2003, 2004; Zhang *et al.*, 2004), for formulating control strategies for primary emission in the future in PRD.

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