

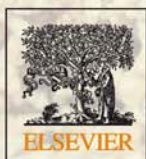
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Chemical composition, mass closure and sources of atmospheric PM₁₀ from industrial sites in Shenzhen, China

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Abstract

Concentrations of atmospheric PM₁₀ and chemical components (including twenty-one elements, nine ions, organic carbon (OC) and elemental carbon (EC)) were measured at five sites in a heavily industrial region of Shenzhen, China in 2005. Results showed that PM₁₀ concentrations exhibited the highest values at 264 µg/m³ at the site near a harbor with the influence of harbor activities. Sulfur exhibited the highest concentrations (from 2419 to 3995 ng/m³) of all the studied elements, which may be related to the influence of coal used as fuel in this area for industrial plants. This was verified by the high mass percentages of SO₄²⁻, which accounted for 34.3%–39.7% of the total ions. NO₃⁻/SO₄²⁻ ratios varied from 0.64–0.71, which implies coal combustion was predominant compared with vehicle emission. The anion/cation ratios range was close to 0.95, indicating anion deficiency in this region. The harbor site showed the highest OC and EC concentrations, with the influence of emission from vessels. Secondary organic carbon accounted for about 22.6%–38.7% of OC, with the highest percentage occurring at the site adjacent to a coal-fired power plant and wood plant. The mass closure model performed well in this heavily industrial region, with significant correlation obtained between chemically determined and gravimetrically measured PM₁₀ mass. The main constituents of PM₁₀ were found to be organic materials (30.9%–69.5%), followed by secondary inorganic aerosol (7.9%–25.0%), crustal materials (6.7%–13.8%), elemental carbon (3.5%–10.8%), sea salt (2.4%–6.2%) and trace elements (2.0%–4.9%) in this heavily industrialized region. Principal component analysis indicated that the main sources for particulate matter in this industrial region were crustal materials and coal/wood combustion, oil combustion, secondary aerosols, industrial processes and vehicle emission.

Key words: PM₁₀; chemical compositions; mass closure analysis; industrial sites; principal component analysis

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Introduction

Atmospheric inhalable particulate matter (PM₁₀) has received wide attention due to its adverse impact on human health and its association with visibility reduction in urban areas (Fang et al., 2000; Hu et al., 2002; Lin, 2002; Duan et al., 2006; Oanh et al., 2006; Terzi et al., 2010). Chemical compositions of particulate matter play an important role in these responses (Lee and Kang, 2001). To test whether the gravimetrically determined mass can be reconstructed by the chemically determined constituents, a mass closure model has been adopted (Celis et al., 2004; Oanh et al., 2006; Viana et al., 2006, 2007; Terzi

et al., 2010). The components of PM₁₀ have always been classed as mineral matter (MIN) (oxides of aluminum, calcium, silicon, titanium, iron, magnesium, manganese, sodium and potassium), organic matter (OM), elemental carbon (EC), secondary inorganic aerosol (SIA), sea salt (SS) and trace elements (TE) (Terzi et al., 2010). Among these components, SIA (sulfate, nitrate and ammonium) and carbonaceous particles were of great concern, as they were crucial factors controlling the degree of acidity (Xiu et al., 2004; Lin et al., 2007) and toxicity of the aerosols (Lee and Kang, 2001; Gutiérrez-Castillo, 2005).

The chemical compositions may vary largely due to the influence of emission sources, meteorology and the chance for dispersion (Viana et al., 2007; Terzi et al., 2010). Former studies on chemical compositions had been

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conducted mainly in coastal sites (Terzi et al., 2010; Viana et al., 2006, 2007) considering the influences of both continental and oceanic sources or of a regional megalopolis (Oanh et al., 2006; Celis et al., 2004; Putaud et al., 2004; Ho et al., 2006) in view of the tremendous pressure on atmospheric environments owing to huge population density and heavy traffic. Tsai and Cheng (2004) reported that energy intensive activities connected with industrial processes and other anthropogenic activities were the dominant contributors to PM₁₀ components. Wang et al. (2003) thought that aerosols were easily concentrated at the downwind of industrial sites. Before establishing effective measures to protect the population from exposure to hazardous atmospheric pollutants at these sites, it was necessary and urgent to investigate the chemical compositions of particulate matter. However, few investigations have been performed in cities or regions with highly centralized industries except for those in Pittsburgh (Rees et al., 2004), Lahore (Stone et al., 2010) and Fushun (Kong et al., 2012). The diversity of chemical compositions for particulate matter in industrial sites when compared with that in coastal sites or in a megalopolis were still not well recognized.

To better understand the influence of industrial sources on the surrounding PM₁₀ concentrations and its chemical composition, a field campaign was conducted at five site regions at Shenzhen, China in 2005. The particle mass was also reconstructed by a mass closure model for each site to identify the main contributors for PM₁₀ at industrial sites. The sources of PM₁₀ were identified by principal component analysis.

1 Methodology

1.1 Sampling site descriptions

The industrial region of this study was located in Shenzhen, in the south of China. It encompasses more than one hundred industrial plants, including four coal-fired power plants, one solid waste incinerator and one glass-producing plant. In the year 2008, the ten key industrial plants emitted 50,000.0 tons of SO₂ and 4000.40 tons of particulate matter, according to data of the local General Survey of Pollution Sources, which was not publically published.

1.2 PM₁₀ sampling and mass measurement

PM₁₀ sampling was carried out concurrently at the five sites (one was near a garbage-fired and a coal-fired power plant (NS), one was adjacent to another coal-fired power plant and wood plant (YL), one was set at a heavy-traffic roadside (CK), one was located by a dock (MT) and the last was in a residential area (JM)) in an industrial during Nov 3 to Nov 17, 2005. Particles were continuously collected for about 24 hr onto polypropylene and quartz filters (QR100, ADVENTEC Co., Ltd., Japan) using samplers (Dike In-

strument Co., Ltd., Beijing, China) operating at a flow rate of 75 L/min with a 10- μ m cut-off point. A total of 70 samples were obtained. Prior to sampling, polypropylene and quartz fiber filters were conditioned at 60°C for 0.5 hr and 800°C for 2 hr to remove any organic compounds that may be present on the filters, respectively. After sampling, the filters were removed from the inlets, folded in half wrapped, and kept in a laminar-flow clean hood until analysis. Filters were equilibrated in a relative humidity (45% \pm 5%) and temperature (21.0 \pm 1)°C controlled environment for 48 hr before gravimetric analysis. Filters were weighed with a sensitive microbalance (Daojin) with balance sensitivity \pm 0.010 mg. After weighing, the filters were stored at -4°C until chemical analysis.

1.3 Analytical techniques

Concentrations of PM₁₀ were obtained by standard gravimetric methods. For elemental analysis, half of each polypropylene filter was cut into portions for individual analysis for 20 elements (P, S, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Zr, Cd, Ba and Pb). Elements were extracted into acid solution in the following sequence: after being cut into pieces, filter samples were placed in a Teflon vessel and treated initially by concentrated acid solutions (0.5 mL HNO₃ and 1 mL HF). After being placed into a stainless steel vessel and covered, they were then put into an oven for 24 hr at 190°C (total digestion). After being taken out and cooled, the Teflon vessel was boiled to dryness on a hot plate (190°C). This process was repeated. Five milliliters HNO₃ was added into the vessel, and then it was kept at 130°C for 3 hr. The solution was cooled and transferred into a clean plastic bottle. Three milliliters of the extracted solution was transferred into a Teflon vial and finally it was diluted to 50 mL using distilled water. The extracts were then analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II, Thermo Electron). A quarter of each quartz filter was used for Na⁺, NH₄⁺, Mg²⁺, K⁺, Ca²⁺, F⁻, Cl⁻, NO₃⁻ and SO₄²⁻ analysis by Ion Chromatography (Dionex DX-500). Another quarter of each quartz filter was used for analysis of OC and EC by the IMPROVE thermal/optical reflectance method with DRI Model 2001 Thermal/Optical Carbon Analyzer. More information for the analysis methods including quality assurance and quality control is available in Kong et al. (2010).

1.4 Data analysis

Sources categories for PM₁₀ constituents were identified by means of principal component analysis (PCA) using SPSS 13.0 software. Briefly, PCA is a tool for analyzing structure in multivariate data sets. It starts with a large number of correlated variables and seeks to identify a smaller number of independent factors that can be used to explain the variance in the data. The derived variables are linear combinations of the original variables (Call  n et

al., 2009). A varimax normalized rotation was applied to maximize (or minimize) the values of the loading factors of each compound analyzed in relation to each rotated principal component (Kong et al., 2010). Factor loadings indicated the correlation of each pollutant species with each component and were related to the source emission composition.

2 Results and discussion

2.1 PM₁₀ mass concentrations

Summary data of PM₁₀ mass concentrations for the five sites are listed in **Table 1**. PM₁₀ concentrations at MT exhibited the highest values (2.2–3.6 times higher than those for the other sites), which may be related to the influence of harbor activities including resuspended soil particles, fuel combustion and dust emitted from the loading activities for corn. It should be mentioned that around MT, there were a number of barns for wheat. Corresponding measures should be undertaken to reduce the dust emission from corn loading and protection measures should also be adopted to prevent the workers being exposed to high levels of particulate matter. The concentrations of PM₁₀ exhibited similar variation trends for sites CK, NS, YL and JM, with the correlation coefficients between every two sites higher than 0.55 ($P < 0.05$), which indicated that the sources of PM₁₀ for the four sites may be similar. There were no correlations of PM₁₀ at MT with those for the other four sites, and this further validated that there were dissimilar sources for PM₁₀ at MT compared with other sites.

Table 1 PM₁₀ mass concentrations at the five sites (unit: $\mu\text{g}/\text{m}^3$)

	CK	MT	NS	YL	JM
Min	48	174	49	54	43
Max	89	384	103	92	80
Median	70	249	73	72	63
Mean ($n = 14$)	70	264	73	72	63
SD	14	62	16	13	13

2.2 Elements

The concentrations of elements in PM₁₀ for the five sites are listed in **Table 2**. Crustal elements Na, Mg, Al, K, Ca, Ti and Fe were abundant at the five sites, followed by elements related to anthropogenic processes (V, Cu, Zn, and Pb). The average concentrations of Al, Fe, Ti, Ca and Mn exhibited the highest values at site MT compared to the others. This implied that these extra PM₁₀ measured at MT site could also be resuspended soil particles. Meanwhile, some anthropogenic elements, such as Pb, Zn, Cr, V and Ni were also high at MT which indicated that anthropogenic activities in the harbor, such as fuel combustion and crane activities etc., could be at least partly responsible for

the observed high PM₁₀ levels. S exhibited the highest concentrations of all the elements, which may be related to the influence of coal used as a feed fuel for industrial plants in this area. This was verified by Kong et al. (2011), who pointed out that in a coal-based city, S was the source marker for almost all the types of fugitive dust, and attributed it to the influence of fugitive coal dust emissions. Ni and V have always been regarded as indicators of heavy oil combustion (Janssen et al., 1997; Hsu et al., 2005; Almeida et al., 2006; Koçak et al., 2007; Wu et al., 2007); Na, Ca, Mg and K were signatures for sea salt (Janssen et al., 1997; Wu et al., 2007; Mazzei et al., 2008; Viana et al., 2008); the combination of Al, Ca and Si were markers for crustal material (Götschi et al., 2005). Therefore, in these coastal industrial sites, sea salt, combustion sources related with harbor activities and crustal materials could be the main sources for particulate matter. At the traffic site CK, Cu showed the highest value at $261 \text{ ng}/\text{m}^3$, which could be related to brake erosion.

2.3 Characteristics of soluble ionic species

Table 3 summarizes the mean concentrations of ionic species for PM₁₀ at the five sites. The dominant ion was SO_4^{2-} , accounting for 34.3%–39.7% of the total ions. The reason was the same as the explanation for the high levels of S discussed above. NH_4^+ also exhibited relatively high mass concentrations. This may be related to industrial activities. Higher NH_4^+ concentrations were also observed by Chen et al. (2003) at an industrial site ($17.9 \text{ }\mu\text{g}/\text{m}^3$) in Taiwan, by Lin (2002) at a coastal traffic site ($14.5 \text{ }\mu\text{g}/\text{m}^3$) in Taiwan and by Lin et al. (2002) at coastal sites in Kaohsiung ($11.75 \text{ }\mu\text{g}/\text{m}^3$). Na^+ , Mg^{2+} , K^+ , Ca^{2+} and Cl^- exhibited significantly ($P < 0.01$) higher concentrations at the MT site when compared with other four sites, indicating that the influence of sea salt was more obvious for PM at this site, as Chen et al. (2003) pointed out that Na^+ and Cl^- were related to marine aerosol.

The sulfate concentration of non-marine origin, non-sea-salt (NSS) SO_4^{2-} , generally of anthropogenic origin, was determined indirectly based on Eq. (1) (Chen, 2003; Almeida et al., 2006; Gupta et al., 2007; Callén et al., 2009) which assumed that: (1) the chemical composition of sea salt particles was the same as that of sea water and (2) Na^+ in particulate samples originated solely from sea salt.

$$[\text{SO}_4^{2-} \text{ nm}] = [\text{SO}_4^{2-}] - [\text{Na}^+] \times 0.252 \quad (1)$$

At the five sites, NSS SO_4^{2-} accounted for 94.3%–96.4% of total SO_4^{2-} , indicating that anthropogenic emissions such as coal combustion and industrial emissions dominated the concentrations of SO_4^{2-} in this region.

The anion/cation (A/C) ratio was a good indicator to study the acidity of particles (Wang et al., 2006). The A/C ratios ranged close to 0.95 for the five sites (**Fig. 1**), all lower than 1.0, indicating anion deficiency. This could

Table 2 Statistical values for elemental concentrations in PM₁₀ at the five study sites (unit: ng/m³)

Elements	Sampling sites				
	CK	MT	NS	YL	JM
P	56.7 ± 11.8 (37.0-73.0)	436 ± 104 (273-632)	39.5 ± 9.3 (27.0-56.0)	66.9 ± 15.4 (45.0-89.0)	51.0 ± 10.7 (33.3-65.7)
S	2687 ± 562 (1890-3427)	3995 ± 721 (3010-5373)	3234 ± 874 (2170-5001)	2824 ± 518 (2170-3715)	2419 ± 506 (1701-3084)
Na	1140 ± 212 (814-1438)	2300 ± 382 (1798-3146)	1412 ± 344 (986-2143)	1662 ± 286 (1198-2069)	1026 ± 191 (733-1294)
Mg	200 ± 44.0 (132-268)	1052 ± 230 (713-1695)	214 ± 46.7 (142-299)	411 ± 70.8 (328-541)	181 ± 39.6 (119-241)
Al	274 ± 69.6 (189-376)	641 ± 168 (345-874)	355 ± 111 (199-553)	423 ± 88.0 (314-553)	247 ± 62.7 (170-338)
K	245 ± 48.6 (179-318)	1679 ± 393 (1160-2531)	291 ± 67.3 (191-413)	231 ± 59.3 (128-328)	220 ± 43.7 (161-286)
Ca	892 ± 213 (613-1240)	2312 ± 63 (1320-3334)	965 ± 292 (658-1570)	971 ± 193 (701-1275)	803 ± 192 (552-1116)
Ti	9.6 ± 2.5 (7.0-13.0)	30.4 ± 6.7 (19.0-43.0)	9.9 ± 2.9 (6.0-15.0)	33.1 ± 5.6 (25.0-43.0)	8.7 ± 2.2 (6.3-11.7)
V	28.3 ± 6.4 (19.0-37.0)	31.6 ± 6.5 (22.0-43.0)	18.2 ± 3.8 (13.0-26.0)	19.9 ± 4.9 (13.0-29.0)	25.5 ± 5.8 (17.1-33.3)
Cr	3.8 ± 1.0 (2.0-5.0)	23.9 ± 5.6 (17.0-34.0)	2.7 ± 0.6 (2.0-4.0)	14.2 ± 4.2 (9.0-21.0)	3.4 ± 0.9 (1.8-4.5)
Mn	27.7 ± 6.3 (17.0-35.0)	66.9 ± 14.9 (42.0-97.0)	27.7 ± 6.9 (18.0-39.0)	29.3 ± 5.3 (22.0-38.0)	24.9 ± 5.7 (15.3-31.5)
Fe	725 ± 140 (512-913)	2105 ± 477 (1479-3028)	944 ± 266 (621-1431)	1220 ± 295 (856-1716)	652 ± 126 (461-822)
Ni	7.1 ± 2.6 (1.0-11.0)	13.4 ± 3.7 (8.0-22.0)	8.0 ± 2.4 (5.0-12.0)	12.9 ± 2.9 (10.0-18.0)	6.4 ± 2.4 (0.9-9.9)
Cu	261 ± 45.2 (193-329)	65.8 ± 21.7 (39.0-112.0)	51.4 ± 10.0 (36.0-67.0)	39.2 ± 7.4 (30.0-50.0)	235 ± 40.7 (174-296)
Zn	215 ± 40.5 (154-270)	463 ± 76.0 (347-608)	195 ± 48.0 (124-279)	253 ± 48.2 (191-325)	193 ± 36.4 (139-243)
Sr	4.5 ± 0.8 (3.0-6.0)	13.9 ± 2.9 (10.0-20.0)	5.4 ± 1.2 (4.0-8.0)	7.3 ± 2.3 (4.0-12.0)	4.1 ± 0.7 (2.7-5.4)
Zr	1.5 ± 0.5 (1.0-2.0)	nd	1.1 ± 0.8 (nd-2.0)	0.1 ± 0.3 (nd-1.0)	1.4 ± 0.5 (0.9-1.8)
Cd	0.8 ± 0.6 (nd-2.0)	0.4 ± 1.6 (nd-6.0)	0.7 ± 0.5 (nd-1.0)	nd	0.7 ± 0.5 (nd-1.8)
Ba	13.7 ± 3.2 (8.0-18.0)	32.3 ± 5.4 (21.0-40.0)	17.4 ± 4.3 (11.0-24.0)	25.9 ± 4.8 (19.0-34.0)	12.3 ± 2.9 (7.2-16.2)
Pb	27.4 ± 5.3 (20.0-35.0)	80.5 ± 28.8 (48.0-148)	27.5 ± 6.5 (18.0-40.0)	73.8 ± 13.4 (57.0-92.0)	24.6 ± 4.8 (18.0-31.5)

Mean ± standard deviation is listed, Min and Max values are given in brackets.

nd: not detected

Table 3 Statistical values for ionic components in PM₁₀ at the five study sites (unit: ng/m³)

Elements	Sampling sites				
	CK	MT	NS	YL	JM
Na ⁺	957 ± 187 (703-1226)	1908 ± 312 (1465-2617)	1173 ± 293 (807-1830)	1380 ± 222 (1031-1674)	957 ± 187 (703-1226)
NH ₄ ⁺	3387 ± 623 (2407-4320)	2985 ± 639 (2216-4317)	4110 ± 930 (2835-5847)	3385 ± 605 (2444-4298)	3387 ± 623 (2407-4320)
Mg ²⁺	165 ± 37 (106-226)	873 ± 233 (605-1376)	177 ± 40 (111-245)	346 ± 60 (282-461)	165 ± 37 (106-226)
K ⁺	207 ± 44 (141-275)	1378 ± 328 (977-2123)	247 ± 58 (147-371)	196 ± 55 (92-285)	207 ± 44 (141-275)
Ca ²⁺	746 ± 174 (517-1031)	1905 ± 527 (1137-2775)	828 ± 251 (579-1322)	826 ± 171 (585-1110)	746 ± 174 (517-1031)
F ⁻	136 ± 25 (99-168)	156 ± 31 (122-228)	122 ± 21 (95-163)	204 ± 67 (122-354)	136 ± 25 (99-168)
Cl ⁻	1432 ± 254 (1020-1808)	2891 ± 555 (2047-3916)	1836 ± 449 (1279-2844)	2229 ± 350 (1683-2739)	1432 ± 254 (1020-1808)
NO ₃ ⁻	4977 ± 1291 (3466-6830)	7025 ± 1741 (4785-10473)	5524 ± 1382 (3697-8102)	5178 ± 1142 (3764-7260)	4977 ± 1291 (3466-6830)
SO ₄ ²⁻	6968 ± 1498 (4877-9042)	10793 ± 1890 (8120-14269)	8642 ± 2414 (5747-13315)	7564 ± 1393 (5811-9809)	6968 ± 1498 (4877-9042)

Mean ± standard deviation is listed, Min and Max values are given in brackets.

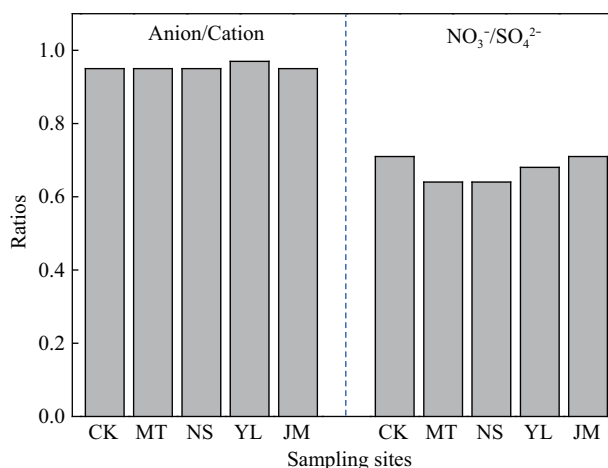


Fig. 1 Ratios for equivalent concentrations of anions and cations at an industrial region in Shenzhen. Cations = [Na⁺]/23 + [NH₄⁺]/17 + [K⁺]/39 + 2 × [Mg²⁺]/24 + 2 × [Ca²⁺]/40; anions = [F⁻]/19 + [Cl⁻]/35.5 + [NO₃⁻]/62 + 2 × [SO₄²⁻]/96 (Lai et al., 2007; Shen et al., 2009).

be explained by the presence of some carbonate ions (HCO₃⁻, CO₃²⁻) and organic water-soluble ions that were not detected (Duan et al., 2006; Behera and Sharma, 2010). The mass ratio of NO₃⁻/SO₄²⁻ has been used as an indicator of the relative importance of mobile vs. stationary sources of sulfur and nitrogen in the atmosphere (Yao et al., 2002; Wang et al., 2006). Arimoto et al. (1996) ascribed high NO₃⁻/SO₄²⁻ mass ratios to the predominance of mobile sources over stationary sources of pollutants. In the current study, the NO₃⁻/SO₄²⁻ ratios for the five sites varied in the range 0.64–0.71, implying coal combustion was predominant as a source for atmospheric particulate matter (**Fig. 1**). The ratios for sites CK and JM were slightly higher than the other sites, which could be attributed to the enhanced vehicle emissions.

Ammonia reacted with acidic gases such as sulfuric, nitric and hydrochloric acid to form ammonium sulfate, ammonium chloride and ammonium nitrate (Lai et al., 2007). Ammonium first combined with sulfate when sul-

fate, nitrate and chloride co-existed, since ammonium sulfate was more stable (Lai et al., 2007; Liu et al., 2008). The sum of SO_4^{2-} , NO_3^- and Cl^- was significantly correlated with NH_4^+ , with correlation coefficients higher than 0.95 ($P < 0.0001$) in **Fig. 2**. All intercepts were close to 0, indicating that ammonia may fully neutralize sulfate, nitrate and chloride. The slopes were all lower than 1.0, implying insufficient ammonium present, and the reason may be the existence of industrial plants with coal as fuel, which may release large amounts of SO_2 .

2.4 Characteristics of elemental and organic carbon

EC is a byproduct of incomplete combustion of organic carbon (OC) and is accepted as a tracer of primary emissions. OC is directly emitted to atmosphere from anthropogenic and biogenic sources and is also formed in the atmosphere from low-volatility products produced by the oxidation of gas-phase precursors (Kong et al., 2010). The separation and quantification of primary and secondary organic carbon (SOC) is of great importance in understanding secondary aerosol formation as well as in controlling particulate carbon pollution (Kong et al., 2010). **Table 4** summarizes the OC and EC concentrations for PM_{10} at the five sites.

The highest concentrations of OC and EC were found both at MT, and were attributed to the influence of harbor activities, such as the emissions from vessels or other engines. The loading and unloading of corn may also increase the amount of organic particulate matter. Field and laboratory studies have showed that mineral dust par-

ticles can serve as reaction surfaces for different species, including those of man-made origin (Koulouri et al., 2008). The large amount of dust emitted from corn loading and unloading activities may act as the reaction surfaces for organic materials. In the study of Kong et al. (2012), OC and EC concentrations both decreased in the order industrial site > traffic site > residential sites > background site in Fushun. In this study, however, except for MT, a higher EC concentration was found at site YL, which could be related with the corresponding incomplete combustion sources. OC/EC ratios larger than 2 have always been used as an indication of secondary aerosol formation (Chen et al., 2003; Guo et al., 2009). The high EC concentrations at YL also led to the lowest OC/EC ratio being found at this site. The ratio peaked at MT at 16.9. The reason was as discussed before.

It is difficult to directly measure SOC species, and SOC concentrations (OC_{sec}) could be estimated based on the following equation (Tao et al., 2009):

$$\text{OC}_{\text{sec}} = \text{OC}_{\text{tot}} - \text{EC} \left(\frac{\text{OC}}{\text{EC}} \right)_{\text{min}} \quad (2)$$

where, OC_{tot} is total OC, and $(\text{OC}/\text{EC})_{\text{min}}$ is the minimum ratio observed. This equation would be reasonable if the minimum ratios $(\text{OC}/\text{EC})_{\text{min}}$ were stable and reproducible at various locations. The $(\text{OC}/\text{EC})_{\text{min}}$ values for the five sites were 3.75, 11.81, 4.2, 1.08 and 3.70, respectively. SOC accounted for about 22.6%–38.7% of OC, with the highest percentage occurring at YL, which indicated that there existed more precursors for SOC from the surrounding coal-fired power plant, wood plant and the heavy traffic. The conclusion was verified by the relationship between OC and EC from linear regression analysis, which could be also used to evaluate the origin of OC and EC (Kong et al., 2010). Significant correlation existed for the other four sites, indicating similar sources for OC and EC as **Fig. 3** shows. The OC and EC exhibited no correlation at site YL, which was different from other sites. As about 38.7% OC were formed by transformation from precursors, the mass percentages of primary OC emitted along with EC were low. This may explain the low correlation between OC and EC at site YL.

2.5 Mass closure of PM_{10}

Mass closure analysis has been widely accepted for analysis of aerosols (Kim et al., 2001; Chow et al., 2002;

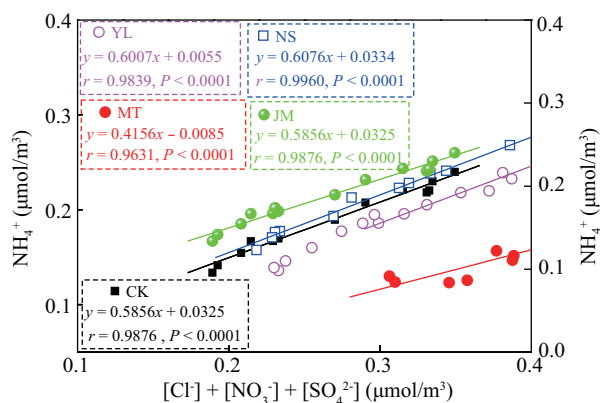


Fig. 2 Relationship between equivalent concentrations of Cl^- , NO_3^- , and SO_4^{2-} and NH_4^+ .

Table 4 Statistical values for organic carbon (OC), elemental carbon (EC) and secondary carbon (SOC) in PM_{10} at the five study sites (unit: $\mu\text{g}/\text{m}^3$)

Elements	Sampling site				
	CK	MT	NS	YL	JM
OC	18.6 ± 3.3 (14.0–23.0)	154 ± 42.0 (94.5–232)	18.4 ± 4.2 (13.0–26.0)	14.0 ± 2.7 (10.0–19.0)	16.7 ± 3.0 (12.6–20.7)
EC	3.9 ± 1.0 (2.0–5.0)	9.2 ± 2.6 (6.0–14.0)	3.4 ± 1.0 (2.0–5.0)	7.8 ± 2.3 (4.0–12.0)	3.5 ± 0.9 (1.8–4.5)
SOC	4.1 ± 2.3 (0.0–7.0)	50.3 ± 20.5 (0.0–75.4)	4.3 ± 2.0 (0.0–7.2)	5.6 ± 3.0 (0.0–9.5)	3.7 ± 2.0 (0.0–6.3)
OC/EC	5.0 ± 0.9 (3.8–7.0)	16.9 ± 2.0 (11.8–19.8)	5.7 ± 0.8 (4.2–7.0)	1.9 ± 0.6 (1.1–3.0)	5.0 ± 0.9 (3.8–7.0)
SOC/OC (%)	22.6 ± 13.5 (0.0–46.4)	28.9 ± 10.3 (0.0–40.3)	24.2 ± 11.3 (0.0–40.0)	38.7 ± 20.0 (0.0–63.9)	22.6 ± 13.4 (0.0–46.4)

Mean ± standard deviation is listed, Min and Max values are given in brackets.

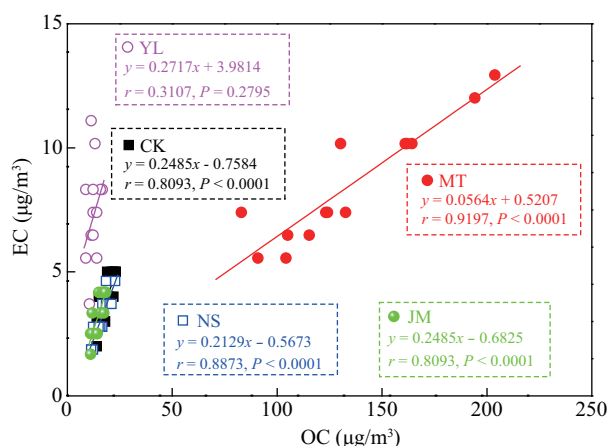


Fig. 3 Correlation between OC and EC for the five sites.

Celis et al., 2004; Duan et al., 2006; Sillanpää et al., 2006; Viana et al., 2006; Koulouri et al., 2008; Terzi et al., 2010), allowing for source reconciliation, quality assurance, health and welfare impacts (Ho et al., 2006). The relative contributions reflected differences in emission sources and processes controlling the aerosol composition (Sillanpää et al., 2006). For the purposes of chemical mass closure, the chemical components were divided into six classes as follows: MIN, TE, OM, EC, SS, SIA and unidentified matter.

MIN was the sum of Al, Mg, Mn, Si, Na, K, Ca, Ti and Fe multiplied by factors to convert them to their common oxides with the equation: $\text{MIN} = 2.14\text{Si} + 1.67\text{Ti} + 1.89\text{Al} + 1.59\text{Mn} + 1.67\text{Mg} + 1.95\text{Ca} + 1.35\text{Na} + 1.21\text{K} + 1.43\text{Fe}$.

Ca was multiplied by a factor of 1.95 to account for CaO and CaCO₃, which were considered its most abundant forms (Terzi et al., 2010). Si was not detected in this study and was calculated according to the contents of Ti, based on the assumption that the percentages of the two elements in atmospheric particulate matter were the same as those in crustal materials (The mass percentages of Si and Ti in crustal materials were 27.2% and 0.68%, respectively). Trace elements only represented a small percentage of PM, however they were also added to the analysis because they have great environmental importance due to their toxicity and anthropogenic origin (Terzi et al., 2010). Except for the above elements in MIN, the sum of all the other elements was defined as trace species. Finally, organic matter was estimated by multiplying OC by a conversion factor (CF), which corresponded to the organic molecular carbon weight per carbon weight (Koulouri et al., 2008), and from previous work CF was found to range from 1.2 to 2.5 (Sillanpää et al., 2006). In this work a conversion factor of 1.4 was applied. The marine contribution was calculated to make comparison to others as the sum of Na⁺ concentration and fractions of the concentrations of Cl⁻, Mg²⁺, K⁺, Ca²⁺, and SO₄²⁻ based on a standard sea water composition, assuming that soluble Na⁺ in aerosol samples comes solely from sea salt. Therefore,

$$\text{Sea salt} = [\text{Na}^+] + [\text{ss-Cl}^-] + [\text{ss-Mg}^{2+}] + [\text{ss-K}^+] + [\text{ss-Ca}^{2+}] + [\text{ss-SO}_4^{2-}] \quad (3)$$

where, ss-Cl⁻ was calculated as total [Na⁺] times 1.8, ss-Mg²⁺ as total [Na⁺] times 0.12, ss-K⁺ as total [Na⁺] times 0.036, ss-Ca²⁺ as total [Na⁺] times 0.038, and ss-SO₄²⁻ as total [Na⁺] times 0.252 (Terzi, et al., 2010). Finally, secondary inorganic aerosol was calculated as the sum of NSS-SO₄²⁻, NO₃⁻ and NH₄⁺. The concentrations of all these species in µg/m³ were adopted.

As shown in Fig. 4, the main constituents of PM₁₀ were found to be OM (30.9%–69.5%), followed by SIA (7.9%–25.0%), SS (2.4%–6.2%), MIN (6.7%–13.8%), EC (3.5%–10.8%) and TE (2.0%–4.9%). The unidentified materials were in the range of 3.9%–7.5%. The remaining unidentified materials probably resulted from aerosol-bound water, unanalyzed chemical components such as non-soluble species, as well as random and possibly systematic errors (Putaud et al., 2004; Sillanpää et al., 2006; Tao et al., 2009; Terzi et al., 2010). MT exhibited the highest OM percentage, which was explained above.

The mass closure fit is shown in Fig. 5. A good model fit was evidenced by three factors: high r^2 , gradient close to 1.0 and a near-zero intercept (Yin et al., 2008). The r^2 values was 0.99, while the gradients and intercepts were 1.05 and 6.5, respectively, which meant some undetected compositions existed and may also be related to the combined uncertainty of the chemical analysis.

The chemical components of PM₁₀ in the current study were compared with former studies, to better understand the compositional diversity at various locations (Table 5). PM₁₀ concentrations in this study were higher than those in most other studies except for Beijing and Chennai (Oanh et al., 2006). MIN and OM were the main contributors to PM₁₀ around the world, accounting for 6%–49% and

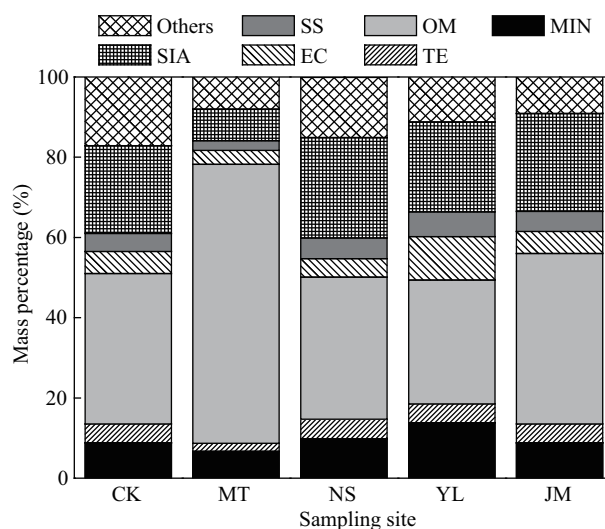


Fig. 4 Chemical mass closure of PM₁₀ at the five sampling sites. MIN: minerals; TE: trace elements; OM: organic matter; EC: elemental carbon; SS: sea salt; SIA: secondary inorganic aerosol; Others: unidentified mass.

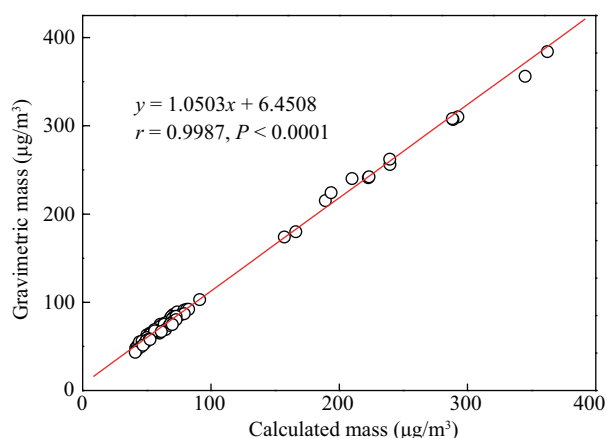


Fig. 5 Relationship between the calculated and the gravimetrically measured particulate mass for PM₁₀ samples in the industrial region.

18%–43.2%, respectively. The contributions reflected the differences in emission sources and processes controlling the aerosol composition (Terzi et al., 2010). The MIN showed a comparatively lower mass percentage while OM had the highest mass percentage, which could be related to the surrounding industrial sources. The mass percentages of SS, EC, TE and SIA were in the range of the corresponding values in other studies.

2.6 Source identification by PCA

Using PCA, it is possible to simplify the interpretation of complex systems and to reduce the set of variables to fewer new ones, called factors. Each of these factors can be identified as either an emission source, or a chemical interaction. Many of these factors indicate more than one possible cause (Callén et al., 2009). Considering that $n > 30 + (V + 3)/2$ (where n = number of samples and V = number of variables) (Callén et al., 2009) and the relatively limited number of samples available for each site, PCA analysis was performed on PM₁₀ data sets for the five sites together (70 samples and 32 variables) with varimax rotation. A total of four components were extracted covering 94.8% of the data variance as shown in **Table 6**. The first factor was related to crustal elements, P, Mg, K, Ca, Mn, Fe, trace elements including Zn and Zr and Mg²⁺, K⁺, Ca²⁺ as well as OC, and it explained 54.5% of the variance. This factor was associated with crustal materials and coal/wood combustion. The second factor explained 20.9% of the variability, heavily loaded on Ni, F and EC. This factor was considered to represent oil combustion. The third factor was mainly related to NH₄⁺, SO₄²⁻ and NO₃⁻, explaining 11.4% of the variance. This factor was considered to be associated with secondary aerosols. The fourth factor was highly related to Cu and Cd and it

Table 5 PM₁₀ mass closure around the world (unit: µg/m³)

Study sites	Description	Periods	PM ₁₀	MIN	OM	EC	SS	TE	SIA	UM
Shenzhen	Industrial sites	03/11/2005-17/11/2005	108.4	9.3 (9.6%)	57.1 (43.2%)*	5.5 (6.0%)	4.1 (4.7%)	3.7 (4.2%)	17.2 (20.3%)	11.3 (12.1%)
Chillán ^a	Urban site	12/2001-4/2003	82.5	22.3 (27%)	23.1 (31%)	6.0 (8%)	/	/	19.0 (23%)	/
Europe ^b	Urban background	1991-2001	–	(9%)	(20%)	(5%)	(4%)	/	(35%)	(27%)
	Curbside		–	(19%)	(22%)	(13%)	(3%)	/	(24%)	(19%)
Hongkong, China ^c	Curbside	2000-2001 winter	73.5	8.8 (12%)	16.2 (22%)	5.9 (8%)	5.9 (8%)	/	22.1 (30%)	14.7 (20%)
	Mixed residential/ commercial/industrial area		55.8	6.1 (11%)	12.2 (22%)	3.9 (7%)	6.7 (12%)	/	18.4 (33%)	8.4 (15%)
	Curbside	2000-2001 summer	–	(6%)	(27%)	(13%)	(9%)	/	(12%)	(34%)
	Mixed residential commercial/industrial area		–	(9%)	(25%)	(11%)	(12%)	/	(15%)	(28%)
Bangkok	Urban site ^d	2001-2004 (other month)	76	10.0 (13%)	26.6 (35%)	9.4 (12%)	3.6 (5%)	0.5 (1%)	11.8 (16%)	16.7 (22%)
Beijing			262	43.1 (16%)	/	/	2.4 (1%)	3.5 (1.3%)	61.7 (24%)	151.9 (58%)
Bandung			83	7.8 (9%)	/	9.8 (12%)	4.6 (6%)	1.2 (1%)	24.4 (29%)	34.9 (42%)
Manila			54	/	/	12.9 (24%)	/	/	/	/
Hanoi			186	23.4 (13%)	/	8.9 (5%)	2.0 (1%)	1.5 (1%)	106.5 (57%)	102.3 (55%)
Bangkok	Urban site ^d	2001-2004 (May-October)	33	6.1 (18%)	/	6.3 (19%)	3.5 (11%)	0.6 (2%)	4.7 (14%)	8.6 (26%)
Beijing			180	24.8 (14%)	/	/	1.1 (1%)	12.1 (7%)	46.8 (26%)	93.6 (52%)
Chennai			145	/	/	/	/	/	/	/
Bandung			62	8.6 (14%)	/	7.5 (12%)	5.8 (10%)	4.6 (7%)	15.9 (26%)	19.8 (32%)
Hanoi			79	19.8 (25%)	/	6.6 (8%)	2.7 (3%)	1.2 (2%)	12.4 (16%)	36.3 (46%)
Barcelona, Spain ^e	Coast, dense road traffic site	09/01/2001-27/12/2001	36.1	10.7 (29%)	10.8 (30%)*	/	2.0 (6%)	/	7.4 (20%)	4.9 (14%)
Tarragona, Spain ^e	Coast, urban background site	09/01/2001-27/12/2001	29.5	8.2 (28%)	6.6 (22%)*	/	2.7 (9%)	/	6.3 (21%)	5.9 (20%)
Ghent ^f	Coastal, urban background site	2004-2005 (summer)	19.9	1.9 (9%)	5.9 (29%)*	/	1.4 (7%)	/	6.5 (33%)	4.3 (22%)
	winter		28.6	2.5 (9%)	8.5 (30%)*	/	4.3 (15%)	/	11.2 (39%)	2.2 (8%)
Barcelona ^f	Coastal, urban background site	summer	29.5	9.8 (33%)	6.8 (23%)*	/	2.3 (8%)	/	6.9 (23%)	3.9 (13%)
	winter		34.0	7.8 (23%)	11.3 (33%)*	/	1.2 (4%)	/	10.7 (31%)	3.1 (9%)
Spain ^g	Urban background sites	1999-2005	38	6.9 (18%)	6.9 (18%)*	/	4.8 (13%)	/	5.8 (15%)	/
	Urban industrial sites		39	11.4 (29%)	7.1 (18%)*	/	2.4 (6%)	/	9.7 (25%)	/
	Urban traffic sites		48	14.4 (30%)	11.9 (25%)*	/	1.8 (4%)	/	11.3 (24%)	/
	Coastal, urban industry site	12/2006-3/2007 (winter)	69	31.1 (45%)	13.8 (20%)	/	0.7-1.4 (1-2%)	0.7 (~1%)	9.7 (14%)	5.5 (8%)
Thessaloniki, Greece ^h	Coastal, urban traffic site	12/2006-3/2007 (winter)	51	18.4 (36%)	11.2 (22%)	/	0.5-1.0 (1-2%)	0.5 (~1%)	7.1 (14%)	11.2 (22%)
	Coastal, urban industry site	6/2007-9/2007 (summer)	58	28.4 (49%)	10.4 (18%)	/	0.6-1.2 (1-2%)	0.6 (~1%)	8.1 (14%)	8.7 (15%)
	Coastal, urban traffic site	6/2007-9/2007 (summer)	42	15.1 (36%)	12.2 (29%)	/	0.4-0.8 (1-2%)	0.4 (~1%)	9.2 (22%)	2.1 (5%)

The values are expressed as µg/m³ and the values in bracket show the percentage average.

^a Celis et al., 2004; ^b Putaud et al., 2004; ^c Ho et al., 2006; ^d Oanh et al., 2006; ^e Viana et al., 2006; ^f Viana et al., 2007; ^g Querol et al., 2008; ^h Terzi et al., 2010.

* OM+EC; UM: undetected; –: accurate PM values can not be obtained; /: not detected.

Table 6 Factorial weight matrix obtained from PM₁₀ samples in Shenzhen

Species	Factor1	Factor 2	Factor 3	Factor 4
P	0.979	0.184	-0.030	-0.010
S	0.665	0.285	0.377	0.025
Na	0.759	0.499	0.353	-0.176
Mg	0.925	0.357	0.032	-0.086
Al	0.769	0.457	0.369	-0.129
K	0.988	0.117	0.030	-0.033
Ca	0.926	0.256	0.241	0.040
Ti	0.465	0.519	0.022	-0.286
B	0.766	0.567	-0.078	-0.268
V	0.575	0.264	0.247	0.707
Cr	0.785	0.582	-0.059	-0.161
Mn	0.936	0.270	0.193	0.051
Fe	0.846	0.447	0.236	-0.151
Ni	0.491	0.710	0.296	-0.181
Cu	-0.224	-0.220	-0.093	0.925
Zn	0.894	0.397	0.141	0.035
Sr	0.870	0.426	0.152	-0.123
Zr	-0.414	-0.352	0.478	0.616
Cd	0.095	-0.140	0.361	0.499
Ba	0.676	0.628	0.240	-0.236
Pb	0.605	0.736	0.074	-0.185
Na ⁺	0.764	0.496	0.353	-0.132
NH ₄ ⁺	-0.165	0.145	0.941	0.185
Mg ²⁺	0.924	0.361	0.023	-0.086
K ⁺	0.986	0.117	0.034	-0.022
Ca ²⁺	0.922	0.256	0.254	0.055
F	-0.034	0.905	0.181	0.086
Cl	0.728	0.529	0.366	-0.190
NO ₃	0.599	0.357	0.648	0.236
SO ₄ ²⁻	0.666	0.277	0.678	0.045
OC	0.992	0.110	0.009	-0.002
EC	0.623	0.695	0.087	-0.087
% of variance	54.5	20.9	11.4	8.0
Cumulative %	54.5	75.4	86.8	94.8
Sources	Crustal materials and coal/wood combustion	Oil combustion	Secondary aerosol	Industrial process and vehicle emission

Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization.

explained 8.0% of the total variance. This component was associated with industrial processes and vehicle emissions like brake or tire wear. The associations of these chemical species with various sources were discussed in detail by Kong et al. (2010). The PCA results were consistent with the explanation for the mass concentrations of PM₁₀ and chemical species discussed above.

3 Conclusions

PM₁₀ mass concentrations and major inorganic chemical compositions were measured in a coastal industrial region at Shenzhen in 2005. The spatial variations of elements, ions and carbonic fractions were discussed and the composition of PM₁₀ was reconstructed. PM₁₀ concentrations were highest at 264 µg/m³ at the site near a harbor. The concentrations of PM₁₀ exhibited similar variation trends

for the other four sites, with the correlation coefficients between every two sites higher than 0.55 ($P < 0.05$). Similarly, most elements, ions, OC and EC demonstrated their highest concentrations at the MT site, pointing to the influence of harbor activities in the vicinity. At this industrial region, coal combustion was more important than vehicle emission, with NO₃⁻/SO₄²⁻ ratios varying in the range 0.64–0.71, and the particulate matter was alkaline, with A/C ratios that ranged close to 0.95. SOC accounted for about 22.6%–38.7% of OC, with the highest percentage at YL, which may be related to various emission sources in the surrounding environment for particulate matter. Meanwhile at this site, the OC and EC exhibited no correlation, which was different from the other sites.

A mass closure model performed well, with significant correlation obtained between calculated and measured PM₁₀ mass concentrations. Organic matter and secondary inorganic aerosol were the main two components of PM₁₀ with the ranges of 30.9%–69.5% and 7.9%–25.0% in this industrial region. When compared with other study sites around the world, the mineral matter showed lower mass percentage while organic matter had the highest mass percentage in this study, which could be related to the specific surrounding industrial sources. Principal component analysis indicated that the main sources for particulate matter in this industrial region were crustal materials and coal/wood combustion, oil combustion, secondary aerosols, industrial process and vehicle emission.

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