Vertical variability of particulate matter and the potential sources in Tianjin, China

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Abstract

PM 10 samples were collected at a meteorological tower in Tianjin. Four height levels (10m, 40m, 120m and 220m) were selected as the sampling sites. During the measurement campaign, highest PM 10 and species concentrations were obtained at 10m while lower concentrations were obtained at higher sampling sites. According to the analysis of vertical variability for species concentrations and fractions, significant difference among different height sites were found for some species such as Al, Si, Ca and OC, while insignificant difference were found for NO 3 - and SO 4 2-. In addition, the source contributions at each sampling site were calculated by chemical mass balance (CMB) model. For all sampling sites, secondary sulfate got the largest contributions (24.11-30.96%), the other estimated contributions were: secondary nitrate (16.19-20.95%), crustal dust (10.74-11.37%), coal combustion (12.47-14.39%) and vehicle exhaust (13.92-14.78%) and cement dust (4.60-9.89%). Finally, the conditional probability function (CPF) plots and potential source contribution function (PSCF) maps show that ambient samples might be mainly attributed from local potential sources at lower height sampling sites; while mainly from regional potential sources at higher height sampling sites, during this measurement campaign.

Keywords: Vertical variability; Sources; Particulate matters; Conditional Probability Function; Potential Source Contribution Function

1. Objective

Vertical distribution characteristics can indicate the PM 10 pollution situation on local and regional scales. In this work, four height sampling sites (10m, 40m, 120m and 220m) at a meteorological tower in Tianjin were selected. The vertical variability of particle matter in Tianjin was studied. The chemical mass balance (CMB) was used to study the potential sources at four height sampling sites. In addition, the likely location of potential source were studied by conditional probability function (CPF) and potential source contribution function (PSCF).

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Main research area:
Receptor model, Air pollution prevention and control
2. Method
2.1 Ambient sampling
Tianjin, with an area of 11200km² and a population of over ten million citizens, is a large industrial city as well as the largest seaport in northern China. PM$_{10}$ samples were collected on a 255-m high meteorological tower (39°04′29.4″N, 117°12′20.1″E) which lies in the observation station of atmospheric planetary boundary layer, set up by the Meteorological Bureau of Tianjin. The observation station is located in a residential and traffic mixing area with no direct industrial sources of atmospheric pollutants near the site. PM$_{10}$ monitoring instruments were set up at the heights of 10m, 40 m, 120 m, and 220 m.

The sampling period was selected in the summer from 24$^{th}$ August to 12$^{th}$ September in 2009 including several different types of weather. At each height sampling site, twenty PM$_{10}$ samples were obtained. Samples were collected for 24h everyday using medium-volume PM$_{10}$ samplers. The sampling method was similar to our prior works (Shi et al., 2009a, Shi et al., 2009b).

2.2 Chemical analysis
Some elements (Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn, Fe, Ni, Co, Cu, Zn, Br, Ba, and Pb) were analyzed by ICP (IRIS Intrepid II, Thermo Electron) (Baldwin et al., 1994; Watson et al., 1999). These elements were extracted from polypropylene membrane filters by using the laboratory system (ETHOS E, Milestone). The quartz fiber filters were cut into pieces for respective analysis of ion, organic carbon (OC). Water soluble NH$_4^+$, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ were extracted by the ultrasonic extraction system (AS3120, AutoScience) and analyzed by ion chromatography (DX-120, DIONEX) (Carvalho, et al., 1995; Chow and Watson, 1999). OC was analyzed by carbon elemental analyzer (Vario EL, GmbH).

3. Results
3.1 PM$_{10}$ concentration
Time-serial PM$_{10}$ concentrations measured at each height are described in Fig.1. During sampling period, 10 m-height site got the highest PM$_{10}$ concentrations; the second highest PM$_{10}$ concentrations were obtained at the 40-height site; while 220 m-height site got the lowest PM$_{10}$ concentrations. PM$_{10}$ concentrations from lower height sampling site were significantly higher (p<0.05, T-test) than those from higher height sampling site (However, 10 m-height site was not significantly higher than 40- height site). The changes of PM$_{10}$ mass concentration showed an obvious periodicity with the period of 6-7days which is attributable to change in synoptic scale.

![Fig. 1 Time-serial PM$_{10}$ concentrations for four sampling heights](image-url)
For each receptor profile, Al, Si, Ca, OC, NO$_3^-$ and SO$_4^{2-}$ were got high levels. So, coal combustion, soil dust, cement dust, vehicle exhaust emission, secondary nitrate and sulfate might be the potential sources which attributed to the receptor samples.

3.2 Analysis of vertical variability

Fig. 2a and 2b describe some species concentrations ($\mu$g/m$^3$) and fractions (%) in receptors from four sampling sites. The plot shows that higher concentrations were obtained at lower height sampling site, for almost all the species (NO$_3^-$ got the highest value in 120 m-height sampling site). For Al, Si, Ca and OC, the T-test studies shows that the differences of concentrations among four sampling sites are significant ($p<0.05$). It indicates that the vertical height have a stronger influence on the concentration of these four species. In contrary, for NO$_3^-$ and SO$_4^{2-}$ concentrations, their differences among four heights are insignificant ($p>0.05$).

In species fractions (%) plot, it can be found that similar levels were observed at four heights, for species Al, Si, and OC. As to Ca fraction (%), higher values were observed at lower height sampling sites; while higher height sampling sites got higher fractions (%) for NO$_3^-$ and SO$_4^{2-}$. However, the T-test results indicate that vertical variability for Ca fraction (%) was significant while NO$_3^-$ and SO$_4^{2-}$ fraction (%) were insignificant. The species fractions can reflect the information of potential source contributions.

![Fig. 2a](image1.png)

Fig. 2a Species concentrations in receptors from four sampling sites

![Fig. 2b](image2.png)

Fig. 2b Species fractions (%) in receptors from four sampling sites
3.3 Source apportionment

Chemical mass balance (CMB) model was used to obtain the contributions of potential sources at each height sampling site. In this work, the source profiles reported in our prior studies (Bi et al., 2007) were used for CMB calculating. The estimated source contributions (%) at each sampling site are shown in Fig. 3. Of all the results, the performance indices such as $\chi^2$ (0.035-0.87), $R^2$ (0.91-1.00) and percent mass (88-97%) all meet the CMB requirements, which indicates that the results can be accepted.

At all the sampling sites, secondary sulfate got the largest contributions (24.11-30.96%) and cement dust got the lowest contributions (4.60-9.89%). The other estimated contributions were: secondary nitrate (16.19-20.95%), crustal dust (10.74-11.37%), coal combustion (12.47-14.39%) and vehicle exhaust (13.92-14.78%).

For crustal dust, coal combustion and vehicle exhaust, four height-sampling sites got similar estimated contributions. While the estimated contribution of cement dust shows a negative correlation with the height of sampling site. For secondary sulfate and nitrate, their estimated contribution has a positive correlation with the height of sampling site.

![Fig. 3. Estimated source contributions (%) for four height sampling sites, by CMB model](image)

3.4 CPF and PSCF function study

The conditional probability function (CPF) (Kim et al., 2005; Song et al., 2007; Song et al., 2008) can be applied to identify the orientation of species based on their emission concentrations and the wind direction data. The CPF plot of all the species at 220m height site was different from those at 10m and 40m height site; while the CPF plots at 10m and 40m height sites were relatively similar to each other. It is because that the ambient samples might be mainly contributed from local potential sources at lower height (10m and 40m) sites, while at higher site (220m) they may be contributed from regional potential sources.
The PSCF model counts the number of trajectory segment end points falling within grid cells (Hopke et al., 1995; Crawford et al., 2007; Dvorska et al., 2008; Gasic et al., 2010). The PSCF results are agreed with CPF results.

4. Conclusion

Overall, higher PM$_{10}$ and species concentrations were obtained at lower height sampling site. According to the vertical variability study of species concentrations and their fractions(%), significant difference among different heights were found for some species such as Al, Si, Ca and OC, while the difference for NO$_3^-$ and SO$_4^{2-}$ was insignificant. CMB model show that secondary sulfate got the largest contributions at each height sampling site. The vertical variability of source contributions are agreed with species concentrations and fractions results. Finally, the CPF and PSCF function show that ambient samples might be mainly contributed from local potential sources at lower height sampling sites; while mainly from regional potential sources at higher height sampling sites, during this measurement campaign.

References


