Concentration and chemical composition of PM$_{2.5}$ in Shanghai for a 1-year period

Boming Ye[a], Xueli Ji[a], Haizhen Yang[a], Xiaohong Yao[b], Chak K. Chan[b], Steven H. Cadle[c,*], Tai Chan[c], Patricia A. Mulawa[c]

[a] *School of Environmental Science & Engineering, Tongji University, Shanghai, China*
[b] *Department of Chemical Engineering, Hong Kong University of Science & Technology, Hong Kong, China*
[c] *GM R&D Center, Chemical and Environmental Sciences Laboratory, MC 480-106-269, Warren, MI 48090, USA*

Abstract

Weekly PM$_{2.5}$ samples were collected in Shanghai, China at two sites, Tongji University and Hainan Road. Sampling started in March 1999 and was conducted for 1 year. The ambient mass concentration and chemical composition of the PM$_{2.5}$ were determined. Chemical analyses included elemental composition, water-soluble ions, and organic and elemental carbon. Weekly PM$_{2.5}$ mass concentrations ranged from 21 to 147 μg/m^3, with annual average concentrations of 57.9 and 61.4 μg/m^3 at the two sites, respectively. Seasonal variation of PM$_{2.5}$ concentrations was significant, with the highest concentrations observed from mid-November through December and the lowest from June through September. Ammonium sulfate and nitrate accounted for 41.6% of the PM$_{2.5}$ mass with sulfate alone accounting for 23.4% of the PM$_{2.5}$ mass. Carbonaceous material accounted for 41.4% of the PM$_{2.5}$ mass, with 73% of that mass being organic, as defined by the TOR analysis method. Crustal components averaged 9.6% of the PM$_{2.5}$ mass. Potassium, which was 95% water soluble, accounted for 2.7% of the PM$_{2.5}$ mass.

1. Introduction

Air quality is an important issue in China and the Chinese government is committed to improving it by establishing more stringent emission control strategies. Particulate matter is a primary concern due to its possible health impacts and visibility degradation. China has a PM$_{10}$ standard, but does not have one for PM$_{2.5}$. Thus, relatively little data is available concerning PM$_{2.5}$ concentrations and trends. In 1999, we initiated a PM$_{2.5}$ monitoring program in Beijing and Shanghai that included chemical characterization of the collected PM. Results from the first year of monitoring in Beijing

have been reported (He et al., 2001). This paper examines the results from 1 year of monitoring in Shanghai.

Shanghai is the largest city of the Shanghai Municipality, which has over 15 million people. It is located at the mouth of the Yangtze river in Jiangsu province and is one of the worlds' largest seaports. It has a strong commercial and industrial base with China's largest petrochemical complex, its largest steel output, and other major industries. Years of rapid economic growth and urban development have burdened its air quality, resulting in visibility reduction and public health concerns (Ye et al., 1999; Brunekreef and Dockery, 1995; He et al., 1993; Shen et al., 1992; Yan, 1989). In addition to local air quality problems, there are also regional concerns. For example, the impact of atmospheric haze on agriculture due to reduced sunlight was

*Corresponding author. Tel.: +1-586-986-1603; fax: +1-586-986-1910.

E-mail address: steven.h.cadle@gm.com (S.H. Cadle).

assessed for the lower Yangtze basin with an estimated 5–30% reduction in crop yields (Chameides et al., 1999). Xu (2001) suggested that the "northern drought with summer flooding"—a recent climatic change phenomenon in China during the last 20 years may be attributable to increases in sulfur dioxide emissions from the industrialization of east China. Despite these serious concerns, there is little published data on atmospheric PM concentration, composition, and sources. Song and Cui (1996) did make total suspended particles (TSP) and SO_2 measurements in Shanghai and four other cities in China under a UNEP-WHO environmental program over a 12-year period. It was observed that the TSP mass concentration was in the 100–300 $\mu g/m^3$ range with the highest concentration in the winter. Recently, Davis and Guo (2000) measured PM_{10} in Shanghai on two separate days and reported the mean geometric particle diameters to be 1.2 and 1.6 μm.

Increased energy consumption from the 1980s to the early 1990s has contributed to the increasing ambient aerosol concentration in Shanghai. According to Tong and Xi (1995), more than 80% of the energy in Shanghai was from low quality coal. The industrial consumption of coal was expected to rise from 19.6 million tons in 1989 to 41.7 million tons in 2000. Further examination of the SO_2 emissions led them to suggest that energy consumption has to shift from the use of coal for power generation to lower sulfur fuel oil or natural gas to improve air quality. Chang et al. (1998) modeled the air quality in Jiangsu province and concluded that the atmospheric SO_2 burden represented a significant health risk to Shanghai. Flue-gas desulfurization (FGD) for power plants and other large coal users was recommended as one key strategy to manage air quality in the region. Similar findings and conclusions were documented by Song and Cui (1996) who reported annual average concentrations of TSP and SO_2 in Shanghai and four other Chinese cities in a 12-year study from 1981 to 1992. More recently, Streets et al. (1999) emphasized the need to deploy advanced technology to control SO_2 emissions from stationary sources. They concluded that without additional controls much of the population will be exposed to SO_2 and sulfate ambient concentrations in excess of World Health Organization guidelines.

There is also concern over mobile source emissions. Ye et al. (1999) noted that mobile sources are increasing rapidly in China and that there are approximately 700,000 cars and 500,000 scooters on the streets of Shanghai. Zhou and Ye (1998) also collected particulate emissions from diesel engines, 2-stroke motorcycles and scooters and reported on the short-term mutagenic activities of the extracts. Meanwhile, Ji et al. (1993) estimated that 12,300 tons of road dusts were re-entrained into the ambient air in Shanghai annually, which is about 8% of the stationary source inventory. It is expected that continued urban development will cause

further increases in population and traffic density for the next 30 years.

The purpose of this work was to conduct weekly monitoring of $PM_{2.5}$ to examine seasonal variations in the $PM_{2.5}$ and gases, and to determine the composition of the PM in an effort to better understand its sources.

2. Experimental

Sampling was conducted at two sites, one on the rooftop of the Environmental Engineering Building on the campus of Tongji University. The other site was at a Shanghai Environmental Protection Bureau rooftop air quality monitoring station on Hainan Road, which is closer to downtown than the University site. The Tongji site was 16 m above the ground while that at the Hainan Road site was 18 m above the ground. Both sites were approximately 50 m from major roads. The distance between the two sites is about 4 km. Sampling at Tongji started on 20 March 1999 and ended on 27 March 2000. For the first 6 weeks of the study, the samplers were co-located at the Tongji site for quality control purposes. Sampling at the Hainan Road site started on 5 May 1999 and ended 20 March 2000.

2.1. Sampling and analysis

$PM_{2.5}$ sampling was performed with low-flow rate samplers (LFS) from Aerosol Dynamics Inc., Berkeley, CA. A schematic of the sampler and details of its operation are included in He et al. (2001). The LFS has three parallel $PM_{2.5}$ sampling inlets. One inlet uses a 47-mm, Gelman PTFE Teflon-membrane filter with a 2-μm pore size for $PM_{2.5}$ mass concentrations and for elemental analysis. The second inlet uses a denuder to remove acidic gases followed by another Teflon membrane filter and a nylon filter (Gelman 47-mm diameter, 1-μm pore size). These filters were used for the determination of ionic species. The third inlet was followed by two quartz filters (47-mm diameter Gelman quartz-fiber filters) that were used for determining organic and elemental carbon. The LFS was well suited to collect integrated weekly samples of $PM_{2.5}$ at a flow rate of 0.41/min through each sampling inlet.

Conventional air quality instruments were used to continuously measure carbon monoxide, nitrogen oxides, and sulfur dioxide at the Tongji site. These instruments were operated by Tongji University. Conventional air quality instruments were also used to monitor carbon monoxide, nitrogen oxides, ozone, sulfur dioxide, and TSP at the Hainan site as part of its normal operation. The instruments were operated by the Shanghai EPB. All data was integrated into weekly averages to compare to the $PM_{2.5}$ data.

The samples on the denuded Teflon-membrane filter were analyzed for mass by gravimetry and for water-soluble ions (sulfate, nitrate, chloride, ammonium, sodium, potassium, magnesium and calcium) by ion chromatography (IC), while the nylon back filter was analyzed for chloride, nitrate and sulfate ions. Most of the IC analyses were conducted at the Hong Kong University of Science and Technology (HKUST). However, 12 weeks of samples were sent to an alternate laboratory for IC analysis. Quality control measures indicated some problems with these analyses, which are discussed below. The Teflon-membrane filter of the single-filter $PM_{2.5}$ cassette was analyzed for mass gravimetrically and for 40 elements (from aluminum to uranium) by X-ray fluorescence (XRF) using standard methods (Chow and Watson, 1994). The front quartz filter of the tandem-filter $PM_{2.5}$ cassette was analyzed for organic and elemental carbon (OC and EC) by the thermal/optical reflectance (TOR) method (Chow et al., 1993). A subset of the backup quartz filters was also analyzed for volatilized/adsorbed carbon. The backup filter data was not used to adjust the OC. The XRF and OC/EC analyses were performed at the Desert Research Institute in Reno, NV. While the TOR method employed in this study is commonly used for PM measurements, it should be recognized that other methods of determining the OC and EC fractions can give different results (Chow et al., 2001). The 1-week sampling periods exacerbate the possible loss of semi-volatile organic compounds during sampling.

2.2. Quality assurance

The two $PM_{2.5}$ samplers were run side by side for 6 weeks at the Tongji site. Fifteen of the Teflon filters were pre-and post-weighed both by Tongji University and by General Motors R&D in Michigan. The correlation between the weight gains measured by the two laboratories had an R^2 of 0.96 and a slope of 1.08. Average weight gain was approximately $250 \mu g$. This was considered excellent agreement considering the number of times the filters were handled and the need to transport the filters to China and back for the weighing at GM R&D Center. The ratio of $PM_{2.5}$ mass from the two undenuded filters ranged from 0.89 to 1.16, with an average of 1.0. The ratios for the denuded filters ranged from 0.81 to 1.11 with an average of 1.0. While there clearly was some variability, the averages show good agreement between both legs of the two samplers.

$PM_{2.5}$ mass was determined from both the denuded and undenuded Teflon membrane filters simultaneously collected by each sampler. Mass on the undenuded filter is the primary measurement, since the denuded filter is expected to lose mass due to nitrate and chloride volatilization. At Tongji, the denuded filter $PM_{2.5}$ mass was lower than that of the undenuded filter for 43 of the

52 samples. A linear correlation had an R^2 of 0.91, with a slope of 1.17. At Hainan Road, 36 of the 45 samples had lower mass on the denuded filter. The correlation had an R^2 of 0.87 with a slope of 0.98. Overall, it was concluded that there was reasonable agreement between the two legs of each sampler at both sites. No outliers were identified by doing these comparisons.

As previously mentioned, some samples were analyzed by IC for sulfate, nitrate, and chloride at a laboratory other than HKUST. To judge the analysis accuracy of the samples from the two laboratories, sulfate–sulfur measured by IC was compared to total sulfur, measured by XRF. The correlation using only the HKUST data had R^2 values of 0.86 and 0.91 with slopes of 0.88 and 0.84 for the Tongji and Hainan Road sites, respectively. Adding the results from the other laboratory reduced the R^2 values to 0.64 and 0.69, respectively, because the IC sulfur was much lower than the XRF sulfur. It appeared that either the sulfate had not been efficiently extracted, or the sulfur standards were in error. Hence, it was concluded that those results could not be used. Rather than having no sulfate data for those 12 weeks, the sulfate was estimated using the linear correlation derived from the HKUST data. The IC and XRF data for chloride were also compared. For HKUST data only, the R^2 values were 0.88 and 0.89 and slopes were 0.73 and 0.72, respectively, for Tongji and Hainan Road. IC chloride is lower than XRF chloride in part because ammonium chloride can volatilize from the denuded filter used for the IC measurement. Adding in the chloride data from the other lab again reduced the R^2 values, in this case to 0.79 and 0.76. While some of the chloride values were in reasonable agreement with the XRF, many others were too high. The differences appeared to be random and looked like chloride contamination of the lower concentration samples. Hence, these values were discarded. The source of the contamination was not identified. As with the sulfate, it was decided that IC chloride could be estimated using the linear correlation. No direct comparisons are possible to judge the quality of the nitrate data. Instead, we looked at ratios of sulfate to nitrate for all weeks, using XRF derived sulfate where needed. The ratios for the data derived from the second laboratory were in line with those obtained from the HKUST data. Hence, the nitrate data was retained.

3. Results and discussion

3.1. Ambient concentrations

The site-to-site comparison of the weekly average $PM_{2.5}$ mass concentration is shown in Fig. 1. There is generally good agreement between the two sites. A linear regression between the mass at the two sites had an R^2 of
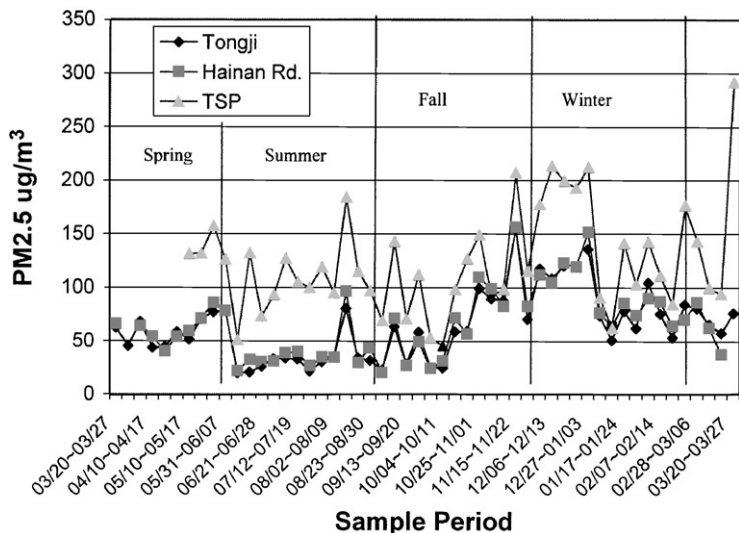
Fig. 1. Weekly $PM_{2.5}$ mass concentrations at Tongji University and Hainan Road compared to the TSP at Hainan Road.
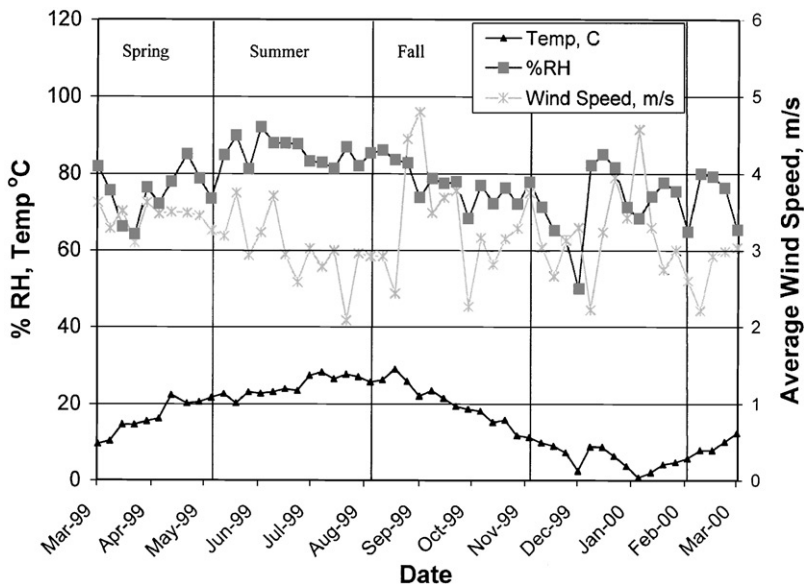

Fig. 2. Ambient conditions in Shanghai.

0.94 and a slope of 0.95. This suggests that there were no significant proximate sources and both sites represent an urban aerosol. The annual average $PM_{2.5}$ at Tongji was 63.4 $\mu g/m^3$ for the entire sampling period. Weekly $PM_{2.5}$ averages ranged from 19.9 to 156 $\mu g/m^3$. For the May through March period when both sites were operating, the average $PM_{2.5}$ concentrations were 64.6 and 67.6 $\mu g/m^3$ for Tongji and Hainan Road, respectively. These values are much higher than the new annual $PM_{2.5}$ ambient air quality standard in the US of 15 $\mu g/m^3$ and

are approximately equal to the 24-h $PM_{2.5}$ US ambient air quality standard.

A strong seasonal variation in $PM_{2.5}$ is apparent in Fig. 1, with the maximum $PM_{2.5}$ concentrations occurring in the late fall and early winter. Fig. 2 gives the average temperature, wind speed and relative humidity during the study. Note that the relative humidity remains high most of the year. For this paper, seasons were defined as lasting 3 months, with spring from March through May. On this basis, the seasonal average

PM$_{2.5}$ concentrations for Tongji from spring to winter were 61.7, 36.8, 64.8 and 88.6 μg/m^3, respectively.

TSP data from Hainan Road was examined since TSP has been monitored for many years in China, and variations in TSP may give information regarding periods when resuspended dust might make a larger contribution to the PM$_{2.5}$ (see Fig. 1). The average PM$_{2.5}$ to TSP ratio for the entire study period was 0.55. The TSP seasonal variation is not as strong as that of PM$_{2.5}$. Hence, the average PM$_{2.5}$/TSP ratio varies seasonally, with values of 0.50, 0.35, 0.62 and 0.68 for the spring, summer, fall and winter, respectively. The ratio was generally high from 4 October through 21 February, averaging 0.73. It has been reported that re-entrainment of road dust increases in the summer in Shanghai due to increased traffic and human activities such as construction (Ji et al., 1993). Since the TSP concentration did not peak in the summer, this may not apply to the sites used in this study, or the increase was offset by higher summer dispersion rates. A lower summer ratio could be explained even with the higher dispersion if the locally generated TSP is impacted less than the PM$_{2.5}$, which has a major regional component. This scenario is consistent with the seasonal behavior observed in this study for gases expected to be dominated by local sources (CO) and regional sources (SO$_2$). Wei et al. (1999) reported the PM$_{2.5}$/PM$_{10}$ ratios for four other cities in China. The average ratios for the suburban sites and urban sites were 0.65 and 0.59, respectively. Our PM$_{2.5}$/PM$_{10}$ measurements in Beijing averaged 0.64. Hence the Shanghai results appear to be roughly in-line with other locations in China.

Fig. 3 shows the average weekly concentrations of carbon monoxide (CO), nitrogen oxides (NO$_x$) and

sulfur dioxide (SO$_2$) at the Hainan Road site for the study period. CO averaged 3.4 mg/m^3 with a range of 1.7–6.6 mg/m^3, NO$_x$ averaged 121 μg/m^3 with a range of 71.3–280 μg/m^3 and SO$_2$ averaged 53.9 μg/m^3 with a range of 20–108 μg/m^3. There is a marked increase in the NO$_x$ and SO$_2$ concentrations during the late October through January period. An increase in PM concentration during the same period is shown in Fig. 3. At the Tongji site, the seasonal pattern in emissions was similar to that at Hainan Road.

The seasonal effect was examined further by comparing average ambient concentrations during the low concentration 14-week period (31 May through 6 September) and the high concentration 12-week period (18 October through 10 January). CO, NO$_x$, SO$_2$, and PM$_{2.5}$ concentrations were 2.25 mg/m^3, and 104, 34.7, and 39.8 μg/m^3, respectively during the low concentration period. During the high concentration period these average ambient concentrations increased by 38%, 63%, 217%, and 266%, respectively. Wintertime increases in ambient pollutant concentrations are frequently attributable to a combination of low level, persistent temperature inversions and increases in emissions related to heating. Both of these are likely factors in this case. It is interesting to note that CO increased the least, while SO$_2$ and PM$_{2.5}$ increased the most. CO is generally considered to be a good tracer for mobile source emissions. Mobile source CO emissions are expected to increase somewhat in the winter due to cold start emissions. The much greater increase in ambient SO$_2$ and PM$_{2.5}$ compared to CO at this location suggests that it is due to increased emissions rather than meteorology. Thus, the higher PM$_{2.5}$ concentration is likely due to increased use of coal and other fuels for
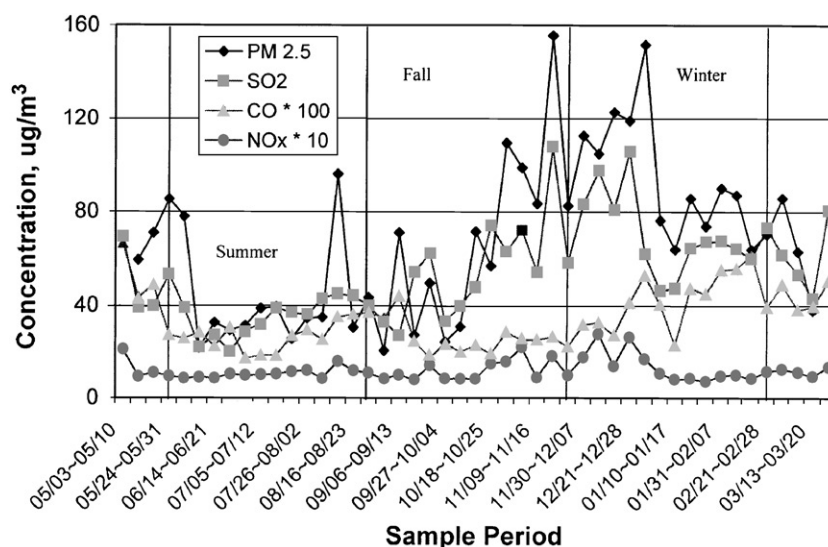

Fig. 3. Carbon monoxide, nitrogen oxides, and sulfur dioxide concentrations at Hainan Road.

winter heating. NO_x increases were intermediate to those of CO and SO_2, while showing the same general pattern in the weekly variation. This suggests that NO_x emissions are more evenly divided between mobile and stationary sources than are the other pollutants.

3.2. Particulate matter composition

The average composition of the $PM_{2.5}$ for the entire sampling period at each site is given in Table 1 along with the minimum and maximum average weekly concentrations. The concentrations of S, Cr, Mn, Cu, Zn, Se and Br are available in Ye et al. (2002) along with the uncertainty in the data. All other XRF measured species were below detection limits. There are several factors to keep in mind when using this data. First, the sampling period was longer at the Tongji site than at Hainan Road, so the two sites are not perfectly matched. Second, both sites include sulfate data derived from the XRF sulfur. Third, ammonium concentrations may be slightly low. Ammonium was measured on the filter from the denuded filter train.

Semi-volatile compounds such as ammonium nitrate and ammonium chloride that are expected to volatilize from that filter are captured on the backup nylon filter. However, ammonium is not captured by this filter. Hence, volatilized ammonium is not measured. The magnitude of ammonium loss can be estimated from the nylon nitrate. For Tongji, the average NO_3^- collected on the nylon filter was $0.55 \mu g/m^3$. If this was all ammonium nitrate, an average of $0.16 \mu g/m^3$ of ammonium was not captured. This is only 2.8% of the 5.67 $\mu g/m^3$ average total ammonium concentration. Hence, this has little impact. Finally, it is noted that, on average,

11% of the nitrate was captured by the backup nylon filter. For low level nitrate samples the percentage was significantly higher. Overall, however, use of the denuder system did not have a major impact on the results at these locations.

The profile of species, as well as their range of concentrations, was very similar at the two sites. In both cases, OC is the largest contributor to the $PM_{2.5}$ mass, followed in decreasing order of contribution by sulfate, elemental carbon, total nitrate, ammonium, potassium, chloride, silicon and iron. Water soluble chloride, sodium, potassium, magnesium and calcium were measured but are not included in Table 1 since data was available for only 38 weeks. At Tongji, a comparison of average weekly concentrations for those weeks with both XRF and IC data showed that 70%, 62%, 95%, 12%, and 23%, respectively, of these species were water soluble. The solubility of the chloride may be underestimated since it was measured from the denuded filter while the total chloride was measured on the filter with no denuder. As noted above volatilization was a minor factor for ammonium nitrate, and hence its impact on ammonium chloride should be minimal. The high solubility of the potassium is significant, since soluble potassium is generally taken as a tracer for biomass. The low solubility of the magnesium and calcium is consistent with their origin as soil or construction related dust.

The seasonal variation in concentration is shown in Table 2. The spring Hainan Road data is not included since the number of samples was small. Sampling was conducted at the same time intervals at both sites for the other three seasons, thus these data are directly comparable. Most species follow the same seasonal

Table 1
Annual average $PM_{2.5}$ composition at the two sites

Species	Hainan Rd., $\mu g/m^3$			Tongji U., $\mu g/m^3$		
	Mean	Min	Max	Mean	Min	Max
$PM_{2.5}$	67.6	20.5	155.6	62.4	19.9	155.3
SO_4^{2-}	14.56	3.30	29.95	13.48	5.68	28.74
NO_3^-	6.30	0.50	16.6	5.77	0.40	18.2
NH_4^+	6.07	1.51	12.44	5.67	1.60	11.99
OC	15.43	5.28	42.22	14.34	4.35	66.10
EC	6.77	3.69	12.72	6.21	2.31	13.04
Cl	1.81	0.00	6.90	1.45	0.01	5.99
Na	0.49	0.00	1.13	0.45	0.19	0.88
K	1.98	0.27	9.82	1.66	0.24	6.09
Mg	0.19	0.03	0.0	0.19	0.0	0.59
Ca	0.55	0.15	1.35	0.54	0.12	2.06
Al	0.48	0.14	1.17	0.46	0.11	1.73
Si	1.27	0.42	3.28	1.26	0.34	5.01
Fe	0.90	0.30	2.10	0.82	0.23	2.78
Pb	0.28	0.08	0.59	0.27	0.06	0.63

Table 2
Seasonal average $PM_{2.5}$ concentrations

Species	Hainan Rd., μg/m^3			Tongji Univ., μg/m^3			
	Summer	Fall	Winter	Spring	Summer	Fall	Winter
$PM_{2.5}$	35.85	67.78	93.91	61.66	36.80	64.77	88.57
SO_4^{2-}	9.32	14.31	19.22	12.60	10.01	13.55	17.78
NO_3^-	4.76	5.12	10.1	5.41	2.92	5.12	9.64
NH_4^+	3.34	6.59	8.09	5.53	3.49	6.26	7.38
OC	13.07	17.28	17.59	16.10	9.62	15.22	16.40
EC	5.71	6.97	8.07	5.27	4.61	6.81	8.16
Cl	0.25	1.65	4.08	0.71	0.22	1.49	3.54
Na	0.47	0.62	0.41	0.48	0.42	0.46	0.44
K	0.89	1.97	3.24	1.36	0.85	1.90	2.61
Mg	0.13	0.21	0.21	0.19	0.16	0.19	0.21
Ca	0.37	0.52	0.78	0.61	0.30	0.56	0.71
Al	0.32	0.43	0.68	0.55	0.26	0.44	0.59
Si	0.75	1.21	1.82	1.64	0.64	1.21	1.56
Fe	0.66	0.89	1.13	1.00	0.52	0.81	0.94
Ni	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pb	0.16	0.32	0.40	0.23	0.16	0.32	0.37

pattern, with concentrations highest in the winter and lowest in the summer. Sodium is the exception to this, having similar average concentrations in all seasons. On the other hand, chloride has the greatest seasonal variation, increasing from an average concentration of 0.22 μg/m^3 in the summer to an average of 3.54 μg/m^3 in the winter. The chloride to sodium molar ratio was 0.96, 0.33, 2.1 and 5.23 for the spring through winter seasons. Hence, for the fall and winter periods, most of the $PM_{2.5}$ chloride could not have been present as sea salt particles. It is possible that the chloride originated in large sea salt particles, but had been displaced by reaction with nitric acid, followed by reaction with ammonia to form small particles. The seasonality of the ambient chloride concentration suggests, however, that it is directly emitted from coal combustion, since the displacement reaction would be favored at high temperatures. Chloride is known to be a minor constituent of particulate matter from coal burning and a major constituent from the briquettes used in Chinese cities (Bond et al., 2002).

3.3. $PM_{2.5}$ mass balance

Table 3 gives the annual average weekly mass balance for sulfate, nitrate, ammonium, organic and elemental carbon, chloride, sodium, potassium and crustal materials (Mg, Ca, Al, Si, and Fe), the sum of the trace elements and the unidentified mass for both sites. To obtain the mass balance, the OC concentration was multiplied by a factor of 1.2. This factor is commonly applied to emission sources to account for the hydrogen and oxygen associated with the organic carbon. A factor

Table 3
Mean percent of the $PM_{2.5}$ mass

Species	Hainan Rd.	Tongji Univ.
SO_4^{2-}	23.1	23.6
NO_3^-	8.84	8.55
NH_4^+	9.38	9.72
OC	31.3	29.2
EC	11.6	10.6
Cl	2.02	1.83
Na	0.97	0.91
K	2.80	2.53
Mg	0.35	0.36
Ca	1.20	1.26
Al	1.49	1.47
Si	4.27	4.52
Fe	2.08	2.00
Trace elements	2.30	2.13
Unidentified	−1.87	1.34

of 1.4 is frequently used for aged ambient samples to account for increased mass due to reaction in the atmosphere. We are not aware of any TOR based data for the mass correction factor for OC for China sources. Since this is a source dominated area we chose to use the factor of 1.2. Using a factor of 1.4 would put the average weekly mass balance in excess of 100%. Aluminum, silicon, calcium, and iron were assumed to be present in the atmosphere as oxides, so their masses were increased accordingly. Other elements measured by XRF were summed and listed as trace elements.

The composition of the $PM_{2.5}$ is very similar at the two sites. For Hainan Road, the average weekly mass

balance exceeded the measured mass by 1.87%, while it averaged 1.34% less than the measured mass at Tongji University. While the average mass balance was excellent, there was variation from week to week. This is shown in Fig. 4, which plots the sum of the masses of the measured species against the measured mass for each week at both sites. The straight line is an equivalence line. The figure shows that for relatively low ambient mass concentrations, 20–40 $\mu g/m^3$, a large fraction of the samples had identified masses significantly in excess of the measured mass. Above 40 $\mu g/m^3$, most of the mass balances were less than the mass, although occasional exceptions did occur. The possibility that the excess measured mass was due to adsorbed organics was investigated. The problem of OC adsorbed on quartz filters is generally greatest at low filter loadings, since the amount of OC that can be adsorbed is fixed. Plots of OC/EC vs. measured mass did not support the hypothesis that adsorbed OC was the cause of the imbalance.

Table 3 shows that OC was the major component of the PM at both sites. In fact, total carbon accounted for 42.9% and 39.8% of the mass at Hainan Road and Tongji, respectively. Sulfate was the second most abundant species, averaging 23.1% and 23.6% at the two sites, respectively. On average, sufficient ammonium was present to neutralize 85% of the sum of the equivalents of the sulfate and nitrate recovered from the Teflon filter. It is further assumed that ammonium was present for the nitrate that was captured by the nylon filter. Hence, it is reasonable to conclude that more than 85% of the sulfate and nitrate were present as ammonium species. If we assume all of the sulfate was present as ammonium sulfate, then it was responsible for

32% of the $PM_{2.5}$ mass, slightly higher than the OC corrected for its corresponding mass of H and O. The sum of sulfate, nitrate and ammonium accounted for an average of 41.3% and 41.8% of the mass at the two sites respectively, essentially equivalent to the total carbon contribution. The sum of the crustal elements (Ca, Mg, Al, Si and Fe) averaged 9.4% and 9.9% of the mass, respectively.

Table 4 gives the seasonal contributions of the various species as a percentage of the identified mass. Percent identified mass was used as opposed to percent measured mass to avoid bias caused by averaging the high percentage values for the low mass days where the identified mass significantly exceeded the measured mass. Results are given for Tongji only since the spring data at Hainan Road was limited. There is very little variation in the percent sulfate, seasonally. Nitrate is highest in the winter and the spring. This is likely due to the shift in equilibrium between the gas and solid phases that is strongly dependent on temperature. OC and EC are somewhat higher in the summer than the winter, on a percentage basis, but the differences are not great. As noted earlier, chloride is highest in the winter. Since sodium is lowest in the winter chloride does not originate from $PM_{2.5}$ salt. It is probably due to coal combustion and a temperature related shift in equilibrium of the ammonium chloride. Potassium is highest in the winter suggesting that some biomass burning is done for heating purposes although it could be from coal burning as well. Ca, Al, Si and Fe were highest in the spring. In Beijing (He et al., 2001), Ca has been found to be a good tracer of construction activity. This is reflected in the seasonal change in the Ca/Si and Ca/Al
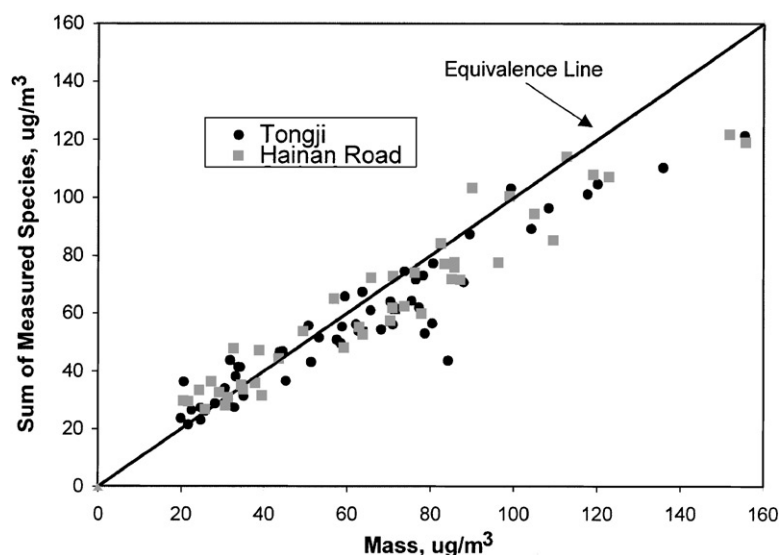

Fig. 4. Comparison of $PM_{2.5}$ mass and the sum of measured species.

ratios, which are highest during the warm months. These ratios were examined for the two Shanghai sites. There was no clear seasonal pattern. The ratios were similar to those during the low construction period in Beijing. Hence, it is uncertain if construction generated Ca is having a significant impact in Shanghai.

3.4. $PM_{2.5}$ sources

A qualitative source apportionment was made since region source profiles are not available for a chemical mass balance apportionment and there was insufficient data for a factor analysis.

Table 4
Seasonal average percent contributions to the total identified mass at Tongji University

Species	Spring	Summer	Fall	Winter
SO_4^{2-}	24.0	26.0	23.9	23.5
NO_3^-	9.89	7.45	7.10	12.0
NH_4^+	10.3	9.20	10.9	9.71
OC	27.3	30.4	28.5	25.0
EC	8.85	12.1	11.5	10.1
Cl	1.36	0.59	1.92	4.38
Na	0.89	1.26	0.95	0.58
K	2.52	2.07	3.00	3.28
Mg	0.35	0.47	0.40	0.27
Ca	1.54	1.14	1.34	1.32
Al	1.94	1.32	1.51	1.53
Si	6.40	3.75	4.58	4.53
Fe	2.60	1.96	2.01	1.79
Trace elements	2.14	2.33	2.30	2.04

Much has been written about coal combustion in China and the associated sulfur dioxide emissions. Steps have been taken in Shanghai and elsewhere to reduce this source. Fig. 5 shows the annual average TSP and sulfur dioxide concentrations for Shanghai from 1981 through 2000. The data for 1981–1992 were abstracted from the report by Song and Cui (1996) while the data from 1993 to 2000 were obtained from the Shanghai Environmental Protection Bureau. The data show an increase in sulfur dioxide from 1981 to 1993 from 50 to $96 \mu g/m^3$. Emissions dropped abruptly after 1993 and have returned to the pre-1981 levels. A major decrease in TSP occurred after 1993 as well, presumably due, in part to reductions in sulfate. Despite this success at controlling sulfur emissions, sulfate remains an important component of the $PM_{2.5}$. Ammonium sulfate, by itself, exceeds the US $PM_{2.5}$ $15 \mu g/m^3$ annual air quality standard. Hence it appears that additional controls will be needed to reduce sulfur emissions.

The nitrate $PM_{2.5}$ contribution is much less than that of sulfate. Understanding the sources of the nitrate requires a good NO_x inventory, which is not currently available. The observation that air quality has worsened as the number of vehicles has increased has led the general public to conclude that mobile sources are a major contributor to the PM problem. While mobile sources undoubtedly contribute to the NO_x emissions, it was noted above that NO_x increases during the winter were intermediate to those of CO, which increased the least, and sulfur dioxide. Hence, it appears that NO_x emissions related to non-mobile source fuel combustion are important as well. The mass ratio of NO_3^- to $SO_4^=$ has been suggested as an indicator to identify sources of sulfur and nitrogen in the atmosphere (Arimoto et al.,
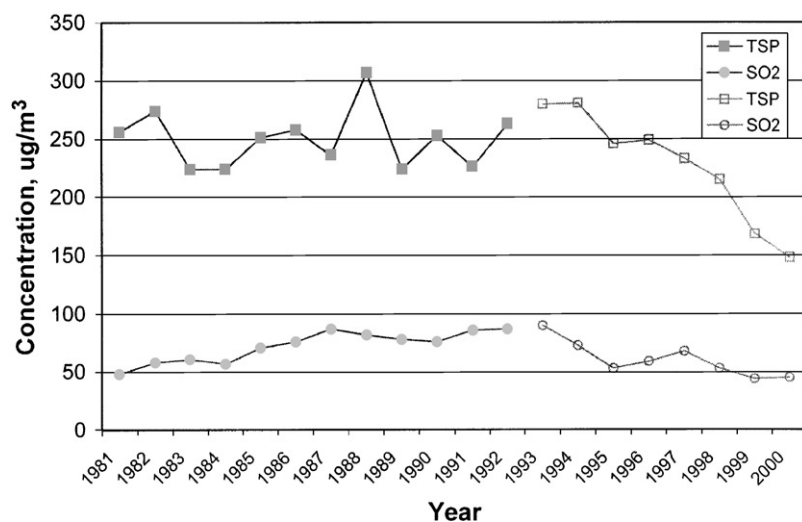

Fig. 5. Historical sulfur dioxide and TSP concentrations in Shanghai. Data from 1980 to 1992 are from Song and Cui (1996), and those after 1993 are from reports by the Shanghai Environmental Protection Bureau.

1996; Carmichael et al., 1997), with high ratios indicating a major contribution from mobile sources. Yao et al. (2002) examined this ratio for both Shanghai and Beijing, using the data from this study. For Shanghai, both sites were similar and yielded a ratio with a strong seasonal average, ranging from 0.2 to 0.7. It was concluded that stationary sources emissions are more dominant than vehicle exhaust.

Carbonaceous material was found to be the largest contributor to the $PM_{2.5}$, with OC alone contributing 30% of the $PM_{2.5}$ mass. An inventory of organic carbon emissions is not available. We examined the seasonal variation in the OC/EC ratio to see if that gave any indication of major sources (Fig. 6). Very high ratios were seen at the start of the study at Tongji, but did not return in the spring at the end of the study. We do not have an explanation for this. For the rest of the study period the OC/EC ratio averaged around 2.0. At the Hainan Road site, the OC/EC ratio increased during the winter, the same period that the $PM_{2.5}$ concentration went up. However, the Tongji data did not show the same increase. The cause of the difference is unknown. Hence, no conclusions regarding sources could be drawn from the OC/EC data.

Diesel emissions are a source of both OC and EC. Old technology gasoline vehicles and poorly maintained vehicles can be a significant source of carbonaceous PM, with considerably more of the carbon present as OC than from diesels. Shanghai has over a million vehicles on the road with an additional 400,000 two stroke motorcycles and scooters. These are undoubtedly a significant source of carbonaceous material. Efficient combustion of coal in boilers should emit little carbon. Coal is also used for residential heating and cooking,

although this use has been greatly diminished recently. Bond et al. (2002) have shown that residential coal burning emits large quantities of both OC and EC. These are greatly reduced when coal briquettes are used. It has also been reported anecdotally that most large cities in China have a significant migrant population that tends to burn all available combustibles for heating and cooking. Finally, emissions from cooking itself can be a major source of OC.

Over 2.5% of the $PM_{2.5}$ mass was potassium, 95% of which was water soluble. Potassium emissions have been found in biomass burning, fugitive dust, coal-fired boiler emissions and meat cooking emissions (Raveendran et al., 1995; Watson et al., 1998). Most of the potassium in fugitive dust is insoluble. Results from coal-fired boilers are variable, but on average 21% of the potassium emitted from boilers was found to be soluble in the Northern Front Range Air Quality Study (NFRAQS) study (Watson et al., 1998). Total potassium in the NFRAQS study was 0.55% of the $PM_{2.5}$ mass from coil fired boilers. Only biomass burning and barbecue meat cooking had potassium emissions that were mostly soluble. The fraction of the $PM_{2.5}$ mass attributable to potassium from these sources is less than 1%, with most of the mass being OC. This clearly cannot be the case in Shanghai, since potassium accounted for 2.7% of the total $PM_{2.5}$ mass. Hence, these profiles cannot be used. It is recommended that future studies strongly consider biomass burning as a potential $PM_{2.5}$ source. C^{14} analysis would be a good way of separating fossil fuel derived carbon from biomass and meat cooking derived carbon.

Silica accounted for about 4.5% of the $PM_{2.5}$ mass, with the highest seasonal value being 6.4% in the spring.
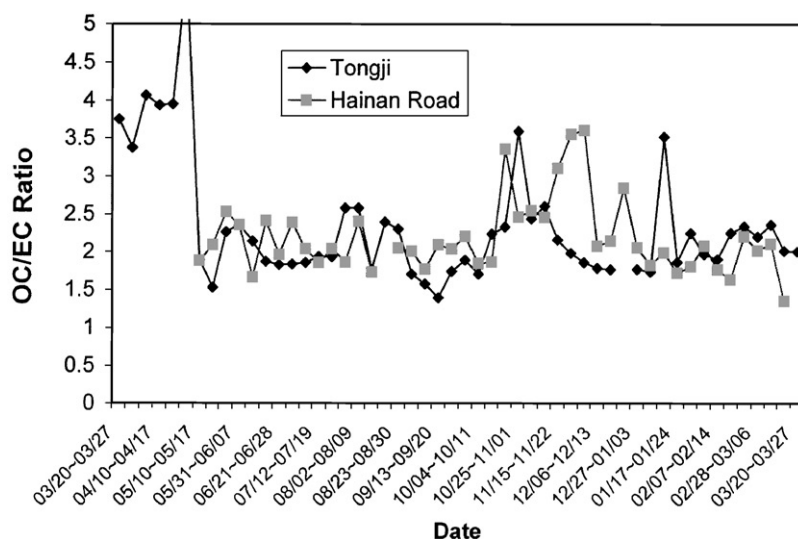

Fig. 6. OC/EC ratio at both sampling sites as a function of time.

This spring high may be due, at least in part, to the long range transport of the severe Asian dust storms in March and April of 2000. These storms raised the 24-hour PM_{10} concentration to an astonishing $1.7\,mg/m^3$ in Beijing (Wang et al., 2002) and resulted in peak continuous PM_{10} concentrations of $250–400\,\mu g/m^3$ as far south as Taiwan (Lin, 2001). Fig. 1 shows a very high TSP value in Shanghai the week of 20–27 March. While $PM_{2.5}$ does not look uniquely high during that week, the crustal component of the $PM_{2.5}$ was clearly elevated with Si, Ca, Al, Fe, and Mg percent contributions of 14.0, 3.77, 4.27, 5.21 and 0.77, respectively. Overall, the crustal elements expressed as oxides, except for magnesium, accounted for 28% of the $PM_{2.5}$ mass that week, much higher than the overall average of 9.7%.

Lead is the traditional tracer for gasoline based mobile sources. The use of leaded gasoline in Shanghai was banned shortly before this study. The annual average airborne lead concentration at the two sites of $0.28\,\mu g/m^3$ is comparable to other cities where unleaded gasoline is used (Thomas et al., 1999). A linear correlation between lead and CO at the Hainan Road site showed no correlation between the species. Hence it is concluded that the observed lead is due to a combination of industrial sources, resuspended dust, and perhaps from long-range transport.

4. Summary and conclusions

Ambient $PM_{2.5}$ mass concentrations were monitored in Shanghai for 52 consecutive weeks for the first time. The annual average concentrations were 57.9 and $61.4\,\mu g/m^3$ at the two sampling sites, with a range from $21\,\mu g/m^3$ in the summer to $147\,\mu g/m^3$ in the winter. The bulk composition of the $PM_{2.5}$ mass was determined, with good overall mass balance. The most abundant species contributing to the $PM_{2.5}$ mass were organic carbon, sulfate, elemental carbon, ammonium, nitrate, silicon, potassium, iron, chloride, and calcium, in decreasing order of contribution. Total carbon, including a correction factor of 1.2 to the OC fraction to account for the mass of hydrogen and oxygen, accounted for 41.4% of the identified species, while the sum of ammonium, sulfates and nitrates accounted for 41.6% of the identified species.

The lack of good emission inventories and Shanghai specific source profiles limit the ability to determine the sources of the $PM_{2.5}$. Use of coal is undoubtedly a major contributor to the $PM_{2.5}$. The biggest uncertainty however, is in the sources of the carbonaceous material, especially the organic carbon. Other issues not addressed in this study are the daily variability of the $PM_{2.5}$ and the impact of long-range transport on the observed $PM_{2.5}$ concentrations. Additional fieldwork is being performed in 2001 that will examine these issues.

References

Arimoto, R., Duce, R.A., Savoie, D.L., Prosperro, J.M., Talbot, R., Cullen, J.D., Tomza, U., Lewis, N.F., Ray, B.J., 1996. Relationships among aerosol constituents from Asia and the North Pacific during PEM-west A. Journal of Geophysical Research 101, 2011–2023.

Bond, T., Quinn, P., Bates, T., 2002. Particulate emissions from residential combustion of coal from the US and China. Presented at the Sixth International Aerosol Conference, Taipei, Taiwan on September 9–13, 2002.

Brunekreef, B., Dockery, D.W., 1995. Epidemiological studies of short-term effects of low levels of major ambient air pollution components. Environmental Health Perspectives 103 (2), 3–14.

Carmichael, G.R., Hong, M.-S., Ueda, H., Chen, L.-L., Murano, K., Park, J.K., Lee, H., Kim, Y., Kang, C., Shim, S., 1997. Aerosol composition at Cheju island, Korea. Journal of Geophysical Research 102, 6047–6061.

Chameides, W.L., Yu, H., Liu, C.S., Bergin, M., Zhou, X., Mearns, L., Kiang, C.S., Saylor, R.D., Luo, C., Huang, Y., Steiner, A., Giorgi, F., 1999. Case study of the effects of atmospheric aerosols and regional haze on agriculture: an opportunity to enhance crop yields in china through emission controls? Proceedings of the National Academy of Sciences 96, 13626–13633.

Chang, Y.S., Arndt, R.L., Calori, G., Carmichael, G.R., Streets, D.G., Su, H., 1998. Air quality impacts as a result of changes in energy use in China's Jiangsu province. Atmospheric Environment 32, 1383–1395.

Chow, J.C., Watson, J.G., 1994. Guidelines for PM-10 Sampling and Analysis Applicable to Receptor Modeling. US Environmental Protection Agency, Office of Air Quality Planning and Standards, Washington, DC, EPA-452/R-94-009.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in US air quality studies. Atmospheric Environment 27A, 1185–1201.

Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Thomas, M., 2001. Comparison of IMPROVE and NIOSH carbon measurements. Aerosol Science and Technology 34, 23–34.

Davis, B.L., Guo, J., 2000. Airborne particulate study in five cities of China. Atmospheric Environment 34, 2703–2711.

He, Q., Lioy, P.J., Wilson, W.E., Chapman, R.S., 1993. Effects of air pollution on children's pulmonary function in urban and suburban areas of Wuhan, PRC. Archives of Environmental Health 48, 382–391.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C.K., Cadle, S., Chan, T., Mulawa, P., 2001. The characteristics of

PM$_{2.5}$ in Beijing, China. Atmospheric Environment 35, 4959–4970.

Ji, X., Jiang, D., Fei, S., Yuan, H., He, P., Ye, B., Lei, Z., 1993. Road dust emission inventory for the metropolitan area of Shanghai city. Atmospheric Environment 27A, 1735–1741.

Lin, T.H., 2001. Long-range transport of Yellow Sand to Taiwan in spring 2000: observed evidence and simulation. Atmospheric Environment 35, 5873–5882.

Raveendran, K., Ganesh, A., Khilar, K.C., 1995. Influence of mineral matter on biomass pyrolysis characteristics. Fuel 74, 1812–1822.

Shen, S., Qin, Y., Cao, Z., Shang, J., Liu, Y., Yang, X., Deng, Y., Huang, J., Fu, Z., Song, X., 1992. Indoor air pollution and pulmonary function in children. Biomedical and Environmental Sciences 5, 136–141.

Song, R., Cui, J., 1996. Dynamic observation on urban air pollution in five cities in China. Journal of Hygiene Research 25, 328–342 (In Chinese with English abstract).

Streets, D.G., Hedayat, L., Carmichael, G.R., Arndt, R.L., Carter, L.D., 1999. Potential for advanced technology to improve air quality and human health in Shanghai. Environmental Management 23, 279–295.

Thomas, V.M., Socolow, R.H., Fanellii, J.J., Spiro, T.G., 1999. Effects of reducing lead in gasoline: an analysis of the international experience. Environmental Science and Technology 33, 3943–3948.

Tong, J.G., Xi, S.T., 1995. Energy consumption structure and atmospheric environment in Shanghai. Proceedings of an International Conference on Energy and Environment in Shanghai, China in May, 1995, pp. 120–123.

Wang, W., Yue, Y., Liu, H., Pan, Z., Tang, D., Wang, Y., Du, R., Su, H., Qian, F., Sakamoto, K., 2002. Study of pollution characteristics of aerosols during sand-dust storm weather in Beijing. Huanjing Kexue Yanjiu (Research of Environmental Sciences (in Chinese, abstract in English), in press.

Watson, J.G., Fujita, E., Chow, J.C., Zielinska, B., Richards, L.W., Neff, W.D., Dietrich, D., 1998. Northern Front Range Air Quality Study Final Report. Desert Research Institute. Available at www.NFRAQS.colostate.edu/index2.html

Wei, F., Teng, E., Wu, G., Hu, W., Wilson, W.E., Chapman, R.S., Pau, J.C., Zhang, J., 1999. Ambient concentrations and elemental compositions of PM$_{10}$ and PM$_{2.5}$ in four Chinese cities. Environmental Science and Technology 33, 4188–4193.

Xu, Q., 2001. Abrupt change of the mid-summer climate in central east China by the influence of atmospheric pollution. Atmospheric Environment 35, 5029–5040.

Yao, X., Chan, C.K., Fang, M., Cadle, S.C., Chan, T.L., Mulawa, P.A., He, K., Ye, B., 2002. The water-soluble ionic composition of PM$_{2.5}$ in Shanghai and Beijing, China. Atmospheric Environment 36, 4223–4234.

Yan, B., 1989. Epidemiologic studies of chronic respiratory diseases in some regions of China. Chest 96 (3), 339S–343S.

Ye, S., Zhou, W., Song, J., Peng, B., Yuan, D., Lu, Y., Qi, P., 1999. Toxicity and health effects of vehicle emissions in Shanghai. Atmospheric Environment 34, 419–429.

Ye, B., Ji, Xueli, Yang, H., Yao, X., Chan, C., Cadle, S., Chan, T., Mulawa, P., 2002. Concentration and chemical composition of PM$_{2.5}$ in Shanghai for a 1 year period. General Motors Research Publication 9342, June, 2002.

Zhou, W., Ye, S.H., 1998. Effects of two new lubricants on the mutagenicity of scooter exhaust particulate matter. Mutation Research 414, 131–137.