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The elemental and organic characteristics of PM2.5 in Asian dust episodes in Qingdao, China, 2002

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Abstract

Eighteen PM2.5 samples that included three episodes were collected in Qingdao, China in spring 2002. Simultaneous total suspended particulate samples were also collected during two of the episodes for comparisons. Meteorological data along the back trajectories suggested that two of the episodes may have been the consequence of Asian dust storms. The chemical characteristics of selected elements and solvent-extractable organic compounds (SEOC) were determined to identify the origin of these materials. The elements Fe, Mg, Ca, Al, Ti, Mn and V in the dust samples were found to be of crustal origin and were transported to Qingdao from outside the area, while Pb and Zn were attributed to local (regional) emissions. Small variations in the distribution patterns and compositions were observed in the SEOC from the PM2.5 samples collected during the two dust episodes although there was a significant increase in total loading. The results suggest that the dust episodic aerosols possess strong local characteristics superimposed with a heavy crustal and possibly pollution influx transported with the dust particles during the storms. Because the sources of the aerosols were different, high pollutant concentrations were observed at Qingdao in two waves: the locally emitted aerosols such as vehicular exhaust rose first before the long-distance transported materials arrived and the locally emitted pollutants tended to stay in the atmosphere for a longer time.

Keywords: Aerosol; Solvent-extractable organic compounds; Metals; Asian dust storm

1. Introduction

Asian dust originates from the arid regions of central and eastern Asia and in regions where loess is deposited south of the Gobi and Ordos deserts. The dust affects the mid-latitudes (25–40°N) and can be detected as far away as the tropical North Pacific and the North American Arctic (Rahn et al., 1977; Duce et al., 1980; Uemastsu et al., 1983; Merrill et al., 1989; Gao et al., 1992). Asian dust storms frequently occur during the dry spring season, particularly during April and May. There have been many studies in East Asia and the Pacific on the composition, particle size distributions, sources and transport paths of Asian dust storms (Liu and Zhou, 1999; Fang et al., 1999; Zhang and Iwasaka, 1999; Ye et al., 2000; Chun et al., 2001; Lin, 2001; Ma et al., 2001; Zhuang et al., 2001; In and Park, 2002; Mori et al., 2002). Recently, the ACE-Asia project (Aerosol Characterization Experiments-Asia), which concentrates on understanding how atmospheric aerosol particles affect the earth's climatic system (Arimoto et al., 2002; Kobayashi et al., 2002; Ito et al., 2002), has been presenting reports on Asian dust. Despite such efforts, information on the chemical characteristics of the

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PM2.5 fraction of the dust, in particular, the solvent-extractable organic compounds (SEOCs), is still scarce.

Qingdao is a coastal city situated at the southern tip of the Shandong Peninsula of Northern China (35°35′N and 119°30′E) with an area of 1102 km^2 and a population of 2.346 million (Fig. 1). Qingdao is located down wind of the origin of the Asian dust storms during spring when northwesterly winds prevail. Qingdao is in the transport path of the storms as they move to the east and is thus an important exit point of the dust storms to the Pacific (Korea and Japan). It is an ideal site to monitor Asian dust storms before dispersion and influx from non-continental atmospheric sources dilutes the air mass.

Eighteen PM2.5 samples were collected in the months of March and April 2002 in Qingdao. In addition, simultaneous total suspended particulate (TSP) samples were collected during two of dust episodes for comparisons. The samples were analyzed for elements and SEOCs to characterize the sources of the particles.

2. Experimental

2.1. Sampling site

The sampling site was on the rooftop of a three-storey meteorological station on top of Baguan Hill on the campus of the Ocean University of China (Fig. 1). The elevation of Baguan Hill is 70 m and is about 500 m from the sea. The campus is in the midst of a seaside tourist district. There are many restaurants and residential areas in the general area, which has abundant trees and vegetation. The main part of the city is north of the sampling site. About 5 km to the north of the sampling site is Qingdao's industrial district.

2.2. Sampling

Samples were collected on quartz fiber filters (Whatman, 90 mm in diameter cut from QM-A $20 \times 25\,cm^2$ filters) using a GIF PM2.5-2 sampler (Beijing Geological Institute). The flow rate was 77 l min^{-1} and the sampling time was nominally 24 h with sampling starting at 10:00 a.m. Three-quarters of the filters was used for the SEOC GC/MS analyses while the remaining was for elemental measurements. TSP samples were collected on quartz fiber filters (Whatman, QM-A $20 \times 25\,cm^2$) using a high-volume sampler (Sibata HV-1000F, Japan). The flow rate was 1.0 $m^3\,min^{-1}$ and the sampling time was nominally 24 h. One-half of the filters was used for organic analysis and one-eighth was used for elemental measurements. The organic samples were stored in 250-ml glass bottles in a refrigerator ($\sim 0°C$) with 5 ml of methylene chloride added to prohibit microbial growth. The elemental samples were stored in pre-washed plastic bags.

2.3. Elemental analysis

The elemental composition of the samples was quantified using a Perkin Elmer 3000 ICP-OES at the

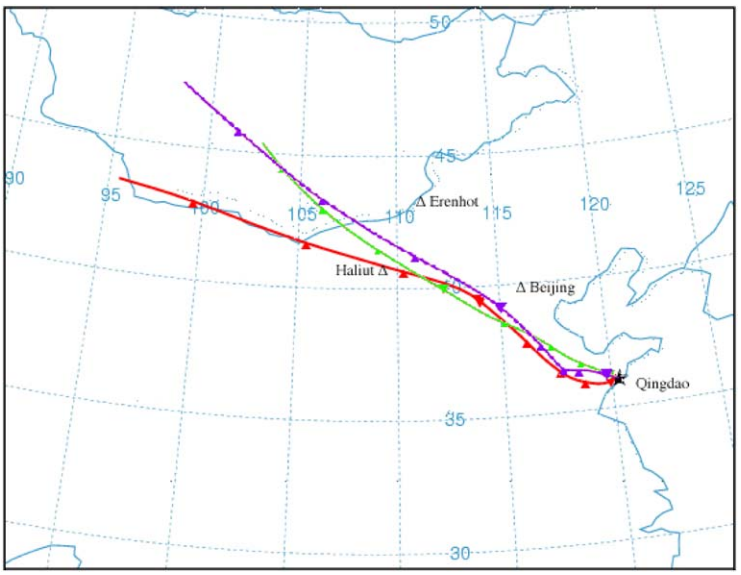

Fig. 1. Back trajectory calculations. (Produced using National Oceanic Atmospheric Administration ARL website (www.arl.noaa.gov.ready/). Duration: 48 h. Vertical motion calculation method: model vertical velocity. Legends: Solid line –20/21 March 2002; Broken line –7/8 April 2002; Grey line –16/17 April 2003.

Center for Atmospheric and Coastal Research, HKUST. Pre- and post-processing of the samples was performed in the class 100 clean room booths in the HKUST Institute for Environment and Sustainable Development. All plastic ware was acid-cleaned prior to use. Filters were digested in a 5 ml mixture of HCl, HNO_3 and HF on a hot plate at 110°C for 4 h. After digestion, the samples were evaporated to dryness at 60°C, redissolved in 2% nitric acid and filtered before ICP-OES analysis. Quantitative analysis was carried out by the external calibration technique using a set of external calibration standards at concentration levels close to that of the samples. Procedural and field blanks were also determined and were subtracted from the samples. Recoveries derived from the analysis of SRM1648 (Standard Reference Material 1648, urban suspended particulates) were in the range of 89% for Fe to 103% for Ti.

Quartz fiber filters contain high Na, Al, Ca and Mg background levels and therefore do not yield accurate enough results for our purpose. On the other hand, Fe, S, Ti, Mn, Pb, Cu, Zn and V are low in these filters and the average respective concentrations of these metals in the samples are 3–10 times higher than in the filter blanks, creating usable results. In addition, despite the high Al, Ca and Mg background levels on the quartz filters, Asian dust samples contain very high Al, Ca and Mg (5–30 times higher than non-episodic samples). The results from the dust samples provide useful information.

2.4. Organic analysis

The samples were analyzed in the Environmental Laboratory at the Hong Kong University of Science and Technology. The analytical procedure used was described in a previous publication (Zheng et al., 1997). Briefly, one half of a filter was used and it was spiked with perdeuterated eicosane (*n*-$C_{20}D_{42}$) prior to sample extraction. The *n*-$C_{20}D_{42}$ was used for recovery tests and also served as an internal standard. The filter was ultrasonically extracted with three 100-ml aliquots of dichloromethane for 15 min each at room temperature. The total extract was concentrated to a volume of 2–3 ml by rotary evaporation before filtration to remove the fiber residues and was further reduced by gentle evaporation with a stream of high purity N_2 to near dryness. The total extract was reacted with 14% BF_3 in methanol to esterify the free organic acids. Hexamethyl benzene was also added as an internal standard before the *total extract* was analyzed using a Gas Chromatograph/Mass-Selective Detector (GC/MSD). The GC-MSD was an HP 5890A GC/HP 5971A MSD. The MSD was operated in the electron impact mode at 70 eV and the scan range was 40–500 amu. An HP-5MS capillary column (30 m × 0.25 mm i.d.; film thickness 0.25 μm) was used.

Relative response factors (RRFs) for 49 standard compounds including 18 alkanes (C_{14}–C_{36}), 16 polycyclic aromatic hydrocarbons (PAHs) and 15 methylated fatty acids (C_7–C_{30}) were calculated and referenced to the internal standards. The target compounds were detected by their typical ions and retention times and were quantified by comparing the areas of their typical ion peaks with those of the internal standards and corrected with the RRFs. For compounds without RRFs, the value of the most similar compound or that deduced from its analogs was used. Field blanks, filter blanks and solvent blanks were also determined. The quantification results using hexamethyl benzene and *n*-$C_{20}D_{42}$ showed good agreement, which indicated good recovery.

3. Results and discussion

3.1. Meteorological conditions

According to the meteorological data and air pollution indices obtained from Qingdao (City of Qingdao, 2002), (www.qingdao.gov.cn) three suspected dust episodes were observed on 20 March, 7–8 April and 17 April of 2002. Strong north and northwesterly winds prevailed during these periods. The air pollution index (API) was 398, 500 and 194 for the three periods. The average API for springtime in Qingdao is 40–100 and it seldom exceeds 120. The pollutant responsible for the high API was respirable suspended particulates (RSP). The samples collected in Qingdao during 20 March and 7–8 April were grayish brown in color in contrast to the grayish black color commonly observed in non-episodic samples.

Back trajectory calculations (Fig. 1) traced the storms to Inner Mongolia, and meteorological data for stations along the path were obtained (Qingdao (N36.07, E120.33), Beijing (N39.93, E116.28), Haliut (N41.57, E108.52) and Erenhot (N43.65, E112.00)). The wind directions, wind speeds and visibility (SYNOP) are plotted in Fig. 2. Considering the accuracy of the back trajectories, the three paths are virtually the same. It can be seen that very low visibility was reported at these sites for 20 March and 7–8 April, but the visibility was good for 16 April except at Qingdao. Relative humidity data were also examined to ensure that the low visibility was not caused by moisture. From the back trajectory calculations, there was about one day difference in time between Haliut and Erenhot, and Qingdao and the same time lag was observed in the visibility data. The fact that good visibility was observed on 16–17 April at Inner Mongolia suggests that this episode may not be the consequence of dust storm. In the following discussion further evidences will be provided as the data are

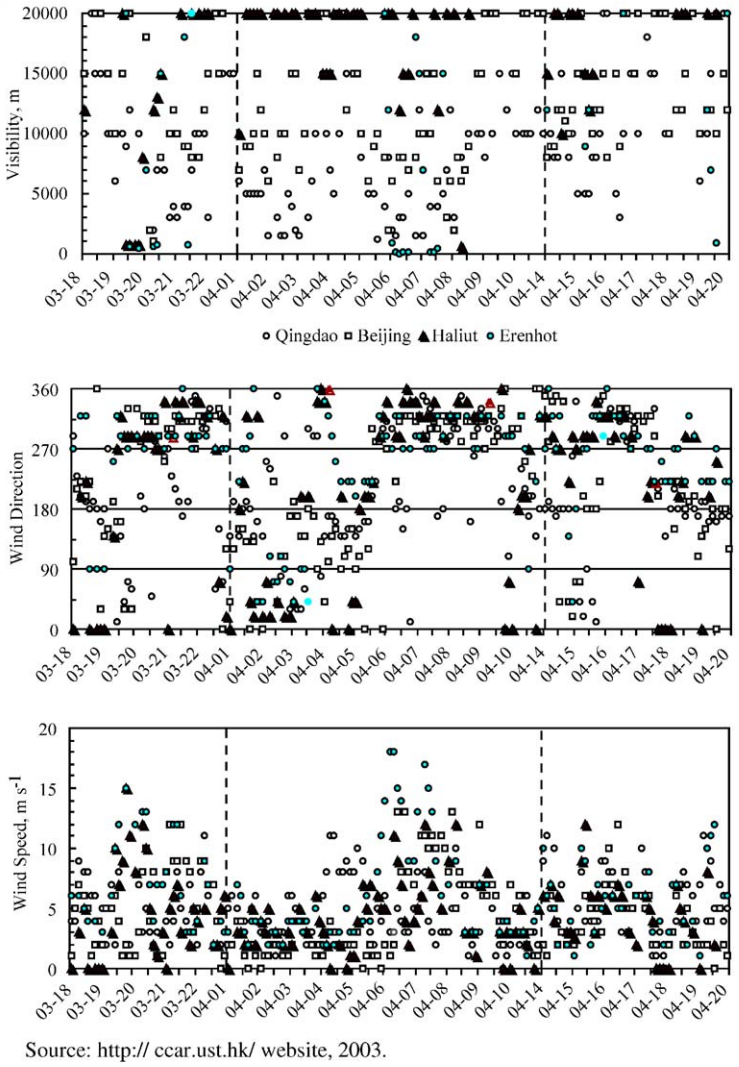

Fig. 2. Visibility and wind data along the back trajectories.

analyzed to support that the 16–17 April event was a local episode.

3.2. Characteristics of elements

The concentrations of Fe, S, Ti, Mn, Pb, Cu, Zn and V of the 18 samples analyzed are listed in Table 1 and in Table 2 are the enrichment factors (with respect to crustal Fe). The abundance of the targeted crustal elements is according to Taylor (1964).

The concentrations of Fe, Ti, V and Mn are significantly higher in the dust samples than the non-dust storm samples with Fe having the highest concentration of all the elements measured followed by S. The exception is in the 21 March sample when S is higher than Fe. In the calculation of the averages of the non-episodic samples, the 16–17 April samples were not included. The average Fe/S ratio for the dust storm events is 1.3 while it is 0.24 for the non-dust storm samples. Ti is higher than Pb and Zn in concentration and the Ti/Pb and Ti/Zn ratios for the dust storm events are 2.1, 1.9, respectively, while they are 0.53 and 0.28, respectively, for the non-episodic days. These trends are consistent with other dust storm studies.

Fe and Ti are abundant in the earth crust and are commonly used as mineral indicators in aerosols (Zhang and Friedlander, 2000; Mori et al., 2002). The enrichment factors for Ti reported in Table 2 for the dust episodes are 0.87–0.97 while they are 0.23–0.88 for the non-dust episode samples. This suggests that the Ti in the dust storm samples could have originated from the soil. Fe could also come from industrial sources such as

Table 1
Concentrations (ng m^{-3}) and ratios of selected elements in PM2.5 samples

	Fe	Ti	Mn	V	S	Pb	Zn	Fe/S	Ti/Pb	Ti/Zn
20/3	5308	507	152	19.8	4583	229	365	1.16	2.21	1.39
21/3	2080	183	69	7.2	3602	190	184	0.58	0.96	0.99
22/3	834	67	46	5.7	2540	96	165	0.33	0.70	0.41
23/3	571	49	22	4.3	1129	44	56	0.51	1.12	0.86
02/4	1242	111	51	14.8	5307	116	392	0.23	0.95	0.28
03/4	963	82	40	6.7	3100	76	160	0.31	1.08	0.51
04/4	232	9	16	5.6	2579	25	165	0.09	0.36	0.05
05/4	1015	79	60	7.1	8597	125	1304	0.12	0.63	0.06
07/4	4763	467	123	14.9	2651	128	137	1.80	3.64	3.41
08/4	2870	266	96	9.1	1893	149	164	1.52	1.78	1.62
15/4	657	44	47	6.5	3794	142	370	0.17	0.31	0.12
16/4	2223	200	65	6.3	1047	79	80	2.12	2.52	2.51
17/4	587	47	31	4.0	1684	122	152	0.35	0.38	0.31
18/4	498	34	28	2.8	2891	103	157	0.17	0.33	0.22
22/4	257	6	21	7.6	3124	89	307	0.08	0.07	0.02
23/4	529	38	21	4.0	1700	73	85	0.31	0.52	0.45
24/4	693	36	33	5.1	2370	111	155	0.29	0.32	0.23
25/4	201	11	12	2.0	1305	78	100	0.15	0.13	0.11
Average										
Eps	3755	356	110	13	3182	174	213	1.3	2.1	1.9
Non-eps	637	47	33	5.9	3086	92	275	0.24	0.53	0.28

Note: The highlighted rows are Asian dust episodes. Eps = episodic samples while non-eps = non-episodic samples.

steel mills and power plants in addition to soil sources. This could be the reason for the low EF values for Ti for the non-episodic days. The EFs for Mn and V in the dust samples were lower than the normal samples, suggesting that they were of soil origin. Vanadium can also be derived from the combustion of heavy residual oil typically used in ships (Nriagu and Pacyna, 1988). Qingdao is a port city. The higher V in Qingdao's atmosphere should not be a surprise. The EFs for S, Pb, Zn were much greater than unity in general and the non-episodic samples had much higher EFs than the dust storm samples. This suggests that these elements were of anthropogenic origin. Sulfur is mainly derived from the combustion of fossil fuels (Zhang and Friedlander, 2000) and Zn can come from industrial sources and the abrasion of rubber tires on roads (Rogge et al., 1993a). Both are not constituents of dust storms. Lead is a known component in automobile emissions (Nriagu and Pacyna, 1988) and in our study, the average dust storm concentrations of lead were higher than in the non-dust storm samples by almost two-fold. The high Pb concentration could be caused by vehicular emissions in Northern China brought into Qingdao by the dust storms. Cu was not studied because it is known that the motor of the sampler could cause contamination to the samples.

From the results of the elemental analysis, it can be seen that the episode on 20 March was apparently stronger than the other two and there was also an across-the-board increase in the elemental concentrations regardless of the source.

3.3. The characteristics of SEOC

The SEOC studied were *n*-alkanes, PAHs and fatty acids. A summary of the yields and indices is given in Table 3 and the distribution diagrams are presented in Fig. 3.

The maximum total yield for the March dust episode at 766.8 ng m^{-3} was higher than that for the April dust event, and the same can also be said for the alkanes, PAHs and fatty acids, suggesting that a more severe episode was experienced in March.

The C_{14}–C_{36} *n*-alkanes in the episodic samples ranged from 110.0 to 184.5 ng m^{-3} (average 145.9 ng m^{-3}) while those for the non-episodic samples were in the range 35.5–197.7 ng m^{-3} (average 82.8 ng m^{-3}). The carbon preference index (CPI) can be used to identify the

Table 2
Enrichment factors, EF = $(X_i/X_{crustal})/(X_{Fe}/X_{FeCrustal})$

	Ti	Mn	V	S	Pb	Zn
20/3	0.94	1.7	1.6	187	194	55
21/3	0.87	2.0	1.4	375	411	71
22/3	0.79	3.3	2.8	659	517	159
23/3	0.84	2.3	3.1	428	344	79
02/4	0.88	2.4	5.0	925	421	254
03/4	0.84	2.5	2.9	697	355	134
04/4	0.38	4.1	10.0	2403	484	572
05/4	0.77	3.5	2.9	1834	555	1034
07/4	0.97	1.5	1.3	121	121	23
08/4	0.92	2.0	1.3	143	234	46
15/4	0.66	4.3	4.2	1251	974	453
16/4	0.89	1.7	1.2	102	161	29
17/4	0.78	3.1	2.8	622	938	209
18/4	0.68	3.3	2.3	1257	934	253
22/4	0.23	4.8	12.3	2636	1565	962
23/4	0.71	2.4	3.2	696	624	129
24/4	0.51	2.8	3.1	741	721	180
25/4	0.52	3.5	4.2	1407	1759	400

Note: The highlighted rows are Asian dust episodes.

distribution of recent biogenic matter and anthropogenic materials (Simoneit, 1986; Zheng et al., 2000) and its range was 1.29–1.56 for the dust storm samples and 1.23–1.40 for the non-dust storm samples, showing almost no difference in the two sets of samples. A CPI equals unity indicates the characteristics of petroleum residues. This suggests that the samples studied contained substantial anthropogenic contributions. The maximum alkane carbon number (C_{max}) was 20 or 21 for the samples taken in March and early April. These samples included the two dust episodes. The exception was 4 April at 25. This suggests that the two sets of samples were very similar. For the samples taken in mid and late April, the C_{max} varied from 21 to 27. This may be caused by the change in seasons. The alkane distribution diagrams in Fig. 3a show only small differences between the episodic and averaged non-episodic samples except for the loading.

The alkanes can be further divided into two sources: plant wax and petroleum residues (Simoneit, 1986; see Table 3). On average, the petroleum residues in the alkanes for the episodic samples was 81% of the alkanes while it was slightly higher at 85% for the normal samples. This suggests that most of the alkanes in the PM2.5 of Qingdao were anthropogenic in origin.

Table 3
PM2.5 SEOC concentrations by family and important indices

	Alkane			Wax %	Petroleum residues	Fatty acid			Wax %	PAH yield	Total yield	Total wax
	Yield	CPI	C_{max}			Yield	CPI	C_{max}				
3/20	176.6	1.33	C_{20}	16.8	147.0	413.1	6.80	C_{16}	36.0	60.5	650.3	178.3
3/21	184.5	1.29	C_{21}	13.6	159.4	526.8	5.26	C_{16}	35.5	55.5	766.8	212.2
3/22	197.9	1.23	C_{21}	12.6	172.9	456.9	6.87	C_{16}	30.0	90.5	745.2	162.0
3/23	92.4	1.23	C_{21}	12.8	80.6	255.4	7.01	C_{16}	23.2	21.5	369.3	71.1
4/02	76.6	1.23	C_{21}	12.4	67.1	282.2	8.50	C_{16}	18.3	36.7	395.6	61.1
4/03	46.7	1.40	C_{21}	20.5	37.1	203.3	5.84	C_{16}	23.0	6.4	256.5	56.3
4/04	35.5	1.35	C_{21}	17.9	29.1	196.2	5.79	C_{16}	17.3	1.8	233.4	40.2
4/05…06	109.1	1.37	C_{25}	18.5	88.9	301.4	6.65	C_{16}	24.8	29.7	440.2	95.0
4/07	112.4	1.44	C_{21}	21.0	88.8	355.3	9.89	C_{16}	28.9	36.4	504.0	126.2
4/08	110.0	1.56	C_{21}	25.6	81.9	384.8	6.42	C_{16}	40.6	42.7	537.6	184.4
4/15	74.1	1.33	C_{23}	15.0	63.0	304.6	9.94	C_{16}	16.8	21.7	400.4	62.4
4/16	59.5	1.53	C_{21}	22.0	46.5	216.9	10.26	C_{16}	13.2	10.0	286.4	41.8
4/17	94.3	1.41	C_{21}	17.9	77.4	481.3	11.47	C_{16}	14.9	26.7	602.2	88.7
4/18	87.8	1.25	C_{27}	12.2	77.1	298.0	7.89	C_{16}	14.1	14.1	399.9	52.9
4/22	55.0	1.22	C_{23}	10.6	49.2	274.2	9.58	C_{16}	11.3	14.4	343.6	36.9
4/23	67.1	1.40	C_{23}	17.6	55.3	445.0	11.57	C_{16}	12.8	16.6	528.7	68.9
4/24	111.9	1.25	C_{23}	11.8	98.7	467.1	12.41	C_{16}	13.9	48.4	627.4	78.0
4/25	62.2	1.27	C_{21}	12.8	54.3	461.2	11.71	C_{16}	10.2	8.9	532.4	55.0

Note: The wax content in the alkanes is calculated after Simoneit (1986): Wax $C_n = C_n - ((C_{n+1}+C_{n-1})/2)$. The highlighted rows are Asian dust episodes.
All concentrations are ng m^{-3}.

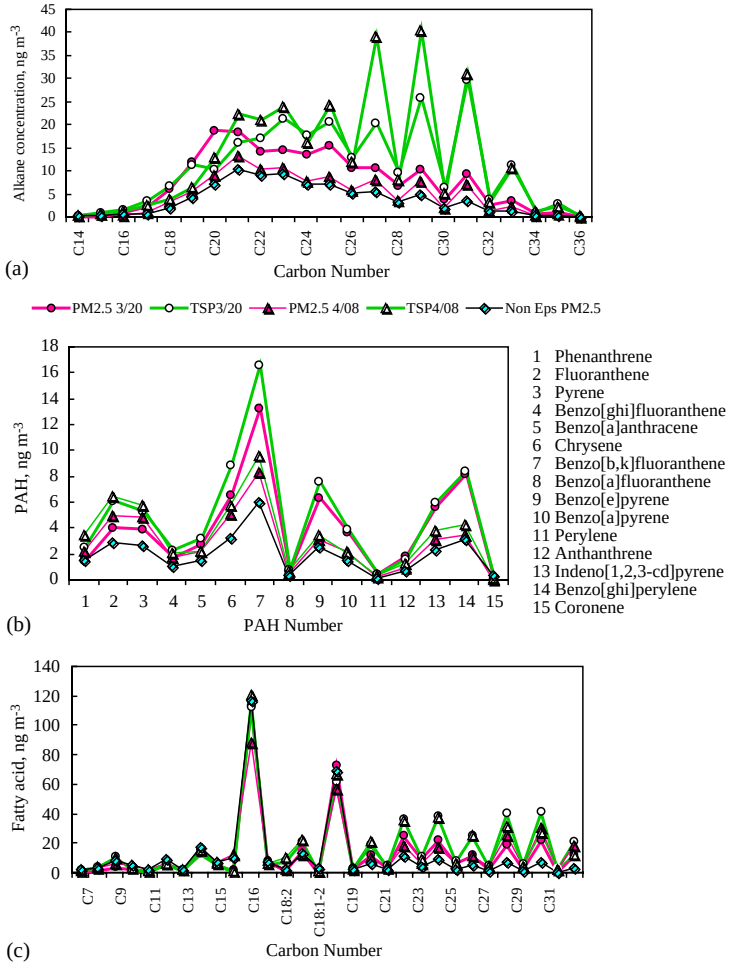

Fig. 3. SEOC distribution diagrams of dust storm and non-episodic samples, PM2.5 and TSP.

Fig. 3b shows the typical distribution diagrams of the 15 quantified PAHs and the names of the PAHs are also given in the figure. The general shape of the distribution diagrams of the episodic and non-episodic samples is by and large the same, only the loading is different. This suggests that the PAHs of the two different types of samples were from the same sources. The total PAHs ranged from 36.4 to 60.5 ng m^{-3} and the average was 48.8 ng m^{-3} for the dust samples. They ranged from 1.8 to 90.5 ng m^{-3} and the average was 24.7 ng m^{-3} for the non-dust storm days.

Fatty acids in the C_7–C_{32} range were the largest fraction of the three families of organic compounds detected. The concentration range was 355.3–526.8 ng m^{-3} and the average was 420.0 ng m^{-3} for the dust events, the range was 196.2–467.1 ng m^{-3} and the average was 320.2 ng m^{-3} for the non-dust storm days. The C_{max} was 16 for all samples. The $<C_{20}$ homologues are thought to be derived in part from microbial sources while $>C_{22}$ homologues are from vascular plant wax (Simoneit and Mazurek, 1982). Besides microbial activities, cooking has also been found to be an important contributor of the $<C_{20}$ fatty acids in urban areas (Rogge et al., 1991). Other sources include vehicular emissions (Schauer et al., 1999) but the contribution is small. The plant wax contribution in the dust storm samples was 28.9–40.6% (average 35%). The kitchen/microbial contribution was estimated to be 65%. In the non-dust storm day samples, the plant wax was 10.2–30.0% (average 18%). The kitchen/microbial contribution was estimated to be 82%. Higher wind speeds were experienced during the dust storms thus promoting more wind abrasion of leaves and vegetation resulting in higher plant wax input (Simoneit, 1986; Zheng et al., 2000). During the mid-April episode, there was a difference of one day between the metals and SEOC peak concentrations. Fe peaked at 2223 ng m^{-3} on 16 April before dropping off to 587 ng m^{-3} the next

day while total SEOC was 286.4 and 602.2 ng m^{-3} for the two days, respectively. Even though the total organic yield was high on 17 April, the fatty acid wax content at 14.9% was much lower than the content detected in the dust samples (35.2%). The wax content of the 17 April sample resembled the non-episodic samples taken during that period (average 13.2%).

Upon further examination of the total plant wax (the sum of alkane and fatty acid plant wax) and petroleum residue concentrations in Table 3, there existed little difference between the concentration of these two families of organic compounds in non-episodic days, with a few exceptions when the petroleum residues were higher than the plant wax. However, the total plant wax contribution was always substantially higher than the petroleum residues during the dust storms. The 17 April sample had 77.4 ng m^{-3} of petroleum residues and 88.7 ng m^{-3} of total wax. This suggests that the 17 April sample may not be a consequence of a dust storm. Unlike the drastic differences observed in the Fe concentrations in the episodic and non-episodic samples, the SEOC, in general, showed much smaller variations suggesting that the storms had less impact on the SEOC.

3.4. Comparison of simultaneous episodic TSP and PM2.5 chemical characteristics

Three simultaneous high-volume TSP samples were taken on 20 March and 7–8 April. The results of these episodic samples were compared to the PM2.5 data discussed above. Because of the very high loading of the PM2.5 samples during the dust storm episodes, the background of the filter medium were less pronounced and the concentrations of Mg, Ca and Al can be reported for qualitative comparisons. Such comparisons shed more light on the chemical characteristics of the dust storm samples according to particle size. A comparison of the TSP and PM2.5 elemental, EF and SEOC data is presented in Tables 4 and 5. Distribution diagrams of the *n*-alkanes, PAHs and fatty acids are shown in Fig. 3.

Zhang et al. (1996) showed that the elements Al, Fe, Mg, and Sc and the ratios of Fe/Al, Mg/Al, and Sc/Al can be effectively used to identify the origin of the dust from different regions. They reported Fe/Al and Mg/Al of the dust in eastern Inner Mongolia to be 0.44 and 0.20, while those from the northwest deserts of China

Table 4

(a) Comparison of simultaneous elemental TSP and PM2.5 during episodes

	Fe	Mg	Ca	Al	Ti	Mn	V	S	Pb	Zn
PM2.5										
3/20	5308	1959	3766	9011	507	152	20	4583	229	365
4/07	4763	777	2690	7623	467	123	15	2651	128	137
4/08	2870	613	938	4548	266	96	9	1893	149	164
Average	4314	1116	2465	7061	413	124	15	3042	169	222
TSP										
3/20	43,057	16,157	42,802	90,765	5818	1221	147	12,439	226	522
4/07	30,001	14,129	26,293	78,290	3722	813	93	5496	145	232
4/08	26,549	11,667	23,001	65,481	3332	696	77	4770	183	268
Average	33,202	13,984	30,698	78,179	4291	910	105	7569	185	341
PM2.5/TSP	0.13	0.080	0.080	0.090	0.096	0.14	0.14	0.40	0.91	0.65

(b) Comparison of the episodic TSP and PM2.5 enrichment factors (referenced to crustal Fe)

	Mg	Ca	Al	Ti	Mn	V	S	Pb	Zn
PM2.5									
3/20	0.89	1.0	1.2	0.94	1.7	1.6	187	194	55
4/07	0.39	0.77	1.1	1.0	1.5	1.3	121	121	23
4/08	0.52	0.44	1.1	0.92	2.0	1.3	143	234	46
Average	0.60	0.72	1.1	0.94	1.7	1.4	150	183	42
TSP									
3/20	0.91	1.3	1.4	1.3	1.7	1.4	63	24	10
4/07	0.79	0.83	1.2	0.85	1.1	0.9	28	15	4.3
4/08	0.65	0.72	1.0	0.76	0.96	0.7	24	19	5.0
Average	0.78	1.0	1.2	1.0	1.3	1.0	38	19	6.4

All concentrations are in ng m^{-3}.

Table 5
Comparison of simultaneous TSP and PM2.5 SEOC during episodes

	Alkanes	ALK Wax	ALK Wax%	ALK C_{max}	ALK CPI	Fatty acids	FA Wax	FA Wax%	PAHs
PM2.5									
3/20	177	25	17	C_{20}	1.3	413	149	36	61
4/07	112	19	21	C_{21}	1.4	355	103	29	36
4/08	110	22	26	C_{21}	1.6	385	156	41	43
Average	133	22	21		1.4	384	136	35	47
TSP									
3/20	253	77	30	C_{31}	1.9	526	239	45	74
4/07	211	74	35	C_{29}	2.1	508	225	44	33
4/08	290	120	41	C_{29}	2.4	501	194	39	51
Average	251	90	36		2.1	512	219	43	53
PM2.5/TSP	0.53	0.25				0.75	0.62		0.88

Note: ALK = *n*-alkanes; FA = fatty acids.
All concentrations are in ng m^{-3}.

are 0.83 and 0.19. From Table 4(a), these ratios based on the 2002 Qingdao dust episodes are 0.42 and 0.18, respectively, suggesting that the source of the dust may be from Inner Mongolia. This is consistent with the back trajectory calculations.

Fe, Mg, Ca, Al, Ti, Mn and V concentrations in the PM2.5 samples were 8–14% of that in the corresponding TSP samples. Chun et al. (2001) reported a substantial increase in the 1.35–10 μm particles in heavy Asian dust storms and the increase was localized in the 2.23–6.06 μm particle size range. Zhuang et al. (2001) measured a Beijing dust episode in the spring of 2000 and found that <2.1 μm particles constituted 16.1% of the TSP. This suggests that fine particles are not the dominant fraction of the total aerosol loading in dust storms, which explains the low PM2.5/TSP ratios for these elements in our samples. The enrichment factors for these elements (Table 4(b)) in both PM2.5 and TSP were very close to unity. This suggests that even though PM2.5 only constituted a small fraction of the TSP, these elements in TSP, nevertheless, came from similar sources, i.e., the Earth's crust.

The PM2.5/TSP ratios for Pb and Zn, on the other hand, were high with values of 0.91 and 0.65, suggesting that the origin of these two elements was mainly anthropogenic with only minor input from geological sources.

Sulfur showed a PM2.5/TSP of 0.4, indicating that 60% of the material was in the larger particles. This is different from the distribution observed in urban areas. Wall et al. (1988) showed that the sulfate particle distribution in Los Angeles had two modes with the condensation mode in the 0.17–0.25 μm range and the droplet mode in the 0.6–0.65 μm range. Sulfate is the dominant species in Hong Kong's fine particles (<1.8 μm), co-existing in the condensation (0.2 μm) and droplet (0.57 μm) modes (Zhuang et al., 1999). The different particle distribution may be the result of the dust storms.

The wind speed during dust storms is usually high, promoting the dispersion of locally generated fine particles as exemplified by the loss of <0.5 μm particles (Chun et al., 2001). Normally, there is less sulfate in the coarse particles than fine ones, yet in a dust storm, the particle loading can be as much as 30 times higher than in the non-episodic samples. From possible contribution from soil and the transformation of SO_2 during transport (Zhuang et al., 2001), more sulfur may be found in the coarse dust storm particles.

The ratio of *n*-alkanes in PM2.5 to that in TSP was 0.53. The composition and distribution of the *n*-alkanes were quite different between PM2.5 and TSP (Table 5). For example, the C_{max} was higher for TSP (29–30) than for PM2.5 (20–21), and the same was true for the plant wax contribution (36% for TSP and 21% for PM2.5). The average PM2.5/TSP ratio of the alkane plant wax was 0.25. The average CPI for TSP was also higher than that for PM2.5. This suggests that the alkane plant wax in the dust storm episode samples may be partially attributable to soil origins while the petroleum residues, residing mostly in the smaller particles, may be from local sources.

The ratio of the fatty acids in PM2.5 to those in TSP was 0.75 and the plant wax fraction of the fatty acids was higher in TSP (43%) than that in PM2.5 (35%). It has been reported that the plant wax in the fatty acids can be attributed to the abrasion of leaves (Simoneit, 1986) and dead leaves contain 5.14 times more fatty acids than in green leaves (Rogge et al., 1993b).

Long-distance dust samples show odd-even dominance in the alkanes, high alkane C_{max} values (29–31), and high plant wax content in both the alkanes and fatty acids (Simoneit, 1977; Fang et al., 1999). The TSP collected in this study exhibited these characteristics but

not the PM2.5. In particular, there was no obvious difference in the alkane distribution between the PM2.5 samples (Fig. 3a). This suggests that the source of the fine and coarse particles was different during the dust storms, i.e., PM2.5 was local while the larger particles were transported from a long distance.

4. Conclusion

The use of a combination of inorganic and organic characteristics of the chemical species in atmospheric aerosols in Asian dust episodes has been demonstrated to reveal more information on the sources and the transport processes. This is due to the fact that elements, especially metals, are good long-distance tracers while SEOC can provide information on local emissions including biogenic and microbial origins (Fang et al., 1999). During the dust storms, the transport of soil-related materials lagged behind local emissions because of the distance of the sources from the sampling site. Furthermore, the local sources tended to have sooner and longer impact while dust storm effects were present only while the storm lasted. Because dust storms are inherently associated with coarse particles, complementary TSP data are very useful in source apportionment.

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