APPENDIX 1

HONG KONG ENVIRONMENTAL PROTECTION DEPARTMENT

PM2.5 STUDY

Tsuen Wan PM2.5 Study (August 1998 - January 1999)

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Summary

The PM2.5 study conducted in the lower half year of 1998 revealed that the monthly means of PM2.5 were attributable to around 69% of PM10 consistently throughout the sampling period. From August 1998 to January 1999, the monthly means of PM2.5 ranged from the lowest 30.5 $\mu g/m^3$ in August 1998 to the highest 54.9 $\mu g/m^3$ in January 1999, with an average of 44.8 $\mu g/m^3$. If the USEPA 24-hour objective (i.e. 65 $\mu g/m^3$) was adopted, there should be four non-compliance in winter (November 1998 to January 1999), with a maximum of 76 $\mu g/m^3$.

Carbon and secondary aerosols were found to be the major constitutes of PM2.5. Elemental carbon should be mainly emitted from the diesel vehicles while part of the organic carbon might be originated from other source or activity that was more active in winter. On the other hand, sodium and chloride should probably be depleted from the sea salt. A lot of secondary nitrate might hence exist in the form of sodium nitrate during the summer season. Aluminum, iron, silicon and calcium should mainly be originated from crustal sources.

1. Introduction

Tsuen Wan was considered to be a representative district of Hong Kong as it was a highly populated area with mixed residential, commercial and industrial development. An one-month sampling for PM2.5 was carried out at the roof-top of Tsuen Wan Alexander Community Center in January 1998. However, the results were suspected to have a high uncertainty on the species concentrations due to uneven distribution of dust on the filters equipped in the ACCU sampling system. On the other hand, the sampling period was short and thus it was impossible to follow the change and trend of species concentrations throughout the summer and winter seasons. A follow-up exercise was therefore commenced in August 1998 using the USEPA designated samplers, and ended in January 1999.

2. Methodology

- 2.1 Samples were collected at 2 m above the roof floor of Alexander Community Center, Tsuen Wan, where was approximately 10 m apart from the EPD's Tsuen Wan Air Monitoring Station.
- 2.2 The sampling was conducted once every three days covering the summer and winter seasons. Samples for PM2.5 and PM10 were collected simultaneously over 24 hours by four co-located Partisol samplers of which two (Model 2025) and the other two (Model 2000) were granted with the USEPA designation for PM2.5 & PM10 sampling respectively. The 47 mm Teflon and pre-fired quartz (QMA) filters were used to collect a full set of sample for each type of particulates for chemical analysis purpose. The pre- and post-sampling filters, including field and laboratory blanks, were weighed in the EPD's Balance Laboratory and subsequently sent to the Desert Research Institute (DRI) for analysis.
- 2.3 The pre-fired QMA filters were used to determine the concentration of organic and elemental carbons by the thermo-optical reflectance method while the ions (including

ammonium, sulphate, nitrate, potassium, magnesium and sodium) were analyzed by automated colorimetry, ion chromatography and atomic absorption methods.

- 2.4 The Teflon filters were used to determine the concentration of elements Aluminum (Al) to uranium (U) by Energy Dispersive X-ray Fluorescence (EDXRF) method.
- 2.5 The species concentrations of each type of particulates were validated by the DRI as valid results. Appendix 1 enclosed the results for reference.

3. Results and Discussions

3.1 Fig.1 (a) & (b) showed the time-series plot for the particulates levels. There was no regular weekly pattern of both PM2.5 and PM10 in Tsuen Wan. The trend of PM2.5 variation throughout the summer and winter seasons was similar to that of PM10. Table 1 summarized the monthly particulates levels. It was noted that the monthly particulate levels were higher in winter. From August 1998 to January 1999, the monthly means of PM2.5 ranged from the lowest $30.5 \ \mu g/m^3$ in August 1998 to the highest $54.9 \ \mu g/m^3$ in January 1999, with an average of $44.8 \ \mu g/m^3$. If the USEPA 24-hour objective (i.e. $65 \ \mu g/m^3$) was adopted, four non-compliance, with a maximum of 76 $\ \mu g/m^3$ were noted in winter season (see Appendix 1 for details). However, the monthly percentage of PM2.5 to PM10 was quite consistently kept at around 69% throughout the summer and winter seasons. This finding coincidentally matched with the previous finding in January 1998, which revealed that 70 percentage of PM10 particulates were mainly of PM2.5 nature.

	Month	ly Averag	ges	Seasonal Statistics							
Month	PM2.5	PM10	PM2.5/PM10	Season	Туре	Average	Max	Min	Stdev		
	$(\mu g/m^3)$	$(\mu g/m^3)$	(%)			$(\mu g/m^3)$	$(\mu g/m^3)$	$(\mu g/m^3)$	$(\mu g/m^3)$		
Aug 98	30.5	42.2	72.2		PM2.5	37.2	62.4	19.3	13.2		
Sep 98	37.0	54.9	67.9	Summer	PM10	54.3	90.5	26.5	19.9		
Oct 98	39.5	57.7	69.5		PM2.5	66.6 %	79.3 %	52.2 %	7.0 %		
					PM10						
Nov 98	49.3	75.4	67.3		PM2.5	52.0	76.0	28.0	13.1		
Dec 98	53.1	76.1	69.9	Winter	PM10	76.2	121.3	37.7	22.8		
Jan 99	54.9	77.8	72.3		PM2.5	69.4 %	83.6 %	55.1 %	6.5 %		
					PM10						

Table 1 : Statistical Summary of Tsuen Wan Dust Levels





		к		SO4		NH4		OC		EC			NO3						
	Month	PM2.5	PM10	PM2.5/1	PM2.5	PM10	PM2.5/1	PM2.5	PM10	PM2.5/1	PM2.5	PM10	PM2.5/1	PM2.5	PM10	PM2.5/1	PM2.5	PM10	PM2.5/1
				0			0			0			0			0			0
Average	Aug-98	0.191	0.375	0.492	7.040	8.804	78.469	1.354	1.163	1.177	6.585	7.919	0.864	8.599	10.197	0.871	0.603	1.632	0.383
	Sep-98	0.753	1.258	0.514	10.307	11.152	90.526	2.485	2.110	1.249	6.859	9.594	0.729	8.271	9.439	0.871	0.900	2.826	0.349
	Oct-98	0.914	1.409	0.636	13.244	14.428	93.022	2.730	2.362	1.193	9.212	12.607	0.727	6.245	6.286	0.997	1.117	3.205	0.407
	Nov-98	1.442	2.210	0.628	11.669	12.643	92.424	3.214	2.892	1.124	12.376	14.889	0.819	9.190	10.369	0.890	1.269	3.967	0.349
	Dec-98	1.539	2.295	0.669	11.240	12.359	89.715	3.788	3.812	0.996	13.954	17.895	0.766	7.047	7.440	0.979	2.269	4.313	0.561
	Jan-99	1.544	2.299	0.678	11.180	11.637	96.427	3.816	3.807	1.015	13.376	15.829	0.855	7.086	8.470	0.841	2.923	4.610	0.677
Summer	Average	0.742	1.199	0.561	10.888	12.025	89.406	2.431	2.084	1.216	7.732	10.482	0.752	7.535	8.337	0.920	0.933	2.767	0.378
	Max	2.267	3.472	0.775	22.425	23.485	129.845	7.069	6.431	1.537	14.663	18.871	1.431	11.950	13.299	1.579	1.559	6.493	0.696
	Min	0.080	0.271	0.276	3.931	3.764	64.509	0.457	0.326	0.838	3.638	5.258	0.500	2.125	3.041	0.571	0.375	0.838	0.202
	Stdev	0.645	0.948	0.136	5.086	4.984	13.481	1.642	1.511	0.187	3.199	4.117	0.191	2.289	2.488	0.213	0.379	1.412	0.146
Winter	Average	1.502	2.263	0.655	11.395	12.313	92.234	3.569	3.451	1.050	13.211	16.270	0.806	7.894	8.810	0.914	2.020	4.242	0.504
	Max	2.467	3.825	0.753	17.350	19.332	108.772	5.995	6.069	1.308	18.600	22.486	0.919	10.792	12.758	1.496	3.825	7.661	0.893
	Min	0.215	0.407	0.428	3.925	5.790	67.789	1.476	1.428	0.910	5.546	7.494	0.570	3.838	4.501	0.731	0.574	1.174	0.195
	Stdev	0.599	0.896	0.069	3.694	3.910	7.738	1.320	1.387	0.096	3.834	4.144	0.085	2.042	2.435	0.172	0.959	1.616	0.212
Overall	Average	1.131	1.743	0.609	11.142	12.169	90.820	3.013	2.783	1.131	10.472	13.376	0.779	7.715	8.574	0.917	1.476	3.504	0.441
	Max	2.467	3.825	0.775	22.425	23.485	129.845	7.069	6.431	1.537	18.600	22.486	1.431	11.950	13.299	1.579	3.825	7.661	0.893
	Min	0.080	0.271	0.276	3.925	3.764	64.509	0.457	0.326	0.838	3.638	5.258	0.500	2.125	3.041	0.571	0.375	0.838	0.195
	Stdev	0.725	1.058	0.116	4.403	4.432	10.962	1.578	1.590	0.168	4.456	5.024	0.149	2.152	2.446	0.192	0.906	1.676	0.191

0.383 0.349 0.407

0.349

0.677 0.378

0.696 0.202 0.146 0.504

0.893 0.195 0.212 0.441 0.893 0.195 0.191

Table 2	•	Major S	Snecies	in	Fine	Mode
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		Total Mass Concentration			Sum of the Above Spec	cies Conc.	Ratio of the Above Species Conc. to Total Mass				
	Month	PM2.5(T)	PM10(T)	PM2.5/10	PM2.5(s)	PM10(s)	PM2.5(s)/PM2.5(T)	PM2.5(s)/PM10(T)	PM10(s)/PM10(T)		
Average	Aug-98	30.54	42.15	72.16	24.37	30.09	0.80	0.58	0.71		
	Sep-98	37.05	54.93	67.94	29.58	36.38	0.80	0.54	0.66		
	Oct-98	39.49	57.69	69.50	33.46	40.30	0.85	0.58	0.70		
	Nov-98	49.34	75.38	67.29	39.16	46.97	0.79	0.52	0.62		
	Dec-98	53.10	76.10	69.85	39.84	48.11	0.75	0.52	0.63		
	Jan-99	54.88	77.83	72.30	39.92	46.65	0.73	0.51	0.60		
Summer	Average	37.16	54.32	66.59	30.26	36.89	0.81	0.56	0.68		
	Max	62.38	90.51	79.31	59.93	72.05	0.96	0.66	0.80		
	Min	19.33	26.52	52.23	10.61	13.50	0.55	0.40	0.51		
	Stdev	13.18	19.94	7.00	13.24	15.46	1.00	0.66	0.78		
Winter	Average	52.02	76.20	69.38	39.59	47.35	0.76	0.52	0.62		
	Max	76.04	121.30	83.63	59.03	72.13	0.78	0.49	0.59		
	Min	28.00	37.70	55.10	15.57	20.79	0.56	0.41	0.55		
	Stdev	13.06	22.76	6.49	12.45	14.39	0.95	0.55	0.63		
Overall	Average	44.75	65.50	69.27	34.95	42.15	0.78	0.53	0.64		
	Max	76.04	121.30	83.63	66.34	77.19	0.87	0.55	0.64		
	Min	19.33	26.52	52.23	10.60	13.50	0.55	0.40	0.51		
	Stdev	14.99	23.90	6.67	14.22	16.23	0.95	0.60	0.68		

Notes : All units are in microgram per cubic meter PM i (s) = Sum of SO4 + NO3 + OC +EC +K + NH4 conc. where i = 2.5, 10

- 3.2 Table 2 indicated the major chemical species that contributed a high percentage of PM2.5 to the PM10 samples. Carbon (i.e., organic carbon (OC) and elemental carbon (EC)) and secondary aerosols (i.e., sulphate $(SO_4^{2^-})$ and ammonium (NH_4^+)) were found to be the main constitutes of PM2.5 & PM10. Fig. 2 & 3 showed their trends and magnitudes. From the Table, it was noted that the sum of sulphate and ammonium levels had nearly reached the 3-three annual objective of PM2.5 ($15 \mu g/m^3$). Since (i) these two species existed in fine mode (PM2.5) and (ii) their levels in PM10 were recorded more or less the same day by day at the four sites, including the one near the boundary between Mainland and Hong Kong, where samples were taken simultaneously were spread in different areas in the territory and (iii) their levels were usually high when wind blew from the north-east to north west, these two species were considered the regional factor rather than local emission factors. Certainly, Hong Kong is possibly to be one of the sources in the Asia. It should be treated on regional scale.
- 3.3 Table 2 revealed that sulphate, ammonium and elemental carbon existed in very fine mode. Nearly all of them were of PM2.5 nature. Although OC was also mainly fine in size, it still had approximately 20% by mass in coarse mode (i.e., 2.5 m < size < 10 m) that might probably be contributed by other sources such as construction and paved road dusts.
- 3.4 Fig.2 revealed that the trend of OC was a little bit different from that of EC, especially during the winter. The EC level was found to be maintained within a range throughout the summer and winter seasons while the OC level tended to increase its level in winter. Table 2 indicated that the averaged monthly and seasonal EC levels of PM2.5 and PM10 were kept at around 7.7 and $8.6 \,\mu g/m^3$ respectively. However, the OC levels of PM2.5 & PM10 were obviously higher in winter and was about 50 % higher than the summer levels. As a result, the winter average of OC to EC ratio was around 50% higher than the summer average. Table 3 showed the figures. It reflected that another OC source might possibly exist and should be arisen from the activities or phenomena that was more active during the winter season. Further study on this issue was required.

Ratio of OC to EC									
	Monthly Ave	rages ($\mu g/m^3$)		Seasonal Averages(µg/m ³)					
Month	PM2.5 PM10		Season	PM2.5	PM10				
Aug 98	0.83	0.85							
Sep 98	0.90	1.04	Summer	1.19	1.43				
Oct 98	1.67	2.12							
Nov 98	1.39	1.47							
Dec 98	2.26	2.69	Winter	1.84	2.03				
Jan 99	1.88	1.87							

Table 3 : The OC to EC Levels

3.5 EC itself was worldwide considered a good indicator of diesel vehicles because most of the sources did not have too much EC in terms of percentage by mass. It was reasonable to have a stable monthly EC value throughout the year as the local diesel vehicles, especially taxi and bus, should have maintained their regular running schedules.



3.6 Crustal sources were found to have a certain amount of OC in the study of local source profile development, being composed of construction aggregates, cement, PFA, natural soil and paved road. It was also well-known that they were mainly of coarse nature. Silicon (Si), aluminum (Al), iron (Fe) and calcium (Ca) were identified to be the major constitutes in the latest PM2.5 and PM10 source profile development. Table 4 and Fig. 4 as an example demonstrated they were of coarse nature in particulates samples, and Fig. 5 showed their consistency in emissions throughout the sampling period which revealed that they should come from the same sources - crustal.

Month	Ratio of PM2.5 to PM10								
	Ca	Al	Si	Fe	Na	K			
Aug 98	0.133	0.116	0.123	0.231	0.044	0.492			
Sep 98	0.114	0.077	0.113	0.225	0.104	0.514			
Oct 98	0.134	0.092	0.115	0.262	0.528	0.636			
Nov 98	0.123	0.090	0.124	0.251	0.000	0.628			
Dec 98	0.103	0.063	0.104	0.243	0.431	0.669			
Jan 99	0.108	0.078	0.109	0.262	0.149	0.678			

Table 4 : Possible Constitutes of Crustal Sources

3.7 Among the elements in Table 4, Fig. 6 revealed that the trend of sodium was quite different from those of the other crustal elements. There was possibly another source attributable to Na. Fig. 8 revealed that sodium (Na) and chloride (Cl) might come from the same source - marine aerosol because their trends showed the similarity. The degree of depletion of marine salt (marine aerosol) depended on a lot of factors such as temperature and humidity. Their composition in form of particulates could be different from each other after depletion, depending on the external factors such as the ammonium and nitrate concentrations. If any of them was attached to the large compounds, their particulates could be big in size and might even be larger than PM10. Nevertheless, there was a very complicated chemistry among these factors. Table 5 indicated that the summer level was normally higher than the winter level. It could be explained that the depletion of sea salt was favourable under high temperature condition.

		Cl			Na		Meteorological Condition		
Month	PM2.5	PM10	PM2.5	PM2.5	PM10	<u>PM2.5</u>	Temperature	Relative	
	$(\mu g/m^3)$	$(\mu g/m^3)$	PM10	$(\mu g/m^3)$	$(\mu g/m^3)$	PM10	(° C)	Humidity (%)	
Aug 98	0.003	0.741	0.001	0.059	0.988	0.044	28.9	83.0	
Sep 98	0.000	0.523	0.000	0.236	1.072	0.104	28.0	73.8	
Oct 98	0.000	0.427	0.000	1.207	2.513	0.528	25.7	71.7	
Nov 98	0.002	0.341	0.002	0.000	0.631	0.000	23.2	72.5	
Dec 98	0.009	0.403	0.030	0.119	0.417	0.431	18.2	65.8	
Jan 99	0.025	0.541	0.059	0.044	0.296	0.149	15.0	66.2	

Table 5 : Nature of Sodium and Chloride









Apart from the above, it was interesting that sodium level was higher in October. Moreover, the ratio of PM2.5 to PM10 was consistently higher in October and occasionally higher in December as compared with the other days, but the chloride level did not vary too much. A certain amount of fine sodium particles might be contributed by other source(s), but was unlikely of crustal nature.

- 3.8 Nitrate could be found in both coarse and fine modes. The size distribution depended heavily on location and weather conditions. Coarse nitrate had often been observed in coastal areas. The formation processes of nitrate had been studied and reported by a few researchers. Yoshizumi and Hoshi (1985) used an Anderson sampler to collect the particulate samples in downtown Tokyo and found that nitrate was mainly distributed in the coarse mode in summer and in the fine mode in winter. Using thermal analysis, they found that the fine mode nitrate was ammonium nitrate and the coarse mode nitrate was sodium nitrate. Ammonium nitrate had a high volatility and therefore easily dissociate into gas-phase nitric acid and ammonium at low humidity and high temperature. As the summer temperature in Hong Kong was high, it would favour the depletion of sea salt. A lower ratio of PM2.5 to PM10 of nitrate in summer was therefore expected. In January 1997, Hong Zhuang of HKUST¹ reported nitrate in Hong Kong to be predominantly in the coarse mode because of high sodium concentration at coarse area. Besides, nitrate could also form coarse particles with calcium and magnesium. It helped explain why Table 2 indicated most of the nitrate were in coarse mode, especially during the summer season.
- 3.9 The EC levels remained more or less the same during the sampling period probably because of a constant number of vehicles running on the streets every day. As the site was located in an area where a number of diesel trucks, including container trucks, buses, vans, taxies, etc., would pass by every day, the EC should mainly originate from diesel vehicle emissions. Taking the average EC level and ~60% of EC in diesel vehicle emission (with reference to the US EPA profile) into account, appropriate control on local diesel vehicle emissions should be undertaken for the achievement of 3-year PM2.5 annual objective (15 μ g/m³).

4. Conclusion

Particulate collected from August 1998 to January 1999 revealed that around 69 % of PM10 was in the form of PM2.5. The monthly means of PM2.5 ranged from the lowest 30.5 μ g/m³ in August 1998 to the highest 54.9 μ g/m³ in January 1999, with an average of 44.8 μ g/m³. If the USEPA 24-hour objective (i.e. 65 μ g/m³) was adopted, four non-compliance, with a maximum of 76 μ g/m³ were found in winter.

Carbon and secondary aerosols were found to be the major constitutes and mainly existed in the fine mode. Elemental carbon was expected to be mainly originated from the diesel vehicles while part of the organic carbon might come from the other source(s) or activity that was more active in winter.

Sodium and chloride might mainly be depleted from the sea salt, and the summer season provided a favourable condition for the formation of sodium nitrate. On the other hand, aluminum, iron, silicon and calcium should be contributed by crustal sources.

Control on local diesel vehicle emission and measures to tackle regional pollution are effective means to reduce the PM2.5 level.

5. References

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