

Correlations between Organic and Inorganic Species in Atmospheric Aerosols

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Correlations between 35 different organic and inorganic species or tracers in the aerosols of Hong Kong were derived based on the GC–MS organic results from our 1993–1994 study and Hong Kong Environmental Protection Department inorganic data. Source apportionment is essential in fingerprinting of air pollutants for cross-boundary studies. It is also important in the development of emissions inventory data, control strategies, and legislature. Traditionally, emission sources are identified from either the inorganic or organic tracers in the aerosols, but not both. Each of these techniques yields much source information; however, each by itself provides only a partial picture due to the complicated nature of ambient aerosols. Since many of the organic and inorganic species in aerosols are from the same source, correlations between the two are to be expected. In this study, such correlations were indeed found. For example, benzo[*b,k*]fluoranthene, the most abundant PAH (polycyclic aromatic hydrocarbon) in all the PAHs detected in Hong Kong, exhibited good correlation with Pb, Zn, As, nss SO₄²⁻ (nonseasalt sulfate), total PAHs, and benzo[*a*]pyrene. This paper further demonstrates that a combination of the two techniques could be an improved method for source apportionment than using either method alone.

Introduction

There have been extensive studies on the sources of aerosols in different areas of the world (1, 2). By studying the inorganic and organic components in the aerosols and sometimes complementing with meteorological data and flow modeling, local emissions and cross-boundary transport of air pollutants can be identified. It has been demonstrated that the concentration change in the trace substances in the atmosphere can be related to the differences in air-mass trajectories and transport pathways (3).

The origins of the inorganic and organic components in the atmosphere can be either natural or anthropogenic, or both. Traditionally, the inorganic tracers in aerosols have been used as a tool for source apportionment because they are source specific and maintain their integrity in the atmosphere while this is not possible for some organic compounds. It is commonly accepted that Al in aerosols is a tracer of crustal material (4, 5), while Pb comes mainly from leaded gasoline and smelters (6, 7), and V is from the combustion of heavy fuel oil rich in V-porphyrins (7, 8).

Solvent-extractable organic compounds (SEOC) in aerosols are also commonly used to identify the sources (9–15). The organic matter in aerosols is derived from two major sources: biogenic detritus (plant wax, microbes, etc.) and anthropogenic emissions (oils, soot, etc.) (11). In general, alkanes, fatty acids, alkanols, and PAHs are the main families of SEOC in aerosols and each possesses characteristic source information. Unsubstituted analogues of PAHs are known to be products of high-temperature combustion processes (16, 17), and unsaturated fatty acids and most *n*-fatty acids (<C₂₀) are from microbial sources (18). Biomarkers are present in the aerosols and are very useful in fingerprinting; some examples are retene from the combustion of coniferous wood and hopanes from petroleum residues (19, 20).

It has thus been demonstrated that inorganic tracers are effective in providing source information on crustal, marine, and anthropogenic sources, while organic markers can provide additional information on the emissions from combustion, microbial activities, and biogenic contribution from higher plant wax.

There are voluminous contributions in the literature on both subjects separately but few on combined studies. Since it is known that some organic and inorganic components in aerosols can be emitted from the same sources, a correlation of the two is to be expected—and is to be expected to yield more and better information. The combination of the two techniques should provide more source information; the combined data set would be more complete and effective and would greatly enhance the study of air pollution dynamics. Biomass burning is a good case in point. It produces abundant soot carbon and excess (noncrustal) fine-particle potassium (21), and at the same time, the total yield of SEOC in the aerosol samples can have a 44-fold increase as compared to the normal samples (22). It would be much more effective to apportion the sources using the combined data set. In this paper, the correlation between organic and inorganic tracers is presented, and its application in source apportionment is demonstrated.

Data Sources

The organic data used in this study come from our previous work (22–24). High-volume samplers were used to collect TSP (total suspended particulates), and the associated SEOC were extracted using organic solvent (dichloromethane), separated by flash column chromatography into fractions, and identified and quantified using GC–FID (gas chromatography–flame ion detector) and GC–MS. Up to 80 organic compounds are reported in our study. The origins of the SEOC are usually categorized as vehicular, biogenic, and microbial (12). For inorganic measurements, the Hong Kong Environmental Protection Department (HKEPD) routine analyses of aerosol samples were used. They report the following species: Al, Ca, Mg, Pb, Na⁺, V, Cl⁻, NH₄⁺, NO₃⁻, SO₄²⁻, Br⁻, Mn, Fe, Ni, Zn, EC (elemental carbon), Cd, K⁺, Ba, Cu, As, Be, Hg, and Cr.

The two independent data sets were combined and used in the correlation analysis. Seven samples collected at Central-Western (CW), Hong Kong South (HKS), Kwun Tong (KT), Kwai Chung (KC), and Mong Kok (MK) by HKEPD during 1993–1994 were in the same sampling period of the organic samples collected by the Atmospheric Research Group at HKUST; i.e., the HKUST and HKEPD samples were collected within one day of each other. Figure 1 is a map of Hong Kong with the sampling sites. Figure 2 shows the TSP loading and some meteorological data on adjacent days at CW (July 14–15, 1993) and KC (December 6–7, 1994) as examples. Over

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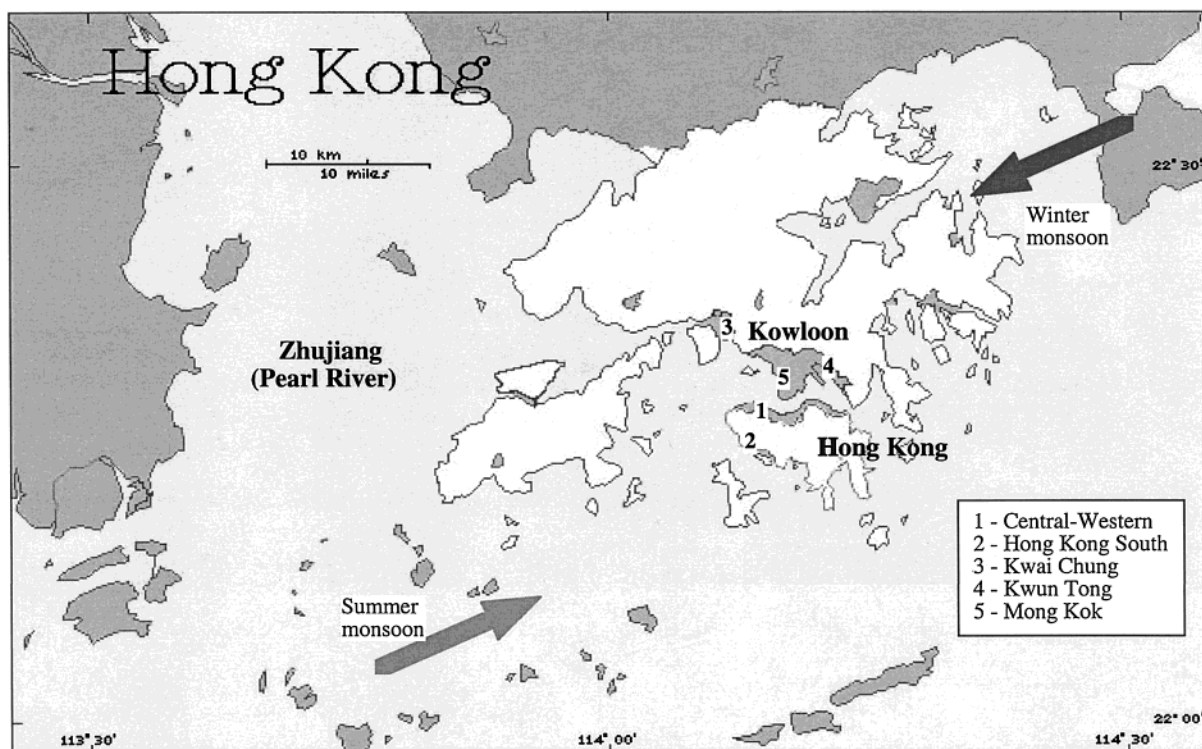


FIGURE 1. Sampling sites.

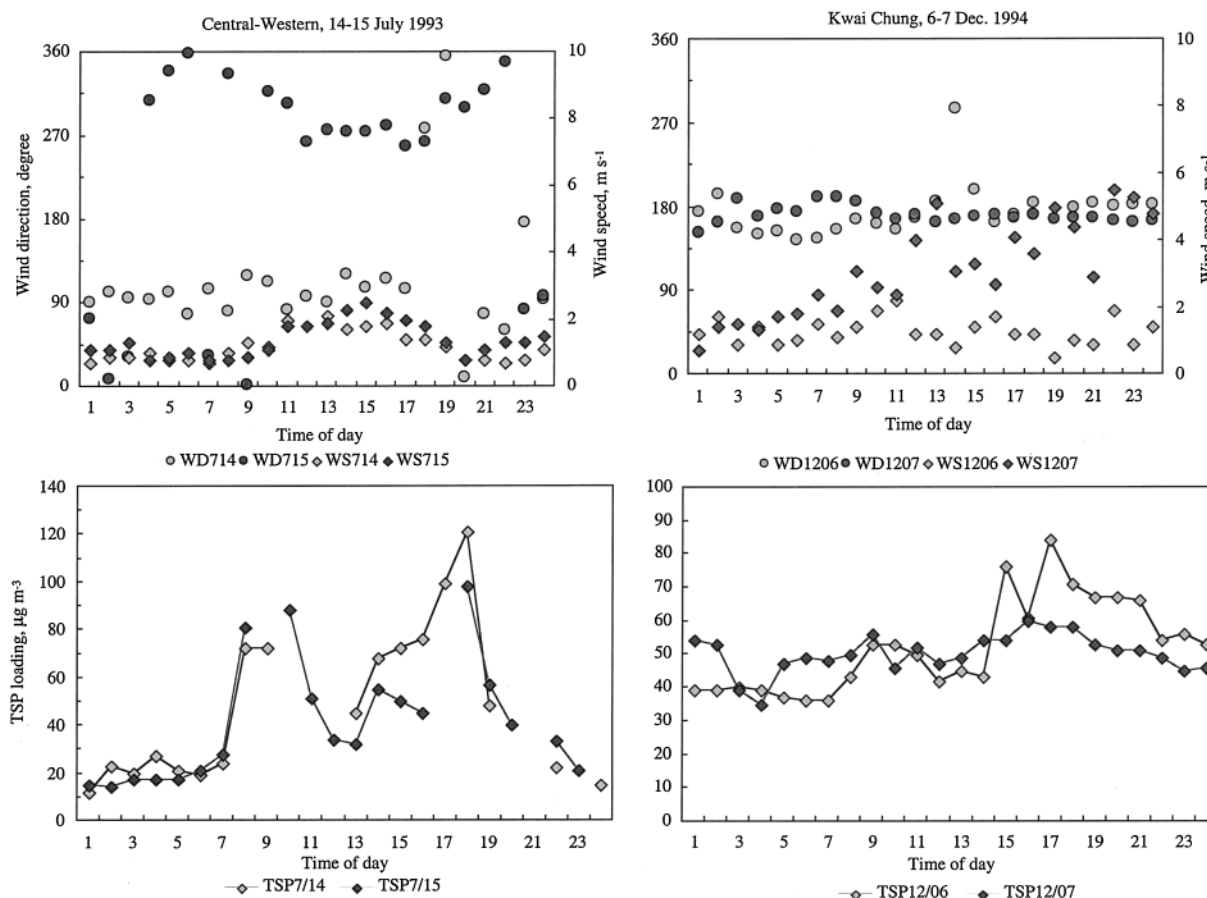


FIGURE 2. Adjacent day aerosol samples. WS, wind speed, m s^{-1} ; WD, wind direction, deg; TSP loading, $\mu\text{g m}^{-3}$. Source: HKEPD.

the 24-h sampling period, low wind speeds ($\sim 2 \text{ m s}^{-1}$) at CW were observed, which meant that there were large uncertainties in wind directions while at KC the wind conditions were very close. The hourly TSP loading for the two sets of

samples were close. The main ambient aerosol source in Hong Kong is vehicular; therefore, the TSP loading and composition on a short-term basis is not expected to change significantly unless under episodic conditions. It was felt

TABLE 1. Summary of Data Used in the Study^a

species	CW150793	CW241293	HKS080893	KT061293	KT131194	KC071294	MK050594
Al	130	350	71	240	92	290	940
Fe	420	690	300	340	230	470	1700
Ca	330	1100	290	580	140	700	3300
Mg	160	210	230	300	110	130	750
Pb	41	190	14	40	44	80	51
V	3.5	13	11	8.5	5.0	9.5	10
Ni	5.9	3.5	1.9	1.6	1.6	1.6	3.3
Zn	63	210	15.5	84	28	140	140
Cd	8.1	1.7	0.2	0.8	0.8	1.6	0.7
Mn	10	33	4.5	15	4.9	9.5	46
Ba	11	12	11.5	12	3.5	23.5	12
Cu	110	42	8.5	20	20	27	42
As	0.4	9.8	0.4	6.1	2.9	5.9	3.8
Be	0.07	0.07	0.06	0.07	0.07	0.07	0.07
Na ⁺	1100	340	2100	2200	1500	850	760
Cl ⁻	700	140	1400	2800	720	430	740
K ⁺	175	1100	185	440	190	1100	180
NH ₄ ⁺	1157	3857	167	2057	1200	1700	690
NO ₃ ⁻	1063	2214	930	2569	600	700	350
SO ₄ ²⁻	5200	12000	3800	8100	6600	8200	5500
nss sulfate	4923	11914	3272	7547	6223	7986	5309
Br ⁻	24	8.5	7.5	6.5	8.0	8.0	14
EC	26300	36200	11600	11410	22400	18500	24700
THC	1700	1800	400	590	1600	1500	8300
total alkanes	105.6	213.6	21.9	149.1	148.1	79.6	272.0
total PAHs	2.51	15.37	1.23	8.19	11.16	5.05	18.72
total fatty acids	670.0	719.4	386.9	519.8	426.2	565.0	1374.5
total alkanols	28.28	64.91	22.76	34.26	50.71	66.34	70.02
benzo[a]pyrene	0.15	0.89	0.03	0.27	0.39	0.16	0.93
benzo[b,k]fluoranthene	0.47	3.16	0.07	1.19	1.49	1.19	2.06
benzo[ghi]perylene	0.57	1.91	0.15	1.18	1.66	0.33	3.05
C ₂₉ alkane	8.13	14.48	0.75	10.47	14.47	7.35	28.14
C ₃₁ alkane	7.53	21.23	4.23	15.5	12.18	6.00	30.72
C _{16:0} fatty acids	222.4	285.9	111.6	235.6	193.1	246.0	549.5
C _{18:0} fatty acids	95.1	113.1	80.5	85.1	79.6	114.0	219.1
C _{18:1} fatty acids	213.8	98.7	132.1	55.6	45.1	37.3	340.1

^a All concentrations in ng m⁻³.

that the conditions were close enough that they could be considered to be simultaneous organic and inorganic samples for the purpose of demonstrating the validity and effectiveness of the proposed method.

Results and Discussion

The concentrations of the following species were used in the correlation analysis: Al, Fe, Ca, Mg, Mn, Ba, Na⁺, Cl⁻, V, Ni, Cd, Cu, Be, Pb, Br⁻, EC, NO₃⁻, NH₄⁺, SO₄²⁻, nss (nonseasalt sulfate) sulfate, Zn, K⁺, As, total alkanes, C₂₉ alkane (C29A), C₃₁ alkane (C31A), total alkanols, total PAHs, benzo[a]pyrene (B(a)P), benzo[ghi]perylene (B(ghi)P), and benzo[b,k]fluoranthene (B(b,k)F), C_{18:1} fatty acid, total fatty acids, C_{16:0} fatty acid, and C_{18:0} fatty acid. These data are summarized in Table 1.

Figure 3 shows the correlation coefficients (CC, same as *r*) of Na and Cl with the rest of the species. Na and Cl have positive correlation only with each other (CC = 0.85) and negative correlation with all other species except NO₃⁻ for Na and NO₃⁻ and Mg for Cl. The formation of seasalt aerosols by wave breaking and bubble bursting is an important natural source for elements such as Na and Cl in a marine atmosphere (3). The South China Sea borders Hong Kong on the east and south and Zhujiang (Pearl River) Estuary on the west while the prevailing wind in Hong Kong is easterly; therefore, marine aerosols are the predominant source of Na and Cl. The fact that positive correlation exists only between these two elements provides a check of the validity and integrity of the two independent data sets.

The strongest negative correlation (CC less than -0.8) with Na is pollutant elements Zn and EC. Cl shows a similar

but smaller trend. This can be explained by the Cl loss reactions in seasalt aerosols due to H₂SO₄ in the atmosphere in Hong Kong (25). The negative correlation of Na and Cl with the pollutants could be due to the Asian monsoon: the southwesterly summer monsoon brings cleaner oceanic aerosols from the oceans (South China Sea and tropical Pacific), while the northeasterly winter monsoon brings polluted air masses from the Asian Continent. The negative correlation reflects the out-of-synchronization contribution of the pollution species and marine particles.

Figure 4 shows the correlation between several selected crustal elements including Al, Fe, Ca, and Mg with 35 inorganic and organic species from all sources, i.e., crustal (Al and Fe), marine (Na and Cl), pollution (Pb, V, SO₄²⁻, EC, alkanes, PAHs, B(ghi)P, and B(b,k)F), and microbial (C_{16:0} fatty acid). The correlation patterns of the crustal elements Al, Ca, and Fe with other elements are very similar, suggesting that they are from a similar source. However, Mg behaves differently because it has two main sources: marine and crustal. The correlation coefficients with the other elements are generally lower than Al, Fe, and Ca. Al, Fe, and Ca correlate well with the crustal elements and fatty acids (total fatty acids, C_{16:0} and C_{18:0} fatty acids) (CC > 0.96); however, much lower CC between the crustal elements (Al, Ca, Fe, and Mg) and other organic species such as B(b,k)F and total alkanols are observed. Negative or very low CC are also found between these crustal elements and inorganic species such as NH₄⁺, SO₄²⁻, NO₃⁻, EC, Cd, Cu, and As, suggesting that they have very different sources.

Figure 5 shows the correlation of Pb, V, and B(b,k)F with other species. V does not show strong correlation with any

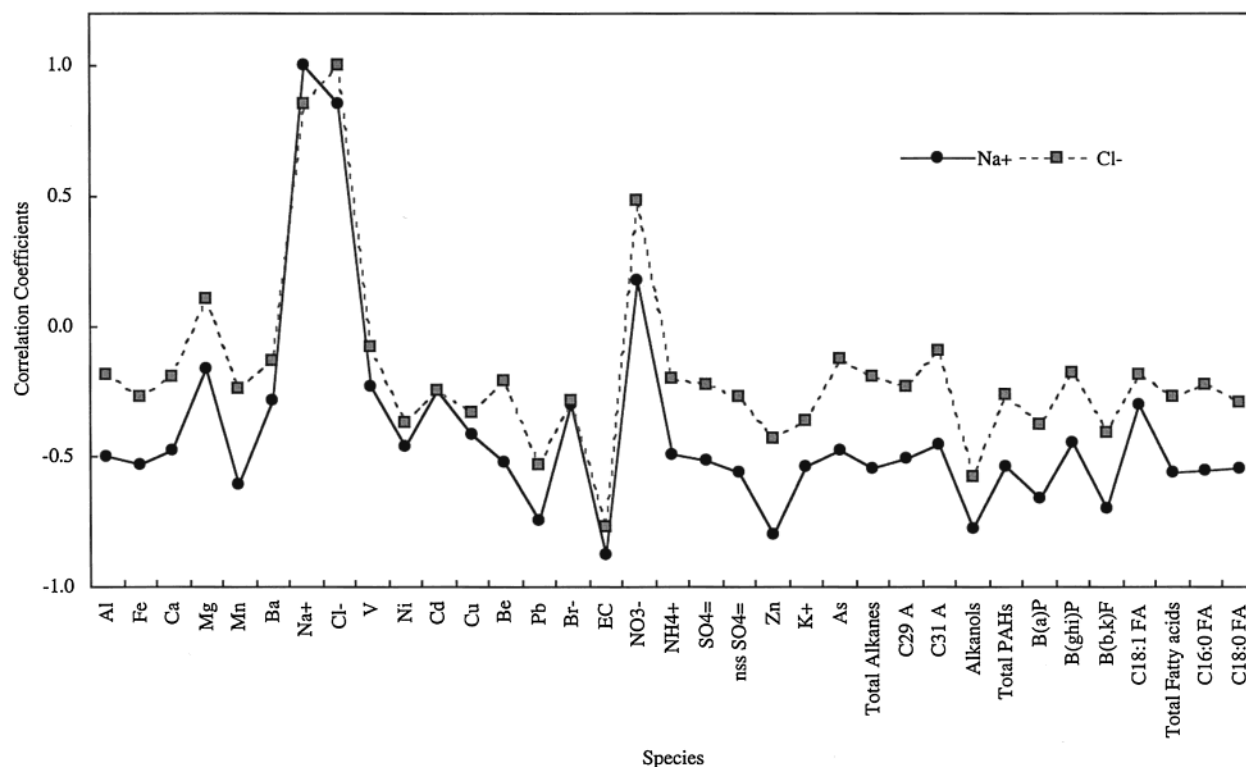


FIGURE 3. Correlation of Na and Cl with 34 other inorganic and organic species demonstrating the integrity of the data sets used.

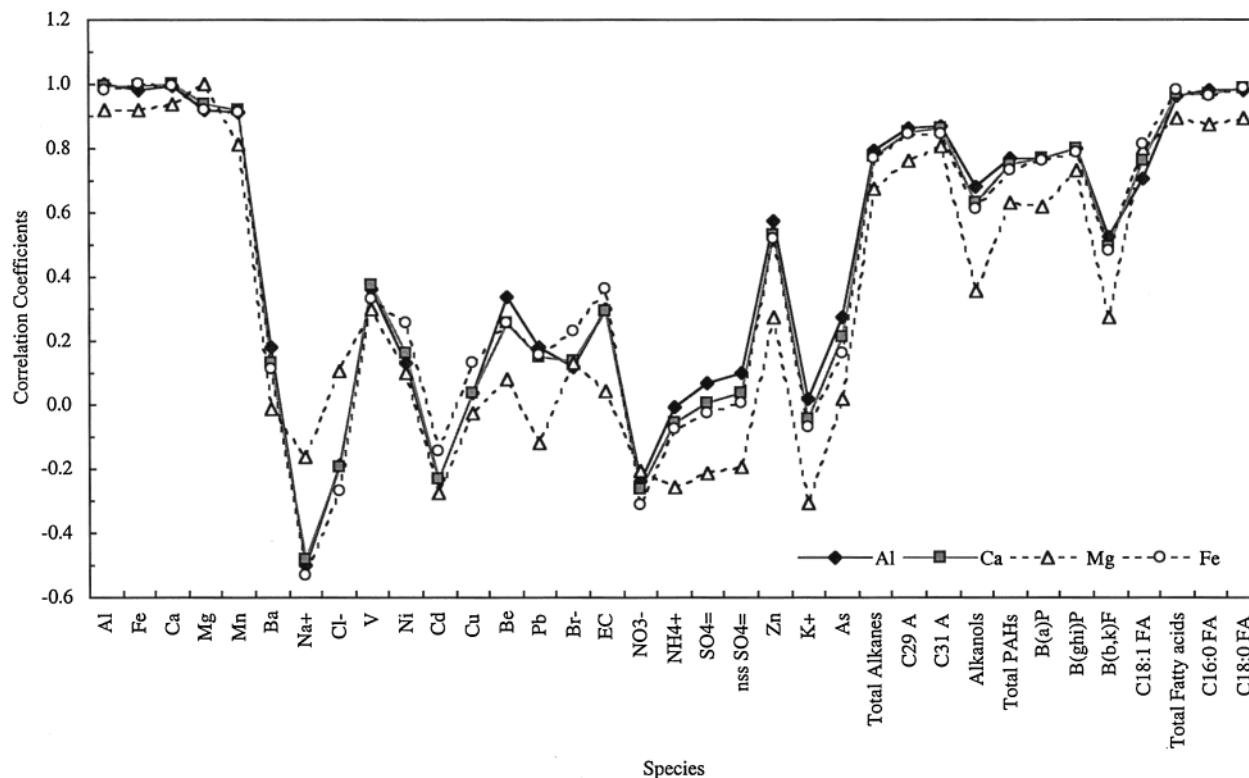


FIGURE 4. Correlation of crustal elements with other species.

of the species; the best correlation is with Zn and As (CC close to 0.6). Lead, on the other hand, has high correlation (CC > 0.8) with NH_4^+ , SO_4^{2-} , nss SO_4^{2-} , Zn, K, As, and B(b,k)F. It is interesting to note that B(b,k)F, a dominant component in vehicular emissions in Hong Kong, has good correlation with Pb, Zn, As, nss SO_4^{2-} , total PAHs, and B(a)P (CC > 0.8). It is the most abundant PAH in all the PAHs (12–25%) detected in the aerosols of Hong Kong, especially in autumn

and in winter (1). The strong correlation of B(b,k)F with Pb, As, and sulfate suggests that it has multiple sources including vehicular emissions and coal combustion. Feng (26) also reported that B(b,k)F was abundant (10–20%) in aerosols collected in Guangzhou, China, where traffic emissions are also heavy. In addition, there exists a strong correlation between Pb and B(b,k)F; they show similar correlation patterns with other species. Compared to Pb, V does not

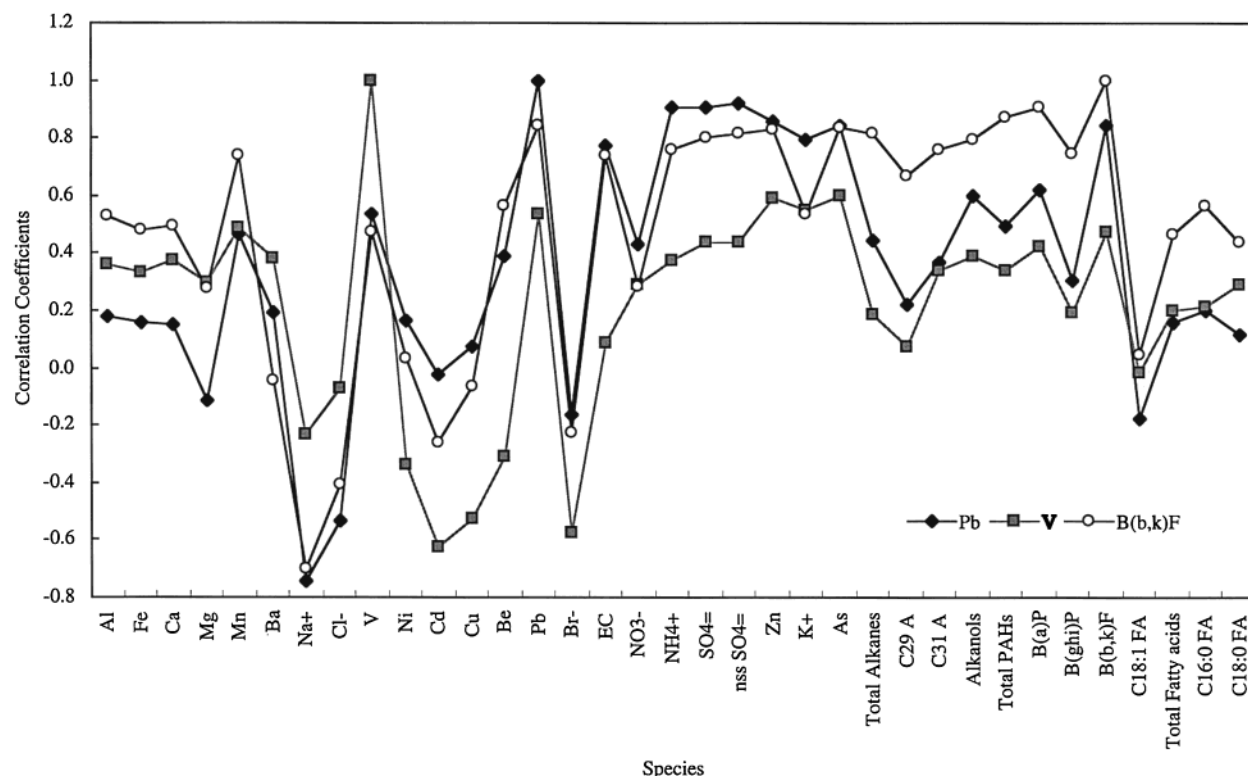


FIGURE 5. Correlation of combustion products with other species.

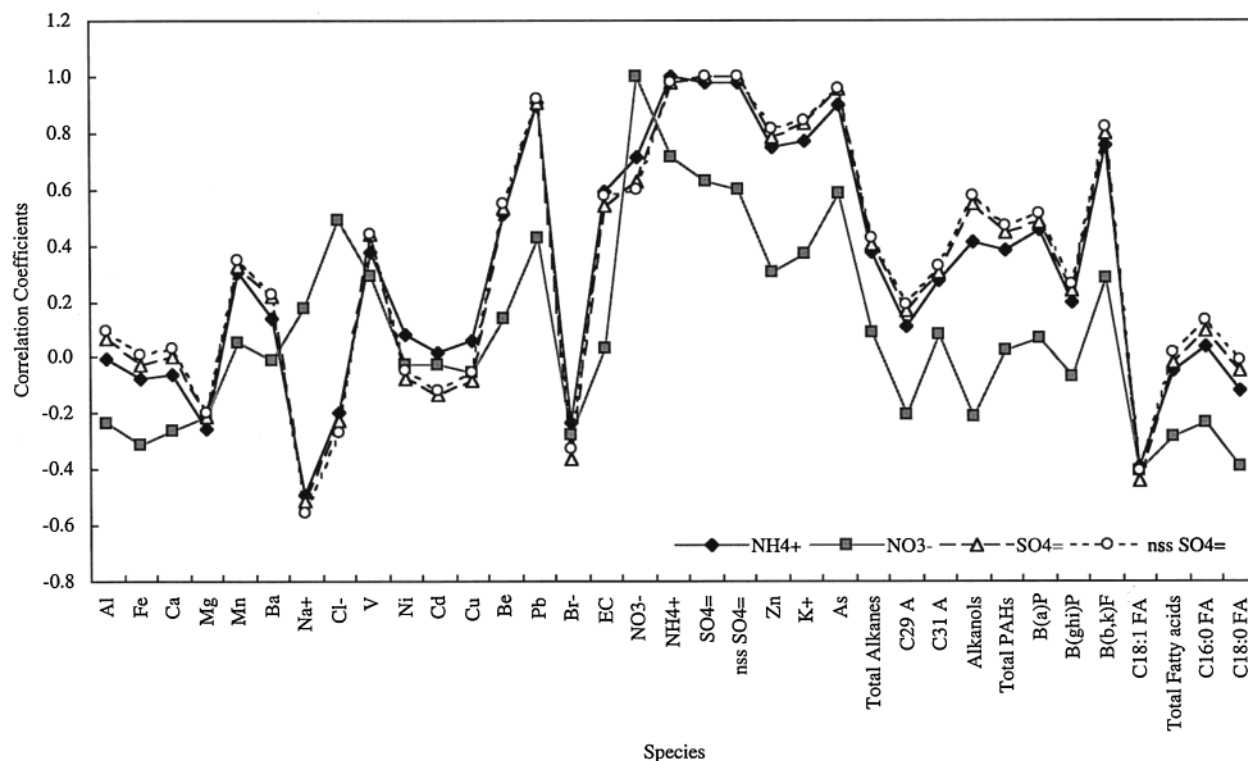


FIGURE 6. Correlation of ionic species with other organic and inorganic components.

exhibit as high a correlation with B(b,k)F, suggesting that vehicular emission and not heavy oil combustion is the most important source of B(b,k)F in Hong Kong. Figure 5 also clearly shows that the pollution species exhibit poor correlation with crustal, marine materials, and fatty acids.

Figure 6 shows the correlation of NH_4^+ , NO_3^- , SO_4^{2-} , and nss SO_4^{2-} with other species. Ammonium and sulfate are

strongly correlated, and they show similar patterns with other species. Nitrate behaves somewhat differently when compared to sulfate and ammonium, suggesting that ammonium associates predominantly with secondary sulfate and not with nitrate. Of all of the species associated with ammonium in the atmosphere, ammonium sulfate is the most stable. For ammonium and sulfate, CC close to 0.8 is found with Pb, K, As, and B(b,k)F.

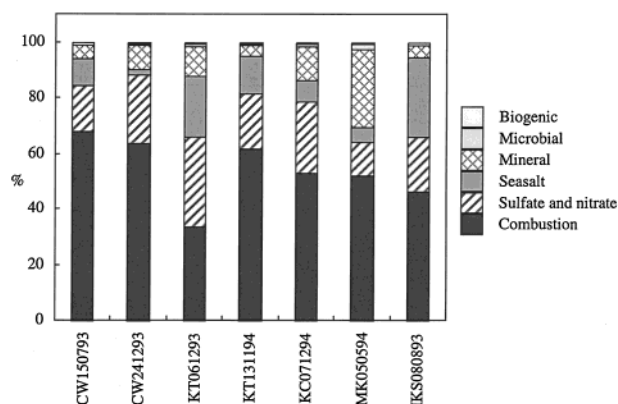


FIGURE 7. Sources of Hong Kong's aerosols.

The histograms in Figure 7 show the various sources of aerosols in Hong Kong. The amount of mineral aerosols is calculated by assuming Al is 7% of the crustal materials. Taylor (4) estimated the Al content in the continental crust to be 8.2%, and Kadowaki (27) reported a value that ranged from 5.1 to 8.2% for loess in China. In general, the Al content in crustal aerosols is estimated to be 6–8% of the averaged soil values (5, 28). Na is a major component in seasalt (30.7%); it can be used to estimate the amount of seasalt in total aerosol (29). The microbial components are estimated by the amount of $<C_{20}$ fatty acids in the aerosols. The biogenic components are the contribution from higher plant wax and are estimated from the amount of alkanes, fatty acids ($>C_{20}$), and alkanols ($>C_{20}$) in the aerosols (12). The largest group is from combustion processes represented by EC, Pb, V, alkanes from petroleum residues, and total PAHs. The secondary pollutants (sulfate and nitrate) are treated as a separate category.

Combustion is the dominant source (34–68%) of all samples (Figure 7). The highest seasalt component (28%) is found at HKS located at the southeastern tip of Hong Kong, representing rural and marine environment. Hong Kong is under the influence of the Asian monsoon system. The CW summer sample collected on July 15, 1993 (CW150793, 9%), exhibited a higher seasalt content than the December 24, 1993, winter sample (CW241293, 2%). This is caused by the relatively clean oceanic aerosols from the southwest brought to this region by the summer monsoon. The MK station was the only roadside station in HKEPD's monitoring network at that time. The highest mineral (28%) and microbial (2%) contents are in the MK May 5, 1994, samples. Very high Al, Fe, and Ca concentrations are also reported by seven other HKEPD stations on the same day (2). This suggests that a possible Asian dust episode occurred on May 5, 1994 (30); the high mineral content in the MK sample could be due to the dust transported from northern China. The high microbial contribution at MK reflects the high human activities in this region, which is in one of the most densely populated areas of Hong Kong.

Results here demonstrate that the levels of SEOC and inorganic elements in aerosols from similar sources exhibit positive correlation. Using a combination of the organic and inorganic tracers identified in the aerosols, it has been

demonstrated that it is possible to better characterize the sources of these aerosols, which include marine, mineral, combustion, microbial, and biogenic contributions.

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