

ELEMENTAL COMPOSITION OF TOTAL SUSPENDED  
PARTICULATE MATTER IN KUALA LUMPUR  
- A PRELIMINARY SURVEY

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ABSTRACT

Eighteen samples of ambient 24-hr average total suspended particulate matter were collected at Universiti Teknologi Malaysia sampling station. A total of 25 trace-elements (Al, Ag, As, Au, Ba, Br, Ca, Cd, Co, Cr, Cu, Dy, Eu, Fe, La, Mg, Mn, Ni, Pb, Sb, Sc, Sm, Ti, V and Zn) were determined from the samples using instrumental neutron activation analysis and atomic absorption spectrophotometry techniques. The use of pairwise correlation statistic and enrichment factors were presented to identify sources. It was demonstrated that the particulate can be related into two specific source categories: soil-derived (Al, Au, Ba, Ca, Cr, Dy, Eu, Fe, La, Mg, Mn, Sc, Sm, Ti and V) and anthropogenic sources (Ag, As, Br, Cd, Co, Ni, Pb, Sb and Zn). Pb and Br were mainly due to automobile exhausts emission.

## INTRODUCTION

Atmospheric aerosols can have significant effects on the environment. At current concentration, the principal effects are associated with the degradation of visibility, local weather modification, soiling and material damage. More importantly, however, airborne particulates have long been known to be associated with deleterious health effect<sup>1</sup>. Many studies have shown that our atmospheric environment does contain number of toxic elements originating from anthropogenic sources. Such studies have been largely confined to major urban areas where the center of human activities as well as the major population area are located. The release of potentially toxic substance to the atmosphere and the possibility of adverse health effects of these substances should be of our great concerned.

Consequently, investigation of the total suspended particulate matter (TSP) in the ambient air has progressed from determination of simple mass loading through particle size classifications and distribution as well as its elemental composition. Characterization of the ambient urban air in terms of its chemical and physical properties have been reported by many researchers<sup>2,3,4</sup>. Measurement of the size distribution and chemical composition of the particles in the ambient air are important in understanding the behaviour and mechanisms of formation of particles in the atmosphere which will eventually lead to the identification of air pollution sources.

The use of the large number of trace elements in the ambient airborne particulate matter to identify air pollution sources have received much attention in recent years. Friedlander<sup>5</sup> formulated and applied the theory of source-receptor chemical element balance to the sources of Pasadena, CA aerosol. The basic assumption is that each type of source emits a characteristic distribution of a set of elements. These sets were determined from an inventory sources emissions.

A comparison were made with the ambient data. Sea-salts, soil, auto-exhaust, fuel-oil, coal combustion and cement dust contributions were estimated and accounted for more than 72% of the Pasadena aerosol. Neustadter et al.<sup>6</sup>, used relatively simple approach using pairwise correlation, cluster analysis and elemental enrichment factors to relate the suspended particulate matter in Cleveland to their respective sources. It was found that some elemental constituents were associated with specific source types: earth's crust (Al, Si, Sc, Ti, V, La, Sn, Eu, Dy, Th), automotive exhaust (Pb, Br), metallurgy (Fe, Cr, Co) and unidentified specific industries (Sb, Hg). In another study, Paciga and Robert<sup>7</sup> analyzed as many as 25 elements in the aerosol samples collected at urban and industrial site in Toronto. An enrichment factor and linear correlation analysis were applied. It was found that Al, Ca, Fe, La, Mg, Sm, Sc, Na, and Ti were appeared to be mainly soil derived aerosols whereas Sb, As, Br, Cl, Pb, V and Zn appeared to have significant anthropogenic sources in the area. Another study of a similar type were also conducted in Indiana<sup>8</sup>. This approach has become increasingly attractive with the availability of sensitive, inexpensive, non-destructive, multielement analytical methods such as instrumental neutron activation.

To date there is no detail and comprehensive study of the airborne trace-elements in this region. Although, Pb has been occasionally determined by few local investigators but it has not been extended to other considered important elements. The purpose of the present study is to describe the level of various trace-elements found in the ambient TSP samples collected at Kuala Lumpur. The elemental analysis were done by both instrumental neutron activation and atomic absorption spectrophotometer. The results were subjected to enrichment and pairwise correlation analysis in order to determine the source, behaviour and fate of airborne trace elements in a complex urban environment. In particular, it was hoped to identify those elements which were abnormally enriched in the atmosphere as well as to differentiate sources of these elements.

## EXPERIMENTAL TECHNIQUES

Sampling. Ambient 24-hr average particulate samples were collected every other day from Jan. through March 1986. Air sampling was carried out on the roof of the Pollution Control Laboratory Building (15 meters high) at the Universiti Teknologi Malaysia, located 2 km northeast of city center of Kuala Lumpur. The location of the sampling site is shown in Figure 1. Total suspended particulate matter was collected with a high volume air sampler (Sierra Anderson UV001/861) calibrated at  $1.13 \text{ m}^3/\text{hr}$  (40 CFM) on every filter changed. All samples were collected on a glass fiber filter (Whatman EPM 1000) conditioned in controlled room temperature for at least 24-hr before pre- and post-weighted with three control filters to avoid any erroneous gravimetric results.<sup>9</sup>

Neutron Activation Analysis. The elemental analysis of Al, As, Au, Ba, Br, Ca, Cl, Cr, Dy, Eu, K, La, Na, Sb, Sc, Sm, Ti, and V were performed with instrumental neutron activation analyzer (Model Triger Mk II). Several  $25 \text{ cm}^2$  filter area were cut for the analysis.

Table I. Neutron Irradiation and Sample Counting Schedule for this study.

Irradiation time	Cooling time	Counting time	Elemental detected
30 s	10 min	5 min	Dy, Eu, Ba, Ti, Br, Na, V, K, Cl, Ca.
10 hr	4 - 5 days	50 min	Sm, Au, Sb, Na, As, K, La, Sc, Br, Cr.

Table I shows the irradiation and counting procedure that was followed.



The short irradiation time was done by the Pneumatic Transfer System (PTS) while the long irradiation was done in the Rotary Rack. The average neutron flux in the reactor is about  $3 \times 10^{12} \text{ n.cm}^{-2} \text{ s}^{-1}$ . The gamma rays emitted by the radionuclide in the irradiated samples were detected by the hyper pure germanium (Hp Ge) semi conductor detector with the resolution of 1.9 KeV at 1332 KeV  $^{60}\text{Co}$ . The relative efficiency of the detector is about 20% of the NaI (Tl) detector (3 x 3"). The analysis of the gamma ray spectra were done by the ND 66/ND 6600 computerised multichannel analyzer system.

The elemental composition in the samples were calculated by direct comparison of the corrected photo-peak activity of the isotop in the sample and the standard (the corrected photopeak activity is the photopeak activity after correction due to blank and radioactive decay). The accuracy and precision of the INAA system at NEU laboratory have been verified by analysis of National Bureau Standard Reference Materials reported elsewhere<sup>10</sup>.

Atomic Absorption Analysis. Eleven elemental concentrations (Pb, Mn, Cd, Zn, Ca, Co, Mg, Cu, Fe, Ag and Ni) were determined by AAS technique (Perkin Elmer 5000). A portion of the effective filter area (3.5 x 17.5 cm) were cut into small pieces and digested with concentrated 5 ml  $\text{HNO}_3$ , 5 ml  $\text{H}_2\text{SO}_4$  and 10 ml of double distilled deionised water. The samples were heated up to boiling for at least 1 hr to reduce the volume to approximately 10 ml, transferred and diluted to 50 ml for flame atomic absorption analysis together with the standard stock solutions. Blank filters were subjected to similar treatment for blank correction before final elemental concentration were obtained.

## RESULTS AND DISCUSSION

As many as 25 elements were determined in the TSP samples. Table II presents the average, standard deviation and ranges of the elemental concentration along with the average TSP mass for the study period. Na, Cl, K, and Ca (for NAA) were not reported in the list due to high concentration of these elements found in the background matrix. This made it almost impossible to detect the actual concentration of these elements deposited on the sample filters. The use of other filter type like cellulose type filter would be strongly recommended to eliminate this interfering effect<sup>11</sup>. Copper contamination from the brush wear on the copper commutator of high volume air sampler motor is significant<sup>12</sup> and was reflected in this study by high daily copper concentration and poor correlations of copper with other elements. A short sampling period of the present study, allow no correlation analysis of copper with meteorological parameters such as wind direction to be performed to further verify the above statement.

The Al, Ag, Ba, Co, Ni concentration showed the greatest range of arithmetic standard deviations compare to other elements for this variable. As expected, the impact of the commercial or industrial source on the sampling site due to variability of the meteorological parameters such as wind speed and wind direction could have brought to this effect. Although, Al which is known to be predominantly soil derived aerosol was no exception. Since at any time the wind could have blown up the uncovered ground area (as there are constructions and development around the city) to the sampling site. As a result, a wider range between the minimum and the maximum concentration of the element found on the sample filter. In other word, the elements with large standard deviation are associated with localized sources. Those with small standard deviations suggest earth crust, weak, or uniformly distributed source contributions. In addition, some elements were poorly resolved (e.g. Ba).



Table II: Average Concentration of Trace-element in the TSP Samples  
( PPM )

	$\bar{X}$	$\sigma$	Range
Al	4.87%	5.86%	981 - 15.4%
Ag	57.8	68.5	3.24 - 186
As	154 (10 $\mu\text{g}/\text{m}^3$ )	57	93.7 - 317
Au	50.9 ppb	28.0 ppb	15.8 - 85.6 ppb
Ba	1067	1181	3.76 - 2431
Br	644	293	142 - 1136
Ca	2.78%	2.01%	0.62% - 6.89%
Cd	12.2 (0.8 $\mu\text{g}/\text{m}^3$ )	10.6	1.61 - 32.5
Co	488	852	8.43 - 2390
Cr	322	110	226 - 443
Cu	6531	3225	3098 - 17523
Dy	12.5	7.57	3.25 - 26.10
Eu	12.5	7.74	3.00 - 26.7
Fe	6135	2181	2017 - 11514
La	14.9	8.44	4.54 - 32.5
Mg	3.46%	2.71%	0.35% - 7.59%
Mn	341	176	60.7 - 807
Ni	4825	7164	119 - 13077
Pb	6710	1997	3205 - 10862
Sb	27.1	14.6	6.17 - 60.5
Sc	1.92	0.44	1.54 - 2.74
Sm	1.69	1.46	0.13 - 4.95
Ti	4471	1626	2235 - 6129
V	52.4	25.8	20.4 - 111
Zn	680	150	430 - 1068
TSP Mass*	66.6	15.3	43.2 - 91.5

\* Mass in  $\mu\text{g}/\text{m}^3$

### Pairwise Correlation

In an attempt to find a common metal source, correlation coefficient of metal concentration have been computed between pairs of element. Table III shows these correlation coefficients for metal pairs which have been detected in at least 15 of the samples. A large correlation coefficient value between metal pair is indicative of a common source and similar behaviour.

The best interelement correlation seen in this study is that between Br and Pb. Automobile is the main source of these elements. Lead is added to petrol in the form of an organic tetraethyl lead (TEL) as anti-knock agent. During combustion this reacts with ethylene (EDH) 'scavengers', also added to petrol, with consequent emission of the lead in an organic particulate form predominantly  $\text{PbBrCl}^{13,14}$ . The stoichiometry of the major compounds reported in automobile exhaust particulate matter is such that the Br/Pb mass ratio should be approximately equal to tetraethyl fluid value (0.386). The average and the maximum Br/Pb rate for this study were 0.096 and 0.138 respectively. Loss of Br from the particulate phase due to irradiation and uncovered of sample filters immediately after sampling are probably responsible for the variation in the Br/Pb ratio. Low wind speed during study period and high sampling point may also contribute to this effect. Nevertheless, Br and Pb have been widely used by many workers to predict the impact of automobile on air quality.

As expected both Br and Pb show a negative correlation with Fe and Mn. While positive correlation between Fe and Mn is observed. Apparently, this indicate that Fe and Mn originate from a common source i.e. soil dust. Pb also shows a positive correlation with Zn. The presence of Zn as one of the many additives used in lubricating oil such as zinc-di-thiophosphate as suggested by Largerwerff and Specht<sup>15</sup> could support this finding. Application of a simple linear correlations analysis as in Table III, may seem to be the easiest and most direct

Table III: Pairwise Correlation Coefficients (  $\times 100$  )

	As	Br	Fe	Mn	Pb	Sb	V	Zn
As	100	15	1.0	12	-9	5	24	-17
Br		100	-49	-29	82	43	29	25
Fe			100	36	-56	-16	-13	-21
Mn				100	-16	-18	-14	51
Pb					100	8	5	37
Sb						100	12	24
V							100	-3
Zn								100

method for such interpretations to be made. It is however, in view of the relatively small size of the data sets measurement, we wish to remind the readers of the necessary caution regarding the interpretation of such information, as has been noted by Bogen<sup>16</sup>.

#### Enrichment Factor

An increasingly popular method of examining the relative importance of selected sources on the measured atmospheric burden of trace-species is to compare the relative abundance of species in source material to that found in the atmosphere<sup>17</sup>. In the case of a soil source, this comparison is made by examining the enrichment of elements in the air over what is found in crustal or soil material. This enrichment is calculated by obtaining the ratio of the air concentration of an element normalized to a reference element to the crustal concentration normalized to the same reference element. For this work, Al has been chosen as the reference element since soil is almost certainly the source for Al. Perhaps Si should be chosen as the reference element because of its high natural abundance (compared to Al) but it is not readily determined by conventional nuclear technique. The enrichment factors, EF, are calculated as follow:

$$EF = \frac{\frac{\text{Air concentration of indicated element}}{\text{Air concentration of Al}}}{\frac{\text{Crustal concentration of indicated element}}{\text{Crustal concentration of Al}}}$$

An enrichment factor close to 1 would indicate that the relative concentration of a given element is identical to that which is present in soil. An enrichment factor increasingly greater than 1 indicate the element is more abundant in the air relative to that found in soil.

Value less than 1 for EF, would suggest a depletion of the element in air over that found in soil. For this study the reference crustal ratios were taken from Wedepohl<sup>18</sup>. The average calculated enrichment factors for the elements is given in Table IV.

An examination of the data in Table IV, indicates that the element Al, Au, Ba, Ca, Cr, Fe, La, Mg, Mn, Sc, Sm, Ti and V had relatively low EF values. Most of these elements were also positively correlated with each other and can be assumed to have a major soil component. However, the presence of local sources cannot be discounted, especially in the case of Cr (EF = 7.4) which is a substantial constituent of metallurgy emission.

An interesting point to note in this study, is the relatively high EF value for mine related elements namely Au, Dy and Eu. The authors believed that the soil in the area is rich with these elements. The area was once known with its tin-mining activities. Therefore, soil or mining dust is the only possible source for these elements. The contribution of soil material to the total atmospheric burden of particulate matter (assuming an Al concentration of 7.8% in soil) is estimated to be 64% at sampling site.

The elements Ag, As, Br, Cd, Co, Cu, Ni, Pb, Sb and Zn are greatly enriched in the atmosphere relative to soil. Contamination of Cu from the high-volume air sampler has been discussed previously. Ag, As, Cd, Co, Ni, Pb and Zn are known to be industrial source chemical species. The As, Cd, Co, Ni and Zn are among the important constituent of combustion related sources (e.g. fuel-oil burning, incineration, smelting). Both Cd and Zn could also be associated with motor-vehicles. Studies have shown that higher level of airborne cadmium concentration were observed in city area than suburban area<sup>19</sup>. Cd, Pb and Zn are positively correlated with each other which suggests that there is a common source for these elements. Higher level of cadmium observed in

Table IV: Enrichment Factors of the Trace-elements

	Conc. (ppm)	Crustal, Wedepohl (ppm)	EF
Al	4.87%	7.80%	1.0
Ag	57.8	0.06	1543
As	154	1.7	145
Au	50.9 ppb	0.004	20.4
Ba	1067	590	2.9
Br	644	2.9	356
Ca	2.78%	2.87%	1.55
Cd	12.2	0.1	199
Co	488	12	65
Cr	322	70	7.4
Cu	6531	30	349
Dy	12.5	3.0	6.7
Eu	12.5	1.4	14
Fe	6135	3.54%	0.28
La	14.9	44	0.54
Mg	3.46%	1.39%	3.99
Mn	341	690	0.79
Ni	4825	44	176
Pb	6710	15	716
Sb	27.1	0.2	217
Sc	1.92	14	0.22
Sm	1.69	6.6	0.41
Ti	4471	4700	1.52
V	52.4	95	0.88
Zn	680	60	18

higher traffic density area or urban environment, support the hypothesis that automobiles tyres are a likely source of Cd as suggested by Lagerwerff and Specht and supported by Burton<sup>20</sup>.

The large Ag, Br, Pb and Sb enrichment values are supportive of anthropogenic sources rather than normal soil-weathering processes for these elements. Lead and bromine are mainly produced by combustion of leaded gasoline. Their source is a significant area source pollution in the urban environment which exhibit negative correlation with increasing wind speed term. A good correlation between these two elements is an indication of their common source origin as has been found by other studies<sup>21 - 23</sup>. It is much more difficult to relate both Ag and Sb to their respective sources. The presence of their potential sources are not fully understood in the area. Sb could be attributed to a chemical factory which specializes in the manufacture of Sb products. Pewter making or an electric-lamp filament manufacturing plant are also possible sources for Sb in this area. In view of the fact that quite a large number of industries are located within few kilometers around the city area, a more detail investigation is necessary to ascertain the sources of these trace-elements.

## CONCLUSION

The concentration of 25 trace-elements in the air over Kuala Lumpur area has been measured by NAA and AAS. On the basis of elemental enrichment analysis calculated base on ratios to Al as the reference element, a soil-derived group of elements were identified. These include Al, Au, Ba, Ca, Cr, Dy, Eu, Fe, La, Mg, Sc, Sm, Ti and V. An enriched level of Au, Dy and Eu in the air indicates that the soil is rich with these elements. Industrial related chemical species includes Ag, As, Cd, Co, Ni, Sb and Zn. Bromine and lead, taken as a pair, are significant and increasingly enriched when normalized to Al as compared with typical earth crustal abundances, can be identified with automotive exhaust.

The use of pairwise correlation statistics can be more meaningful if more data sets were obtained. Determination of other important trace-elements should be sought in the future as to enhance the identification of potential air pollution sources. Subsequently, more monitoring stations should be set up in the area for this would improve the statistical reliability of the results and help to locate sources of pollutants. Although, this paper was based on a short term study, an overall understanding of Kuala Lumpur aerosol emerges from the present study would provide a basis for future work.

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# REFERNECES

1. Airborne Particulate; Subcommittee on Airborne Particles, Committee on Medical and Biological Effects of Environmental Pollutants, National Research Council, University Park Press, Baltimore, MD, 1979.
2. Whitby, K.T, et al.; The Aerosol Size Distribution of Los Angeles Smog. J. of Colloid and Interface Science. 39: 77, 1972.
3. John W, et al., Trace Element Concentrations in Aerosol from the San Francisco Bay Area. Atmos. Environ. 7: 107, 1973.
4. Lee, R.E. Jr. and Von Lehmden, D.J; Trace Metal Pollution in the Environment. J. Air Pollut. Contr. Assoc. 23: 853, 1973.
5. Friedlander, S.K.: Chemical Element Balance and Identification of Air Pollution Sources. Environ. Sci. Technol. 7:235; 1973.
6. Neustadter, H.E., Fordyce, J.S. and King, R.B.; Elemental Composition of Airborne Particulate and Sources Identification. Data Analysis Technique. J. Air Pollut. Contr. Assoc. 26: 1979, 1976.
7. Paciga, J.J. and Robert, E.J.; Multielement Size Characterization of Urban Aerosols. Environ. Sci. Technol. 10: 1124, 1976.
8. Harrison, P.R.;, Rahn, K.A., Dams, R., Robbins, J.A., Winchester, J.W., Brar, S.S., and Nelson, D.M.; Areawide Trace Metal Concentrations Measured by Multielement Neutron Activation Analysis. J Air Pollut. Contr. Assoc. 21: 563, 1971.
9. Neustadter, H.E. et al.; The Use of Whatman - 41 filters for High Volume Air Sampling. Atmos. Environ. 9:101, 1975.
10. Suhaimi Hamzah et al.; Initial Testing of the NAA Facilities at PUSPATI by Analysis of SRM. Seminar on the Effective Management and Utilization of Research Reactor, 1983 Kuala Lumpur.
11. Dams, R., Rahn, K.A., and Winchester, J.W.; Evaluation of filter materials and impaction surfaces for non-destructive neutron activation analysis of aerosols. Environ. Sc. Technol. 6:441, 1972.

12. Hoffman G.L. and Duce. R.A.; Copper contamination of atmospheric particulate matter samples collected with Gelman hurricane air sampler. Environ. Sci. Technol. 5:134. 1971.
13. Habibi, K.; Characterization of Particulate Matter in Vehicle Exhaust. Environ. Sci. Technol. 7:223, 1973.
14. Ter Haar; G.L., Lenane, D.L., Hu, J.N., and Brandt, M., Composition, Size and Control of Automotive Exhaust Particulates. J Air Pollut. Contr. Assoc. 22:39, 1972.
15. Lagerwerff, J.V and Specht, A.W.; Contamination of roadside soil and vegetation with cadmium, nickel, lead and zinc Environ. Sci. Technol. 4:583, 1970.
16. Bogen. J; Discussion Concerning: Trace elements in atmospheric aerosol in the Heidelberg area, measured by instrumental neutron activation analysis. Atmos. Environ. 8:298. 1974.
17. Zoller, W.H., Gladney, E.S., Duce, R.A.; Atmospheric concentration and sources of trace metals at the South Pole. Science 183, 198. 1974.
18. Wedepohl, K.H., "Origin and Distribution of the Elements". p 99, L.H. Ahren, Ed. , Pergamon Press, London, England, 1968.
19. Khandekar, R.N., Kelkar, D.N and Vohra, K.G.; Lead, cadmium, zinc, copper and iron in the atmosphere of greater Bombay. Atmos. Environ, 14:457, 1980.
20. Burton, K.W and John, E. Study of heavy metal concentration in the Rhodda Fawa, South Wales. Water, Air, Soil Pollut. 7:45, 1977.
21. Winchester, J.W, Zoller W.H., R.A, Benson C.S. Lead and halogens in pollution aerosol and snow Fairbanks, Alaska. Atmos. Environ. 1:105, 1967.
22. Bowman, H.R, Conway J.G., and Asaro F.; Atmospheric lead and bromine concentration in Berkeley, California. Environ. Sci. Technol. 6:558, 1972.
23. Hammerle R.H. and Perrson W.R. Sources and elemental composition of aerosol in Pasadena California by energy dispersive x-ray fluorescence. Environ. Sci. Technol. 9, 1058, 1975.