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# Statistical Analysis of the Aerosol Elemental Composition in an Industrial Belt

T. Jayasekhar,[1] S. Kumaresan,[2] S. L. Radhika,[3] B. Biju,[3] M. Sindhu,[3]
C. S. P. Iyer[3]

[1] Tamilnadu Pollution Control Board, Tirunelveli 627 010, India
[2] Manonmaniam Sundarner University, Tirunelveli-627012, India
[3] Center for Marine Analytical Reference and Standards (C-MARS), Regional Research Laboratory (CSIR), Trivandrum 19, India

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In recent years, the accelerated industrial activity releases more anthropogenic particulate matter into the atmosphere. This anthropogenic particulate matter, together with natural mineral particulate matter is then transported by wind and distributed throughout the local, regional and continental areas. Since the concentration of different species in the atmospheric aerosol is significantly affected by the human activities, the study of the chemical composition of the particles is crucial for environmental management on local, regional and continental scales (Choi et al. 2001). The knowledge of the chemical composition of the aerosols, especially of the trace metals, is important to understand their role in atmospheric chemistry. High temperature processes such as coal combustion emit various trace elements into the atmosphere, which affect natural cycles of climate (Gao et al.1997). Many researchers have reported in detail the characteristics of metals in atmospheric particulate matter (Marshall et al. 1985, Pacyna 1984, Virkkula et al. 1999, Siefert et al. 1999). In the present study, we report the distribution of the trace elements Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Se, Hg and As in the aerosol of an industrial belt. Based on multivariate and principal component analysis of the results, the sources of the trace metals have been identified. It is expected that the findings of the study would lead to a better management of the environment.

## MATERIALS AND METHODS

The study is carried out in the industrial area, which is on the coastal belt. The area is rapidly getting industrialized due to proximity to a natural harbour. Fertilizer, Chemical and Thermal power plants besides Copper Pyrite Processing and Smelting units exist at the site.

Being a coastal site, the land /sea breeze modifies the prevailing winds within the boundary layer leading to unstable conditions. The sea breeze usually sets in between 08.00 and 10.00 hrs local time in the morning and land breeze sets in between 18.00 and 20.00 hrs in the evening. Around the periods of reversal, near-neutral conditions prevail for a long time. The predominant wind directions are NE and NW, with an average wind speed of 5.2km/hr. The minimum temperature recorded is $27^0$C and the maximum is $34^0$C. The average relative humidity is 67%.

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*Correspondence to:* C. S. P. Iyer

Five sampling stations were selected in the middle of the industrial belt, having a fertilizer factory, a thermal power plant and a metallurgical unit. For measuring the background levels, a station fifteen kilometer away from the industrial belt was taken.

Aerosol sampling was carried out using high volume air sampler, fitted with preconditioned and weighed Whatman glass microfibre filter paper (Whatman 20.3 cm x 25.4 cm). A minimum airflow of 1.1 cubic meters per minute was maintained throughout the experiment. The aerosols were collected on 8 hourly basis (10hr to 18hr, 18hr to 2 hr, 2hr to 10hr) over a full day. After sampling, the filter papers were carefully enclosed in clean polythene paper and brought to the laboratory for further analysis. Total suspended particulate concentration was determined from the weight of atmospheric aerosols collected on the filter paper and the volume of air sampled. The weighing procedure involves equilibrating the filters to standard atmospheric conditions. These are maintained the same for pre-weighing and for the final weighing.

Portions of the filter paper were cut into circles of about 1.0 $cm^2$ area. Ten such circles were cut from different portions of the filter paper. At all stages, extreme care was taken to prevent contamination. The cut circles were transferred to a 125 ml griffin beaker.15ml of mixed acid (65ml $HNO_3$ and182ml HCl diluted to 1L with double distilled water) was added and agitated for 60 minutes in an ultrasonic bath at $85^0$C. After cooling to room temperature, it was filtered using a vacuum filtration unit and the filtrate was collected in a 25 ml volumetric flask and made up to the mark with double distilled water. A blank was prepared in the same way with identical fresh filter paper. T he samples were stored in polythene sampling bottles, which had been subjected to a rigorous cleaning procedure. The bottles were initially washed with distilled water, then filled with 3N nitric acid and kept for one day. Subsequently they were subjected to ultrasonic agitation for 15 minutes. After removing the nitric acid and repeatedly washing with Millipore water, the bottles were filled up with Millipore water, till use. Supra pure acids, analytical grade reagents and millipore water were used in the analysis.

The samples were handled in a clean room conforming to Class 100 specifications. Analysis of the trace elements was carried out using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) – Thermo Jarrel Ash Atom 25. The wavelength calibration was performed using internal calibration, by a mercury vapour lamp. The standardization for the different elements was carried out using multi elemental standards. The measurements for emission were carried out at the optimum wavelengths- Cr (205.55nm); Mn(257.61nm); Fe(238.20nm); Co(238.89nm); Ni(221.65nm); Cu(324.75nm); Zn(213.86nm); Cd(214.44nm); Pb(220.35nm); Se(196.03nm); Hg(194.23nm); As(193.70nm). The minimum, maximum and mean concentration along with the standard deviation are given in Table 1. The mean background levels obtained at the sampling point G are also included.

**Table 1.** Concentration of trace elements in the aerosol samples.

| Parameter | Minimum μg/m$^3$ | Maximum μg/m$^3$ | Mean μg/m$^3$ | SD μg/m$^3$ | Background concentration μg/m$^3$ |
|---|---|---|---|---|---|
| SPM* | 82.32 | 310.4 | 141.9 | 52.6 | 48.17 |
| Cu | < 0.1 | 1.26 | 0.44 | 0.41 | 0.34 |
| Fe | 0.54 | 4.01 | 1.46 | 0.65 | 0.89 |
| Zn | 2.30 | 13.07 | 6.69 | 4.07 | 0.41 |
| Cd | < 0.001 | 0.009 | 0.003 | 0.003 | < 0.001 |
| Mn | < 0.001 | 0.123 | 0.029 | 0.040 | 0.002 |
| Cr | < 0.01 | 0.172 | 0.028 | 0.046 | < 0.01 |
| Co | < 0.005 | 0.019 | 0.006 | 0.007 | < 0.005 |
| Ni | < 0.05 | 0.294 | 0.075 | 0.10 | < 0.05 |
| Pb | < 0.005 | 0.547 | 0.83 | 0.13 | 0.009 |
| Se | < 0.1 | 1.35 | 0.29 | 0.38 | < 0.1 |
| Hg | 0.08 | 2.7 | 0.58 | 0.76 | < 0.01 |
| As | 0.81 | 5.07 | 2.6 | 1.72 | < 0.05 |

*Suspended particle matter

## RESULTS AND DISCUSSION

Proper quality assurance procedures have been followed in site selection, sampling preservation and analysis (Malcom.J.R.Clark2000). In the present study, specific importance is given to the trace elements of anthropogenic origin such as Cu, Fe, Zn, Cd, Mn, Cr, Co, Ni, Pb, Se, Hg and As, in suspended particulate matter. As seen from Table 1, compared to the background levels, measured at station G, the concentrations of trace metals in the industrial belt are higher. It is also observed that the concentrations are comparatively higher in the samples collected during the period 18hr to 2hr. This may be due to the fact that there is inversion during this period.

From the data, the correlation coefficients have been calculated and are entered in Table 2. It is seen that positive correlations predominate over the negative correlations, which suggest common sources. High positive correlation is found for the elements, As, Hg and Se. Besides these elements, Zn, Mn, Cr, and Co are also correlated with the above mentioned elements to a certain extent. The logical inference is that the sources are common. The source is mainly the fly ash resulting from the combustion of coal. Although Hg, Se and As are volatilized in the combustion zone, they are captured by the fly ash. Thus, the behavior of these elements generally follows the overall behavior of the particulate matter of the power station (Sandeline and Beckman 2001). It is observed in our studies that Cu, Cd and Pb are not correlated with As, Hg, Se, Cr and Co. The logical explanation is that the sources of these elements are different. This is attributed to the presence of smelter units in the urea.

**Table 2.** Correlation matrix of the studied element.

| | SPM | Cu | Fe | Zn | Cd | Mn | Cr | Co | Ni | Pb | Se | Hg | As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SPM | 1.00 | | | | | | | | | | | | |
| Cu | 0.01 | 1.00 | | | | | | | | | | | |
| Fe | 0.46 | 0.14 | 1.00 | | | | | | | | | | |
| Zn | 0.04 | 0.11 | 0.8 | 1.00 | | | | | | | | | |
| Cd | -0.24 | -0.21 | 0.05 | 0.22 | 1.00 | | | | | | | | |
| Mn | 0.04 | 0.41 | 0.58 | 0.64 | 0.23 | 1.00 | | | | | | | |
| Cr | -0.02 | -0.01 | 0.59 | 0.57 | 0.08 | 0.69 | 1.00 | | | | | | |
| Co | -0.08 | 0.29 | 0.52 | 0.61 | 0.43 | 0.31 | 0.52 | 1.00 | | | | | |
| Ni | 0.11 | -0.34 | -0.09 | -0.02 | 0.45 | 0.28 | 0.03 | -0.05 | 1.00 | | | | |
| Pb | -0.16 | 0.59 | 0.14 | 0.06 | 0.22 | -0.16 | 00 | 0.50 | -0.30 | 1.00 | | | |
| Se | 0.18 | -0.03 | 0.64 | 0.63 | -0.06 | 0.64 | 0.54 | 0.54 | -0.16 | 0.03 | 1.00 | | |
| Hg | 0.02 | 0.13 | 0.53 | 0.45 | -0.22 | 0.61 | 0.81 | 0.15 | -0.01 | -0.10 | 0.54 | 1.00 | |
| As | 0.27 | 0.15 | 0.85 | 0.93 | 0.07 | 0.58 | 0.68 | 0.58 | -0.04 | 0.01 | 0.68 | 0.59 | 1.00 |

The principal component analysis is used to classify the elements into groups, which due to their composition, can be attributed to particular sources. The results of the principal component analysis are given in Table-3. Only three factors were found to be statistically significant, accounting for 71% of the total variance.

**Table 3.** Principal component analysis of the analytical data of the aerosol sample

| Variables | P1 | P2 | P3 |
|---|---|---|---|
| SPM | 0.077201 | -0.110264 | -0.109499 |
| Cu | 0.001589 | 0.810438 | -0.283465 |
| Zn | 0.837408 | 0.181626 | 0.222535 |
| Fe | 0.808294 | 0.191248 | 0.053300 |
| Cd | 0.052339 | 0.068822 | 0.925881 |
| Mn | 0.813707 | -0.359807 | 0.261057 |
| Cr | 0.868554 | -0.037932 | -0.015766 |
| Co | 0.561595 | 0.577652 | 0.440391 |
| Ni | -0.030556 | -0.508987 | 0.621492 |
| Pb | -0.015455 | 0.861334 | 0.171955 |
| Se | 0.800885 | 0.058009 | -0.061277 |
| Hg | 0.797207 | -0.133075 | -0.353610 |
| As | 0.884959 | 0.146941 | 0.065267 |

The first factor ($P_1$) accounting for 40% variation is mainly due to elements As, Hg, Se, Zn, Fe, Mn, Cr, and Co. As discussed earlier, these highly correlated elements can be traced to the fly ash emitted from the burning of coal. Since Hg is correlated with As and Se, it may be concluded that the main contribution for Hg in the area is from the thermal plant and not from the chlor alkali plant.

The second factor ($P_2$) accounting for 17% variation is due to Cu and Pb. The source for these elements can be traced to the smelting industry. The third factor ($P_3$), which is totaling 14%, is attributed to Cd with lesser contributions of Co and Ni. The exact source for Cd could not be established though some of the smelting operations can give rise to cadmium. The presence of Co and Ni can be attributed to the burning of oil.

As expected, the mean concentration in the industrial sites was higher compared to background levels. It was also seen that the ratio of the concentration of iron in the industrial area to that of the background was not very high as compared to the other elements. This means that the contribution of iron in the area was both natural and industrial.

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