

# Sources of atmospheric pollutants in the North West province of South Africa: a case of the Rustenburg municipality

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## Abstract

A number of activities are known to generate substantial quantities of atmospheric pollutants in the form of uncontrolled emissions. Such sources include mineral extraction and stockpiling, landfill sites, materials handling operations and long term construction operations. In this study, the composition of air particulate matter was determined using Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry (SEM/EDS) and the following elements were identified: Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, C, Cl, S, F, P, V, Pb, Ni and O. Correlation and regression analysis, together with Principal Component Analysis (PCA) were used to determine the sources of atmospheric pollutants; the sources were identified in order of decreasing abundance as: soil dust, industry, biomass burning, and traffic.

*Keywords:* particulate matter, SEM/EDS, sources, PCA, correlation and regression.

## 1 Introduction

A better understanding of the chemical constituents as well as the sources of ambient particles is fundamental in bridging the existing knowledge gap between the air quality and its health effects. Exposure to ambient particulate matter (PM) has been associated with a range of adverse health effects including: premature



mortality, aggravation of existing respiratory conditions, changes to lung tissues and structures, and altered respiratory defence mechanisms, damages to the immune system, neurological damages, reproductive (i.e. reduced fertility) problems [1].

The major components of PM include sulphate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic and transition metals); organic material; elemental carbon (or soot) and crustal components [2]. PM can also be classified as primary and secondary particles. Primary particles are the direct products from combustion processes while secondary particles are a result of the physical and chemical reactions in the atmosphere [3].

Nriagu [4] observed that metal smelting and fuel combustion are usually the source of non-crustal volatile metals in the atmosphere. The elements Zn and Mn can be used as tracers for smelting sources, K can be used for biomass burning, Cl for sea salt, sulphate for anthropogenic sources, and Al, Si, Ti for soil dust. Zn, excess Mn, Cu and Ni are an unambiguous signal of anthropogenic smelting [5].

The occurrence of Cr with Co or Ni indicates the anthropogenic origin of particulate aerosols while, the co-presence of both Pb and Zn, and moderate correlations (between Pb and V) as observed by Mishra *et al* [6] in Seoul, indicates that the contribution from fuel combustion may be important. The co-presence of high Al, Mg, Si, Ca mixed with K, Fe, Mn, Zn observed by Begum *et al* [7] also indicates contribution of metal smelting source to particulate aerosols.

Different approaches have been proposed to understand the source diversity of aerosol particles, including particle size and chemical composition [8, 9]. The objective of this study was to determine the source contributions to the chemical composition of particulate matter in the Rustenburg municipality of the North West province.

## 2 Experimental

Sampling of PM was done at Boshhoek Primary School (BPS) located at latitude 25°30'15"S and longitude 27°5'45" E, within the Rustenburg municipality, which is situated at 25°39'00"S and 27°13'59"E, and is one of the biggest mineral producing districts in South Africa. The site is representative of well-defined environments, exposure situations or source activities like remote areas, urban background, traffic, and industry. The map showing the exact location of BPS is given in Figure 1.

The PM samples were collected onto Teflon-coated borosilicate fibreglass filters using the tapered element oscillating microbalance (TEOM). The ambient sample stream was allowed to pass through the PM<sub>10</sub> inlet at the flow rate of 16.7 L/min, which was then isokinetically split into a 3L/min sample stream that is sent to the mass transducer and a 13.7L/min exhaust stream.

The scanning electron microscope for environmental samples (ESEM FEI QUANTA 200) coupled with the energy dispersive spectroscopy (OXFID ENCA 200 EDS) was used for analysis of filters. The samples were analysed at high



vacuum, with a voltage of 15kV and the working distance of 10mm. The filters were mounted onto sample studs to ensure good electrical connection between the specimen and the microscope stage. The samples were not coated. The filters were scanned several (10) times (1 scan per 10 second) to ensure that the representative portion of the sample is covered. No extraction was performed.

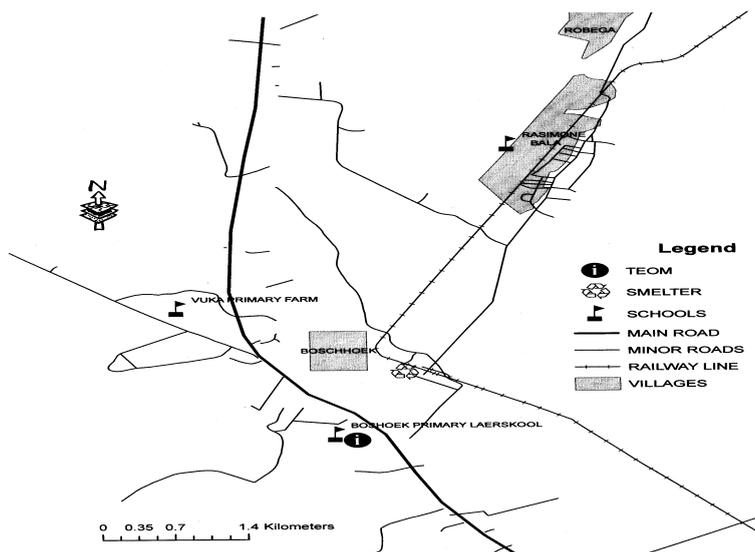


Figure 1: A map showing the Boshhoek Primary School (BPS) sampling site in the Rustenburg municipality.

The statistical analysis methods, correlation and regression analysis, together with principal component analysis (PCA) were used to determine the sources of atmospheric pollutants. It is worth noting that a strong correlation between any two elements suggests that the two have a common source whereas the absence of correlation between any two elements may indicate that the two do not have a common source [10].

### 3 Discussion of results

#### 3.1 PM<sub>10</sub> levels

The results obtained from the TEOM levels in the form of monthly concentrations of the inhalable particulate matter at BPS are given in Figure 2. The PM<sub>10</sub> levels for the spring season (August, September, and October) are relatively higher than the summer (November and December) levels at BPS. A

peak in PM10 levels was observed during the month of October (spring season), which agrees well with the fact that high wind speeds of 6.4 to 17.1 ms<sup>-1</sup> reported by the South African Weather Services (SAWS) favour resuspension and transportation of atmospheric pollutants.

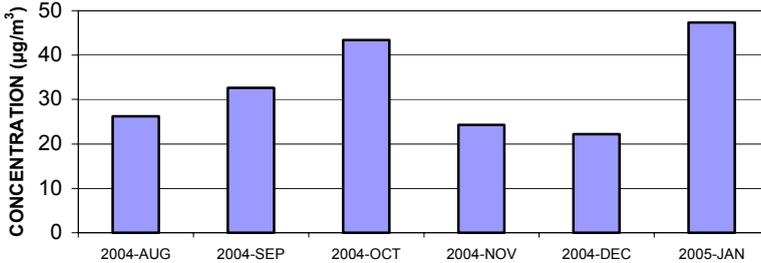


Figure 2: Monthly mass concentrations of PM10 at BPS.

The six-month average concentration at BPS is 33 µg m<sup>-3</sup>, which is the same as the annual average levels obtained in 1999 at the Goodwood site in Cape Town, South Africa [11]. This agreement in results shows that the same level of pollution can result from urbanisation and industrialisation.

The levels observed from August to October 2004 (26 to 43 µg m<sup>-3</sup>), and in January 2005 are within the average range observed by Querol *et al* [12], at different countries (Germany, Spain, Sweden, Austria, United Kingdom, and Netherlands) within the European Union, where the PM10 levels (annual mean) ranged from 28 to 42 µg m<sup>-3</sup> at urban background, and from 37 to 53 µg m<sup>-3</sup> at kerbside sites.

Characterisation of the fine airborne particulates is becoming increasingly important to regulators and researchers due to their potential impacts on human health, trans-national migration and influence on climate forcing and global warming [13, 14]. In the light of this, the composition of particulate matter and the estimation of source contributions within the Rustenburg area are discussed.

### 3.2 Composition of PM

Schneider [15], observed that an ordinary particle from traffic or fuel combustion source contain carbon at the core, with toxics and carcinogenic substances attached to their surfaces. This shows the importance of using the composition (elements and their oxides) of pollutants in source determination studies. The composition of PM10 obtained after filter analysis using SEM/EDS is given in Table 1. The levels of oxides of Al, Ca, Si, Na, Cl, S, O, and Fe observed in the samples suggest according to Chong *et al* [16] the presence of aluminosilicates with traces of sulfate or sulfite, and chloride. For most of the samples, the content of oxides of sulphur is the forth highest content.

The S concentration is important because it includes the sulphates and most toxic trace metals exist in the atmosphere in the form of sulphates and/or nitrates.

The relatively high S on the filters is according to Chong *et al* [16], indicative of the presence of sulphur dioxide, sulphuric acids, ammonium sulphate, ammonium bisulphate. The S levels are relatively stable for August, September, November and December. A peak is observed in October and an unusually low value is observed in January. There is a proportionality correlation between S and Pb, and between S and Ni from August to December. The correlation also applies to Cr but from August to November. Further studies need to be conducted to ascertain the cause of these correlations.

Table 1: Concentrations (in  $\mu\text{g}\cdot\text{m}^{-3}$ ) of oxides of the elements identified by SEM/EDS analysis of filters.

Sample	PM10	Si	Fe	Al	Ca	Mg	K	Na	Ti	Cr	C	Cl	S	F	V	Ni	Pb	O
Aug 2004	26.2	1.55	0.1	0.58	0.05	1.55	1.55	0.24	0.02	0.03	4.27	-	0.24	4.66	0.01	-	0.03	14.23
Sep 2004	32.62	2.12	0.26	0.88	0.13	0.2	0.13	0.26	0.03	0.1	5.41	0.03	0.29	4.14	-	0.01	0.05	18.56
Oct 2004	43.38	2.47	0.87	0.95	0.26	0.43	0.21	0.48	0.03	0.3	6.68	-	1.69	3.86	-	0.03	0.21	24.99
Nov 2004	24.26	1.77	0.34	0.58	0.12	0.12	0.15	0.32	0.05	0.07	3.2	-	0.27	5.26	-	0.02	0.04	11.94
Dec 2004	22.21	1.18	0.07	0.6	0.09	0.11	0.07	0.14		0.04	4.69	-	0.22	-	0.01	-	0.06	14.93
Jan 2005	36.15	3.15	1.05	1.34	0.14	0.29	0.14	0.11	0.07	0.22	6.04	0.07	0.07	1.59	0.01	-	0.1	21.76
Mean	31.74	2.02	0.46	0.81	0.13	0.46	0.37	0.26	0.03	0.08	5.35	0.01	0.46	3.12	0.01	0.01	0.09	18.49
SD	8.31	0.27	0.18	0.12	0.02	0.19	0.20	0.05	0.01	0.06	0.78	0.01	0.22	0.84	0.00	0.00	0.02	2.53

The oxides of Ni were measured mainly in spring (September and October) and ranged from 0.01 to 0.03  $\mu\text{g}\cdot\text{m}^{-3}$ . The levels of V were found to be lowest (0.01  $\mu\text{g}\cdot\text{m}^{-3}$ ) for the months August, December and January. Pb and Cr were identified throughout the sampling period, and their concentrations were measured as 0.03 to 0.21  $\mu\text{g}\cdot\text{m}^{-3}$  for Pb and 0.03 to 0.32  $\mu\text{g}\cdot\text{m}^{-3}$  for Cr.

The concentrations of the oxides of crustal elements identified in this study are similar to the levels obtained by Baron and Willeke [17] from four study sites in Atlanta, Rubidoux, Shenandoah National Park, and Meadview between May 1998 and May 1999 in the USA. The Ca concentrations at BPS ranged from 0.05 to 0.14  $\mu\text{g}\cdot\text{m}^{-3}$  whereas the Ca levels at the four sites in the US ranged from 0.03 to 0.16  $\mu\text{g}\cdot\text{m}^{-3}$ . The 0.1  $\mu\text{g}\cdot\text{m}^{-3}$  Fe measured at BPS in August 2004 compares with the 0.13  $\mu\text{g}\cdot\text{m}^{-3}$  in August 1999 in Atlanta. The levels of the oxides of Cr determined ranged from 0.03 to 0.42  $\mu\text{g}\cdot\text{m}^{-3}$  for this study. This shows that the limit of 1000  $\text{ng}/\text{m}^3$  (1  $\mu\text{g}\cdot\text{m}^{-3}$ ) set by NIOSH was not exceeded.

The SEM/EDS technique in this study revealed the presence of atmospheric particles of complex composition including S, Si, Al, Mg, Ca, Pb, Fe, Cr, Ni, V, and Pb among other elements. These particles can be harmful not only to human health, but also to the cultural heritage and the ecosystem as a whole. It is thus advisable for purposes of proper monitoring, to determine the sources of atmospheric pollutants using the elements identified. The world health organization (WHO) [18] also suggests that besides physical aspects such as particle number, size, or surface, the chemical composition of particles is likely to play a crucial role in regard the health implications of particulate matter.



Various health effects of PM, from less serious to very serious ones, are associated according to Sharma and Maloo [19] with its specific chemical and physical components.

### 3.3 Correlation and regression analysis

The following regression equations (eqns 1 – 2) show a clear relation relationship between the levels of PM10 and the toxic trace metals Cr, and Pb observed during this study.

$$\text{PM10} = 22.6 + 62.7 \text{ Cr} \quad (1)$$

$$\text{PM10} = 22.3 + 123 \text{ Pb} \quad (2)$$

These relations suggest an increase in the levels of toxic trace metals as the levels of PM10 increases. This imply the possibility of having high levels of trace metals within the PM, thus even when the standards set by the environmental protection agencies are not exceeded, the levels of the cancer-causing agents may still be hazardous to human health.

The relation between carbon and the trace metals is also important since the carbon determined can form part of the elemental and organic carbon. The oxides of carbon may imply the presence of Cr in the form chromium carbonate or even a gas. The carbon content can thus help give an indication of the main trace metals in the area. The  $r^2$  values obtained for trace metals were low, except for C and Cr for which an  $r^2$  value of 0.87 was obtained. The regression equation for C and Cr is given as:

$$\text{C} = 3.52 + 12.9 \text{ Cr} \quad (3)$$

According to Al-Momani [20], crustal material is the main source of Al. It is therefore logical to use Al as a tracer for crustal material source. The  $r^2$  values obtained from regression analysis ranged from 0.008 to 0.01 for Al and V, 0.008 to 0.32 for Al and Pb, and 0.62 to 0.63 for Al and Cr, 0 and 0.014 for Al and Ni. These rule off the possibility of same source for Al and the trace metals of concern, except for Al and Cr. The high  $r^2$  value for Al and Cr presents the possibility of Cr being from a crustal source. This however, does not rule out anthropogenic activities since they cause resuspension of particulate matter.

Metal smelting and fuel combustion are usually the source of non-crustal volatile metals in the atmosphere [4]. Held *et al* [5] suggests that the elements Zn and Mn can be used as tracers for smelting sources, K for biomass burning, Cl for sea salt, sulphate for anthropogenic sources, and Al, Si, Ti for soil dust. Zn, excess Mn, Cu and Ni are suggested as unambiguous signals of anthropogenic smelting. The correlation between K and Si in this study is  $r^2 = 0.58$ , and 0.55 between K and Fe, and 0.55 between K and Ca. This suggests that biomass burning is not the major source of the elements identified, since K and Si may be from the same source, and Si and Fe are tracers for soil dust source. The contribution of biomass burning may be observed as a result of some regional source.

In a similar study conducted in an industrial area of Taejon, Korea, Pb was also found to be strongly correlated with crustal elements (Ba, Sb, Co, Fe, etc.) and fuel combustion (V), strong correlations were also noticed by Chow *et al* [21] among Pb, Fe, Zn, and Ti from a study conducted in Los Angeles. The



correlations observed during this study are however, very small  $r^2 = 0.008$  for Pb and Ti,  $r^2 = 0.006$  for Pb and Fe. This indicates that Pb identified in this study cannot be of crustal origin, but is mainly due to fuel combustion (traffic).

The correlation and regressions discussed in this section suggest soil dust, traffic, and biomass burning as the sources of atmospheric pollutants in the Rustenburg municipality. It is important to note that the regression analysis could not quantify the contribution from different sources of particulate matter thus principal component analysis was used.

### 3.4 Principal Component Analysis (PCA)

Principal component analysis was also used to apportion the sources of atmospheric pollutants in the Rustenburg municipality. Figure 3 gives the PCA for BPS. Five factors that accounted for 98.4% of the PM were identified. The other 1.6% is labeled as unknown in the figure. This is the part that has eigenvalues less than one and thus could not be apportioned. The first factor, which accounted for 46.1% of the variance contained Si, Fe, Al, Cr, C and O. This is indicative of a soil dust source according to Held *et al* [5]. The occurrence of C in this factor could not be explained since elemental carbon (EC) was suggested by Ito *et al*, Ho *et al* and Salvador *et al* [22–24] as an emission from vehicles. The O is not used as a tracer or signature in this study since it may be linked with carbon or any other element identified thus implying any oxide in the PM10 analysed. The occurrence of Cr is not surprising since it may have been deposited on the earth crust as a result of the long-term ferrochrome mining activities in the area. There may be however, a justification for the co-occurrence of Cr, C and O, since Cr may be present in the form of carbonates.

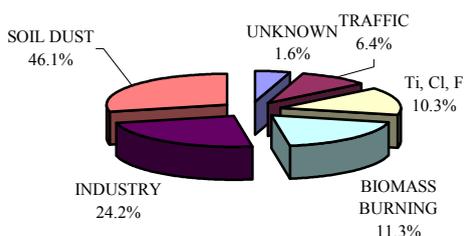


Figure 3: PCA for BPS.

Factor 2, which formed 24.2% and contained Na and Ni, was linked with industrial activities. This is mainly because Ni is linked with smelting, and other anthropogenic activities like oil-fuelled plant emissions [5, 26], while the presence of Na may be due to agricultural activities since it may be found in fertilisers. The third factor accounted for 11.3% of the variance with loadings of Mg and K. The factor was linked to biomass burning [5].

Factor 4, which formed 10.3% of the PM, contained Ti, Cl and F. The source of this factor could not be properly identified, mainly because of the presence of

high loadings of F, which may also be from the filters used. The Cl was identified by Salvador *et al* [24] as an additive to petrol in the form of ethylene dihalide ( $C_2H_4Cl_2$ ), and Ti has been linked to soil dust by Held *et al* [5] and to building industrial activities by Zhu *et al* [25].

The fifth factor (6.4%), which was linked to traffic, contained Ca, S, V and Pb, with high loadings of V. The co-occurrence of Pb and V was also linked to fuel combustion in a study by Mishra *et al* [6]. The source of S was also identified by Watson and Chow [26] as oil-fuelled emissions.

The PCA method suggests the following sources in order of decreasing abundance: soil dust, industry, biomass burning, and traffic.

## 4 Conclusion

Identification of source contributions to the elemental components of particulate matter within the Rustenburg area was achieved in this study. Both the correlation and regression analysis, and the principal component analysis suggested soil dust, biomass burning and traffic (fuel combustion) as sources of atmospheric pollution. The PCA method proved to be the relevant tool for apportionment of sources atmospheric pollutants, since it yielded quantifiable information about the sources of pollutants within the area. Contributions to the sources of atmospheric pollutants are thus given in order decreasing abundance as soil dust, industry, biomass burning, and traffic.

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