



Composition of Inhalable Atmospheric Particulates in Rustenburg, South Africa

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ABSTRACT

In this study, inhalable particulate matter was sampled using the TEOM series 1400a, the elemental composition of the particulate matter was determined using Scanning Electron Microscopy coupled with Energy Dispersive Spectrometer (SEM/EDS) and the concentration of particulate nitrates and sulphates was analyzed using Ion Chromatography (IC). These parameters were evaluated to obtain an estimate of the composition of inhalable particulate matter (PM₁₀) in Rustenburg, South Africa. The toxicity was also determined in terms of ratios of toxic metals to PM₁₀, as well as to elemental carbon, nitrates and sulphates. The components of PM₁₀ were obtained as follows: organic, halides, sulphates, crustal metals, toxic metals, nitrates, and carbon. The main toxic metals were obtained in order of decreasing abundance as Cr>Pb>Ni>V. Seasonal variations showed high levels of PM₁₀ and sulphates in spring and high nitrate levels in summer. The SEM/EDS showed the presence of atmospheric particles of complex composition including S, Si, Al, Mg, Ca, Pb, Fe, Cr, Ni, V, and Pb.

Keywords: *Inhalable particulate matter; toxic metals; particulate sulphates; particulate nitrates.*

1. INTRODUCTION

The primary goal of air pollution research is to identify and quantify sources and effects in order to understand and prevent adverse environmental and health outcomes. Airborne particulate matter is a mixture of thousands of different substances, diverse in characteristics

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like solubility, persistence in the atmosphere and in human tissue, reactivity, toxicity and carcinogenicity, as well as chemical structure and elemental composition. Major components of particulate matter (PM) include sulphates, nitrates, ammonium and hydrogen ions, trace elements (including toxic and transition metals), organic material, elemental carbon (or soot), and crustal components (Khlystov, 2001). PM can also consist of at least 160 organic compounds and 20 metals (Ag, As, Ba, Be, B, Cd, Ce, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sr, Ti, V and Zn) (Los Alamos national laboratory, 2003).

The World Health Organization (WHO, 2003) suggests that besides physical aspects such as particle number, size, or surface, the chemical composition of particles is likely to play a crucial role with regards the health implications of particulate matter. Various health effects of PM, from less serious to very serious ones, are associated with its specific chemical and physical components (Sharma and Maloo, 2005). The characteristics of chemicals in particulate matter are an important determining factor in their toxicological effect. The presence of dioxins and metals in particulate matter explains their carcinogenic effect (Environment Canada, 2004).

A number of studies link particulate matter with increases in premature deaths, hospitalizations, asthma symptoms, bronchitis and other respiratory illnesses (Sicard et al., 2011). Senior citizens and persons with existing cardiovascular and respiratory illnesses appear to be more sensitive than the rest of the population. Some scientists link these effects with particulate matter combined with other pollutants such as ozone, sulphur dioxide and metals. The studies on particulate sulphates state that, even at ambient concentrations of between 30 and 150 microns per cubic meter, these pollutants are linked with increased fatal cardiovascular attacks, particularly when combined with high-risk activities such as smoking (Burnett, 1997). These pollutants are also linked to child hospitalizations, school absences and increased use of medication by asthmatics. There are some possible indirect processes through which sulfate and nitrate in PM may affect health-related endpoints, including interactions with certain metal species and a linkage with production of secondary organic matter (Reiss et al., 2007).

The inorganic fraction of particulate matter includes nitrates, metals and a high percentage of sulphates. Nitrogen oxides form when fuel is burned at high temperatures, as in a combustion process. The primary sources of NO_x are motor vehicles, electric utilities, and other industrial, commercial, and residential sources that burn fuels. Natural sources for nitrogen oxides include soil, volcanic emissions and lightning; they make up less than 10% of the total emissions (Erisman et al., 1998). Because there is no primary source for particulate nitrate, it is considered a secondary pollutant and assumed to originate from atmospheric reactions of gaseous nitrogen species with coarse particles (Evans and Poor, 2001; Blanchard, 1999). Secondary pollution or aerosol formation includes the gas-to-particle conversion of emitted primary pollutants, such as the oxidation of SO₂ to sulfate compounds (Evans, 2003). Particulate sulfates can be formed from the gas-to-particle conversion of biogenically emitted SO₂ on sea salt particles (Roth and Okada, 1998).

A better understanding of the chemical constituents of ambient particles is fundamental in bridging the knowledge gap between the air quality and its health effects (Kgabi, 2011). In this study, the elemental components, particulate nitrate and sulphate concentrations were determined to obtain an estimate of the composition of inhalable particulate matter (PM₁₀). The toxicity was also measured in terms of ratios of toxic metals to PM₁₀, as well as to elemental carbon, nitrates and sulphates. The findings from this study are crucial for

development of appropriate monitoring and control measures, source apportionment studies, as well as health impact studies.

2. MATERIALS AND METHODS

Sampling of the air particulate matter was done using the TEOM series 1400a incorporated with the PM₁₀ inlet. The TEOM sampler was located between the latitude 25°30'15"South and 27°5'45" East (Figure 1). The ambient sample stream was allowed to pass through the PM₁₀ inlet at a flow rate of 16.7 L/min, which was then isokinetically split into a 3 L/min sample stream that was sent to the instrument's mass transducer and a 13.7 L/min exhaust stream. The filters were changed monthly using forceps and placed in plastic containers with caps.

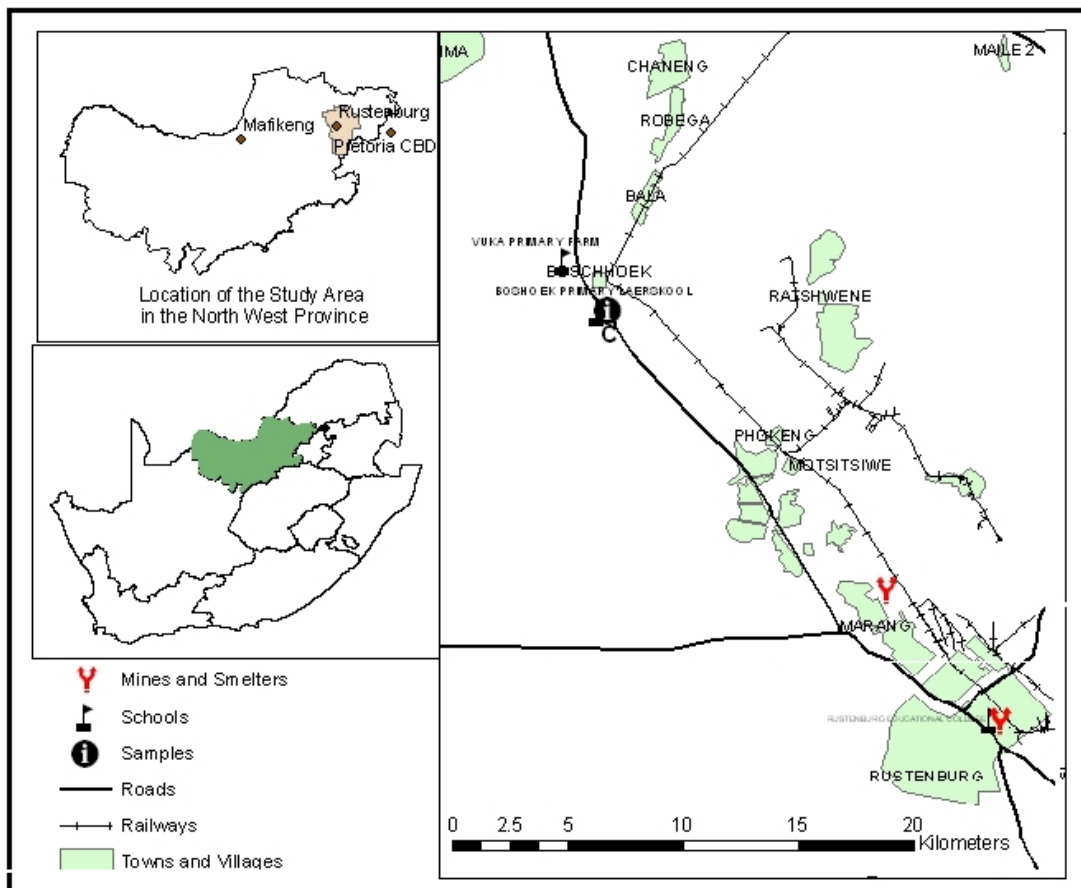


Fig. 1. Location of the sampler (shown with symbol C) within Rustenburg

Boshhoek is a semirural area and the sampling site (Site C) is located next to a main road used as bypass from the city (Rustenburg) to an internationally recognized hotel/entertainment complex (Sun City). The road also forms part of the route to Bafokeng Stadium in Phokeng (~10 Km). The vehicular density on the road therefore increases during holiday seasons and according to the type of event. The possible industrial sources are

mines and smelters situated towards the east (Platinum mine) and south east (ferrochrome mines) The site is also situated close to trees that may affect the concentration levels of the pollutants in the vicinity of the sampler. It was also upwind of industrial sources for most of the time. Relatively strong winds of 31.4 Km/h, low temperatures (mean = 16°C) and wind direction of 239 degrees (WSW) were reported by Kgabi and Mokgwetsi (2009) for the Boshoeck area.

Analysis of PM was performed using Scanning Electron Microscopy coupled with Energy Dispersive Spectrometer, and Ion Chromatography (IC). The ESEM FEI QUANTA 200, coupled with the OXFID ENCA 200 EDS, was used for elemental analysis of samples. The samples were analyzed at high vacuum, with a voltage of 15 kV and the working distance of 10 mm. A dead time of forty percent, which corresponds to a lifetime of 100 s, was used during the analysis of samples. The filters were fixed 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 s) to ensure that a representative portion of the sample is covered. No extraction was performed.

Detection limits and analytical precision vary widely with analytical protocol, instrumental response, blank contamination, interferences, matrix composition, and isotope abundance, but range from <100 ppb to <1 ppt in aqueous solution. Analytical precision is typically ~2%, of one standard deviation. The method detection limits for SEM/EDS are not easy to determine since they depend on different factors such as size and density of the sample, resolution of the detector and the working voltage. In this study, the spectrum range of 0 – 20 keV was maintained throughout, and quant-optimization of the system was done with Ni to standardise the system. On each filter, the fault boundaries (weight % sigma) were observed to be ranging from ± 0.05 to 0.3.

Ion chromatography (IC), a separation technique by which two or more chemical compounds are physically separated according to their affinity in the stationary phase where the solute that has a greater affinity for the stationary phase moves through the column slower than the one that has less affinity for the stationary phase (USEPA, 2005) was used for determination of sulphates and nitrates. Solute ions of the opposite charge are attracted to the stationary phase by electrostatic force. Anions such as SO_3^- or cat ions such as $\text{N}(\text{CH}_3)_3^+$ are covalently attached to the stationary phase. The retention of these ions and polar compounds in the stationery phase depends on their charge density and the higher the charge the longer the compound will be retained on the stationery phase (Rouesacc & Rouesacc, 2001). In this study, each filter was immersed into a beaker containing 50ml of distilled water and then sonicated in a steam bath at $50 \pm 3^\circ\text{C}$ for 7 minutes. The samples were then removed and stored in the refrigerator overnight before analysis by IC.

3. RESULTS AND DISCUSSION

3.1 PM₁₀ and Meteorological Parameters

Figure 2 shows monthly PM₁₀ levels and meteorological parameters for the period August 2004 to January 2005. The levels observed from August to October 2004 (26 to 43 μgm^{-3}) and in January 2005 were within the average range observed by Querol et al. (2004) in 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 μgm^{-3} at urban background, and from 37 to 53 μgm^{-3} at kerbside sites.

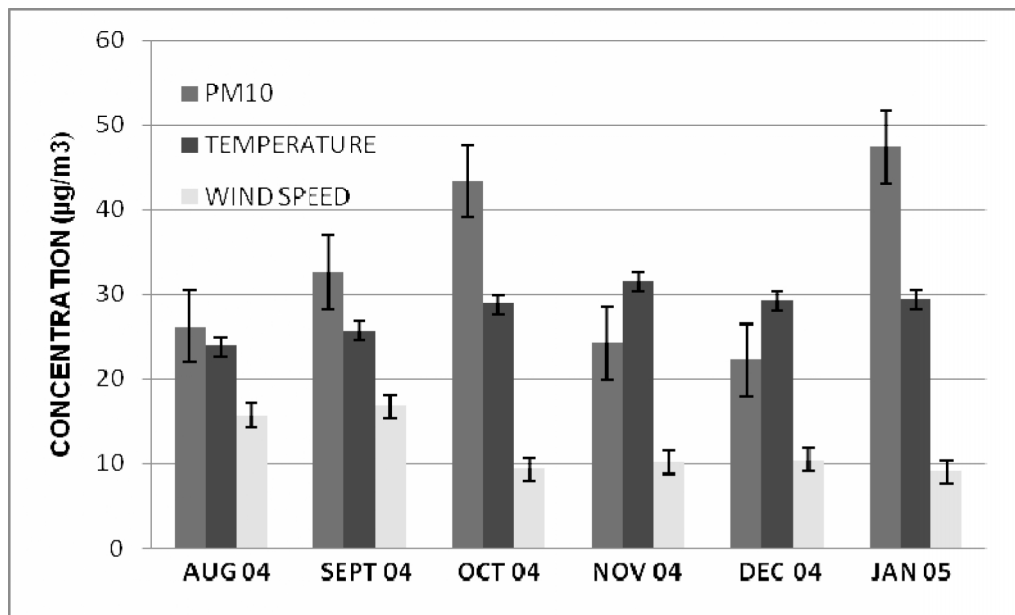


Fig. 2. Monthly PM₁₀ concentrations and meteorology for the period August 2004 to January 2005

The PM₁₀ levels for the spring season (August, September and October) were relatively higher than the summer (November, December), which agrees well with the fact that high wind speeds favor re-suspension and transportation of atmospheric pollutants. Relatively strong winds (speed of 31.4 km/h) dilute more concentrated pollutants from the sampling point (Kgabi and Mokgwetsi, 2009). The wind direction of 239 degrees (WSW), the location of possible sources of PM like the main road and the high temperatures may account for the high levels in January.

An increase in PM₁₀ levels as temperature and wind speed increased was also observed during this study.

3.2 The Elements Identified

The elements identified using the SEM/EDS are given in Table 1. These include Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, C, Cl, S, F, V, Ni, and Pb. The element O mentioned hereafter, imply all the oxides that could not be explicitly identified by the SEM/EDS. According to Miranda and Andrade (2005), elements produced during combustion usually appear in the form of oxides such as magnesium oxide, aluminum oxide, silicon dioxide, calcium trioxide, titanium oxide, iron trioxide, phosphorus pentoxide, ammonium sulfate, copper oxide, zinc oxide, sodium chloride, potassium oxide, vanadium oxide, nickel oxide and manganese oxide.

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 S levels were relatively stable for August, September, November and December. A peak was observed in October and an unusually low value was observed in January. The high levels in October may be caused by high wind speeds (spring season) and the low levels in January are likely to be caused by the autumn rainfall in the area.

Table 1. Concentrations (in μgm^{-3}) of the elements identified for spring (August to October 2004) and summer (November 2004 to January 2005)

	PM ₁₀	Si	Fe	Al	Ca	Mg	K	Na	Ti	Cr	C	Cl	S	F	V	Ni	Pb	O
AUG	26.20	1.55	0.10	0.58	0.05	1.55	1.55	0.24	0.02	0.03	4.27	-	0.24	4.66	0.01	-	0.03	14.20
SEP	32.60	2.12	0.26	0.88	0.13	0.20	0.13	0.26	0.03	0.10	5.41	0.03	0.29	4.14	-	0.01	0.05	18.60
OCT	43.40	2.47	0.87	0.95	0.26	0.43	0.21	0.48	0.03	0.30	6.68	-	1.69	3.86	-	0.03	0.21	25.00
NOV	24.30	1.77	0.34	0.58	0.12	0.12	0.15	0.32	0.05	0.07	3.20	-	0.27	5.26	-	0.02	0.04	11.90
DEC	22.20	1.18	0.07	0.60	0.09	0.11	0.07	0.14	-	0.04	4.69	-	0.22	-	0.01	-	0.06	14.90
JAN	47.35	3.05	1.12	1.26	0.14	0.36	0.12	0.10	0.06	0.32	7.83	0.04	0.06	0.80	0.01	0.01	0.12	26.30
MEAN	31.70	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	18.50
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	2.530

It could be expected that high levels of Pb be measured during spring mainly due to resuspension of soil dust from the roads. The high levels observed in December may be due to the fact that, Pb occurs in the atmosphere mainly in the form of Lead carbonate and Lead-phosphate. The increased usage of transportation during December (holiday period) may also be an important contributing factor to the increased Pb levels observed.

Heavy metals originate from a variety of industrial processes such as incineration, manufacturing, and smelting (Pinto & Lester, 1998). The oxides of Ni were measured mainly in spring (September and October) and ranged from 0.01 to 0.03 μgm^{-3} . The levels of V were found to be lowest (0.01 μgm^{-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 μgm^{-3} for Pb and 0.03 to 0.32 μgm^{-3} for Cr.

3.3 Toxic Metal-PM Correlations

According to Zhang et al. (2000), dust offers a good surface for chemical reactions. Determination of the element to PM_{10} ratios in percentages give an indication of the relative abundance of the toxic metals in the particulate matter and hence an estimation of the toxicity of the dust in the vicinity of the study area. The ratio of toxic metals to PM_{10} was very small (less than 0.001) for V and Ni. For Cr and Pb, the ratio was determined in the range from 0.001 to 0.007. The ratios are small but have a maximum in the month of October as one would expect. The maximum in the ratio is measured as a result of high PM_{10} levels and high toxic metal concentrations observed in October as shown in Table 2.

The F/PM_{10} ratio showed a maximum in November while the concentrations of S/ PM_{10} were high in October (spring season) and low throughout summer. The high F/PM_{10} ratio could not be explained because Teflon filters may be responsible for the F identified. The fact that South Africa is characterized by dry and windy spring seasons may account for the high S/PM_{10} ratio in October. The high rainfall which contributes to particle wash-out accounts for the low S/PM_{10} in summer.

Table 2. Percentage of Element/ PM_{10} ratios

MONTH	Cr/ PM_{10}	Ni/ PM_{10}	V/ PM_{10}	Pb/ PM_{10}	S/ PM_{10}	C/ PM_{10}
AUG	0.10	-	0.04	0.10	0.90	16.30
SEP	0.30	0.03	-	0.20	0.90	16.60
OCT	0.70	0.09	-	0.50	3.90	15.40
NOV	0.30	0.08	-	0.20	1.10	13.20
DEC	0.20	-	0.04	0.30	1.00	21.10
JAN	0.50	-	0.04	0.20	0.10	12.80
Min	0.10	0	0	0.10	0.10	12.80
Max	0.70	0.09	0.04	0.50	3.90	21.10
Ave	0.36	0.04	0.02	0.26	1.49	16.16

The correlation between carbon and the trace metals is also important because the carbon determined can be elemental or organic and may indicate the existence of toxic metals in the form of carbonates. The oxides of carbon may imply the presence of Cr in the form of chromium carbonate or even gas. The r^2 values obtained for trace metals and carbon were

low, except for C and Cr for which an r^2 value of 87% was obtained. The regression equation for concentration of C and Cr is given as:

$$C_C = 3.52 + 12.9 C_{Cr} \quad (1)$$

The Equation 1 implies that an abundance of C indicates abundant Cr, thus it is important to note the possibility of a large fraction of C existing with Cr in the particulate matter. The relation between C and Cr may not necessarily suggest Cr to be in an organic form, it may also imply the occurrence of Cr as a carbonate.

The following regression equations show a clear relationship between the levels of PM₁₀ and the toxic trace metals of interest (Cr, Ni, V, and Pb) observed at the study site.

$$C_{PM10} = 22.6 + 62.7 C_{Cr} \quad (2)$$

$$C_{PM10} = 22.3 + 123 C_{Pb} \quad (3)$$

These correlations are important since they suggest an increase in the levels of toxic trace metals as the level of PM₁₀ increases. Many metal smelters emit significant amounts of heavy metals into the atmosphere. Lead for instance, occurs in the atmosphere mainly in the particulate form (in the fine particle fraction), but a small part occurs in vapor as organic lead compounds (European Environment Agency, 1996). This further suggests the possibility of having high levels of trace metals at relatively low levels of PM₁₀. 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.

Figure 3 gives the PCA model results for Site C generated from concentrations of the elements identified. Five factors, which accounted for 98.4% of the PM were identified. The other 1.6% is the part with eigenvalues of less than one, which could not be apportioned and is labeled as 'other' in the figure.

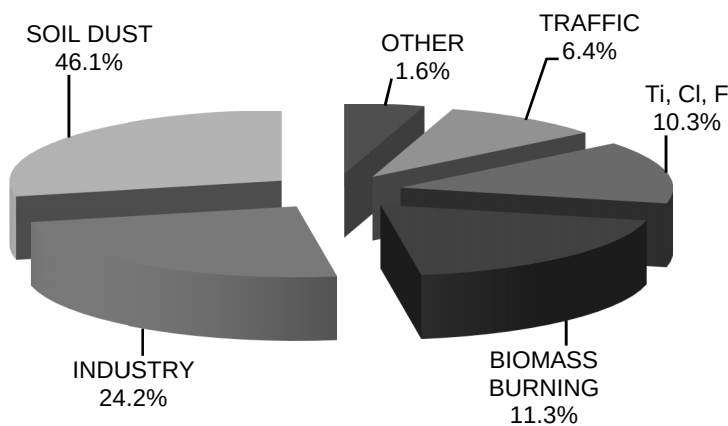


Fig. 3. Source contributions for site C

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. The occurrence of Cr may indicate that the toxic metal have been deposited on the earth crust as a result of the long-term ferrochrome mining activities in the area. Factor 2, which formed 24.2% and contained Na and Ni, was linked to industrial activities. This is mainly because Ni is linked to residual oils and other anthropogenic activities.

The third factor accounts for 11.3% of the variance with loadings of Mg and K. The factor was linked to biomass burning. 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 fifth factor (6.4%), which was linked to traffic, contained Ca, S, V and Pb, with high loadings of V.

The PCA results show source contributions of soil dust>industry>biomass burning>Ti, Cl, F (unknown)>traffic>other. This needs further investigation mainly because Site C is located next to a main road and close to a railway line. It is also far from the Mine (~20 Km South East) and Central Business District (Rustenburg ~25 Km South East), which are expected to account for the industrial sources. The predominant wind direction of WSW, as well as the seasonality of vehicular density also influenced the results for traffic sources. Further analysis was performed on the filters using ICP to determine the particulate sulphate and nitrate concentrations because most of the toxic metals occur in the form of sulphates, nitrates, carbonates, phosphates and other oxides.

3.4 Particulate Sulphates and Nitrates

The concentrations of sulphates and nitrates determined in this study are given in Figure 4. The concentration of nitrates ranged from 0.11 to 0.71 μgm^{-3} with a peak in December, while the sulphate concentrations ranged from 1.35 to 7.93 μgm^{-3} , with a peak in October. These particles, especially the sulfates can absorb water and become larger on days of high humidity, scattering light and creating hazy conditions. Power plants that use coal release oxides of sulfur and nitrogen, which can change into sulfate and nitrate particles.

The sulphate concentrations are higher than the nitrates. The high levels of sulphates and nitrates create an expectation of high toxic trace metals within the area, since the metals (especially Cr, Ni and Pb) exist as sulphates and nitrates in the atmosphere and Pb exist mostly in the form of carbonates and/or phosphates.

It should however be noted that retention of sulfur dioxide on filters, followed by oxidation to sulfate, which is referred to as artifact sulfate formation, a phenomenon which increases with increasing filter alkalinity, might contribute to the high sulfate levels (Coutant, 1977).

The low nitrate levels observed might be caused by loss of true atmospheric particulate nitrate occurring during or following sampling mainly due to dissociation or chemical reaction (Appel et al., 1981). This phenomenon has been observed on Teflon filters and inferred for quartz fiber filters (Pierson et al., 1980; Dunwoody, 1986). The magnitude of nitrate artifact errors in PM_{10} mass concentration measurements may vary with location and ambient temperature; however, for most sampling locations, these errors are expected to be small.

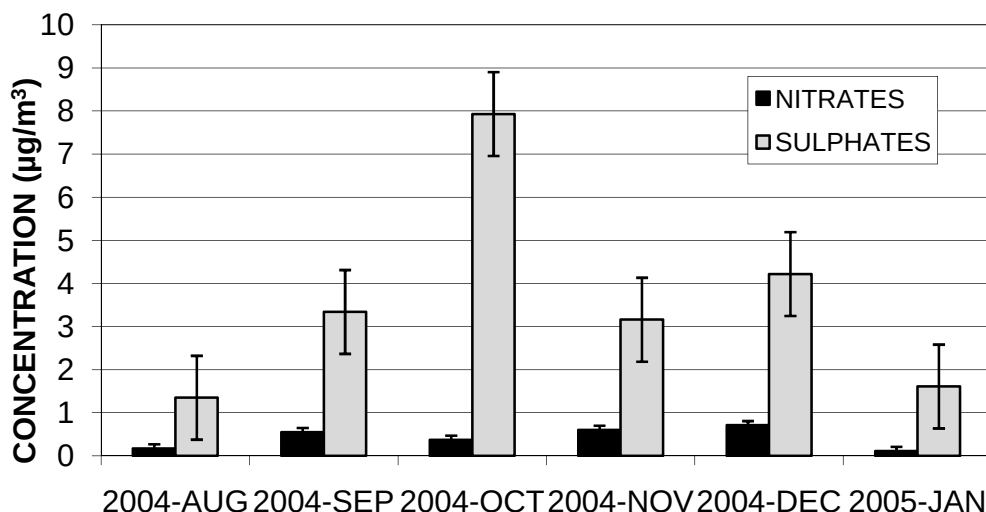
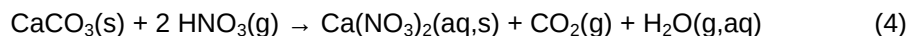


Fig. 4. Concentrations of sulphates and nitrates measured

The 46% soil dust and 24% industrial contributions to PM_{10} , obtained from the PCA results also explains the low nitrate concentrations which are in line with Evans (2003), who stated that mineral dust play an important role as a sink for nitric acid, converting it into a coarse mode species, $Ca(NO_3)_2$ following the reaction:



Dentener et al. (1996) however, suggests that the uptake of HNO_3 can take place only in mineral dust aerosols with a high enough alkalinity to overcome the acidity associated with uptake. The alkalinity of the mineral dust is to a great extent determined by the concentration of $CaCO_3$.

Mamane and Gottlieb (1989) have shown that 25 - 150 mg of SO_4^{2-} and 0.5 - 4.5 mg of NO_3^- can be formed per gram of mineral particle in highly polluted atmospheric conditions. The ratios of nitrate and sulphate with PM_{10} in percentages in Table 3 thus indicate the relative abundance of nitrates and sulphates in the PM_{10} . Metals are also inhaled mostly in the form of sulphates and nitrates thus the ratios also provide information about the occurrence of metals in their inhalable form, which can also help with inference to toxicity of the PM_{10} .

The mean NO_x/PM_{10} and SO_x/PM_{10} ratios (in percentages) for the study area were obtained as 1.51 and 11.51 respectively. The fact that high ratios of toxic metals to nitrates were measured as compared to sulphates shows the extent to which the sulphate and nitrate is linked to these metals. The rest might be linked with any of the other elements observed depending on their reactivity. It is thus vital to determine the overall composition of the PM_{10} measured.

Table 3. Oxide/ PM₁₀ and Element/oxide ratios (in percentages)

Month	NOx/ PM ₁₀	SOx/ PM ₁₀	Cr/SOx	V/SOx	Ni/SOx	Pb/SOx	Cr/NOx	V/NOx	Ni/NOx	Pb/NOx
Aug	0.64	5.15	2.20	.00.70	-	2.20	17.60	5.80	-	17.60
Sep	1.68	10.23	2.90	-	0.30	1.50	18.10	-	1.80	9.10
Oct	0.85	18.28	3.70	-	0.40	2.60	81.00	-	8.10	56.70
Nov	2.47	13.02	2.20	-	0.60	1.20	11.60	-	3.30	6.60
Dec	3.19	19.00	0.90	0.20	-	1.40	5.60	1.40	-	8.40
Jan	0.23	3.40	19.80	0.60	0.60	7.40	29.09	9.10	9.10	10.91

3.5 Components of Particulate Matter

The relative abundance of different components of the inhalable particulate matter sampled from the Boshhoek municipal area of Rustenburg can be represented in percentages (Figure 5).

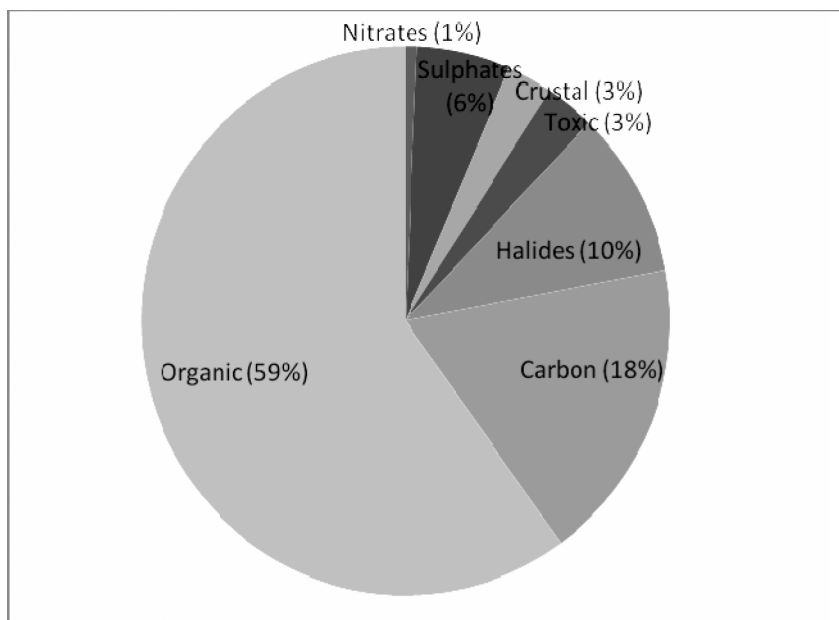


Fig. 5. Composition of PM10

The metals, Si, Fe, Al, Ca, Mg, K, Na, Ti, and S were grouped together and represented as the crustal, Cl and F as halides, and Cr, Ni, V, Pb as toxic metals. These together with the nitrates and sulphates determined in this study account for 41% of the PM₁₀ sampled, which is inorganic. It was thus assumed that the remaining 59% accounts for the organic part of the PM₁₀. The assumption can be verified in future studies taking into account the fact that the inorganic fraction of inhalable particulate matter may also contain carbonates and by laboratory analysis and quantification of both the organic and elemental carbon content. The composition obtained is in line with Watson et al. (1997) who observed that crustal and trace metals contribute only a very small fraction of the total PM₁₀ mass, and the remaining portion may be attributed to organic carbon (OC), elemental carbon (EC), silicon and water-soluble constituent of atmospheric aerosol. The fact that particulate matter can contain 30 - 50% of organic species contributes to low masses of the inorganic species determined above and may also be a result of the one limiting factor of the Ion Chromatography analysis, which is the difficulty in assessing the efficiency of extracting the PM from different filters. This has been reported before by Li et al. (1996) who estimated an efficiency of 20–50% of PM removed from filters, and Gilmour et al. (1996) who estimated an efficiency of 10–30%.

4. CONCLUSION

The composition of atmospheric particulates was obtained with the following main components: organic, halides, sulphates, crustal metals, toxic metals, nitrates and carbon,

showing that the complex composition of particulate matter can vary according to location, and domestic and industrial activities in the vicinity of the sampling location.

The elements identified during this study can be presented in order of decreasing abundance as C>F>Si>Al>Fe>Mg>S>K>Na>Ca>Pb>Cr>Ti>Ni>V>Cl and the toxic metals linked to industries around the study area were obtained in order of decreasing abundance as Cr>Pb>Ni>V. The sulphate levels were higher than nitrate levels for the entire study period.

The seasonality of PM₁₀, nitrates and sulphates, was also observed high levels of PM₁₀ and sulphates in spring and high nitrate levels in summer.

The source contributions to the inhalable particulate matter were obtained in decreasing order as soil dust>industry>biomass burning>Ti, Cl, F (unknown)>traffic.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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