Occurrence of Toxic Trace Metals in Health-Significant Atmospheric Particles

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***Abstract*-In this study, the sampling of size segregated particulates was performed by using a three-stage Dekati PM_{10} Cascade Impactor. The concentration of toxic elements in the different particle sizes was determined using Particle Induced X-ray Emission. This study focused on determination of the concentration of toxic elements in different particle sizes. The highest level of particulate matter (PM) at daytime was 90 $\mu g.m^{-3}$ while at night-time, the concentrations ranged between 0.04 $\mu g.m^{-3}$ and 0.8 $\mu g.m^{-3}$. The toxic elements Cr, Ni, V and Pb were identified in the PM_{10}, $PM_{2.5}$, $PM_{1.0}$ and PM<1 samples. The Cr concentrations exceeded the limits of 1 $\mu g.m^{-3}$ for NIOSH and also the 1.5 $\mu g.m^{-3}$ limit for APCEL. The WHO standards of 0.5 $\mu g.m^{-3}$ and 1 $\mu g.m^{-3}$ for Pb and V respectively were not exceeded. The study suggests the need for more prolonged, continuous studies so as to establish trends and seasonal variations in particulate matter and toxic metals.**

***Keywords*-Toxic Metals; Particulate Matter; Size Distribution; Sources of Atmospheric Particles; Particle Induced X-Ray Emission**

I. INTRODUCTION

Health effects of aerosol particles have raised great interest in the investigation of aerosol properties. The World Health Organization (WHO) has identified atmospheric particulate pollution as one of the most important contributors to ill-health [1]. Numerous studies suggest that health effects can occur at or below the levels permitted under national and international air quality standards. According to WHO [2], particulate pollution does induce adverse health effects, especially for the more susceptible populations.

It has been suggested that the extremely small size of the fine particulate matter (PM) promotes efficient entry and adherence to the lungs, and the toxicity of the particles is mainly responsible for inflicting damage to the organ [3]. There is therefore a need for the determination of size distribution of atmospheric aerosols.

Particle size distributions play an important role in understanding both the detailed aerosol processes, the long-term changes in the atmosphere, and their impact on health. The size distribution functions describe how the aerosol number (or area or volume) is distributed with respect to size.

The fine fraction includes particles with aerodynamic diameters of ≤2.5 μm, and is referred to as $PM_{2.5}$. The $PM_{2.5}$ has shown a closer association with human adverse health effects than either particles ≤10 μm (PM10) or total suspended particles (TSP) [4]. Kim et al. [5] confirmed that $PM_{2.5}$ is mainly produced by particles emitted directly into the atmosphere (primary particles) and particles formed in the air from the chemical transformation of gaseous pollutants (secondary particles).

The size distribution mainly depends on the production mechanism or source [6]. Particle size distribution is also crucial in apportionment of sources and effects on climate and on human health. The fine particles contain aerosols such as sulphates, nitrates, combustion particles, re-condensed organic and metal vapours. Toxic heavy metal particles have also been found in fine particles [7].

It is well known that fine particles have high concentrations of many potentially toxic trace metals, such as cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn), which can be incorporated into the body through inhalation [8].

The objective of this study is to determine the concentration of the toxic elements in different particle sizes.

II. METHODOLOGY

Atmospheric PM samples were collected from Impala Platinum mine, which is located in Rustenburg. The mine is situated in close proximity to the community of Luka, a semi-rural area within the Rustenburg district. Fig. 1 shows the location of the Impala Platinum mine, one of the biggest platinum mines in Rustenburg, the North West Province of South Africa.

According to the North-West Freight Transport Databank [9], Rustenburg is reported to be the fastest growing city in South Africa and is home to the two largest platinum mines and the largest platinum refinery in the world, which processes 70% of the platinum mined in the world. Chrome is also mined extensively in the nearby town of Brits.

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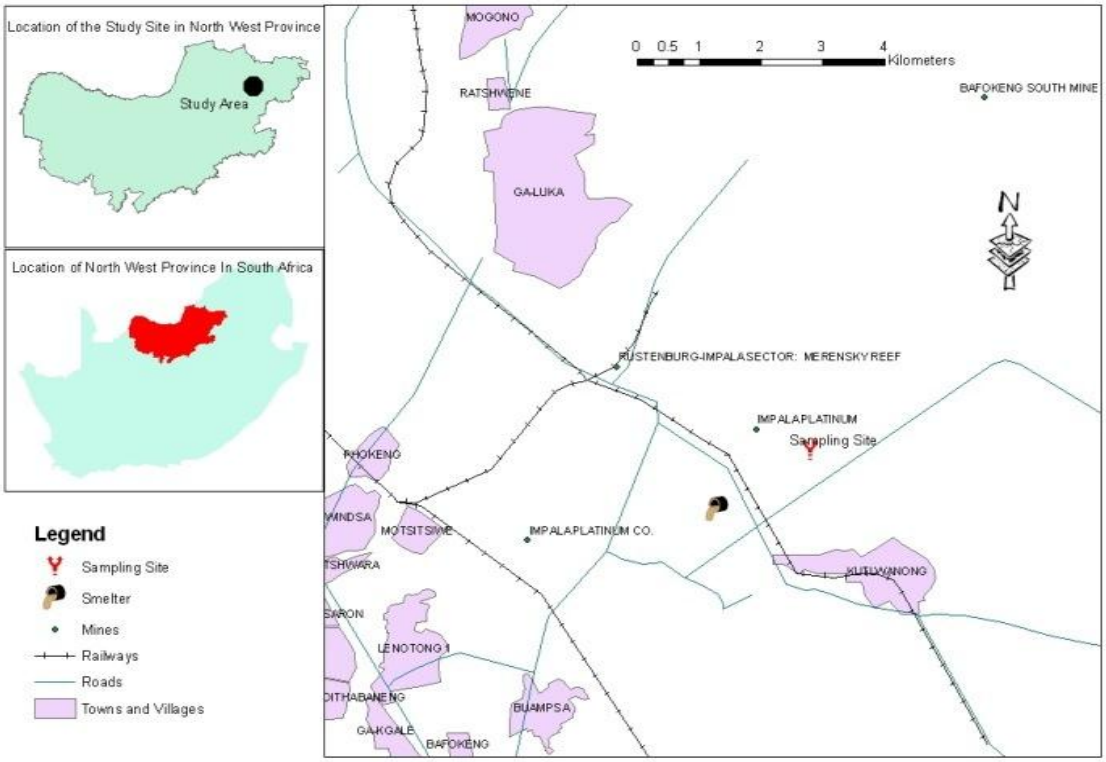

Fig. 1 Location of impala mines study site in Rustenburg

The sampling procedure was done in two stages, namely the pre-treatment, which included greasing the polycarbonate foil filters with Apiezon-toluene mixture, and weighing on a Sartorius Analytic A2005 electronic balance; and the sampling of particulates. The foils were placed on a collection plate and fastened with a stainless steel holder ring while ensuring that there were no bubbles underneath, and that no wrinkles appeared before applying the grease mixture.

The sampling of PM was conducted by using a three-stage Dekati PM_{10} Cascade Impactor connected to a pump system which was set to give a flow rate of 30 L/min. Successive impactor stages were stacked so that each slot is above an impaction plate. The collection substrates were carefully placed between the collection plates so that the slots were exposed. The collection substrate was centred over the slots with the rough side up.

The aerosol data were collected at three hourly intervals on weekdays and weekends during the day. At night time, the data were collected over twelve hours from 18h00 to 06h00 the following morning. In addition to the aerosol data, meteorological data were also collected continuously and recorded at 3 hourly intervals. This study reports on a total of 46 measurements made during the short campaign/study. These include 36 three-hourly (day-time: 6h00-9h00, 9h00-12h00, 12h00-15h00, 15h00-18h00) samples and 10 twelve-hourly (night-time: 18h00-6h00) samples. The researchers planned to make 50 measurement sets but had to disregard a few daily measurements due to logistic reasons. Each of the 46 measurement sets yielded 5 filters, i.e. 4 day-time and 1 night-time filters for each PM size (PM_{10}, $PM_{2.5}$, $PM_{1.0}$, and PM<1). Meteorological data (temperature, wind speed, wind direction and pressure) were also measured for each measurement set.

Elemental analysis of the PM filters collected was performed at South African Nuclear Energy Corporation (NECSA) using Particle Induced X-ray Emission (PIXE).

PIXE analysis consists of two parts. The first is to identify the atomic species in the target from the energies of the characteristic peaks in the X-ray emission spectrum, and the second part is to determine the amount of a particular element present in the target from the intensity of its characteristic X-ray emission spectrum. This normally requires knowledge of the ionization cross-sections, fluorescence yields and absorption coefficients [10]. The MicroPIXE technique is useful for the non-destructive analysis. Although it provides only an elemental analysis, MicroPIXE technique can be used to determine the distribution of trace elements in a wide range of samples. In this study, the MicroPIXE was used to determine the elemental composition of PM samples.

III. Results and Discussion

Elemental composition of PM was determined by using PIXE for all elements, but the main focus was on determining the occurrence and concentrations of the toxic elements: Vanadium (V), Chromium (Cr), Nickel (Ni) and Lead (Pb).

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A. Day-Time Elemental Composition of PM in Rustenburg on Weekdays

Fig. 2(a) shows that Pb is the element with a high concentration in all particle sizes. This is followed by Cr which has a high concentration in PM_{10}, $PM_{2.5}$ and PM_1. Vanadium was also found to be present in all particle sizes while Ni occurred only in PM < 1.

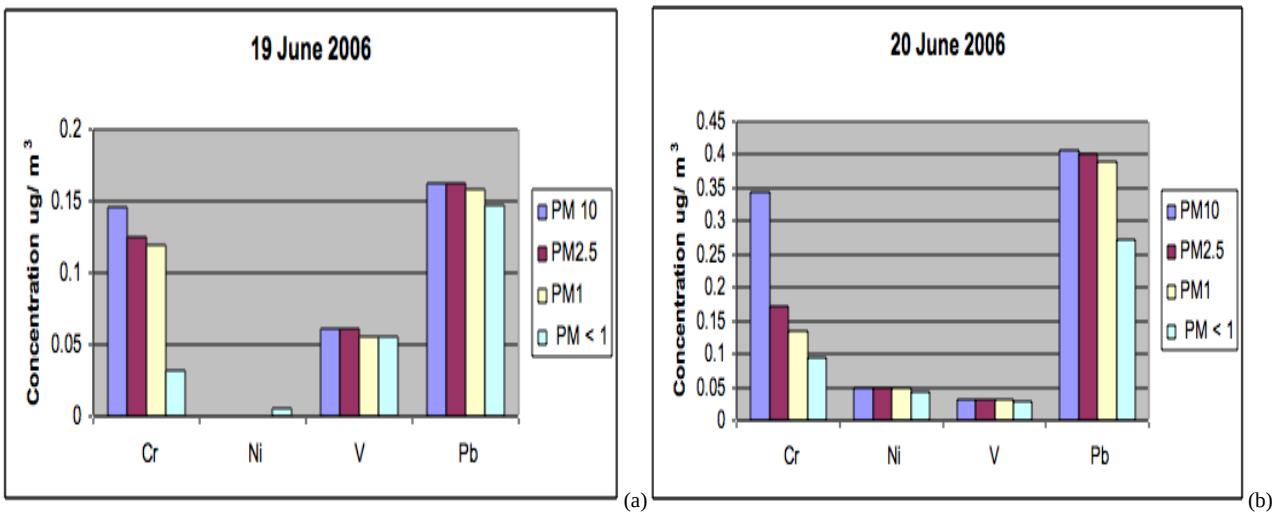

Fig. 2 (a) Elemental Composition for Monday (b) Elemental Composition for Tuesday

It is noted that on this particular day, the wind speed was high from morning to about noon, and it changed direction from south-easterly (102^0) to north-westerly (205^0) to north-easterly (53^0). From the location of the sampling site shown in Fig. 1, it is observed that vehicle emissions from the neighboring mining areas resulting from transportation of raw materials by the trucks and the trains contributed to the collected data. In addition, close to the sampling site there is a smelting operation, whose raw material is transported to two concentrator plants via rail where it is milled. The milled ore is introduced to flotation banks where particles containing precious metals are separated as a concentrate leaving non-valuable tails which are deposited onto tailings dams. The production of platinum from the mines includes Cr which is also produced as part of the waste.

The occurrence of Cr and Ni indicates the anthropogenic origin of particulate aerosols while the occurrence of V and Pb in the early morning hours is due to road dust and local traffic. The elements Cr and Fe may be the results of abundant ferrochrome mining activities in Rustenburg. Fig. 1 shows that there is a road and a railway track on the south side of the sampling site which might have been the cause of the increase of emissions of Pb. Vanadium is also observed in all PM. With the wind coming from east-southerly, the emission could be influenced by a vanadium plant and the burning of fuel oils on the easterly side.

In Fig. 2(b), the elements identified as abundant in the PM_{10} are Pb and Cr with a concentrations of 0.41 $\mu g/m^3$ and just below 0.35 $\mu g/m^3$ respectively. From the prevailing meteorological parameters and the PM concentrations already given, it is clear that the main sources of the toxic elements found in the emissions are the local industries.

The measured concentrations of Cr during the week in Fig. 2(a) and (b) did not exceed the limits of 1 $\mu g.m^{-3}$ for NIOSH and 1.5 $\mu g.m^{-3}$ for APCEL; the values obtained in this study were largely between 0.1 $\mu g.m^{-3}$ and 0.6 $\mu g.m^{-3}$. Cr had high concentration levels even though the standards were not exceeded. Lead (Pb) did not exceed the WHO standard since it is 0.5 $\mu g.m^{-3}$ and the lead concentrations found in this study were 0.41 $\mu g.m^{-3}$. For V, the level of 1 $\mu g.m^{-3}$ recommended by WHO was not exceeded since V had the lowest concentration on this day with less than 0.05 $\mu g.m^{-3}$; while Ni, which is considered to be not safe at any level, was found to be 0.05 $\mu g.m^{-3}$ on the same day.

B. Day-Time Elemental Composition of PM on Weekends

Fig. 3(a) shows the four toxic elements which were determined for all size particles on the weekend of 24th June. It shows that the concentration of Cr was high particularly in PM_{10} and that it exceeded the NIOSH standard. The concentration of Cr in the $PM_{2.5}$ sample was also high even though it did not exceed the standards.

In Fig. 3(b), the NIOSH standard for Cr was exceeded in both PM_{10} and $PM_{2.5}$. The wind speed on this day was 1.7 m/s and it came from the direction of the platinum mine, a ferrochrome mine and waste dumps. These Cr concentrations were identified for all size particles.

The high speed wind also came from the direction of the smelter (250^0) in the platinum plant. The wind direction in the morning was 20^0 north-easterly and changed in the afternoon to north-westerly. In the vicinity of the sampling site are the community residence, road, railway track, a vanadium plant and a platinum plant on the east side. The pollutants from the industries and mines are thus responsible for high concentrations of all the four toxic elements. On the weekend, the wind

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speed was high in the afternoon and caused the particles to move in the north-westerly direction of (345^0), and the $PM_{2.5}$ episode may have been caused by the waste dumping of chrome to the west of the site. Cr concentration levels were very high at more than 1 $\mu g.m^{-3}$, and they were identified for all mass size particles. The occurrence of Cr and Ni indicates the anthropogenic origin of particulate aerosols while that of V and Pb indicates the contribution from road dust and local traffic.

In summary, it is shown in Fig. 3(a) that Cr exceeded the limits of 1 $\mu g.m^{-3}$ for NIOSH and also the limit of 1.5 $\mu g.m^{-3}$ for APCEL. Pb did not exceed the WHO standard of 0.5 $\mu g.m^{-3}$, neither did V exceed the levels of 1 $\mu g.m^{-3}$ set by WHO. It is also noted that V had the lowest concentration on this day. In Fig. 3(b), the Cr exceeded the limits of 1 $\mu g.m^{-3}$ for NIOSH but did not exceed 1.5 $\mu g.m^{-3}$ for APCEL. Pb did not exceed the WHO standard of 0.5 $\mu g.m^{-3}$ nevertheless lead concentrations were very high at 0.3 $\mu g.m^{-3}$. The V limit of 1 $\mu g.m^{-3}$ for WHO were not exceeded and V had the lowest concentration of all elements on this day.

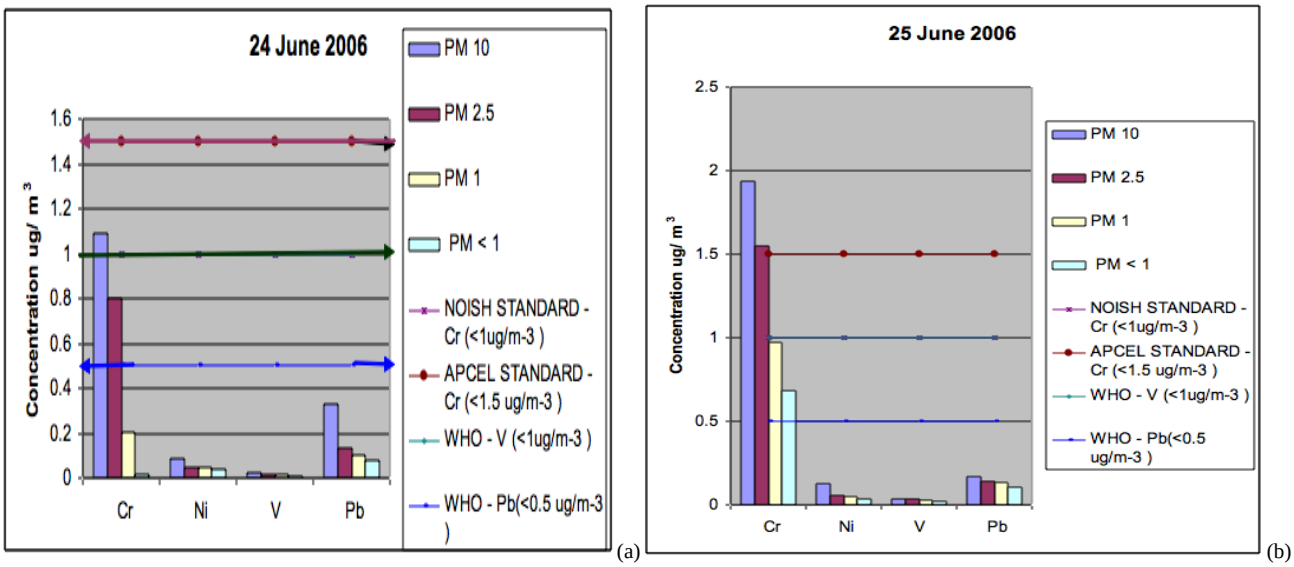

Fig. 3 (a) Elemental Composition for Saturday, (b) Elemental Composition for Sunday

C. Night-Time Elemental Composition of PM on Weekdays

Fig. 4 shows the four toxic elements identified in all particle sizes. The distributions of the metals in different size particles showed similar patterns but the concentrations of Cr and Pb were higher than those of Ni and V. Even though all the elements were identified, the amount of exposure was however low. This could have been as a result of some operations not continuing during the night. The standards for all elements were not exceeded during night time for weekdays. This helps with regards to health considerations.

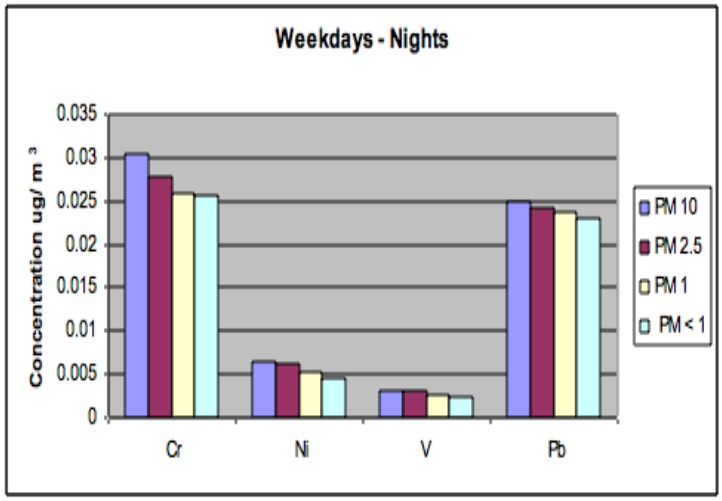

Fig. 4 Elemental Composition of Particulate Matter (PM) for Weekdays Night – times

D. Night-time Elemental Composition of PM in Rustenburg on Weekends

Fig. 5 on the weekend shows that the concentrations were very high for Cr in PM_{10}, $PM_{2.5}$ and PM_1. With the wind from the direction of 244^0 which is the direction of a smelter relative to the sampling site, the smelter and waste dumps of platinum

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were likely emission sources. Cr had a night concentration of 0.1 μg.m^{-3}, which was very high when compared with the concentration during weekdays and suggested that there could have been a different mode of operation during this period. All four toxic elements were observed in all particle sizes.

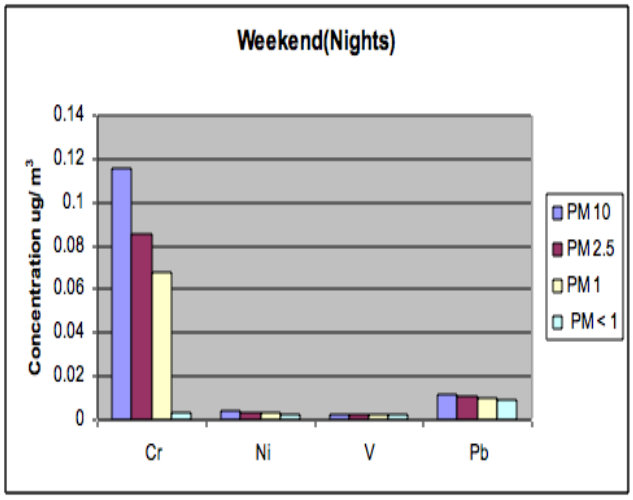

Fig. 5 Elemental composition for particulate matter (PM) for weekend – night

E. Comparison of Toxic Elements (Pb, Cr, Ni, V) Concentrations with International Air Quality Standards

The toxic element concentrations were compared with the international air quality standards. This type of comparison is useful in determining the health risks associated with these toxic elements. The mean concentration of the toxic metals obtained from each study site is compared with the available exposure limits in Table 1.

TABLE 1 SUMMARY OF THE CONCENTRATION OF THE POTENTIAL TOXIC TRACE METALS IN RUSTENBURG AND KHUMA AREAS

Toxic Metal	**Three Hourly Concentration Range (μg.m^{-3})**	**Exposure Limit(μg.m^{-3})**
Cr	0.02 – 5.2	1 - NIOSH 1.5 - APCEL
Ni	0.0012 – 0.04	No safe level – WHO
V	0.003 – 0.06	1 - WHO
Pb	0.004 – 0.3	0.5 - WHO

The levels of Cr exceeded the limits set by NIOSH and APCEL. This metal is one of the harmful substances which should be managed well. Since the concentrations of Ni were in the range from 0.0012 to 0.04 μg.m^{-3} and there is no safe level, any concentration of Ni that is released into the air is harmful. The concentrations of V and Pb were on an acceptable level since they did not exceed any standards.

F. Health Implications of the Toxic Trace Metals

The toxic elements Cr, V, Ni and Pb were identified during day-time sampling periods with Cr dominating. The Pb identified in the morning and afternoons maybe indicative of traffic. The night-time elemental levels were lower than day-time concentrations; which indicates that the elements are linked to domestic, vehicular emissions and industrial activities. These suggest that the exposure and hence the health impacts are high in this area since people are mostly outdoors during the day as opposed to the night time.

During weekends, the occurrence and concentration of Cr were higher than the other elements at night-time. The concentrations can be related to the crustal deposits of Cr in the area as observed by Kgabi et al. [11] in Rustenburg, which is the result of long term (years) ferrochrome mining activities in the area.

For the health implications of these metals, Cr and Ni in particular cannot be underestimated considering the fact that they occur even in the smallest (PM_1 and PM<1) particle sizes. Figueroa et al. [12] confirmed that most of the toxic metals in the air occur in the form of fine particles. It is suggested that these metals can produce lung tissue damage by catalyzing oxidant

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formation [13]. Frampton et al. [14] observed that the metals also promote the release of inflammatory mediators and cyto-toxicity. While larger particles are usually deposited onto the cilium at the bronchus or in the nose and mouth region, and can cause tickling and irritation with coughing for short periods; smaller ($PM_{2.5-1}$) and especially ultra-fine particles (UFPs, PM<1) can travel all the way to the lungs and the alveoli without being deposited in the bronchus [15]. The membrane at the bottom of the alveoli is exceptionally thin so that oxygen can effectively enter the bloodstream. UFPs and fat-soluble compounds on the surface of bigger PM are so small that they may be able to pass through this thin membrane [16]; and can travel anywhere within the bloodstream and their effects in the body are hard to recognize. The body can also get rid of larger particles through exhalation but the smaller particles in the lungs may remain inside the body for months or years. Some particles in the bloodstream may never exit the body [15]. The fine particle size also determines the residence time and mobility of particles, which in turn determines the exposure time and hence the health impacts. Raes et al. [17] found that the atmospheric lifetime of $PM_{2.5}$ is in the order of days to weeks, and showed that they can travel hundreds to thousands of kilometers. These characteristics can result in prolonged exposure and promoting or aggravating health problems [12]. The toxic levels observed in the Rustenburg area thus confirmed to be of long term health significance.

IV. CONCLUSIONS

The occurrence of the toxic metals chromium (Cr), Lead (Pb), Nickel (Ni) and Vanadium (V) in atmospheric aerosols of different sizes in the Rustenburg was successfully determined. The main objective of this study (determination of toxic metals in different sizes of particulate matter) was achieved by using the Particle Induced X-ray Emission technique.

Particle induced X-ray emission analyses of samples collected have shown that several heavy metals were emitted into the atmosphere from industries and area-based sources, and these metals were associated with particulate matter in air. The toxic metals were mostly determined on the finer particles, which can penetrate much deeper into the lungs.

Lead emissions from motor vehicles and petroleum services were found to be in large amounts; and while lead is a critical air pollutant, it did not exceed the South African Standards. The reason could be that most of the cars use unleaded petrol, but trucks still use diesel containing a fair amount of lead. Chromium was abundant in almost all PM sizes while vanadium had the lowest concentrations.

All the four toxic metals (Cr, Ni, V and Pb) were identified in the fine particles (PM < 1) for the Rustenburg area. This is an important finding in view of their negative health effects because of their deeper penetration into the human system. This also implies that more people living around Rustenburg area are at risk of respiratory diseases due to high levels of ambient concentration of heavy metals measured in particulate matter. The results obtained on one weekday showed that Cr exceeded the limit of 1 $\mu g.m^{-3}$ for NIOSH and also the limit of 1.5 $\mu g.m^{-3}$ for APCEL. Pb did not exceed the WHO standards of 0.5 $\mu g.m^{-3}$ neither did V exceed the levels of 1 $\mu g.m^{-3}$ set by WHO on that same day. The results obtained on another day also showed that Cr exceeded the limits of 1 $\mu g.m^{-3}$ for NIOSH but did not exceed 1.5 $\mu g.m^{-3}$ for APCEL. Pb did not exceed the WHO standard of 0.5 $\mu g.m^{-3}$ nevertheless Pb concentrations were generally very high at 0.3 $\mu g.m^{-3}$. The Cr concentration at night on weekend was found to be high when compared with the concentration during weekdays and this was likely attributed to a different mode of operation. It was further shown that the type of domestic and industrial activity around a pollution source relates to the type of elements present in the particulate matter for the specific area.

Particle induced X-ray emission thus proved to be effective in the determination of the elemental composition of atmospheric aerosols. This technique is sensitive, fast, and accurate since it could measure several metals simultaneously.

There is a need for more prolonged and continuous studies so as to establish trends and seasonal variations in particulate matter and the toxic metals.

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