Screening of various diesel particulate matter samples from various commodity mines

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ABSTRACT: This paper presents qualitative analysis results of diesel particulate matter (DPM) from various mining commodities in South Africa. The objective of this work was to determine the concentrations of elements in DPM samples. For this screening exercise, inductively coupled plasma (ICP) spectrometry was used to identify trace elements and other metal elements in the DPM samples. Most of the trace elements did not give a sufficient instrument response to warrant further evaluation. However, the concentrations of calcium (Ca), nickel (Ni), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), and chromium (Cr) for most samples were detectable.

1 INTRODUCTION

Diesel exhaust emissions consist of a mixture of gases, vapours and particulate matter and were classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) in 2012 (IARC 2012). Diesel particulate matter (DPM) is the ultra-fine carbon-based particulate fraction (< 1 µm) of diesel engine exhaust. Due to their particle size they remain airborne in the atmosphere for extended periods of time and can be inhaled by humans long after they were formed as a result of incomplete combustion. These particulates pose a serious health hazard to humans because of their toxicity (Choi, Mochida 1990), (Sydbom et al. 2001).

Diesel engine exhaust is a complex mixture and studies have been conducted to determine the composition thereof (Watson, Chow & Chen 2005). Polyaromatic hydrocarbons (PAHs), soot particulate matter, non-organic compounds such as sulphates and metal ash were discovered in samples investigated during these studies (Liati et al. 2013), (Forbes et al. 2013).

This paper aims to investigate the inorganic composition of DPM within the context of the South African mining industry.

2 BACKGROUND

Diesel exhaust emission is the result of combusted diesel fuel and has a complex composition. The composition depends on a number of factors such as the engine technology, the type of fuel used, condition of the engine etc. (Birch 2003).

DPM consists mainly of elemental carbon (EC) and organic carbon (OC) and for this reason EC was chosen as a marker (Birch 2003). The employee exposure monitoring for DPM is carried out against the EC marker using the National Institute of Occupational Safety and Health’s (NIOSH) analytical method, NIOSH 5040.

A comprehensive study was carried out in three South African Platinum mines to determine the health outcomes of mine employees that were exposed to DPM (Pretorius et al. 2014). One part of the project aimed to characterise the OC fraction of DPM. It was found that heavier PAHs, such as pyrene and fluoranthene were associated with DPM (Forbes et al. 2013), (Geldenhuys et al. 2015). These compounds have been linked to environmental cancers (Dybing et al. 2013) and pyrene in particular, is considered to be a co-carcinogen with other PAH carcinogens such as benzo[a]pyrene (Baturay, Kennedy 1986).

DPM forms as a result of incomplete combustion of diesel fuel in diesel engines. In the ideal process, it is expected that there are very little or no metal elements associated with DPM since the source of diesel emissions is from the combustion of diesel fuel. However, in reality other particulates that form during diesel combustion are metal ash (Liati et al. 2013). When metal elements are detected from the exhaust samples, it is an indication that a different, unwanted process was taking place during the combustion of the diesel fuel. In some cases the fuel or combustion chamber could also be contaminated.

The health effects of metal ash have not been comprehensively studied (Liati et al. 2013) even though metals bound to particulate matter in ambient air have been associated with respiratory and cardiovascular diseases (Betha, Balasubramanian 2013). The ash may contain metal oxides, sulphates or phosphate compounds that originate from the combustion of lubrication oil or contaminated diesel. Alternatively, metals present in ash may originate as a result of wear and corrosion of the engine parts (Liati et al. 2013).

Proper maintenance of diesel powered engines has been found to be the most effective control measure for DPM (Stachulak 2003). In a pilot study that was carried out in South African platinum mines, a positive correlation was found between the wear metals in engine oil and the DPM concentrations that mine employees are exposed to (Pretorius 2015). Although oil and diesel fuel are often analysed and tested, there is the potential to analyse DPM samples for wear metals.

This paper shows the results that were obtained from the metal screening of DPM filters.

3 METHODOLOGY

Ten DPM samples were randomly chosen for the screening exercise. These samples were taken from storage after they were submitted to the laboratory for DPM analysis. Nine samples were collected in an underground mining environment from different commodity mines. It was not known to the laboratory whether these samples were personal monitoring or exhaust emission samples. One sample was collected in a controlled environment directly from the diesel exhaust. A blank tissue quartz filter was included in the analysis to take trace elements in the filter media into account.

The DPM was sampled onto a 37 mm tissue quartz filter as per the NIOSH 5040 method. Samples with different DPM concentrations were chosen for the elemental screening. Table 1 lists the different samples and the source mines where they originated from.

Table 1: Sample numbers and commodity mine source

Sample nr	Commodity
Blank	Blank filter
V01	Platinum mine A
V02	Platinum mine B
V03	Platinum mine B
V04	Copper
V05	Coal
V06	Gold mine A
V07	Gold mine B
V08	Gold mine B
V09	Controlled environment
V10	Chrome

The samples were first analysed for DPM using method NIOSH 5040. A 1.5 cm^2 specimen was taken from the sampled filter and analysed on a thermo-optical DPM analyser. A blank filter was also analysed to record the trace EC and OC for the filter media. Another 1.5 cm^2 specimen from each filter was chemically digested in a mixture of hydrochloric (HCl) and nitric acid (HNO3). The elemental screening was carried out using ICP optical emission spectrometry (ICP-OES) and ICP mass spectrometry (ICP-MS) to cover a range of the trace metal concentrations.

The samples were qualitatively analysed for 43 elements and the results were reported in mg/l. The results from the 1.5 cm^2 specimen were converted back to the filter deposition area (8.04 cm^2) as an even distribution was assumed based on the findings of previous studies.

4 RESULTS AND DISCUSSION

The results relate only to the samples that were qualitatively analysed and cannot be extrapolated to the broader population of an individual mine, or the broader mining industry. The analysis results from the blank filter are also only representative of the individual filter that was analysed and is not necessarily representative of all tissue quartz filters.
Table 2 shows the results obtained from the DPM analysis. The EC concentrations ranged from 0.001 to 4.93 mg (median 0.24) and the OC concentrations from 0.04 to 0.66 mg (median 0.16 mg). When sample V04 is excluded, all the samples have DPM concentrations below 2 mg (Figure 1).

Sample	OC (mg)	EC (mg)	TC (mg)
Blank	0.046	0.000	0.046
V01	0.040	0.010	0.050
V02	0.080	0.010	0.090
V03	0.350	0.890	1.240
V04	0.660	4.930	5.590
V05	0.210	1.260	1.470
V06	0.240	0.240	0.480
V07	0.130	0.090	0.220
V08	0.090	0.050	0.130
V09	0.160	0.390	0.540
V10	0.447	0.719	1.166

Table 2: Comparison of the OC, EC and TC concentrations on selected samples

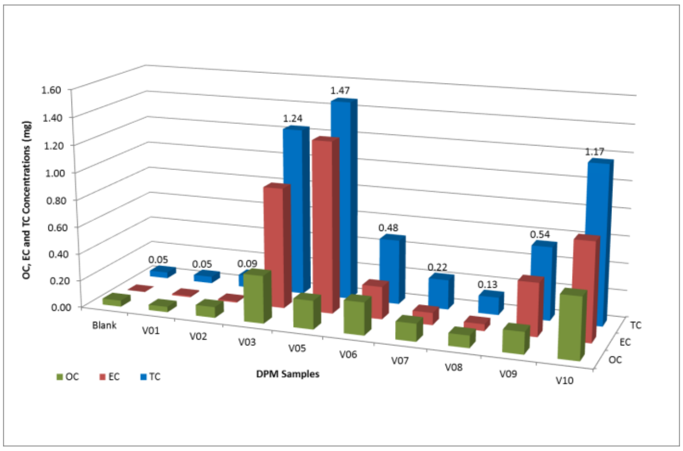

Figure 1: OC, EC and TC concentrations excluding sample V04

The samples were qualitatively analysed for 43 elements. Since this was a screening exercise the analytical detection limit for each element was not determined. The exclusion of some elements were made as a result of the low qualitative response from the instrumentation. For this reason only 16 elements were selected for further evaluation. Figure 2 summarises the ICP results (in mg/L) for the 16 elements on all the DPM samples.

Sample V10 stands out as having significantly higher concentrations of chrome (Cr), iron (Fe) and nickel (Ni) when compared to the other samples. The Cr may be attributed to the presence of some ore dust on the filter as the sample originates from chrome mine. The Ni may be attributed to the combustion of diesel fuel and engine oil but the presence of Ni from mineral ore dust may not be excluded. Fe may be attributed to wear metals.

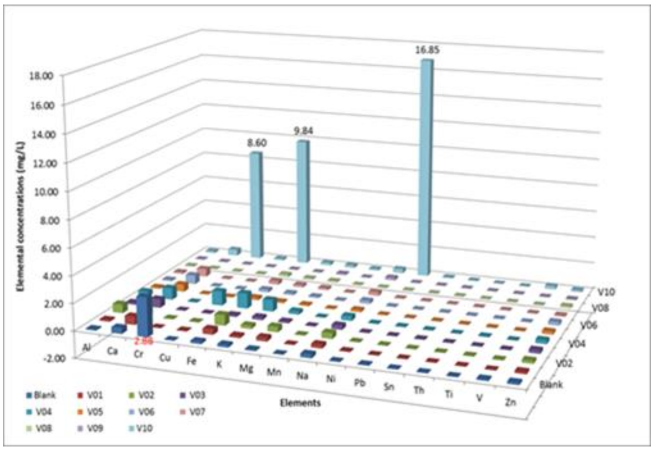

Figure 2: Comparison of the ICP results (mg/L) for the DPM filters

Sample V04 had significant concentrations of aluminium (Al), calcium (Ca), copper (Cu), iron (Fe), potassium (K), sodium (Na), and zinc (Zn) present. Fe may be as a result of engine wear but then it would be expected that the presence of other wear metals would have been higher. Although the other elements may be from additives in the engine oil, the presence of ore dust was not excluded.

It is not clear if the Cr in the blank filter sample originates from the filter media itself or if it was a contamination. Other notable elements in the filter media were Al, Fe, K, magnesium (Mg), Na, vanadium (V) and Zn.

For the sake of clarity the samples Blank filter, V04 and V10 were excluded from the graph and Figure 3 shows the comparison of metal elements in the remaining samples. All the samples contain substantial concentrations of Al, Ca, Fe, K, magnesium (Mg), Na, and Zn. The Al, Ca, Mg, K and Zn may originate from some additives that are found in engine oil (Liati et al. 2013). Fe may be as a result of engine wear but then it would have been expected that the concentrations of elements such as Cr, nickel (Ni) and Pb would have been higher.

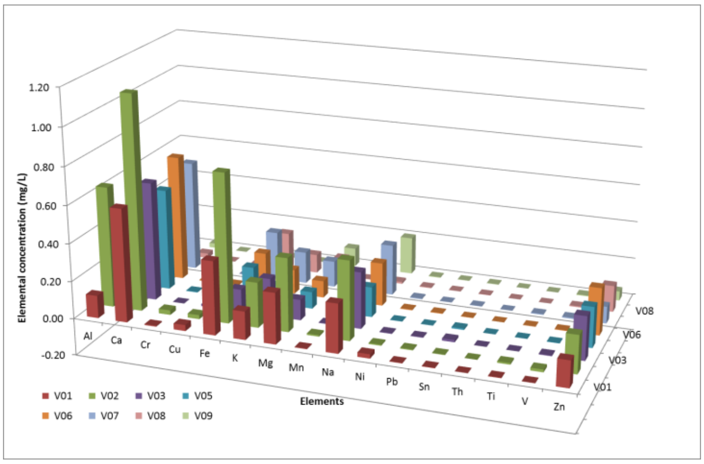

Figure 3: Comparison of the ICP results (mg/L) when the Blank, V04 and V10 were excluded

5 CONCLUSION

DPM filters were qualitatively analysed for 43 inorganic elements to determine the presence and estimated concentrations of metals. Only 16 elements were selected for further evaluation since the qualitative response from the instrumentation were sufficient enough for this screening exercise.

Two samples stood out because of the significantly higher concentrations of some elements when compared to the other samples: Sample V04 from the copper mine (Al, Ca, Cu, Fe, K, Na, , and Zn) and sample V10 from the chrome mine (Cr, Fe and Ni). The other filters had substantial concentrations of Al, Ca, Fe, K, Mg, Na and Zn present. These elements can be attributed to engine oil or wear of engine components.

On some of the samples (e.g. V10), there may have been interference from mineral ore dust. The blank filter also contained substantial concentrations of certain elements. For further method development, corrections should be made for the trace elemental content of the blank and the mineral ore dust.

Further characterisation of the inorganic components of DPM is planned with the use of scanning electron microscopy (particle size and element concentration) and laser light-scattering (particle size).

The qualitative analysis of DPM samples for metal elements may be used as part of the occupational hygiene risk assessment and/or diesel engine conditions monitoring programmes.

The conditions under which the samples were taken were not known (i.e. volume of personal exposure sample). But it should be noted that some of the DPM and elemental concentrations may be above regulated limits for personal occupational exposure to airborne pollutants.

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