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Spatial Distribution and Source Identification of Mercury in Dust Affected by Gold Mining in Johannesburg, South Africa

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Abstract - Mercury concentrations (Hg_{TOT}) were analysed in total and size fractions in urban dust. The results showed that Hg_{TOT} ranged from 270 to 1350 µg kg^{-1} for PM_{25} particle size fraction. The distribution was as follows: $Hg_{Industrial} > Hg_{CBD} > Hg_{Residential}$. The Hg_{TOT} showed a positive correlation with percent volume of the PM_{25} size fraction. This indicated that as the particles size decreased, the Hg_{TOT} increased. The dust was mainly characterized by high concentration levels of quartz (74.3 to 97.6 wt. %). The tailings dumps showed similar levels of quartz (65 to 81 wt. %), which indicated that tailings are the major anthropogenic sources of mercury in the dust. Both, the tailings dumps and the dust samples showed well defined crystalline structures of the quartz coated with trace elements.

Keywords**:** Mercury, Particulate Matter, Dust, Tailings dumps

1. Introduction

Gold mining in the Witwatersrand basin commenced in 1886, and the initial method of extraction was the mercury amalgamation. This process led to the generation of sand dumps, which are characterized by large particle sizes, are often domed shaped, and still contain small amount of gold (0.6 g t^{-1}) [1]. As mining became deeper, unoxidised sulphidic pyrites ores interfered with the extraction. This led to the introduction of the MacArthur-Forrest cyanide extraction process. The waste generated after extraction was pumped into large tailings dumps known as slimes dumps[2,3].

To date, approximately 270 tailings dumps covering an area of 181 km^2 have been identified in Gauteng, South Africa [2], of which about 70 were reclaimed, resulting in about 13 km^2 of land becoming available for potential development. However, tailings footprints contain significant variable quantities of residual material. The exposure of surfaces to oxygenated rain water, led to the oxidation of pyrites, forming acid mine drainage (AMD), and leaching minerals into groundwaters [4]. The surfaces remained acidic, lacked normal levels of soil nutrients and did not develop normal soil structure hence could not support the establishment of plant cover. The exposed surfaces are subjected to wind erosion and led to increased dust fallout incidents and eventually dust pollution. This is excessibated by the prevailing north westerly winds, which are dominant from July to October, where winds speeds > 7 m s^{-1} can be achieved [5], and when the surface of the mine dumps are dry. The effect of prevailing winds in redistribution of contaminants plays a significant role in the soil contamination accumulating trace elements a distance away from the source [6,7,8]. The milled slimes dams have a greater fraction of finer material than older sand dumps, and also contain a higher fraction of respirable and inhalable particles [5].

Dust and aerosol emissions from gold mining operations are commonly associated with significantly elevated levels of metals, which accumulate in soils, natural waters and vegetation [9,10]. Contaminants commonly associated with particulates from mining operations are mostly concentrated in the finer particle fraction, which travelled greater distances [11]. Resuspension of the dust and fine soil fraction can contribute a significant amount to the inhalable trace element load of urban aerosol or it can be washed-out where it can become an important component of suspended and dissolved solids in street run-off.

Mercury in South Africa occurs together with the gold ore, ranging from 1.2 to 4.6 wt. % [1]. The amalgamation process used for gold mining up until 1920 is currently used by increasing artisanal gold mining. The inefficiencies of the amalgamation process resulted in massive release of mercury into the atmosphere and pollution of the water system and the land [12]. A lot of work had been done in the world and in South Africa on mercury in coal, with emphasis on the mode of

occurrence, and its release into the atmosphere [13]. However, little is known about mercury release due to gold mining activity in South Africa.

2. Materials and Methods

2.1. Sampling Protocol

Dust samples were collected across the city using a brush and pan, on impervious pavements along both sides of the road, transferred to zip lock polyethylene bags, and transported to the laboratory. The samples collected were distributed as follows: industrial area (28), CBD (9), and residential areas (13), represented in Figure 1. Samples were collected during the dry and sunny weather conditions. These samples were dried in an oven at 40°C for two days and then separated into three particle size fractions (PM_{25}; PM_{50}; PM_{100}). PM_{25} was chosen as the particle size fraction of choice because finer fractions generally contain higher heavy metal concentrations [14], are considered to be hazardous and furthermore are easily inhalable. After separation, the sieved samples were preserved in acid washed plastic containers at 4°C until the total mercury determination and characterization of dust experiments.

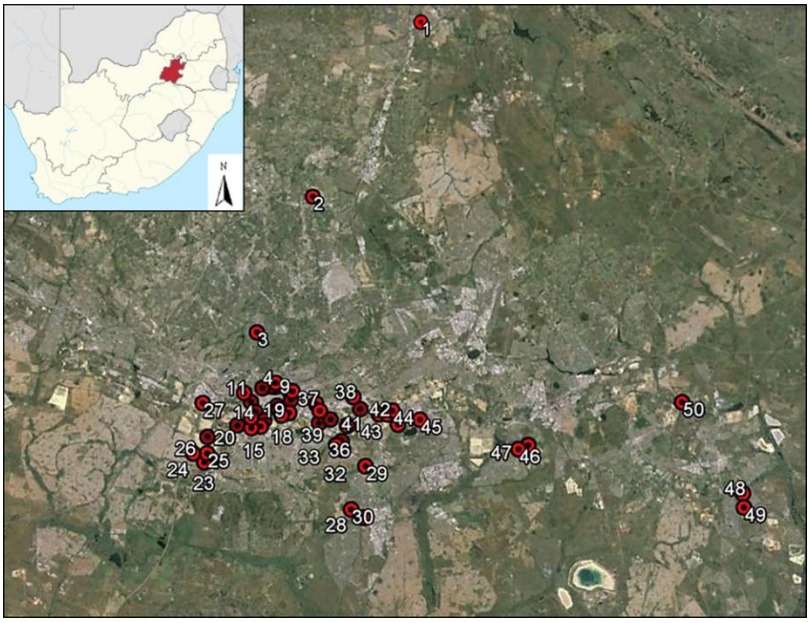

Fig. 1: The location of the dust samples from the study sites in Johannesburg, South Africa.

2.2. Analytical Procedures and Characterization Techniques

Total Mercury Determination

Dust samples were extracted using a microwave system (Multiwave 3000, Anton Paar, Graz, Austria). Aliquots (0.25 g) of dust (PM_{25}) were mixed with 13 mL of concentrated acids ($HCl:HNO_3:HF$ = 9:3:1 (v/v/v)). After digestion, the HF was neutralized with 4% (w/v) boric acid (H3BO3) and filtered using the 0.45 µm membrane filter paper. The filtrate was stored in plastic bottles and kept in a refrigerator. HgTOT was determined by mercury analyser (FIMS 400 FIAS-AAS, Perkin Elmer, Norwalk, Connecticut, USA) with an AS-91 auto sampler.

Calibration standards were prepared using mercury standards (Ultraspec, Merck, Dorset, UK), and suprapur grade chemicals for ultra-trace analysis (99.999% purity) (Sigma Aldrich, Germany). The accuracy of the extraction and determination of mercury in dust procedure was checked using standard reference material, LGC 6187 analysed routinely. The total mercury value of 1.44 ± 0.03 mg kg^{-1} were in agreement with the certified concentration of 1.40 mg kg^{-1}. Procedural blanks were simultaneously processed with dust samples, and were analysed after every 10 measurements. The limits of detection were determined as 3 × standard deviation (SD) of the blank samples, which was 0.1310 µg L^{-1} The relative standard deviation for each replicate was less than 10%, and the recovery of the reference material for mercury was between 98 and 105%.

Characterization Methods

Particle size distribution. was determined by the MS-14 Particle Sizer (Malvern Instruments Ltd., Worcestershire, UK). *Mineralogy and elemental composition of the dust samples* was determined by D2 Phaser X-ray diffraction (XRF, Bruker-AXS Gmbh, Karlsruhe, Germany) and Energy dispersive X-ray fluorescence spectrometry (ED XRF tracer SD II, Bruker-AXS Gmbh, Karlsruhe, Germany). The X-ray diffractograms were analysed using Eva diffract plus evaluation software. *Surface morphology of dust* was determined using the high vacuum scanning electron microscopy (FEI Nova Nanolab 600 Dual beam FIB/SEM) equipped with EDS.

Statistical Analysis

Pearson's correlation coefficients (r) were used to calculate correlations between Hg_{TOT} in the dust and particle size distribution. To determine the significant differences at different sampling sites, a one-way analysis of variance (ANOVA), Tukey's honest significant difference test was employed, because of normalisation of the data. All statistical analyses were computed by using Minitab version 16.

3. Results and Discussion

3.1. Hg_{TOT} Concentration in Dust Fractions

Hg_{TOT} in the greater Johannesburg dust ranged from 80 to 243 (PM_{100}), 122 to 499 (PM_{50}), and 270 to 1349 (PM_{25}) µg kg^{-1}, with a mean of 151, 291, and 600 µg kg^{-1}, respectively (Figure 2). These values were about 2, 3, and 7 times higher than the crustal value of Hg in soils (85 µg kg^{-1}) for PM_{100}, PM_{50}, and PM_{25}, respectively.

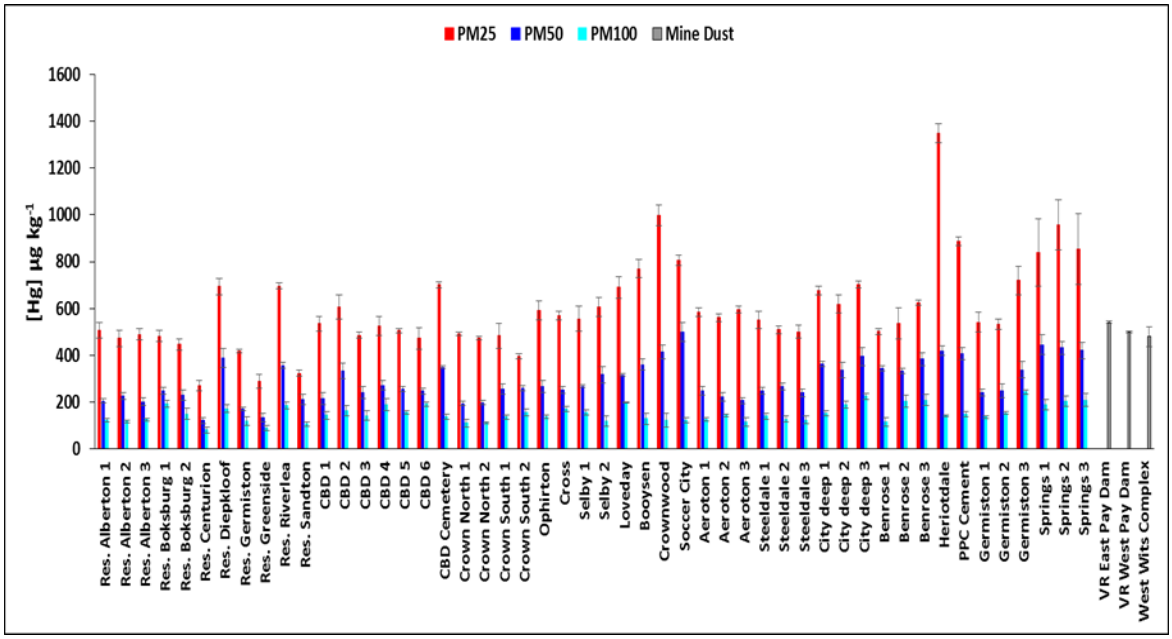

Fig. 2: Comparison of mean HgTOT concentration in three different particle size fractions of dust samples.

The highest concentration of $Hg_{TOT,}$ was observed in the industrial sites followed by the Central Business District (CBD) and lastly residential areas (Figure 3). This trend was evident in all the three particle size fractions with the highest Hg_{TOT} in PM_{25}. This showed that the Hg_{TOT} increased with a decrease in the particle size.

HgTOT in PM25 from industrial area ranged from 500 to 1349 µg kg-1, with a mean of 687 µg kg-1. The highest HgTOT was found in the tailings storage facilities (TSF) presently under reprocessing (Heriotdale), followed by industrial sites built on TSF footprints (Selby 1 & 2, Loveday, Rosettenville, PPC cement, and Trump), and lastly industrial sites built next to TSF (Aeroton, Benrose, Booysen, City Deep, Germiston, PPC, and Steeldale). PPC site was also affected by the presence of the cement factory in the vicinity [15].

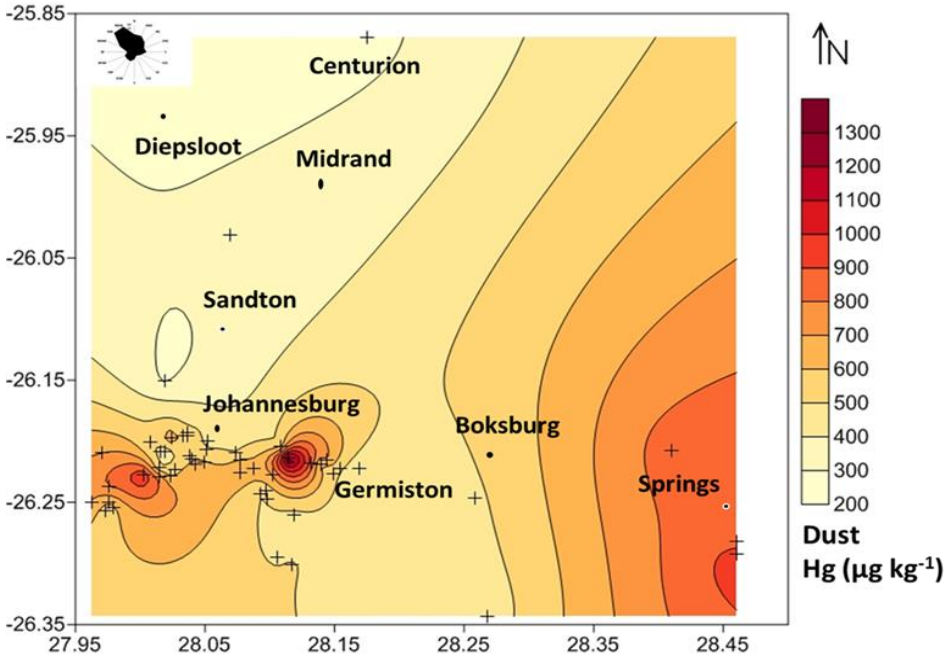

Fig. 3: The spatial distribution of Hg_{TOT} in PM25 in dust samples from the greater Johannesburg, South Africa.

Significant quantities of tailings (footprints and reprocessed tailings) left behind due to gold mining are responsible for the Hg pollution. These tailings are susceptible to wind erosion particularly the unrehabilitated tailings. Heavy metals, including Hg contained in the tailings, are distributed through windblown dust, re-emission and resuspension of dust, leaching by rain water, and seepage to ground water [3, 5, 16, 17]. The prevailing wind plays an integral role in the distribution of metal pollutants laden dust from the tailings. The recorded dominant prevailing wind direction were north north-westerly, north westerly, northerly, and north north-easterly with 13.9%, 13.5%, 9.1%, and 8.9%, respectively. Therefore, the highest Hg_{TOT} were observed in the south-eastern to the south-western parts of Johannesburg CBD. However, the lower Hg_{TOT} was observed to the north of Johannesburg CBD where there is no mining activity.

In the CBD, Hg_{TOT} range from 473 to 702 µg kg^{-1}, with a mean of 548 µg kg^{-1}. The highlight was the highest Hg_{TOT} (702 µg kg^{-1}) coming from the Braamfontein cemetery, with a crematorium whilst the rest of CBD averaged 497 µg kg^{-1}. Meanwhile, the Hg_{TOT} gradually decreased as you move further away from the cemetery.

In the residential areas, Hg_{TOT} ranged from 270 to 697 µg kg^{-1}, with a mean of 462 µg kg^{-1}. The highest Hg_{TOT} was recorded in Riverlea and Diepkloof (Soweto), respectively. This was attributed to the old sand dumps being re-processed in Riverlea while Diepkloof is surrounded by sand dumps in the north-west and tailings slimes dams to the north-east of the township. During heavy dust storms, dust fallout from the tailings was in excess of 2 400 mg m^{-3} day^{-1} [5], having 53% vol. and 37% vol. of PM_{10} and PM_5 (i.e. thoracic and respirable fractions), respectively.

Comparison between sampling sites using one-way analysis of variance (ANOVA). The F_{test} (217.09) > $F_{critical}$ (1.41) implies that the means of the different sampling sites are significantly different. This is expected as they are greatly influenced by the presence of the tailings. The sampling sites were grouped according to their means (Hg_{TOT} concentration). The higher mean values were representative of the sampling sites surrounded by tailings dumps or built on tailings footprint or close to tailings under reprocessing. The lower mean were experienced by sampling sites in the residential areas, further away from the tailings dumps.

3.2. Size Distribution of Dust Samples

The PM_{25} fraction in dust samples ranged from 0.8 to 10.1 % volume from Sandton to Heriotdale, respectively, (Figure 4).

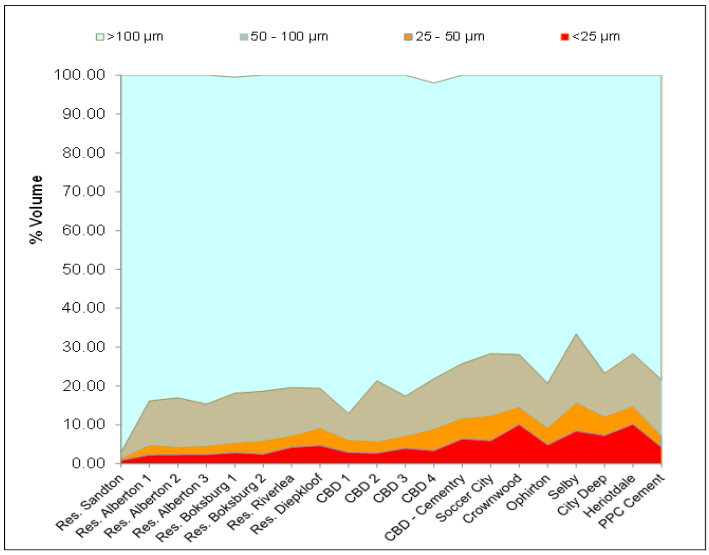

Fig. 4: Particle size distribution in dust.

The particle size analysis showed that the contents of PM_{25}, PM_{50}, PM_{100}, and $>PM_{100}$ in the dust samples of Johannesburg ranged from 0.8 to 10.1, 0.6 to 7.4, 1.4 to 15.9 and 71.7 to 97.2% with averages of 4.6, 3.9, 12.0, and 79.4%, respectively. These results show that about 21% of dust could become suspended into the atmosphere, of which about one twentieth (i.e. less than 0.05%) could enter the respiratory system. The highest % volume of PM_{25} fraction was recorded in industrial samples. The least % volume of PM_{25} fraction was recorded in residential area of Sandton, which was 0.8%. Particles less than 25 µm from industrial areas made up a mean of 7.2% of the dust, which is about 2 times higher than the CBD's mean (3.8%), and 3 times higher than the residential area's mean (2.3%). The remaining particle size fractions (PM_{50} and PM_{100}) followed the same trend as PM_{25} with the order: industrial area > CBD > residential area. Therefore, dust from the industrial areas consisted of higher proportions of inhalable, thoracic and respirable particles with increased risk of adverse health effects to human beings.

The samples that contained low Hg_{TOT} also had low % volume of PM_{25} and vice versa. (Figure 5(a)). However, when considering the PM_{25} size fraction, the correlation analysis showed that mercury concentration positively correlated with the % volume of PM_{25} in dust samples (R^2 = 0.51) (Figure 5 (b)). This explains the significant decrease of mercury levels observed in dust samples moving away from the vicinity of the gold mine tailings dams to the residential areas and also confirmed that gold mining tailings are the main source of mercury pollution in the area.

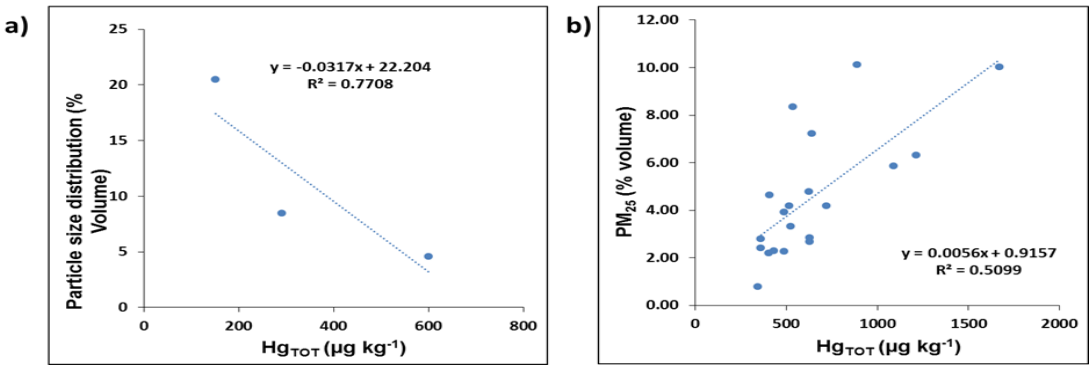

Fig. 5: Correlation coefficients (a) between particle size fractions and Hg_{TOT}, and (b) between % volume in PM_{25} and Hg_{TOT}.

3.3. Mineralogy and Morphology of Dust

The dust is predominantly composed of quartz (SiO_2) (XRD spectra at 21°, 26°, 31°, 50°, and 59° *2θ*) (Figure 6). These results were confirmed by ED-XRF, where the major oxide concentrations were: SiO_2 (30.5 - 86.3%), alumina, Al_2O_3 (13.5 – 19.8%) and hematite, Fe_2O_3 (3.7–7.1%). From this, quartz is the principal oxide with an average of 66.3%,

followed by small concentrations of alumina, arsenic, calcium, chromium, copper, manganese, nickel, potassium, and titanium oxides. In comparison to the tailings material, both from East and West rand, quartz was by far the most dominant mineral phase ranging from 65 to 81 wt. % and 70 to 93 wt. %, averaging 71 and 78 wt. % [5].

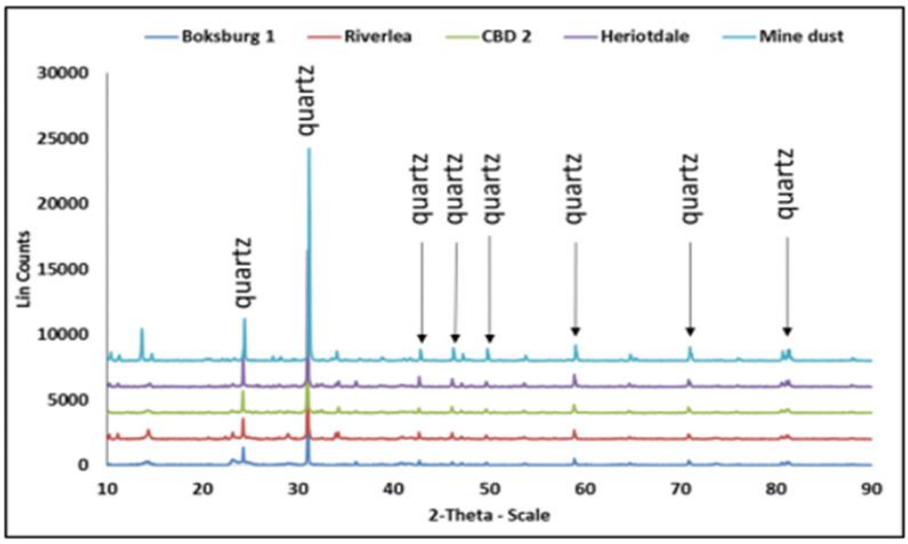

Fig. 6: The mineralogical composition of selected dust samples.

Since dusts are solid particles mobilized by winds into the atmosphere, their chemical composition is similar, if not identical to the source, which is the tailings material. However, dust had the higher amount of quartz as compared to the tailings materials. This could be attributed to the larger concentration of smaller particle size fractions with a large surface area, which allows enrichment of different minerals and mineral phases to take place [18,19,20]. The presence of quartz in large quantities reflects the original type of rock present in this region. Mercury concentration in the environment has a close relation with the regional geography and geology, and the development of the social economy [20].

The minor mineral phases determined from tailings dumps both from the east and west rand were as follows: mica, chlorite, chloritoid, pyrophyllite, clay, gypsum, pyrite, jarosite, pyrite, rutile, hematite, clinochlore, muscovite, and k-feldspar. Total elemental analysis determined the following trace elements: Al. As, Ca, Cd, Co, Cu, Cr, Fe, Hg, Ni, Mn, Mo, Si, Ti, Pb, S, U, V, and Zn, and enrichment of Al, Ca, Fe, Mn, Ti, and Si was observed in the tailings material, street dust and windblown dust (PM_{10} and PM_5 fractions) [5]. However, Al, Ca, Fe, Mn and Si elements are of geologic nature.

The morphology of dust samples was determined by scanning electron microscopy (SEM) (Figure 7).

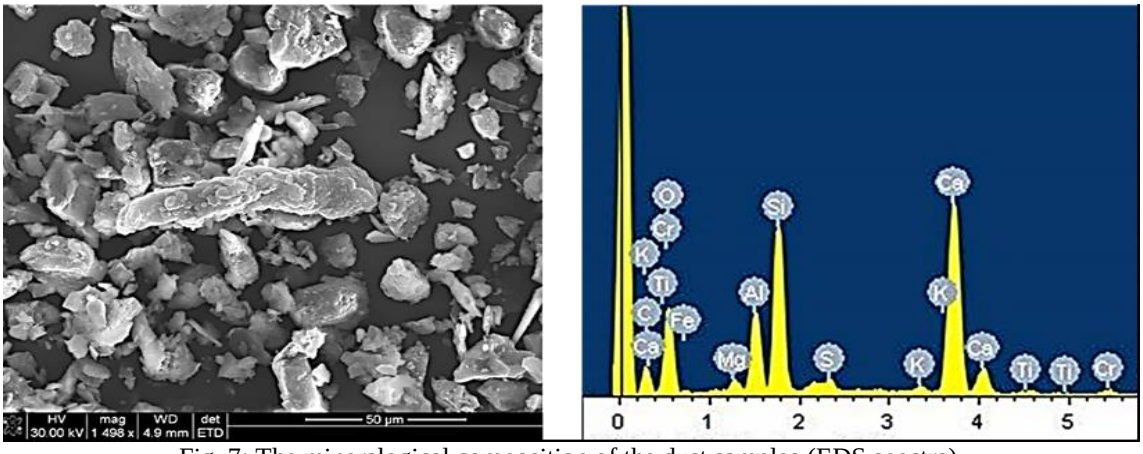

Fig. 7: The mineralogical composition of the dust samples (EDS spectra).

A larger percentage of the particulate matter consisted of quartz with well define crystalline structures and at times coated with other elements such as sulphur, manganese.

3.4. Carbon and Sulphur Analysis

The carbon and sulphur content in the dust are presented in the Figure 8. CBD experienced high carbon content mainly to the proximity of the rail marshalling yard, where oil based products are used in large quantities. The same can be said about industrial areas, where large machinery use oil based products as lubricants and fuel. The sulphur content in dust is extremely low, as expected. The pyrites in top layer of the tailings undergoes oxidation forming AMD, and the sulphur leaches out, as sulphates, into the groundwater or seepage at the sides or foot of the tailings dumps. This result also acts as confirmation that the dust source is the tailings dumps.

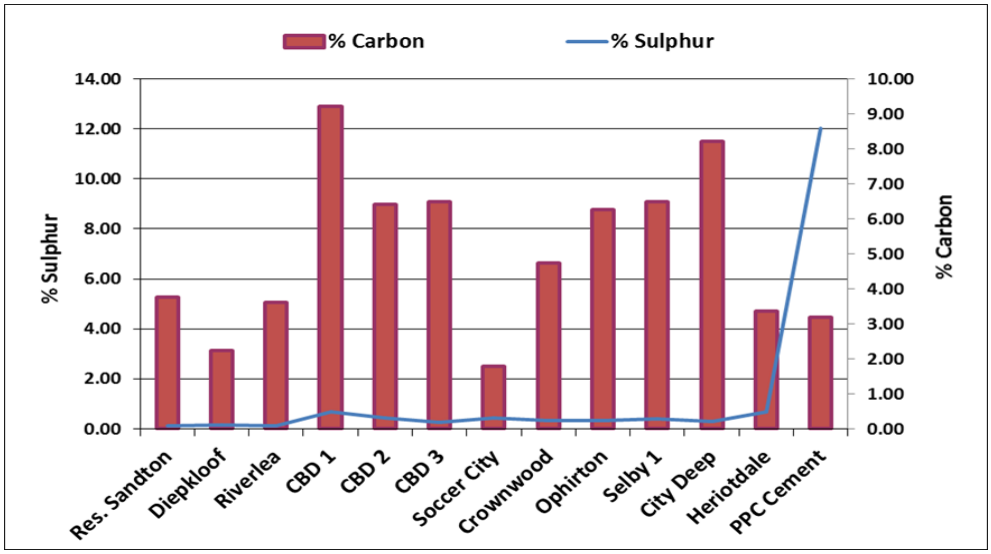

Fig. 8: Carbon and sulphur content in the dust PM25 size fractions.

4. Conclusion

The results of the study show that the distribution of mercury in the dust samples collected from various sites in greater Johannesburg varied widely, and was greatly impacted by the gold mining. The source of the mercury in the dust samples was anthropogenic and appeared to be coming from the tailings dumps. Higher concentration of Hg_{TOT} was observed in areas surrounding the tailings dumps or tailings dumps under reprocessing or build on tailings footprints. Lower Hg_{TOT} was observed in residential areas far from the influence of the tailings dumps. However, residential areas in close proximity to the tailings were highly affected and exhibited high levels of Hg_{TOT}. Both the dust and the tailings dumps samples were characterized by high levels of quartz, and contained similar concentration of trace elements. It was concluded that both sets of samples were almost identical, and therefore, confirming that the source of the mercury in the dust was the tailings dumps.

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