

MEASUREMENT AND CHARACTERIZATION OF DUST-FALL SAMPLES FROM MPUMALANGA PROVINCE, SOUTH AFRICA

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ABSTRACT

Exposure of asbestos dust comes from several sources that include mine dumps, unpaved road made of asbestos materials, blasting, crushing, grinding and milling activities, as well as spillages from trucks carrying the asbestos materials. The threat to human health is exacerbated by wind blowing over uncovered asbestos dust, making it airborne and inhaled by nearby local communities. The aim of this case study is to measure the dust-fall rates, characterize the dust and determine the metal levels in the resulting filtrate solutions within the Mpumalanga study area. The standard method for collection and analysis of dust-fall rates adopted by the American Standard Test Method (ASTM D 1739, 1970) and the South African National Dust Control Regulations (NDC R 827, 2013) was used. Filtrate solutions generated after filtering the collected falling dust were analyzed with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to determine the levels of some trace metals. Dust samples were characterized with a Scanning Electron Microscopy–Energy Dispersive Spectrometry (SEM–EDS) to determine the morphology such as shape, size, length and width of asbestos fibers. Dust-fall rates measured from January to June 2016 were all below the residential standard limit of 600 mg/m²/day at all five sampling sites. Site E was the highest with 478 mg/m²/day measured in May 2016, possibly due to its close proximity to the asbestos mine dump. All trace metals of interest (manganese (Mn), iron (Fe), nickel (Ni), cadmium (Cd) and lead (Pb)) exceeded the local and international standard limits. SEM–EDS results confirm the dominance of silicates minerals that include the serpentine (Mg₃(OH)₄(Si₃O₅), amphibole (NaCa₂(Mg,Fe,Al)₅(Al,Si)₈O₂₂(OH)₂, quartz (SiO₂), plagioclase (NaAlSi₃O), kaolinite (Al₂Si₂O₅(OH)₄Mg,Fe⁺⁺⁵Al(Si₃Al)O₁₀(OH)₈, feldspar (KAISQ₃O₈) and mica (KAl₂(Si₃Al)₁₀(OH)₂. The presence of poisonous metals and asbestos fibers could have negative health impacts to the exposed individuals.

Keywords: asbestos mining, asbestos dust, dust fall rates, mine dumps, NDC R 827-2013, minerals, ASTM D 1739-1970, SEM–EDS, ICP-MS.

1 INTRODUCTION

Asbestos mining has left behind major environmental and health challenges. Wind blowing across the old and abandoned mine dumps transport dust to nearby communities. Asbestos is one of the oldest mineral mined in South Africa (Hart [1]). The risk of being exposed to asbestos dust is increased by the close proximity of human settlements to areas where asbestos minerals were mined and milled (Muculloch [2]). Asbestos materials were used by the rich and royals in the past to preserve the ashes after cremation (Abratt et al. [3]). Inhalation of asbestos dust or fibers is known to cause lung diseases such as asbestosis (scarring of the lungs), lung cancer and mesothelioma (a malignant and fatal tumor that grows on the lining of the lung) (Felix et al. [4]). The purpose of this study is to measure dust fall rates and characterize the resulting dust and filtrate solution samples collected within residential areas that are close to un-rehabilitated mine dumps around the Mpumalanga Province with the intention of assessing the asbestos pollution levels.



2 EXPERIMENTAL DESIGN

2.1 Study area, geology and sampling points

The study area is situated in Mpumalanga Province around residential areas that are near un-rehabilitated asbestos mine dumps within Mbombela (previously known as Nelspruit), Malelane and Carolina towns as shown in Fig. 1. Mbombela is the capital city of the Mpumalanga Province and is located centrally, but on the eastern direction. The province is known to have pine tree and escarpment and mountainous. Dust fall dust samples were collected around five local communities and the sampling sites were within 5 km of the nearby old and abandoned asbestos mine dumps. Asbestos minerals are products of metamorphic rock such banded iron formation and occur in narrow veins as cross fiber extending from wall to wall or as slip fiber “needle like” parallel to the vein walls. The asbestos mass fiber is an aggregate of various oriented fibers and differ in structure, chemistry and physical properties. Fig. 2 shows the geological make-up within the province and contains Komatiipoort Group and Transvaal SuperGroup. The common rocks are sandstones, shale, murchison, greenstone belt and intrusive granite, etc. Komatities often display spectacular textures of skeletal crystals (known as spinifex textures) which branch out like fern leaves. The textures and the chemical make-up of the rocks can be deduced komatities lavas crystallized exceptionally rapidly from very hot and probably water-rich molten magma (Ehlers and Vorster [5]).

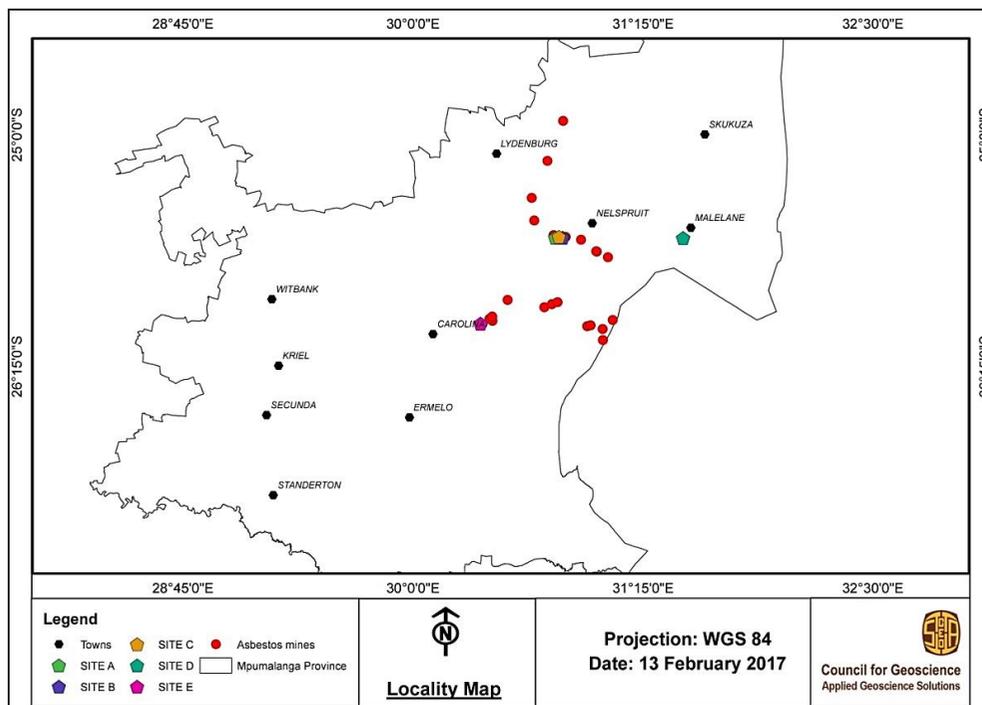


Figure 1: A map showing the location of asbestos mine dumps and five sampling points in Mpumalanga Province.

2.3 Sample preparation and analyses methods

The mass concentration expressed as dust-fall rate (D in $\text{mg}/\text{m}^2/\text{day}$) was determined by calculating the total weight mass (W_m in mg) divided by the cross-section area of the dust-fall bucket diameter (A in m^2) and multiplied by the number of days (30 days) on site as shown below:

$$D = \frac{W_m}{A \times \text{number of days}} \quad (1)$$

Filtered dust samples (stored in transparent closed plastic containers as shown in Fig. 4) were studied further using an X-Ray Diffraction (XRD) analytical technique to evaluate the mineralogical composition. SEM–EDS was used to determine morphology which includes the size, shape and types of asbestos groups detected on the filtered dust samples (Perkins and Harvey [6]). Both instruments were conditioned according to the CGS Mineralogy Laboratory Methods (Atanasova [7]). All specimens for SEM–EDS were homogenized by light grinding by hand in agate mortar. The powder subsamples were then pressed into plastic holders preparing them to be analyzed as whole rock in a BRUKER D8 ADVANCE instrument. It has a 2.2 kW Cu long fine focus tube ($\text{Cu K}\alpha$, $\lambda = 1.54060$) and 90 position sample changer. The system is equipped with LynxEye detector with 3.7° active area. Samples are scanned from 2 to 70.2 at a speed of 0.02 – 2 steps size/3 sec, and generator settings of 40 kV and 40 mA. Phase identification is based on BRUKER DIFFRACPlus – EVA evaluation program. The ICDD Inorganic/Organic Data base is used for phase search. Filtrate solutions samples (in plastic containers with white caps, Fig. 4) were analyzed using ICP-MS to determine the trace metals pollution levels.



Figure 4: Dust samples filtration process in the laboratory.

3 RESULTS AND DISCUSSIONS

3.1 Dust-fall rates results

Table 1: Dust fall rates results from January to June 2016.

Sampling sites	Jan-16	Feb-16	Mar-16	Apr-16	May-16	Jun-16
Site A	89	37	43	22	39	59
Site B	32	43	74	37	54	39
Site C	43	91	77	39	102	76
Site D	22	50	67	106	478	126
Site E	52	57	26	32	37	44

All the dust-fall rates are below the local residential limit of 600 mg/m²/day from all the sites (NDC R 827, 2013) (NDCR [8]). Site D measured the most dust of 478 mg/m²/day in May 2016, followed 126 mg/m²/day in June and 106 mg/m²/day in April at the same site, and 102 mg/m²/day at site C in May 2016. The lowest dust fall rates were detected at Site A in April 2016 and Site D in January with 22 mg/m²/day.

3.2 Metal filtrate results from January to May 2016.

The concentration levels of essential metals (Mn, Fe, Ni and Cu) and non-essential metals (Cr, Cd and Pb) in filtrate solution samples, together with relevant standard levels are shown in Table 2. The data measured from January to February represent the summer season, while the period from April to May represent the winter period.

Table 2: Metal concentration (mg/L) ranges for filtrate results ranges from January until May 2016.

Sampling points	Mn USEPA=0.05 WHO=0.1 RSA=0.05	Fe RSA=0.1	Ni USEPA=0.07 WHO=0.07 RSA=0.02	Cu RSA=1	Cr WHO=0.05 RSA=5	Cd USEPA=0.003 WHO=0.003 RSA=5	Pb USEPA=0.05 WHO=0.01
Site A	<0.5–15.4	<23.9–141.9	<0.04–34.1	<0.20–204	<0.6–1.9	1.1–17.2	5.2–25.7
Site B	<0.5–128	<23.9–38.8	<0.04–2.8	<0.20–1.4	<0.6	<0.06–1.2	<0.06–45.3
Site C	2.9–48.5	<23.9–297.4	<0.04–8.4	<0.20–3.3	<0.6–3.3	1–17.1	1.9–25.7
Site D	1.7–57.9	<23.9–57.9	<0.04–5	<0.20–14	<0.01–2.3	<0.06–1.1	7.1–17
Site E	<0.5–99.3	<23.9–652.8	<0.04–8.9	<0.20–20	<0.01–4.7	<0.06–17.7	7.9–1204.7



Seasonal levels for essential metals are discussed per site, starting with site A in Mpumalanga, manganese (Mn) metal concentration is <0.5 mg/L in summer and in the range of <0.5–15.4 mg/L in autumn, which were all exceeded (RSA [9]) and (USEPA [10]) limits of 0.05 mg/L and (WHO [11]) limit of 0.1 mg/L. Iron (Fe) metal concentration ranged <23.9–44.2 mg/L in summer and ranged <23.9–141.9 mg/L in autumn, which all exceeded the RSA (1995) limit of 0.1 mg/L. Nickel (Ni) metal concentration is <0.04 mg/L in summer and ranged 2.7–34.1 mg/L in autumn, all of which exceeded WHO (2011) and USEPA (2003) limits of 0.07 mg/L and RSA (1995) limit of 0.02 mg/L. Copper (Cu) metal concentration is <0.20 mg/L in summer and ranged <0.20–2.4 mg/L in autumn, which were all exceeded RSA limit of 1 mg/L. The non-essential metal concentration for cadmium (Cd) exceeded the limits of USEPA (2003) and WHO (2011) of 0.03 mg/L and are below RSA (1995) limit of 5 mg/L with summer 2.5 mg/L and ranged from 1.1–17.2 mg/L in autumn. According to the USEPA (2003) limit of 0.05 mg/L and WHO (2011) limit of 0.01 mg/L, the lead (Pb) metal concentration is 7.8 mg/L in summer and ranged from 5.2–15.8 mg/L in autumn. Chromium (Cr) metal concentration is 1.1 mg/L in summer and ranged from <0.6–1.9 mg/L in autumn, which all exceeded the limits of WHO (2011) of 0.05 mg/L, USEPA (2003) of 0.03 mg/L and RSA (1995) limit of 5 mg/L.

Table 3: Metals concentration (mg/L) for filtrate results from January to May 2016.

Sampling points and dates	Mn USEPA=0.05 WHO=0.1 RSA=0.05	Fe RSA=0.1	Ni WHO=0.07 USEPA=0.07 RSA=0.02	Cu RSA=1	Cr WHO=0.05 RSA=5	Cd WHO=0.005 USEPA=0.003 RSA=5	Pb USEPA=0.05 WHO=0.01
Jan-16							
Site A	No data	No data	No data	No data	No data	No data	No data
Site B	No data	No data	No data	No data	No data	No data	No data
Site C	No data	No data	No data	No data	No data	No data	No data
Site D	No data	No data	No data	No data	No data	No data	No data
Site E	No data	No data	No data	No data	No data	No data	No data
Feb-16							
Site A	<0.5	<23.9	<0.04	<0.20	<0.6	2.5	7.8
Site B	27.2	38.8	2.8	1.4	<0.6	1.2	45.3
Site C	5.6	36.6	1.2	1.9	3.3	1	1.9
Site D	5.9	57.9	5	14	2.3	1.1	7.1
Site E	76.5	204.2	14.3	6.1	4.7	1.1	1204.7
Mar-16							
Site A	<0.5	<23.9	34.1	<0.20	<0.6	1.1	5.2
Site B	<0.5	<23.9	<0.04	<0.20	<0.6	1.1	2.8
Site C	2.9	297.4	<0.04	<0.20	<0.6	1.1	25.7
Site D	36.3	<23.9	<0.04	<0.20	<0.6	1.1	9.6
Site E	<0.5	<23.9	<0.04	<0.20	<0.6	1.1	7.9

Table 3: Continued.

Apr-16							
Site A	15.4	141.9	2.7	2.4	1.9	17.2	15.8
Site B	64.4	44.2	<0.04	<0.20	<0.01	<0.06	15.4
Site C	48.5	181.8	8.4	3.3	2	17.1	15.6
Site D	1.7	<23.9	<0.04	<0.20	<0.01	<0.06	17
Site E	99.3	652.8	8.9	20	2.6	17.7	15.7
May-16							
Site A	No data						
Site B	128	<23.9	<0.04	<0.20	<0.01	<0.06	15.2
Site C	11	<23.9	<0.04	2	<0.01	<0.06	15.2
Site D	No data						
Site E	57.6	80.1	<0.04	<0.20	<0.01	<0.06	15.3

Note: Summer (Feb), Autumn (Mar–May).

Site B metal concentration of manganese (Mn) is 27.2 mg/L in summer and ranged from <0.5–128 mg/L in autumn, were all exceeded limits of USEPA (2003) and RSA (1995) of 0.05 mg/L and WHO (2011) limit of 0.1 mg/L. Iron (Fe) metal concentration is 38.8 mg/L in summer and ranged from <23.9–44.2 mg/L in autumn, which all exceeded RSA (1995) limit of 0.1 mg/L. Nickel (Ni) is <0.04 mg/L in summer and <0.04 mg/L in autumn, all of which exceeded WHO (2011) and USEPA (2003) limits of 0.07 mg/L and RSA (1995) limit of 0.02 mg/L. Copper (Cu) metal concentration is <0.20 mg/L in summer and ranged from <0.20–<0.20 mg/L in autumn, which were all within RSA (1995) limit of 1 mg/L. The non-essential metal concentration of cadmium (Cd) exceeded the limits of USEPA (2003) and WHO (2011) of 0.003 mg/L but below RSA (1995) limit of 5 mg/L in summer with 2.5 mg/L and ranging from <0.06–1.1 mg/L in autumn. According to USEPA (2003) limit of 0.05 mg/L and WHO (2011) limit of 0.01 mg/L exceeded the lead (Pb) metal concentration is 45.3 mg/L in summer and 2.8–15.4 mg/L in autumn. Chromium (Cr) metal concentration is <0.6 mg/L in summer and ranged from <0.01–<0.6 mg/L in autumn, which were below the limits of WHO (2011) of 0.005 mg/L and USEPA (2003) of 0.003 mg/L and RSA (1995) limit of 5 mg/L.

Site C manganese (Mn) metal concentration is 5.6 mg/L in summer and ranged from 2.9–48.5 mg/L in autumn, which were all exceeded USEPA (2003) and RSA (1995) limits of 0.05 mg/L and WHO (2011) limit of 0.1 mg/L. Iron (Fe) metal concentration is 36.6 mg/L in summer and ranged from <23.9–297.4 mg/L in autumn exceeded the RSA (1995) limit of 0.1 mg/L. Nickel (Ni) is 1.2 mg/L in summer and ranged from <0.04–8.4 mg/L in autumn, which were all exceeded USEPA (2003) and WHO (2011) limits of 0.07 mg/L and RSA (1995) limit of 0.02 mg/L. Copper (Cu) metal concentration is 1.9 mg/L in summer and ranged from <0.20–3.3 mg/L in autumn exceeded RSA (1995) limit of 1 mg/L. The non-essential metal concentration for cadmium (Cd) with summer is 1 mg/L and ranging from <0.06–17.1 mg/L in autumn, which were all exceeded the WHO (2011) and USEPA (2003) limits of 0.03 mg/L, but below RSA (1995) limit of 5 mg/L. Lead (Pb) metal concentration is 1.9 mg/L in summer and ranged from 2.8–15.6 mg/L in autumn exceeded the USEPA (2003) limit of 0.05 and WHO (2011) limit of 0.01 mg/L. Chromium (Cr) metal



concentration is 3.3 mg/L in summer and ranged from <0.01–2 mg/L in autumn which were all exceeded limits of USEPA (2003) of 0.003 mg/L, WHO (2011) of 0.05 mg/L and RSA (1995) limit of 5 mg/L.

Site D manganese (Mn) metal concentration is 5.9 mg/L in summer and ranged from 1.7–36.3 mg/L in autumn, which were all exceeded USEPA (2003) and RSA (1995) limits of 0.05 mg/L and WHO (2011) limit of 0.1 mg/L. Iron (Fe) metal concentration in summer is 57.9 mg/L and ranged from <23.9–652.8 mg/L which were all exceeded the limit of RSA (1995) of 0.1 mg/L. Nickel (Ni) metal concentration is 5 mg/L in summer and ranged from <0.04–0.04 mg/L in autumn which were all exceeded USEPA (2003) and WHO (2011) limits of 0.07 mg/L and RSA (1995) limit of 0.02 mg/L. Copper (Cu) metal concentration is 6.1 mg/L in summer and ranged from <0.20–<0.20 mg/L in autumn, which were all exceeded RSA (1995) limit of 1 mg/L except in autumn. The non-essential metal concentration for cadmium (Cd) is 1.1 mg/L in summer and <0.60–1.1 mg/L in autumn, which were all exceeded USEPA (2003) and WHO (2011) limits of 0.003 mg/L and RSA (1995) limit of 5 mg/L. The lead (Pb) is 7.1 mg/L in summer and ranged from 9.6–17 mg/L in autumn, which were all exceeded USEPA (2003) limit of 0.05 mg/L and WHO (2011) of 0.01 mg/L. Chromium (Cr) metal concentration is <0.6 mg/L in summer and ranged from <0.01–<0.6 mg/L in autumn which were all exceeded the limit of WHO (2011) of 0.05 mg/L, USEPA (2003) of 0.003 mg/L and RSA (1995) limit of 5 mg/L.

Site E manganese (Mn) metal concentration is 76.5 mg/L in summer and ranged from <23.9–99.3 mg/L in autumn, which all exceeded USEPA (2003) and RSA (1995) limit of 0.05 mg/L and WHO (2011) limit of 0.1 mg/L. Iron (Fe) metal concentration in summer with 204.2 mg/L and ranged from <23.9–652.8 mg/L in autumn, which were all exceeded the RSA (1995) limit of 0.1 mg/L. Nickel (Ni) in summer is 14.3 mg/L and ranged from <0.04–8.9 mg/L in autumn, which were all exceeded USEPA (2003) and WHO (2011) limits of 0.07 mg/L and RSA (1995) limit of 0.02 mg/L. Copper (Cu) metal concentration is 6.1 mg/L in summer and ranged from <0.20–20 mg/L in autumn, which were all exceeded the limits of WHO (2011) of 0.05 mg/L, USEPA of 0.003 mg/L and RSA (1995) of 5 mg/L. Chromium (Cr) metal concentration is 4.7 mg/L in summer and ranged from <0.01–2.6 mg/L in autumn, which exceeded the limits of WHO (2011) of 0.05 mg/L, USEPA (2003) of 0.003 mg/L and RSA (1995) limit of 5 mg/L. Cadmium (Cd) metal concentration is 1.1 mg/L in summer and ranged from <0.06–17.7 mg/L in autumn, which were all exceeded USEPA (2003) and WHO(2011) of 0.03 mg/L and below RSA (1995) limit of 5 mg/L. Lead (Pb) metal concentration is 1204.7 mg/L in summer and ranged from 7.9–15.7 mg/L in autumn exceeded USEPA (2003) limit of 0.05 mg/L and WHO (2011) limit of 0.01 mg/L.

Comparing the study results with research done by (Moja and Mnisi [12]) the essential metals concentration for Mn ranged from 5.06–10.23 mg/L whereas for the study results ranged from <0.5–99.3 mg/L both in autumn and ranged from 2.5–4.31 mg/L the study results ranged from <0.5–76.5 mg/L both in summer, which were all exceeded WHO (2011) limit of 0.1 mg/L, USEPA (2003) and RSA (1995) limits of 0.05 mg/L. Iron (Fe) metal concentration ranged from 2.45–8.56 mg/L comparing with the results <23.9–297.4 mg/L both in autumn and ranged from 2.3–7.23 mg/L comparing with the study results ranged from <23.9–204.2 mg/L both in summer comparing with the results which were all exceeded RSA (1995) limit of 0.1 mg/L. Nickel (Ni) ranged from 1.2–3.45 mg/L comparing with the study results ranged from <0.04–34.1 mg/L both in autumn and 0.14–3.54 mg/L in summer comparing with the study results ranged from <0.04–14.3 mg/L both in Autumn, which all exceeded WHO (2011), USEPA (2003) limits of 0.07 mg/L and RSA (1995) limit of 0.02 mg/L. Copper (Cu) ranged from 1.01–2.57 mg/L comparing with the study results ranged from <0.20–3.3 mg/L both in autumn and ranged from 0.1–2.26 mg/L comparing with

the study results ranged from $0.20\text{--}6.1\text{ mg/L}$ both in summer, which exceeded RSA (1995) limit of 1 mg/L.

3.3 SEM-EDS results

The results confirm the presence of chrysotile ($\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$) of the serpentine ($\text{Mg}_3(\text{OH})_4(\text{Si}_3\text{O}_5)$) group and amphibole ($\text{NaCa}_2(\text{Mg,Fe,Al})_5(\text{Al,Si})_8\text{O}_{22}(\text{OH})_2$) mineral group and other silicate minerals is quartz (SiO_2), mica ($\text{KAl}_2(\text{Si}_3\text{AlO}_{10})(\text{OH})_2$), and plagioclase ($\text{NaAlSi}_3\text{O}_8$). The non-silicate mineral detected was kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), feldspar (KAISQ_3O_8) and chlorite ($(\text{Mg, Fe})_3(\text{Si, Al})_4\text{O}_{10}$). At site A and site B the size particles is 100 μm for semi-rectangular and the shape characterized by straw or bundle clustered together and also organic fiber detected. The size particles measured ranged from 300 μm to 400 μm for semi-rectangular and the shape characterized by bundle clustered together for Site D. According to the research reported by (Harris et al. [13]) determining of mixed mineral dust particles and characterizing particles confirms the presences of the following the minerals amphibole using field emission scanning electron microscopy (FESEM). FESEM indicated the morphology features such as shape fiber-like cleavage fragments which are presence from the mixed mineral dust samples. The fibers were thin particles with width $0.05\ \mu\text{m}$ with parallel side smooth surface and ratios detected 20:1 to 100:10 or even higher and often displayed on curvature. Include the results on SEM-EDS results detected not of sites C and E.

4 CONCLUSIONS

All of the dust-fall rates exceeded the residential limit of 600 $\text{mg/m}^2/\text{day}$ at all the five sites. All the essential and non-essential metal concentration exceeded the local and

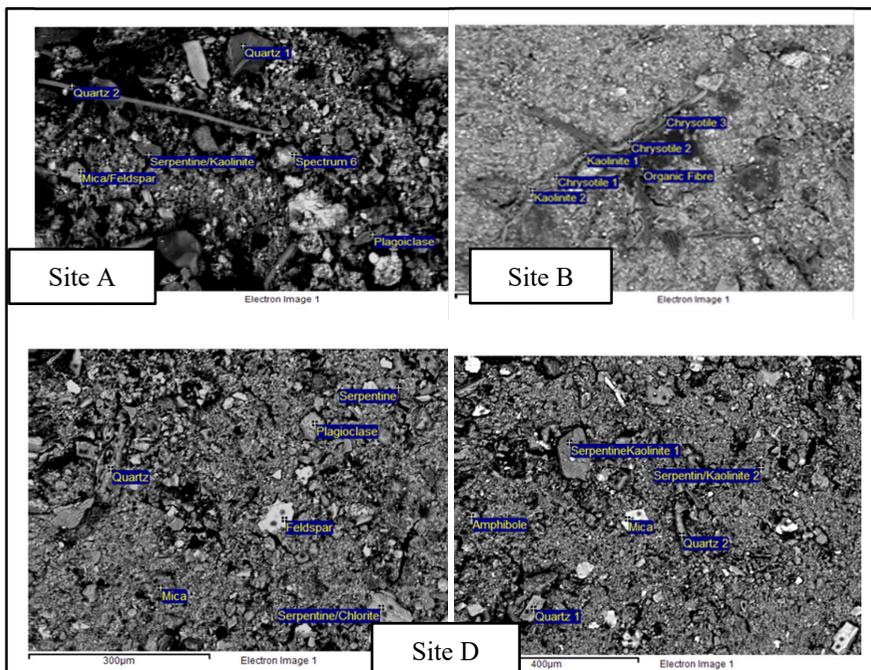


Figure 5: SEM-EDS results.

international limits/standards for all the sites except for Chromium (Cr) which is below RSA (1995) limit of 5 mg/L. The SEM–EDS results confirm the presence of chrysotile ($\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$) of the serpentine ($\text{Mg}(\text{OH})_4(\text{Si}_3\text{O}_5)$) group and amphibole ($\text{NaCa}_2(\text{Mg,Fe,Al})_5(\text{Al,Si})(\text{OH})_2$) minerals groups. The other silicate minerals detected were quartz (SiO_2), plagioclase ($\text{NaAlSi}_3\text{O}_8$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_4$), feldspar (KAISQ_3O_8) and mica ($\text{KA}_2\text{Si}_2\text{Al}_3(\text{OH})_2$). The data will be used to motivate for the acceleration of the rehabilitation of the non-rehabilitated mine dumps. Rehabilitation process should involve vegetation, back filling and sealing of shafts. This approach will go a long way in reducing the physical safety of unstable sloped and reducing possible airborne asbestos dust or fibers.

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