Investigation of nanomaterial and hazardous emissions at coal-fired power stations in Mpumalanga, South Africa

AUTHORS:
Simphiwe Nundze[1]
Adeniyi Ogunlaja[2]
Kirstie Eastwood[3]
Melusi Thwala[1,4]
Paula Melariri[1]

AFFILIATIONS:
[1]Environmental Health Department, Nelson Mandela University, Gqeberha, South Africa
[2]Chemistry Department, Nelson Mandela University, Gqeberha, South Africa
[3]Stastical Consultation Unit, Nelson Mandela University, Gqeberha, South Africa
[4]Science Advisory and Strategic Partnerships, Academy of Science of South Africa, Pretoria, South Africa

CORRESPONDENCE TO:
Paula Melariri

EMAIL:
paulaezinne.melariri@mandela.ac.za

DATES:
Received: 29 Apr. 2023
Revised: 02 July 2024
Accepted: 12 Sep. 2024
Published: 04 Dec. 2024

HOW TO CITE:
Nundze S, Ogunlaja A, Eastwood K, Thwala M, Melariri P. Investigation of nanomaterial and hazardous emissions at coal-fired power stations in Mpumalanga, South Africa. S Afr J Sci. 2024;120(11/12), Art. #16062. https://doi.org/10.17159/sajs.2024/16062

ARTICLE INCLUDES:
☒ Peer review
☐ Supplementary material

DATA AVAILABILITY:
☐ Open data set
☐ All data included
☒ On request from author(s)
☐ Not available
☐ Not applicable

EDITORS:
Michael Inggs
Thywill Dzogbewu

KEYWORDS:
coal-fired power stations, soil, emissions, nanoparticle

FUNDING:
Health and Welfare Sector Education and Training Authority

Coal-fired power stations remain the main source of electricity generation in South Africa. The combustion of coal creates fly ash and slag, and increases emissions of particulate matter, which is composed of nano-sized materials. In this study, we investigated nanoparticle emissions from coal-fired power stations. Soil samples were collected at 500 m and 1 km radii from Matla and Kriel power stations. The soil samples were examined using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray fluorescence (XRF) spectrometry. SEM images confirmed polydisperse particles in the form of semi-spherical, semi-oval, irregular-shaped and amorphous particles in dust and soil samples. The particle size range was 4–150 nm. Carbon sheet–metal oxide composites of As, Zn, Cu, Cr, Ni and V were observed. We found that coal-fired power stations are a potential source of nano-pollution, pointing to elevated human and environmental exposure around such sites. Currently, there are no environmental limits for nanomaterials due to the lack of robust risk assessment; however, this study suggests that coal-fired power stations may be hotspots that could be used as priority cases to examine the environmental implications of nano-pollution.

Significance:

Coal-fired power stations are a potential source of nano-pollution, pointing to elevated human and environmental exposure around such sites. Currently, there are no environmental limits for nanomaterials due to the lack of robust risk assessment; however, our findings suggest that coal-fired power stations may be hotspots that could be used as priority cases to examine the environmental implications of nano-pollution.

Introduction

Approximately 30% of the global energy need is met through coal, with the remainder from oil, natural gas, nuclear energy, hydroelectricity, and renewable sources.[1] South Africa is the fifth largest producer and sixth largest consumer of coal globally[2]; about 90% of its electricity is from coal-fired power stations supplied by the Electricity Supply Commission (Eskom)[3]. Eskom operates 13 coal-fired power stations with an estimated 39 342 Megawatt (MW), excluding Kusile and Medupi power stations that are yet to operate at full capacity. An additional 46 540 MW capacity comes from nuclear (1940 MW), hydropower (2732 MW), open cycle gas turbine (2426 MW) and wind farming (100 MW).[4]

Coal combustion and processing lead to the formation of particulate matter (PM) and ultrafine particles (UFPs) that are released into the environment due to vaporisation of inorganic substances in coal.[5] These vaporised particles form a variety of nanoparticles (NPs) as by-products through nucleation, which then coagulate and aggregate when they condense to form accumulated mode aerosols.[6] Generally, nanomaterials (NMs) have at least one size dimension within the 1–100 nm range, and they can be in any phase of matter. NMs can be natural (e.g. ocean sprays, fine sand, dust, volcanoes, biological matter) or anthropogenic (incidental and engineered). Incidental NMs are by-products of human activities, for instance, motor vehicle emissions, mining, coal-based power stations and fires.[7,8] Engineered nanomaterials (ENMs) are specifically designed and synthesised for applications; examples include quantum dots, carbon nanotubes, gold NPs and fullerenes, among others.[9]

Burning of coal emits various airborne pollutants, for instance, trace metals, mercury (Hg), sulfur dioxide (SO_2), sulfur trioxide (SO_3), nitrogen oxides (NO_x), condensable PM, and radioactive nucleoids, which can be persistent in the environment.[10] However, the emission properties depend on the type and quality of coal.[11] The elemental composition of NPs emitted from coal combustion includes proportions of aluminium (Al), carbon (C), calcium (Ca), iron (Fe), magnesium (Mg), sodium (Na), sulfur (S), silica (Si), arsenic (As), chromium (Cr), lead (Pb), vanadium (V) and zinc (Zn) among others.[6]

Approximately 25% of coal combustion emissions are associated with trace metals[12], and relatively more volatile trace elements, such as Hg and Se, are released in abundance as compared to As.[13] Concentrations of Ni, Zn, Cr, Cd and Pb notably above background natural soil levels have been recorded globally in coal-fired power station surroundings, including in South Africa.[14] Coal burning emits substantial amounts of $PM_{2.5}$ μm or UFPs through the process of mineral transformation at high temperatures, causing negative environmental implications, such as the release of fly ash particulates, acid rain, and emission of greenhouse gases (GHG) like carbon dioxide (CO_2).[15,16] A study conducted at the Coal Terminal in Richards Bay (South Africa) found that coal dust harms the local aquatic (mainly photosynthesis inhibition in mangroves) and terrestrial ecosystems.[17]

Attention has been given to PM_{10} and smaller particulates because of their relatively large surface area, which is associated with enhanced potential to induce human health effects such as lung cancer, heart diseases and asthma.[18] When considering the health risks associated with NPs and UFPs, the more hazardous forms tend to be the smaller sized, which have higher adsorptive and absorptive potential and can, with relative ease, reach organs such as the kidneys and brain.[19]

The aim of the current study was to investigate NP emissions in coal-fired power stations and further examine compliance witha the South African soil quality regulations for trace metals. The study objectives were to:

1. Determine levels and physicochemical characteristics of NPs in soil samples collected at various points at the Matla and Kriel power stations.
2. Assess the measured values of arsenic, lead, chromium, copper, zinc, vanadium and nickel against the acceptable levels as per the National Norms and Standards for the Remediation of Contaminated Land and Soil Quality in the Republic of South Africa.

Materials and methods

Description of the study area

The study was conducted at Eskom's Matla and Kriel coal-fired power stations (hereafter Matla and Kriel) (Figure 1). The proximity of the two power stations was ideal for practical purposes as they are both located within the Emalahleni Local Municipality in Mpumalanga province. The two coal-fired power stations are located in the Highveld Priority Area (HPA), which is associated with poor air quality due to intense mining, the concentration of coal-fired power stations, and industrial and agricultural activity. The HPA covers 31 106 km^2 that includes parts of Gauteng and Mpumalanga provinces.[20]

Matla is approximately 10 km outside the town of Kriel, and when it was completed in 1979, it was the largest coal-fired power station in the southern hemisphere, being among the first to be supplied with coal from a fully mechanised coal mine. Matla generates 3000 MW and has approximately 694 employees.[21]

Kriel has a generation capacity of 3600 MW; it was the first of the giant coal-fired power stations that were commissioned in the 1980s. Kriel was designed for an operating lifespan of 30 years, but it has since been extended to 50–60 years. A total of 3800 tons of coal per hour can be transported by conveyor from a nearby colliery to the power station, resulting in the consumption of approximately 1 150 000 tons of coal per month. There are approximately 700 employees (excluding students and contractors) at this station.[22] Geographic information system (GIS) mapping was done using QGIS software[23] to show NP distribution levels across Matla and Kriel power stations.

Sample collection

Soil and dust samples were collected at Matla and Kriel to determine the physicochemical properties and levels of NPs and heavy metal concentrations following procedures described by the US Environmental Protection Agency Laboratory Services & Applied Science Division.[25] At both power stations, 30 samples were collected: 10 soil samples at a 1 km radius, 10 soil samples at a 500 m radius and 10 dust samples from windows, desks and filing cabinets of offices in the power stations (Figures 2 and 3).

Soil samples

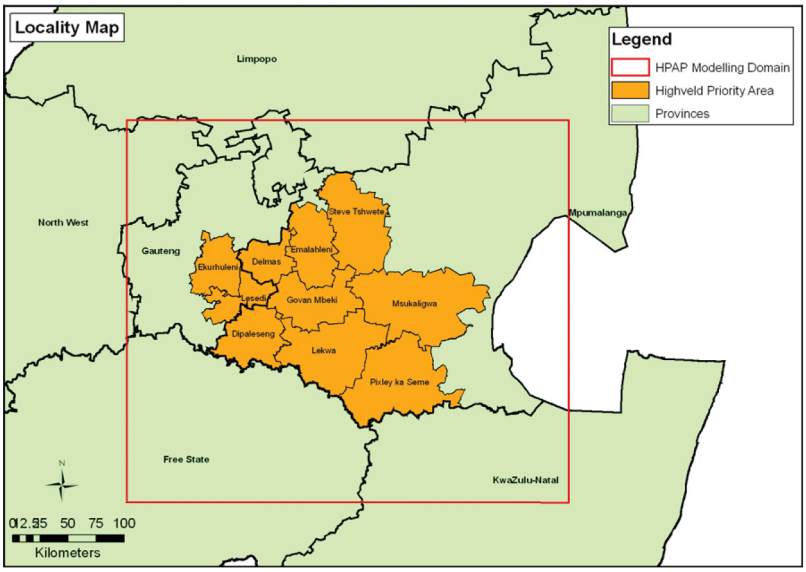
Soil samples at each power station were collected using a metal scoop at a depth of 1.2 cm. The obtained samples were placed in paper trays and thoroughly mixed, and foreign materials such as stones, roots, gravels and pebbles were removed. Each soil sample was placed in a ziplock plastic container and labelled according to the sampling point, the name of the power station and radius. To prevent the cross-contamination of samples, wipes and distilled water were used to disinfect the metal scoop until the soil was completely removed before taking another sample.

Dust sample collection

Dust samples were collected from windows, desks and filing cabinets of offices at the power stations using the ASTM E 1728-03 procedure, a standard practice for the collection of settled dust samples using wipe sampling methods for subsequent hazardous material determination. The dust samples were collected from surfaces of 30 X 30 cm to standardise the size of the collection surface areas. Ten dust samples were collected from each power station. The sampling area was wiped from the left to the right at either corner to the furthest. Wipes were folded to keep the sampling side in and to prevent loss of dust samples collected. A second wiping was from the top to the bottom repeating the same procedure, and then the wipes were folded in half again, with the sample side inside. Lastly, wiping was around the perimeter of the sampling area, and the wipes were folded as previously described. For each sample, wipes were stored in a sterile plastic container, sealed with a lid and labelled.

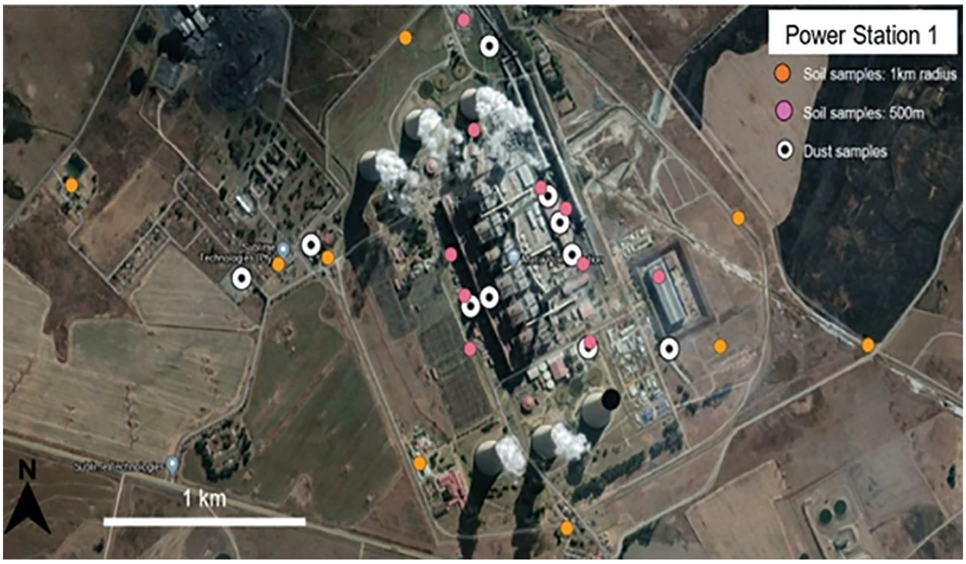
Heavy metal analytes

Seven heavy metals, namely As, Cr, Cu, V, Ni, Pb and Zn, were prioritised for analysis due to their notable adverse environmental health effects.[26] Their concentrations were assessed against the norms and standards for the remediation of contaminated land and soil quality of the *National Environmental Management: Waste Act, 2008 (Act No. 59 of 2008)*.[27] Based on the known land usage (i.e. in the HPA), the application of commercial/industrial soil screening values (SSVs) in the norms and standards for contaminated land and soils was justified, as the study examined human exposure through direct and indirect routes.



Source: South African Department of Environmental Affairs[24] (non-commercial re-use permitted)

Figure 1: An illustrative map of the Highveld Priority Area in South Africa.



Source: Map created using open-source QGIS

Figure 2: Soil and dust sample collection points at Matla Power Station.

Source: Map created using open-source QGIS

Figure 3: Soil and dust sample collection points at Kriel Power Station.

Analytical instruments

Transmission electron microscopy

The transmission electron microscope (TEM; Carl Zeiss Libra 120 equipped with an energy-dispersive X-ray analysis (EDX) detector and Gatan Crystorage, Germany) was used to characterise the particle size and morphology of the soil samples. All soil samples collected were placed in methanol. The solution was then spread out using a plastic Pasteur pipette onto a 3.05 mm carbon-coated copper grid and left to dry at room temperature. The samples were mounted on a TEM carbon-coated specimen holder using a fine-point tweezer. The images were captured using the embedded self-imaging system with a MegaView III digital camera.

Scanning electron microscopy

The scanning electron microscopy (SEM) analysis of soil samples was undertaken using the TESCAN Vega TS 5136LM (TESCAN, Czech Republic) operating at 20 kV at a working distance of 20 mm. The SEM was coupled with EDX for elemental analysis. A double-sided carbon adhesive tape was used for sample attachment on sample stubs. The samples were sprinkled evenly but lightly on an SEM sample stub with double-sided sticky tape and a hand blower used to blow away the loose particles. They were mounted on the SEM stubs using Storkbill forceps to avoid unintentional damage to the sample.

Data analysis

Data analysis was performed using the IBM SPSS Statistics version 27. Descriptive and inferential statistics were used to analyse and describe the data and included the Student's *t*-test and chi-square (χ^2) tests (Table 1). Hypothesis testing was conducted with a significance level of $\alpha = 0.05$; significant associations were further interrogated using Cohen's d for tests involving sample means, and Cramer's V for tests involving frequencies to determine practical significance. Cohen's values larger than 0.20 and Cramer's V larger than 0.10 indicate practically significant results.

Table 1: Independent samples test

	Levene's test for equality of variances		*t*-test for equality of means		
	F	Significance	*t*	d.f.	*p*-value
Arsenic	3.593	0.074	1.779	18	0.092
Total chromium	1.783	0.198	0.304	18	0.765
Copper	0.802	0.383	0.224	17	0.826
Lead	3.813	0.067	0.621	18	0.542
Nickel	0.651	0.430	-1.082	18	0.294
Vanadium	0.239	0.631	-3.522	18	0.002
Zinc	0.000	0.986	-0.803	18	0.432

Results and discussion

Determination of NPs

SEM Analysis

The SEM images of soil samples collected at the 500 m and 1 km radius are provided in Figure 4. In the dust samples from the power station offices (Figure 4B and C) and soil samples (Figure 4A, D, E and F), individual NPs within agglomerates could be identified and some were embedded within the organic matrix, indicating that NPs are hardly found as individual particles but rather as agglomerates. The particles were polydisperse in terms of size and morphology. There was a mixture of semi-spherical, semi-oval and irregular-shaped particles in the soil samples. Due to agglomeration influence, there was size polydispersity. The interaction occurring between particles may be influenced by environmental conditions and physicochemical characteristics of the particles, which determine the size dynamics of NPs.[28] Generally, the soil samples were predominantly aggregated, possibly indicative of swelling due to organic combustion as observed by bubbles produced around the sampled coal-based materials.[29]

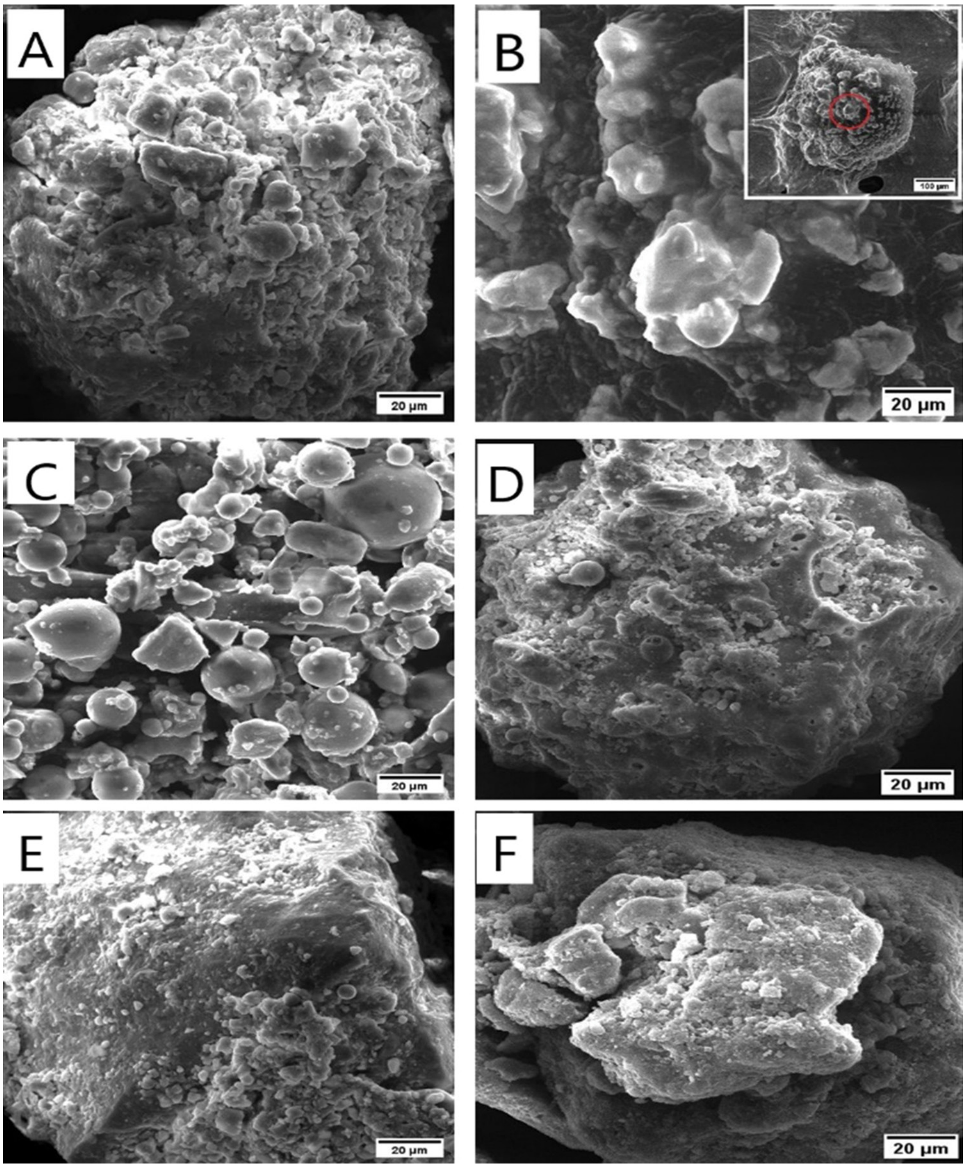


Figure 4: SEM images of dust and soil samples collected at Matla and Kriel: (A) soil samples collected outside the Mechanical Maintenance Department, 500 m, (B) dust sample collected at environmental offices, (C) dust sample collected at slurry offices, (D) soil samples collected outside the outage offices, 500 m, (E) soil samples collected at contract area west, 1 km and (F) soil sample collected at the coal stock yard, 1 km.

Furthermore, the semi-spherical morphology is distinct for coal combusted at high temperature through the process of decomposition, nucleation, coagulation and condensation of vaporised material.[29] The degree of solid organic matter was more prominent on samples collected within the 500 m radius for both Matla and Kriel, compared to samples from the 1 km radius. Such findings indicate carbonic signatures are stronger close to the point of emission, that is, the power station.

TEM Analysis

The TEM analysis enabled the identification of individual primary particles within agglomerates in all samples (Figure 5A–G). Layers of carbon sheets and graphitic carbon-based NMs were observed on the images with no dispersed particles within the images, meaning that the nanocomposites were mainly non-metal-based. Metal-based NPs embedded within carbon-based sheets were observed and were sized approximately 6–9 nm (Figure 5E–G). The average NP size was 4 nm and 1 nm in Matla and Kriel dust samples, respectively. For soil samples, the average NP size was 15 nm at Matla and 1 nm at Kriel. The average length of NPs in dust was 14 nm and 2 nm in Matla and Kriel, respectively. In soils, the average length of NPs was 113 nm at Matla and 3 nm at Kriel.

Size is a major factor determining the reactivity of NPs, including toxicity potential. The smaller the size of the particle, the greater the surface-area-to-volume ratio, and thus the higher the reactivity and toxicity potential. For instance, UFPs with sizes ranging from 12 nm to 20 nm (Figure 5H) have the ability to penetrate the alveolar lining and enter the lungs at a rapid rate compared to larger counterparts.[30,31]

Assessment of samples

Dust samples

The results of heavy metal concentrations (mg/kg) in dust samples from Matla and Kriel are presented in Table 2. There was generally a concentration variation within each power station, and there was no uniform trend when comparing concentrations between the power stations. As, Cr, Cu, V, Ni, Pb and Zn were found in all dust samples collected at both Matla and Kriel. The concentration of As at Matla (30 404 mg/kg) and Kriel (13 551 mg/kg) was higher than those of the other heavy metals, whereas Ni at both sites was the least abundant. A study conducted at Baotou city, China, showed that human activities have a significant impact on emissions of heavy metals. High concentration values for As, Co and C were observed in areas where steel smelting and thermal power stations are located.[32]

The South African SSV of 150 mg/kg for As in industrial/commercial areas was exceeded in dust samples from both power stations. The considerably high extent of the As SSV exceedance levels suggests the need for precautionary measures (e.g. frequent cleaning of surfaces and utilisation of necessary protective personal equipment), and establishment of monitoring to establish trends in order to safeguard human health. It is noteworthy that As was only detected in dust samples and not in soil samples for both power stations, suggesting that emissions were probably indoors, although such a source(s) was not investigated further as this extended beyond the original scope of the study. As is widespread but rarely found naturally and average concentration levels could be 2 mg/kg in the natural environment[33], hence the recorded values considerably above natural background levels strengthen credence for an anthropogenic source. Pesticide application, waste incineration and smelting are among the known As sources in the environment.[34]

The study focused on total Cr using X-ray fluorescence (XRF) to determine the elemental composition of soil. Cr average concentrations were 751 and 599 mg/kg, respectively, for Matla and Kriel dust samples; these were above the limit for South African industrial/commercial areas of 40 mg/kg. This may be due to the large amount of Cr compounds (e.g. $FeCr_2O_4$) present close to coal fire plants.[35] All other heavy metals (Cu, Pb, Ni, V, Zn) examined in both power stations fell below the respective SSVs as outlined in South African norms and standards. Average As, Cr, Cu and Pb in dust samples were relatively higher at Matla than at Kriel; however, Ni, V and Zn were relatively higher at Kriel.

Soil samples

<u>Soil samples from 500 m radius</u>

Cr, Cu, V, Ni, Pb and Zn were detected in soil samples from both Matla and Kriel; however, As was not detected (Table 3). Cr exists in a variety of oxidation states, the most common of which are Cr (III) and Cr (VI). The

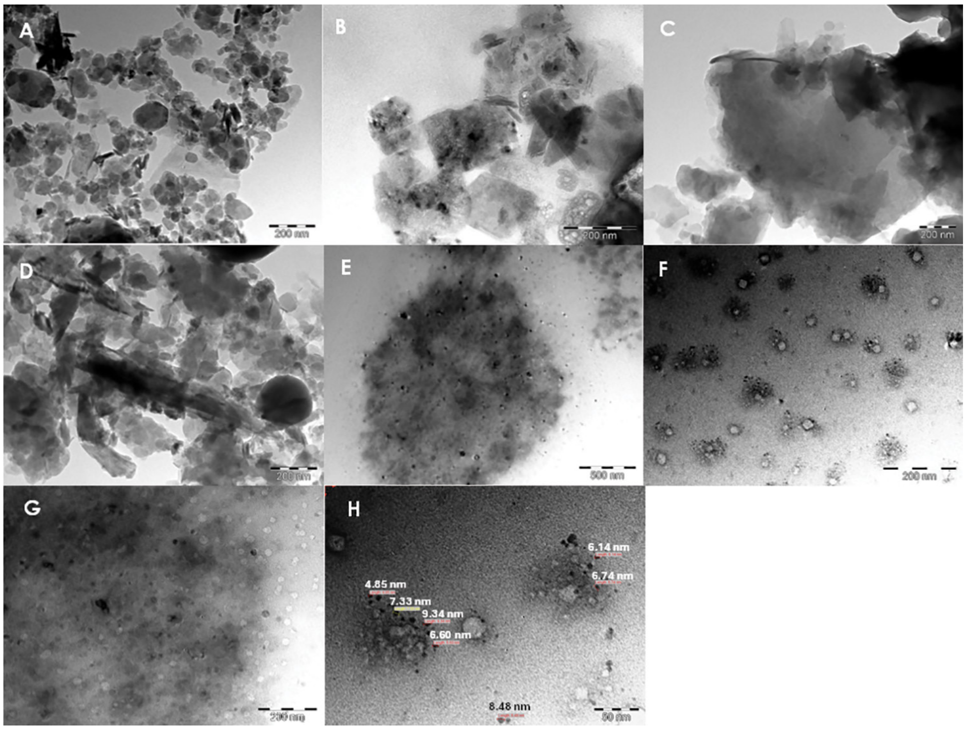


Figure 5: TEM images of (A) soil sample collected outside the outage offices, 500 m, (B) soil sample collected at the coal stock yard, 1 km, (C) soil sample collected outside the Mechanical Maintenance Department, 500 m, (D) TEM image showing spherical oval and rod-like particles, (E) dust sample collected at slurry offices, (F) soil sample collected at contract area west, 1 km, (G) dust sample collected at the environmental offices and (H) particle size distribution for metal-based nanoparticles.

difference between these two species is critical because Cr (III) is often regarded as benign or even needed for some biological activities, but Cr (VI) is extremely toxic and carcinogenic. The average Cr concentrations were 328 mg/kg and 815 mg/kg at Matla and Kriel, respectively, which exceed the SSVs for metals and organics per South African norms and standards (40 mg/kg).

The prevalence of heavy metals in mining operations can be explained by their natural occurrence in the earth's crust, soil, air and water. According to Kalagbor and Kiadum[36], when Ni is present in tiny amounts, several enzymes become active. It plays a role in fat metabolism and serves as a biocatalyst necessary for body pigmentation. Higher doses are thought to be carcinogenic, can irritate the skin, and cause damage to the heart and liver. On the other hand, Cu is a naturally occurring metal that builds up in plants and animals and is a micronutrient that is necessary for overall health. However, excessive concentrations can have negative consequences, such as nausea, diarrhoea, stomach cramps, and irritation of the nose and eyes. Brain tumours and liver cancer may potentially be related to excess Cu.[36] Zn is regarded to be rather non-toxic, particularly when taken orally. Zn toxicosis has been associated with symptoms such as vomiting, bloody urine, liver failure, renal failure and anaemia. It has been known to give similar symptoms to Pb poisoning and is easily misdiagnosed. The average soil concentrations for Cu Pb, Ni, V and Zn at both Matla and Kriel were below the respective SSVs (Table 3 and Figure 6).

Pb has no health benefits of any sort. It is biotoxic and has major consequences, including teratogenicity. Pb poisoning inhibits haemoglobin synthesis and causes kidney, joint, reproductive and cardiovascular problems as well as long-term harm to the central and peripheral nervous systems.[36] Concentrations of Pb at Matla (43 mg/kg) and Kriel (60 mg/kg) were below the South African allowable limit of 19 000 mg/kg for industrial/commercial areas. Natural background Pb concentrations in surface soils can be 3–65.8 mg/kg.[37] Pb was found in 27 of the 30 samples collected at Kriel and 20 of the 30 samples collected at Matla. Agricultural material, metallurgic industries, waste disposal and automotive fuels are some of the known sources of Pb.[37-39] The road network around Matla and Kriel, which commonly carries trucks and employee transport, possibly contributes to the detected Pb concentrations. Although leaded fuels are being phased out in South Africa, there are vehicles that still use leaded petrol or diesel.[40]

Table 2: Descriptive statistics for dust samples collected at Matla and Kriel (mg/kg)

Site	Heavy metals	Mean	Median	Standard deviation	Range	%> South African norms and standards	South African norms and standards
Matla	As	30 404.30	22 018.50	28 026.51	96 546	100%	150
	Total Cr	751.10	266.00	1521.95	5000	80%	40
	Cu	114.00	122.00	90.40	264	80%	19 000
	Pb	158.20	49.50	360.17	1174	60%	1900
	Ni	44.30	31.50	37.87	98	30%	10 000
	V	40.40	0	56.63	153	10%	2600
	Zn	824.30	675.50	656.48	2157	80%	150 000
Kriel	As	13 550.90	9921.50	10 584.737	31 470	100%	150
	Total Cr	598.80	481.00	439.096	1263	90%	40
	Cu	101.40	55.00	145.430	460	60%	19 000
	Pb	87.10	80.50	34.411	130	100%	1900
	Ni	62.70	58.50	38.178	137	10%	10 000
	V	132.10	140.00	59.773	213	40%	2600
	Zn	1080.30	987.00	765.219	2609	100%	150 000

Table 3: Average metal concentrations in soil at Matla and Kriel, with respective limits at 500 m and 1 km radius

Heavy metal	Matla soil average 500 m (mg/kg)	Matla soil average 1 km (mg/kg)	Kriel soil average 500 m (mg/kg)	Kriel soil average 1 km (mg/kg)	Allowable limit of heavy metals in soil for industrial/commercial areas (mg/kg)
					South African national norms and standards
As	–	–	–	–	150
Total Cr	328	558	815	212	40
Cu	132	106	58	62	19 000
Pb	43	28	60	40	1900
Ni	82	100	62	71	10 000
V	148	136	164	222	2600
Zn	192	105	261	152	150 000

Soil samples from 1 km radius

Between the two power stations, Cr, Cu and Ni average concentrations were relatively higher at Matla, whereas concentrations of Pb, V and Zn were higher at Kriel (Table 3); however, all were below the respective SSVs.

Cr was high at both power stations (Matla: 558 mg/kg, Kriel: 212 mg/kg) against the 40 mg/kg limit for South Africa and was detected in 29 of the 30 samples from Kriel and 24 of the 30 samples from Matla. Cr is primarily released from coal combustion and waste slurry.[10] Natural in origin and extensively utilised in industrial operations, it is regarded as one of the most dangerous heavy metals. The exceeded soil contamination limit values for South Africa demonstrated that Cr in coal is closely associated with ash-forming minerals.[35] High Cr in coal ash may also stem from the grinding media or as a result of stainless-steel erosion of power plant installation.[41] Human exposure to Cr can occur through inhalation and accumulate in the lungs (among other parts); nasal ulcers, skin hypersensitivity and chronic oral effects' have been reported in exposed humans.[42,43]

Average Pb concentrations were 28 and 40 mg/kg at Matla and Kriel, respectively; this was below the South African set limit of 1900 mg/kg. The South African limits for Ni and V were not exceeded at Matla and

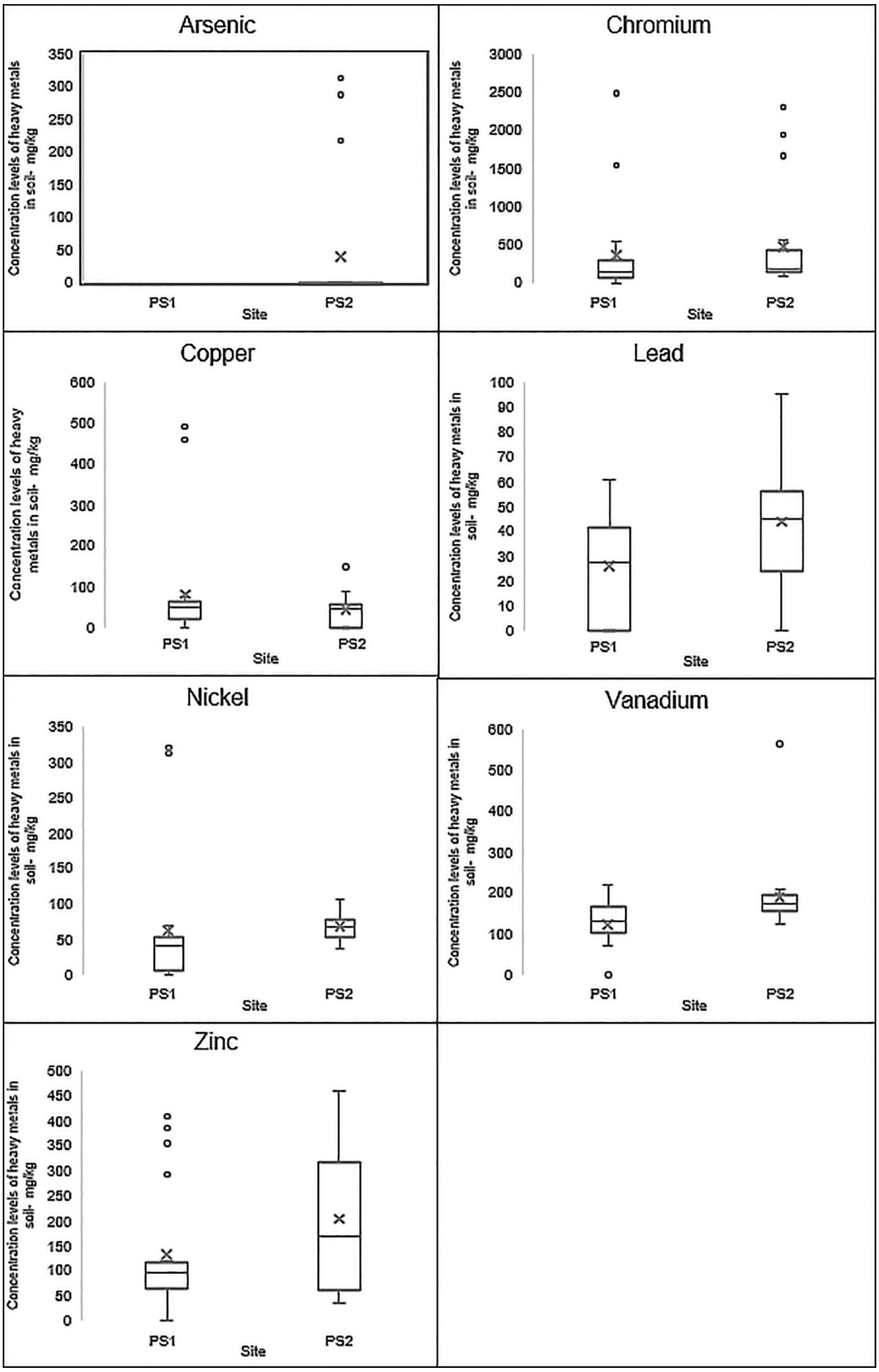


Figure 6: Graphical presentation of descriptive statistical parameters of analysed soil concentrations from Matla and Kriel. (The x symbols represent mean; • depicts outliers; PS1 = Matla; PS2 = Kriel.)

Kriel. The Zn average concentration was 105 mg/kg and 152 mg/kg at Matla and Kriel, respectively. These averages were below the 150 000 mg/kg guideline for South Africa (Table 3).

In soil samples, the average range for Matla was 2419 mg/kg, and for Kriel, it was 32 149 mg/kg. Additionally, the data pointed to Cr, Cu and Ni at a radius of 1 km at Kriel being higher compared to Matla. On the other hand, the concentration levels of Zn, V and Pb at Kriel were higher at a radius of 1 km compared to those at Matla. In 2015, the power utility applied for exemptions for 13 of its existing power stations as contained in GNR 893 as amended by GNR 1207 (31 October 2018), which were granted.[44] The high concentrations of heavy metals in soil could be a result of the non-compliance of both power stations to minimum emission standards (PM$_{50}$ mg/Nm^3).

Comparison of hazardous material concentrations in study sites

On comparing inter-site differences in concentrations of As, Cr, Pb, Ni, V and Zn, no significant difference between the power stations was observed for As ($p = 0.092$), Cr ($p = 0.765$), Cu ($p = 0.826$), Pb ($p = 0.542$), Ni ($p = 0.294$) and Zn ($p = 0.432$) for both 500 m and 1 km radius. However, for V, the average concentrations varied significantly for both power stations between 500 m and 1 km radius ($p = 0.002$), being relatively higher at 500 m .

Natural V soil concentration can reach 100 mg/kg. Combustion of heavy fuels, especially in coal-fired power stations, refineries, industrial boilers and coal mines are major sources of anthropogenic emissions of V.[45] In the case of Kriel, V emissions could be additionally to a coal mine located 5 km from the power station.

Conclusion and recommendations

We have confirmed the presence of anthropogenically derived NMs in the soil samples that were collected at both power stations. The presence of NPs in the soil confirmed environmental and potential occupational exposure. Currently available studies have generally focused on UFPs, NMs and heavy metals in coal, stockpile and air samples[12,46] and not on exposure assessments in soil and dust samples, as in the current study. In South Africa, coal fly ash has been predominantly the medium of interest[47]; as a result, comparative analysis with other local findings is not possible. Furthermore, comparison with values from other countries would not be suitable due to natural geological differences. In this regard, the current study will support comparative assessment with future local studies.

The study confirmed the presence of Cr at levels that exceeded the South African average metal concentrations in soil. The average levels of Cr in the soil samples from both power plants were higher than what the South African norms and standards permitted, associated with the release of Cr in coal and ash-forming minerals. High Cr in coal ash might also stem from the stainless-steel erosion of power plant installations. Average concentrations of Pb at both power stations were below the South African recommended limit. However, Pb can also be derived from other sources, for instance, emissions from vehicles.

Average concentrations for V and of Matla and Kriel soil samples were below the South African maximum allowable limit. Likewise, Zn concentrations at both power stations did not exceed the South African allowable limit. Furthermore, for Zn and Pb, it was observed that concentrations varied between sampling distances.

The common exceedance of heavy metal limits in soil is a concern for human and environmental health. This concern calls for more stringent pollution control measures at the power stations; however, other activities should not be overlooked. Due to the presence of anthropogenically derived NPs in soil at power stations, such sites present likely hotspots for human and environmental exposure to NMs. Such power stations can be prioritised to establish environmental exposure guidelines for NMs. As part of the corporate health, safety, and environment policies, it is recommended that exposure analysis through dust in work settings be incorporated as part of long-term monitoring in order for the establishment of credible exposure and effects data.

Acknowledgements

We thank Eskom for their knowledge sharing and for providing information without which this publication would not have been possible. We also thank the anonymous reviewers for their constructive inputs.

Funding

We thank the Health and Welfare Sector Education and Training Authority for funding this research project.

Data availability

Data are available on request from the corresponding author.

Declarations

We have no competing interests to declare. We declare no use of AI tools.

Authors' contributions

S.N.: Conceptualisation; methodology; data collection; sample analysis; data analysis; validation; writing – the initial draft; writing – revisions; funding acquisition. A.O.: Conceptualisation; methodology; sample analysis; data analysis; validation; writing – revisions; student supervision; project management. K.E.: Data analysis; validation; data curation; writing – revisions. M.T.: Conceptualisation; methodology; data analysis; validation; writing – revisions; student supervision; project management. P.M.: Conceptualisation; methodology; data analysis; validation; writing – revisions; student supervision; project leadership; project management. All authors read and approved the final manuscript.

References

1. International Energy Agency (IEA). Report extract coal [webpage on the Internet]. c2019 [cited 2020 Aug 30]. Available from: https://www.iea.org/reports/world-energy-outlook-2019/coal#abstract

2. World Coal Association. Coal statistics [document on the Internet]. c2020 [cited 2020 Aug 30]. Available from: https://www.worldcoal.org/file_validate.php?file=WCA_South%20Africa_0.pdf

3. Todd I, McCauley D. Assessing policy barriers to the energy transition in South Africa. Energy Policy. 2021;158, Art. #112529. https://doi.org/10.1016/j.enpol.2021.112529

4. Eskom Fact Sheet. Generation plant mix, revision 19 [document on the Internet]. c2017 [cited 2020 Oct 21]. Available from: https://www.eskom.co.za/AboutElectricity/FactsFigures/Documents/GX0001GenPlantMixRev19.pdf

5. Hochella MF Jr, Mogk DW, Ranville J, Allen IC, Luther GW, Marr LC, et al. Natural, incidental, and engineered nanomaterials and their impacts on the Earth system. Science. 2019;363(6434), eaau8299. https://doi.org/10.1126/science.aau8299

6. Saikia BK, Saikia J, Rabha S, Silva LF, Finkelman R. Ambient nanoparticles/nanominerals and hazardous elements from coal combustion activity: Implications on energy challenges and health hazards. Geosci Front. 2017;9(3):863–875. https://doi.org/10.1016/j.gsf.2017.11.013

7. Lohse S. Nanoparticles are all around us [webpage on the Internet]. c2013 [cited 2021 May 28]. Available from: https://sustainable-nano.com/2013/03/25/nanoparticles-are-all-around-us/#:~:text=Naturally%20occurring%20nanoparticles%20can%20be,than%20their%20naturally%20occurring%20counterparts

8. Ray U. What are the different types of nanoparticles? [webpage on the Internet]. c2018 [cited 2021 May 28]. Available from: https://www.azonano.com/article.aspx?ArticleID=4938

9. Occupational Safety and Health Administration (OSHA). OSHA fact sheet, working safely with nanomaterials [webpage on the Internet]. c2020 [cited 2020 Aug 30]. Available from: www.osha.gov/dsg/nanotechnology/nanotechnology.html

10. Savic D, Nisic D, Malic N, Dragosavljevic Z, Medenica D. Research on power plant ash impact on the quality of soil in Kostolac and Gacko coal basins. Minerals. 2018;8(2):54. https://doi.org/10.3390/min8020054

11. Shahzad BK, Yousaf M. Coal-fired power plants: Emission problems and controlling techniques. J Earth Sci Clim Change. 2017;8:404. https://doi.org/10.4172/2157-7617.1000404

12. Okedeyi OO, Dube S, Awofolu OR, Nindi MM. Assessing the enrichment of heavy metals in surface soil and plant (*Digitaria eriantha*) around coal-fired power plants in South Africa. Environ Sci Pollut Res. 2013;21:4686–4696. https://doi.org/10.1007/s11356-013-2432-0

13. Nalbandian H. Trace element emissions from coal. IEA Clean Coal Centre, 601, CCC/203 [document on the Internet]. c2012 [cited 2021 Jun 27]. Available from: https://usea.org/sites/default/files/092012_Trace%20element%20emissions%20from%20coal_ccc203.pdf

14. Dalton A, Feig GT, Barber K. Trace metal enrichment observed in soils around a coal-fired power plant in South Africa. Clean Air J. 2018;28(2), Art. #1. https://doi.org/10.17159/2410-972x/2018/v28n2a1

15. Lelieveld J, Evans JS, Fnails M, Giannadaki D, Pozzer A. The contribution of outdoor air pollution sources to premature mortality on a global scale. Nature. 2015;525:367–371. https://doi.org/10.1038/nature15371

16. Finkelman RB, Wolfe A, Hendryx MS. The future environmental and health impacts of coal. Energy Geosci. 2021;2(2):99–112. https://doi.org/10.1016/j.engeos.2020.11.001

17. De Place E. Coal dust threatens cascadia's water and wildlife. Seattle, WA: Sightline Institute; 2016 [cited 2021 Apr 25]. Available from: https://www.sightline.org/2016/05/12/coal-dust-threatens-cascadias-water-and-wildlife/

18. World Health Organization (WHO). Ambient air pollution: A global assessment of exposure and burden of disease. Geneva: WHO; 2016 [cited 2021 Jun 27]. Available from: https://iris.who.int/bitstream/handle/10665/250141/?sequence=1

19. Mahar BA, Ahmedb IAM, Karloukovski V, MacLaren DA, Foulds PG, Allsop D, et al. Magnetite pollution nanoparticles in the human brain. Proc Natl Acad Sci USA. 2016;113(39):10797–10801. https://doi.org/10.1073/pnas.1605941113

20. Pauw C, Garland RM, Oosthuizen R, Albers P, John J, Wright CY. Air quality and human health among a low-income community in the highveld priority area. Clean Air J. 2011;20(1):12–20. https://doi.org/10.17159/caj/2011/20/1.7180

21. Matla Power Station. Generation plant mix, generation division corporate affairs division [webpage on the Internet]. c2020 [cited 2020 Nov 30]. Available from: https://www.eskom.co.za/Whatweredoing/ElectricityGeneration/PowerStations/Coal/Pages/Matla_Power_Station.aspx

22. Kriel Power Station. Generation plant mix, generation division corporate affairs division [webpage on the Internet]. c2020 [cited 2020 Nov 30]. Available from: https://www.eskom.co.za/Whatweredoing/ElectricityGeneration/PowerStations/Coal/Pages/Kriel_Power_Station.aspx

23. GIS Development Team. Spatial without compromise | QGIS web site. 2021 [cited 2021 Jun 27]. Available from: https://qgis.org/

24. South African Department of Environmental Affairs (DEA). Highveld Priority Area air quality manage-ment plan. Pretoria: DEA; 2011 [cited 2021 Jun 27]. Available from: https://www.gov.za/sites/default/files/gcis_document/201409/35072144.pdf

25. United States Environmental Protection Agency (USEPA). Soil sampling operating procedure [Online]. 2023 [cited 2023 July 01]. Available from: https://www.epa.gov/sites/default/files/2015-06/documents/Soil-Sampling.pdf

26. Holland M. Health impacts of coal-fired power stations in South Africa [document on the Internet]. c2017 [cited 2021 Jun 27]. Available from: https://cer.org.za/wp-content/uploads/2017/04/Annexure-Health-impacts-of-coal-fired-generation-in-South-Africa-310317.pdf

27. South Africa. Notice 467 of 2013, National Environmental Management: Waste Act, 2008 (Act No 59 of 2008): National norms and standards for the remediation of contaminated land and soil quality [document on the Internet]. c2008 [cited 27 Jun 2021]. Available from: https://faolex.fao.org/docs/pdf/saf90450.pdf

28. Tourinho PS, Van Gestel CAM, Lofts S, Svendsen C, Soares AMVM, Loureiro S. Metal-based nanoparticles in soil: Fate, behavior, and effects on soil invertebrates. Env Toxicol Chem. 2012;31(8):1679–1692. https://doi.org/10.1002/etc.1880

29. Lighty JS, Veranth JM, Sarofim AF. Combustion aerosols: Factors governing their size and composition and implications to human health. Air Waste Manag Assoc. 2000;50:1565–1618. https://doi.org/10.1080/10473289.2000.10464197

30. Morabet RE. Effects of outdoor air pollution on human health. In: Reference module in earth systems and environmental sciences. Amsterdam: Elsevier; 2018 https://doi.org/10.1016/B978-0-12-409548-9.11012-7

31. Yang Y, Ruan Z, Wang X, Yang Y, Mason TG, Lin H, et al. Short-term and long-term exposures to fine particulate matter constituents and health: A systematic review and meta-analysis. Environ Pollut. 2019;247:874–882. https://doi.org/10.1016/j.envpol.2018.12.060

32. Han X, Lu X, Qinggeletu, Wu Y. Health risks and contamination levels of heavy metals in dusts from parks and squares of an industrial city in semi-arid area of China. Int J Environ Res Public Health. 2017;14, Art. #886.https://doi.org/10.3390/ijerph14080886

33. Tabelin CB, Igarashi T, Villacorte-Tabelin M, Park I, Opiso EM, Ito M, et al. Arsenic, selenium, boron, lead, cadmium, copper, and zinc in naturally contaminated rocks: A review of their sources, modes of enrichment, mechanisms of release, and mitigation strategies. Sci Total Environ. 2018; 645:1522–1553. https://doi.org/10.1016/j.scitotenv.2018.07.103

34. Chung JY, Yu SD, Hong YS. Environmental source of arsenic exposure. J Prev Med Public Health. 2014;47:253–257. https://doi.org/10.3961/jpmph.14.036

35. Li Z, Wang Q, Xiao Z, Fan L, Wang D, Li X, et al. Behaviors of chromium in coal-fired power plants and associated atmospheric emissions in Guizhou, Southwest China. Atmosphere. 2020;11(9), Art. #951. https://doi.org/10.3390/atmos11090951

36. Kalagbor I, Kiadum D. Evaluation of the presence and concentrations of nine heavy metals: Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in five crops harvested from farms located in Kpean and Zaakpon in Khana Rivers State Nigeria using AAS and XRF. Res Rev J Chem. 2022;11(6):6–12. Available from: https://www.rroij.com/open-access/evaluation-of-the-presence-and-concentrations-of-nine-heavymetals-cr-mn-fe-co-ni-cu-zn-cd-and-pb-in-five-cropsharvested-.pdf

37. Bakshi S, Banik C, He Z. The impact of heavy metal contamination on soil health. In: Reicosky D, editor. Managing soil health for sustainable agriculture. Vol 2: Monitoring and management. Sawston: Burleigh Dodds Science Publishing Ltd; 2018. p. 63–95. https://doi.org/10.19103/AS.2017.0033.20

38. Hassaan MA, El Nemr A, Madkour FF. Environmental assessment of heavy metal pollution and human health risk. Am J Water Sci Eng. 2016;2(3):14–19. Available from: https://sciencepublishinggroup.com/article/10.11648/j.ajwse.20160203.11

39. Mast L. Coal ash contain lead, arsenic and mercury – and it's mostly unregulated. Environmental engineering - Georgia Institute of Technology [webpage on the Internet]. c2019 [cited 2021 Mar 25]. Available from: https://massivesci.com/articles/coal-ash-water-health-hazard/

40. Zhu C, Tian H, Hao J. Global anthropogenic atmospheric emission inventory of twelve typical hazardous trace elements, 1995–2012. Atmos Environ. 2020;220, Art. #117061. https://doi.org/10.1016/j.atmosenv.2019.117061

41. Wilczyńska-Michalik W, Janusz Dańko J, Michalik M. Characteristics of particulate matter emitted from a coal-fired power plant. Pol J Environ Stud. 2020;29:1411–1420. https://doi.org/10.15244/pjoes/106034

42. Holmes AL, Wise SS, Wise JP Sr. Carcinogenicity of hexavalent chromium. Indian J Med Res. 2008;128:353–372. Available from: https://digitalcommons.usm.maine.edu/cgi/viewcontent.cgi?httpsredir=1&article=1000&context=appmedsci

43. Ray S, Ray MK. Bioremediation of heavy metal toxicity-with special reference to chromium. Al Ameen J Med Sci. 2009;2(2):57–63.

44. Naledzi Environmental Consultants. Application for postponement of the Minimum Emission Standards (MES) compliance timeframes for Eskom's coal and liquid fuel-fired power stations in the Mpumalanga Highveld, Vaal Triangle and Cape Region, Revision 2 [document on the Internet]. c2019 [cited 2021 Mar 03]. Available from: https://www.eskom.co.za/MESapplications/Documents/Annexure%204.2%20%20Final%20IRR_Updated%20Feb%202019%20v2.pdf

45. Guagliardi I, Cicchella D, Rosa R, Buttafuoco G, Ricca N. Geochemical sources of vanadium in soils: Evidences in a southern Italy area. J Geochem Explor. 2018;184:358–364. https://doi.org/10.1016/j.gexplo.2016.11.017

46. Duarte AL, DaBoit K, Oliveira MLS, Teixeira EC, Schneider IL, Silva LFO. Hazardous elements and amorphous nanoparticles in historical estuary coal mining area. Geosci Front. 2019;10:927–939. https://doi.org/10.1016/j.gsf.2018.05.005

47. Akinyemi SA, Gitari WM, Thobakgale R, Petrik LF, Nyakuma BB, Hower JC, et al. Geochemical fractionation of hazardous elements in fresh and drilled weathered South African coal fly ashes. Environ Geochem Health. 2020;42:2771–2788. https://doi.org/10.1007/s10653-019-00511-3