Feasibility study of portable sampling techniques for combustion related airborne particulates in a platinum mine

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ABSTRACT Hazardous compounds such as airborne particulate polycyclic aromatic hydrocarbons (PAHs) and black carbon (BC) require special attention. The toxicological effects caused by the inhalation of such substances depend mainly on the concentration of each health relevant compound inhaled. In this feasibility study, portable aerosol samplers were utilised for the first time together with portable Aethalometers in different areas of a South African underground platinum mine. The preliminary results showed the highest mean toxicity equivalent (TEQ) values from 3.2 to 3.9 ng m⁻³ in the mechanised mining areas, indicating the largest extent of diesel exhaust emissions at those sampling sites. Furthermore, very high mean equivalent black carbon (eBC) concentrations from 264 to 1439 µg m⁻³ were found in the same areas and give therefore, a cause of concern regarding occupational health aspects. In summary, both, the aerosol samplers and the Aethalometers delivered valuable data regarding the occupational exposure to airborne pollutants originating from combustion sources in mining activities. For such mining activities, the exposure to eBC was shown to be of greater concern than the exposure to PAHs.

Machbarkeitsstudie zu personengetragenen Probenahmetechniken für Partikel aus Verbrennungsmotoremissionen in einer Platinmine

ZUSAMMENFASSUNG Luftgetragene Gefahrstoffe, wie partikelförmige polyzyklische aromatische Kohlenwasserstoffe (PAK) und Ruß (schwarzer Kohlenstoff, engl. black carbon, BC), erfordern unter arbeitsmedizinischen Gesichtspunkten besondere Aufmerksamkeit. Toxikologische Auswirkungen, verursacht durch die Einatmung dieser Substanzen, hängen im Wesentlichen von der Konzentration der gesundheitlich relevanten Verbindungen ab. In dieser Machbarkeitsstudie wurden erstmals personengetragene Aerosolsammler zusammen mit tragbaren Aethalometern in verschiedenen Bereichen einer südafrikanischen Platinmine angewendet. Die vorläufigen Ergebnisse zeigten die höchsten Toxizitätsäquivalent-Werte (TEQ-Werte) von 3,2 bis 3,9 ng m-3 in den mechanisierten Bergbaubereichen, welche auf die hohen Dieselabgasemissionen in diesen Minenbereichen zurückzuführen sind. Außerdem konnten in denselben Bereichen sehr hohe Ruß- bzw. BC-Konzentrationsmittelwerte von 264 bis 1439 µg m-3 festgestellt werden, was im Hinblick auf arbeitsmedizinische Aspekte ein Grund zur Besorgnis ist. Die mit den Aerosolsammlern und Aethalometern ermittelten Ergebnisse liefern wertvolle Daten hinsichtlich der berufsbedingten Exposition luftgetragener Schadstoffe aus Verbrennungsquellen bei Abbau- und Transportarbeiten unter Tage. Bei diesen Bergbauarbeiten konnte gezeigt werden, dass die Exposition mit Ruß bzw. BC besorgniserregender ist als die Exposition mit PAK.

1 Introduction

The health of underground workers in the mining sector worldwide is a matter of concern. Noise, thermal stress, whole body vibration, musculoskeletal disorders and the inhalation of hazardous substances such as coal dust, silica or diesel exhaust emissions are some examples for risks mine workers are confronted with [1; 2]. Severe occupational diseases might result in the case of continuous inhalation of polluted air over a long period of time. For instance, if heavy diesel powered vehicles are used for ore mining and transportation, diesel exhaust emissions above a threshold limit value should be considered as a potential trigger of cancer [3; 4]. More precisely, diesel engine exhaust was categorised by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Group 1) [4]. In general, particle-bound diesel engine emissions are considered of great concern as they can penetrate deep into the lungs. Therefore, in addition to the implementation of technical and organisational protection measures, regular occupational monitoring of hazardous substances is vital to control the potential exposure of workers.

Diesel exhaust emissions consist of a complex mixture of gaseous substances and particulate matter (PM), resulting from unburned fuel, lubricant oil and combustion products [5]. Diesel emission PM comprises mainly elemental carbon (EC) as core and organic compounds adsorbed on the large surface area of the core [6]. These organic compounds in turn contain polycyclic aromatic hydrocarbons (PAHs) as well as methylated, nitrated and oxygenated PAHs [5]. Besides carcinogenic PAHs [7], the high quantity of carcinogenic EC also indicates a high health risk potential [8]. Furthermore, various metals from additives can be found in diesel exhaust [9]. If diesel exhaust is emitted to the surrounding environment, particle ageing additionally leads to mixed particles by coagulation of engine emission and dust particles

	Sampling location					
	Mechanis	Conventional mining				
	Tipping point	LHD vehicle area				
Aethalometer measurements						
Number of instruments N	3	3	2			
Measurement duration [min]	64, 32, 29	55, 27, 50	66, 65			
Mean air temparature [°C]	33, 30, 32	34, 31, 33	31, 31			
Mean relative humidity [%]	48, 49, 40	53, 47,40	42, 40			
Flow rate [ml min ⁻¹]	150, 50, 50	150, 50, 50	50, 50			
Time resolution [s]	60	60	60			
Aerosol sampling						
Number of samples N	4	4	5			
Flow rate [I min ⁻¹]	0.5	0.5	0.5			
Sampling duration [min]	31, 33, 45, 88	14, 20, 57, 60	7, 15, 28, 50, 60			

Table 1 Sampling parameters for the Aethalometer and aerosol sampling measurements in the platinum mine [22].

from working activities. The discussion of the fate of those particles after lung deposition highlights the need for a single particle analysis to better assess potential health outcomes. A method to characterise individual particles is the aerosol time-of-flight (ATOF) mass spectrometer [10; 11], which is able to deliver for each single particle both the PAH profile and the inorganic composition. However, personal exposure data would be particularly beneficial for occupational or environmental health studies, which include ideally personal biomarkers of exposure (e.g. from blood [12] or urine [13; 14]).

The extent of adverse health effects depends on the concentration of the compounds inhaled as well as on their physico-chemical properties. While hygroscopic gases are predominantly deposited in the extrathoracic region like nose, larynx and upper airways due to their high diffusivity, non-hygroscopic gases can penetrate further into deep lung regions, depending on absorption, translocation and metabolism in the airway lining cells [15]. In contrast, particles are deposited mainly depending on their aerodynamic diameter [16]. Micron-sized particles mainly deposit on the air conducting extra thoracic and bronchial part of the respiratory tract by gravitational sedimentation and impaction at the airway bifurcations [17; 18]. There, they can be cleared by the mucus covering the airways and transported to the larynx by ciliated cell activity [19; 20]. If sub-micron-sized fine and ultrafine (<100 nm) particles reach the alveoli, an unspecific immune defence in the alveolar region is performed by freely moving macrophage cells, removing particles from the epithelium by phagocytosis. However, ultrafine particles from diesel emissions deceive this mechanism by their small size and by depositing widely spread over the alveolar surface with a local dose of up to several particles per pneumocyte (6,940 nm² [21]). Those particles could be taken up by the cells or could be translocated through the epithelium, for instance to the blood circulation.

The goal of our study was the analysis of the diesel emission PM fraction inside an underground platinum mine in the North West Province of South Africa. The mine was a perfect location

to compare different work exposures dominated by one combustion source, the load haul dump (LHD) vehicles. Since these LHD vehicles were operated without any emission reduction measures and were responsible for high emissions of soot particles. In order to assess the workers' exposure to PM in different areas of the mine, personal sampling was undertaken in the mechanised (i.e. diesel engine based) as well as conventional (i.e. electrical power based) mining areas. For this purpose, portable Aethalometers and personal aerosol samplers were carried by workers to measure their exposure for different tasks. The direct-reading portable Aethalometers provided online measurements of equivalent black carbon (eBC) originating from emitted soot particles. The particle mass collected by the personal aerosol samplers provided useful information towards the exposure against polycyclic aromatic hydrocarbons (PAHs), their oxygenated and methylated derivatives as well as aliphatic compounds with carbon ranges from C_{12} to C_{40} . Applying these personal aerosol sampling techniques, concentrations of hazardous compounds as well as PAH toxicity equivalent (TEQ) values could be determined.

2 Materials and methods 2.1 Sampling sites

The field measurements took place in the underground shafts of a platinum mine in the North West Province of South Africa [22]. The underground platinum mine is one of approximately 17 Merensky Reef mines in the Bushveld Igneous Complex. The mined ore contains a wide range of various platinum- and palladium based compounds such as platinum sulphides, which can be found with a content of up to 74 % in some ore layers [23]. The depth of the mine, where our field studies were carried out, had a depth of between 620 and 1,290 m below surface.

In this mine, aerosol sampling and Aethalometer measurements were carried out in three different areas: two in mechanised mining areas and one in a conventional mining area. In the mechanised mining areas, heavy diesel powered LHD vehicles were used. The LHD vehicles transported the mined platinum ore to a central location called the tipping point, where it was dumped by the tipping point operator above a conveyor belt that transferred the ore to the ground level. Workers who carried the personal samplers and Aethalometers in the mechanised mining area were LHD vehicle operators and the tipping point operator. These workers were not protected by any pressurised cabins, thus they were directly exposed to the diesel engine emissions. This means the LHDs had no cabins and there was also no housing around the control panel for the tipping point. Workers were only protected from getting injured due to impacts of larger objects by open cages.

At the tipping point, there was a steady but infrequent arrival of LHD vehicles to dump their load. In contrast, in the conventional mining area, no LHD vehicles were present (non-diesel shaft). Here, miners were collecting ore by means of electrically powered drilling and blasting operations. Compared to the mechanised mining area, no diesel exhaust emissions were expected here.

The conditions in the mine were characterised by high temperatures around 32 °C and a relative humidity around 45% (**Table 1**). All of the investigated areas had similar conditions. The non-diesel shaft was slightly cooler at around 31°C, whereas LHD vehicle drivers had to work at temperatures of up to 34 °C due to heat radiation from the engines.

2.2 Sampling of particles with personal aerosol samplers

For the purpose of this feasibility study, personal aerosol samplers were used to trap airborne particulate organic compounds found underground (Figure 1 a/b). A detailed description and characterisation of the samplers can be found elsewhere [22; 24].

For the purpose of this study, only the particle-bound hazardous compounds were considered. The particle phase was sampled on 13 mm quarz fibre filters. Before use, the commercially available quartz fibre filters (T293, Munktell, Sweden) were heated in an oven at 550 °C for 12 h and stored in sealed glass vials.

Inside the mine, 13 workers were equipped with personal aerosol samplers connected to GilAir Plus pumps (Sensidyne, USA) in order to perform workplace air measurements inside the platinum mine (Figure 1 d/e and Table 1). Four personal aerosol samplers were applied each in the tipping point area as well as in the LHD vehicle area, while five aerosol samplers where used in the conventional mining area. All filter samples were taken at a flow rate of 0.5 1 min¹. The sampling duration varied widely from 7 to 88 min. The reason for the different sampling durations was that portable aerosol samplers were attached to workers in the underground mine and it was not possible for them to return after a certain predetermined time. For example, every LHD operator had individual driving routes and therefore, varying distances which had to be covered. The variation in sampling time and thus sample volume was corrected for in the calculation of the analytical results from the aerosol samplers.

In addition to the portable filter samples, five field blank samples were taken underground and treated in the same way as the real samples except they were not connected to a sampling pump. The determined background levels of analysed organic compounds were finally subtracted from sample values. After sampling, all filters were stored in capped glass vials. The samples



Figure 1 a: Portable aerosol sampling device; b: open filter holder (top) and disassembled filter holder; c: portable Aethalometer; d, e: sampling set up as carried by the workers. *Photo: Authors*

were transported in a cooler box to ground level and stored in a freezer until analysis.

The off-line analysis of the particulate matter from quartz fibre filters by thermal extraction was carried out with an OPTIC-4 (GL Sciences, Netherlands) direct thermal desorption injector. Prior to extraction, samples were spiked with internal standard (ISTD) mixtures (Table 2). For the first 50 s, the split flow was set at 50 ml min⁻¹, at a column flow rate of 1 ml min⁻¹. Afterwards the injector was switched to splitless mode for 20 min. After 135 s vent time the sample was heated up to 300 °C with a heating rate of 50 °C s⁻¹. Extracted compounds were trapped on the separation column at 40 °C. The gas chromatography (GC) column was a 25 m BPX-5 non-polar column (0.22 mm ID, 0.25 µm film thickness, SGE, Australia). After a sampling time of 15 min for thermal extraction, the column was heated at a rate of 20 °C min-1 up to 150 °C, 5 °C min-1 up to 350 °C followed by 10 min of isothermal operation. The mass spectrometer (MS) of the GC-MS-System (Shimadzu GCMS-QP2010 Ultra, Shimadzu, Japan) was operated in scan mode (m/z 35 to 500, scan rate 3.3 Hz). Quantification of analysed compounds was based on internal standard calibration of certain compounds using internal (ISTD) and a calibration standard mixture in toluene (Table 2).

2.3 Determination of the PAH based toxicity equivalent values

An estimation of potential carcinogenicity resulting from PAH exposure was achieved by the calculation of toxicity equivalent (TEQ) values based on an approach of the German Research Foundation [25] for occupational exposure. Briefly, the TEQ was calculated by summing up the multiplication products of the concentration of single compounds with a corresponding toxicity equivalent factor (TEF). The TEFs were set by a DFG expert commission (MAK commission for maximum work place concentrations). The toxicity of eleven PAHs is related to

 Table 2 Overview of (isotope labelled) compounds used for the internal and calibration standard mixture for filters used underground. The precision processing was determined for the calibration and was given as the relative standard deviation (RSD) in % [22].

Isotope labelled inter- nal standard mixture	Calibration standard mixture	Precision in % RSD	
Naphthalene d ₈	Naphthalene	8	
Biphenyl d ₁₀	Biphenyl	11	
Acenaphthylene d ₈	Acenaphthylene	10	
Acenaphthene d ₁₀	Acenaphthene	10	
Fluorene d ₁₀	Fluorene	7	
Phenanthrene d ₁₀	Phenanthrene	5	
Anthracene d ₁₀	Anthracene	6	
Fluoranthene d ₁₀	Fluoranthene	7	
Pyrene d ₁₀	Pyrene	7	
Benz[<i>a</i>]anthracene d ₁₂	Benzo[c]phenanthrene	7	
Chrysene d ₁₂	Benz[a]anthracene	8	
sum Benzo[<i>b,k</i>]fluo- ranthene d ₁₂	Chrysene	7	
Benzo[e]pyrene d ₁₂	2,2'-Binaphthalene	12	
Benzo[<i>a</i>]pyrene d ₁₂	sum Benzo [b,j,k]fluo- ranthene	15	
Perylene d ₁₂	Benzo[e]pyrene	12	
Indeno[1,2,3-cd]pyrene d ₁₂	Benzo[<i>a</i>]pyrene	13	
Dibenz[<i>ah</i>]anthracene d ₁₄	Perylene	15	
Benzo[<i>ghi</i>]perylene d ₁₂	Indeno[1,2,3-cd]pyrene	9	
Coronene d ₁₂	Dibenz[ah]anthracene	15	
Dibenzothiophene d_8	Picene	13	
9,10-Anthracenedione ${}^{13}C_{6}$	Benzo[ghi]perylene	15	
Benz[a]anthrace- ne-7,12-dione d ₁₀	Coronene	18	
<i>n</i> -Hexadecane d ₃₄	1,4-Naphthoquinone	30	
<i>n</i> -Octadecane d ₃₈	1-Naphthaldehyde	13	
<i>n</i> -Docosane d ₄₆	1(2H)-Acenaphthyle- none	13	
<i>n</i> -Tetracosane d ₅₀	9H-Fluoren-9-one	12	
<i>n</i> -Triacontane d ₆₂	9H-Xanthen-9-one	17	
	9,10-Anthracenedione	5	
	1,8-Naphthalic anhy- dride	30	
	<i>4H-</i> Cyclopen- ta[<i>def</i>]phenanthren- 4-one	6	
	Benzo[<i>b</i>]naph- to[<i>2,3-d</i>]furan	22	
	11H-Benzo[a]fluo- ren-11-one	9	

Isotope labelled inter- nal standard mixture	Calibration standard mixture	Precision in % RSD	
	<i>11H</i> -Benzo[<i>b</i>]fluo- ren-11-one	11	
	Benzo[<i>b</i>]naph- to[<i>2,1-d</i>]furan	11	
	Napht- ho[<i>2,1,8,7-klmn</i>]xan- thene	7	
	Benz[<i>a</i>]anthrace- ne-7,12-dione	17	
	5,12-Naphthacenedio- ne	10	
	1,2-Dimethylnaphtha- lene	7	
	1-Methylpyrene	6	
	C ₁₂ H ₂₆	15	
	C ₁₃ H ₂₈	10	
	C ₁₄ H ₃₀	14	
	C ₁₅ H ₃₂	15	
	C ₁₆ H ₃₄	2	
	C ₁₇ H ₃₆	10	
	C ₁₈ H ₃₈	20	
	C ₁₉ H ₄₀	15	
	C ₂₀ H ₄₂	5	
	C ₂₁ H ₄₄	8	
	C ₂₂ H ₄₆	9	
	C ₂₃ H ₄₈	6	
	C ₂₄ H ₅₀	6	
	C ₂₅ H ₅₂	7	
	C ₂₆ H ₅₄	9	
	C ₂₇ H ₅₆	8	
	C ₂₈ H ₅₈	9	
	C ₂₉ H ₆₀	6	
	C ₃₀ H ₆₂	16	
	C ₃₁ H ₆₄	25	
	C ₃₂ H ₆₆	14	
	C ₃₃ H ₆₈	16	
	C ₃₄ H ₇₀	20	
	C ₃₅ H ₇₂	20	
	C ₃₆ H ₇₄	21	
	C ₃₇ H ₇₆	22	
	C ₃₈ H ₇₈	25	
	C ₃₉ H ₈₀	16	
	C ₄₀ H ₈₂	17	
	2-Methylnaphthalene	8	
	1-Methylnaphthalene	8	
	Cyclopenta[cd]pyrene	7	

benzo[a]pyrene (B[a]P, TEF = 1), due to higher or lower health risk potential compared to B[a]P [25].

In a number of European countries like Austria, Poland, Sweden and Switzerland, an occupational exposure limit of 2 μ g m⁻³ is in place for benzo[*a*]pyrene. Other countries (Germany, Latvia, the Netherlands) have enforce even lower exposure limits for B[*a*]P [26].

2.4 Black carbon monitoring with portable Aethalometers

Black carbon (BC) is a product of incomplete combustion processes and is emitted for example by vehicles operated on diesel fuel, such as LHDs. Due to the large surface area thereof, BC is capable of absorbing various organic substances. In order to characterise BC, portable Aethalometers (microAeth®, MA 200 series, AethLabs, USA) were used during our field campaign (**Figure 1 c**). These Aethalometers enabled the online monitoring of carbonaceous aerosol particles within a sampling period. The instrument is operated with an internal pump, which allows continuous measurements over about 8 h with a time resolution between 1 s and 5 min. It measures the light attenuation (ATN) by aerosol particles continuously deposited on a polytetrafluoroethylene (PTFE) filter tape at five wavelengths (375, 470, 528, 625 and 880 nm) ranging from ultraviolet (UV) to near infrared (IR).

BC is characterised by its strong wavelength independent absorption of visible light, from near UV up to near IR and is defined by its absorbance at 880 nm [27]. The conversion of the attenuation to a mass concentration is done by an internal algorithm considering mass absorption cross section and different optical parameters, device design and filter material. The achieved values are given as equivalent black carbon (eBC) [28]. Another fraction of carbonaceous aerosols, excluding BC, which absorbs light primarily at the short visible wavelengths (UV-VIS) is called brown carbon (BrC). BrC can be calculated from the difference between the absorbance at 370 nm and 880 nm [27; 29; 30].

Because of the toxicological effects of elemental carbon, the European Commission has set a binding occupational exposure limit value (BOELV) of 50 µg m⁻³, which shall be adhered to in underground mining and tunnelling starting from February 2026. This quite low BOELV can raise issues for measurements using traditional personal filter sampling techniques, as long sampling times and high flowrates are necessary to achieve a low enough LOQ. On the other hand, portable Aethalometers are much more sensitive, which can be found very useful for occupational monitoring purposes. Beside shorter sampling times, exposure profiles can also be measured with such direct-reading instruments. Even though the BC measured by the Aethalometer doesn't directly translate into an EC concentration, validated calibration factors could be used for the purpose of workplace measurements. A similar device [31; 32] was successfully used to measure diesel particulate matter in underground mines. Because the particles emitted form diesel engines are below 1 µm in size [33], the portable Aethalometers could be operated without a size-selective inlet.

Here, in order to measure the ambient eBC concentrations online in different mine regions, eight workers in total were equipped with portable Aethalometers (Table 1). Six Aethalometers were worn by workers at the tipping point and the LHD ve-



Figure 2 Mean PAHTEQ values and mean PM concentrations of health relevant PAHs. The health relevant PAHs are naphthalene (Nap), phenanthrene (Phe), pyrene (Pyr), chrysene (Chy), 1methylpyrene (Pyr 1 M), benz[a]an-thracene (B[a]A), sum benzo[b,j,k]fluoranthenes (sum B[b,j,k]F), cyclopenta[cd]pyrene (Cp[cd]P), indeno[1,2,3-cd]pyrene (I[1,2,3-cd]P), benzo[a]pyrene (B[a]p) and dibenz[ah]anthracene (Db[ah]A). The PAHs are listed from left to right with increasing TEFs [25]. TEFs of each PAH are shown on the top of the bars. *Graphic: Authors*

hicle area. In the conventional mining area, two workers were equipped with one Aethalometer each.

3 Results and discussion

3.1 Health relevant organic compounds found underground

The mean and median concentrations of aromatic analytes associated with PM in different areas of the underground platinum mine, as well as the calculated TEQ values are presented in Table 3. The mean TEQ values and mean PM concentrations of health relevant PAHs found underground are listed with increasing TEFs in Figure 2. The bar diagram represents the results determined for the tipping point (blue), LHD vehicle (red) and conventional mining (green) area. Here, the highest mean concentrations of up to 45 ng m3 (median: 46 ng m3) could be found for pyrene, its methylated derivatives and for phenanthrene in the LHD vehicle area. This is due to the highest frequency of LHD vehicles passing by in this area and therefore the largest extent of diesel exhaust emissions. However, one exception was dibenz[ah]anthracene, a heavier PAH, for which much higher concentrations were found at the tipping point. In contrast, the LHD vehicle and conventional mining area, the dibenz[ah]anthracene concentrations found were below the limit of quantification (LOQ). Also the green bars starting with pyrene represent values below the LOO.

In general, considering the sampled health relevant PAHs in this feasibility study, the highest mean TEQ value of 3.9 ng m³ (median: 3.5 ng m⁻³) was calculated for the LHD vehicle area. In the area of the tipping point, LHD vehicles were not continuously present and therefore, lower concentrations of health relevant PAHs were present in the surrounding air. Consequently, a lower mean TEQ value of 3.2 ng m⁻³ (median: 3.1 ng m⁻³) was determined for that area. These measured TEQ values or B[a]P equivalents are several orders of magnitude below the OEL of 2 μ g/m³ imposed in most European countries. These findings

 Table 3 GC-MS quantification results for aromatic analytes found on filter samples as PM and calculated toxicity equivalent (TEQ) values. The toxicity equivalent factors (TEFs) for different PAHs are listed in the right column [25]. Less than (<) values were below the limit of quantification (LOQ).</th>

	Sampling location						
	Mechanised mining PM		Conventional mining PM				
	Tippin	g point	LHD vehicle area				
Aromatic analytes	Mean [ng m ⁻³]	Median [ng m ⁻³]	Mean [ng m ⁻³]	Median [ng m ⁻³]	Mean [ng m ⁻³]	Median [ng m ⁻³]	TEF
τεο	3.2	3.1	3.9	3.5	<0.1	<0.1	
Naphthalene	8.6	7.8	13	14	5.1	4.3	0.001
1-Methylnaphthalene	2.1	1.6	2.7	2.9	1.7	1.3	
2-Methylnaphthalene	3.0	2.5	5.2	5.0	1.7	1.6	
Biphenyl	2.5	1.9	3.7	3.4	2.3	1.1	
Acenaphthylene	0.4	0.3	1.4	1.4	<0.1	<0.1	
Acenaphthene	0.1	<0.1	33	2.3	1.8	<0.1	
Fluorene	1.9	1.6	3.2	2.9	0.8	<0.1	
Phenanthrene	11	9.4	19	13	0.6	0.2	0.001
Anthracene	4.8	4.7	11	7.9	0.5	0.3	
Fluoranthene	10	10	10	9.9	<0.1	<0.1	
Pyrene	36	34	45	46	<0.1	<0.1	0.001
1-Methylpyrene	15	14	19	17	<0.1	<0.1	0.1
2-Methylpyrene	21	20	29	27	<0.1	<0.1	
4-Methylpyrene	20	18	26	24	<0.1	<0.1	
Benzo[c]phenanthrene	0.2	<0.1	0.5	<0.1	<0.1	<0.1	
Benz[a]anthracene	3.2	3.2	3.4	3.4	<0.1	<0.1	0.1
Chrysene	5.1	5.4	7.5	7.3	<0.1	<0.1	0.01
2,2'-Binaphthalene	0.1	0.1	1.0	0.9	<0.1	<0.1	
sum Benzo[<i>b,j,k</i>]fluo- ranthenes	2.9	3.3	5.1	5.0	<0.1	<0.1	0.1
Cyclopenta[cd]pyrene	0.9	0.9	1.1	1.0	<0.1	<0.1	0.1
Benzo[e]pyrene	1.1	1.1	1.6	1.6	<0.1	<0.1	
Benzo[a]pyrene	0.6	0.7	0.8	0.8	<0.1	<0.1	1
Perylene	0.2	0.1	0.5	0.1	<0.1	<0.1	
Indeno[1,2,3-cd]pyrene	0.4	0.1	0.3	0.2	<0.1	<0.1	0.1
Dibenz[<i>ah</i>]anthracene	0.2	0.2	<0.1	<0.1	<0.1	<0.1	1
Picene	6.7	5.0	6.1	4.8	<0.1	<0.1	
Benzo[ghi]perylene	1.4	1.3	1.0	1.2	<0.1	<0.1	
Coronene	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	
1,4-Naphthoquinone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
1-Naphthaldehyde	1.2	1.5	2.4	2.6	<0.1	<0.1	
1(<i>2H</i>)-Acenaphthyle- none	0.5	0.5	0.5	0.4	<0.1	<0.1	
9H-Fluoren-9-one	2.1	1.8	3.3	2.5	<0.1	<0.1	
9H-Xanthen-9-one	0.6	0.7	0.6	0.5	<0.1	<0.1	
9,10-Anthracenedione	8.9	8.6	7.1	7.1	<0.1	<0.1	
1,8-Naphthalic anhy- dride	7.5	3.8	5.1	6.1	<0.1	<0.1	

	Sampling location						
	Mechanised mining PM			Conventional mining PM			
	Tipping	g point	LHD veh	icle area			
Aromatic analytes	Mean [ng m ⁻³]	Median [ng m ⁻³]	Mean [ng m ⁻³]	Median [ng m ⁻³]	Mean [ng m ⁻³]	Median [ng m ⁻³]	TEF
4-H-Cyclopen- ta[<i>def</i>]phenanthren- 4-one	2.3	2.0	4.0	2.8	<0.1	<0.1	
Benzo[<i>b</i>]naph- to[<i>2,3-d</i>]furan	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
<i>11H</i> -Benzo[<i>a</i>]fluo- ren-11-one	5.0	4.9	6.7	6.4	<0.1	<0.1	
<i>11H</i> -Benzo[<i>b</i>]fluo- ren-11-one	4.3	4.1	13	13	<0.1	<0.1	
Benzo[<i>b</i>]naph- to[<i>2,1-d</i>]furan	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	
Naph- to[<i>2,1,8,7-klmn</i>]xanthe- ne	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
Benz[a]anthrace- ne-7,12-dione	0.2	<0.1	0.8	<0.1	<0.1	<0.1	
5,12-Naphthacenedio- ne	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
7-lsopropyl-1-methylp- henanthrene	1.6	1.7	7.3	6.4	0.7	<0.1	

suggest that the exposure to PAHs is not a main concern in similar mining environments. Currently, no OELs are defined for PAHs in South Africa.

In contrast to the mechanised mining areas, no LHD vehicles were present in the conventional mining shaft at all. Therefore, with a few exceptions, almost all detected compounds were below the LOQ. Here, the low concentrations of health relevant components resulted in mean and median TEQ values below LOQ. One possibility for the occurrence of PAHs in a LHD vehicle free area could be wooden poles, which were utilised as roof supports underground. If these wooden poles were treated with PAH containing mixtures such as creosote before use, the release of PAHs such as naphthalene into the surrounding air is not unlikely [34]. However, the existence of trace amounts of PAHs in a section without any diesel emissions could also result from the transference of airborne compounds from the outer environment of the ground level via the air inlet [35]. Further investigations concerning airborne compounds, transmitted from the external environment via the air inlet, should be taken into account. In this way, the quantity of air pollutants found underground can be assigned to emission sources in the mine considering the incoming external air quality. The dispersion of gases and PM from diesel mechanised mining sections to conventional mining sections may be possible, depending on the configuration of the shafts and the ventilation system, thus the linkages between diesel engine emissions, ventilation system parameters and occupational exposure need to be considered in assessing potential health risks underground.

Besides aromatic compounds, aliphatic substances were also found on filters in all three sampling sites. The mean and median concentrations are listed in **Table 4**. In general, aliphatic substances found on filter samples originated from combustion aerosols and from aerosols generated by the evaporation of lubrication oil. Thus C_{12} to C_{24} aliphatics can be assigned to diesel exhaust emissions, while aliphatic compounds with carbon numbers higher than C_{17} originate from the exhaust of unburned lubricant oil [36]. Our results revealed the highest mean concentrations in the range of 64 to 204 ng m⁻³ (median: 69 to 199 ng m⁻³) for C_{21} to C_{29} aliphatics found on filter samples taken in the LHD vehicle area. However, for carbon numbers greater than 30, higher concentrations could be found on filters applied in the conventional mining area. Here, the utilisation of greased pneumatic drills as conventional mining tools was considered as a potential source of aerosolised aliphatic components.

3.2 Equivalent black carbon concentrations

Table 5 shows all determined eBC concentrations as mean and median values, while **Figure 3** represents the online concentrations of eBC measured by four portable Aethalometers in all three sampling locations. The measurements were not carried out simultaneously, except the two measurements illustrated in Figure 3c.

In the section of mechanised mining, fluctuating eBC concentrations, partially with high peak values could be observed (Figure 3 a/b). Very high eBC concentrations of up to 1.5 mg m⁻³ were measured particularly at the tipping point, where LHD vehicles arrived to dump the ore onto the conveyor belt (Figure 3a). The fluctuations in Figure 3a are the result of time slots, where LHD vehicles either arrived at the tipping point or were absent. The evaluation of the measurement data of all three devices worn in this area revealed a high mean concentration of 326 μ g m⁻³ (median: 279 μ g m⁻³) (Table 5). However, higher

	Sampling location					
	Mechanised mining PM				Conventional mining PM	
	Tippin	g point	LHD vehicle area			
Aliphatic analytes	Mean in ng m ⁻³	Median in ng m ⁻³	Mean in ng m ⁻³	Median in ng m ⁻³	Mean in ng m ⁻³	Median in ng m ⁻³
$C_{12}H_{26}$	11	5.0	5.3	3.6	<0.1	<0.1
C ₁₃ H ₂₈	6.4	6.4	6.6	5.1	<0.1	<0.1
C ₁₄ H ₃₀	4.9	4.7	10	9.5	<0.1	<0.1
C ₁₅ H ₃₂	5.0	5.4	9.7	7.6	<0.1	<0.1
C ₁₆ H ₃₄	5.8	6.4	9.0	8.5	<0.1	<0.1
C ₁₇ H ₃₆	12	13	21	21	<0.1	<0.1
C ₁₈ H ₃₈	11	10	18	16	<0.1	<0.1
C ₁₉ H ₄₀	13	10	18	16	4.4	2.8
C ₂₀ H ₄₂	22	15	28	29	7.3	6.2
C ₂₁ H ₄₄	44	30	64	69	13	11
$C_{22}H_{46}$	95	54	148	153	12	13
C ₂₃ H ₄₈	113	67	204	199	15	11
$C_{24}H_{50}$	131	103	200	184	35	20
C ₂₅ H ₅₂	97	91	146	144	36	14
$C_{26}H_{54}$	93	92	130	122	46	25
C ₂₇ H ₅₆	70	79	99	85	54	25
C ₂₈ H ₅₈	66	78	98	96	54	28
C ₂₉ H ₆₀	54	60	103	102	52	23
C ₃₀ H ₆₂	30	31	52	54	53	31
C ₃₁ H ₆₄	25	28	32	30	50	23
C ₃₂ H ₆₆	21	24	31	29	49	26
C ₃₃ H ₆₈	22	25	33	30	46	23
C ₃₄ H ₇₀	17	19	28	25	38	15
C ₃₅ H ₇₂	21	22	22	19	34	18
C ₃₆ H ₇₄	17	15	21	21	27	9.6
C ₃₇ H ₇₆	12	13	18	17	22	8.3
C ₃₈ H ₇₈	16	17	18	19	22	8.2
C ₃₉ H ₈₀	17	19	14	10	24	14
C ₄₀ H ₈₂	21	21	23	21	45	27

Table 4 GC-MS quantification results for aliphatic analytes found on filter samples. Less than (<) values were below the limit of quantification (LOQ).

mean and median concentrations were found in the LHD vehicle area.

In the LHD vehicle area a high overall mean eBC concentration of 657 μ g m⁻³ (median: 350 μ g m⁻³) could be observed (Table 5). Here, the highest mean concentration overall of 1,439 μ g m⁻³ (median: 450 μ g m⁻³) was measured. The other instrument measured lower concentrations with a mean value of 307 μ g m⁻³ (median: 295 μ g m⁻³). The very high eBC concentrations observed in this area are the result of the direct exposure of miners to diesel exhaust emissions or their work was performed in areas with a steady operation of diesel engines. In view of this, Figure 3b shows the online eBC concentrations correlated to

the operating procedures of the LHD vehicle engine. It transpires that the engine loads were changing quickly depending on the three working steps load, haul and dump. In addition, these vehicles often reversed. This resulted in fluctuating peak values as well as the higher eBC concentrations the drivers were exposed to. The high eBC concentrations measured are of concern, when compared to the BOELV of 50 μ g m⁻³ for EC, which will be in place in the European Union from 2026. Even though a calibration factor is needed to convert eBC measurements in EC equivalents, the high eBC concentrations measured in the mechanised mining area show that exposure to diesel exhaust can be an issue in mining environments.

	eBC concentrations					
	Mean in µg m ⁻³	Median in µg m ⁻³				
Tipping point						
Worker 1	334	336				
Worker 2	264	245				
Worker 3	379	231				
Overall mean / median values	326	279				
LHD vehicle area						
Worker LHD 1	1439	450				
Worker LHD 2	307	295				
Worker LHD 3	559	540				
Overall mean / median values	657	350				
Conventional mining						
Worker 1	2.0	1.9				
Worker 2	2.0	2.2				
Overall mean/median values	2.0	2.1				

Table 5 Mean and median eBC concentrations determined via online

 Aethalometer measurements in different mine areas [22].

Figure 3c shows the online eBC concentrations within the conventional mining section. Each of the two workers wore one instrument simultaneously. Compared to the mechanised mining area, these eBC concentration levels were much lower and rather constant during the whole measurement interval since no LHD vehicles were present at all. The total mean and median eBC concentrations in the conventional mining area were 2 μ g m⁻³ (Table 5).

As expected, there was no BrC measured, neither in the conventional nor in the mechanised mining section. This is in agreement with *Corbin* et al. [37], who found that BrC is commonly negligible for diesel engine exhaust due to the high temperature of combustion. Moreover, the low concentrations of organic compounds, such as PAHs and alkanes, underline the huge disproportion of organic material to eBC emitted by diesel engines.

4 Conclusion

The objective of this feasibility study was to perform an assessment of the potential exposure of mine workers to health relevant particulate compounds, such as eBC and PAHs, using a portable Aethalometer and a personal aerosol sampler. The results obtained revealed that the area with the highest exposure measured by the personal samplers was the LHD vehicle area, followed by the tipping point. Compared to the conventional mining area, the eBC concentrations measured in the mechanised mining sections were much higher. Since BC is an emission product and has a large surface area, it is capable of adsorbing high concentrations of PAHs. Therefore, the calculated TEQ values assigned to the mechanised mining areas were much higher than those values



Figure 3 eBC_(880 nm) Concentrations measured online at three different sampling locations; 3a shows the eBC concentration at the tipping point; 3b shows the eBC concentration in the LHD vehicle area; 3c shows the eBC concentration in the conventional mining area. Here, two workers wore the instruments at the same time. The red straight lines indicate the mean eBC concentrations measured in each area. *Graphic: Authors*

determined for the non-diesel shaft, where no BC was emitted. However, compared to the eBC concentrations, the determined PAH concentrations were much lower by around four orders of magnitude.

Finally three main outcomes were found in this feasibility study which require further investigation:

- 1. Sampling duration for PM also requires further consideration, as variations in eBC concentration were detected by the Aethalometer, which infers large changes in organic compounds concentrations during a working shift as well.
- 2. The portable Aethalometer is well suited for occupational monitoring of soot emissions, as areas of high exposure and exposure peaks can be easily identified, given the direct-reading measurement principle. We showed in this feasibility study that the Aethalometer can be an appropriate instrument for measuring black carbon in underground metal mines. A calibration factor for diesel soot, between the eBC concentration measured by the Aethalometers and the concentration of elemental carbon, such as the established NIOSH 5040 [38] or DGUV Information 213-544 [39] methods could be very advantageous for occupational monitoring purposes. This parameter should be monitored in general in diesel mechanised underground working areas.
- 3. Last but not least, in further studies the number of workers wearing personal samplers should be increased. The sampling strategy should take into consideration that the sampling duration shall be representative for a work shift and personal sampling should be conducted over several working days/shifts in order to obtain a statistically reliable number of samples.

4.1 Study limitations

The eBC measurements with the portable Aethalometer without a size-selective inlet can only be performed in mines where interference from coal dust is not expected. Coal dust can interfere with the eBC reading of soot, making a particle size-selective inlet a prerequisite for coal mining environments. Occupational exposure limits for diesel emissions are usually set for the concentration of elemental carbon, as measured by the NIOSH 5040 or DGUV Information 213–544 [39] methods. For occupational studies, a conversion factor between eBC and elemental carbon would be necessary.

Our study did not consider the exposure against silica, metals, nitrogen oxides or volatile organic compounds, which may also be of concern in mining environments.

4.2 Conflicts of interest

There are no conflicts to declare.

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