Research article
An exploratory characterisation of the carbon and stable isotope composition of atmospheric particulate matter from opencast coal mining activities and adjacent communities

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Abstract

Standard source apportionment techniques for atmospheric particulate (PM) collected near opencast coal mines using inorganic markers only are limited by the similarity in the mineral components in the overburden and at adjacent residential locations. This study explores the use of the stable carbon (C) and nitrogen (N) isotope ratios ($^{13}C/^{12}C$ and $^{15}N/^{14}N$) and thermal optical methods to differentiate sources of carbonaceous material in the atmospheric PM samples from the opencast coal mines and adjacent communities. Results show isotopic and OC/EC ratio differences between atmospheric PM samples from the opencast coal mines and communities, although distinguishing between the contributions of coal combustion, liquid fuel combustion and the domestic use of biomass requires further analysis.

Keywords

Atmospheric PM, coal, opencast, elemental carbon, organic carbon, IRMS, thermal optical.

Introduction

Atmospheric particulate matter

Air pollution in South Africa has been identified as one of the critical threats to human health, the environment and sustainability in general (see for instance Lim et al. 2011). High air pollution levels in some of the highly industrialised parts of the country have resulted in severe air quality degradation and the declaration of priority air quality management areas. The three priority areas which have been declared thus far in South Africa include the Vaal Triangle Airshed Priority Area (VTAPA) in Gauteng Province, the Highveld Priority Area (HPA) in Mpumalanga Province and Waterberg-Bojanala Priority Area (WBPA) in the North West and Limpopo Provinces. Anthropogenic sources of air pollution in all these areas include industrial facilities, power generation, transport, agricultural activities and coal mining (DEA, 2011). Elevated atmospheric concentrations of criteria pollutants such as sulphur dioxide (SO_2), nitrogen oxides (NOx) and atmospheric particulate matter (PM_{10} and $PM_{2.5}$; particles with an aerodynamic diameter less than 10 µm and 2.5 µm, respectively) have been observed in these priority areas, resulting in stakeholder concerns on the resultant negative health and environmental impacts thereof (DEA, 2017). The health impact of atmospheric PM is historically measured by the concentration of particulate smaller than 10 µm or PM_{10} (Albers et al. 2015; Kunzli and Tager 2000; Mannucci and Franchini 2017) while $PM_{2.5}$ is increasingly recognised as being of importance due to its higher toxicity and increased penetration into the gas exchange regions of the respiratory system (Hartmann et al. 2016).

Opencast coal mining activities have been associated with significant contributions to atmospheric PM emissions (Gautam et al. 2012). During opencast coal mining, atmospheric PM is generated from various sources which include drilling and blasting, excavation, materials handling, vehicle entrainment of dust, crushing and screening, wind erosion of mine residue dumps, tailings dams and open areas (Chaulya 2004). The handling of overburden, defined as the earth and rock that must be removed to gain access to the coal layers, can play a major part in dust generation, as the ratio of overburden to coal (also called the stripping ratio) in South African opencast coal mines varies between 2 and 6 (Mohutsiwa 2015, Moolman 2000). The impact of these activities on air quality in adjacent communities has become a matter of concern (see for instance Huertas et al. 2012, 2014); for Mpumalanga, this has been quantified by the Highveld Priority Area baseline study (DEA 2012).

Source apportionment

Source apportionment techniques such as principal component analysis (PCA) and principal matrix factorisation (PMF) are frequently used for atmospheric particulate matter (see for instance McGuire et al. 2011). As the inorganic components of atmospheric particulates from opencast mines and from other sources in their vicinity are often very similar, this paper explores the use of carbon- and nitrogen-related parameters of the atmospheric PM_{10} collected from opencast coal mines and from sites in adjacent residential communities to establish whether significant differences occur. Such differences could occur if the fuel mix used in the residential areas contains components originating from sources other than the adjacent mine and, if found, could augment existing source apportionment techniques. In this paper, the possible use of these parameters by the analysis of single samples taken at three pairs of mine and adjacent residential locations is explored.

Methodology

Selection of study areas

Areas located in the HPA and WBPA air quality management priority areas were selected for the study and consisted of three opencast coal mines and an adjacent community for each mine. Selection criteria for the community samples take into consideration site accessibility, security considerations for placement of PM_{10} monitoring equipment and the distance from industrial or commercial activities. Two opencast coal mines were selected in Mpumalanga due to a high concentration of opencast coal mining activities in the province. The adjacent communities to these mines are Delmas and Clewer in Emalahleni (Figure 1 and Figure 2). In the case of Delmas, a site in a residential backyard as close as possible to the centre of the Delpark residential area was used. At Clewer, the grounds of the local primary school were used. One opencast coal mine was selected in Limpopo given its proximity to the adjacent community of Marapong in Lephalale (Figure 3). The community monitoring site in this case was located at the local public library. Mine samples were taken as close as possible to the coal processing facilities so as to represent coal properties; in one of the Mpumalanga mines and for the Limpopo mine, samples were also taken in areas where overburden handling took place so as to represent the composition of overburden material.

Sampling

Portable Minivol (Airmetrics, Springfield, Oregon) samplers were deployed for the active sampling of atmospheric PM_{10} over 24h at 5 l/min at the selected opencast coal mines and adjacent communities during March 2018. PM_{10} impactors were used to selectively sample PM_{10} with quartz fibre filters (47 mm in diameter). After sampling, each filter was removed from the filter holder using forceps and was placed in a marked container for post sampling weighing and analysis using Isotope Ratio Mass

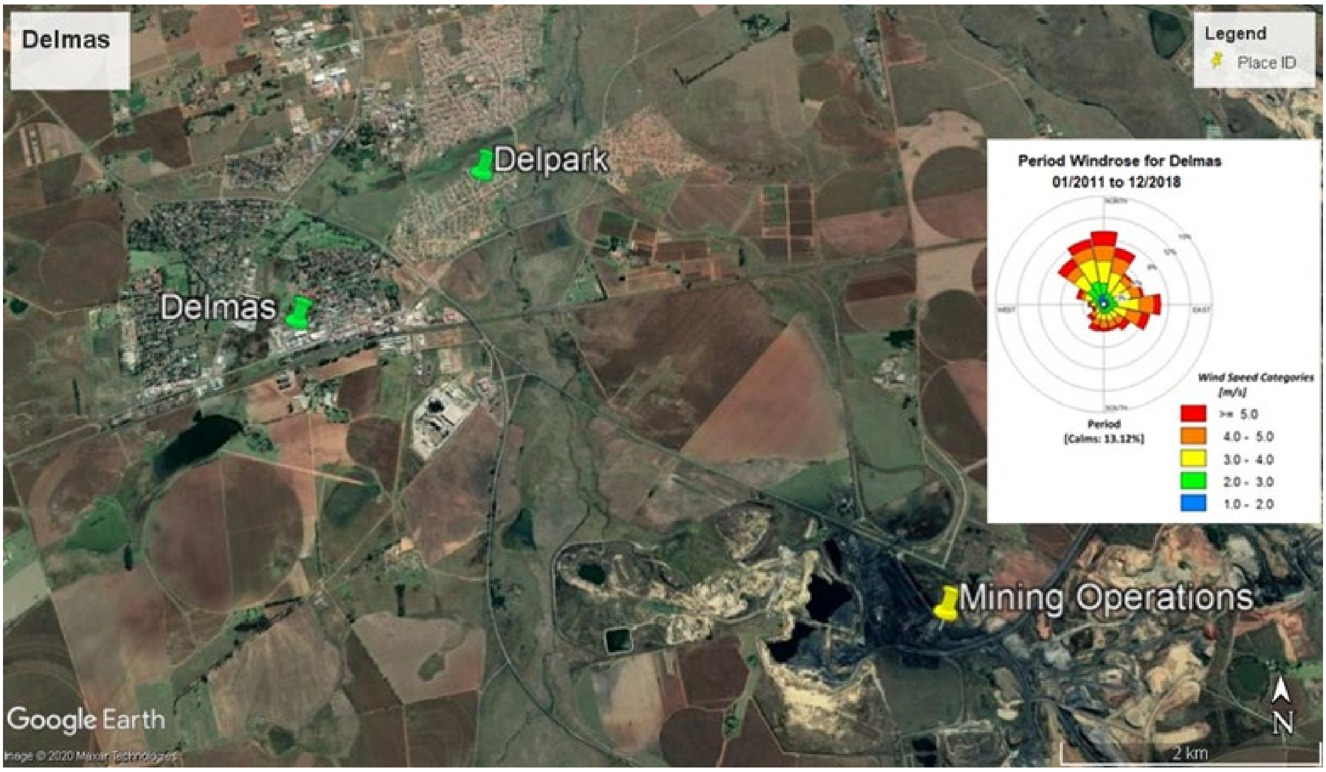

Figure 1: *Location of the community of Delpark in relation to current opencast coal mining activities in the town of Delmas, Mpumalanga (Google Earth Maps, 2018).*

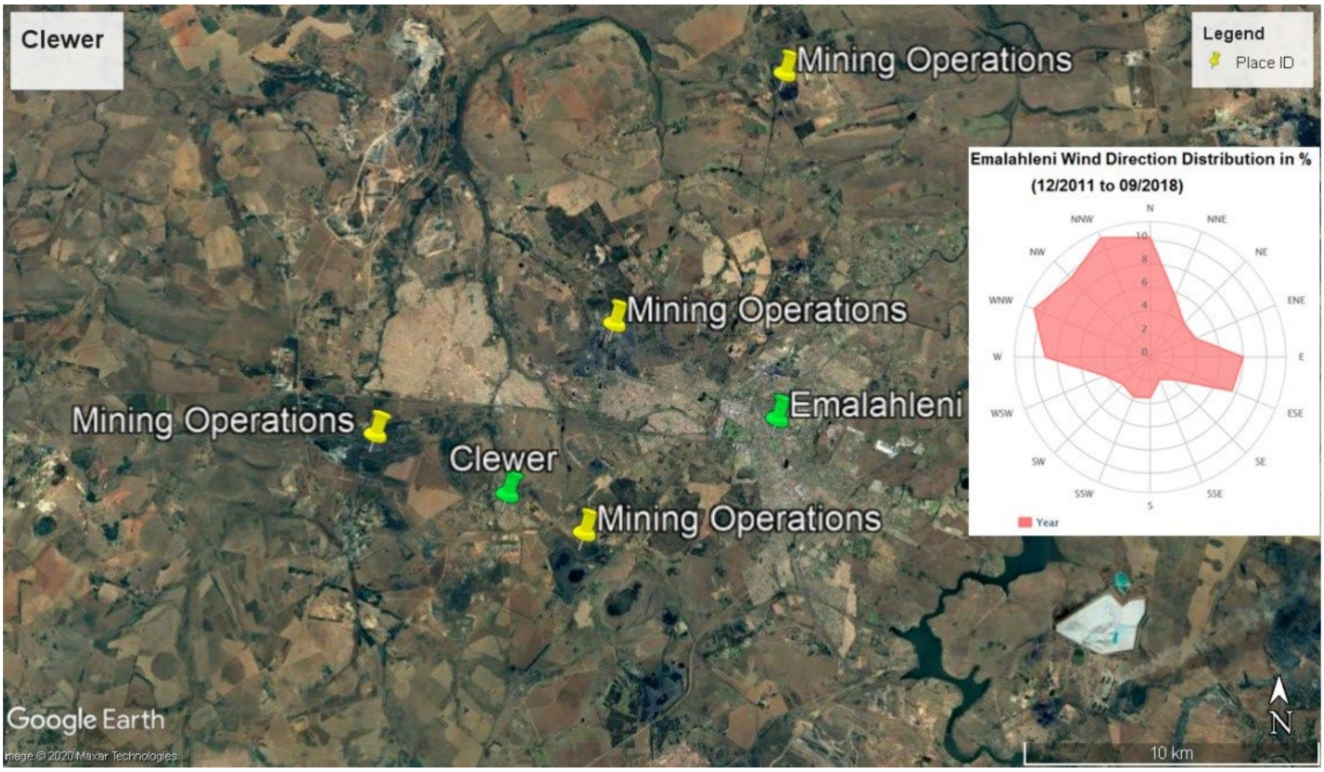

Figure 2: Location of the community of Clewer in relation to current opencast coal mining activities in the town of Emalahleni, Mpumalanga (Google Earth Maps, 2018).

Figure 3: Location of the community of Marapong in relation to current opencast coal mining activities in the town of Lephalale, Limpopo (Google Earth Maps, 2018).

Spectrometry (IRMS) and thermal optical techniques. Within the mine area, samplers were located in coal handling areas and overburden handling areas to determine possible differences in the properties being evaluated.

Analysis

Isotope Ratio Mass Spectroscopy

Atmospheric PM samples were combusted at a temperature of 1020°C using an elemental analyser (EA) (Flash EA 1112 Series) coupled to a Delta V Plus stable light isotope ratio mass spectrometer (IRMS) via a ConFlo IV system (all equipment supplied by Thermo Fischer, Bremen, Germany), housed at the UP Stable Isotope Laboratory, Mammal Research Institute, University of Pretoria. Two laboratory running standards (Merck Gel: $\delta^{13}C$ = -20.26‰, $\delta^{15}N$= 7.89‰, C%= 41.28, N%=15.29) and (DL-Valine: $\delta^{13}C$ = -10.57‰, $\delta^{15}N$=-6.15‰, C%=55.50, N%=11.86) and a blank sample were run after every 11 unknown samples. Data corrections were done using the values obtained for the Merck Gel during each run. The standard deviations of the nitrogen and carbon values for the DL-Valine standard provided the ± error for $\delta^{15}N$ and $\delta^{13}C$ values for the samples. The C and N ratios for all secondary (NIST) and lab running (Merck & DL-Valine) standards were all calibrated using the following primary standards:

- IAEA-CH-3 (Cellulose),
- IAEA-CH-6 (Sucrose),
- IAEA-CH-7 (Polyethylene foil),
- IAEA N-1 & IAEA N-2 (Ammonium sulphate),
- IAEA NO-3 (Potassium nitrate).

All the results were referenced to Vienna Pee-Dee Belemnite for carbon isotope values and to air for nitrogen isotope values. Results were expressed in delta notation using a per mille scale using the standard equation:

$$\delta X\ (‰) = [(R_{sample}-R_{standard})/R_{standard}-1]$$

where X= ^{15}N or ^{13}C and R represents $^{15}N/^{14}N$ or $^{13}C/^{12}C$ respectively.

Thermal Optical Characterisation of OC and EC

The quartz filters from the PM_{10} active monitoring campaign were analysed using a thermal-optical carbon analyser (Sunset Laboratory Inc Lab OC-EC Aerosol Analyser). The blank filters were pre-fired in air (700°C for one hour) for the removal of residual carbon contaminants. The detection limit of the instrument is 0.2 µg cm^{-2} and the relative standard deviation (RSD) 5%. The instrument and analysis process followed during this investigation is shown in Figure 4.

Punch aliquots of 1.5 cm^2 of the filter deposits were used for the analysis. Each aliquot was heated in a sample oven in four increasing temperatures of 140°C (OC1), 280°C (OC2), 480°C (OC3) and 580°C (OC4) in a non-oxidizing helium (He) atmosphere (Afrox Ltd, 99.999%) for the removal of all organic carbon (OC) on the filter. The carbon that evaporated at each temperature was catalytically oxidized by MnO_2 into CO_2 in the oxidiser oven. The CO_2 entrained in the He gas flow, was converted to CH_4 in the methanator oven. The detection and quantification of methane was undertaken through a flame ionisation detector while the pyrolitic conversion was continuously monitored by measuring the transmission of a He-Ne laser through the quartz filter. The darkness of the filter was also continuously monitored throughout all stages of the analysis. Ramping up to the next tsemperature or atmosphere was undertaken when the flame ionization detector's response returned to baseline or a constant value (subject to the condition of the time spent in any segment (OC1, OC2, etc).

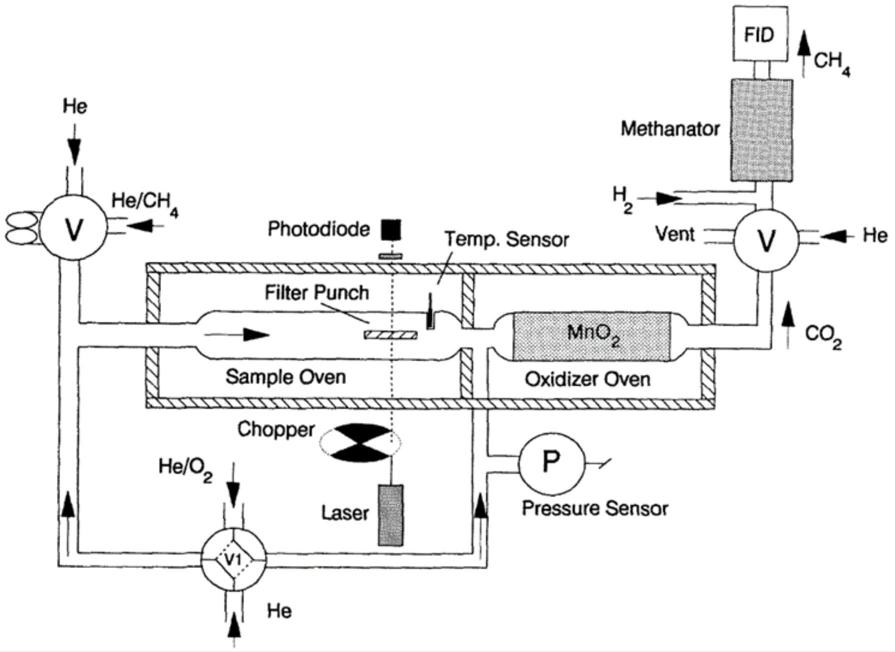

Figure 4: *Schematic of thermal-optical instrumentation (Birch & Cary, 1996).*

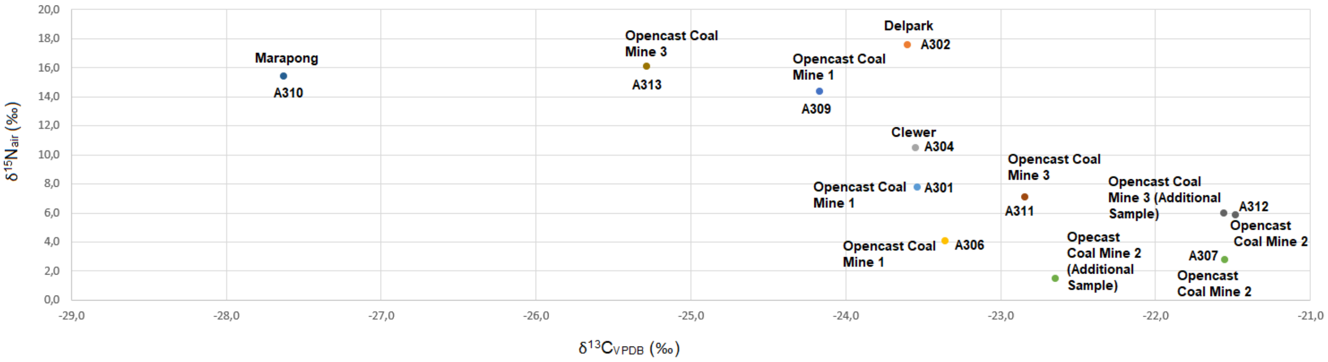

Figure 5: *Biplot of mean carbon and nitrogen isotope ratios for opencast coal mines and adjacent communities.*

Table 1: *Results of stable carbon and nitrogen isotope analysis for atmospheric PM samples.*

Sample ID	Weight	δ15N (‰)	%N	δ13C (‰)	%C	C/N ratio
A301 Opencast Coal Mine 1 Sample 1	10,1	7,8	0,13	-23,5	1,21	10,8
A302 Delpark Community	12,4	17,5	0,24	-23,6	2,89	14,3
A304 Clewer Community	17,6	10,5	0,03	-23,6	0,53	18,4
A306 Opencast Coal Mine 1 Sample 2 (plant area)	10,7	4,1	0,06	-23,4	1,80	34,8
A307 Opencast Coal Mine 2 Sample 1 (overloaded)	2,8	2,8	1,37	-21,6	56,55	48,1
A309 Opencast Coal Mine 1 (overburden area)	13,0	14,4	0,08	-24,2	1,08	16,5
A310 Marapong Community	14,6	15,4	0,07	-27,6	0,83	14,7
A311 Open cast Coal Mine 3 Sample 1	10,0	7,1	0,23	-22,8	5,27	27,1
A312 Open Cast Coal Mine 2 Sample 2	12,9	5,8	0,39	-21,5	12,87	38,9
A313 Opencast Coal Mine 3 Sample 2 (overburden area)	16,4	16,1	0,04	-25,3	0,33	9,7
Opencast Coal Mine 2 Additional Sample 2	2,8	1,5	1,02	-22,6	33,58	38,5
Opencast Coal Mine 3 Additional Sample	9,8	6,00	0,46	-21,6	16,32	41,2

Table 2: *Organic, elemental and total carbon concentrations for the opencast coal mines and adjacent communities atmospheric PM samples.*

Sample ID	OC (μg cm^{-2})	EC(μg cm^{-2})	TC(μg cm^{-2})	OC/EC Ratio
A301 Opencast Coal Mine 1 Sample 1	24	16	39	1.53
A302 Delpark Community	112	25	136	4.50
A304 Clewer Community	21	4	25	6.03
A306 Opencast Coal Mine 1 Sample 2	30	19	48	1.60
A307 Opencast Coal Mine 2 Sample 1 (filter overloaded)	4,7E+09	5,1E+09	9,9E+09	0.92
A309 Opencast Coal Mine 1 Sample 3 (overburden area)	33	7	40	5.01
A310 Marapong Community	24	3	27	8.13
A311 Open cast Coal Mine 3 Sample 1	91	58	150	1.56
A312 Open Cast Coal Mine 2 Sample 2	285	310	596	0.92
A313 Opencast Coal Mine 3 Sample 2 (overburden area)	16	3	19	5.61

The sample oven was then cooled to 525°C and the pure helium eluent was switched to a 2% O2/98% He mixture. Peaks were integrated at 580°C (EC1), 740°C (EC2), and 840°C (EC3). The sample oven temperature was then stepped up to 850°C (EC4). During this phase, both the original EC and the EC produced through the pyrolysis of OC during the first phase were oxidized to CO_2 due to the presence of oxygen in the eluent. The CO_2 was then converted to CH_4 and detected by the flame ionisation detector. The darkness of the filter was also continuously monitored throughout all stages of the analysis by reflectance of 633 nm of light from a He–Ne laser. During this phase, original and pyrolized black carbon were combusted and the increases in the reflectance were observed. The amount of carbon that was measured after the addition of oxygen until the reflectance achieved its original value was reported as optically detected pyrolized carbon (PC).

After the oxidation of all the carbon from each sample, a known volume of methane (Afrox Ltd 99.95%) was injected into the sample oven, resulting in each sample being calibrated to a known quantity of carbon. Based on the Flame Ionisation Detector (FID) response and laser transmission data, the quantities of OC and EC were calculated for each sample. The concentration of OC and EC on each filter punch aliquot was calculated by multiplying reported values by the sample deposit area. The concentrations were reported in μg/cm² of deposit area. This approach assumed a homogenous filter deposit. The precision of this technique (Sunset Laboratory method of OC/EC analysis), measured as a relative standard deviation, typically falls into the 4-6% range for samples that are in the afore-mentioned OC and EC concentration ranges. This relative standard deviation range is applicable to the OC/EC speciation values as well as to the total carbon.

Results and discussion

For this exploratory study, only single samples were taken per location and the conclusions below are preliminary.

Stable Isotope Analysis

For the mining samples, those representing coal handling and those taken in overburden handling areas (A309 and A313) show different characteristics on the plot of $\delta^{15}N$ against $\delta^{13}C$ (Figure 5) As shown in section 3.2, the OC fraction of these samples is also much higher than those of the coal-rich samples, indicating that the carbon in these samples is of a different origin. The mine samples representing mainly coal dust and the residential area samples have distinct characteristic fingerprints, with the community samples having higher $\delta^{15}N$ values than the coal samples (Table 1 and Figure 5). The high $\delta^{15}N$ values for the residential areas Marapong (average annual precipitation 437 mm/annum), Clewer (average annual precipitation 693 mm/annum) and Delpark (average annual precipitation 1230 mm/annum) are unexpected. Amundsen et al. (2003) indicate the South African average for soils to be 6.2 to 7.6‰, while they found values to decrease with increased annual precipitation. Savard et al. (2017) give a value of 3.4 to 6.1‰ for coal-fired power station emissions, while Moroeng et al. (2018) give a value of 2.66‰ for Witbank no 4 seam coal, which is the predominant coal at Opencast Coal Mines 2 and 3. This suggests a contribution by biomass-related particulate for the residential samples. This is confirmed by the $\delta^{13}C$ value (see below) for the more rural area around Marapong, but not for Clewer and Delpark where biomass is less readily available; the $\delta^{15}N$ for C_3 and C_4 biomass-related PM_{10} is given as 13.7 ± 2.2‰ by Mkoma et al. (2013), while for C_4 biomass-related particulate Bikkina et al. (2016) give a value of 11.5±2.1‰. The $\delta^{15}N$ isotope ratios for the opencast coal atmospheric PM samples are lower than those for the residential samples, but higher than that given for South African coals by Moroeng et al. (2018) at 2.66‰. This may be due to the extensive use of liquid fuels (diesoline) in opencast coal mining, for which the $\delta^{15}N$ is given as between 3.9 and 5.4±0.5‰ by Widory (2007), or to the presence of mineral dust in the mine samples.

The carbon isotope fingerprint ratios for the opencast coal mines' atmospheric PM samples were within the $\delta^{13}C$ ranges measured for coal in various parts of the world (-27.4‰ to –23.7‰) (Suto and Kawashima, 2016; Garbarienė et al. 2016). For the coal mined at mines 2 and 3, Moroeng et al. (2018) give a value of -23.27‰. The impact of coal combustion products cannot be distinguished from coal dust itself; values for atmospheric particulate related to coal combustion are given as -23.5±1.3 (Andersson 2015, Fang and Andersson 2017) and -24.5±0.5‰ (Garbarienė et al. 2016, Engelbrecht et al. 2002). The lower carbon isotope values for the residential area, especially for the rural area (sample A310) can be attributed to the use of biomass (mainly wood) or the contribution of traffic-derived particulate. The $\delta^{13}C$ values for wood is given by Garbarienė et al. (2016) as -26 to -27‰, with little fractionation with combustion, while Bikkina et al. give a value of -25.8±0.5‰ for C_4 plant-related combustion particulate. For traffic-related particulate, Engelbrecht et al. (2002) provide a $\delta^{13}C$ value of -28 to -29‰.

Thermal optical characterisation

The OC, EC and TC concentrations (μg cm^{-2}) and the OC/EC ratio obtained from the thermal optical analysis of the opencast coal mines and adjacent communities' atmospheric PM samples are shown in Table 2. Again not taking samples that represent mainly overburden (A309 and A313) into account, OC/EC ratios confirm the observations of the section "Stable Isotope Analysis". Mine samples have a low ratio, commensurate with the ratio between volatile matter and fixed carbon in the coal before combustion. The filters for the samples from mine 2 were both overloaded, and the results are accordingly less accurate. The best range for the deposit concentration is 5-400 μg/cm^{-2} for OC and 1-15 μg/cm^{-2} for EC. Concentrations of OC that are greater than this range may result in exceedances of the detection limits of the OC/EC instrument and interference with the EC measurements, particularly when low concentrations of EC are found in the sample (Desert Research Institute, 2019).

Samples from the residential communities have higher values, but source contributions cannot be determined from this ratio only. Sources that may contribute are coal combustion at OC/EC of 7.0, liquid fuel combustion at 9.7 (Engelbrecht et al. 2002), the combustion of C_3 biomass at 16±5 and the combustion of C_4 biomass (grasses) at 18±4 (Salma et al. 2017). The higher ratio for Marapong would suggest a higher contribution by the latter two sources.

Conclusion and recommendation

This exploratory work on the use of IRMS and thermal-optical methods for characterising carbon-containing particles near opencast coal mines indicates the possibility of applying the results of these techniques to improve source apportionment for atmospheric PM in such locations. Additional sampling and analysis of the coal itself, with the use of operational data on mine stripping ratios and/or dispersion modelling and the standard source apportionment techniques would be required to allow more exact characteristics to be determined.

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References

Albers, P. N., Wright, C. Y., Voyi, K. V. V. and Mathee, A. (2015) Household fuel use and child respiratory ill health in two towns in Mpumalanga, South Africa, South African Medical Journal. South African Medical Association NPC, 105(7), pp. 573–577. doi: 10.7196/SAMJnew.7934.

Amundson, R., Austin, A.T., Schuur, E.A.G., Yoo, K., Matzek, V., Kendall, C., Uebersax, A., Brenner, D. and Baisden, W.T. (2003) Global patterns of the isotopic composition of soil and plant nitrogen. Global biogeochemical cycles 17(1) pp1031-1040 doi:10.1029/2002GB001903

Andersson, A., Deng, J., Du, K., Zheng, M., Yan, C., Sköld, M. and Gustafsson, Ö. (2015) Regionally-Varying Combustion Sources of the January 2013 Severe Haze Events over Eastern China. Environ. Sci. Technol. 49, 2038−2043 doi:10.1021/es503855e

Bikkina, S., Kawamura, K. and Manmohan S. (2016) Stable carbon and nitrogen isotopic composition of fine mode aerosols ($PM_{2.5}$) over the Bay of Bengal: impact of continental sources. 31 68 pp 31518-31533 doi 10.3402/tellusb.v68.31518

Birch, M. E. and Cary, R. A. (1996) Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust, Aerosol Sci Tech 25(3), pp. 221–241. doi: 10.1080/02786829608965393.

Chaulya, S. K. (2004) Assessment and management of air quality for an opencast coal mining area, J Env Man 70(1), pp. 1–14. doi: 10.1016/j.jenvman.2003.09.018.

Department of Environmental Affairs (DEA) (2017) The Management of Air Quality in South Africa. Available at: www.saaqis.org.za (Accessed: 29 November 2019).

Department of Environmental Affairs (DEA) (2012) Highveld Priority Area Air Quality Management Plan. Government Gazette 35072 of 2 March 2012.

Desert Research Institute (2019) EAF Capabilities- Carbon Analysis (TOR/TOT). Available at: https://www.dri.edu/eaf-lab (Accessed: 29 November 2019).

Engelbrecht, J.P., Swanepoel, L., Chow, J.C., Watson, J.G. and Egami, R.T. (2002) The comparison of source contributions from residential coal and low-smoke fuels, using CMB modeling, in South Africa. Envl Sci & Policy 5 157–167. doi:10.1016/S1462-9011(02)00029-1.

Fang, W., Andersson, A., Zheng, M., Lee, M., Holmstrand, H., Kim, S., Du, K. and Gustafsson, Ö. (2017) Divergent Evolution of Carbonaceous Aerosols during Dispersal of East Asian Haze. Scientific Reports 7 10422-10433 doi:10.1038/s41598-017-10766-4

Garbarienė,I., Šapolaitė, J., Garbaras, A., Ežerinskis, Ž., Pocevičius, M., Krikščikas, L., Plukis, A. and Remeikis, V. (2016) Origin Identification of Carbonaceous Aerosol Particles by Carbon Isotope Ratio Analysis. Aerosol and Air Quality Res, 16: 1356–1365 doi: 10.4209/aaqr.2015.07.0443

Hartmann, S., O'Brien, G., Warren, K. and Krahenbuhl, G. (2016) Characterisation of urban dust samples using reflected light microscopy methods, Air Quality and Climate Change, 50(3), p. 34.

Huertas, J.I., Huertas, M.E., Izquierdo, S. and González, E.D. (2012) Air quality impact assessment of multiple open pit coal mines in northern Colombia. J Env Man 93 pp 121-129 doi: 10.1016/j.jenvman.2011.08.007

Huertas J.I., Huertas, M.E., Cervantes, G. and Díaz, J. (2014) Assessment of the natural sources of particulate matter on the opencast mines air quality. Sci Total Env 493 pp 1047-1055 doi: 10.1016/j.scitotenv.2014.05.111

Kunzli, N. and Tager, I. B. (2000) Long-Term Health Effects of Particulate and Other Ambient Air Pollution: Research Can Progress Faster If We Want It to, Env Health Perspectives 108(10), p. 915. doi: 10.2307/3435048.

Lim, S.S. et al. (2012) A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and risk factor clusters in 21 regions, 1990–2010: a systematic analysis for the Global Burden of Disease Study 2010 Lancet 380 pp 2225-2260

Mannucci, P. and Franchini, M. (2017) Health Effects of Ambient Air Pollution in Developing Countries, Intl J Envl Res and Public Health 14(9), p. 1048. doi: 10.3390/ijerph14091048.

Mkoma, S.L., Kawamura, K., Tachibana, E. and Pingqing Fu (2014) Stable carbon and nitrogen isotopic compositions of tropical atmospheric aerosols: sources and contribution from burning of C3 and C4 plants to organic aerosols. Tellus B 66(1) pp 20176-20190, doi: 10.3402/tellusb.v66.pp 20176

McGuire, M.L., Jeong, C.-H, Slowik, J.G., Chang, R.Y.-W, Corbin, J.C., Lu, G., Mihele, C., Rehbein, P.J.G., Sills, D.M.L., Abbatt, J.P.D., Brook, J.R. and Evans, G.J.(2011) Elucidating determinants of aerosol composition through particle-type-based receptor modeling. Atmos. Chem. Phys., 11, 8133–8155. doi:10.5194/acp-11-8133-2011.

Moolman, C.J. (2000). *Evaluation of stripping techniques*. Coaltech 2020 report on task 3.14.1.

Mohutsiwa, M. (2015) *Estimation of capital costs for establishing coal mines in South Africa*, MEng thesis, Faculty of Engineering and the Built Environment, University of the Witwatersrand.

Moroeng O.M., Wagner, N.J., Hall, G. and Roberts, R.J. (2018) Using $\delta^{15}N$ and $\delta^{13}C$ and nitrogen functionalities to support a fire origin for certain inertinite macerals in a No. 4 Seam Upper Witbank coal, South Africa. Org Geochem 125 pp 23-32. doi: 10.1016/j.orggeochem.2018.10.007.

Salma, I., Németh, Z., Weidinger, T., Maenhaut, W., Claeys, M., Molnár, M., Major, I., Ajtai, T., Utry, N., and Bozóki, Z. (2017) Source apportionment of carbonaceous chemical species to fossil fuel combustion, biomass burning and biogenic emissions by a coupled radiocarbon–levoglucosan marker method. Atmos. Chem. Phys., 17pp 13767–13781. doi: 10.5194/acp-17-13767-2017.

Savard, M.M., Cole, A., Smirnoff, A. and Vet, R (2017) $\delta^{15}N$ values of atmospheric N species simultaneously collected using sector-based samplers distant from sources - Isotopic inheritance and fractionation. Atm Env 162 pp 11-22. doi: 10.1016/j.atmosenv.2017.05.010.

Suto, N. and Kawashima, H. (2016) Global mapping of carbon isotope ratios in coal. J Geocheml Expl 167, pp 12-19. doi: 10.1016/j.gexplo.2016.05.001.

Widory, D. (2007) Nitrogen isotopes: Tracers of origin and processes affecting PM_{10} in the atmosphere of Paris. Atm Env 41 (2007) 2382–2390 doi:10.1016/j.atmosenv.2006.11.009 Australia, pp. 180-185.