academicJournals

Vol. 8(4), pp. 210-218, April 2014
DOI: 10.5897/AJEST2013.1567
Article Number: B0CC71B44340
ISSN 1996-0794

http://www.academicjournals.org/AJEST

African Journal of Environmental Science and Technology

Full Length Research Paper

Determination of some polycyclic aromatic hydrocarbons (PAHs) associated with airborne particulate matter by high performance liquid chromatography (HPLC) method

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Received 01 August, 2013; Accepted 27 February, 2014

In this study, polycyclic aromatic hydrocarbons (PAHs) associated with airborne particulate pollutants of aerodynamic size 10 µm (PM10) were studied for three months, from October to December 2010 in the Vanderbijlpark area. Some PAHs are highly carcinogenic and could be more harmful when combined with inhalable PM10. A dual E-Sampler which combines the light scatter and the gravimetric filter methods was used. A 10 mg/L standard stock solution that contained naphthalene (Naph), 2-methyl naphthalene (2-MNaph), phenanthrene (Phe), anthracene (Anth), benzo(b)fluoranthene (BbFl), benzo(k)fluoranthene (BkFl), benzo(a)pyrene (BaPy) and dibenzo(a,h)anthracene (DiBahAn) was prepared, compounds were indentified and quantified with an Agilent high performance liquid chromatography (HPLC). A dichloromethane (DCM) and n-hexane (1:1) extraction mixture was used to extract the pollutants from both exposed and unexposed (blank) filters. Detection limits obtained ranged from 0.001 to 0.0305 mg/L and R-values ranged from 0.996 – 0.999. Very good percentage recoveries were obtained with the lowest 97.63% and highest 101.57% associated with DiBahFl and 2-MNaph, respectively. Total concentration of 2-MNaph obtained per month were 325.2 ng/L (October 2010), 162.4 ng/L (November 2010) and 381.2 ng/L (December 2010). Relatively high levels of 2-MNaph were detected consistently when compared with other pollutants in the three months. Concentration ranges of other PAH compounds were Anth (7.2 - 14.76 ng/L), BbFl (6.7 - 13.6 ng/L), BaPy (6.8 - 13.0 ng/L) and BkFl (6.7 - 10.8 ng/L). Daily and monthly mass concentration levels obtained were lower than the strict regional daily limit of 0.075 µg/m^3, as well as national and international daily limits of 0.150 µg/m^3. These results could be used as the basis for undertaking a comprehensive study on the status of these organic compounds from the heavily industrialized Vaal Triangle region.

Key words: Polycyclic aromatic hydrocarbons (PAHs), PM10, distribution, concentration, high performance liquid chromatography (HPLC), Vanderbijlpark.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants which are known to be carcinogenic to animals (Hailin et al., 1998; Menzie et al., 1992). They are lipophilic and present in the atmosphere due to emissions from vehicles, residents heating systems that utilize coal, wood, gas and industrial processes

(Söderström et al., 2005). PAHs are composed of carbon and hydrogen atoms arranged in the form of fused benzene ring as cluster, linear or angular (Maliszewska-Kordybach, 1999). They exist in the atmosphere in both vapor and particulate phase (Guo et al., 2003; Van Jaarsveld et al., 1997). PAHs with low molecular weight have propensity to be more concentrated in the vapor-phase whereas those with higher molecular weight are often associated with particulates (Maliszewska-Kordybach, 1999; Guo et al., 2003). When in air, PAHs can be transported over a long distance before they are deposited with atmospheric precipitation on soils, vegetation, sea and inland (Wania and Mackay, 1996; Wild and Jones, 1995). PAHs have been associated with adverse health effects in the human population (Halsall et al., 1994; IARC, 1987). They are linked to morphological, physiological and developmental abnormalities in test animals, increased allergic immune responses in human at low levels and may act synergically with other air toxics to cause adverse health effects (Li et al., 2005; ATSDR, 1995; Diaz-Sanchez et al., 1996; Harvey, 1991). Estimated potential doses of carcinogenic PAHs by inhalation to range is between about 0.02 and 3 µg/day with a median value of 0.16 µg/day, which is about 20 times more than the calculated food dose and about 25 times more than the potential dose with drinkable water (Menzie et al., 1992).

Vanderbijlpark city is located close to anthropogenic pollution sources such as mining, a coal power station, steel manufacturing companies, an oil refinery, major roads and fossil fuel burning residential areas. This city has been identified as one of the national air pollution hot spots according to the National Environment Management Air Quality Act 2004 (Act No. 39 of 2004) of South Africa (Vaal Environmental News, 2011). A number of reports exist on the general environmental pollution by PAHs within this city and the surrounding areas, however, not much if any has been reported on airborne pollution by PAHs.

The aim of this study was to evaluate the levels of PAHs associated with airborne PM10 particles from the Vanderbijlpark. Cities of Vanderbijlpark, Sasolburg and Meyerton form the Vaal Triangle region. These cities are also close to townships such as Sebokeng, Evaton and Sharpville.

MATERIALS AND METHODS

Sample collection, preparation and analyses

Sample collection

A particulates E-Sampler from Met One Instruments Inc, Oregon United States of America, was used to collect PM10 samples (Figure 1). The E-sampler is a dual technology instrument that combines the real time measurement of the light scatter method and the gravimetric filter method where particles are pre-concentrated. An internal rotary vane pump draws air at the rate of 2 L per minute (LPM) into the visible laser light sensing chamber used for measuring the number of particles in a particular volume of air. The instrument is capable of making 40 measurements per second and averaging them to get a representative particulate data per hour, day or month. Rugged state of the art electronics measure the intensity of the focused light and output a signal to the central processing unit (CPU).

The E-Sampler was placed in the backyard of a suburban house (26°42′01″S, 27°51′15″E) and sampling occurred in three consecutive months from October to December 2010. Continuous daily samples were averaged every 30 min and then arranged per month. Data measured on the day which experienced the highest PM10 loading was further arranged per hour to study the diurnal distribution. High purity quartz filters (20 x 25 cm Whatmann 41, Whatman Corp, USA) were used and dried in a desiccator overnight. A mass of filter paper was weighed before and after exposure to attain the total particulate mass loading per sampling period on a Mettler Toledo AG245 analytical balance.

Standard and sample preparation

A 1.0 mg/L standard stock solution was prepared by dissolving 1.0 mg of each of Naph, 2-MNaph, Phe, Anth, BbFl, BkFl, BaPy and DiBahFl PAH compounds (Dr. Ehrenstorfer Reference Materials, Atlanta, U.S.A.) in 1000.0 ml acetonitrile solvent. All solvents used were of analytical grade and were obtained from Sigma-Aldrich, Johannesburg, S.A. A series of calibration standard solutions ranging between 0.01 and 1.0 mg/L were prepared from the stock solution.

A benchmark method for the extraction of PAHs from soils and sediments (was adopted during this study (Lau et al., 2010). The soxhlet extraction apparatus were cleaned by evaporating methanol at 180°C in a rotaevaporator three times, followed by three times evaporation of the extraction mixture of dichloromethane (DCM) and n-hexane (1:1) for an hour. The fourth extract of the extraction solvent mixture was collected from the receiving flask for analysis. PAH compounds were extracted from both unexposed and exposed filters with the prepared extraction mixture for an hour at 180°C in the rotaevaporator. Extracts were analyzed on the same day or stored in amber sample bottles in a fridge at below 4°C temperatures. About 20.0 µl of sample were injected five times per sample in a high performance liquid chromatographic (HPLC) instrument.

Instrumentation

An Agilent 1100 model HPLC (Agilent Technology Inc, Santa Clara, California, U. S. A) with a programmable wavelength diode array and ultraviolet (on 254 nm) detectors were used. Operating conditions were: sample volume = 20.0 µL, run time = 25 min, flow rate = 1.0 mL/min, column temperature = 23.0°C (ambient), column = eclipse XDB-C18 column (4.6 mmID x 250.0 mm (5.0 µm) 80.0 Á), mobile phase = 50.0% DCM and 5.00% n-hexane.

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Figure 1. Filter loading area of the E-Sampler (Model 9800 Rev G).

Table 1. Average daily and monthly PM10 mass concentration results levels (mg/m^3).

Day of the month	2010		
	October	November	December
1	0.00067	0.00042	0.00025
2	0.00038	0.00004	0.00025
3	0.00033	0.00033	0.00067
4	0.02283	0.00063	0.00042
5	0.01477	0.00033	0.00054
6	0.03554	0.00021	0.00067
7	0.00121	0.00046	0.00071
8	0.00079	0.00008	0.01413
9	0.00017	0.00021	0.01158
10	0.00021	0.00001	0.00573
11	0.00025	0.00002	0.00688
12	0.01225	0	0.00013
13	0.01396	0.02046	0.00042
14	0.00008	0.01883	0.00071
15	0	0.0001	0.00021
16	0.00183	0	0.00017
17	0.00425	0.00046	0.00042
18	0.00225	0.00108	0.00021
19	0.00975	0.00146	0.00004
20	0.048	0.00188	0.00001
21	0.00204	0.00104	0.00002
22	0.01542	0.00029	0
23	0.00967	0.00046	0.00004
24	0.0001	0.00021	0.01387
25	0.0007	0.00013	0.01667
26	0	0.00008	0
27	0	0.00633	0.00001
28	0.01809	0.02754	0.00017
29	0.02196	0.00046	0.00025
30	0.00038	0.00021	0.00004
Sum	0.23788	0.08376	0.07522

RESULTS AND DISCUSSION

PM10 mass concentration

Average daily and monthly PM10 mass concentrations for three months are shown in Table 1. The highest mass concentration data per month were: 0.048 mg/m^3 (20th), 0.03554 mg/m^3 (6th), 0.02283 mg/m^3 (4th) and 0.02196 mg/m^3 (29nth) in October; 0.02754 mg/m^3 (28th); 0.02046 mg/m^3 (13th) in November and the December data were all below 0.02 mg/m^3. These results are also in agreement with those obtained in summer seasons as reported (Moja et al., 2012). Average daily mass concentrations were below the stringent Vaal Triangle regional standard of 0.075 mg/m^3. Department of Environmental Affairs (DEA's) national daily limit together with international EPA's standard and WHO's guidelines of 0.150 mg/m^3 were also not exceeded (NAAQS, 2009; Annergan and Scorgie, 2002).

The highest daily PM10 loading was obtained on the 20th October. Hourly distribution of this data is shown in Figure 2, with the largest peak starting from 2:00 (0.0001 mg/m^3) and ending at 16:00 (0.0011 mg/m^3) with a peak maxima occurring at 13:00 (0.0043 mg/m^3). A smaller peak was measured from 18:00 (0.0011 mg/m^3) to 22:00 (0.001 mg/m^3) with a peak maxima at 19:00 (0.0021 mg/m^3). Similar PM10 diurnal distribution pattern within this study area was previously reported (Moja et al., 2012). This distribution pattern resemble the morning traffic flow to work, as well as the optimized industrial activities at around midday.

Concentrations of PAHs

Detection limits for the instrument were taken as three times the standard deviation of the lowest detectable concentration of PAHs from the mean of triplicate analyses and ranged from 0.001 to 0.0305 mg/L (Table 2).

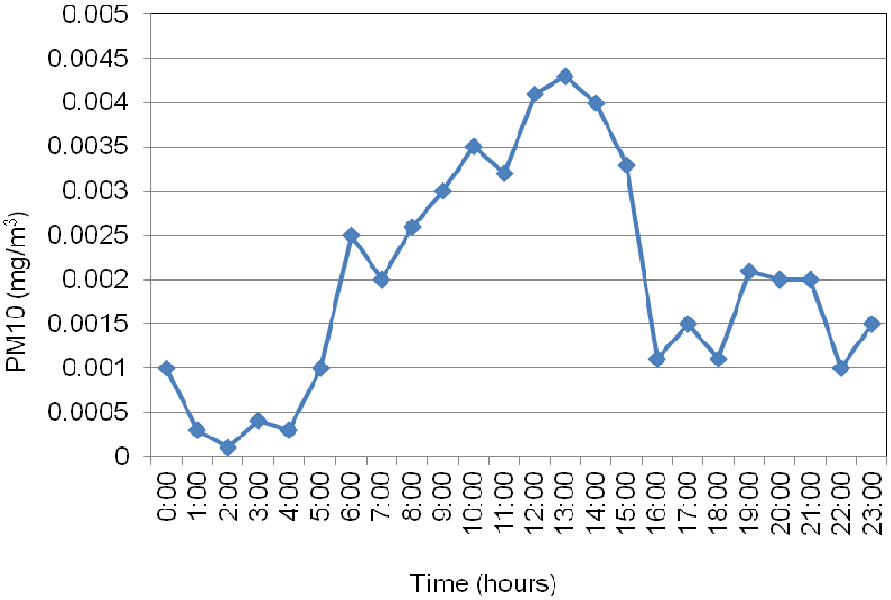

Figure 2. Hourly PM10 distribution on the 20th of October.

Table 2. Calibration data.

PAHs	Linear calibration ranges (mg/L)	Detection Limits (mg/L)	Linear equation	R^2	Recovery (%)
Naph	0.2 - 1.0	0.0305	y = 23.73x + 0.11	0.999	98.34
2-MNaph	0.2 - 1.0	0.0301	y = 27.17x + 0.06	0.999	101.57
Phe	0.02 - 1.0	0.0035	y = 335.4x + 0.04	0.998	100.39
Anth	0.01 - 1.0	0.001	y = 1135x + 0.15	0.999	100.82
BbFl	0.03 - 1.0	0.0062	y = 174.5x + 0.09	0.996	100.7
BkFl	0.04 - 1.0	0.0032	y = 132.9x + 0.12	0.999	101.01
BaPy	0.04 - 1.0	0.0057	y = 132.2x + 0.31	0.996	100.68
DiBahFl	0.2 - 1.0	0.0146	y = 35.53x + 0.14	0.999	97.63

R-values obtained during the standard calibration process ranged from 0.996 - 0.999. Very good percentage recoveries were obtained with the lowest 97.63% and highest 101.57% associated with DiBahFl and 2-MNaph, respectively.

2-MNaph and Anth compounds were detected from a prepared extracting solvent mixture at 8.967 (min) and 10.979 (min) retention times (t_R), respectively (Figure 3). Their peak areas were 249.907 for 2-MNaph and 10.6032 for Anth.

Three PAH compounds were also detected after extracting an unexposed blank filter paper with the prepared solvent mixture. Figure 4 shows a chromatogram with peaks of 2-MNaph (t_R = 8.976 min), Anth (t_R = 10.976 min) and BbFl (t_R = 11.830 min). Peak areas were 222.465 for 2-MNaph, 7.94263 for Anth and 8.17125 for BbFl. Since higher peak areas of 2-MNaph and Anth were obtained from the prepared extracting solvent mixture than from the extract of a blank filter paper, it could be concluded that the blank filter did not contain these two compounds. However, this filter did contain BbFl.

The highest concentration of PAHs standard mixture (1.0 mg/L) was used to optimize the HPLC. Standard PAH compounds had the following retention times: Naph (6.933 min), 2-MNaph (8.712 min), Phe (9.700 min), Anth (10.119 min), BbFl (13.936 min), BkFl (14.108 min), BaPy (14.454 min) and DiBahFl (14.976 min) as shown in Figure 5.

PAH compounds detected from the exposed filters are shown in Figures 6a to c. The five PAH compounds detected from all the samples analyzed in the order of appearance of the peaks on the chromatogram are 2-MNaph, Anth, BbFl, BkFl and BaPy and the retention

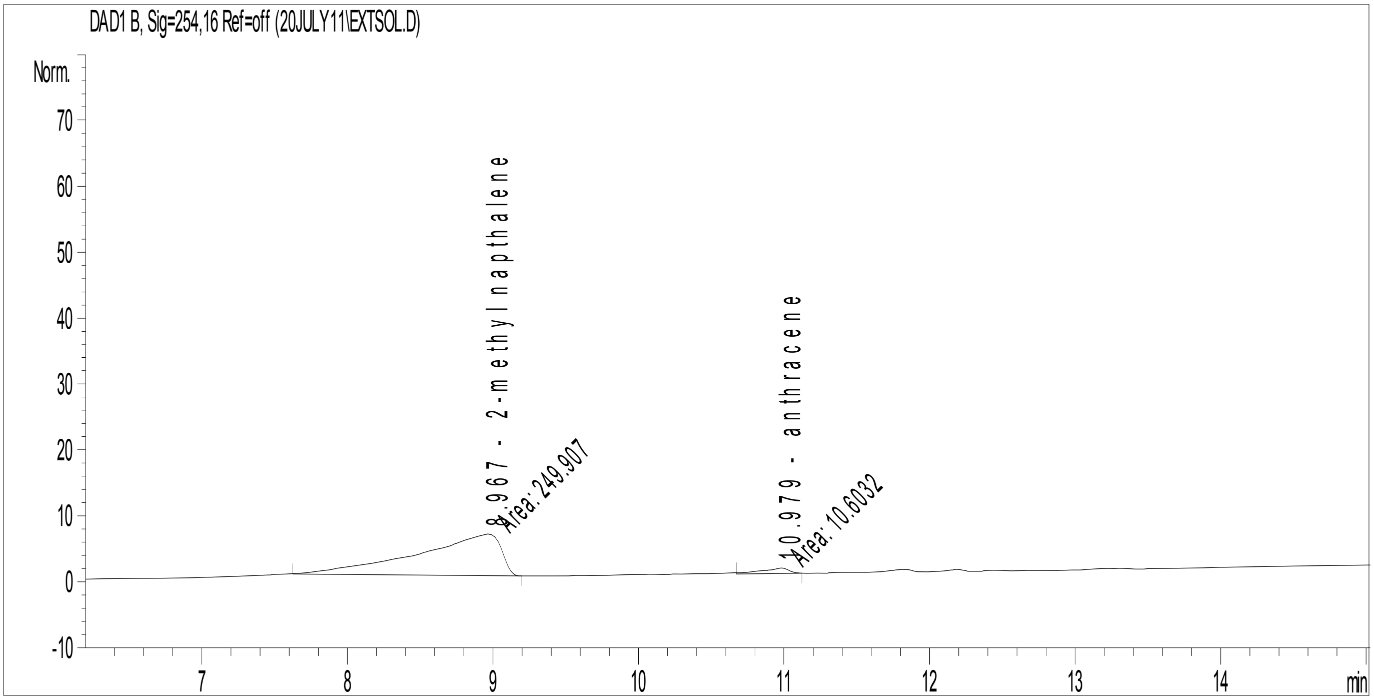

Figure 3. Chromatogram of PAHs from the prepared extracting solvent mixture.

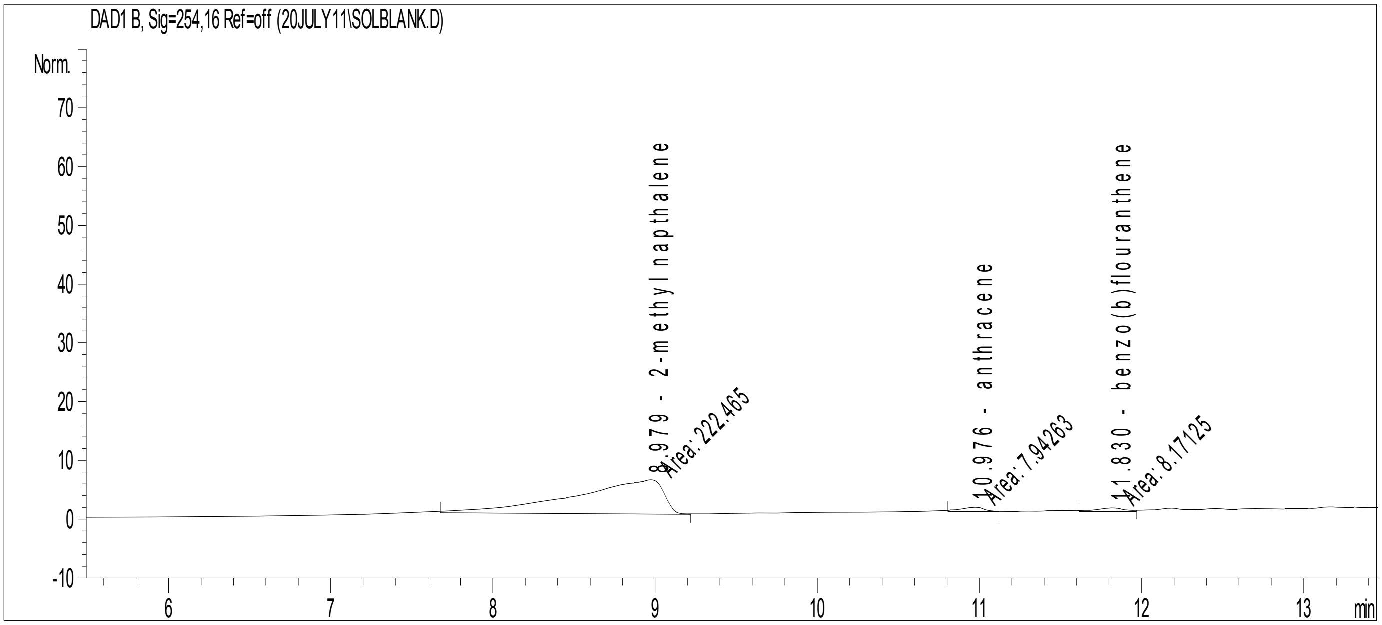

Figure 4. Chromatogram of PAHs extracted from an unexposed filter paper.

times are listed in the same order. Figure 6a had retention times: 9.007, 11.026, 11.871, 12.232 and 13.200 min. Figure 6b had 8.978, 10.998, 11.834, 12.209 and 13.288 min and Figure 6c had 9.008, 11.019, 11.869, 12.225 and 13.172 min.

Total concentration of 2-MNaph obtained per month were 325.2 ng/L (October 2010), 162.4 ng/L (November 2010) and 381.2 ng/L (December 2010). Relatively high

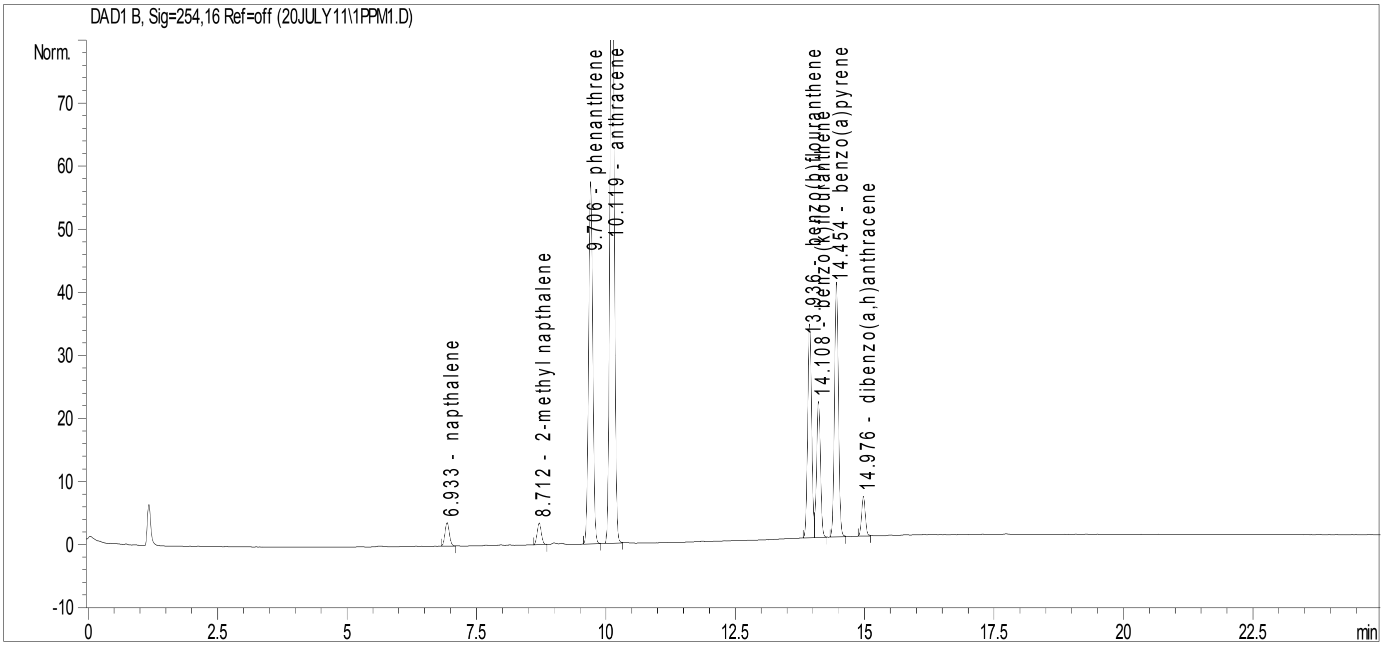

Figure 5. A chromatogram of standard PAHs mixture.

levels of 2-MNaph were detected consistently when compared with other pollutants in the three months of this study (Figure 7). Concentration ranges of other PAH compounds were Anth (7.2 - 14.76 ng/L, BbFl (6.7 - 13.6 ng/L), BaPy (6.8 - 13.0 ng/L and BkFl (6.7 - 10.8 ng/L).

2-MNaph is formed through the distillation of methylnaphthalene, where 1-methylnaphthalene is removed leaving behind 2-MNaph (ATSDR, 1995). Mixtures containing 2-MNaph are used in the formulation of alkyl-naphthalenesulfonates (used for detergents and textile wetting agents), chlorinated naphthalenes, and hydronaphthalenes (used as solvents). Pure 2-methylnaphthalene is a component used in the manufacture of vitamin K and the insecticide carbaryl (1-naphthyl-N-methylcarbamate) (HSDB, 2002). Possible PAH sources within the study area would include combustion activities from a coal power station, coal using steel manufacturing companies, an oil refinery and diesel and petrol powered vehicles or informal burning of solid waste. Another possible source could be insecticides used at a nearby farm area.

Since inhalable PM10 particles are a cause of health concern on their own, the elevated presence of 2-MNaph adsorbed on the surfaces of these particles could exacerbate these health effects (ATSDR, 1995; Diaz-Sanchez et al., 1996; Harvey, 1991; Vaal Environmental News, 2011; Lau et al., 2010; Moja et al., 2012). Collectively, PAHs cause skin irritation and inflammation, while Anth, BbFl, BkFl and BaPy cause adverse health effects to humans (ADH, 2009; WHO-IPCS, 1998). BbFl and BaPy are known as animal carcinogens, but together with BkFl are also classified as possible human carcinogens (HSDB, 2002; WHO-IPCS, 1998; Wang et al., 2011).

This study successfully evaluated the levels of some PAHs association with airborne PM10 particles within the Vanderbijlpark study area. Based on these results and the outcome of other similar studies (Liu et al., 2006), airborne PAHs and PM10 pollutants could be used as indicators of urban air pollution.

Conclusion

Average daily and monthly mass concentration levels obtained were lower than the strict regional daily limit, as well as national and international daily limits.

The presence and wide distribution of some PAHs within the Vanderbijilpark environment is a major challenge Moja et al. (2013) reported the presence of some carcinogenic compounds such as BbFl and InPy in water samples used for domestic and agricultural purposes in the same study area. The current study also reports the existence in the atmosphere of PAH compounds that could cause adverse human health effects, for example, Anth, BbFl, BkFl and BaPy. The association of respirable fraction of airborne particles with toxic PAHs elevates local air to dangerous levels. These results could be used as the basis for undertaking a comprehensive study on the status of these organic

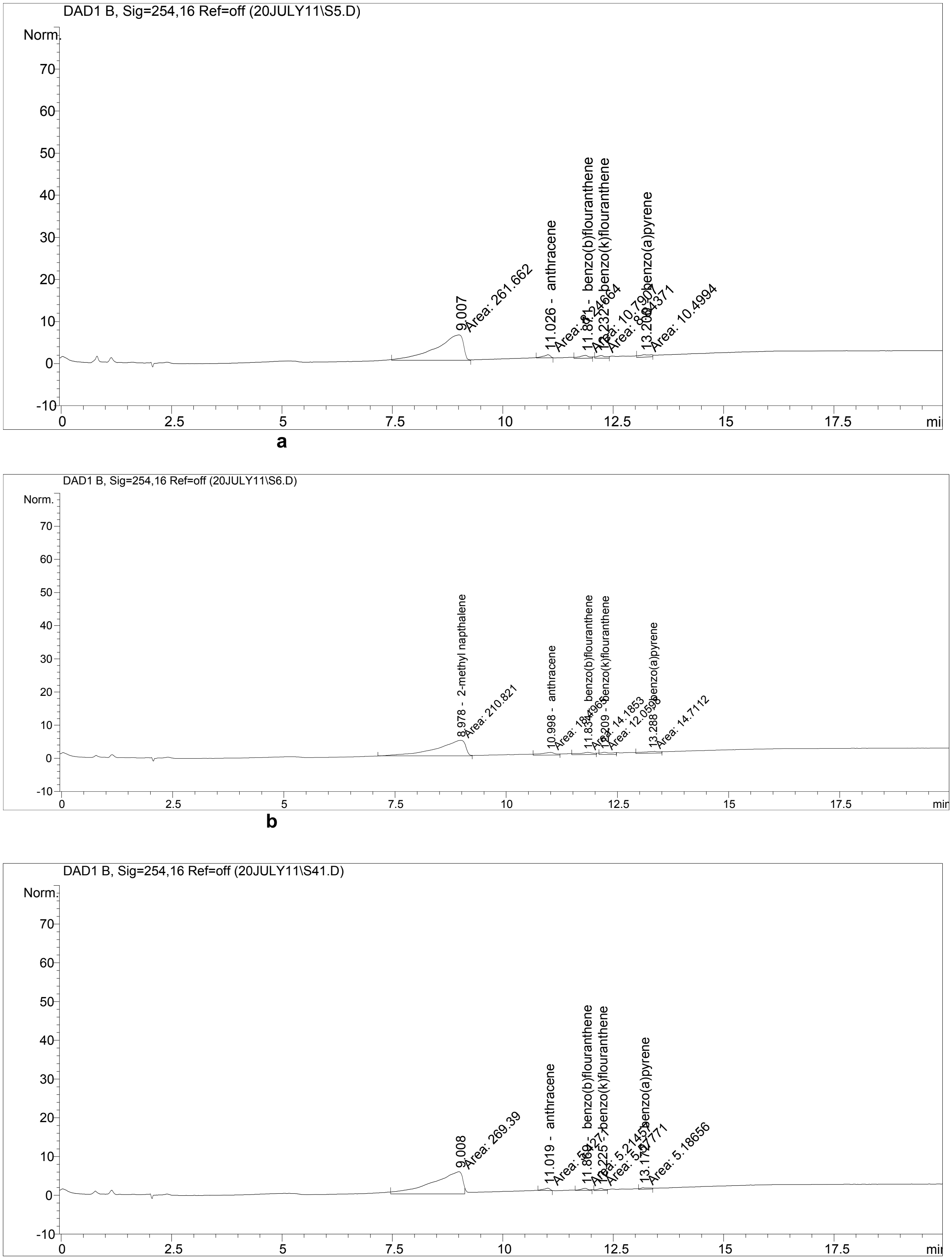

Figure 6. Chromatograms of (a) October sample, (b) November sample and (c) December sample.

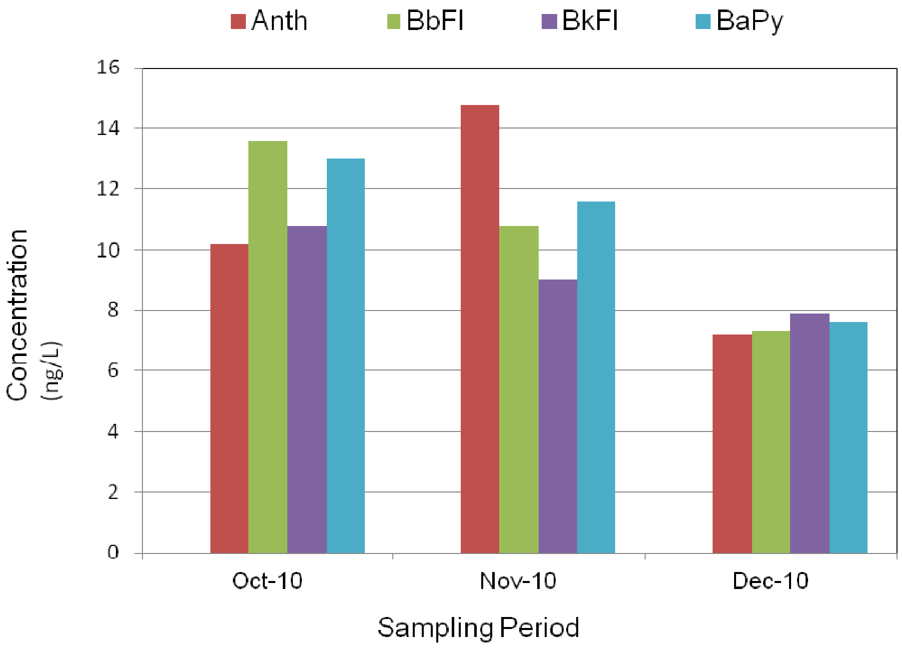

Figure 7. Concentration of different PAH compounds detected from samples.

compounds from the heavily industrialized Vaal Triangle region.

Conflict of Interests

The author(s) have not declared any conflict of interests.

ACKNOWLEDGEMENTS

The research and HPLC analyses were done in the Chemistry Department at Vaal University of Technology. The particulate E-Sampler was provided by the Department of Environmental Sciences at the University of South Africa.

REFERENCES

ADH (Australian Department of Health) (2009). Polycyclic aromatic hydrocarbons - health effects. Public Health Fact Sheet. Environment of Southern Australia. 1 - 4

Annergan H, Scorgie Y (2002). Physics and chemistry of the urban atmosphere. Course No GEOG 525. MSc Course Work Notes. Wits University, Johannesburg.

ATSDR (Agency for Toxic Substances and Disease Registry) (1995). Toxicological profile for naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene (update). U.S. Department of Health and Human Services, Public Health Service. Atlanta, GA. PB95/264362. http://www.atsdr.cdc.gov/toxprofiles/tp67.html. Published online.

ATSDR (1995). Toxicological profile for polycyclic aromatic hydrocarbons (PAHs). Agency for toxic substances and disease registry. US department of Health and Human Services, Washington DC.

Diaz-Sanchez D, Tsien A, Casillas A, Dotson AR, Saxon A (1996). Enhanced nasal cytokine production in human beings after in vivo challenge with diesel exhaust particles. J. Allergy Clin. Immunol. 98: 114-123.

Guo H, Lee SC, Ho KF, Wang XM, Zou SC (2003). Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. Atmos. Environ. 37:5307-5317.

Hailin S, Yizeng L, Ruqin Y (1998). Analysis of PAHs in air-borne particulates in Hong Kong City of heuristic evolving latent projection. Sci. China B 41(1):21-29.

Halsall CJ, Coleman PJ, Davis BJ, Burnett V, Waterhouse KS, Harding-Jones P, Jones KC (1994). Polycyclic aromatic hydrocarbons in U.K. urban air. Environ. Sci. Technol. 28:2380-2386.

Harvey RG (1991). Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity. Cambrige University Press, New York, NY.

HSDB (Hazardous Substances Data Bank) (2002). 2-Methylnaphthalene. The National Library of Medicine. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen. Accessed July 22.

IARC (International Agency for Research on Cancer) (1987). Overall evaluations of carcinogenicity: an updating of IARC monographs volumes 1-42. IARC Monogr. Eval. Carcinog. Risks Chem. Hum. Suppl. 7.

Lau EV, Gan S, Ng HK (2010). Extraction Techniques for Polycyclic Aromatic Hydrocarbons in Soils. Int J Anal Chem. doi: 10.1155/2010/398381. PMCID: PMC2853853. 1-9.

Li A, Schoonover TM, Zou Q, Norlock F, Conroy LM, Scheff PE, Wadden RA (2005). Polycyclic aromatic hydrocarbons in residensial air of ten Chicago area homes: Concentrations and influencing factors. Atmos. Environ. 39. 3491-3501.

Liu Y, Liu L, Lin JM, Tang N, Hayakawa K (2006). Distribution and characterization of polycyclic aromatic hydrocarbon compounds in airborne particulates of East Asia. China Particuology 4(6):283-292.

Maliszewska-Kordybach B (1999). Sources, Concentrations, Fate and Effects of Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment. Part A: PAHs in Air. Pol. J. Environ. Stud. 8(3):131-136.

Menzie CA, Potocki BB, Santodonato J (1992). Exposure to carcogenic

PAHs in the environment. Environ. Sci. Technol. 26:1278-1284.

Moja SJ, Mtunzi F, Madlanga X (2013). Determination of polycyclic aromatic hydrocarbons (PAHs) in river water samples from the Vaal Triangle area in South Africa. J. Environ. Sci .Health A Tox. Hazard. Subst. Environ. Eng. 48(8):847-54.

Moja SJ, Mnisi JS, Nindi MM, Okonkwo JO (2012). Characterization of PM10 samples from Vanderbijlpark in South Africa. J. Environ. Sci. Health: Part A. http://www.tandfonline.com/doi/abs/10.1080/10934529.2012.707859.

NAAQS (National Ambient Air Quality Standards) (2009). Notice No. 1210. 2009, 24 December

Söderström H, Hajšlova J, Kocourek V, Siegmund B, Kocan A, Obiedzinski MW, Tysklind M, Bergqvist P (2005). PAHs and nitrated PAHs in air of five European countries determined using SPMDs as passive samplers. Atmos. Environ. 39:1627-1640.

Vaal Environmental News (2011). Air Quality Management in Vaal Triangle. http://vaalenvironmentalnews.blogspot.com/2011/09/air-quality-management-in-vaal-triangle.html.

Van Jaarsveld JA, Van Pul WAJ, De Leeuw FA (1997). Modelling transport and deposition of persistent organic pollutants in the European region. Atmos. Environ. 31:1011-1024.

Wang W, Huang M, Kang Y, Wang H, Anna OW, Leung AOW, Cheung KC, Wong MH (2011). Polycyclic aromatic hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: Status, sources and human health risk assessment. Sci. Total Environ. 409:4519-4527.

Wania F, Mackay D (1996). Tracking the distribution of persistent organic pollutants. Environ. Sci. Technol. 30:390-396.

WHO-IPCS (World Health Organization / International Programme on Chemical Safety) (1998). Selected non-heterocyclic policyclic aromatic hydrocarbons. Geneva. Environmental Health Criteria 202: 1-701

Wild SR, Jones KC (1995). Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. Environ. Pollut. 88:91-108 .