Determination of polycyclic aromatic hydrocarbons (PAHs) in river water samples from the Vaal Triangle area in South Africa

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ABSTRACT

PAHs are fused ring aromatic pollutants some of which are highly carcinogenic to humans and are persistent in the environment. The objective of this study was to develop a suitable extraction method for PAHs from river water samples, identify and quantify the individual compounds.

An optimized reverse solid phase extraction (SPE) method was used after conditioning the sorbent to extract and preconcentrate compounds of polycyclic aromatic hydrocarbons (PAHs) in river water samples. The following ten compounds were

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identified and quantified with a High Performance Liquid Chromatography (HPLC): naphthalene (Naph), acenaphthylene (Ace), phenanthrene (Phe), anthracene (Anth), fluoranthene (Fluo), benzo(b)fluoranthene (BbFl), benzo(k)fluoranthene (BkFl), benzo(a)pyrene (BaPy), dibenzo(a,h)anthracene (DiAn) and indeno(1,2,3-cd)pyrene (InPy).

An LC-18 sorbent showed good recoveries after extracting PAHs standard mixture of 1.0 mg/L. The best performing eluting solvent was acetone and very good percentage recoveries that ranged from 97.17-101.18% were obtained for seven compounds. Poor recoveries were also obtained for Fluo (1.03%), BbF1 (0.22 %) and BkF1 (0.7%). The standard deviation ranged from 0.05 to 2.26 and the detection limits of less than 0.2 were obtained. Average concentration ranges of PAHs identified within the study area were: Naph (0.0339 – 0.0382 mg/L) at the Klip river site; Ace (00815 - 0.0828 mg/L) at Vaal river, (0.0538 - 0.0591 mg/L) at Klip river and (0.001 – 0.0073 mg/L) at Vaal barrage; Phe (0.0214 - 0.0263 mg/L) at Vaal river, (0.0487 - 0.0521 mg/L) at Klip river and (0.3837 - 0.4373 mg/L) at Vaal barrage; Anth (0.0073 - 0.0092 mg/L) at Vaal river, (0.3582 - 0.4072 mg/L) at Klip river and (0.3457 - 0.4022 mg/L) at Vaal barrage; Fluo (0.0985 - 0.1205 mg/L) at Vaal river, (0.0552 - 0.0593 mg/L) at Klip river and (0.1321 – 0.1612 mg/L) at Vaal barrage; BbFl (0.0681 - 0.1151 mg/L) and InPy (0.2561 ± 0.3067 mg/L) at Vaal barrage sites only. Benzo(k)fluoranthene, benzo(a)pyrene and dibenzo(a,h)anthracene were not detected. The obtained data will be useful as baseline information when similar studies are undertaken in the future and could also be useful to policy makers.

Keywords: Solid phase extraction, LC-18 sorbent, polycyclic aromatic hydrocarbons, high performance liquid chromatography.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are fused ring aromatic compounds classified by the number of carbon rings they possess. [1,2] They are highly lipholic and have relatively low solubility in water. [3] PAHs have for many years attracted attention, because some of them are highly carcinogenic or mutagenic. [4] The two and three ring PAHs are non-carcinogenic, while several of the four, five and six ring PAHs are carcinogenic. The US Environmental Protection Agency (EPA) has promulgated sixteen (16) unsubstituted PAHs as priority pollutants. [5] Eight (8) of them are considered to be possible carcinogens, namely: benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene, indenol(1,2,3-cd)pyrene and benzo(g,h,i)perylene. [3, 6]

PAHs are found in air, soil, water, in many members of both animal and plant kingdoms, marine and non-marine sediments and also in different kinds of food. [7] Most of them are formed as a result of anthropogenic activities which include incomplete combustion of organic substances during pyrolysis of organic materials due to some processes used in the iron and steel industry, heating and power generation and petroleum. [8] It has been estimated that 230 000 metric tons of PAHs enter the global environment annually from

spills and seeps of petroleum, direct discharges from industrial/domestic sources, aerial transport and biosynthesis. [1, 9,10] PAHs are more prevalent or concentrated near urban centers. [11] Their fate is determined by their physico-chemical properties, especially nonpolarity and hydrophobicity which are responsible for their persistence in the environment. [3]

There are wide varieties of techniques that can be used to determine the concentrations and prevalence of PAHs in different matrices. For the characterization and quantitation of PAHs, capillary gas chromatography with flame ionization detection/photo-ionization detection, [12] mass spectrometric detection (MS), [13] supercritical fluid chromatography, [14] and high performance liquid chromatography (HPLC) using mass spectrophotometric detection [15] or florometric detection, [16] have been used. In this paper, an HPLC coupled to wavelength diode array detector and a UV detector was used. HPLC was preferred since it gives excellent separation, good resolution and it is non destructive for the selected PAHs.

Solid-phase extraction (SPE) is an extraction and pre-concentration technique that has been used successfully when trace levels of organic compounds were characterized. [17-18] Cartridges and disks consist of variable stationary phases, each of which is able to separate analytes according to different chemical properties. In most cases, stationary phases are made on silica that has been bonded to a specific functional group. These functional groups include hydrocarbon chains of variable length (for reversed phase SPE), quaternary ammonium or amino groups (for anion exchange), and sulfonic acid or carboxyl groups (for cation exchange). [11]

Therefore, the objective of the present study was to develop a suitable extraction method for polycyclic aromatic hydrocarbons from river water samples and quantify the identified compounds.

MATERIALS AND METHODS

Chemicals

About 1.0 mg of each of naphthalene, acenaphthylene, phenanthrene, anthracene, fluoranthene,benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene standard PAHs were dissolved in 1000 mL solvent to produce a 1.0 mg/L stock solution (obtained from Dr. Ehrnestorfer, U.S.A.). All solvents used were obtained from Sigma-Aldrich S.A. Acetonitrile, methanol and acetone solvents were of HPLC grade and the acetone was of analytical grade. Double distilled water was also used.

Instrumentation

An Agilent 1100 Series HPLC (Agilent Technology Inc, S.A.) with a programmable wavelength diode array and ultraviolet (on 254 nm) detectors were used. Operating conditions were: run time = 35 min, sample volume = 20 µL, flow rate = 1 mL/min, column temperature = 23^{o}C (ambient), column = eclipse XDB-C18 column [4.6 mmID x 250 mm (5 µm) 80Å], mobile phase = 25 % water and 75 % acetonitrile.

Optimization of SPE sorbents and solvents

The following three 3.0 mL reverse solid phase extraction columns were used: Strata X – 500.0 mg (Phenomenox, USA), MFC18 – 500.0 mg and LC-18 – 500.0 mg (Sulpeco, USA). The columns were arranged in a cartridge or syringe barrel form. [20] The cartridge was made of polypropylene with a wide sample entrance and narrow exit openings or frits. The sorbent material was packed at the base of cartridge towards the exit frit, which held the sorbent in place. The exit frit was made from polyethylene of ± 20 µm pore size and allows separation of mixtures to take place when transported by a solvent.

The sorbents were wetted and conditioned first with 5.0 mL methanol at 5.0 mL/min and equilibrated with 5.0 mL ultra-pure water at 5.0 mL/min. Columns clean-up of the water extracts were carried out using a 12-port SPE Visi-prep vacuum manifold (Sulpeco, U.S.A.). A 10.0 mL blank solution was spiked with the standard solution containing 100.0 mg/L PAHs and was then loaded to the columns at a flow rate of 3.0 mL/min. The lipophilic interferences were then removed by 5.0 mL of 10.0 % (v/v) methanol at 5.0 mL/min. Columns were dried under vacuum for 10.0 min and then eluted by passing 3 x 1.0 mL of eluting solvents at a flow rate of 1.0 mL/min (sorbents were soaked for 10.0 min with the elution solution before each elution). The eluates were collected into 2.0 mL GC vial and made up to volume with the elution solutions before being analysed by an HPLC. Care was taken that the surface of the sorbent in the column was not dry during conditioning and loading of the sample extracts. The performances of methanol, acetonitrile and acetone solvents were investigated to select the best elution solvent. The

capacities of the three sorbent phases to retain or recover the analytes were also compared. The breakthrough volume of different PAHs was determined using sample blank.

Linear ranges and detection limits

A series of calibration standards ranging from 0.1 to 5.0 mg/L were prepared from the stock solution. Detection limits for the instruments were taken as three times the standard deviation of the lowest detectable concentration of PAHs from the mean of triplicate analyses.

Application

Three sampling sites were selected based on socio economic activities taking place, which include industrial operations, agricultural and tourism activities. The Vaal river (29°4'15"°S, 23°38'10"°E / 29.0'70''83°S, 23.6'36"11°E / -29.0'70"83°S; 23.6'36"11°E) is 1,120 km in length and forms the border between Mpumalanga, Gauteng and North West Provinces on its north bank, and the Free State on its south. It then flows westwards where it combines with the Orange river southwest of Kimberley in the Northern Cape. Vaal river is the primary source of water for human usage, irrigation and industrial activities within the region. [21]

The Klip river (26°35'0" °S, 28° 1' 0" °E) system is one of the catchment areas that drains into the Vaal Dam. The Vaal barrage catchment (6°45′53″S 27°41′30″E / 26.76472°S

27.69167°E / -26.76472; 27.69167) is a dam on the Vaal River near Vanderbijlpark and forms a border between Gauteng and Free State provinces. This catchment supplies water to Gauteng province, which contributes 37,6 % of the country's GNP and is a home to 18,1% of the population. [21]

Composite water samples were collected every Friday (7, 14, 21 and 28) in October 2011 per site. A sub-surface grab sampling method was followed where samples were collected at 30.0 cm below the surface of the stream at 45 degrees angle to the direction of the flow. Samples from the three points where mixed to produce a composite sample per site. 1.0 Litre amber bottles with caps were thoroughly cleaned with soap and water, rinsed with tap water, then soaked overnight with dilute nitric acid (HNO_3) solution, rinsed with deionized water several times in the Laboratory. Bottles were further rinsed twice with sample water before filing them at the sampling points. An organic modifier, 10.0 mL acetonitrile was added to the samples before performing SPE procedures. Unspiked samples (i.e. “blank” samples) were also processed, in an identical manner to the spiked samples. Samples were transported to the Laboratory in a cooler boxes filled with ice. The samples were then stored in the freezer at 5˚C until they were used.

RESULTS AND DISCUSSION

Sorbent material, solvent choice and break through solvent volume

The relative performances of MFC-18, Strata-X and LC-18 sorbent material in retaining standards PAHs compounds are shown (Figure 1). An LC-18 sorbent produced good

recoveries after extracting PAHs standard mixture of 1.0 mg/L. Both LC-18 sorbent and PAHs analytes are nonpolar and interact with water hydrophobically. [4]

The choice of the solvent is an important parameter in any organic compound extraction process since the extraction efficiency depends on the solvent nature. The performances of eluting solvents between methanol, acetone and acetonitrile relative to chosen LC-18 sorbent are shown (Figure 2). Both acetone and acetonitrile were found to be the best performing eluents and several similar studies used acetonitrile successfully. [17-18] In this study, acetone was chosen because of its non-polar character, it's cheaper and easily accessible than acetonitrile.

The break through volume of the extracting solvent was optimized by evaluating the extracting and recovering efficiencies from 1.0 mg/L PAHs standard solution with the following volumes of the extractant: 10.0, 50.0, 100.0, 500.0 and 1000.0 mL. A 100.0 mL volume of the extractant solvent was found to be more efficient (Table 1). There was no significant difference among extractive efficiencies with 2.0, 4.0, 6.0 and 10.0 mL of acetonitrile solvent when determining PAHs in kerosene and bio-kerosene soot. [17]

Linear calibration curves were obtained with linear ranges from 0 to 5.0 mg/L for napthalene and acenaphthylene, 0 – 1.0 mg/L for the eight other PAHs compounds (Table 2). Very good correlations were obtained with R-values ranging from 0.999-0.9994 during the standard calibration process. Good percentage recoveries that ranged from 97.17-101.18% were obtained for seven compounds. Poor recoveries were also obtained for Fluo (1.03 %), BbFl (0.22 %) and BkFl (0.7 %). The standard deviation ranged from 0.05 to 2.26 and the detection limits of less than 0.2 mg/L were obtained.

An HPLC chromatogram of ten narrow and well-separated compounds of the PAHs standard mixture with LC-18 fused silica sorbent is shown (Figure 3). Peaks appeared at the following retention times: Naph: 6.881 min; Ace: 7.518 min; Phe: 9.608 min; Anth: 10.157 min; Fluo: 11.691 min; BbFl: 19.990 min; BkFl: 20.621 min; BaPy: 22.119 min; DiAn: 25.431 and InPy: 30.982 min. The analytical method development was successful as shown by relatively narrow and well-separated peaks of individual PAHs compounds. Also, a relatively flat background, which runs parallel to the x-axis, was obtained.

Concentrations of PAHs

The concentrations of individual PAH components were automatically calculated by Chemstation software of the Aligent HPLC used. PAHs tend to build up in fatty tissues due to their hydrophobicity. [22] Their lipophilic characteristics and limited biodegradation make PAHs to be classified as persistent organic pollutants. [23] PAHs and other organic componunds have high affinity for environmental matrices such as sediments, soils and biota. Generally, PAHs in water is low (about 100.0 mg/L) mainly due to their weak solubility, but sometimes their concentrations may be elevated after leaching from sediment. [24] The presence of trace levels of PAHs in water samples makes them difficult to detect.

Figure 4(a) shows a chromatogram with clearly separated peaks of Ace (t_R = 7,186 min), Phe (t_R = 8.440 min), Anth (t_R = 8.951 min) and Fluo (t_R = 10.375 min) after being treatment through the SPE cartridge. SPE provides a means for pre-concentrating water phase organics to make them detectable. [25]

Similarly, Figures 4(b) and 4(c) show the previously undetected PAHs. Naph (t_R = 6.514 min min), Ace (t_R = 7.180 min), Phe (t_R = 8.431 min), Anth (t_R = 8.845 min and Fluo (t_R = 10.367 min) were determined from composite Klip river water samples and Ace *(t_R = 7.134 min)*, Phe *(t_R* = 8.437 min*)*, Anth *(t_R* = 8.947 min*)*, Fluo *(t_R* = 10.370 min*)*, BbFl *(t_R* = 18.628 min*) and* InPy *(t_R* = 27.404 min) from composite Vaal barrage water sample after treatment through the SPE.

A total of seven PAHs compounds were identified and quantified (Table 3). The following PAHs were detected at the Vaal river, Klip river and Vaal barrage sampling sites: Ace was 0.0822 ±, 0.0558 ± and 0.0073 ± mg/L, respectively; Phe was 0.0235 ±, 0.0506 ± and 0.4176 ± mg/L, Anth was 0.0083 ±, 0.3870 ± and 0.3663 ± mg/L) and Fluo was 0.1108 ±, 0.0572 ± and 0.1487 ± mg/L. Naph was detected only at the Klip river site (0.0357 ± mg/L), while BbFl (0.0873 ± mg/L) and InPy (0.2561 ± mg/L) were detected at the Vaal barrage site. BkFl, BaPy and DiAn were not detected under the current experimental conditions. Based on the possible carcinogenic list of PAHs which was reported by [26], only BbFl and InPy were detected at the Vaal barrage site. This is significant since farmers in this region use the barrage untreated water for irrigation. It may lead to these carcinogenic organic compounds finding their way into the food chain. The Vaal barrage is also the main supplier of water for domestic and industrial usage. Ineffective treatment processes of contaminated raw water will expose many users to these toxic pollutants.

Several studies have demonstrated the toxicity of PAHs, [24] reported on their genotoxicity in humans; a list of possible carcinogenic PAHs has been reported on [26],

two of which were detected in the study area as discussed earlier. People living in urban and suburban areas near industrial chemical sites were more vulnerable to PAHs exposure. [23] Since the study was located in heavily industrialized and polluted regions of central South Africa, there is a very high possibility that locals will be exposed to some levels of PAHs in water and other environmental media.

CONCLUSIONS

The LC–18 extraction and pre-concentration column method used was very effective in improving the detectable levels of PAHs in river water samples. Identified PAHs compounds, together with their concentration ranges were: Naph (0.0358 mg/L) only at the Klip river site; Ace (0.0026 – 0.0822 mg/L), Phe (0.0083 – 0.3663 mg/L); Anth (0.0572 – 0.1487 mg/L) and Fluo (0.0873 mg/L) only at Vaal barrage; BbFl (0.1151 mg/l) and InPy (0.2561 mg/L) only at the Vaal barrage site. BkFl, BaPy and DiAn were not detected under the current experimental conditions.

The carcinogenicity of some of the detected compounds (BbFl and InPy) within the study area is of concern. The sampling sites are popular holiday destinations within South Africa. Water from these sites is also used for domestic and agricultural purposes. Regular monitoring and management of these toxic organic pollutants is essential in order to minimize their negative health and environmental effects. This study recommends that a more wider and larger scale study be undertaken to ascertain the environmental levels of Persistent Organic Pollutants (POPs) in general and BbFl and InPy in particular.

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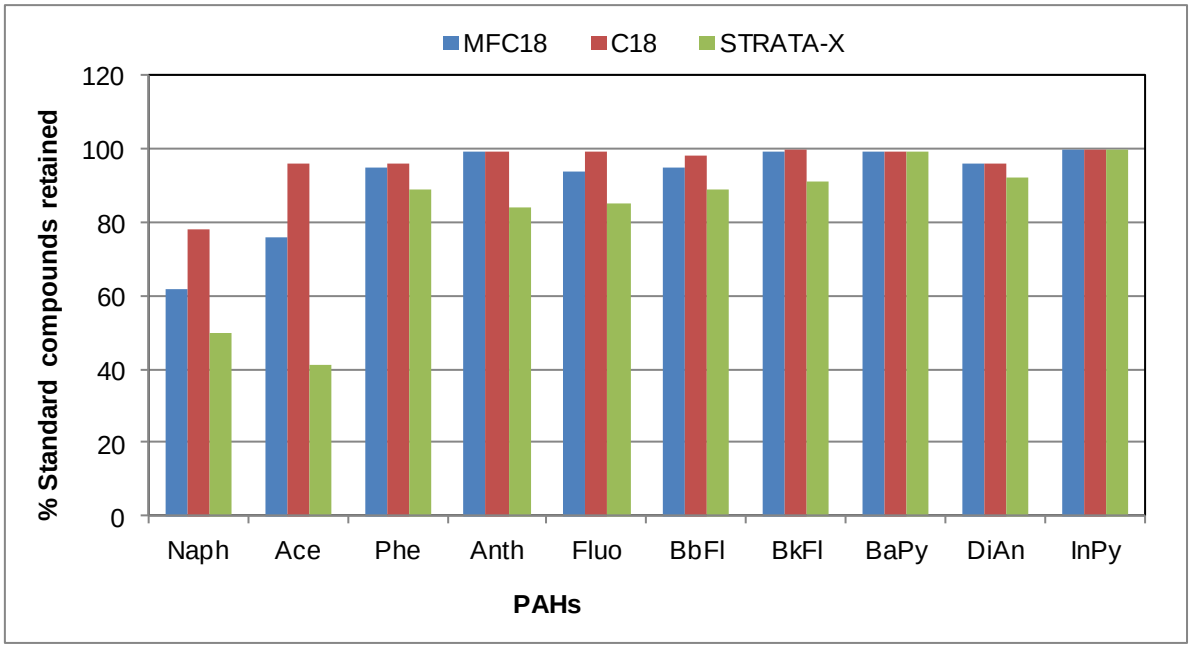
FIGURE CAPTIONS

Figure 1: The comparison between the efficiencies of the three sorbent phases using 1.0 mg/L PAHs standard solution.

Figure 2: Comparison between the three solvents in a C18 column using 100 mg/L PAHs standard solution.

Figure 3: A chromatogram of PAHs standard mixture

Figure 4: Chromatograms of (a) Vaal river water, (b) Klip river water and (c) Vaal barrage water samples after extraction and pre-concentration with SPE cartridges.



410
411 **Fig. 1**

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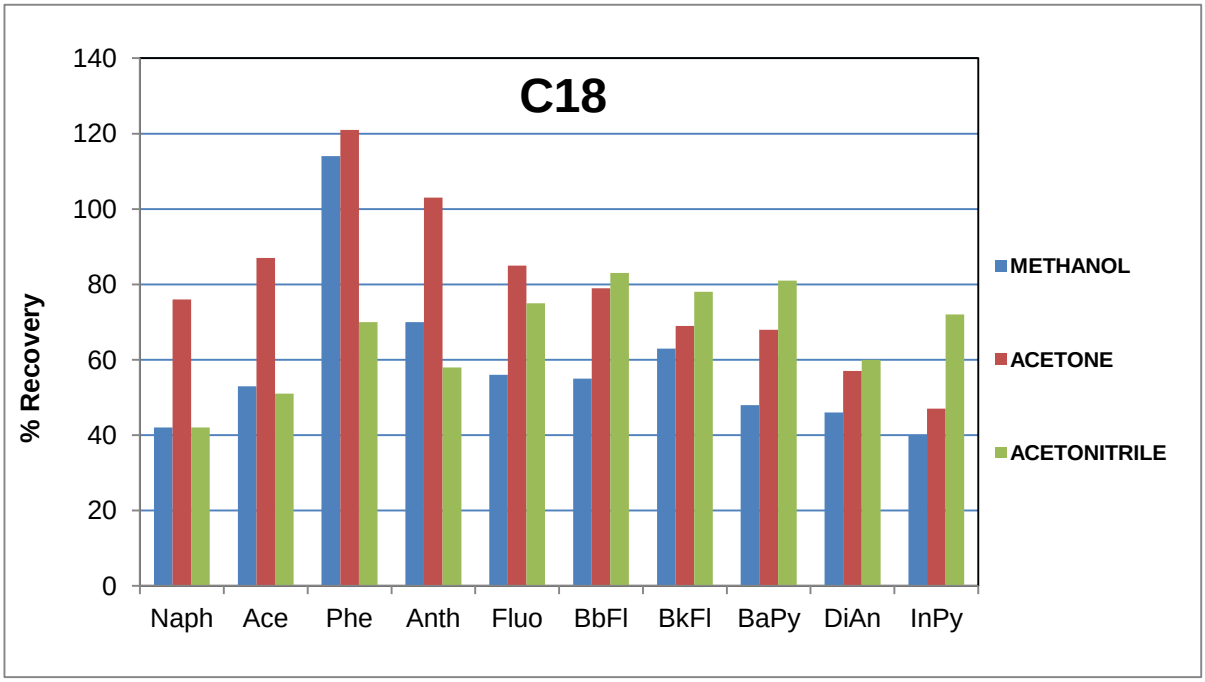

413
414 **Fig. 2**

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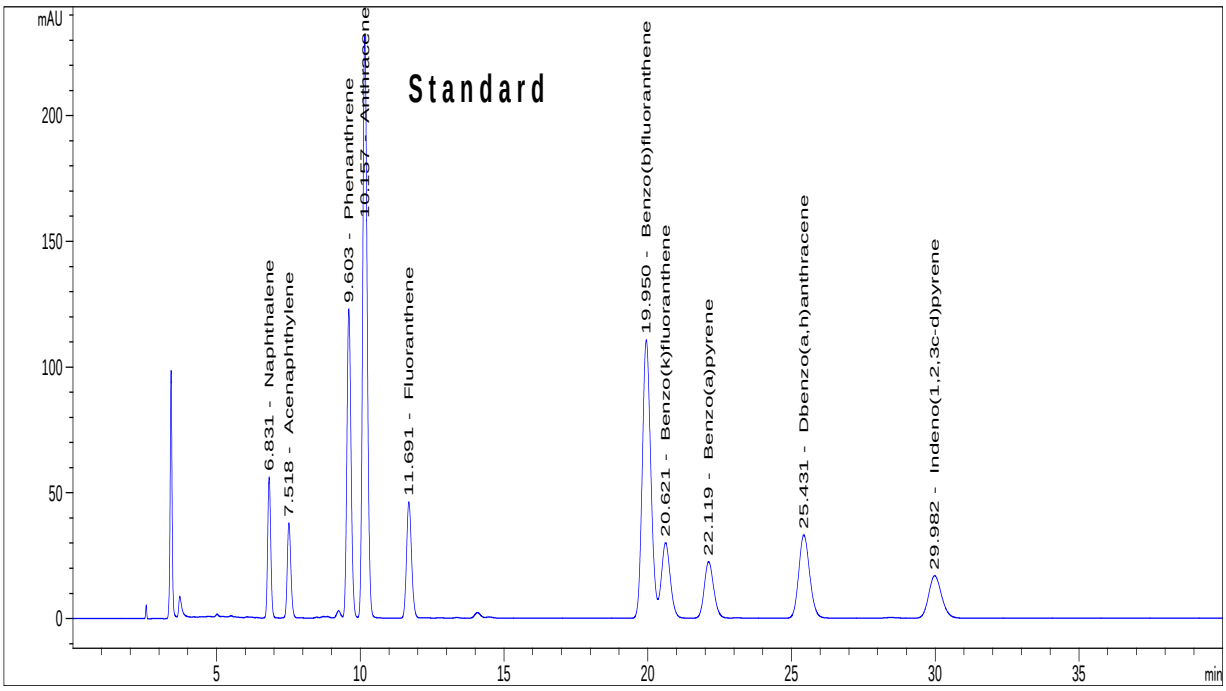
Standard
mAU
6.831 - Naphthalene
7.518 - Acenaphthylene
9.603 - Phenanthrene
10.157 - Anthracene
11.691 - Fluoranthene
19.950 - Benzo(b)fluoranthene
20.621 - Benzo(k)fluoranthene
22.119 - Benzo(a)pyrene
25.431 - Dbenzo(a,h)anthracene
29.982 - Indeno(1,2,3c-d)pyrene
min

Fig. 3

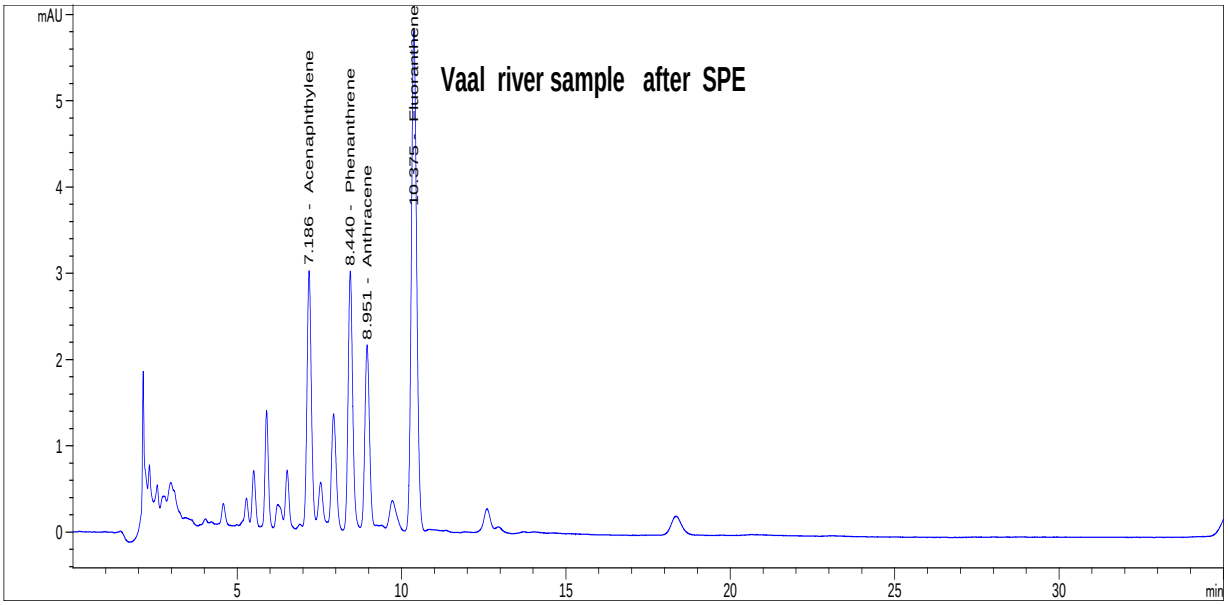
Vaal river sample after SPE
mAU
7.186 - Acenaphthylene
8.440 - Phenanthrene
8.951 - Anthracene
10.375 - Fluoranthene
min

Fig. 4(a)

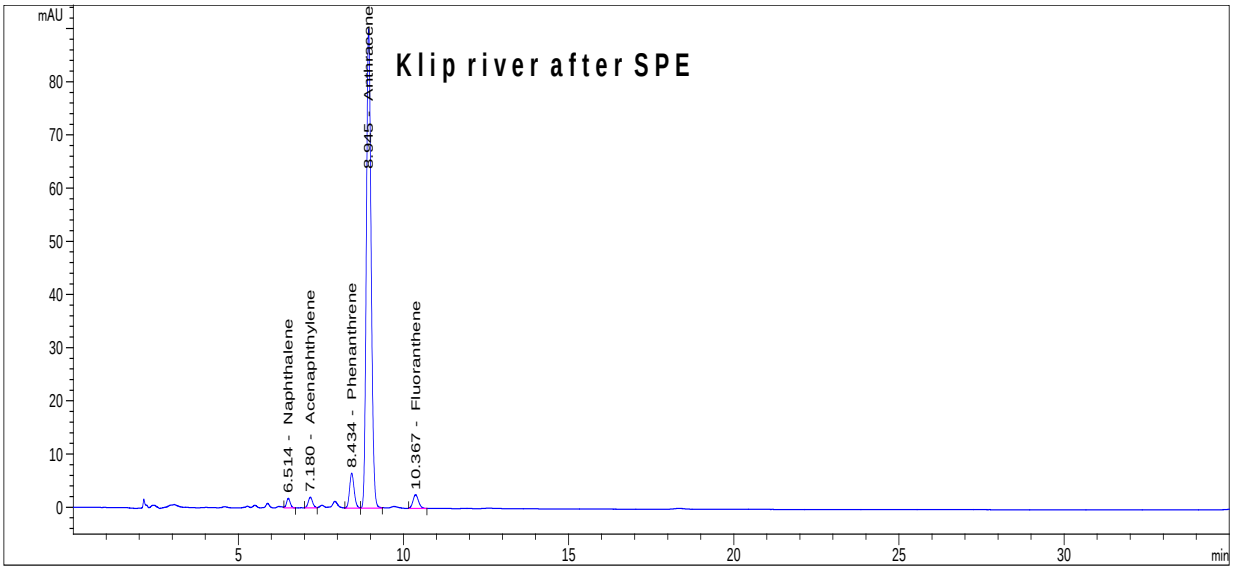
Klip river after SPE
mAU
6.514 - Naphthalene
7.180 - Acenaphthylene
8.434 - Phenanthrene
8.945 - Anthracene
10.367 - Fluoranthene
min

Fig. 4(b)

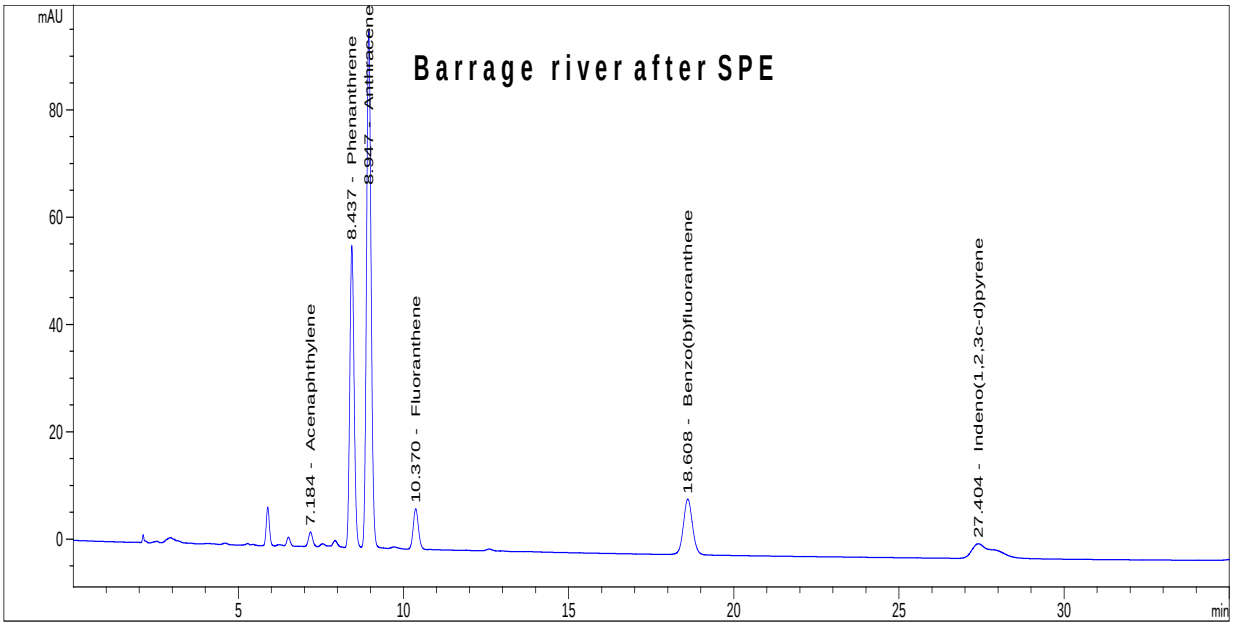
Barrage river after SPE
mAU
7.184 - Acenaphthylene
8.437 - Phenanthrene
8.947 - Anthracene
10.370 - Fluoranthene
18.608 - Benzo(b)fluoranthene
27.404 - Indeno(1,2,3c-d)pyrene
min

Fig. 4(c)

435 **TABLE CAPTIONS**

436

437 **Table 1:** HPLC operating conditions

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439 **Table 2:** Effect of Breakthrough volume

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441 **Table 3:** Linear range, calibration data of standard solution and detection limits for
442 extraction of PAHs by LC-18 sorbent.
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444

445 **Table 1:** Effect of Breakthrough volume

PAHs	% Recovery				
	10 mL	50 mL	100 mL	500 mL	1000 mL
Naph	66	73	88	56	34
Ace	61	70	82	58	73
Phe	83	84	93	83	84
Anth	54	68	68	82	50
Fluo	20	57	87	36	19
BbFl	25	34	70	54	23
BkFl	41	39	51	38	24
BaPy	58	56	64	54	20
DiAn	57	56	64	50	14
InPy	34	42	43	22	6

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454 **Table 2:** Linear range, calibration data of standard solution and detection limits for
455 extraction of PAHs by LC-18 sorbent.

PAHs	Linearity range (mg/L)	Linear equation	R^2	Detection limits (mg/L)	% Recovery
Naph	0 - 5	y = 18.486x + 4.8589	0.9994	0.1509	97.17
Ace	0 - 5	y = 10.98x + 0.2778	0.9993	0.1669	99.5
Phe	0 - 1	y = 350.84x + 2.0813	0.9999	0.0112	99.32
Anth	0 - 1	y = 690.48x + 21.215	0.9987	0.046	101.18
Fluo	0 - 1	y = 102.01x + 3.3605	0.9988	0.0444	1.03
BbFl	0 - 1	y = 172.27x + 0.5584	0.9999	0.01	0.22
BkFl	0 - 1	y = 130.43x + 1.216	0.9994	0.0311	0.7
BaPy	0 - 1	y = 128.51 + 1.3812	0.9996	0.0239	100.49
DiAn	0 - 1	y = 36.81x + 1.453	0.999	0.11	98.75
InPy	0 - 1	y = 127.1x + 0.183	0.999	0.0282	100.64

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458 **Table 3:** Average concentrations of PAHs in composite in water samples per site.

	Concentration per site (mg/L), n = 4		
PAHs	Vaal river	Klip river	Vaal Barrage
Naph	ND	0.0358 ± 0.002	ND
Ace	0.0822 ± 0.001	0.0558 ± 0.002	0.0026 ± 0.0027
Phe	0.0235 ± 0.002	0.0497 ± 0.002	0.4176 ± 0.0188
Anth	0.0083 ± 0.001	0.387 ± 0.0187	0.3663 ± 0.02214
Fluo	0.1108 ± 0.008	0.0572 ± 0.003	0.1487 ± 0.011
BbFl	ND	ND	0.0873 ± 0.02
BkFl	ND	ND	ND
BaPy	ND	ND	ND
DiAn	ND	ND	ND
InPy	ND	ND	0.2561 ± 0.0333

459 ND= not detected
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