ORIGINAL PAPER

Source identification of polycyclic aromatic hydrocarbons in sediments of a creek around a flow station

A. K. Inengite · N. C. Oforka · C. Osuji Leo

Abstract Sources of the sixteen polycyclic aromatic hydrocarbons (PAHs) in the United States Environmental Protection Agency priority pollutants list were determined in sediments of Kolo Creek using diagnostic ratios of parent PAHs[phenanthrene/phenanthrene + anthracene; fluoranthene/fluoranthene + pyrene; benz(a) anthracene/ benz(a) anthracene + chrysene and indeno(1,2,3-d)pyrene/ indeno(1,2,3-cd)pyrene + benzo(ghi)pyrelene]. The study was conducted over four seasons (dry, late dry, rainy and late rainy seasons). Applying cross plots of the diagnostic ratios revealed that PAHs in Kolo Creek sediment have pyrogenic origins except in the rainy season that had petrogenic origins. Comparison of diagnostic ratio values obtained from this study with literature values enabled the further classification into types of pyrogenic and/or petrogenic sources. While the pyrogenic sources of PAHs were mainly as a result of Grass/Wood combustion, the petrogenic PAHs were as result of drained diesel and lubricating oil. The predicted sources corresponded with the prevailing human activities in the vicinity, especially samples collected near a petrol station and an abattoir. This study further affirms the simplicity and accuracy of the use of diagnostic ratios for PAHs source prediction.

Keywords Aquatic environment · Gas flaring · Organic pollutants

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment and can travel long distances from their sources (Lunde and Bjorseth 1977; Halsall et al. 2001), therefore separation of PAHs based on their origins poses a great challenge in environmental studies, especially when there are cumulative impacts on the environment from various sources of PAHs (Readman et al. 1987; Yunker et al. 2002), each having adverse health effects (Yunker et al. 2002; Zhang et al. 2004; Ana et al. 2009). Therefore, there is a desperate need to evaluate and determine the sources of PAHs in the environment to enable proper monitoring and control of emissions into the environment.

PAHs can be classified as being of petrogenic (petroleum) or pyrogenic (combustion) origins; they can also be classified as being of natural and anthropogenic origins. Anthropogenic PAHs, however, contribute the major proportion of PAHs in the environment (Fine et al. 2001; Aichner et al. 2007; Morillo et al. 2008).

Sixteen PAHs listed in the United States Environmental Protection Agency (USEPA) priority pollutants list were considered. They include: naphthalene(Naph); acenaphthene (Ace); acenapthylene (Acen); fluorene (Flu); phenanthrene (Phe); anthracene (Ant); fluoranthene (Fluo); pyrene (Pyr); 1,2-benzanthracene (BaA); chrysene (Chry); benzo(b)fluorathene (benzo(b)); benzo(k)fluoranthene (benzo(k)); benzo(a) pyrene (BaP); 1,2,5,6-dibenzanthracene (Diben); indeno(1,2,3-cd) pyrene (Ind); 1, 12-benzopyrelene (BghiP). Various methods are being applied in source identification and apportionment of PAHs. These include emission inventory modelling approaches, multivariate statistical methods and the use of diagnostic ratios (DRs) of selected PAHs (Li and Kamens 1993; Westerholm and Li 1994; Sjogren et al. 1996; Wang et al. 1999;

Dvorska et al. 2011). Source identification using DRs holds advantages due to the ease of application (Yunker et al. 2002; Morillo et al. 2008; Wang et al. 2010; Dvorska et al. 2011) and unlike inventory modelling approaches; DRs do not rely on emissions inventories which may not be available in most countries especially developing countries.

Morillo et al. (2008) determined the sources of PAHs in urban environments of Sevilla (Southern Spain) using principal mass PAH ratios and low molecular weight (LMW)/high molecular weight (HMW) ratios, while Re'-Poppi and Santiago-Villa (2005) applied PAHs ratios as source determination of PAHs in ambient air of Campo Grande City, Brazil. Four PAHs ratios; Phe/Phe + Ant; Fluo/Fluo + Pyr; BaA/BaA + Chry and Ind/Ind + BghiP were applied to cover for both LMW and HMW PAHs.

Due to the overlap of characteristic PAH profiles from each source and selective decay of more labile compounds, instead of using single ratio, coupling of two is helpful to provide better estimation of PAH sources (Yunker et al. 2002; Lehndorff and Schwark 2004).

In this study, for the first time, PAHs DRs (Phe/Phe + Ant; Fluo/Fluo + Pyr; BaA/BaA + Chry and Ind/Ind + BghiP) were applied for source determination of PAHs in Kolo Creek surface sediments. The study was conducted within April 2008 to January 2009.

Kolo Creek is a fresh water non-tidal creek that flows through a region of Niger Delta that has been urbanised and industrialised due to the quest for crude oil and natural gas, a natural resource that is in abundance in the area and also a likely source of PAHs into the environment. As result of the exploitation and exploration of crude oil and natural gas, Kolo Creek receive loads of human and industrial effluents which may be detrimental to the quality of the Creek (Inengite et al. 2010a).

It is noteworthy that Kolo Creek serves as a source of water for domestic use and also serves as a recreational facility to the inhabitants of the adjoining communities.

Materials and methods

Sampling sites

Nine points were sampled, eight along Kolo Creek and one point located at Epie Creek (Fig. 1). Three points (SS1, SS2, SS5) were around Kolo Creek Flow station and SS4, SS7 and SS8 were within Imiringi, Otuasega and Oruma communities, respectively; while SS3 and SS6 were within uninhabited farmland environments. SS9 was in Epie Creek within Tombia Junction which is relatively urbanised when compared to Imiringi, Otuasega and Oruma. Tombia Junction is situated within Yenagoa with an estimated population of 152,817 as at 2004 (Tamuno 2005). While the other communities were pre-occupied by mainly domestic activities except for the flow station; Tombia junction is busy with a lot of vehicular emissions from automobiles.
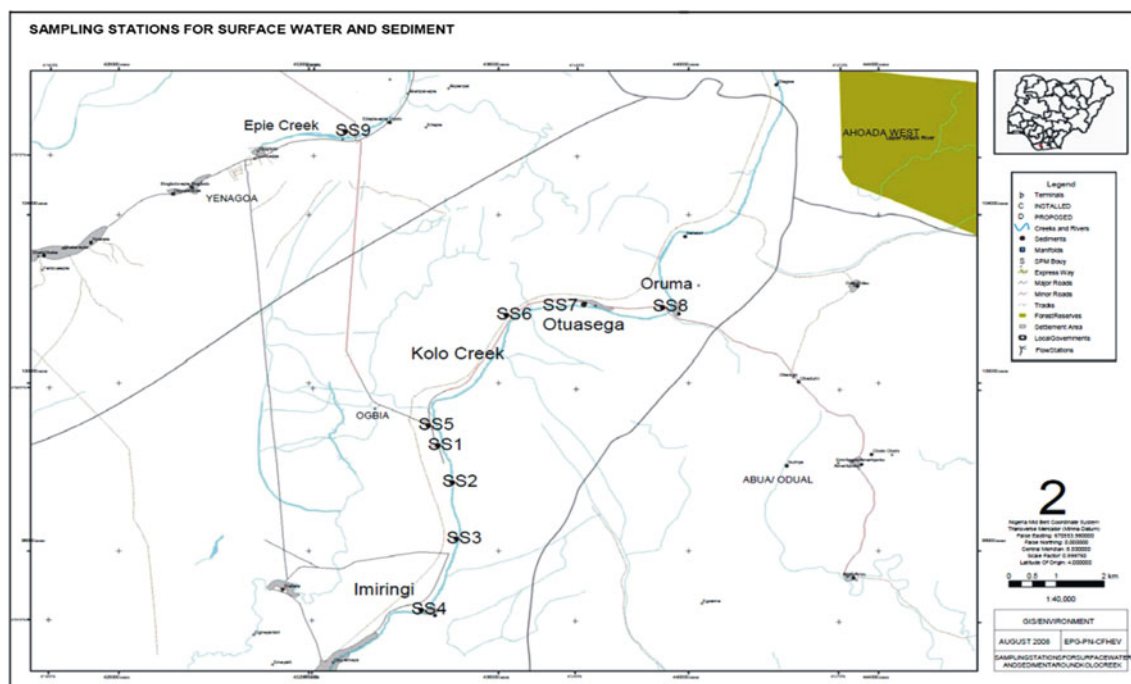
The sampling field data are as shown in (Table 1).

Fig. 1 Map showing sampling stations

Table 1 Sampling field data for sediment

Sampling stations (SS)	Dates sampled	Times sampled	Station location/description	Latitude (N)	Longitude (E)
SS1	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	10:03 am; 9:45 am 10:30 am; 9:30 am	Kolo Creek flow station/gas flaring point	4°53′ 15.855″	6°22′ 25.640″
SS2	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	10:40 am; 10:32 am 11:05 am; 9:50 am	Kolo Creek Flow station/field logistics base	4°52′ 47.289″	6°22′ 35.497″
SS3	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	11:10 am; 11:05 am 11:30 am; 10:30 am	Imiringi/Roadside and fallow bushy area	4°52′ 03.614″	6°22′ 38.551″
SS4	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	11:45 am; 11:40 am 12:00 pm; 11:05 am	Imiringi/Inhabited community with domestic activities	4°51′ 08.229″	6°22′ 14.620″
SS5	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	12:35 pm; 12:30 pm 12:45 pm; 11:30 am	Kolo Creek Flow station/ roadside, fallow bush with farmlands	4°53′ 31.426″	6°22′ 19.121″
SS6	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	1:25 pm; 1:25 pm 1:48 pm; 12:40 pm	Otuasega/roadside and farmland	4°54′ 56.765″	6°23′ 12.185″
SS7	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	2:10 pm; 2:15 pm 2:45 pm; 1:50 pm	Otuasega/inhabited community with domestic activities	4°55′ 05.089″	6°24′ 04.921″
SS8	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	3:05 pm; 3:05 pm 3:40 pm; 3:05 pm	Oruma/inhabited community	4°55′03.037″	6°24′58.92″
SS9 (Tombia)	6th April, 2008; 29th June, 2008 19th Oct., 2008; 24th Jan., 2009	4:10 pm; 4:15 pm 4:40 pm; 4:00 pm	Tombia junction Yenagoa/ urbanised community, busy roadside, petrol station and abattoir	4°57′18.776″	6°21′21.604″

LD (late dry season) = 6th April, 2008; *R* (rainy season) = 29th June, 2008; *LR* (late rainy season) = 19th Oct. 2008; *D* (dry season) = 24th Jan. 2009

Sampling

Sediment samples were collected using a stainless steel Van Veen grab sampler. Triplicate sediment samples were collected at each point to form one composite sample and another composite sample collected about 5 m away from the first point at the same sampling station, forming a total of 72 composite sediment samples for the four sampling seasons. The average PAHs concentrations were as stated in (Table 2). The samples were wrapped in aluminium foil stored in an ice chest and taken to the laboratory and stored at −20 °C prior to analysis.

Extraction of PAHs from sediment samples

The samples were dried, crushed and sieved using 0.5 mm sieve. 2.0 g ± 0.01 of samples were weighed and spiked with pre-deuterated PAHs mixture (naphthalene-d8, phenanthrene-d10, chrysene-d12, and perylene-d12) as an internal standard, to determine the extraction efficiency. The recovery was >90 %. 10 ml of extraction solvent (pentane) was added into the samples and mixed thoroughly and allowed to settle. The mixtures were carefully filtered into clean solvent rinsed extraction bottles using filter paper fitted into Buchner funnels. The extracts were concentrated to 2 ml using a rotary evaporator and then transferred for clean-up/separation.

Sample clean-up

In a 10-mm id × 250 mm long chromatographic column, 1 cm of moderately packed glass wool was placed at the bottom. Slurry of 2 g activated silica gel in 10 ml of dichloromethane (DCM) was prepared and placed into the chromatographic column. To the top of the column was added 0.5 cm of sodium sulphate. The column was rinsed with additional 10 ml of DCM. The column was pre-eluted with 20 ml of Pentane; this was allowed to flow through the column for about 2 min until the liquid in the column was just above the sulphate layer. Immediately, 1 ml of the extracted sample was transferred into the column, the extraction bottle was rinsed with 1 ml of pentane and added to the column as well. The stop-cock of the column was opened and the eluent was collected with a 10-ml graduated cylinder. Just prior to exposure of the sodium sulphate layer to air, pentane was added to the column in 1–2 ml increments. Accurately measured volume of 8–10 ml of the eluent was collected. This was labelled "ALIPHATIC". Following recovery of the "ALIPHATIC" fractions just prior to exposure of the sodium sulphate layer, the column

Table 2 Mean PAHs concentrations in Kolo Creek sediments (mg/Kg) dry weight

Sampling stations	Seasons	Naph	Ace	Acen	Flu	Phe	Ant	Fluo	Pyr	BaA	Chry	Benzo (b)	Benzo (K)	BaP	Ind	Diben	BghiP	Total
SS1	LD	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.009	0.025	0.058	0.013	<0.001	0.014	0.014	0.033	0.166
	R	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	0.002	0.004	0.002	0.078	0.128	0.049	0.027	0.014	0.009	0.313
	LR	0.278	0.005	0.008	0.009	0.037	0.027	0.013	0.006	0.018	0.010	0.009	0.003	0.006	0.009	0.015	0.004	0.456
	D	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.009	0.004	0.013	0.028	0.033	0.017	0.003	0.028	0.026	0.007	0.167
SS2	LD	<0.001	0.007	<0.001	<0.001	0.009	0.006	0.013	0.008	0.010	0.050	0.110	0.028	0.008	0.029	0.011	0.064	0.353
	R	0.001	<0.001	<0.001	<0.001	0.001	0.002	<0.001	0.003	0.012	0.005	0.115	<0.001	0.040	0.061	0.162	0.067	0.467
	LR	<0.001	<0.001	0.006	0.008	<0.001	0.006	<0.001	<0.001	0.002	<0.001	0.002	0.003	0.003	<0.001	<0.001	<0.001	0.030
	D	<0.001	0.018	0.011	0.006	0.005	0.013	0.004	0.004	0.015	0.016	0.091	0.012	0.005	0.017	0.019	0.002	0.238
SS3	LD	<0.001	<0.001	<0.001	<0.001	0.011	0.007	0.021	0.015	0.019	0.062	0.098	0.027	0.012	0.023	<0.001	0.052	0.346
	R	<0.001	<0.001	<0.001	<0.001	0.002	0.002	0.001	0.003	0.008	0.004	0.136	0.001	0.011	0.047	<0.001	0.011	0.224
	LR	<0.001	<0.001	0.004	0.008	<0.001	0.005	<0.001	<0.001	0.002	<0.001	0.002	0.003	0.003	<0.001	<0.001	<0.001	0.027
	D	<0.001	<0.001	0.008	0.006	0.004	0.011	0.004	0.002	0.010	0.015	0.099	0.005	0.009	<0.001	0.004	0.002	0.179
SS4	LD	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	R	<0.001	<0.001	<0.001	<0.001	0.001	0.002	<0.001	0.004	0.008	0.005	0.008	<0.001	0.007	0.004	0.007	<0.001	0.057
	LR	<0.001	<0.001	<0.001	0.003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	D	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	0.005
SS5	LD	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.009	0.008	0.012	0.031	0.009	0.012	0.008	<0.001	<0.001	0.009	0.097
	R	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	0.003	0.001	<0.001	0.003	<0.001	0.010	0.001	<0.001	0.003	0.021
	LR	<0.001	<0.001	<0.001	0.003	<0.001	0.002	<0.001	<0.001	0.002	0.004	0.004	0.005	0.004	0.009	0.008	0.004	0.044
	D	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	0.002	0.003	0.011	0.007	0.009	0.010	0.014	0.001	0.012	0.072
SS6	LD	<0.001	<0.001	<0.001	<0.001	0.013	0.015	0.010	0.009	0.027	0.035	0.032	0.020	0.017	0.014	<0.001	0.023	0.215
	R	<0.001	<0.001	<0.001	<0.001	0.001	0.001	0.002	0.002	0.002	0.003	0.037	<0.001	0.101	0.032	0.007	0.003	0.189
	LR	<0.001	<0.001	<0.001	0.004	<0.001	0.003	<0.001	<0.001	0.003	0.003	0.005	0.005	0.003	0.009	0.005	0.003	0.042
	D	<0.001	<0.001	<0.001	0.002	<0.001	<0.001	0.010	0.009	0.010	0.016	0.018	0.004	0.015	0.023	0.003	0.005	0.115
SS7	LD	<0.001	0.005	<0.001	0.007	0.015	<0.001	0.026	0.027	0.036	0.086	0.023	0.031	0.022	<0.001	0.012	0.018	0.308
	R	<0.001	<0.001	<0.001	<0.001	0.002	0.002	0.001	0.004	0.011	0.005	0.004	0.003	0.007	0.016	<0.001	0.003	0.058
	LR	<0.001	<0.001	<0.001	0.004	<0.001	0.005	<0.001	<0.001	0.005	0.004	0.005	0.009	0.002	0.011	0.004	0.003	0.051
	D	<0.001	0.012	<0.001	0.008	0.011	0.005	0.002	0.004	0.019	0.009	0.011	0.016	0.008	0.019	0.002	0.013	0.138
SS8	LD	<0.001	<0.001	<0.001	0.007	0.090	<0.001	0.023	0.015	0.030	0.052	0.025	0.024	<0.001	<0.001	<0.001	0.019	0.283
	R	<0.001	<0.001	<0.001	0.001	0.001	0.001	<0.001	0.002	0.002	0.003	0.070	0.001	0.088	0.003	0.002	0.005	0.177
	LR	<0.001	<0.001	<0.001	0.001	<0.001	0.001	<0.001	<0.001	0.004	0.003	0.005	0.007	0.003	0.010	0.004	0.003	0.040
	D	<0.001	<0.001	<0.001	<0.001	0.010	0.001	0.010	<0.001	0.008	0.010	0.026	0.019	0.001	0.006	0.002	0.010	0.104

Table 2 continued

Sampling stations	Seasons	Naph	Ace	Acen	Flu	Phe	Ant	Fluo	Pyr	BaA	Chry	Benzo (b)	Benzo (K)	BaP	Ind	Diben	BghiP	Total
Tombia	LD	<0.001	<0.001	<0.001	<0.001	0.007	<0.001	0.013	0.013	0.017	0.042	0.012	0.017	0.013	<0.001	<0.001	0.012	0.146
	R	<0.001	<0.001	<0.001	<0.001	0.002	0.002	0.056	0.003	0.006	0.003	0.002	<0.001	0.003	<0.001	<0.001	0.003	0.078
	LR	<0.001	0.002	0.001	0.002	0.005	0.039	0.004	0.007	0.027	0.002	0.013	0.025	0.012	0.005	0.004	0.004	0.154
	D	<0.001	<0.001	<0.001	0.003	0.009	0.018	0.016	0.016	0.020	0.007	0.032	0.019	0.019	0.002	<0.001	0.009	0.169
Mean		0.008	0.001	0.001	0.002	0.007	0.005	0.007	0.005	0.010	0.015	0.033	0.013	0.014	0.012	0.009	0.011	0.154
Std. Dev.		0.046	0.004	0.003	0.003	0.016	0.008	0.011	0.006	0.009	0.021	0.039	0.022	0.022	0.014	0.027	0.017	0.126

LD late dry season, *R* rainy season, *LR* late rainy season, *D* dry season, *Naph* Naphthalene, *Ace* Acenaphthene, *Acen* Acenaphthylene, *Flu* Fluorene, *Phe* Phenanthrene, *Ant* Anthracene, *Fluo* Fluoranthene, *Pyr* Pyrene, *BaA* 1,2-Benzanthracene, *Chry* Chrysene, *Benzo(b)* Benzo(b)fluoranthene, *Benzo(k)* Benzo(k)fluoranthene, *BaP* Benzo(a) pyrene, *Diben* 1,2,5,6-Dibenzanthracene, *Ind* Indeno(1,2,3-C.D) pyrene, *BghiP* 1, 12-Benzopyrelene

was eluted with 1:1 mixture of propanone and DCM in 1–2 ml increments. Another accurately measured 8–10 ml of the eluent was collected and was labelled "AROMAT-ICS". The "AROMATICS" fraction was concentrated to 1 ml for PAHs analysis using gas chromatography.

Gas chromatographic (GC) analysis

The concentrated "AROMATICS" fractions were transferred into labelled glass vials with teflon rubber crimp caps for GC analysis. 1 µl of the concentrated sample was injected by means of hypodermic syringe through a rubber septum into the column. Separation occurs as the vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column (at a constant flow rate) by a flame ionisation detector (FID) whose response is dependent upon the composition of the vapour, by measuring the retention time.

The GC was calibrated by calibration curve method, using standard solutions.

The operational conditions for GC analysis are as stated in Inengite et al. (2010b).

Detector: Hydrogen—35 ml/min; Air—250 ml/min; Nitrogen—30 ml/min.

Inlet: Pressure—14.8 psi; Total flow—65.5 ml/min.

Oven: Initial Temperature—65 °C; Final Temperature—325 °C; Run time—29.0 min.

The limit of detection (LOD) was 0.01 µg/g for the various PAHs studied.

Results and discussion

The results of the PAHs concentrations in the sediments are as stated in Table 2. The PAHs DRs for the various periods of the year that the study was conducted are as stated in Table 3. Half the values of the detection limit of the gas chromatograph were used to represent values below the detection limit of the gas chromatograph, to take care of missing values.

The choice of Epie Creek (SS9) was to serve as control to Kolo Creek. Within the route of Epie Creek there was no gas flaring, while the major concern in the Kolo Creek axis is the gas flare. However, the presence of the gas flare did not show much difference between the two creeks in terms of PAHs concentration rather there were similarities because both SS1 and SS9 portrayed combustion as the main source of PAHs. Henceforth, for the purposes of source prediction of PAHs, Kolo Creek represent all the sampling stations.

The mean levels of PAHs in Kolo Creek sediment at the time of study was (0.154 ± 0.126) mg/Kg. This value is below the critical value of 4.0 mg/Kg for total PAHs in

Table 3 PAHs ratios for source and composition determination in kolo creek sediment

Stations	Ant/Ant + Phe				Fluo/Fluo + Pyr				BaA/BaA + Chry				Ind/Ind + BghiP			
	LD	R	LR	D	LD	R	LR	D	LD	R	LR	D	LD	R	LR	D
SS1	0.50	0.77	0.42	0.50	0.50	0.19	0.70	0.68	0.26	0.63	0.65	0.31	0.29	0.76	0.68	0.80
SS2	0.40	0.63	0.92	0.71	0.62	0.14	0.50	0.45	0.17	0.72	0.82	0.48	0.31	0.48	0.50	0.89
SS3	0.39	0.56	0.91	0.74	0.59	0.18	0.50	0.65	0.23	0.69	0.80	0.41	0.31	0.82	0.50	0.19
SS4	0.50	0.14	0.50	0.50	0.50	0.12	0.50	0.50	0.50	0.61	0.50	0.41	0.50	0.89	0.50	0.50
SS5	0.50	0.39	0.81	0.81	0.51	0.15	0.50	0.20	0.28	0.55	0.27	0.24	0.05	0.28	0.69	0.53
SS6	0.53	0.44	0.85	0.50	0.52	0.46	0.50	0.50	0.44	0.34	0.55	0.38	0.39	0.91	0.75	0.82
SS7	0.03	0.49	0.91	0.32	0.49	0.17	0.50	0.38	0.29	0.70	0.54	0.67	0.03	0.84	0.78	0.60
SS8	0.01	0.39	0.67	0.12	0.61	0.25	0.50	0.95	0.36	0.41	0.57	0.44	0.03	0.40	0.77	0.37
Tombia	0.01	0.47	0.89	0.68	0.50	0.95	0.35	0.49	0.29	0.69	0.92	0.75	0.04	0.14	0.48	0.18
Mean	0.32	0.48	0.76	0.54	0.54	0.29	0.51	0.53	0.31	0.59	0.62	0.45	0.22	0.61	0.63	0.54
Std. Dev.	0.23	0.18	0.19	0.22	0.05	0.27	0.09	0.21	0.10	0.13	0.20	0.16	0.18	0.29	0.13	0.26

Stations	Ant/Ant + Phe	Fluo/Fluo + Pyr	BaA/BaA + Chry	Ind/Ind + BghiP
SS1	0.55 ± 0.15	0.52 ± 0.24	0.46 ± 0.21	0.63 ± 0.23
SS2	0.67 ± 0.21	0.43 ± 0.20	0.55 ± 0.29	0.55 ± 0.25
SS3	0.65 ± 0.22	0.48 ± 0.21	0.53 ± 0.26	0.46 ± 0.27
SS4	0.41 ± 0.18	0.41 ± 0.19	0.51 ± 0.08	0.60 ± 0.20
SS5	0.63 ± 0.22	0.34 ± 0.19	0.34 ± 0.14	0.39 ± 0.28
SS6	0.58 ± 0.18	0.50 ± 0.03	0.43 ± 0.09	0.72 ± 0.23
SS7	0.44 ± 0.37	0.39 ± 0.15	0.55 ± 0.19	0.56 ± 0.37
SS8	0.30 ± 0.30	0.58 ± 0.29	0.45 ± 0.09	0.39 ± 0.30
Tombia	0.51 ± 0.38	0.57 ± 0.26	0.66 ± 0.27	0.21 ± 0.19

Phe phenanthrene, *Ant* anthracene, *Fluo* fluoranthene, *Pyr* pyrene, *BaA* 1,2-Benzanthracene, *Chry* chrysene, *ind* indeno(1,2,3-C.D) pyrene, *BghiP* 1, 12-benzopyrelene, *LD* late dry season, *R* rainy season, *LR* late rainy season, *D* dry season

sediment (ANZECC 2000). According to Maliszewska-Kordybach (1996), Kolo Creek sediment is classified as not contaminated. Comparing the levels of PAHs from this study with other studies in the Niger Delta reveal that Kolo Creek sediments had higher PAHs levels than Warri and Elelenwo (Olajire et al. 2005; Opuene et al. 2007) in the Niger Delta, but lower when compared with values from the other studies (Budzinski et al. 1997; Zhang et al. 2004).

The distribution of total PAHs in the study area is as follows: SS2 > SS1 > SS3 > SS8 = SS9 > SS6 = SS7 > SS5 > SS4, while the individual PAHs were in the order: Benzo(b) ≫ Chry > BaP > Benzo(k) > Ind > BghiP > BaA > Diben > Naph > Phe = Fluo > Ant = Pyr > Flu > Acen = Ace. The PAHs concentration ranged from (0.00 to 0.467) mg/Kg. The highest PAHs concentration was observed in SS2 in the rainy season. PAHs concentration in the seasons follows the trend: late dry season > rainy season > dry season > late rainy season.

Higher ringed PAHs (4–6) rings were more predominant than the lower ringed PAHs (2 and 3) rings, which is indicative of PAHs having pyrogenic origin.

The observed trend of PAHs concentrations in the various sampling stations is an indication that the flare within the proximity of SS1, SS2 and SS3 contributed greatly to PAHs in the environment as compared to other sources of PAHs in the other sampling stations.

PAHs sources were predicated using diagnostic ratios conventionally reported in literature (Yunker et al. 2002; Olajire and Brack 2005; Morillo et al. 2008). These ratios include Ant/Ant + Phe; Fluo/Fluo + Pyr; BaA/BaA + Chry And Ind/Ind + Bghip. The Ant/Ant + Phe ratio presumes that ratios <0.1 indicate PAHs source to be of petroleum origin, while ratios >0.1 indicate PAHs source to be of combustion origin (Budzinski et al. 1997). The Fluo/Fluo + Pyr ratio presumes that ratios in the range ≥0.4 and ≤0.5 indicate petroleum combustion and ratios <0.4 indicate petroleum sources, while ratios >0.5 indicate grass, wood and coal combustion. BaA/BaA + Chry presumes that ratios <0.2 are of petroleum origin, ratios in the range ≥0.2 and ≤0.35 as mixed sources and >0.35 as combustion sources. Lastly, Ind/Ind + BghiP presumes that PAHs ratios <0.2 indicate petroleum sources, ratios in the range ≥0.2 and ≤0.5 as petroleum combustion sources and >0.5 as grass, wood and coal combustion sources (Budzinski et al. 1997; Yunker et al. 2002; Olajire et al. 2005; Morillo et al. 2008). These ratios and their cut-off values for the various predicted sources explicitly elaborated into (Fig. 2) five for the four periods of the year that the study was conducted. Applying a single PAH ratio may not be adequate and can be misleading (Yunker et al. 2002). This, however, is ameliorated by the use of PAH cross plots to enable the determination of PAH sources.

In the late dry season (cf. Fig. 2), the PAHs cross plots separated the sampling stations into groups of possible PAH sources. In (Fig. 2), BaA/BaA + Chry versus Fluo/Fluo + Pyr, two major groups were observed, the largest having four sampling stations (SS1; SS3; SS5 and SS9) and a likely PAH source of mixed sources/grass, wood and coal combustion. While the second largest group has two sampling stations (SS6 and SS8) with a likely PAH source of combustion/grass, wood and coal combustion. The other groups had single sampling stations. Sampling Station 4(SS4) had possible PAH source of petroleum combustion/combustion, SS7 had Mixed sources/petroleum combustion, while SS2 had petroleum/grass, wood and coal combustion.

Sampling Station 1 (SS1) in the late dry season exhibited combustion as sources of PAHs. The combustion is combined petroleum and wood combustion. This is expected for petroleum combustion, since SS1 is the point at which the gas flare is situated. It therefore corresponds with petroleum combustion. Also, grass, wood and coal combustion were predicted as sources of PAHs. This also corresponds with human activities in the vicinity because the host communities of the flow station (Imiringi) and the other bordering communities main source of energy for cooking and other domestic activities is firewood. Also, some minor bush clearing and burning may have contributed to the prediction that grass, wood and coal combustion is a source of PAHs in SS1. Morillo et al. (2008) determined PAHs sources based on the land use, they, however, observed no correlation between the land use and the sources of PAHs basically because of the ubiquitous nature of PAHs, but were able to conclude that PAHs of pyrogenic origin were the major sources of PAHs.

Imiringi (SS4) which is a habited community with all its attendant activities tends to stand out. Its sources of PAHs were combustion, petroleum combustion, grass, wood and coal combustion and petroleum. This could be ascribed to the multifaceted activities embarked upon by inhabitants of this community such as bush burning (Masclet et al. 1995) and generation of energy through the combustion of fossil fuels (Oros and Simoneit 2000). This is similar to SS7 (Otuasega) and SS8 (Oruma) that have settings like SS4 (Imiringi). SS2, SS3, SS5 and SS6 were also similar in their sources of PAHs and closely resemble that of SS1. These stations lie along the creek in parts that traverse farmlands.

In the rainy season (cf. Fig. 3), majority of the sampling stations fell between petroleum and combustion sources, which can be regarded as mixture of extreme sources. Within this area, Kolo Creek serves as the major drainage and all the rain water finally flow through their courses to Kolo Creek. It is likely that petroleum products such as fuel and lubricating oil both in use and as wastes were washed

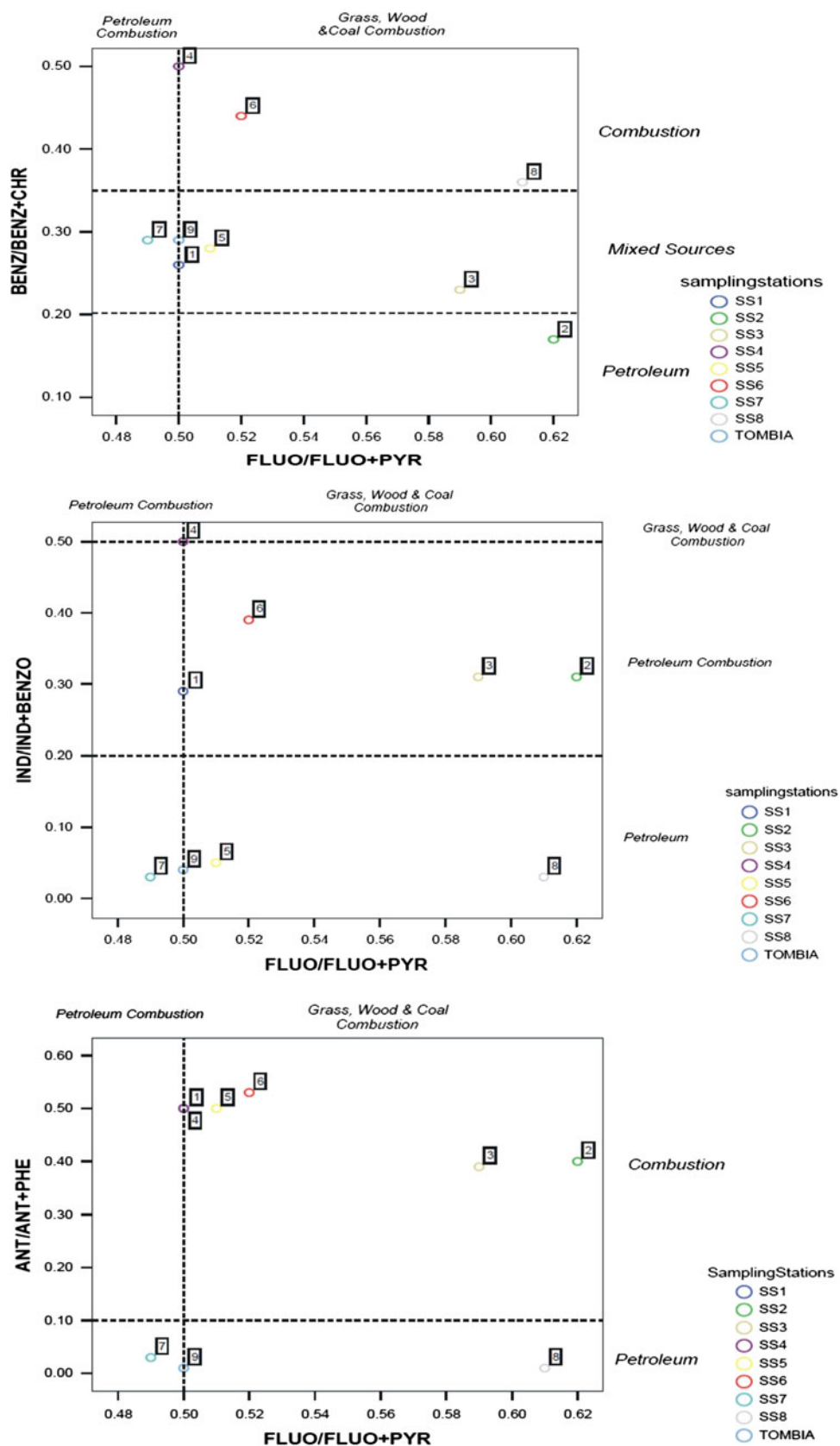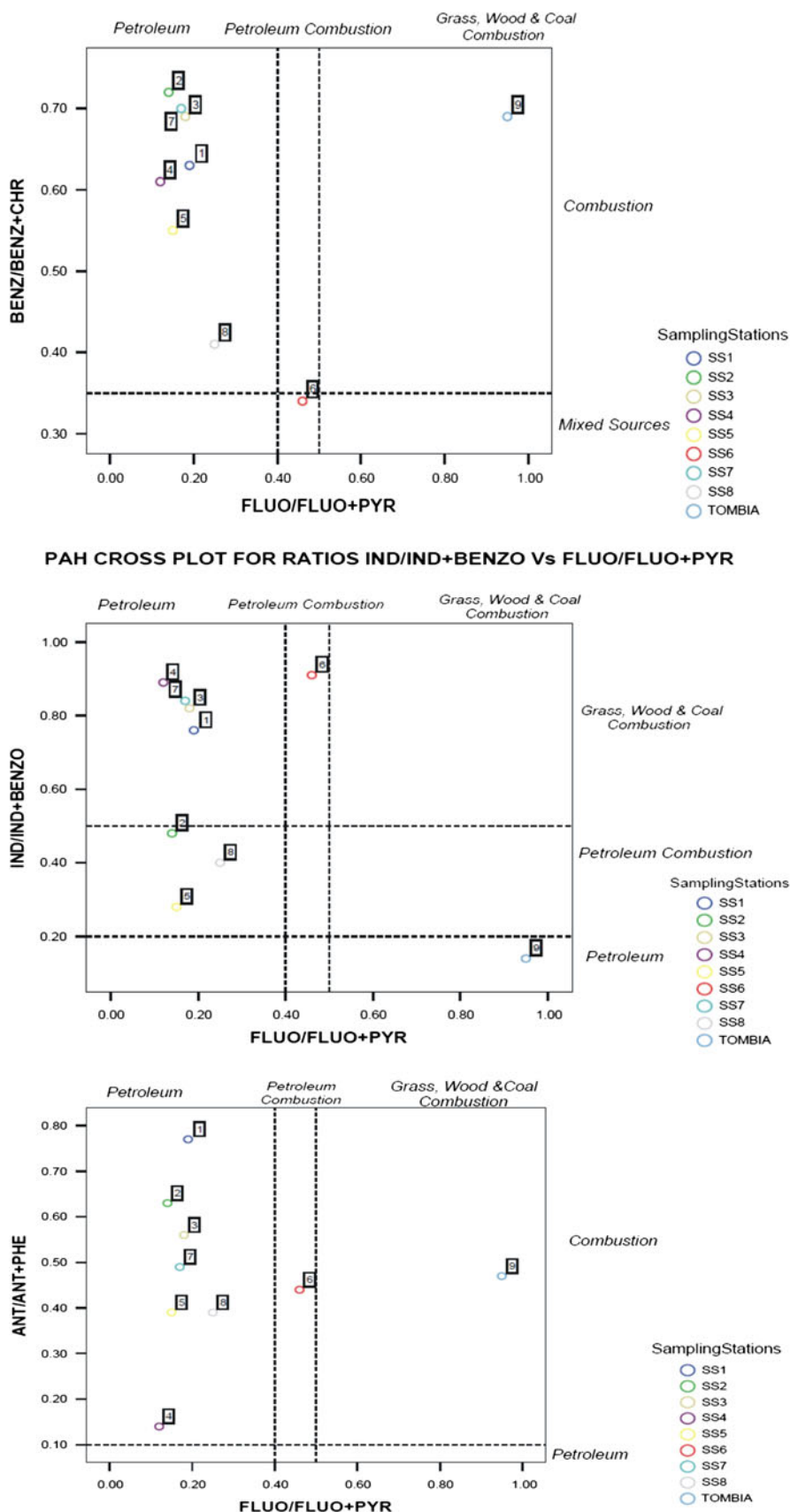**Fig. 2** PAH cross plots for the varios ratios in the late dry season

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Fig. 3 PAH cross plots for the various ratios in the rainy season

PAH CROSS PLOT FOR RATIOS IND/IND+BENZO Vs FLUO/FLUO+PYR

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down into the creek (Laflamme and Hites 1978), thus contributing greatly to the sources of PAHs in Kolo Creek in the Rainy season to be more of petroleum origin. Karlsson and Viklander (2008) reported similarly that Gully Pots water and sediment which were mainly drained from the city centre had mixed sources of PAHs, because the drains collect all manner of waste from the environment. Wang et al. (2010) also reported similar findings.

Tombia Junction (SS9) which is situated close to an abattoir and a petrol station mainly indicated combustion (grass and wood combustion) and petroleum as sources of PAHs in SS9 situated in Epie Creek. This is expected due to high level of wood burning during the preparation of the meat in this abattoir and the fuel and other petroleum products that were likely washed-off and drained into the creek. This observation is consistent with the findings of Olajire and Brack (2005). In their study, soil samples collected from a fuel tanker loading point had PAHs ratios that were indicative of petrogenic origins.

SS6 had a vividly established source of petroleum/petroleum combustion in all the three cross PAHs ratios, which strongly indicated some form of power generation and automobile vehicular activities. During the period of sampling, a bridge construction was on-going at SS6 where heavy duty vehicles were in use. This may have contributed to petroleum/petroleum combustion source of PAHs at SS6.

In the late rainy season (cf. Fig. 4), the major group was combustion/petroleum combustion. Grass, wood and coal combustion also contributed. SS9 was classified to have PAHs sources as petroleum/petroleum combustion, while SS1 was combustion/grass, wood and coal combustion. The other stations were classified as more of petroleum combustion. The sampling stations except SS1 and SS9 had PAHs sources similar to those of the rainy season. Sampling Stations SS1 and SS9 having PAHs sources of wood combustion and petroleum combustion, respectively, is linked to the activities in the immediate environment. SS1 is the flare point and SS9 lies along a busy road with heavy vehicular traffic in the heart of Yenagoa Metropolis. It is, therefore, expected that some of the PAHs may have condensed, and dissolved in rain water, bound to particles and eventually flow to the creek to form sediments.

In the dry season, the PAHs cross plots separated the sampling stations as shown in Fig. 5.

Majority of the stations in the dry season fell under petroleum combustion and also in the broad class of combustion. SS5 fell under petroleum in all three ratio cross plots. This is a strong indication that there may have been some release of petroleum products into the environment during this period of sampling. However, in the dry season, airborne PAHs travel far and wide, and therefore, it is expected that mixed sources of PAHs will more likely represent PAHs in the dry season. Wania and Mackay (1996) reported similarly

that gaseous and particle bound PAHs can be transported over long distances before deposition, especially at low relative humidity. This phenomenon can generate a pot-pouri of PAHs with diverse origins.

The annual modal PAHs sources in the various sampling stations are summarised in Table 4. Most of the sampling stations had combustion as the major source of PAHs in all the seasons of the year. This is a combination of petroleum combustion and grass, wood and coal combustion, which had equal contributions in the considered sampling stations. The in next ranking to combustion (petroleum and wood) is petroleum and the least in ranking is mixed sources.

Sampling station 9 (SS9) had petroleum as an outstanding source of PAHs. As earlier stated, this may have been as a result of the contribution from fuel station that is adjacent to the sampling station. Also, SS9 lies along a busy road with high volume of automobile traffic in an urban setting and that may have contributed greatly to petroleum combustion being the next ranking PAHs source in SS9.

From the literature values in Table 5, the likely predominant PAH sources in Kolo Creek are of petroleum origin (diesel and lubricating oil) in the rainy season. In the other seasons, there was no corresponding petroleum source when values from this study were compared with the literature values. It is suggested that during the rainy season, the storm water would have washed-off diesel and lubricating oil from various sources and drained to the creek. Comparing DR values of this study with literature values reveal that the likely combustion sources were wood/grass and gasoline combustion in all the seasons that the study was conducted except in the rainy season.

The petroleum source from literature that was close to the values obtained in this study is the fluo/fluo + pyr ratio for kerosene (0.46). SS2, SS3 and SS4 had 0.43, 0.48 and 0.41, respectively. The literature value for kerosene for the ind/ind + BghiP ratio was 0.48. The value for SS3 (0.48) was closest to it. SS1 and SS2 had 0.63 ± 0.23 and 0.55 ± 0.25, respectively. In general, the values were also close to literature values for diesel, (0.26 ± 0.16) for fluo/fluo + pyr and $0.40 \pm 0.18)$ for ind/ind + BghiP.

The environmental samples sources from literature that were close to values from this study are bush fire (0.61 and 0.70); lubricating oil re-refined (0.74 and 0.36); used engine oil (gasoline cars) (0.30 and 0.18) and used engine oil (diesel cars) (0.37 and 0.29) for fluo/fluo + pyr and ind/ind + BghiP, respectively.

The literature values for combustion sources that were close to values from this study were those for: grasses; wood; kerosene; gasoline and diesel combustion (cf. 3 and 5). All the sampling stations had elements of combustion; however, for environmental samples SS1 pronounced bush fire as a source of PAHs, while SS4 and SS5 showed used oil as sources of PAHs.

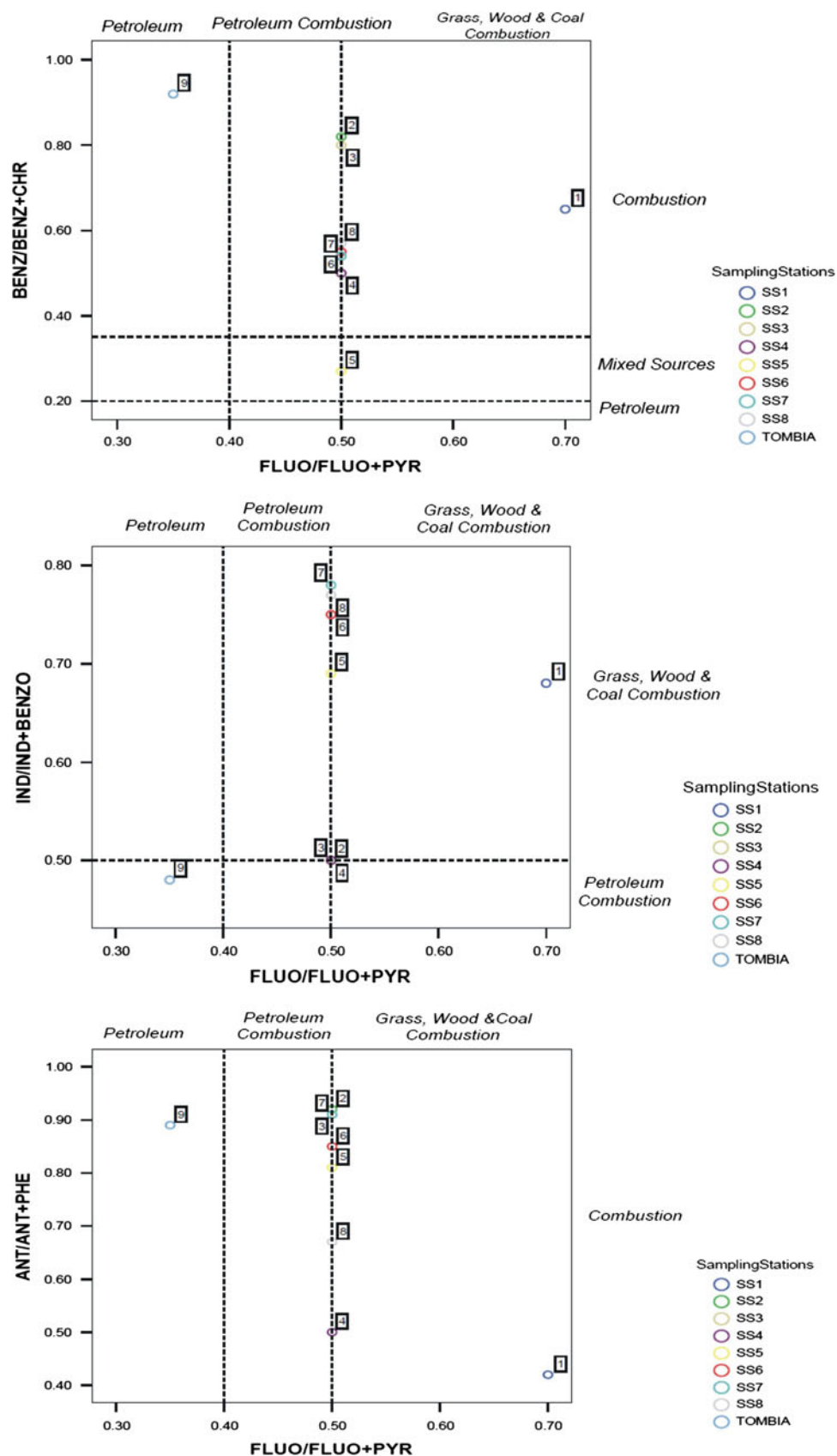**Fig. 4** PAH cross plots for the various ratios in the late rainy season

Fig. 5 PAH cross plots for the
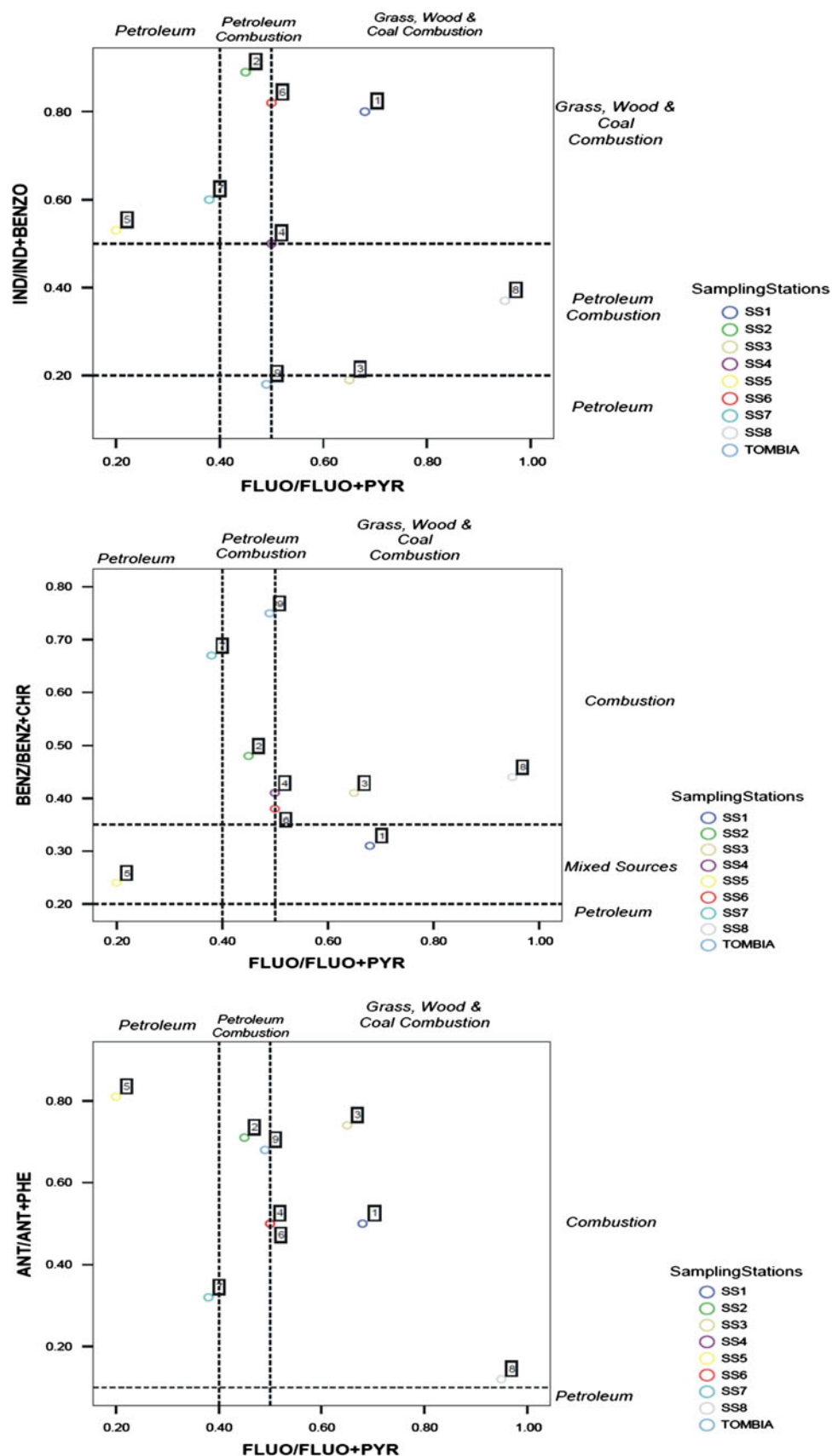various ratios in the dry season

Table 4 Identified PAHs Sources in the Sampling Stations for the Various Seasons

	Petroleum	Petroleum combustion	Grass, wood & coal combustion	Combustion	Mixed sources
Late dry season	SS2, SS7, SS9, SS5, SS8	SS1, SS3, SS4, SS6, SS7, SS9	SS1, SS2, SS3, SS5, SS6, SS8, SS9	SS1, SS2, SS3, SS4, SS5, SS6, SS8	SS1, SS3, SS5, SS7, SS9
Rainy season	SS1, SS2, SS3, SS4, SS5, SS6, SS7, SS8, SS9	SS2, SS5, SS6	SS1, SS3, SS4, SS7, SS9	SS1, SS2, SS3, SS4, SS5, SS6, SS7, SS8, SS9	SS6
Late rainy season	SS9	SS2, SS3, SS4, SS5, SS6, SS7, SS8, SS9	SS1, SS5, SS6, SS7, SS8	SS1, SS2, SS3, SS4, SS5, SS6, SS7, SS8, SS9	SS5
Dry season	SS3, SS5, SS7, SS9	SS2, SS4, SS6, SS8, SS9	SS1, SS3, SS5, SS7, SS8	SS1, SS2, SS3, SS4, SS5, SS6, SS7, SS8, SS9	SS1, SS5
Annual frequency	SS1 = 1	SS1 = 1	SS1 = 4	SS1 = 4	SS1 = 2
	SS2 = 2	SS2 = 3	SS2 = 1	SS2 = 4	SS2 = 0
	SS3 = 2	SS3 = 2	SS3 = 3	SS3 = 4	SS3 = 1
	SS4 = 1	SS4 = 3	SS4 = 1	SS4 = 4	SS4 = 0
	SS5 = 3	SS5 = 2	SS5 = 3	SS5 = 4	SS5 = 3
	SS6 = 1	SS6 = 4	SS6 = 2	SS6 = 4	SS6 = 1
	SS7 = 3	SS7 = 2	SS7 = 3	SS7 = 3	SS7 = 1
	SS8 = 2	SS8 = 2	SS8 = 3	SS8 = 4	SS8 = 0
	SS9 = 4	SS9 = 4	SS9 = 2	SS9 = 3	SS9 = 1
Total	19	22	22	34	9

Table 5 PAH ratios for petroleum, single source combustion and environmental samples

Source	Fluo/Fluo + Pyr	Ind/Ind + BghiP
Petroleum		
Kerosene	0.46	0.48
Diesel oil	0.26 ± 0.16 (0.01–0.47)	0.40 ± 0.18 (0.25–0.65)
Crude oil	0.22 ± 0.07 (0.14–0.26)	0.09
Lubricating oil	0.29 (0.17–0.30)	0.12 (0.00–0.13)
Asphalt		0.52–0.54
Combustion		
Bituminous coal	0.53 ± 0.05 (0.48–0.58)	0.48 (0.35–0.62)
Coal tar	0.58	0.53
Wood soot	0.50	0.55
Wood	0.51 ± 0.06 (0.41–0.67)	0.64 ± 0.07 (0.49–0.77)
Grasses	0.58 ± 0.04 (0.53–0.63)	0.58 ± 0.10 (0.52–0.69)
Gasoline	0.44	0.09–0.22
Kerosene	0.50	0.37
Diesel	0.39 ± 0.11 (0.20–0.58)	0.35 ± 0.1 (0.19–0.50)
Crude oil	0.44 ± 0.02 (0.42–0.46)	0.47 ± 0.01 (0.46–0.48)
Environmental samples		
Bush fire	0.61	0.70
Savannah fire particulate	0.59 ± 0.01 (0.58–0.60)	0.39 ± 0.07 (0.31–0.44)
Road dust	0.42	0.51
Lubricating oil, re-refined	0.74	0.36
Used engine oil (gasoline car)	0.30	0.18
Used engine oil (diesel car)	0.37	0.29
Urban air	0.56 ± 0.01 (0.55–0.57)	0.40 ± 0.11 (0.27–0.48)
Creosote treated wood pilling	0.62 ± 0.01 (0.61–0.64)	0.64 ± 0.04 (0.59–0.68)

Adapted from Yunker et al. (2002)

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Conclusion

The major anthropogenic sources of PAHs in the sediment of Kolo Creek were of pyrogenic origin. There were, however, petrogenic sources that were close to point sources as in the case of SS9 that is in the proximity of a petrol station and also in the rainy season that petroleum products were allegedly washed into the creek by storm water. The pyrogenic sources were a combination of grass/wood combustion and petroleum combustion. These predictions corresponded with the types of activities within the vicinity of the sampling stations in question. This study further affirms the accuracy of the predictive use of diagnostic ratios of PAHs for source determination.

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