Comparison and Optimization of Extraction Methods for The Determination of Polycyclic Aromatic Hydrocarbons in Sediment from Blood River in Limpopo Province, South Africa

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Abstract **-** Polycyclic aromatic hydrocarbons (PAHs) are highly persistent, hazardous (cause cancer), and widespread pollutants. Their presence in the environment is a public health concern. Identifying and determining these PAHs are first step in developing measures for the removal of these compounds from water and sediment. The aim of this study was to compare and optimize three different extraction methods for the detection of PAHs in sediment samples. The optimized methods include microwave assisted extraction (MAE), ultrasonication (U), and a combination of ultrasonication and mechanical shaking (UAM). PAHs in the certified reference material of sediment (CRM-104) were quantified to confirm the accuracy of the proposed methods. Gas chromatography coupled with flame ionization detector (GC-FID) was used for analysis of 16 PAHs. Due to its superior precision compared to ultrasonication and combined ultrasonication and mechanical shaking, which both displayed subpar precision, the MAE was preferred for the extraction of PAHs from sediment. Furthermore, the MAE was found to be the most versatile technique due to its easy handling and fast extraction time when many samples are analysed; also, it implies low operation costs. The MAE was successfully applied in determining the concentrations of 16 PAHs in real sediment samples with good precision and excellent percentage recoveries (between 83.8 and 125%). The concentrations of PAHs obtained using the three extraction methods ranged between 0.016 and 10.8 mg/kg. In general, lower molecular weight compounds showed lower concentration than higher molecular weight PAHs, and the values displayed spatial variation.

Keywords **-** Polycyclic aromatic hydrocarbons, Microwave-assisted extraction, ultrasonication, mechanical shaking

I. BACKGROUND

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds without a heteroatom that are made up of two or more fused aromatic rings arranged in a cluster or linear pattern. The greater molecular weight PAHs are more hazardous, more stable, and last longer in the environment than lower molecular weight compounds [1, 2]. There are numerous routes for PAHs to develop in the environment. These include the direct biosynthesis by microbes and plants, low to moderate temperature fossil fuel formation from sedimentary organic compounds, and high temperature pyrolysis of organic compounds [3, 4]. However, they are the byproducts of incomplete organic combustion that arise from sources that are growing because of human activities like burning or cooking, industrial or vehicle gases from diesel and petroleum engines [5]. According to their origin PAHs are divided into two classes (pyrogenic and petrogenic) that are present in the environment in varying amounts [1].

In addition, it is well known that PAHs linger in the environment for a very long time [6]. According to research by Nemirovskaya [7], these substances are among the hydrocarbon families' most dangerous contaminants. Considering this, PAHs are regarded as environmental pollutants that may harm humans, animals, and microorganisms, leading to the buildup of toxic substances in the food chain and, in rare cases, to serious health issues and genetic disorders [8].

In order to accurately determine the degree of contamination in the sample matrix, a variety of reagents, extraction methods, and instrumental analyses may be used during the study of PAHs in the sample matrix [9]. In analytical processes used to find PAHs in solid samples, extraction is typically the initial step. The choice of an appropriate extraction method influences sample throughput by affecting the analysis duration as well as the precision and accuracy of the results. For the separation of PAHs from solid materials, several effective extraction techniques have been created and are often utilized [2, 9].

Conventional methods for extracting PAHs from sediments have a number of drawbacks, including expensive sample preparation, a high risk of laboratory contamination, and lengthy extraction timeframes [10]. It is highly interesting to develop efficient extraction methods for identifying these PAHs in environmental samples. Conventional extraction methods like MAE, mechanical agitation, Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS), Soxhlet, and ultrasonication can be used to extract these chemicals from sediments [10, 11]. Various extraction methods have been investigated in recent years to lower the amount of organic solvent used, as well as the overall extraction time and sample preparation [2, 9, 11, 12].

When PAHs are released into river waters, they do not stay in solution but are immediately absorbed by particulate matter, avoiding detection in water samples during monitoring them [9]. Sediment analysis can be used to efficiently identify the sources of these PAHs. PAHs have a limited solubility in water and are extremely hydrophobic, which causes them to stick to other particles and build up in sediments. As a result, river sediments that have considerable concentrations of organic

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chemicals can serve as a significant PAH repository [13]. Therefore, in order to identify the optimum extraction approach that will generate the largest yield of PAHs from sediments, this study set out to identify the PAHs in sediment samples from the Blood River using various extraction procedures.

II. MATERIALS AND METHODS

A. Study sites description

Blood River is found in Seshego area, Limpopo Province. Most uses of Blood River water are for residential and agricultural purposes. Blood River serves as a source of water for nearby animals as well. Sewage leaks, home and commercial trash, and other activities taking place in the region and close to Polokwane might all be sources of pollution in Blood River. Therefore, all of these wastes and activities could potentially be sources of PAHs in the river. Sand mining by locals and visitors to Polokwane is another activity going on in Blood River's upper stream. The river system can suffer as a result of sand mining in this location. The sampling sites along the Blood Rivers in the Limpopo Province are depicted on a map of South Africa in Figure 1.

B. Sampling points

The Blood River was sampled at six different locations. The locations of the sampling points weren't equally spaced apart. Sewage pipes that drain into the Blood River at barriers places may be seen as the river travels through the Seshego residential area. While some sampling stations were by the Seshego area, others were chosen to be upstream and downstream of the Seshego residential area.

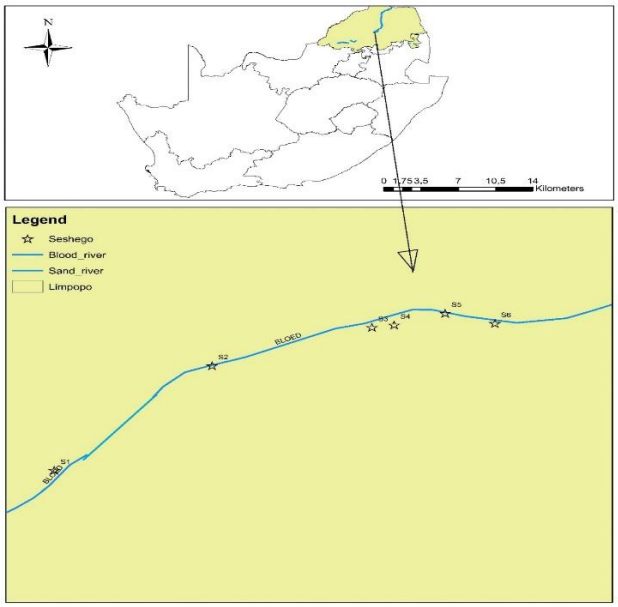

Fig. 1. The map showing Blood River.

The sampling locations were selected at points on the rivers that were close to anthropogenic activities so that the effects of these activities on the river could be evaluated.

C. Reagents and Apparatus

The following chemicals were purchased from Sigma-Aldrich (Chemie GmbH, Calbe, Germany): acetone, methane, hexane, nitric acid and hydrochloric acid. Anhydrous sodium sulfate, Na_2SO_4 was supplied by (Sigma-Aldrich Chemie GmbH, Calbe, Germany). Copper powder (Alfa Aesar GmbH& Co KG, Calbe, Germany) and 35% hydrochloric acid were combined to produce activated copper, which was used to clean up extracts. A Buchi-evaporator R-200, equipped with a heating bath and vacuum pump v-700 was obtained from Labotec SA, RSA. A Reacti-Vap™ Evaporating Unit used to control a gentle stream of nitrogen was obtained from Pierce (Illinois). An automatic pipette (Glison Inc., Middleton, USA) was used to measure the volume of liquids, and a Vortex (Lasec SA, Cape Town, RSA) was used to mix vials containing samples. The United States Environmental Protection Agency (US EPA's) 16 priority PAHs standards: naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fln), pyrene (Pyr), benzo(a)anthracene (BAnt), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (InP), dibenzo(a,h)anthracene (DahAnt), and benzo(g,h,i)perylene (BghiP) were acquired from Supelco (Bellfonte, USA). To verify the precision of the method, certified reference material (CRM-104) of sediments from Sigma-Aldrich Chemie GmbH in the United States was used. A CEM MARS Microwave system (CEM, Charlotte, USA) was used to extract PAHs from sediments. An Agilent 7820A GC with FID (Agilent Technologies, USA) was used to analyse the samples.

D. Sample collection and preservation

Sediment samples were collected from 6 sampling sites in Blood River. Samples were taken at a depth of around 15 cm below the sediment's surface. Samples were air dried for 5–6 days. Samples were pulverized using an agate mortar and pestle, sieved using a 250 µm mesh size sieve, and stored until extraction of PAHs.

E. Extraction of PAHs

Microwave assisted extraction.

For extraction of PAHs, methods reported by Seopela et al. [14] and Mogashane et al. [1] were applied with slight modifications. A 5.00 g sample that has been homogenized and powdered was put in the microwave vessels. A 30 mL 1:1 (v/v) combination of acetone and hexane was used for the extraction, which was carried out for 30 minutes at 110 °C, 800 psi of pressure, and 1,600 W of power. The extracts were collected in 250 mL round bottom flasks after the vessels had cooled to room temperature, and they were then evaporated to around 2 mL in a Buchi-evaporator that was outfitted with a heating bath and vacuum pump at a temperature of 40 ^{0} C. Activated copper was added to each sample for desulfurization, anhydrous sodium sulfate for drying the extract, and a 0.45 µm PVDF syringe filter for filtration, as described by Seopela et al. [14]. The extract was dried using a moderate nitrogen stream. The extract was combined with the internal standards Ace-D10,

Chr-D12, and Per-D12 before being transferred to a 1.5 mL brown vial with 1 mL of dichloromethane (DCM). Prior to GC-FID analysis, all the samples were completely mixed using a vortex.

Ultrasonication procedure.

An ultrasonic bath was used for extraction of PAHs from sediments. During the process, 1.00 g of sediment was accurately weighed into a 25 mL amber bottle. A 20 mL portion of 1:1 (v/v) acetone: hexane was added to the bottle. The bottles were sealed with screw cap closure lined with PTFE-faced silicon rubber washer and shaken vigorously to suspend the contents. The bottles were sonicated in an ultrasonic bath for 60 min at ±50 °C. The extraction solutions were then centrifuged for 10 min at 2000 rpm. The volume of the extracts was reduced to approximately 2 mL using a rotary evaporator. Activated copper was added to the sample to desulfurize the solution. The extracts were dried with anhydrous sodium sulphate and filtered through a 0.45 µm PVDF syringe filter. The solution was evaporated to dryness under a gentle stream of nitrogen. Suitable volumes of internal standards, Ace-D10, Chr-D12 and Per-D12 were added to all the extracts and reconstituted to 1 mL with DCM by using an automatic pipette and mixed thoroughly using a vortex before analysis by GC-FID.

Combination of mechanical shaking and ultrasonication procedure.

Mechanical shaking (Orbirtal platform sharker, 120 W, 50 Hz) and ultrasonication were used for extraction of PAHs from sediment samples. A 1.00 g of sediment sample was accurately weighed into 25 mL amber bottle. A 20 mL portion of 1:1 (v/v) acetone: hexane mixture was added to the bottle. The bottles were sealed with screw cap closure lined with PTFE-faced silicon rubber washer. A platform shaker was used to shake the contents for 25 min at 2000 rpm. The bottles were sonicated in an ultrasonic bath for 60 min at ±50 °C. The extraction solutions were then centrifuged for 10 min at 2000 rpm. The volume of the extracts was reduced to approximately 2 mL using a rotary evaporator. Activated copper was added to the sample to desulfurize the solution. The extracts were dried with anhydrous sodium sulphate and filtered through a 0.45 µm PVDF syringe filter. The solution was evaporated to dryness under a gentle stream of nitrogen. Suitable volumes of internal standards, Ace-D10, Chr-D12 and Per-D12 were added to all the extracts and reconstituted to 1 mL with DCM by using an automatic pipette and mixed thoroughly using a vortex before analysis by GC-FID.

F. Determination of limit of detection and limit of quantification

Reagent blanks were obtained by following the sample preparation process to assess the limit of detection (LOD) and limit of quantification (LOQ). Stock solutions of 1,000 mg/L of the 16 PAHs and three internal standards, were prepared from pure standards using DCM. A 1.00 µL of the prepared reagent blanks was injected and the GC run as usual. When calculating the LOD and LOQ from the calibration slope, signal to noise ratios of 3 and 10 were used, respectively. Table 1 displays the LOD and LOQ computed values.

G. Accuracy and precision

The microwave assisted extraction, ultrasonication, and a combination of sonication and mechanical shaking methods were validated using certified reference material of sediment containing PAHs. By examining CRM-104, which has PAH quantities in sediment that have been certified, the accuracy of the results was confirmed. To assess the precision of the results, the percentage relative standard deviation (% RSD) was determined.

H. Instrumentation and analytical conditions

An Agilent 7820A gas chromatograph (GC) with flame ionization detector was used to analyze the samples. Prior to sample analysis, essential instrumental parameters were optimized as reported by Mogashane et al. [1]. The GC analysis was conducted on HP-5 column of 30 m length, 320 µm id and 0.25 µm film thickness to detect 16 PAH compounds. Helium was used as a carrier gas, whereas hydrogen was used as a make-up gas. The instrumental conditions of GC-FID were programmed as follows: oven temperature: starting at 75 ^{0} C and holding for 0.5 min, followed by ramping to 200 ^{0} C at 10 ^{0} C min^{-1} and holding for 5 min and then ramping to 280 ^{0} C at 10 ^{0} C min^{-1} and holding for 10 min; flow rate of carrier gas: 6.5 mL min^{-1}; FID temperature: 300 ^{0} C; flow rate of H_2: 30 mL min^{-1}; flow rate of air: 400 mL min^{-1}. The sample injection port was kept at 280 ^{0} C. A 1 µL sample was injected in splitless mode.

I. Statistical analysis

To examine the statistical significance of variations in the mean concentration of the 16 PAHs identified in the sediment samples, the data was analyzed using one-way analysis of variance (ANOVA). A probability level of P = 0.05 was considered statistically significant. For statistical analysis, the Statistical Package for the Social Sciences (SPSS) software was utilized.

III. RESULTS AND DISCUSSION

A. Calibration and linearity of the method

Calibration curves for the 16 PAHs were constructed by plotting the response ratios, As/Ais versus the concentration ratios, Cs/Cis, where, As and Ais are the peak areas of the analyte and internal standard and Cs and Cis are their concentrations, in mg/L, respectively. Linear calibration curves were obtained for all standard concentration ranges that were determined. The coefficient of determination (R^2) for the linear regression obtained ranged between 0.9367 and 0.9973 (Table 1). The lowest regression value obtained was for DahAnt, Fln, Pyr and BaP with values lower than 0.99. The calibration curves were used to determine concentrations of each PAH in sediment samples.

B. Limit of detection and limit of quantification

The LOD for each PAH in the samples were calculated as 3 times the standard deviation of the mean whereas, LOQ as 10 times the standard deviation of the mean. The LODs ranged from 0.00214 to 0.0214 mg/kg while the LOQs ranged between 0.0223 and 0.0801 mg/kg as obtained for MAE. The LODs

ranged from 0.00605 to 0.359 mg/kg and 0.0121 to 0.322 mg/kg as obtained for combination of ultrasonication and mechanical shaking and ultrasonication, respectively. However, the LOQs ranged from 0.0202 to 1.21 for combination of ultrasonication and mechanical shaking and between 0.0403 and 1.07 mg/kg for ultrasonication. Furthermore, the lowest LODs and LOQs are observed for MAE as compared to other two extraction techniques. Any PAH concentration in sediment with values less than the LOD were recorded as below LOD. The LODs and LOQs obtained in the current study are comparable to those reported by Seopela et al. [14]. Chemical formulae of PAHs, number of rings, retention times, regression parameters, LODs and LOQs obtained from analysis of standards by GC-FID for methods applied for analysis of sediment are presented in Tables 1.

C. Validation of the methods

Various extraction methods of PAHs from sediments have been proposed and several studies have been conducted to compare the different extraction techniques [2, 9, 11, 12]. The MAE, ultrasonication and combination of ultrasonication and mechanical shaking techniques were compared by evaluating the percentage recoveries of the 16 PAHs from CRM-104 as determined by GC-FID. The percentage recoveries obtained for these PAHs are shown in Table 2. The percentage recoveries obtained from ultrasonication ranged from 32.4 to 98.5% with the % RSD values ranging between 0.279 and 8.91%. Benzo(b)fluoranthene demonstrated lowest percentage recovery of 32.4% while the highest percentage recovery of 98.5% was obtained for chrysene. The percentage recoveries obtained from a combination of ultrasonication, and mechanical shaking ranged from 23.1 to 86.5% with the % RSD values ranging between 0.261 and 8.7%. However, the results from this study showed that extraction performed using ultrasonic bath and a combination of ultrasonication and mechanical agitation gave lower percentage recoveries and was less efficient. The low extraction efficiencies might be caused by losses of PAHs that occur during extraction and concentrating of extracts with the rotary evaporator before analysis. These two extraction techniques require more extraction times, and this might lead to losses of PAHs because purification and centrifugation techniques are usually applied after extraction. The percentage recoveries obtained from MAE ranged from 83.8 to 125% with % RSD values ranging between 0.317 and 7.53%. Phenanthrene had the lowest percent recovery of 83.8% while the highest percentage recovery of 125% was obtained for Indeno(1,2,3-cd) pyrene. The percentage recovery for lower molecular weight (LMW) PAHs (Nap-Ant) ranged from 83.8 to 117%, whereas the percentage recovery for higher molecular weight (HMW) PAHs (Fln-BghiP) ranged from 92.7 to 125% and this shows that higher percentage recoveries were obtained for HMW compounds. The LMW compounds might have been lost during the evaporation step.

The percentage recoveries obtained in the present study indicated that MAE is more efficient than ultrasonication and combination of ultrasonication and mechanical shaking since the percentage recoveries for all the PAHs are above 80% for the MAE method. Mekonnen et al. [15] and Mogashane et al. [1] all reported average percentage recoveries of more than 80% for selected PAHs obtained with MAE, which is comparable to the percent recoveries obtained in the current study. As can be seen in Table 2, higher percentage recoveries and better precision were obtained by MAE using GC-FID analysis. From these results it can be concluded that MAE is a suitable technique for extraction of PAHs from sediment samples.

D. Quantification of PAHs in sediments

The concentration of PAHs in the sediment samples ranged between 0.016 to 3.10 mg/kg as obtained by MAE. Most of the 16 PAHs quantified in sediments from the same river were found to be above the LOD. The LMW compounds (two to three ringed PAHs) including naphthalene and acenaphthylene had lower concentrations, while HMW compounds (≥ 4 ringed PAHs) were present in higher concentrations. Since the HMW PAHs are more lipophilic than LMW PAHs, concentrations of HMW PAHs in sediments are expected to be higher than those obtained for LMW compounds [5]. Moreover, the concentration of all the PAHs increased slightly from sampling site 1 to 6, this might be caused by different sources of PAHs found around the river. Generally, the LMW compounds were detected in lower concentration than the HMW PAHs (≥ 4 aromatic rings) after extraction of PAHs by ultrasonication. The level of PAHs ranged from 0.056 to 8.59 mg/kg. The concentration of PAHs ranged from 0.045 to 10.8 mg/kg as obtained following extraction by a combination of ultrasonication and mechanical shaking. Most of the LMW compounds (Nap, Ace, Acy, Flu, Phe and Ant) were detected at lower concentrations, while the HMW PAHs showed higher concentrations in most of the sampling sites. Concentrations of PAHs obtained by the three extraction methods are demonstrated in Figure 2.

E. Comparison of three extraction methods

To compare the three extraction techniques used in the current study, sediment samples from Blood River were selected and the PAHs extracted and measured using GC-FID with the same column and instrumental conditions. Three extraction techniques (MAE, ultrasonication and combination of ultrasonication and mechanical shaking) were optimised for the quantification of PAHs in the samples. Results from this study showed that ultrasonication and combination of ultrasonication and mechanical shaking yielded higher concentrations of PAHs than the measured concentrations after MAE. The results obtained using the three extraction techniques showed that higher concentrations were obtained for HMW compounds than LMW compounds. This agrees with the findings of Bayowa, [3], who reasoned that HMW PAHs, which are hydrophobic compounds and are less soluble in water and tend to settle mostly in sediments.

The MAE was preferred and found to be suitable for the extraction of PAHs from sediment samples. Generally, the precision obtained for ultrasonication and combined

ultrasonication and mechanical shaking was poor, since the % RSD values for both methods ranged between 0.0477 and 20.5% and 0.314 to 20.9%, respectively. The MAE had the lower % RSD compared to the other two techniques with the value ranging between 0.055 and 9.98% for all PAHs. Furthermore, the results from MAE were evaluated using the CRM of sediment for efficiency of the extraction method and the results were satisfactory with the average percentage recoveries ranging from 83.8 to 125% (Table 2). Several studies indicated that extraction performed using an ultrasonic bath gave lower percentage recoveries and was less efficient [9, 11]. Sonication and combination of ultrasonication and mechanical agitation require more time because further separation techniques such as centrifugation or filtration are usually applied after the extraction process [11]. Seopela et al. [14] applied combined ultrasonication and mechanical shaker for the extraction of PAHs from sediment samples. However, the precision of the results was poor with the % RSD ranging between 1.01 and 26.8%, and the time spent for combined ultrasonication, and mechanical shaker was 1h30 min while MAE took 30 min. The reproducibility and extraction efficiency obtained using MAE were higher than those obtained with other two methods. For these reasons, namely the higher percentage recoveries and better precision obtained using MAE; the MAE was selected as the most suitable method for extraction of PAHs from sediment. Shu et al. [10], Mekonnen et al. [15], and Mogashane et al. [1] successfully applied MAE for the extraction of PAHs from sediment samples and obtained higher percentage recoveries. The ANOVA was used to determine the statistical significance of results obtained by MAE, ultrasonication and the combined ultrasonication and mechanical shaking methods. The null hypothesis is rejected since there is significant difference ($P<0.05$) between the results from these three methods at 95% confidence level.

IV. Conclusions

The results obtained in the present study indicated that PAHs concentrations in sediment samples in all sampling sites were lower (0.016 to 10.8 mg/kg). In general, LMW compounds showed lower concentration than HMW PAHs, which showed larger concentrations and whose values varied at different sample sites.

The most efficient method for extraction of PAHs in sediment with different levels of contamination was MAE. A longer extraction time was required for the combination of ultrasonication, and mechanical shaking method as compared to the MAE and ultrasonication under improved conditions. The MAE method was successfully validated by using a suitable CRM, obtaining quantitative percentage recoveries (above 80%). The MAE was preferred for the extraction of PAHs from sediment samples due to higher extraction efficiency and better precision than ultrasonication and combined ultrasonication and mechanical shaker, which demonstrated poor precision. The quantities of PAHs found in sediment samples may be a result of commercial and agricultural operations carried out by locals and traders that are not properly regulated by the appropriate authorities.

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VI. CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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TABLE 1. REGRESSION PARAMETERS, LIMIT OF DETECTION AND QUANTIFICATION (mg/kg) APPLIED TO SEDIMENTS OBTAINED BY GC-FID

PAHs	Chemical formula	No. of rings	Retention time (Min)	R^2	LOD (MAE)	LOQ (MAE)	LOD (UAM)	LOQ (UAM)	LOD (U)	LOQ (U)
Nap	$C_{10}H_8$	2	3.759	0.996	0.0124	0.0412	0.0927	0.309	0.185	0.618
Acy	$C_{12}H_8$	3	6.911	0.9946	0.0214	0.0715	0.0536	0.179	0.322	1.07
Ace	$C_{12}H_{10}$	3	7.327	0.9956	0.0140	0.0467	0.351	1.17	0.0701	0.234
Flu	$C_{13}H_{10}$	3	8.447	0.9965	0.0110	0.0368	0.0276	0.0921	0.0552	0.184
Phe	$C_{14}H_{10}$	3	10.537	0.9945	0.0110	0.0385	0.0288	0.0961	0.0578	0.193
Ant	$C_{14}H_{10}$	3	10.640	0.9973	0.0103	0.0342	0.0257	0.0855	0.0513	0.171
Fln	$C_{16}H_{10}$	4	13.249	0.9786	0.0117	0.0392	0.0293	0.0979	0.0587	0.198
Pyr	$C_{16}H_{10}$	4	13.782	0.9715	0.0117	0.0391	0.0293	0.0976	0.0585	0.195
BAnt	$C_{18}H_{12}$	4	19.240	0.9953	0.00999	0.0333	0.248	0.826	0.0499	0.167
Chr	$C_{18}H_{12}$	4	19.411	0.9956	0.0144	0.0479	0.359	1.21	0.0719	0.239
BbF	$C_{20}H_{12}$	5	23.044	0.9973	0.00743	0.0248	0.0186	0.0619	0.0371	0.124
BkF	$C_{20}H_{12}$	5	23.108	0.9953	0.00743	0.0239	0.0167	0.0557	0.0356	0.119
BghiP	$C_{22}H_{12}$	6	23.806	0.9952	0.00668	0.0223	0.0171	0.0571	0.0334	0.111
InP	$C_{22}H_{12}$	6	26.225	0.9951	0.0195	0.0649	0.0487	0.162	0.0974	0.325
DahAnt	$C_{22}H_{14}$	5	26.349	0.9367	0.00241	0.0801	0.00605	0.0202	0.0121	0.0403
BaP	$C_{20}H_{12}$	5	26.711	0.9807	0.0210	0.0702	0.0525	0.175	0.105	0.350

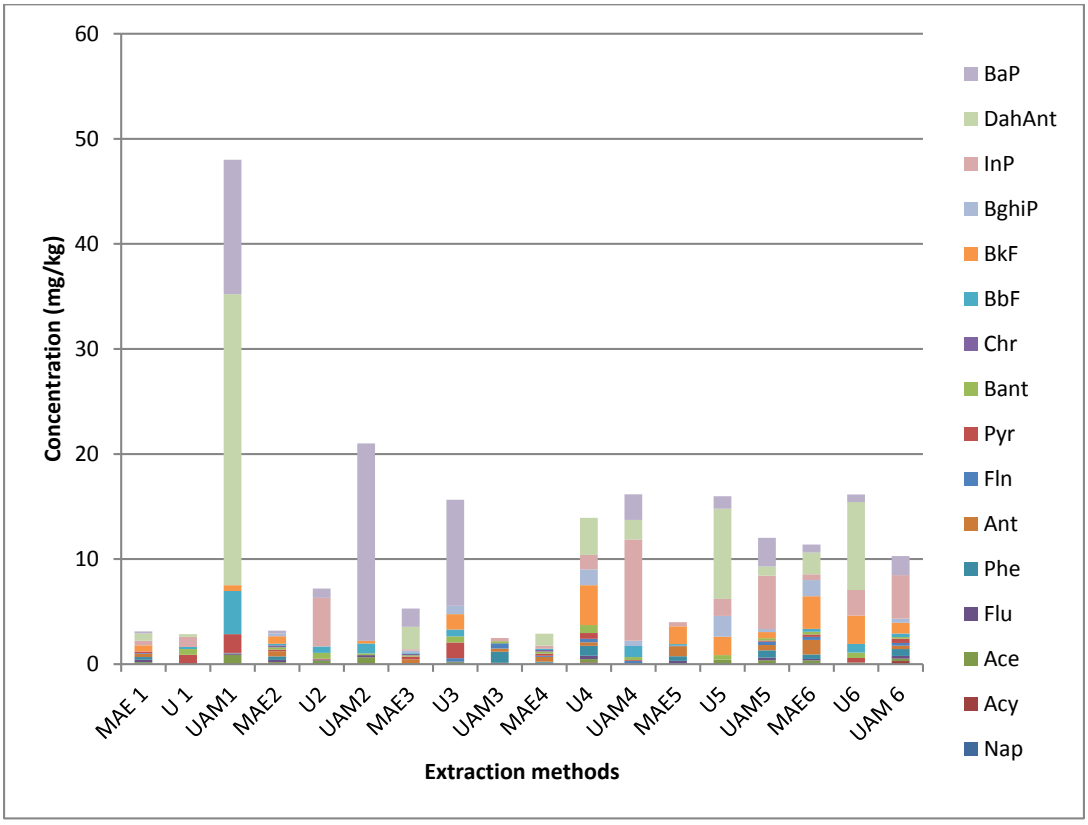

Fig. 1. Comparisons of the concentration of sediment from Blood River as obtained following MAE, U, and combination of UAM.

Table 2: Certified and measured concentrations, %RSD and percentage recoveries of PAHs in CRM-104

PAH	measured value (µg/Kg) (MAE)	certified value (µg/Kg)	%Recovery (MAE)	%RSD (MAE)	Measured value (µg/Kg) (U)	%Recovery (U)	%RSD (U)	Measured value(µg/Kg) (UAM)	%Recovery (UAM)	%RSD (UAM)
Nap	398±2.84	414	96.1	0.715	239±8.5	57.7	3.56	189±1.45	45.7	0.767
Acy	599±1.9	511	117	0.745	412±1.15	80.6	0.279	365±0.954	71.4	0.261
Ace	604±4.5	528	114	0.317	187±4.5	35.4	2.41	122±2.9	23.1	2.39
Flu	369±14.1	392	94.3	3.82	269±3.41	68.6	1.28	338±5.5	86.2	1.62
Phe	397±21.6	474	83.8	5.44	421±9.8	89	2.32	325±12.5	68.6	3.85
Ant	237±1.63	282	84.3	0.688	255±7.1	91	2.78	238±19.8	84.4	8.3
Fln	394±28.5	456	86.4	7.23	285±20.5	63	7.2	216±8.9	47.4	4.12
Pyr	331±16.1	302	109	4.86	286±15.6	95	5.46	247±1.45	81.8	0.587
BAnt	364±3.2	412	88.4	0.879	189±7.1	45.8	3.8	322±14.9	78.2	4.63
Chr	203±12.4	201	101	6.12	198±17.7	98.5	8.91	128±1.35	63.7	1.05
BbF	70.6±0.9	58.6	120	1.27	19±0.15	32.4	0.78	28.4±2.47	48.4	8.7
BkF	299±2.6	323	92.7	0.869	323±5.6	82	2.1	271±0.98	83.9	0.361
BghiP	298.8±9	305	97.9	3.01	256±2.3	84	0.898	189±5.75	61.9	3.04
InP	338±35.5	270	125	10.5	131±1.91	48.5	1.45	224±16.7	82.9	7.45
DahAnt	164±3.3	164	100	2.01	139±4.9	84.7	3.53	142±4.3	86.5	3.03
BaP	215±36.2	180	119	7.53	145±6.2	81.1	4.28	154±6.2	85.6	4.03