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Determination of Polycyclic Aromatic Hydrocarbons in Batman River by Liquid-liquid and Solid-phase Extractions and the Statistical Comparison of the Two Extraction Techniques

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs), which have detrimental health effects such as cancer and mutation, abound in rivers. To employ effective mitigation strategies, accurate determination of PAHs in water bodies is essential. In this study, PAHs in the Batman River were investigated. Specifically, the study has two aims: (1) determining whether there are any statistical differences between the Liquid-liquid (LL) and Solid-phase (SP) extraction techniques of PAHs; and (2) investigation of PAH contamination and the potential sources of PAHs in the Batman River. Methodologically, four different samples were collected and one part of each sample was extracted with the LL and the other part with the SP. Later, each extract was analyzed using gas chromatography-mass spectrometry. Subsequently, the analysis results of the LL and SP extracts were statistically compared. PAH concentrations were 85.5 and 76.7 ng/L for the means of the LL and SP extracts, respectively. Based on the t-test, the differences between these two means were not significant ($p\text{-value}=0.684 > 0.05$). Similarly, no statistical differences were observed between the analysis results of the LL and SP extracts for any individual PAHs. As for the source analysis, the results indicated that road vehicles and coal combustion were the possible sources of PAH contamination in the river. This study provides the first data set for PAH contamination in the Batman River.

Keywords: Polycyclic Aromatic Hydrocarbon, Extraction, Source Determination, River Contamination, Batman River

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are organic chemicals containing 2 to 7 aromatic rings that are fused together and formed by incomplete combustion of organic materials (Kadri et al., 2017; Abdel-Shafy and Mansour, 2016; Bansal and Kim, 2015; Kural et al., 2018). They can be found in all types of environments due to their physicochemical properties (Cachada, et al., 2016; Rubio-Clemente, et al., 2014). The sources of PAHs can be both natural and anthropogenic (Cachada et al., 2016). The natural sources include volcano eruptions and forest fires as well as the subsequent recombination of organic compounds (pyrosynthesis) (Maisto, et al., 2006). Examples of PAHs' anthropogenic sources are the activities such as setting fire on organic materials (stubble burning), burning of solid wastes, and incomplete combustion of fossil fuels (Zhang, et al., 2017; Patrolecco, et al., 2010). Moreover, industrial emissions caused by burning coal, gas, and oil can increase the atmospheric PAH concentration (Bandowe and Meusel, 2017). PAHs also have the ability for long-range transport; hence, they deposit via precipitation in waters, soils, sediments, and vegetation (Khuman, et al., 2018; Eremina, et al., 2016). Last but not least, the fate of PAHs depends on chemical oxidation, volatilization, adsorption to soil and dust particles, and leaching (Bandowe and Meusel, 2017; Cachada et al., 2016; Rubio-Clemente et al., 2014).

PAHs have toxicological impacts on public health since some members are teratogens, mutagens, and carcinogens (Abdel-Shafy and Mansour, 2016; Bansal and Kim, 2015). Their detrimental health effects can be seen as a result of both acute and chronic exposures. Acute effects, which are seen as a result of short-term exposures to high concentrations of PAHs, include nausea, eye irritation, diarrhea, and vomiting (Ha, et al., 2019). The chronic effects, on the other hand, are seen in long-term exposures (Hsu et al., 2014). These chronic effects can be different types of cancer such as bladder, skin, lung, and gastrointestinal (Kim, et al., 2013; Bansal and Kim, 2015; Rengarajan et al., 2015). Kim et al (2013) also reported that chronic PAH exposure could be the reason for impaired lung function in asthmatic patients, and thrombotic complications in people who have coronary heart disease.

There is a global concern on PAHs' wide range distribution to water sources because of their ubiquitous presence and negative health effects (Zhao et al., 2021; Sarria-Villa, et al., 2016; Wilson, et al., 2014). To manage PAH pollution in water, there are several removal techniques exist, including, but not limited to, bioremediation (Silva, et al., 2009), photocatalytic degradation (Zhang, et al., 2008), chemical oxidation (Lian et al., 2017), and adsorption (Yakout and Daifullah, 2013). The efficiency of these treatment

techniques heavily depends on the accurate determination of PAH concentration in water (Smol, et al., 2014; Adeola and Forbes, 2021). Likewise, the accurate determination of PAHs is highly influenced by extraction techniques (Mahgoub, 2016).

Liquid-liquid (LL) and solid-phase (SP) extractions are two commonly-used techniques for sample preparations. While in the LL, water-insoluble solvents are used to extract target chemicals (analytes) from a liquid solution, the SP involves a liquid matrix in which analytes are extracted with the help of an absorbent (Hennion, 1999; Müller, et al., 2000). Although both techniques can be useful for sample preparation, the statistical comparison of their analysis results has not been studied before to the best of my knowledge. To address this, samples from the same body of water (Batman River) were extracted by using both techniques and analyzed with gas chromatography-mass spectrometry (GC-MS). Then, the

concentration results were statistically compared. The current study also aims to provide a data set for PAH concentration in Batman River.

Materials and Methods

Sampling site and procedure

Figure 1 shows the study area, which is located in Batman Province of Turkey. The samples were collected from a 2.5 km-long section of the Batman River. This sampling site was chosen due to its high environmental influence on the river. The site is surrounded by cornfields and sand extraction activities. Moreover, it is located in the west entrance of the city thus experiencing more traffic compared to those in interprovincial roadways. There are also picnic activities nearby the river in the spring and summer seasons. Therefore, these properties provide a good opportunity to study PAHs in the area.

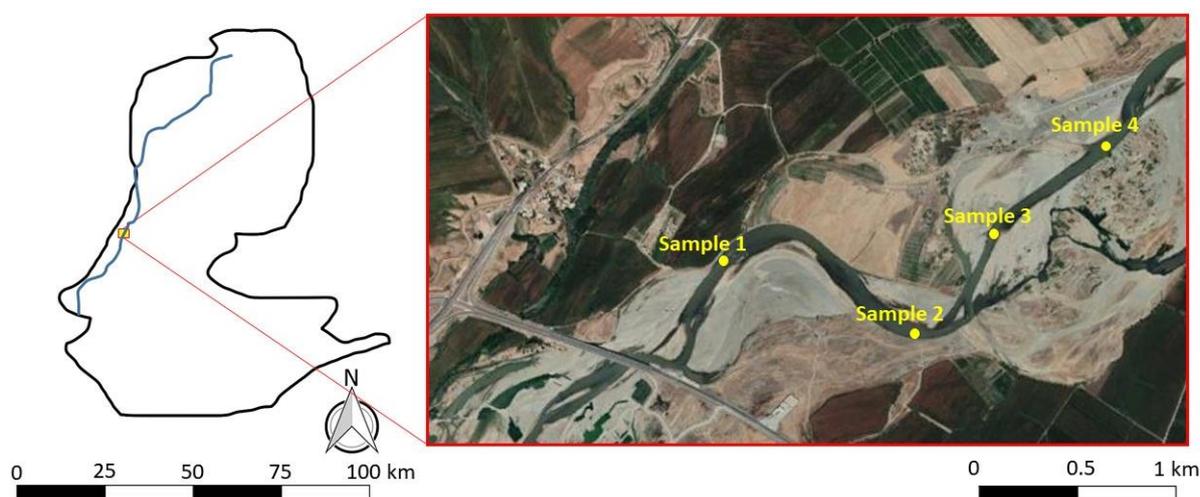


Fig. 1. The study area: Batman Province with Batman River (blue line) on the left side, sampling site with the location of samples (yellow dots) on the right side. For the zoomed map on the right side, the corner coordinates of the left bottom are 37° 52' 54.33" N and 41° 01' 33.94" E; and the corner coordinates of the right top are 37° 54' 05.63" N and 41° 04' 06.01" E.

The samples were collected from four different points along the river (figure 1). The sampling procedure took place in May (the year 2020) since human activities usually increase during that time. A pre-cleaned amber glass bottle was used to collect a 5-liter water sample for each point. The collected samples were then immediately capped and stored at 4°C until extraction. LL and SP extraction procedures have been explained in detail and proven to be effective before. Nevertheless, a brief explanation of extraction steps is provided below.

Chemical reagents

The PAHs to extract include acenaphthylene (Acy), fluoranthene (Fla), phenanthrene (Phe), naphthalene (Nap), anthracene (Ant), acenaphthene (Ace), pyrene (Pyr), benzo[b]fluoranthene (BbF), benzo[a]anthracene (BaA), chrysene (Chr). Additionally, dichloromethane (DCM), hexane, n-hexane, dodecane, and acetone were the solvents used in the study. All chemicals used were of analytical grade and provided by Armadalab

Occupational Health, Safety and Environment Laboratory.

The extraction techniques (LL and SP) and the analysis method used in this study have been explained in detail and proven to be effective before (Galindo-Reyes, et al., 1999; Soyak, et al., 2001; Jaward, et al., 2012; Mahgoub, 2016). Nevertheless, a brief explanation of each step is provided below.

The solid-phase extraction

The SP extraction consisted of sorption of the sample onto a sorbet and a soxhlet extraction. XAD-2 resins were used as polymeric sorbent. The system installation of XAD-2 resins included a bidirectional tube placed on the top of a stainless steel filter holder and a glass fiber filter connected to the top of the tube. In addition, a peristaltic pump was connected to the bottom of the tube. To ensure efficient pulling, the pump was buffered with glass wool and its venting tap was completely closed. With this system, the pump was able to draw the sample

through XAD-2 resins and perform filtration. After the filtration, the relevant extract was left in the XAD-2 resins.

The relevant extract was then subject to a soxhlet extraction. Firstly, 250 mL of DCM was added into a pre-cleaned flat bottomed flask containing anti-bumping granules attached to soxhlet's vein. Secondly, the extraction with a soxhlet extractor was performed, and subsequently, the sample was left to cool down. Thirdly, the samples were evaporated to approximately 2 mL on a rotary evaporator. Finally, after the evaporation completed, each sample was transferred to a 10 mL amber bottle and then evaporated to 1 mL using a stream of nitrogen gas.

The liquid-liquid extraction

1000 mL sample was transferred to a separatory funnel, in which a total of 300 mL of DCM and n-hexane mixture was gradually added. The separatory funnel was then carefully shaken to obtain an admixture in it. Afterward, the funnel was left for 10 minutes to observe two distinct layers. Later, a flat bottom flask was placed under the separatory funnel and the tap of the funnel opened slowly. Finally, the solvent layer was left to drain into the flat bottom flask dropwise.

The clean-up process and the instrumental analysis

The clean-up process and the instrumental analysis are the same for both SP and LL extractions. The column chromatography technique was used to clean extracted sample. A small piece of glass wool was squeezed into the bottom of each column. A slurry of silica (4 g), basic silica (4 g), acidic silica (8 g), sodium sulfate (4 g) was then prepared for each sample. Later, the samples were introduced into the column and eluted with 100 mL hexane and DCM mixture (1:1). Afterward, cleaned samples were collected dropwise into flat bottom flasks. The samples in the flasks were first reduced to 5 mL by a

rotary evaporator and then concentrated to 50 μ L using nitrogen gas. Lastly, cleaned samples were transferred to bottles, which also contains 50 μ L of dodecane for instrumental analysis.

The instrumental analyses of the extracts were conducted by a gas chromatography (Agilent, 6890), using splitless injection with an injection pulse pressure of 25 psi for one minute. This was followed by a purge flow-to-split vent of 50ml/min onto a 30m DB-5MS analytical column (2.5 mm i.d., 2.5 μ m film thickness) using helium as a carrier gas with a flow rate of 1.2 ml/min. The injection temperature was set to 280°C. The oven's temperature program was started at 60°C, at which the temperature was held for 1 minute, then ramped up at a rate of 20°C per minute until 180°C. Later, this temperature was held for another 1 minute, then ramped up at a rate of 6°C per minute to 280°C and held for 10 minutes. The gas chromatograph was coupled to a mass spectrometry (Agilent, 5973) operated in electron ionization (EI) mode using selected ion monitoring (SIM). Operating conditions were as follows; transfer line, ion source, and single quadruple are 300°C, 200°C, and 150°C, respectively.

Statistical comparison

The approach to choose an appropriate test based on data has been described in detail elsewhere (Sullivan, et al., 2016; Mishra et al., 2019). Nevertheless, the flowchart, which was used to compare the means of SP and LL extractions, is provided in figure 3. Briefly, when the assumption of normality and equality of variances were both met, the Unpaired two-sample t-test was used. Otherwise, the Wilcoxon rank-sum test was used for non-normal data. Welch's two-sample t-test was used if normality was assumed but not equality of variances. In this way, every individual PAH (Total 10) and their cumulative concentrations were statistically compared between SP and LL results

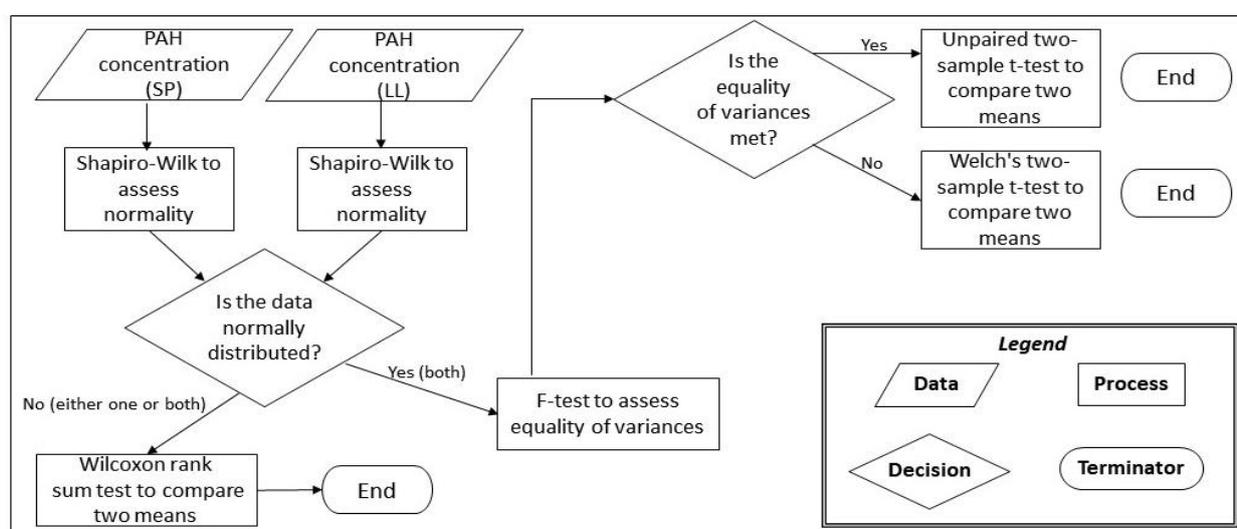


Fig. 2. The flowchart for the determination of the appropriate test to compare the means of SP and LL extractions.

Results and Discussion

Statistical comparison of LL and SP extraction results

Statistical comparison of LL and SP extraction results for every PAH as well as total PAHs is given in table 1. The Wilcoxon rank-sum test was not needed in this study since all data were found to be normally distributed according to the Shapiro-Wilk test results. Additionally, Welch's two-sample t-test was only used for Acy, Ace, BaA, and Chr because equality of variances between LL and SP for these PAHs was not provided. For the rest, the unpaired two-sample t-test

was used to compare the means of LL and SP extracts. According to the test results, statistically, significant mean differences were not observed for any PAH (see Table-1). For the total PAHs, the p-value (0.684) of the Unpaired t-test was greater than the significance level (0.05) thus also indicating that the two means were not significantly different from each other. Based on these results, although SP and LL extraction techniques are methodologically different from each other, their analysis results might not be statistically different from each other with a 95 % confidence interval.

Table 1. Statistical comparison of the analysis results between LL and SP extractions.

PAH Name	Mean (ng/L)		Shapiro-Wilk ¹		F-test for equality of variances ²	Unpaired two-sample t-test ³	Welch's two-sample t-test ⁴
	LL	SP	LL	SP			
Acy	0.025	0.091	0.680	0.408	0.004	ANM ⁵	0.178
Fla	28.483	33.056	0.984	0.504	0.914	0.512	ANM
Phe	17.297	11.320	0.498	0.289	0.835	0.448	ANM
Nap	8.261	7.665	0.805	0.171	0.813	0.863	ANM
Ant	15.987	7.227	0.077	0.351	0.394	0.220	ANM
Ace	2.357	0.705	0.461	0.767	0.0249	ANM	0.088
Pyr	11.251	13.081	0.579	0.607	0.266	0.610	ANM
BbF	0.725	0.306	0.554	0.945	0.129	0.111	ANM
BaA	0.717	1.657	0.962	0.759	0.046	ANM	0.302
Chr	0.388	1.578	0.721	0.886	0.009	ANM	0.109
TOTAL PAHs	85.491	76.686	6.321	5.687	0.662	0.684	ANM

¹P-value_{Shapiro-wilk} > 0.05 → normally distributed

²P-value_{F-Test} > 0.05 → no significant difference between the two variances

³P-value_{Unpaired T-Test} > 0.05 → no significant difference between the two means

⁴P-value_{Welch's T-Test} > 0.05 → no significant difference between the two means

⁵ANM stands for assumption is not met

PAH analysis and source determination

Figure 3 shows the concentrations (ng/L) of each PAH as a clustered column chart. In the chart, the concentration results obtained from LL and SP for each sample are given separately. Fla, Phe, Ant, Pyr, and Nap were the dominant PAHs in all samples. They were made up about 95 % of the total PAH concentration. However, Ace, BbF, BaA, Chr, and Acy were found in trace amounts.

Fla concentration (dark orange bar) was found to be highest among 10 PAHs in all samples except for the LL of sample 3. This might thus indicate road vehicles' influence on PAHs in the river as suggested by Eremina et al (2016). Moreover, PAH concentration was higher in sample 1, whose location is closer to two roadways (see figure 1), than in the other samples. This might also be another indicator that road vehicles might be a major PAH source in the study area.

The ratio of some PAHs has also been used in the relevant literature to determine potential sources of PAHs. For example, Fla/(Fla + Pyr) < 0.4 implies petroleum origin (Yunker et al., 2002). If Fla/(Fla + Pyr) is between 0.4 and 0.5, the source may be liquid fossil fuels. In case of the ratio is greater than 0.5, the source

may be coal, grass or wood combustion. Similarly, other PAH ratios used in the literature to determine potential sources of PAHs include but not limited to ((methyl-phenanthrenes + methyl-anthracenes)/phenanthrene), (dimethyl-phenanthrene/(methyl-phenanthrenes + methyl-anthracenes)), (1,7-dimethylphenanthrene / 2,6-dimethylphenanthrene), BaA/(BaA+Chr) and (Indeno[1,2,3-cd]pyrene/Indeno[1,2,3-cd]pyrene + Benzo[ghi]perylene) (Colombo, et al., 1989; Budzinski, et al., 1995; Pereira et al., 1999; Oros and Simoneit, 2000; Yunker et al., 2002; Lima, et al., 2005).

In this study, BaA/(BaA+Chr) and Fla/(Fla+Pyr) ratios were used to determine possible PAH sources. BaA/(BaA+Chr) ratio ranged from 0.23 to 0.74 across all four samples but it was 0.58 on average thus indicating combustion origin (Yunker et al., 2002). Similarly, the Fla/(Fla+Pyr) ratio of 0.71 (as the average of SP and LL) indicates coal, grass, or wood combustion origin. According to these ratios and based on the fact that coal use for residential heating is common in Batman Province (Vural, 2001), coal combustion might be another major PAH source in this study. There are also oil wells in Batman Province. However, based on the BaA/(BaA+Chr) and Fla/(Fla+Pyr) ratios, the influence of these wells on the concentration of PAHs in the river

was not observed. The reason for this might be that the closest well is 10 km away from the sampling site. The sampling work in this study covers a roughly 3 km distance along the 115 km long river. Therefore, it

cannot represent all the areas where the river flows. For this reason, to conduct a source apportionment analysis of the whole river, further investigations that have more representative samples along the river are required.

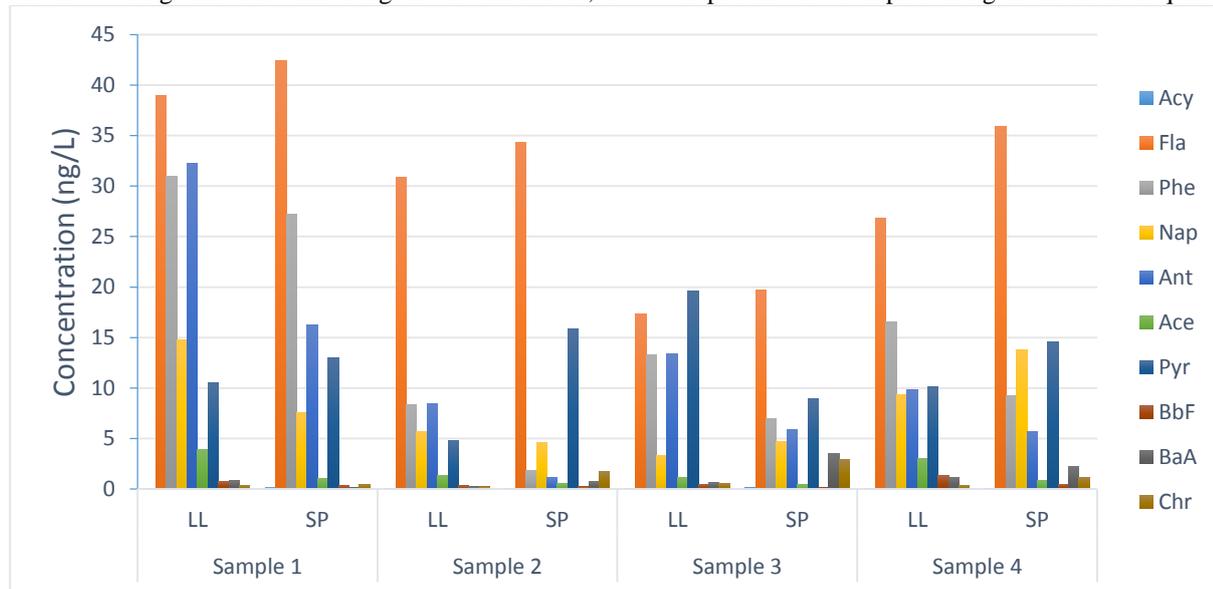


Fig. 3. The concentrations (ng/L) of PAHs in each sample. LL and SP results are shown separately.

Comparison to other rivers worldwide

PAH presence in this study and its potential sources were compared to other studies, which focus on PAHs pollution in rivers (Table 2). The mean PAH concentration (81.1 ng/L) of Batman River was found to be relatively smaller than those that have industrial and petroleum sources. Contrarily, it was slightly higher than those that have vehicular activities or/and mixed combustion sources. This outcome supports the findings

of Meng et al (2012). Accordingly, high population along with dense petroleum and industrial activities are heavily influential on the concentrations of PAHs in surface waters (Meng et al., 2012). As suggested in the previous section (3.2), road vehicles and coal combustion are the possible sources of PAHs in Batman River. This thus explains why the PAH level of the river was found to be lower than the level in Pearl, Huai, Hooghly, and Cauca rivers.

Table 2. Comparison of PAHs occurrence (ng/L) and their possible sources in surface waters worldwide

Study	Location	Total PAHs	Mean [min – max] (ng/L)	Possible Sources
Froger et al., 2019	Orge River, France	13	41 [11–221]	Road vehicles, Urban sewage sludge Atmospheric fallout
Patrolecco et al., 2010	River Tiber, Italy	6	43.4 [23.9–72]	Road vehicles Pyrolytic sources
Gateuille et al., 2014	Orgeval River, France	13	72 [60 – 112]	Heating devices
Eremina et al., 2016	Moscow River, Russia	7	75.8 [50.6 – 120.1]	Road vehicles, Railways Herbicides
This study	Batman River, Turkey	10	81.1 [60.7 – 121] ¹	Road vehicles Coal combustion
Niu et al., 2018	Pearl River, China	62	864.7 [393.1–1195]	Petroleum emissions Road vehicles Wood combustion
Zhang et al., 2017	Huai River, China	16	1204 [891–1951]	Coal combustion Petroleum refinery
Khuman et al., 2018	Hooghly River, India	16	4000 [n.d. – 32000]	Road vehicles Industrial activities Biomass burning
Sarria-Villa et al., 2016	Cauca River, Colombia	12	4476.5 [52.1–12888.2]	Industrial activities Motor oils Biomass burning

¹ The data of this study is the average of LL and SL results.

Conclusion

In this study, 10 PAHs had been extracted from four samples in the Batman River. Each sample was separately extracted by both the LL and SP techniques. After the GC-MS analysis, the corresponding PAH concentrations of analyzed LL and SP extracts were statistically compared by using an appropriate test. There weren't any meaningful differences between the two techniques for any individual PAHs or the total PAH with 95 % confidence. These results suggest that the LL and SP extractions can be used interchangeably for water samples. Consequently, which one to choose for PAH extraction depends on the availability of resources.

PAH concentration in the Batman River ranged from 60.7 to 121 ng/L. The high proportion of Fla in the samples suggested vehicular emission as a potential source of PAHs that contaminate the river. Moreover, BaA/(BaA+Chr) and Fla/(Fla+Pyr) ratios showed that coal combustion might be another major source for the PAH contamination. Based on these results, decreasing coal use for heating purposes in households could increase water quality in the river.

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