



A Review on Available Techniques to Evaluate Polycyclic Aromatic Hydrocarbon Concentration Dependency on Certain Chemical Properties

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Abstract: Organic pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs) perform hydrophobic properties presented in high K_{ow} values. PAHs stick onto particles in the aquatic environment then settles on the sedimentary bed for deposition. The correlation of PAHs concentration with chemical properties of the particles remained less explained. This review highlights the current techniques, limitations and advantages and recommends new methods to be implemented in order to find PAHs concentrations' correlation with chemical properties of hosting media. Size distribution methods follow wet and dry sieving where wet sieving is susceptible discarding pore water from the more fine particles results less PAHs concentration. Among Distillation methods such as Accelerated Solvent Extraction (ASE), Microwave, Sonication, Solid Phase Micro Extraction (SPME) and Soxhlet, the latest method was chosen due to the accuracy and high recovery percentage. The clean-up and compound fractionation methods were preferred using hand packed glass silica gel where identically and specially designed for PAHs rather than commercially packed cartridges due to high recovery percentage. There are possible scenarios to correlate the concentration with chemical properties such as relation with sizes, organic material, total organic carbon and black carbon among others. Future researches are suggested to evaluate the recommended method in order to determine a better dependency of concentration with chemical and physical properties of the hosting media such as particles.

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1. Introduction/ Background Study

The growing concern of human and environmental health leads scientists to study various pollutants such as organic chemicals. These materials are consisting of various types of organic structures in which release to the environment through various kinds of human activities. Polycyclic aromatic hydrocarbons (PAHs) as an important class of organic pollutants are harmful to living organisms where show carcinogenic, mutagenic and toxic properties to mammals (Neff, 1979; Macias-Zamora et al., 2002; Baumard et al., 1998; Guo et al., 2009). PAHs are introduced to the environment throughout processes such as incomplete combustion fossilfuels that contains dense organic materials, slow maturation of organic matter under geochemical gradient conditions (diagenesis), oil spill and biogenic precursors (Baumard et al., 1998; Luca et al., 2005; Soclo et al., 2000; Wilcke, 2000). High concentration of PAHs can be found mainly in coal storage, coke oven plants, manufactured gas plants

and coal tar spillage (Li et al., 2010; Paria and Yu, 2006; Viglianti et al., 2006).

PAHs are ubiquitous in the environment (Neff, 1979; Beyer et al., 2010; Nehyba et al., 2010; Boonyatumanond et al., 2006) especially in the sediment (Guo et al., 2009; Ahrens and Depree, 2004; Baumard et al., 1998). Sediments act as a final sink for PAHs where they travel laterally as well as atmosphere and get deposited in dry and wet forms in the sedimentary environment. PAHs do not bind strongly to the inorganic fraction of the sediment grains like heavy metals (Ahrens and Depree, 2004; Baumard et al., 1998; Bertolotto et al., 2003), due to their low vapor pressure and hydrophobic nature (Luca et al., 2005; Meyers and Quinn, 1973; Knap and Williams, 1982; Chiou et al., 1998) instead strongly adhere into organic fractions of the sediment. Moreover, concentrations of dissolved PAHs in water are very low because of their high Octanol-Water partition coefficient ($\log K_{ow}=3.4-7.6$) and high organic carbon partition coefficient ($\log K_{oc}= 3.8-6.74$) (Oblolade et al., 2012). Hence, higher

concentration of PAHs can be found in sediments rather than water. Sedimentary PAHs show strong resistance to any types of degradation providing opportunity for longer life span (Magi et al., 2002; Soclo et al., 2000).

Due to the above mentioned importance, scientists employ methods in order to identify the concentrations, characterization and source identification of PAHs in the sedimentary environment. There are several methods that facilitate monitoring of PAHs in the sedimentary environment however all the methods are based on identical stages such as sample preparation, extraction, clean-up, fractionation and instrumentation. The development of new technologies have introduced machine assisted methods in order to provide faster processes in which save more consumable materials as chemicals, aiming higher efficiency and accuracy. The processes of selection of the methods for PAHs studies depend on availability of the required materials. In order to choose these methods, this study reviewed several available scientific methods from pure analytical chemistry to modern mechanized instruments.

2. Methods for sample preparation

2.1 Drying methods

Drying sediments are required before running grain size separation and extraction. There are two techniques involved, which either use sodium sulfate, or freeze drier. Freeze drying method is widely used by scientists (Simpson et al., 1998; Yang et al., 2008). The advantages of freeze drying of sediment includes minimize the loss of volatile constituents, low temperature can avoid chemical changes, disperse particles of dried sediments for higher sieving and extraction efficiency, minimize the aggregation of particles, maintain sterility, and minimize or eliminate oxidation of various minerals or organic compounds (Mudroch and Azcue, 1995). However, the freeze drying is time consuming and it is rather expensive for the freeze dryer itself and also the equipment used. Sodium sulfate can also be used as a drying agent, but the use of it is inappropriate when grain size is taken into account. This is because sodium sulfate, which comes in as granular form, will affect the grain size distribution of the sediment samples.

2.2 Grain Size Separation

Sedimentary particles consist of several sizes from fine (<63 μm) to bigger particles (>1 mm). Particles in different sizes perform various surface areas where provide opportunity to adsorb chemicals regardless of its chemistry (i.e. organic or inorganic) where bigger surface tend to adsorb more chemicals. Due to this, scientists are interested to study the size fraction of sediments (Ahrens and Depree, 2004;

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Huang et al., 2011; Kim et al., 1999; Li et al., 2010; Luca et al., 2005; Ololade et al., 2012; Oen et al., 2006; Opel et al., 2011; Simpson et al., 1998; Wang et al., 2001; Yang et al., 2008; Yu et al., 2009). Bathi et al. (2012) stated that particle sizes of the sediments greatly influence the fate and transportation of PAHs. With three or more aromatic rings, PAHs are most abundant in particulate-associated form (Bathi et al., 2012) and accumulate in humus layer of soils (Pena et al., 2007). During dredging processes, low density particles are easily re-suspended in the water column (Huang et al., 2011), which will result in transportation of particles and PAHs to other area by water current. The coarse particles are usually carried via bottom currents, whereas, the finer particles are reintroduced into the upper water column and carried as suspended matter (Sun et al., 2008). Hence, long exposure of lower density particles can adsorb more PAHs concentration during transportation. This theory is proved by Ahrens and Depree (2004) and Ghosh et al. (2003), which they stated that low density particles may contain 10-200 times higher PAHs concentration. Size fractionation of sedimentary particles for PAHs analysis is basically implemented by wet or dry sieving machine. There are advantages and disadvantages in application of any of these techniques that is summarized and listed in Table 1.

Grain size distribution is one of the major factors to consider when analyzing sediment samples (Opel et al., 2011). Non-polar PAHs will adsorb and accumulate in different particle sizes, therefore, showing a different concentration in various grain sizes (Owabor and Ogunbor, 2007). However, most of the studies made did not only focus in particle sizes, some of them also concentrate in other factors, such as total organic carbon (TOC) or black carbon (BC), which will influence the PAHs concentration in different particle sizes. For example, recent finding by Ololade et al. (2012) highlighted that PAHs concentration have a strong correlation among clay and silt, however, they also show positive correlation with organic carbon content. Other than that, back to the year 1999, Kim et al. (1999) stated that PAHs were positively correlated with organic carbon content, but negatively correlated with mean sediment grain size. Hence, we can hypothesize that PAHs concentration not only can be affected by sediment grain size, however, also can be influenced by other factors. To find out what factors that cause the differential in PAHs concentration, various methods can be used to verify them. This review compares a few methods, which are used widely by many other researchers to run the test for PAHs concentration in different particle sizes.

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To separate the sediment into different particle sizes, the sediment is usually passed through a sieve with desired mesh size. The sieving method is done either by using wet sieving or dry sieving. Sieving method is to sort out different particle sizes, so that there will be no overlapping of grain size, Table 1. Pros and cons of different sieving techniques

which will affect the solvent from flowing throughout the samples while running Soxhlet extraction. The mesh size used can vary from <63 μm to >2 mm. Some other researchers, such as Simpson et al. (1998), used a mesh size

Sieving Technique	Advantages	Disadvantages	References
Dry Sieving	1. Effective against coarse particles.	1. Fine sieve becomes clog when sediments contain fine particles. 2. Possible contamination.	1. Mudroch and Azcue (1995) 2. UNEP (2006)
Wet Sieving	1. Effective against fine particles.	1. Porewater will be affected by water used, hence, influence analytical results 2. Possible contamination for organic samples. 3. Time consuming.	1. McGroddy and Farrington (1995) 2. Mudroch and Azcue (1995) 3. UNEP (2006)

ranging from <38 μm to >1180 μm . Although researchers like Ahrens and Depree (2004), Huang et al. (2001), Yang et al. (2008), and Wang et al. (2001), use wet sieving method, dry sieving is still the recommended technique. This is because wet sieving uses distilled water or salt water to run with the sediment samples, which the PAHs in different particle sizes will be influenced by the surrounding water. Although PAHs have a very low aqueous solubility, the presence of porewater organic colloids can strengthen these compounds in porewater concentration (McGroddy and Farrington, 1995). Hence, when the water is discarded, the PAHs will be flowed out with the water, and causes an inaccurate result. Therefore, by using dry sieving after freeze drying is the most desirable technique, which can also prevent the loss of PAHs.

3. Extraction Methods

There are several methods for extracting the sediment samples, which include Soxhlet extraction, ultrasonic agitation, mechanical agitation, accelerated soxhlet extraction (ASE), supercritical and subcritical fluid extraction (SFE), microwave-assisted extraction (MAE), solid phase extraction (SPE), thermal desorption, high temperature distillation (HTD), and fluidized-bed extraction (FBE). All of these extraction methods have their own advantages and disadvantages. Among all of them, Soxhlet extraction is still the widely used method.

Although Soxhlet extraction requires a large volume of solvent, usually more than 150 mL, time consuming and labor intensive, this method yields the

similar result with other methods, and show a small variations with low relative standard deviations (Lau et al., 2010; Flotron et al., 1999; Saim et al., 1997; Berset et al., 1999). Hawthorne et al. (2000) criticized that Soxhlet extraction have a poor selectivity for PAHs, in contrast to Smith et al. (2006), who reported that Soxhlet extraction provided an efficiency range of 84 – 100% of PAHs with higher molecular weights.

Other than Soxhlet extraction, ultrasonic agitation or also known as sonication, can also be used for extraction method. However, sonication may degrade the contaminants and reduce extraction rates of PAHs in a sample (Lau et al., 2010). Although Sun et al. (1998) and Guerin (1998) reported that sonication provided a higher and similar efficiency compared to Soxhlet extraction, Lau et al. (2010) stated that the sample matrix and concentration of pollutants in the sample played an important role when comes to extraction process. Song et al. (2002) found out in their research that ultrasonic agitation is effective against PAHs extraction from low polluted dried and moist soils. In order for a better result shown, separation techniques have to be done followed by sonication process, which does not required by Soxhlet extraction.

Mechanical agitation is an easily handling extraction method, which is also cost efficiency. This method is less preferable because it has a lower extraction efficiency and unsatisfactory quantitative (Dean and Xiong, 2000; Graham et al., 2006; Lau et al., 2010). To obtain better and comparable results, a

longer shaking time is suggested by Linares et al. (1998) and Kalbe et al. (2008), so that the contact time with solvent is extended.

For accelerated solvent extraction (ASE), or also known as pressurized fluid extraction (PFE), is a commercially used system nowadays, which reported by Wang et al. (2007) to be having two times higher recovery rate of PAHs compared to Soxhlet extraction method. Other than that, ASE has the accuracy of less than 10% relative standard deviation, and also lesser time and solvent required when running the extraction (Lau et al., 2010; Berset et al., 1999). The procedure can be fully automated, where heavy preparation and contamination can be prevented (Liguori et al., 2006; Olivella, 2006).

Another extraction method is supercritical and subcritical fluid extraction (SFE). This method shows a recovery rate almost similar with Soxhlet extraction (Miege et al., 1998). Moreover, this method provides a cleaner extract, and can be directed into cleanup column, without the need of removing eluate manually (Lau et al., 2010). In some of the SFE systems, the extracts can also be analyzed by gas chromatography without any clean up processes. This also prevents extra contamination while transferring the extract (Berset et al., 1999; Reimer and Suarez, 1995). However, this method is harder to optimize and may show an inconsistent result due to high complexity (Anitescu and Tavlarides, 2006).

Microwave-assisted extraction (MAE) is cost efficiency and lesser time consuming method (Lau et al., 2010). Other than that, the extraction efficiency of PAHs is also enhanced by using MAE (Letellier et al., 1999; Letellier and Budzinski, 1999). In contrary to the benefits, the solvents of MAE needed to be removed physically for further analysis, and if there is activated copper in the extraction process, the copper has to be removed for a cleaner extract (Flotron et al., 2003). Hence, prior removing physically, there is a chance that inducing contaminants into the samples. Moreover, there is a limitation in sample analysis, which is 1.0g, and this is insufficient for homogeneous analysis (Shu et al., 2000).

Solid phase microextraction (SPME) is a fast, simple and convenient technique to use when extracting PAHs. Only small volume of sample is required for extraction, and can be analyzed without pretreatment (Lau et al., 2010). However, there is a study stating that SPME can only detect lower molecular weight (LMW) of PAHs (Eriksson et al., 2001).

For thermal desorption and fluidized-bed extraction (FBE) method, both of these methods are less discussed in depth about their efficiency in

extracting PAHs. Yet, the advantage of using thermal desorption method is that this method does not require the use of solvents or high pressure extraction equipments. But, this method requires prior calibration for nonlinear response to sample size and concentration of contaminants (Banerjee and Gray, 1997; Lau et al., 2010). Fluidised-bed extraction (FBE), however, has the advantages of lesser time and solvent used under optimised condition (Lau et al., 2010).

In contrast with thermal desorption, pyrolysis (Py) or high temperature distillation (HTD) method is a technique where faster extraction speed, providing more samples to be analysed in a period of time (Lau et al., 2010). Moreover, the contamination risk for this method is lower because re-concentration and cleanup steps are excluded in this technique. Hence, the cost can be reduced. But, the sample size used in this method is small, therefore, an insignificant data can be provided. Nevertheless, the temperature has to be carefully controlled for this method (Lau et al., 2010).

After all, the most preferable method for running extraction of semi-volatile and non-volatile organics from solid matrixes is still the Soxhlet extraction technique. A technique which time consuming and labour intensive, yet providing a high recovery rate compared to other techniques discussed (Oluseyi et al., 2011; Ramos et al., 2000).

4. Clean-up and Fractionation

Clean-up procedure is important during the analysis of PAHs, because the extracts can contain polar compounds, such as animal and plant fats, proteins, and small biological molecules, which may be unintentionally or improperly identified as petroleum constituents. Without clean-up and fractionation, the mixtures can interfere with the analysis machine, hence providing an inaccurate result. Moreover, the compounds in the mixture can contaminate the machine, which will again causes problems prior analysis. Therefore, clean-up is to remove non targeted compounds as much as possible, isolation of particular fraction, and also concentration of interested analytes. There are three types of clean-up techniques, which include using alumina, silica gel, or mixing of both alumina and silica gel.

Clean-up using silica gel is a more satisfying and common clean-up technique used on extracts designated for PAHs and phenol analyses (Jang and Li, 2001; TPH Criteria Working Group, 1998). By using silica gel, the result provided a higher reliability for PAHs with higher molecular mass. In the finding of Jang and Li (2001), silica gel was deactivated in four levels ranging from 0%, 1%, 2% and 3%, the result show that the higher activation level need a longer elution time, which is also the

same observation presented by Later et al. (1985). The activation level of silica gel will cause the overlapping of lower molecular weight compound, where higher deactivation level will result in a more severe overlapping situation. Thus, clean-up using silica gel must be preceded with care especially when deactivating silica gel.

Other than silica gel, alumina is used as a clean-up agent as well. Alumina clean-up is designed to remove any interfering compounds and to fractionate petroleum wastes into aliphatic, aromatic and polar fractions (TPH Criteria Working Group, 1998). These separated fractions can either be analyzed separately or combined for a total petroleum hydrocarbon measurement.

There are two types of column being used for clean-up and fractionation. Hand-packed column is the packing of silica gel, or alumina, or the both of them into a column, which intended for cleaning up the samples and separating different.

Table 2. Pros and cons of different extraction method

Method of Extraction	Advantages	Disadvantages	References
Soxhlet Extraction	<ol style="list-style-type: none"> 1. Yields similar result compared to other methods. 2. Results show small variations with low relative standard deviations. 3. High efficiency, range from 84 to 100%, for PAHs with more than 4 rings. 	<ol style="list-style-type: none"> 1. Large volumes of solvent. 2. Time consuming. 3. Labour intensive. 4. Sample carryover. 	<ol style="list-style-type: none"> 1. Lau et al. (2010) 2. Flotron et al. (1999) 3. Saim et al. (1997) 4. Berset et al. (1999) 5. Hawthorne et al. (2000) 6. Smith et al. (2006)
Ultrasonic Agitation	<ol style="list-style-type: none"> 1. Cost efficiency. 2. Easily operated. 	<ol style="list-style-type: none"> 1. May degrade pollutants, in result of reduction of PAHs extraction rates. 2. Further separation techniques required. 3. Less efficient. 	<ol style="list-style-type: none"> 1. Guerin (1998) 2. Smith et al. (2006) 3. Lau et al. (2010) 4. Sun et al. (1998) 5. Song et al. (2002)
Mechanical Agitation	<ol style="list-style-type: none"> 1. Simple to operate. 2. Low cost. 	<ol style="list-style-type: none"> 1. Lower extraction efficiency. 2. Unsatisfactory quantitative results. 	<ol style="list-style-type: none"> 1. Dean and Xiong (2000) 2. Graham et al. (2006) 3. Lau et al. (2010)
Accelerated Soxhlet Extraction (ASE)	<ol style="list-style-type: none"> 1. Recovery of PAHs is twice higher than Soxhlet extraction method. 2. High accuracy with less than 10% relative standard deviation. 3. Consume lesser solvent and total time. 4. Fully automated, avoiding heavy preparation and contamination. 	–	<ol style="list-style-type: none"> 1. Wang et al. (2007) 2. Liguori et al. (2006) 3. Lau et al. (2010) 4. Olivella (2006) 5. Berset et al. (1999)
Supercritical and Subcritical Fluid Extraction (SFE)	<ol style="list-style-type: none"> 1. Similar recovery rate with Soxhlet extraction. 2. Cleaner extracts. 3. Direct concentrated extract into cleanup column, without manually remove eluate. 4. Extract direct into GC without any cleanup. 	<ol style="list-style-type: none"> 1. More difficult to optimize. 2. High complexity, which may cause inconsistent result. 	<ol style="list-style-type: none"> 1. Miede et al. (1998) 2. Lau et al. (2010) 3. Berset et al. (1999) 4. Reimer and Suarez (1995) 5. Anitescu and Tavlarides (2006)

Microwave-assisted Extraction (MAE)	<ol style="list-style-type: none"> 5. Prevent extra contamination. 1. Cost efficiency. 2. Less time consuming. 3. Higher PAHs extraction efficiency. 	<ol style="list-style-type: none"> 1. Physically remove solvent and activated copper. 2. Chance to induce contaminants. 3. Limited sample in analysis, which is insufficient for homogenous analysis. 	<ol style="list-style-type: none"> 1. Lau et al.(2010) 2. Letellier et al.(1999) 3. LetellierandBudzinski(1999) 4. Flotron et al. (2003) 5. Shu et al.(2000)
Solid Phase Extraction (SPE)	<ol style="list-style-type: none"> 1. Fast, simple and convenient. 2. Small volumes of extraction can be analysed without pretreatment. 	<ol style="list-style-type: none"> 1. Only volatile compounds can be detected. 	<ol style="list-style-type: none"> 1. Eriksson et al. (2001) 2. Lau et al. (2010)
Thermal Desorption	<ol style="list-style-type: none"> 1. Does not require solvents or high pressure extraction equipments. 	<ol style="list-style-type: none"> 1. Requires calibration to allow for nonlinear response to sample size and concentration of contaminants. 	<ol style="list-style-type: none"> 1. Banerjee and Gray (1997). 2. Lau et al. (2010)
High Temperature Distillation (HTD)	<ol style="list-style-type: none"> 1. Lesser time during extraction. 2. More samples can be analysed. 3. Lower contamination risks and higher sensitivity. 4. Does not require reconcentration and clean-up steps. 5. Cost efficiency. 	<ol style="list-style-type: none"> 1. Small sample size causes insignificant data analysis errors. 2. Controlled temperature must be done carefully. 	<ol style="list-style-type: none"> 1. Lau et al. (2010)
Fluidized-bed Extraction (FBE)	<ol style="list-style-type: none"> 1. Lesser solvent and time used under optimised conditions. 	–	<ol style="list-style-type: none"> 1. Lau et al. (2010)

Table 3. Pros and cons of hand-packed column and pre-packed cartridge

Fractionation method	Advantages	Disadvantages
Hand-packed column	<ol style="list-style-type: none"> 1. Cost efficiency. 2. Effective in purifying and separating components of samples. 	<ol style="list-style-type: none"> 1. Very small amount of samples can passed through. 2. Time consuming. 3. Solvent level needs to be top up from time to time.
Pre-packed Cartridge / Solid Phase Cartridges	<ol style="list-style-type: none"> 1. Simple to carry. 2. Lesser time required. 	<ol style="list-style-type: none"> 1. Limited capacity.

To target compounds, it is time consuming because of small sample size can be passed through the column, and the solvent level have to be topped up from time to time to prevent silica gel from being dried up (TPH Criteria Working Group, 1998). Other than that, if poor technique were to be performed, some analytes or target compounds were to be removed.

Solid phase cartridges or pre-packed cartridges can be used for clean-up purpose as well. These cartridges are available in a wide variety of adsorbents with special chemical selectivities. However, these cartridges have very limited capacity (TPH Criteria Working Group, 1998), although they are simple to carry and time saving when being used.

5. Conclusions

Comparing the drying techniques and separation of grain sizes, the conventional way of doing it is by wet sieving following freeze drying. Through these techniques, different particle sizes can be separated under a wet condition and being dried up with freeze dryer, which can minimize the lost of PAHs compounds. Moreover, of all PAHs extraction techniques, soxhlet extraction is the most widely used because of the high efficiency, where small variations of results were shown with relative standard deviations. Lastly, is the clean-up and fractionation technique before sending the samples for instrumentation analysis. The widely used technique in cleaning up and fractionation is by using hand-packed column, that is highly efficient and cost effective way. It is crucial that there is no recognized single technique in analyzing PAHs in sediments. However, cost and time effective, results yield, as well as technical competence is factors to be considered before running the analysis.

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