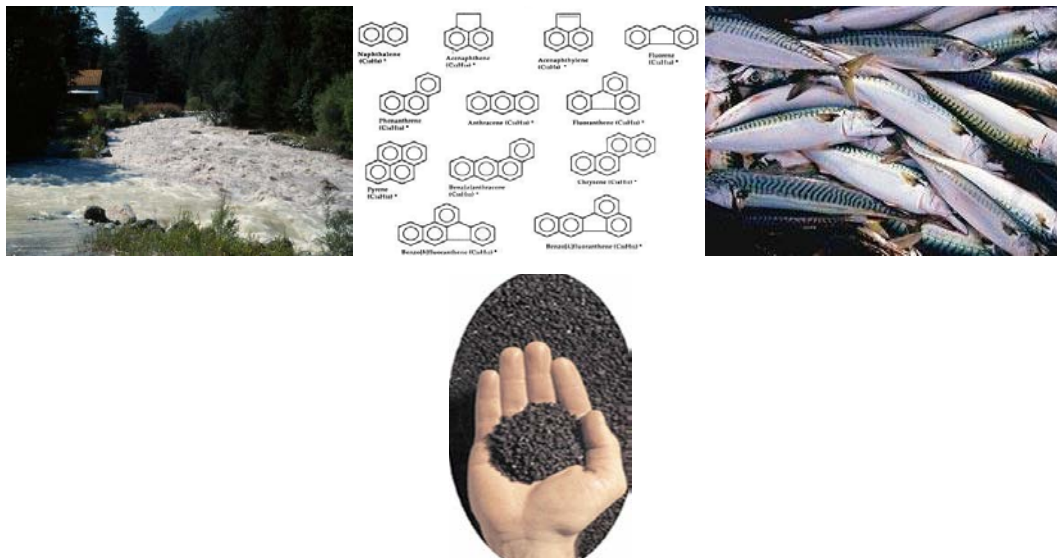# Measuring concentrations of freely dissolved polyaromatic hydrocarbons in sediment-pore water using passive sampling with polyoxymethylene
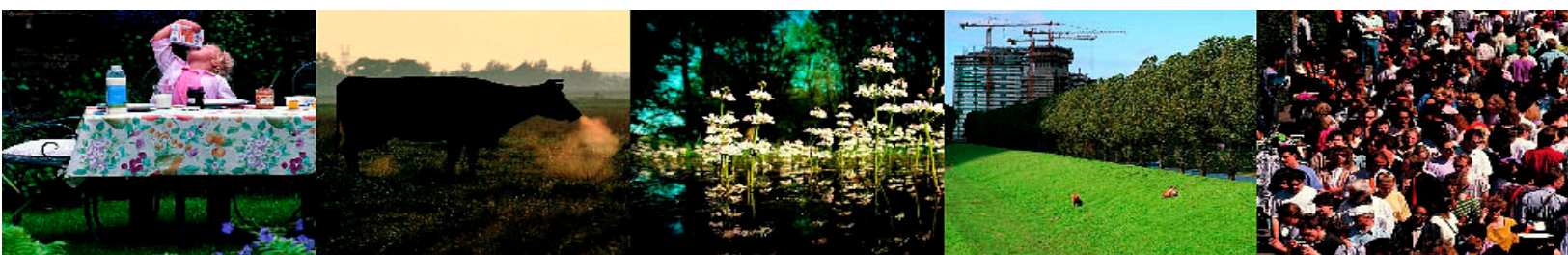
Wageningen, 013/2011

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are one of sediment contaminants drawing great concerns in relation to adverse impacts on aquatic organisms. Dredging and dispose is one of the methods used to eliminate such problem. Due to the concern of massive destruction of aquatic environment, activated carbon (AC) application is proposed as an alternative aiming to reduce bioavailable dissolved PAHs. To quantify the effectiveness of AC, dissolved PAHs (Cw) needs to be assessed. Current approach used is liquid-liquid extraction. This approach possibly affects the accuracy of Cw quantification due to PAHs adsorption onto dissolved organic matter in aqueous phase. This leads to the main aim of this research which is to measure freely dissolved PAHs in sediment pore water using passive sampling with polyoxymethylene (POM-76). By submerging POM-76 in methanol-water systems (0-0.5 methanol volume fraction) to extrapolate linear regression of Log Kpm (methanol-water partition coefficient) (L/Kg) to pure water, Log Kpom can be obtained and eventually freely dissolve PAHs fraction can be analyzed. Log Kpom show strongly linear relationship over methanol fraction (0.3-0.5) and ranges from 4.6 to 6.9 log unit for phenanthrene (PHE) and benzo(ghi)pyrene (B(ghi)PER), respectively. However, correlation with Log Kow is very low (R^2 = 0.3609) due to the significant levelling off at Log Kpom value of dibenzo(a)anthracene (dB(ah)ANT) and benzo(ghi)pyrene (b(ghi)PYR). Total 13 PAHs mass measured in the sediment was approximately 391,459 μg/Kg d.w. Based on Log Kpom, the reduction of freely dissolve PAHs in sediment-pore water increase as %AC d.w doses increases (1, 3, 6, 15, 30%). To be more precise, the decrease of freely dissolve PAHs was 58, 98, 98.7, 99.4 to 99.99%, respectively. In terms of AC doses, 3% AC dose seems to be the most effective in freely dissolved PAHs reduction.

Since AC is used to treat PAHs contaminated sediment, it is also important to be accurate with the quantity of AC used and left in the sediment after sometimes, chemothermal oxidation method (CTO-375°C) and wet oxidation method (WOM) were also tested to claim which method can outweigh other in relation to the capacity in analyzing AC mass mixed in sediment. 2, 4, 6, 10%AC d.w were mixed with sediment samples. In the end, WOM was found to be more effective than CTO-375°C as up to 94% recovery of AC can be obtained from WOM while all AC used in the system (2, 4, 6, except 10%AC) was completely oxidized by CTO-375°C.

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1. Introduction

1.1. Background

Due to their mutagenic (Westerholm et al., 1988; 1994; Ross and Nesnow, 1999), carcinogenic (Goldman et al., 2001; Carl-Elis et al., 2002) and endocrine (Monteiro et al., 2000) properties, polycyclic aromatic hydrocarbons (PAHs) have drawn serious attention to health. When they are discharged from point source, they become sequestrated in sediment (U.S.EPA, 1998; Jonsson et al., 2007) because of their hydrophobic property which is strongly sorbed to soil and sediment (Ahn et al., 2007). With various levels of their concentrations, they have been found globally from in land lake, rivers to open ocean (Zakaria et al., 2002). Some areas have been detected to have very high in concentrations such as at around areas of Chesapeake Bay in Baltimore ranging from 90 to 46,200 μg/Kg (Ashley and Baker, 1999), from 100 to 380,000 μg/Kg at Sydney Harbour, Australia (McCready et al., 2000) and from 2,790 to 224,000 μg/Kg in 10 reservoirs and lakes in six U.S metropolitan areas (Van Metre et al., 2000). Even though the concentration of this contaminant has been decreasing in water environment during past decades, they can pose adverse impacts on the aquatic species due to their persistence and toxicity (U.S.EPA, 1998).

When PAHs settle in the sediment, it does not seem to cause any risks on aquatic organisms. However, Puglisi et al. (2007) acknowledged that bioaccumulation of these organic pollutants is caused by the up taking of the pollutants through the fraction that is readily dissolved in water phase and the fraction which sorbs on particles, which will be available within days through desorption. This has been found consistent with Valsaraj et al. (1997) informing that, especially in in-equilibrium condition, exposure of aquatic species to contaminants is even higher as a result of their desorptions from sediment. This desorbing concentration could simply be taken up in many ways through diffusion across biological membranes, gill and gut uptake (Bjork, 1995).

In response to the problem of contamination, National Research Council (2001) has concluded that many approaches have been applied such as socioeconomic options (focusing on institutional controls, source control, natural attenuation and recovery by biodegradation and sedimentation), in situ treatment and multi-component removal coupling with ex-situ treatment

(involving dredging technologies, pre-treatment technologies, and technologies for management of residual contaminants).

Concerning possible options to tackle the sediment contamination with PAHs, Zimmerman et al. (2004) and Tomaszewski et al. (2007) pointed out that widely used remediation techniques mainly rely on dredging and disposal of dredged materials in depots but they have argued the fact that these techniques could lead to a massive destruction of benthic habitat as well as to a short-term increase of contaminant concentration in the water phase. National Research Council (2001) also emphasized that insufficient removal of contaminated sediment by dredging could result in residual concentration of the compounds, which, in turn, poses a risk to aquatic organisms. Due to sediment dredging to remove an organic pollutant, Weston et al. (2002) found fish and invertebrate body burden increased (2 to 76 folds) and also found that the concentration was comparable or even higher after 18 months of dredging. Being aware of the adverse impacts of the dredging, in European regulation, water legislation has been extensively changed and it discourages sediment contamination by dredging but encouraging to leave the sediment and treat it in environmentally friendly ways (Köthe, 2003).

With concerns relating to benefits, effectiveness, costs, adverse consequences, an alternative to dredging has been proposed. In situ treatment by activated carbon (AC) addition to contaminated sediments with organic pollutants has been very often mentioned by many researchers including Millward et al. (2005), Tomaszewski (2007), Zimmerman et al. (2004), Zimmerman et al. (2005), Werner et al. (2005) and Cho et al. (2007) because this technology is more cost effective without removal of contaminated sediment (Zimmerman et al., 2004). The preliminary study of scale up AC application at Hunter Point Shipyard Parcel F, San Francisco bay, found that using AC treatment method could save total cost about 70 to 75% when compared to that from dredging and disposal method (STANFORD UNI CA, 2008). In addition to that, activated carbon can effectively reduce aqueous PAHs concentration due to its high affinity to organic compounds (Zimmerman et al., 2004). To this fact, AC application seems to be one of key techniques used in cleaning up contaminated sediment.

1.2. Problem Analysis

It is crucial to be certain that amount of AC required and its capacity are well documented when it is used to treat contaminated sediment. However, the question is that how to obtain a more effective and reliable method of AC capacity quantification in relation to reducing PAHs desorbing into water.

Many studies analyze this capacity by directly inferred from the aqueous concentration quantified with aqueous equilibrium liquid-liquid extraction (Zimmerman et al., 2004; Zimmerman et al., 2005). However, one assumption is that freely dissolved fraction could be affected by inclusion of dissolved solute in the water, which adsorb on dissolved organic matter (DOM) (Hermans et al., 1992; Seth et al., 1999; Jonker and Smedes, 2000) because it does not seem possible to separate the freely dissolved fraction from the fraction that is bound to DOM by filtration (Hermans et al., 1992; Smedes et al., 2009).

Hawthorne et al. (2009) suggested that the methods used to quantify accurate aqueous concentration has to be able to differentiate the contaminant that is associated with the DOM and those that is freely dissolved.

Next to SPMDs, polyoxymethylene (POM) is another method which has drawn attention by many research groups. Scientifically, POM was claimed to be a reliable material which has the property of absorb the hydrophobic contaminant (PCBs and PAHs), which, inturn, gives no adsorption site competition impact (Jonker and Koelmans, 2001). POM has been widely used not only in situ but also in the lab quantifying hydrophobic organic contaminant especially in sediment. Additional benefit of POM is that the resulting concentration is quantified over a certain period of time while direct measurement would only provide the results based on one particular point of time (Cornelissen et al., 2008a). Moreover, it has capacity of detecting extensive low aqueous concentration, appropriate $K_{SORBENT}$ values and low cost (Hawthorne et al., 2009). Based on POM-water partitioning coefficient found in Jonker and Koelmans (2001) and Cornelissen et al. (2008a), POM was confirmed to be qualified materials to obtain PAHs aqueous concentration.

Consequently, many different types and thickness of POM have been used for partition coefficient (Kpom) to analyze PAHs and PCBS aqueous concentration such as POM-55 and POM-550 by Cornelissen et al. ([2008a](#)) in assessing PAH and PCB emissions from the relocation of harbour sediments, Oen et al. ([2011](#)) using POM-17 and POM-51 for in situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment, POM-76 used by Hawthorne et al. ([2009](#)) to measure low picogram concentrations of freely dissolved PCBs in sediment pore water and Jonker and Koelmans ([2001](#)) applying POM-500 for soot-water partition coefficient for hydrophobic compounds in soot-sediment environment. One interesting thing is that even same method and same target compounds used in the experiment, POM partition coefficient yield different values. Such difference was found in Cornelissen et al. ([2008a](#)) as an example.

To my knowledge, quite numbers of researches have focussed on using different thickness of POM for Kpom to quantify PCBs aqueous concentration. Therefore, the main aim of this research is using POM-76 in analyzing PAHs aqueous phase in sediment pore water.

The principle behind equilibrium passive samplers with POM is that they make it possible to quantify PAHs concentration in water by analyzing what is found on POM for the target compounds. In this experiment, they would also be used to generate Kpom of the target compound as well. The freely dissolved concentrations can be calculated using the following equation.

Equation 1 : Concentration of PAHs in aqueous phase

$$C_W = \frac{C_{POM}}{K_{POM}}$$

Where C_{POM} (µg/Kg) and C_W (µg/L) refer to the concentration of PAHs on POM and in water, respectively. K_{POM} (L/Kg) is POM-water partition coefficient.

In the end, by comparing the difference of aqueous PAHs concentration in water systems (control and treatment), it is possible to see the efficiency of AC (with different doses) on desorption reduction.

In addition to this, due to the concerns of losing AC quantity possibly over a period of time, two main AC quantification methods are discussed to see which method could be a more effective

method for AC quantification. These include thermal oxidation method (CTO-375°C) and wet oxidation method (WOM).

1.3. Literature Review

Activated carbon

Activated carbon is a highly crystalline form of carbonaceous substance (CPL Carbon Link, NA) with large internal pore structure and high specific surface area stimulating its sorption capacity (see figure: 1) (Mcdougall, 1991; Thomas J. Barton et al., 1999; Strand, 2001). Activated carbon can be manufactured from any materials that retain elemental carbon content (Khadija et al., 2008). Its production bases on two major techniques. The first is physical activation. This includes two main steps, carbonization (by converting raw material in char by heat) and activation (by increasing heat with oxidizing agent) (Wigmans, 1989; Mcdougall, 1991; Valix et al., 2004). Another is chemical activation. This also requires two main steps, dehydration carbonization with (Mcdougall, 1991). Each choice of material and technique (with careful treatment controlling conditions) will give different characteristics of the products such as the pore sizes and shapes, pore connectivity and the contacting specific area (Thomas J. Barton et al., 1999; CPL Carbon Link, NA).

Property related to PAHs adsorption

The structure of an activated carbon is composed of different pore sizes classified into three groups (figure: 1), namely micropores, mesopores and macropores (Yalçln and Sevinç, 2000), with the diameter of 8 - 100 Å, 100 - 500 Å and 500 - 20000 Å, respectively (Mcdougall, 1991). For typical activated carbons, surface areas available for adsorption ranges from 800-1500 m^2g^{-1} (Hu et al., 2000) but micropore account for over 95% of the total surface area (Yalçln and Sevinç, 2000).
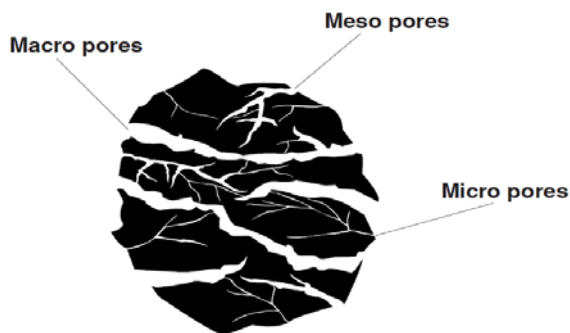
Figure 1: An example of granular activated carbon with fundamental pore size
Source: (Strand, 2001)

Polycyclic aromatic hydrocarbons

The chemistry of PAHs

PAHs are organic compounds (Miller et al., 2003) comprising of two or more benzene rings, attaching to one another by two or more carbon atoms (Watts et al., 2006). Some examples of different PAHs congeners are shown in figure: 2. There are over 100 compounds within PAHs group (Department of Health, 2009) but 13 compounds seem to be significant including PHE, ANT, FLU, PYR, B(a)ANT, CHR, B(e)PYR, B(b)FLU, B(k)FLU, B(a)PYR, B(ghi)PER, dB(ah)ANT, Ind(123)PYR.

PAHs have strong ultraviolet and visible radiation absorption causing them less stable in the environment and they are also biodegradable to an extend depending on the environmental conditions (Connell, 2005). However, some congeners such as anthracene and pyrene were found phototoxic due to some certain increase of UV light (Ankley et al., 1997).

In general, PAHs are compounds that have significantly low solubility in water depending on their ring structures and molecular sizes and weights (Dabestani and Ivanov, 1999; Miller et al., 2003). Low molecular weight congeners (with two or three fused rings) have higher extent water solubility than larger ones (with four to six aromatic rings) (Jonsson et al., 2007). For example, the water solubility can get down from 31,690 µg/L to1.8 µg/L for naphthalene to Chrysene, respectively (May et al., 1978). Thereby, they seem to have strong affinity to non-polar compounds and their level of polarity can be seen from their Kow values. They were analysed in Quantitative Structure-Property Relationship model study by Ribeiro and Ferreira (2003) showing that in 60 tested PAHs compounds Log Kow ranks from 3.37 (naphthalene) to 6.80 (pentacene).

Most PAHs are usually solids in their pure state at ambient temperature (Peters et al., 1997) with ranges boiling point among compounds depending on molecular weights. From the experiment of Ribeiro and Ferreira (2003), it was found that increasing in boiling of PAHs compounds is proportional to the increasing of their molecular weights.

Figure 2: The chemical structure of some typical PAHs frequently encountered in the environment
Source: (Connell, 2005)

PAHs occurrence and distribution in water environment

PAHs is a group of organic pollutants derived from natural process (whenever organic substances are exposed to high temperatures) (Blumer, 1976). For instance, the aromatic hydrocarbons of crude oil have been formed over millions of years from organic matter in sediments at 100 to 150°C or they are processed from falling out of soot due to forest and prairie fires) (Blumer, 1976). However, there is a claim that the level of PAHs present in nature has been found significantly triggered by anthropogenic sources (Connell, 2005). This mainly through burning such as coal-fired electricity power plants, incinerators, open burning, emission from vehicles, etc (Manahan, 2011) especially when carbon from combustion is not completely converted into CO or CO_2 (Ribeiro and Ferreira, 2003). In water environment, they tend to strongly bind to organic matter in sediment and to some extent desorb back to water (Zhou et al., 2000) and disperse through absorbing to organisms and re-sorbing to "clean" particles, which can be transported to other "clean" places (Birdwell et al., 2007).

PAHs sorption mechanism to AC

There are two main mechanisms which help explain organic compound sorption to activated carbon. One is chemical sorption. This is caused by the attraction of electron of adsorbates and activated carbons (Strand, 2001). Another one is physical sorption. This occurs when molecule of compounds are bound to the surface area of activated carbon by means of Van der Waals electrostatic force. This phenomena is also explained by Belfort (1979) that very high cohesive energy density of water squeeze non-polar molecules (PAHs and AC) out of water environment

and if those non-polar molecules are close enough to one another, they become associated with one another.

However, van Noort et al. (2004) pointed out that, like soot, the PAHs adsorption capacity to AC also depends on the characteristic and dimension of the sorbate as well as the sorbent such as the diameter of AC pore, contacting surface areas and the compound thickness due to planarity (which is related to accessible site reduction because thicker molecules might not be able to penetrate to (or even block thinner molecules to access) the site available in the narrow pores).

2. Materials and methods

2.1 Materials

Virgin powder coal based activated carbon (Norit SAE Super) was obtained from Norit Activated Carbon (particle size 1-150 µm) (Amersfoort, The Netherlands). AC was washed prior to experiments, as described previously by Jonker et al.(2009).

Acetone (picograde) and n-Hexane (picograde) (both with purity >99%) were obtained from Promochem, Germany. Acetonitrile (HPLC grade) with purity >99% was supplied by Lab-Scan, Poland. Methanol HPLC with more than 99% purity was bought from J.T. Baker. Hydrochloric acid 37% purity was from Sigma-Aldrich supplier. Sulfuric acid and potassium dichromate ($K_2Cr_2O_7$) with 97% and 99% purity, respectively were delivered from EMSURE, Merck KGaA, Germany.

Three sorbents/reagents including aluminiumoxide, sodium sulphate, silica gel, aluminium oxide (Super I, ICN: 4569) was purchased from MP Biomedicals, Germany. Before used, aluminiumoxide was deactivated with 10% (w/w) nanopore water. Sodium sulphate and silica gel (70-230 mesh) were delivered by Merck KGaA, Germany. Before use, sodium sulphate was heated at 550°C for 2 hours to remove water and silica gel was activated for 16 hours at 180°C. Phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, dibenzo[a,h], and indeno[1,2,3,c,d]pyrene, were obtained from Sigma-Aldrich or Acros Organics, The Netherlands, and all had a purity of 98%. 2-methylchrysene (purity 99.2%) was supplied by The Community Bureau of Reference (BCR), Geel, Belgium as

internal standard. Throughout this report thirteen tested compounds would be referred as PHE, ANT, FLU, PYR, B(a)ANT, CHR, B(e)PYR, B(b)FLU, B(k)FLU, B(a)PYR, B(ghi)PER, dB(ah)ANT, Ind(123)PYR.

Polyoxymethylene film with the thickness of 76 (POM-76) μm was purchased from CS Hyde Company, Lake Villa, IL, USA. The film was cut with scissors into small sizes. Before use, the strips were washed (cold-extracted) with hexane (30 min) and methanol (3 X 30 min), after which they are air-dried and kept in glass bottles (Jonker and Koelmans, 2001; Hawthorne et al., 2009).

Silver cups (8 X 5 mm and 12.5 X 5 mm). They were obtained from Elemental Microanalysis Limited suppliers in UK.

Sediment

The natively contaminated sediment was taken from a previously stored batch, which had originally been dredged from Petroleum Harbor (PH), Amsterdam, the Netherlands. Uncontaminated freshwater sediment was sampled at Station Veenkampen (VKP), Wageningen, The Netherlands, using a sampling bucket. Sediments were sieved through a 2 mm sieve, homogenized and amended with AC to obtain AC concentrations of 0, 1, 3, 6, 15 and 30% d.w. (PH) and 0, 2, 4, 6 and 10% d.w. (VKP). Subsequently, sediments were homogenized on a roller bank for 48 hours and stored at 4°C until use. Total organic carbon and black carbon found for both PH and VKP was 6.2 g/kg d.w and 2.1 g/kg d.w (for PH) and 9.8 g/kg d.w and 1.8 g/kg d.w (for VKP), respectively.

2.2 Methods

Total PAH sediment analysis

In order to estimate total concentration of PAHs in PH and VKP, the sediment subsamples were extracted. The procedures were described in Jonker and Koelmans (2001) and Jonker and Koelmans (2002) for solid phase extraction. In short, around 0.18 (PH1) and 0.33 g d.w (PH2) and around 0.30 (VKP1) and 1.30 g d.w (VKP2) were Soxhlet-extracted for 16 hours with 160 ml of hexane/acetone (3:1). The extracts were then concentrated to 2-3 ml using Kuderna-Danisch apparatus and then further gently condensed to 1-1.5 ml by a stream of nitrogen. Then extracts

were cleaned up over of Al_2O_3 columns. Subsequently, the eluates were reconcentrated again by using the same procedure as mentioned above. The eluates were exchanged into acetonitrile (5 ml) and concentrated again by Kuderna-Danisch apparatus and nitrogen stream successively to 0.9 ml was obtained and transferred in vials with 100 µl of internal standard before they were instrumentally analyzed.

For quality assurance of PAHs extraction and clean up, triplicates of blank plus one recovery also performed for sediment. Due to PAHs can be photolyzed in the presence of light all glasswares used during the extraction and clean up were amber glasswares otherwise wrapped with aluminium foil to create light-free systems. All values were corrected for blank.

Instrumental analysis: Samples were analyzed using a Hewlett-Packard model 1100 HPLC. This device is equipped with a 250 X 4.6 mm Vydac guard to protect the column from insoluble or strongly adsorbed sample components and analytical reverse phase C^{18} column (201GD54T and 201TP54, respectively), with mobile phase consisted of methanol/water (mixture and flow gradient). These were kept at 22.00 °C. PAHs were detected on an HP 1100 multiwavelength fluorescence detector operating in the multi-emission wavelength mode. The injection volume was 20 µL. After each run, the columns were rinsed with acetronitrile. Quantified mass is based resulting light intensity peak converted for each compound by HPLC analyzer. A series of PAH standard solutions was prepared and run together with sediment samples.

Polyoxymethylene-water partition coefficient (co-solvent method)

Due to low aqueous concentration in water environment and difficulty for detection (Hawthorne et al., 2009; Smedes et al., 2009), cosolvent method (methanol-water ratio) is applied. Adding cosolvent can increase aqueous solubility and stabilize the solution consequently lowering Kpm (Smedes et al., 2009).

Based on different ratio of methanol fraction (0, 10, 15, 20, 30, 40 and 50%), each duplicate contains 200 ml of solvent solution in 250 ml dark brown bottle (the water contains 0.01 M $CaCl_2$ and 25mg/L of sodium azide (NaN_3). All systems were then spiked with 100 µl of PAHs solution. After this, POM stripes (0.0255-0.5493 g) were added into the system. After that the bottles were properly sealed with parafilm and shaken for 6 weeks at 120 rpm to achieve

equilibrium condition at room temperature. According to some equilibrium experiments on POM with different thickness and its water environment, it has been found that the POM-water system could reach equilibrium after 30 days. For instance, in situ equilibrium experiment found in Cornelissen et al. (2008b) was 30 days for all PAHs congeners (for POM-55 and POM-500) and within 10 days for POM-500 were found in lab experiment reached equilibrium (Jonker and Koelmans, 2001) and it was also found in Cornelissen and Gustafsson (2004) that 30 days of kinetic experiment was the time for equilibrium on POM-500. After weeks, POM strips were taken out from the bottles, cleaned with nanopore water, dried with a soft tissue, and Sohxlet-extracted with 70 ml methanol for 3 hours.

To quantify concentration of PAHs in aqueous phase (methanol-water mixture), procedures were adapted from (Jonker and Smedes, 2000). In short, after equilibrium was obtained, the aqueous phase was extracted twice using 20 ml of hexane, then phases were separated using separatory funnels. The extracts were combined, the volume was reduced to 1 ml and samples cleaned over Al_2O_3/Na_2SO_4 columns. Then, the condensed solution was exchanged into acetonitrile before analysis with HPLC as described above.

To reassure the quality, blanks and recovery were also prepared and all the values of samples were corrected for blank.

Effects of AC on PAHs desorption reduction

PH sediment amended with AC (0, 1, 3, 6, 15, and 30%) in the amount of 0.2 g d.w was added to 50 ml amber glass vial. Subsequently, 40 ml of nanopore water (mixed with 25mg/L of sodium azide (NaN3) and 0.01M calcium chloride as biocide was added. After that, stripped POM (0.0055-0.013g) was added. The bottles were closed tightly with the stoppers and completely sealed with parafilm. Then the bottles were shaken at about 120 rpm to reach equilibrium condition at room temperature.

After 28 days, POM were taken out from the system, rinsed with nanopore water and dried with a tissue to remove fine particulates attached on them, and then Sohxlet-extracted for 3 hours with 70 ml methanol. Further work-up procedure was done in the same way as for sediment

samples. From what was found on POM and Kpom was obtained from cosolvent experiment, aqueous PAHs (Cw) could be quantified.

AC quantification by chemothermal oxidation method (CTO-375°C)

Total organic carbon, native black carbon and AC contents of sediments can be determined using the thermal oxidation and descaling method described by Gustafsson et al. (1997), according to which organic carbon is removed by thermal oxidation at 375°C, inorganic carbon by in situ acidification.

Subsamples of VKP sediment with initial AC concentrations of 2, 4, 6 and 10% d.w were taken from the field after 3 and 15 m. Sediment was homogenized, dried at 105°C over night, grinded and stored at room temperature before use.

For TOC quantification, 10 mg of VKP sediment was put into a silver cup (12.5 X5 mm). Then 25μl of nanopore water was added, followed by 25 μl of 2 M HCl and let cool down for 1 hour at room temperature before another 50 μl of 2 M HCl was added. After 30 minutes, samples were heated up in the oven for 16 hours at 60° C. Then, 50 μl of 2 M HCl was added one more time, samples were left at 60° C for 16 hours, silver cups were folded.

For black carbon (AC+BC) quantification, samples were heated up at 375°C for 24 hours in muffle furnance to remove OC. After that, BC samples were treated in the same way as TOC samples.

CHN Elemental Analysis: Samples were analyzed using CHN elemental analyzer (Fisons Instruments EA 1108, CE Instruments, Milan, Italy).

AC quantification by Wet Oxidation Method (WOM)

VKP sediment (prepared in the same way as for CTO 375°C) in the amount of 0.2 g d.w was put into 10 ml test tubes. Then, 5 ml of 0.1 M potassium-dichromate/sulphuric acid solution (30g/L) (Brändli et al., 2009) was added and samples were left at 60°C for 30 minutes. After that, samples were vortexed and heated at 60°C for another 30 minutes. Then, 10 ml of methanol was added, samples were votexed, centrifuged for 10 minutes (2,500 rpm) and the supernatant was decanted. The procedure of rinsing samples with methanol was repeated, afterwards, the

sediment was dried at 60°C for 16 hours, transferred to silver cups, and analyzed using a CHN analyzer. For quality assurance, duplicate recovery was also prepared. 2 g of mixture of silica gel and AC were made (10% and 20% of AC) and treated as other samples.

3. Result

Total PAHs quantification

For PH (figure 3: A), the total PAHs was 391,459 µg/Kg d.w (SD = 4-15%). The recovery ranged from 37– 53%. In figure 3: B, with standard deviation up to 15%, the result of total PAHs analyzed for VKP sediment was 24,474 µg/Kg d.w (SD = 4-15%). Mass of individual compound found were various and the reasons are discussed in the discussion part.
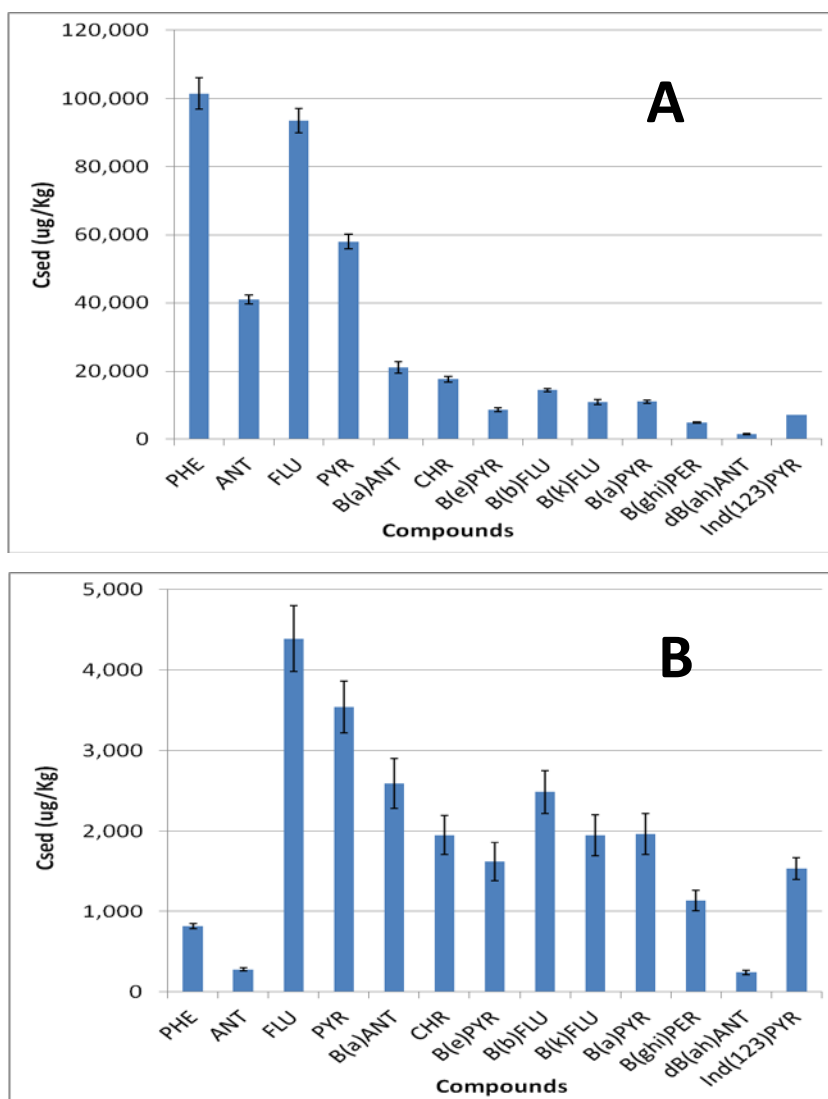
Figure 3: A and B illustrate the concentration of 13 PAHs in PH and VKP sediment, respectively.

Polyoxymethylene-water partition coefficient (co-solvent method)

The Cw and Cpom found were various based on different PAHs congeners as well as methanol-water volume fraction. This can be seen from the mass ratio of the summation of Cw and Cpom to Qtotal. For instance, for PHE the ratio found was 0.00044 (SD=0.00%), 0.63 (SD=0.10%), 0.59(SD=0.10%), 0, 65 (SD=0.01%), 0.80 (SD=0.10%), 0.67 (SD=0.07%) and 0.52 (SD=0.01%) responding to methanol-water volume fraction at 0, 0.1, 0.15, 0.2, 0.3, 0.4 and 0.5, respectively (appendix: 1). The quality assurance was claimed by recovery of 97% (SD=5%) - 146 % (SD=54%) and 69% (SD=8%)-115 % (SD=20%) for Cw and Cpom, respectively (appendix: 2). From dissolved phase found on POM and in aqueous phase, partition coefficient of POM and methanol-water mixture (Kpm) was obtained and Log Kpom was estimated by extrapolation.

Smedes et al. (2009) claimed that Kpom is actually obtained by extrapolation Kpm values and methanol mole fraction of 0<x<0.3 which is equivalent to mehanol volume fraction of 0-0.5 (0<f<0.5). In some cases, Cornelissen et al. (2008a) suggested by extrapolation based on 0.1<f<0.5 backward to 0% to obtain Log Kpom when they determined Kpom for PCBs by using POM-55 and POM-500.

Therefore, in this experiment to obtain Log Kpom, extrapolation based on methanol volume fraction on both ranges, 0<f<0.5 and 0.1<f<0.5, respectively. The ultimate concept of using both is to compare and better select Log Kpom in the end.

When log Kpm values were plotted as the functions of methanol volume fraction, at range 0<f<0.5, the results showed that only four less hydrophobic compounds (PHE, ANT, FLU and PYR) had relatively high correlation coefficient (R^2) (figure: 4 A) while that of other 9 compounds turned out to be very low (figure: 4 B). As the value of 0% methanol was omitted, the linear regression started increased. This can be seen from PHE (figure 4. A) as an example with the stronger relation. However, even though there was some increase of linear relationship, 9 compounds such as B(a)PYR (figure: 4. B) still stayed at very weak correlation.
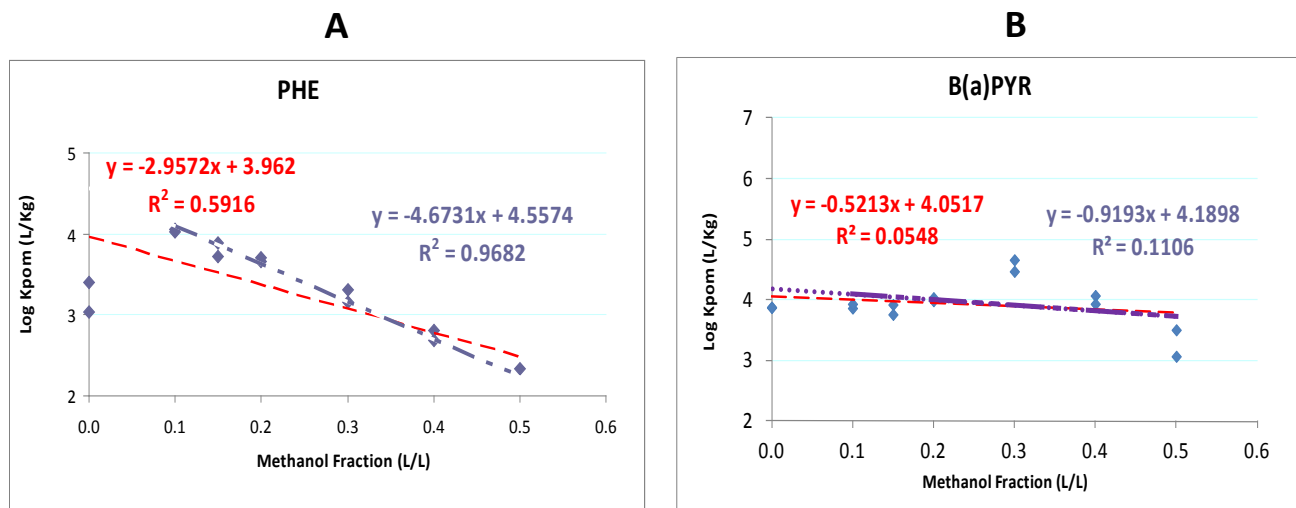
Figure 4: Relationship between Log Kpm (L/Kg) and methanol volume fraction.

A: PHE and **B:** B(a)PYR represent strong and weak linear relationship, respectively based on methanol volume fraction

Dash line refers to log linear relationship based on full range (0<f<0.5).

Dash dot line refers to log linear relationship based on excluded 0% methanol.

This nonlinear relationship is the cause of levelling off of Log Kpm starting from f≤0.3. This phenomena was also observed by Smedes et al. (2009). Moreover, Cornelissen et al. (2008a) noticed in their determination of Kpom for PCBs by using POM-55 and POM-500 that Log Kpm values yielded even lower than that from Log Kpm at f = 0.1 system. In addition to this, it has also been found that methanol fraction below 20% (especially for higher hydrophobic compounds) could not generate high solubility of tested compounds (Kimble and Chin, 1994; Li and Andren, 1994; Li et al., 1994; Hegeman et al., 1995; Jonker and Smedes, 2000). Consequently, it was suggested to extrapolate from f>20% methanol to 0% methanol by Hegeman et al. (1995) when they were trying to obtain Koc from methanol -water systems. Moreover, Jonker and Smedes (2000) further pointed out that to quantify Koc by using cosolvent methanol-water method, it was suggested to extrapolate Log Koc as a function of >16% methanol fraction of mass base (which equivalents to 24% volume fraction of methanol) to 0% methanol. The results from this present experiment based on both ranges (0<f<0.5 and 0.1<f<0.5) yield below acceptable correlation level for many compounds. These analyzing outputs played a great important role on obtaining log Kpom because, with unacceptable correlation coefficient, log Kpom could not be reliable.

System analysis

In response to these unexpected outcomes, one question was raised on how the systems behaved like this. One assumption was that the systems with low methanol content could get

saturated due to too high concentration of tested compounds put into the systems. This inference turned out to be very convincible when systems solubility capacity is estimated by Log

Sm = Log Sw + fc σ

Equation 2: Solubility models

Source: ([Morris et al., 1988](#); [Pinal et al., 1990](#))

Sm = Solubility of HOC in mixture (mg/L). Sw = solubility of HOC in water (mg/L). fc = Methanol fraction (L/L).   σ = cosolvency power)

using some models found in some other sources as the following

To predict if the PAHs stock concentration was too height to completely get dissolved by system, two models were used (equation 2 and 3).

Cosolvency powers are of importance for solubility quantification. However, not all cosolvency powers for all tested compounds in methanol-water system were found in literature. Consequently, a cosolvency model from Li and Yalkowsky ([1998](#)) was used.

$\sigma_{0.5}$ = $M_{0.5}$Log Kow + $N_{0.5}$

Equation 3: Cosolveny power model for methanol-water system.

Source: ([Li and Yalkowsky, 1998](#))

$\sigma_{0.5}$ = Cosolvency power. $M_{0.5}$ and $N_{0.5}$ = slope and intercept of linear regression between $\sigma_{0.5}$ and LogKow, respectively. 0.5 = linear regression between 0-50 % of methanol in mixture system

To claim this model is applicable the value of $\sigma_{0.5}$ (predict values) with the σ taken from literature were compared. Even though the cosolvency powers derived from literatures was higher, the difference between the predicted cosolvency powers and that found in the literature turned out to be acceptably close with standard deviation of 0.4-6% (table: 1).

Table 1: Comparison between σ calculated and σ directly from literature

Compound	LogKow[a]	σ_{50} (Predict)[b]	σ (literature)	% Stdev
PHE	4.6	4.06	4.42 ([Bouchard, 1998](#))	6
ANT	4.6	4.06	4.21 ([Morris et al., 1988](#))	3
FLU	5.2	4.50	4.73 ([Pinal et al., 1990](#))	4
PYR	5.2	4.50	4.30 ([Morris et al., 1988](#))	3
B(a)ANT		4.93 ([Li and Yalkowsky, 1998](#))	-	-

CHY	5.8	4.93	4.96 (Morris et al., 1988)	0.4
B(e)PYR		5.37 (Li and Yalkowsky, 1998)	-	-
B(b)FLU		4.93 (Li and Yalkowsky, 1998)	-	-
B(k)FLU		4.93 (Li and Yalkowsky, 1998)	-	-
B(a)PYR		5.23 (Li and Yalkowsky, 1998)	-	-
B(ghi)PER		5.74 (Li and Yalkowsky, 1998)	-	-
dB(ah) ANT		5.69 (Li and Yalkowsky, 1998)	-	-
Ind(123)PYR		5.50 (Li and Yalkowsky, 1998)	-	-

[a] Log Kow values were obtained from (Cornelissen et al., 2008b), except for PYR taken from (Bayona et al., 1991). [b] Predict values by using equation from (Li and Yalkowsky, 1998).

After all calculation was done (table: 2), the predict solubility and measured Cw (mg/L) found from each systems were compared. Cw (mg/L) values in this experiment found exceeded that of predicted values at 0.1<f<0.3 systems for 8 higher hydrophobic compounds (CHR, B(E)PYR, B(b)FLU, B(k)FLU, B(a)PYR, B(ghi)PER, dB(ah)ANT, Ind(123)PYR). This can be observed in table: 2 (with values in "bald"). Consequently, one conclusion was made from this finding is that once the stock concentration was transferred in to 0.1<f<0.3 systems, some fraction of the eight compounds became saturated.

Table 2: Comparison of predict solubility values and concentration in the systems.

Compo-und	Sw (mg/L)	fc (L/L)	Sm (mg/L)	Cw (mg/L)	Compo-und	Sw (mg/L)	fc (L/L)	Sm (mg/L)	Cw (mg/L)
PHE	1.29 (Mackay and Shiu, 1977)	**0**	**1.29**	**0.0002**	B(b)FLU	0.0015 (Wise et al., 1981)	**0**	**0.0015**	**0.0001**
		0.1	3.569	0.11			**0.1**	**0.005**	**0.10**
		0.15	5.937	0.12			**0.15**	**0.01**	**0.09**
		0.2	9.88	0.14			**0.2**	**0.01**	**0.05**
		0.3	27.33	0.07			0.3	0.05	0.01
		0.4	75.61	0.12			0.4	0.14	0.02
		0.5	209.21	0.16			0.5	0.44	0.06
ANT	0.073 (Mackay and	**0**	**0.073**	**0.0002**	B(k)FLU	0.0008 (Wise et	**0**	**0.0008**	**0.0001**
		0.1	0.192	0.13			**0.1**	**0.002**	**0.16**

Compound	Value				Compound	Value			
	Shiu, 1977)	0.15	0.312	0.15		al., 1981)	0.15	0.004	0.16
		0.2	0.51	0.15			0.2	0.01	0.16
		0.3	1.34	0.06			0.3	0.02	0.01
		0.4	3.53	0.11			0.4	0.08	0.02
		0.5	9.30	0.16			0.5	0.23	0.05
FLU	0.26 (Mackay and Shiu, 1977)	0	0.26	0.0002	B(a)PYR	0.0038 (Mackay and Shiu, 1977)	0	0.0038	0.0003
		0.1	0.773	0.06			0.1	0.013	0.14
		0.15	1.332	0.08			0.15	0.023	0.13
		0.2	2.30	0.09			0.2	0.04	0.12
		0.3	6.82	0.04			0.3	0.14	0.01
		0.4	20.28	0.08			0.4	0.47	0.02
		0.5	60.25	0.14			0.5	1.559	0.07
PYR	0.135 (Mackay and Shiu, 1977)	0	0.135	0.0002	B(ghi)PER	0.00026 (Mackay and Shiu, 1977)	0	0.00026	0.0001
		0.1	0.363	0.06			0.1	0.001	0.15
		0.15	0.596	0.07			0.15	0.002	0.16
		0.2	0.98	0.09			0.2	0.004	0.17
		0.3	2.63	0.03			0.3	0.01	0.01
		0.4	7.08	0.08			0.4	0.05	0.01
		0.5	19.07	0.14			0.5	0.19	0.05
B(a)ANT	0.014 (Mackay and Shiu, 1977)	0	0.014	0.0001	dB(ah)ANT	0.0006 (Mackay and Shiu, 1977)	0	0.0006	0.0001
		0.1	0.044	0.13			0.1	0.002	0.15
		0.15	0.077	0.13			0.15	0.004	0.17
		0.2	0.14	0.12			0.2	0.01	0.17
		0.3	0.42	0.01			0.3	0.03	0.01
		0.4	1.32	0.04			0.4	0.114	0.01
		0.5	4.10	0.09			0.5	0.42	0.04
CHY	0.002 (Mackay and Shiu, 1977)	0	0.002	0.0001	Ind(123)PYR	0.00019 (Mackay and Shiu, 1977)	0	0.00019	0.00001
		0.1	0.006	0.17			0.1	0.001	0.03
		0.15	0.011	0.17			0.15	0.001	0.03
		0.2	0.02	0.18			0.2	0.002	0.02
		0.3	0.06	0.01			0.3	0.0085	0.001
		0.4	0.19	0.04			0.4	0.0302	0.002
		0.5	0.60	0.09			0.5	0.1073	0.01
B(e)PYR	0.0056 (from Log Sm = -2.25)	0	0.0056	0.0001					
		0.1	0.019	0.15					
		0.15	0.036	0.14					
		0.2	0.07	0.12					

(Ferreira, 2001)	0.3	0.23	0.01
	0.4	0.79	0.02
	0.5	2.73	0.09

The bold values indicate the assumption that the concentration (Cw) in the systems could exceed the systems solubility and these values are excluded when extrapolate Log Kpm value to derive Log Kpom.

One remarkable finding is that aqueous system at 0% methanol the concentration found was extremely low for all 13 compounds and below solubility capacity level (Table: 2). However, one conclusion from this finding is that it was not because the pure water system could dissolve all the stock PAHs concentration but because the larger fraction of the PAH compounds become precipitated and very less aqueous fraction was available. This can be inferred from that some fractions of PAH stock solution was possibly be precipitated even from 0.1<f<0.3 systems. Therefore, at pure water system, it was unlikely to be possible for all tested PAH stock solution to be able to dissolve in such system as tested compounds are considered hydrophobic compounds which apparently would more like methanol rather than water. At 0% methanol system, both concentration found in aqueous system and on POM was very low which, in turn, causes log Kpm at pure water to be low and even low than that of f = 0.1 system for some compounds.

Another hypothesis on the unfavourable correlation is whether hexane used as liquid-liquid extraction solvent would works effectively compared to that when it is used for extraction the contaminant in pure water system. Then, hexane-water and hexane-methanol-water partition coefficient were compared. The principle of this is that one can deduce the extraction efficiency from partitioning coefficient of hexane-water and hexane-methanol-water (Log Khw and Log Khmw, respectively). The Log Khw and Log Khmw values are hardly found from sources, basic model were developed from POM-water partition coefficient.

$$C_{POM} = K_{POM} C_w$$

Source: (Koelmans et al., 2009)

Equation 4: Illustrating hexane-water partition coefficient

$$LogK_{hw} = 0.0152V_S + 1.977$$

Source: (Gobas et al., 1988)

Where Vs refers to molar volume (cm^3/mol) of tested compounds

Equation 5: Illustrating hexane-water partition coefficient

$$K_{hmw} = \frac{C_h}{C_{MW}}$$

Where K_{hmw} refers to hexane-methanol-water partition coefficient. C_h and C_{MW} (mg/L) refer to concentration in hexane and methanol-water, respectively. For C_{MW} is the same as Smw (mg/L) in table

To obtain C_h, equation 5 is needed.

Equation 6: Illustrating concentration of PAHs derived from partition coefficient equation

$C_h = K_{hw} * C_w$

Where Cw (mg/L) is PAHs solubility (Sw) mg/L in table 2 above

The results (table: 3) found that at 0.1<f<0.5 only four low hydrophobic compounds (PHE, ANT, FLU AND PYR) show relatively similar Log K_{hwm} or even higher than Log K_{hw} predicted. This could also be one of the reasons why these four compounds have stronger R^2 when compared to that from others. For other congeners, Log K_{hmw} starts to decrease as increasing fraction of methanol. This means that the capacity of PAHs liquid-liquid extraction by hexane gradually gets weak as the methanol fraction increase. Jonker and Smedes (2000) who also used hexane to extract PAHs from methanol-water system and found that the resulting recovery show 64-97%.

Thus, the interpretation from this is that some fraction might be left in the aqueous systems, and this would even support the first assumption that the Cw exceeds the capacity of the systems (0<f<0.3) to dilution all the Cw used.

Table 3: Comparison of predict hexane-water and tested hexane-methanol-water partition coefficient (log scale).

Compound	Molar volume (cm³/mol)	Methanol Volume fraction (L/L)	Sm (mg/L)	Cw (mg/L)	Predict Log K(hw)	Tested Log K(hmw)	Compound	Molar volume (cm³/mol)	Methanol Volume fraction (L/L)	Sm (mg/L)	Cw (mg/L)	Predict Log K(hw)	Tested Log K(hmw)
PHE	199 (Gobas et al., 1988)	0.10	3.57	0.11		**6.08**	B(b)FLU	223 (Ruelle and Kesselring, 1997)	0.10	0.004	0.10		3.5
		0.15	5.94	0.12		**6.02**			0.15	0.01	0.09		3.6
		0.20	9.88	0.14	5.00	**5.97**			0.20	0.01	0.05	5.36	3.8
		0.30	27.33	0.07		**6.28**			0.30	0.05	0.01		4.7
		0.40	75.61	0.12		**6.05**			0.40	0.14	0.02		4.2
		0.50	209.21	0.16		**5.92**			0.50	0.44	0.06		3.7
ANT	197 (Gobas et al., 1988)	0.10	0.19	0.13		4.72	B(k)FLU	223 (Ruelle and Kesselring, 1997)	0.10	0.0026	0.16		3.1
		0.15	0.31	0.15		4.67			0.15	0.0048	0.16		3.1
		0.20	0.51	0.15	4.97	4.67			0.20	0.01	0.16	5.36	3.1
		0.30	1.34	0.06		**5.03**			0.30	0.03	0.01		4.5
		0.40	3.53	0.11		4.78			0.40	0.10	0.02		4.0
		0.50	9.30	0.16		4.64			0.50	0.33	0.05		3.6
FLU	217 (Gobas et al., 1988)	0.10	0.77	0.06		**5.89**	B(a)PYR	263 (Miller et al., 1985)	0.10	0.01	0.14		4.41
		0.15	1.33	0.08		**5.81**			0.15	0.02	0.13		4.44
		0.20	2.30	0.09	5.28	**5.73**			0.20	0.04	0.12	5.97	4.48
		0.30	6.82	0.04		**6.14**			0.30	0.13	0.01		5.76
		0.40	20.28	0.08		**5.77**			0.40	0.41	0.02		5.23
		0.50	60.25	0.14		**5.55**			0.50	1.32	0.07		4.71
PYR	214 (Gobas et al., 1988)	0.10	0.36	0.06		**5.58**	B(ghi)PER	277 (Miller et al., 1985)	0.10	0.0009	0.15		3.42
		0.15	0.60	0.07	5.23	**5.50**			0.15	0.002	0.16	6.19	3.39
		0.20	0.98	0.09		**5.43**			0.20	0.004	0.17		3.36

Compound	Source	Fraction					Compound	Source	Fraction				
		0.30	2.63	0.03		**5.86**			0.30	0.01	0.01		4.86
		0.40	7.08	0.08		**5.47**			0.40	0.05	0.01		4.48
		0.50	19.07	0.14		**5.23**			0.50	0.19	0.05		3.86
B(a)ANT	248 (Miller et al., 1985)	0.10	0.04	0.13		4.77	dB(ah) ANT	300 (Gobas et al., 1988)	0.10	0.002	0.15		4.15
		0.15	0.08	0.13		4.77			0.15	0.004	0.17		4.09
		0.20	0.14	0.12	5.75	4.81			0.20	0.01	0.17	6.54	4.09
		0.30	0.44	0.01		**5.80**			0.30	0.03	0.01		5.43
		0.40	1.41	0.04		5.26			0.40	0.13	0.01		5.32
		0.50	4.46	0.09		4.92			0.50	0.48	0.04		4.68
CHR	241 (Miller et al., 1985)	0.10	0.01	0.17		3.71	Ind(123)PYR	257 (Ruelle and Kesselring, 1997)	0.10	0.001	0.03		3.4
		0.15	0.01	0.17		3.70			0.15	0.001	0.03		3.4
		0.20	0.02	0.18	5.64	3.69			0.20	0.002	0.02	5.53	3.5
		0.30	0.06	0.01		4.86			0.30	0.01	0.00		4.9
		0.40	0.19	0.04		4.34			0.40	0.03	0.00		4.5
		0.50	0.60	0.09		3.99			0.50	0.11	0.01		3.8
B(e)PYR	263 (Miller et al., 1985)	0.10	0.02	0.15		4.56							
		0.15	0.04	0.14		4.59							
		0.20	0.07	0.12	5.97	4.64							
		0.30	0.23	0.01		5.88							
		0.40	0.79	0.02		5.40							
		0.50	2.73	0.09		4.78							

The bald values refer to hexane-methanol-water partition coefficient which relatively similar to or higher than hexane-water partition coefficient.

In response to the findings and claims, it can be motivated that extrapolation to obtain Log Kpom from linear regression of log Kpm as a function of methanol volume fraction (0.3<f0.5) is the option for this experiment. Table: 4 show Log Kpom values (intercept) for all compounds. It can be seen that the relationship of Log Kpom in the range 0.3<f<0.5 is strongly linear. As the higher molecular weight of the tested compounds get higher, R^2 has a tendency to go down. It starts from 0.97-0.79 (PHE to Ind(123)PYR, respectively). The standard error among Log Kpom ranges from 0.08-0.5 at PHE and Ind(123)PYR, respectively. Graph plotted for each congener is shown in appendix: 3.

Table 4: Statistics of Log Kpom of 13 tested compounds and Log Kpom-Log Kow relationship.

Statistics	LogKpom-LogKow	PHE	ANT	FLU	PYR	B(a)ANT	CHR	B(e)PYR	B(b)FLU	B(k)FLU	B(a)PYR	B(ghi)PER	dB(ah)ANT	Ind(123)PYR
Intercept	2.17	4.56	4.29	5.11	5.13	6.24	6.21	6.44	6.58	6.47	6.51	5.41	5.57	5.92
SE	1.44	0.08	0.11	0.09	0.09	0.35	0.36	0.40	0.37	0.37	0.37	0.50	0.45	0.45
CI Lower 95%	-1.00	4.37	4.03	4.92	4.93	5.27	5.22	5.33	5.55	5.44	5.49	4.01	4.33	4.66
CI Upper 95%	5.33	4.74	4.54	5.31	5.33	7.22	7.20	7.55	7.61	7.50	7.53	6.80	6.81	7.18
Slop	0.61	-4.67	-3.89	-5.16	-5.09	-6.69	-6.57	-6.40	-6.71	-6.21	-6.39	-3.65	-3.76	-4.35
SE	0.24	0.27	0.37	0.28	0.29	0.86	0.87	0.98	0.91	0.91	0.90	1.23	1.09	1.11
R^2	0.36	0.97	0.92	0.97	0.97	0.94	0.93	0.91	0.93	0.92	0.93	0.69	0.75	0.79

SE refers to standards error of log Kpom. CI (confidence interval) Lower and Upper 95% refer to the confident interval showing the range of the values within which log Kpom will be found. R^2 refers to the correlation coefficient.

Effects of AC on PAHs desorption reduction.

In table: 5, there was an influence of AC doses on desorbing of PAHs into water environment. As dose of AC increases, PAHs aqueous concentration decreases (graphs of individual compounds are shown in appendix: 4). Based on the total concentration, PAHs aqueous reduction gradually decreases by 59.46, 98.10, 98.73, 99.37 and 99.84% with doses of 1, 3, 6, 15 and 30%. The standard deviation was in a range of 0.5-25% and the recovery was 66-96%.

Table 5: Responding AC doses on PAHs aqueous reduction (Cw) in μg/L.

Compounds	AC doses					
	0%	1%	3%	6%	15%	30%
PHE	0	56.08	97.25	98.21	99.35	99.79
ANT	0	57.95	98.66	99.22	99.41	99.90
FLU	0	62.11	98.64	98.95	99.38	99.89
PYR	0	61.63	98.71	98.86	99.55	99.78
B(a)PYR	0	75.65	98.70	98.92	99.41	99.59
CHR	0	75.41	98.62	99.02	99.46	99.34
B(e)PYR	0	51.62	93.61	95.20	97.75	99.10
B(b)FLU	0	58.07	93.71	96.30	98.24	99.69
B(k)FLU	0	58.27	93.63	95.79	97.23	99.32
B(a)PYR	0	67.38	90.61	92.25	98.50	99.68
B(ghi)PER	0	58.95	60.81	66.02	88.06	97.93
dB(ah)ANT	0	46.05	61.78	77.13	80.46	99.18
Ind(123)PYR	0	65.10	73.20	80.76	90.76	96.48
Total	0	58.46	98.10	98.73	99.37	99.84

Chemothermal and Wet Oxidation methods

Results of 3 month AC mixed sediment

The standard deviation found was 7-11% and 1-8% for CTO 375°C and WOM, respectively. In figure 5: A, CTO-375°C turned out to be decreasing in % TOC as increasing % AC added to the systems. This decrease started from 1.57, 1.14, 0.68 to 0.49% as % AC added increased from 0, 2, 4, 6%, respectively. However, only the system with 10% AC was found a bit high (3.84% TOC). On the other hand, WOM showed an increase of %TOC as the systems was added with higher AC doses. TOC started from 1.81, 3.40, 5.00, 6.51 to 7.65% as added AC got higher from 0, 2, 4, 6 and 10%, respectively (appendix: 5).

Results of 15 month AC mixed sediment

With the standard deviation around 1-10% and 3-14% for CTO 375°C and WOM, respectively, it is interesting to point out that, 15 months later, percentage of C found from both CTO 375°C and WOM turned out to follow the similar pattern even though the % TOC from CTO 375°C was lower than that from WOM (figure 5: B). The results from CTO-375°C increased from 0.23, 1.05, 1.19, 2.02 and 4.07% in the 0, 2, 4, 6 to 10% AC systems, respectively. At the same time, WOM yielded from 2.08, 3.64, 5.38, 5.27 to 5.51% in 0, 2, 4, 6 to 10% sediment system, respectively.
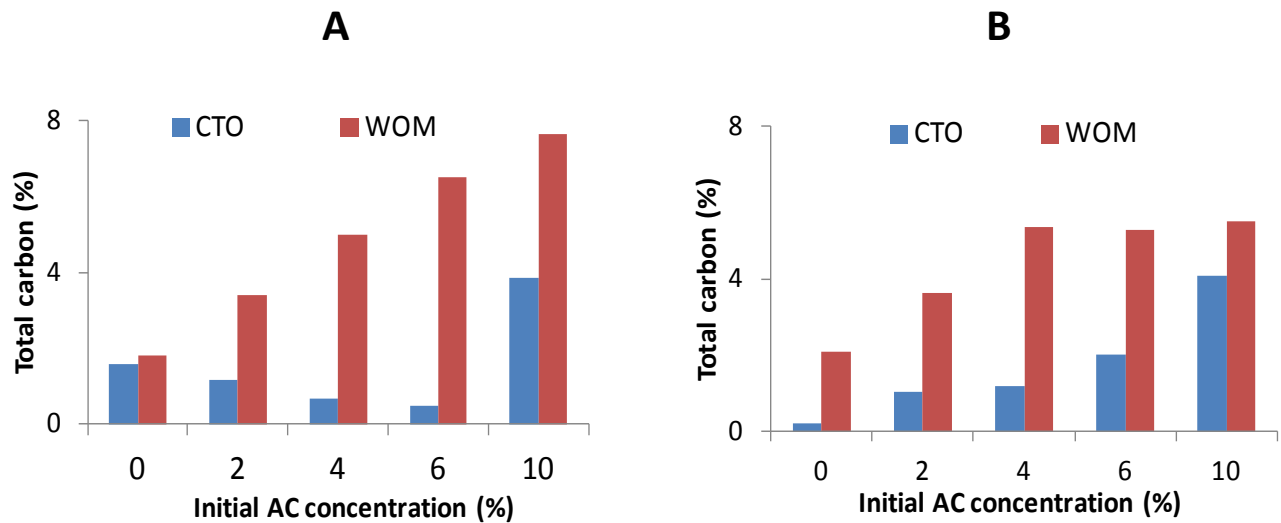
A   **B**

Figure 5: Comparison of CTO-375°C and WOM methods for AC quantification

A: refers to sediment sampled mixed with AC after 3 months

B: refers to sediment sampled mixed with AC after 15 months

4. Discussion

Total PAHs quantification.

PAHs composition in sediment samples turned out various. For example, in PH sediment PHE, ANT, FLU and PYR seemed to be relatively abundant while in VKP sediment only PHE and ANT seem to be among the less dominant compounds. However, this could be explained by Doong and Lin (2004) and Macias-Zamora et al. (2002) that the variation can be attributed to their petrogenic or perolytic point sources. It was added that PHE, CHR and FLUO[1] will become dominant in sediment environment if PAHs are petrogenic originated while FLU and PYR concentration are often found relatively higher compared to others if PAHs are perolytic originated. In align with the claim, PH obtained from Harbor could be concluded that PH has been contaminated from both point sources as the dominant compounds derived from both sources were found very high. This covers 75% of the total concentration found. As VKP were taken from ditch, the main source of the dominant compounds could come from pyrolytic source (table: 6).

Table 6: Concentration in µg/Kg and in percentage of PAHs congeners.

Petroleum Harbor				Veenkampun			
Compounds	Concentraton (µg/Kg)	Sub-Total Concentration (µg/Kg)	%	Compounds	Concentration (µg/Kg)	Sub-Total Concentration (µg/Kg)	%
PHE	101,403			PHE	812	1,091	4
ANT	41,048	293,921	75	ANT	279		
FLU	93,434			FLU	4,390	7,926	32
PYR	58,035			PYR	3,536		
B(a)ANT	21,117			B(a)ANT	2,590		
CHR	17,650			CHR	1,952		
B(e)PYR	8,719			B(e)PYR	1,616		
B(b)FLU	14,475			B(b)FLU	2,485		
B(k)FLU	10,967	97,539	25	B(k)FLU	1,945	15,457	63
B(a)PYR	11,050			B(a)PYR	1,961		
B(ghi)PER	4,943			B(ghi)PER	1,135		
dB(ah)ANT	1,469			dB(ah)ANT	244		
Ind(123)PYR	7,149			Ind(123)PYR	1,529		
Total (µg/Kg)		391,459	100	Total (µg/Kg)		24,474	100

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[1] Fluorene

Polyoxymethylene partition coefficient

Relationship of log Kpom with log Kow

In this experiment, POM-76 was used while other two thicknesses (POM-55 and POM-500) used by Cornelissen et al. (2008b), POM-500 used by Jonker and Koelmans (2001) and log Kpom-76 used by Hawthorne et al. (2009) were discussed. Figure: 6 showed that as Log Kow increase, test Log Kpom also increases. However, even though individual compounds yielded very strong correlation over range of 0.3<f<0.5, the regression line of the pooled relationship between log Kpom and Log Kow turned out to be very weak (R^2 = 0.3609) and also relative weak when compared to R^2 found from other literatures such as 0.947, 0.8268, 0.763 and 0.8838 from Hawthorne et al. (2009), Jonker and Koelmans (2001), Cornelissen et al. (2008a), repectively. The cause of this weak correlation is the significant low POM-water partitioning of dB(ah)ANT and Ind(123)PYR. This observation is also found in Hawthorne et al. (2009), Jonker and Koelmans (2001), Cornelissen et al. (2008a) when Log Kow is in the range of 6.5-7.5. When Kow becomes relatively large (i.e., for compounds which are very hydrophobic and have high molar volumes), a loss of linear correlation is often observed (Veith et al., 1983). This means that once the adsorption on POM goes down, the resulting Log Kpom of higher hydrophobic would also goes down.

It is interesting to note that POM-76 used from Hawthorne et al. (2009) yielded very close to tested log Kpom values. Another remark is that the difference between log Kpom values from this experiment and log Kpom-55 and log Kpom-550 was significant. This difference was assumed to be attributed to variation materials used among manufactures (Cornelissen et al., 2008a). Cornelissen et al. (2008a) further analyzed the dissimilarity of log Kpom value and stated that the difference such as Log Kpom-500 values from in their experiment and in Jonker and Koelmans (2001) is because Jonker and Koelmans (2001) overestimated of concentrations in the (pure) water phase in the study. Based on this claim, tested log Kpom can plausibly be higher than that found in Jonker and Koelmans (2001), Cornelissen et al. (2008a). One possible reason is that, from the assumption made earlier, the low capacity of hexane in extracting the tested contaminant (especially the higher hydrophobic ones) when methanol fraction goes up, which results in lower Cw and higher log Kpom.
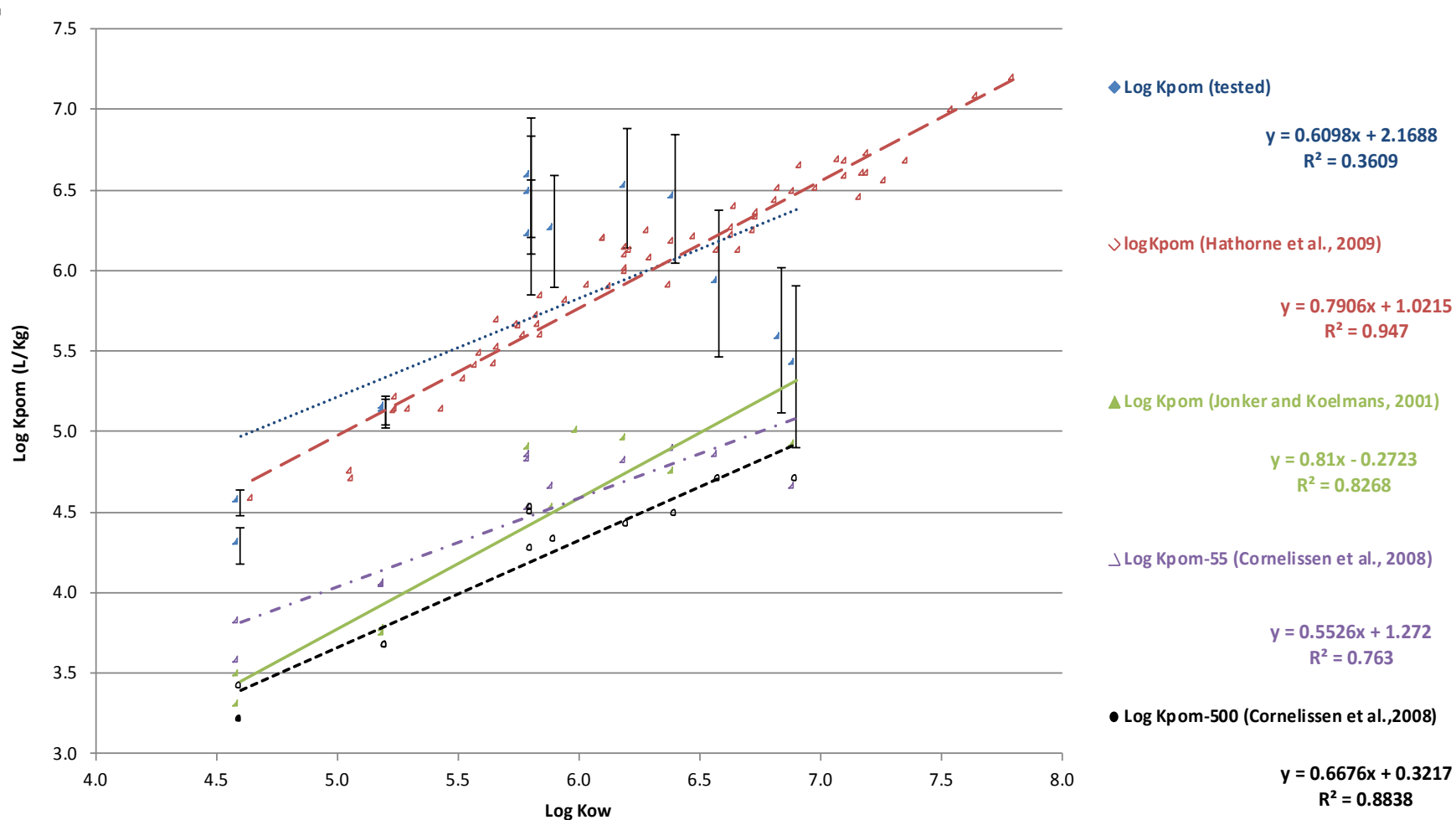
Figure 6: Correlation of Log Kpom and Log Kow for individual congener of PAHs

◆ Tested Log Kpom-76   ◇ Log Kpom-76 from Hawthorne (2009) ▲ Log Kpom-500 Jonker and Koelmans (2001) , ● and △ Log Kpom-55 and Log Kpom-500 values from Cornelissen et al (2008a). Log Kow values were obtained from (Cornelissen et al., 2008b), except (PYR, B(a)PYR (Bayona et al., 1991), dB(ah)ANT and Ind(1,2,3)PYR) (Meharg et al., 1998)). However, only Log Kow used for Jonker and Koelmans (2001) was adopted from Booij et al (1998).

Effect of AC on PAHs aqueous reduction

Some important remarks could be noticed from the results. One is that at 1% AC, total Cw reduction was comparably small (59%). Brändli et al. (2008) explained that this small reduction is attributed to saturation of AC sorption sites to high concentration PAHs as they found in their experiment that adding 2% powder AC could only remove 63% of PAHs from the tested soil.

It is interesting to point out that the extent of the reduction of all freely aqueous PAHs reduction does not seem to correspond to the quantity of AC added. At 1% AC dose, the reduction was 58.46% and it went up to 98.10% when % AC dose was three times higher (3%), which was 49.54% increase. However, little PAHs reduction was observed when there was an addition of % AC dose from 3 to 6, 15 and 30%, which was from 98.10 to 98.73 and 99.37%, respectively. This was also in align with the finding from Zimmerman et al. (2005) who claimed that AC doses after 3.4% had no remarkable PAHs aqueous reduction.

Moreover, even though at 3% AC d.w gave the most effective Cw reduction, this reduction varied for the individual compounds. Zimmerman et al. (2005) pointed out that Cw reduction of less hydrophobic compounds was greater than that of the more hydrophobic ones due to mass transfer kinetics of individual compounds. This claim also agreed with the finding in this experiment in that at 3% ≤ AC ≥ 3% six compounds yielded significant reduction (PHE, ANT, FLU, PYR, B(a) PYR and CHR). For instant, at AC dose = 3%, the values ranged from 97.25% - 98.71% while the Cw reduction of others (B(e)PYR, B(b)FLU, B(k)FLU, B(a)PYR, B(ghi)PER, dB(ah)ANT, Ind(123)PYR) ranged 46.05 − 93.71%. This was also even more confirm when aqueous concentration of the later compounds still could be detected while that of PHE, ANT, FLU, PYR, B(a) PYR and CHR was below detection level.

However, confirmed reducing pattern above did not fit to the reduction quantified at 1% AC. All compounds showed very similar percentage of reduction. The reduction variation among 13 tested compounds at 1% AC was quantified by standard deviation of 8%. In this case, saturation claimed by Brändli et al. (2008) could be plausible cause for this phenomena.

Comparison of Chemothermal and Wet Oxidation methods

Results of 3 month AC mixed sediment

From CTO 375°C, after correcting %TOC found in the free AC system (0% AC), it was found that only the system (10% AC) is assumed to show some recovery of AC while the rest not only all AC but also some fraction of BC was oxidized. This extensive loss of AC was also found by Brandli et al., (2009) that almost of added AC was oxidized after 2% AC was mixed with sediment sample (4% recovered). One notice from Ghosh and Grossman (2009) is that mixing AC with freshwater sediment result in AC burn off at temperature of 375°C. One possible reason could help explain this underestimation is that at high temperature (300-600°C) AC was found to have self-ignition (Hassler, 1974) resulting in the loss. Another is that BC including amended AC can be oxidized as the result of catalyzation of material composition in the sediment sample such as metal or mineral oxides (Elmquist et al., 2006).

From WOM, it was found that by comparing TOC in 0% AC system and other TOC found in 2, 4, 6 10% AC systems, recovered % AC can be quantified, which is about 80%, 80%, 78%, 58%, respectively (appendix: 5). One remark is that the more %AC is added, the analyzed %TOC seems to be diminished. The variation could be because of loss of small particles during decanting and handling (Gélinas et al., 2001). The variation was also found in Brandli et al., (2009) but they also pointed out in their AC quantification experiment that more AC was added, AC recovery become lower (92% and 81% AC recovered when the sample was added with 2 and 5%, respectively).

Results of 15 month AC mixed sediment

One remarkable point is that after 15 month of deploying AC, CTO-375°C showed concurrent increase of % TOC as more %AC added to the sediment (from 0.23%-4.07% TOC) (appendix: 5). This seems to be very opposite to that found in the 3 month AC mixed sediment. However, this addition of carbon can not be possible to claim that it the %AC recovered from the system from this method because this method showed no % AC recovered at all at after 3 months of adding AC. The basic assumption for this occurrence is that there might be a replenishment of other type of carbon added to the system during the time gap.

While CTO-375°C yield unfavourable results, WOM method used for 15 month sediment to quantify AC showed similar % AC recovery of 78, 82, 53 and 34% from the systems added with 2, 4, 6 and 10 % AC.

5. Conclusion

From this study, it can be concluded that using polyoxymethylene (POM) in measuring PAHs concentration in sedeiment-pore water can be possible. However, several issues have to be taken into account. One is that using hexane as PAHs solvent can be affected by methanol content. Second, to derive Kpom values for PAHs from binary system (methanol-water), appropriate concentration should be considered as at low methanol fraction systems, PAHs solubility can be very low causing saturation to occur.

In relation to the efficiency of AC on PAHs desorption reduction with the help of POM, AC can prove that dissolve PAHs from sediment can be extensive reduce and more AC doses are added better result it provides. However, to use AC as an option to solve PAHs sediment contamination problem, one should bare in mind that AC doses and types used could be dependent on the total dissolved PAHs available in the system because too little doses might not give good results if dissolve concentration is too high (Zimmerman et al., 2005). On the other hands, if too much AC applied, AC can pose significant adverse impacts on aquatic organisms (Jonker et al., 2009).

For CTO-375°C and WOM, it can be concluded that WOM can be a very effective method for AC quantification because it is not only be able to preserve the most quantity of AC (up to 82% from this experiment) but it also extensively remove natural organic matter but one problem with this method is that some fraction of AC can be easily loss during decanting step.

6. Appendix

1. The table shows the average mass ratio of measured mass quantification (Qpom and Qw) and total mass used (Qtotal).
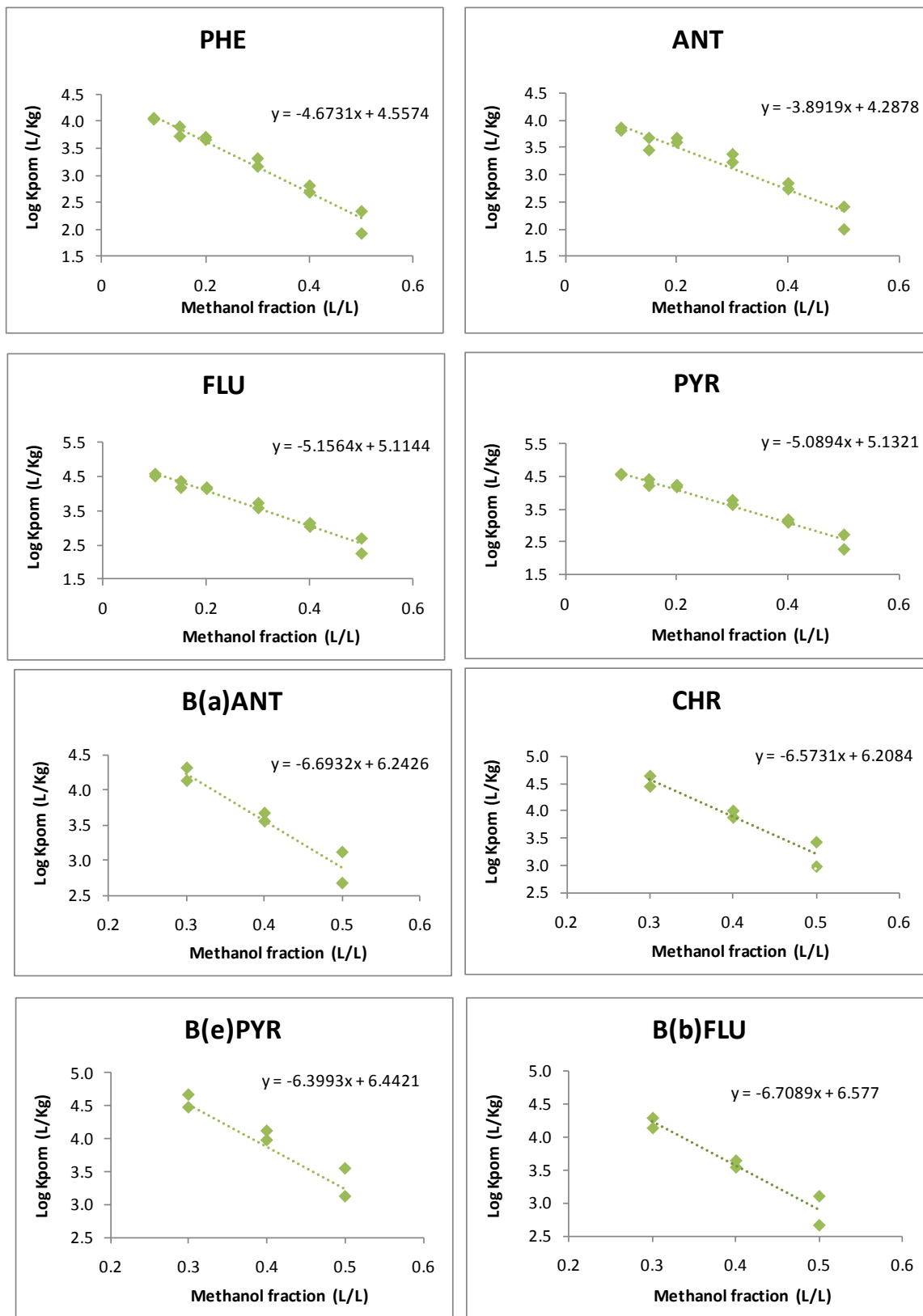
Compound	Volume methanol fraction (L/L)	Average mass ratio (Qpom +Qw) / Qtotal	Compound	Volume methanol fraction (L/L)	Average mass ratio (Qpom +Qw) / Qtotal
PHE	0	0.00044 (SD=0.00)	B(b) FLU	0	0.00024 (SD=0.00)
	0.1	0.63 (SD=0.10)		0.1	0.81 (SD=0.09)
	0.15	0.59 (SD=0.10)		0.15	0.74 (SD=0.18)
	0.2	0.65 (SD=0.01)		0.2	1.06 (SD=0.02)
	0.3	0.80 (SD=0.10)		0.3	1.16 (SD=0.23)
	0.4	0.67 (SD=0.07)		0.4	1.23 (SD=0.16)
	0.5	0.52 (SD=0.01)		0.5	1.05 (SD=0.39)
ANT	0	0.00036(SD=0.00)	B(k) FLU	0	0.00021 (SD=0.00)
	0.1	0.61 (SD=0.11)		0.1	0.54 (SD=0.08)
	0.15	0.56 (SD=0.10)		0.15	0.52 (SD=0.06)
	0.2	0.66 (SD=0.01)		0.2	0.63 (SD=0.00)
	0.3	0.85 (SD=0.12)		0.3	1.15 (SD=0.22)
	0.4	0.72 (SD=0.07)		0.4	1.23 (SD=0.15)
	0.5	0.56 (SD=0.00)		0.5	1.10 (SD=0.42)
FLU	0	0.00042 (SD=0.00)	B(a) PYR	0	0.00019 (SD=0.00)
	0.1	0.90 (SD=0.08)		0.1	0.66 (SD=0.08)
	0.15	0.77 (SD=0.21)		0.15	0.63 (SD=0.13)
	0.2	0.90 (SD=0.01)		0.2	0.83 (SD=0.01)
	0.3	1.01 (SD=0.18)		0.3	1.13 (SD=0.20)
	0.4	0.87 (SD=0.10)		0.4	1.22 (SD=0.16)
	0.5	0.65 (SD=0.08)		0.5	1.08 (SD=0.42)
PYR	0	0.00040 (SD=0.00)	B(ghi) PER	0	0.00025 (SD=0.00)
	0.1	0.86 (SD=0.11)		0.1	0.50 (SD=0.08)

	0.15	0.75 (SD=0.20)		0.15	0.50 (SD=0.04)
	0.2	0.88 (SD=0.01)		0.2	0.58 (SD=0.01)
	0.3	0.98 (SD=0.18)		0.3	1.10 (SD=0.20)
	0.4	0.88 (SD=0.10)		0.4	1.23 (SD=0.13)
	0.5	0.65 (SD=0.08)		0.5	1.19 (SD=0.48)
B(a)ANT	0	0.00024 (SD=0.00)	Db (ah) ANT	0	0.00023 (SD=0.00)
	0.1	0.69 (SD=0.09)		0.1	0.48 (SD=0.07)
	0.15	0.63 (SD=0.11)		0.15	0.47 (SD=0.07)
	0.2	0.81 (SD=0.00)		0.2	0.55 (SD=0.01)
	0.3	1.14 (SD=0.21)		0.3	1.10 (SD=0.18)
	0.4	1.13 (SD=0.13)		0.4	1.21 (SD=0.13)
	0.5	0.86 (SD=0.24)		0.5	1.20 (SD=0.48)
CHR	0	0.00024 (SD=0.00)	Ind (123) PYR	0	0.00017 (SD=0.00)
	0.1	0.54 (SD=0.08)		0.1	0.66 (SD=0.13)
	0.15	0.52 (SD=0.05)		0.15	0.62 (SD=0.10)
	0.2	0.60 (SD=0.01)		0.2	0.88 (SD=0.03)
	0.3	1.10 (SD=0.22)		0.3	1.04 (SD=0.22)
	0.4	1.10 (SD=0.14)		0.4	1.22 (SD=0.19)
	0.5	0.85 (SD=0.23)		0.5	1.21 (SD=0.49)
B(e) PYR	0	0.00027 (SD=0.00)			
	0.1	0.73 (SD=0.11)			
	0.15	0.68 (SD=0.11)			
	0.2	0.92 (SD=0.01)			
	0.3	1.30 (SD=0.24)			
	0.4	1.37 (SD=0.17)			
	0.5	1.15 (SD=0.43)			

2. The table shows the averaged recovery of concentration on POM (Cpom) and aqueous
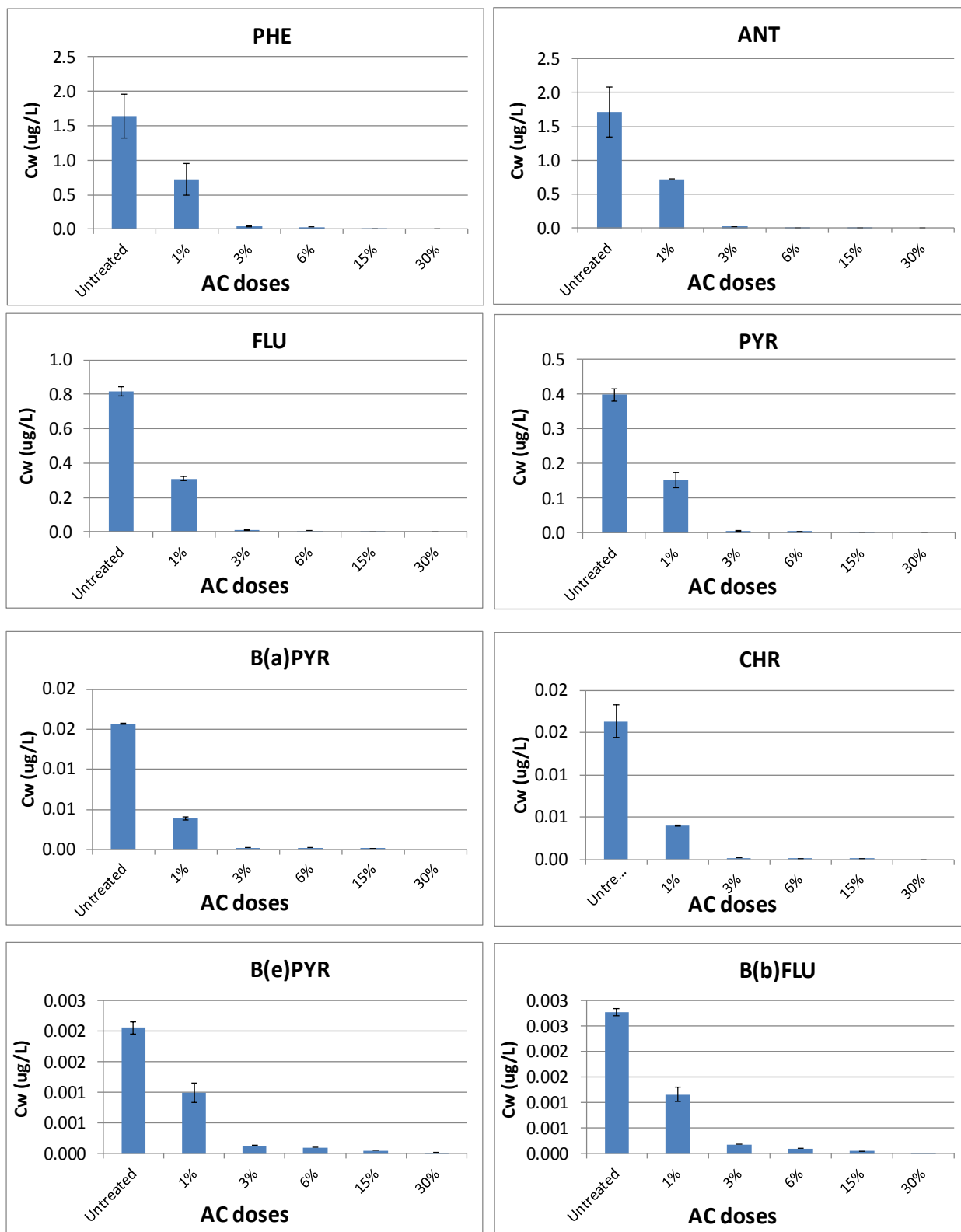   concentration (Cw) for quality assurance on extraction method.

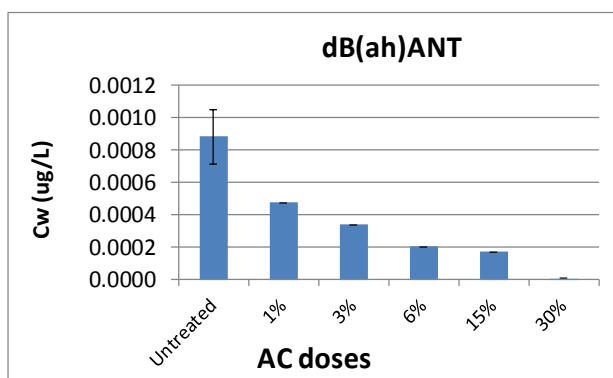| Compound | Recovery (Cpom and Cw) in % | | Compound | Recovery (Cpom and Cw) in % | |
	Cw	Cpom		Cw	Cpom
PHEN	146 (SD=54%)	69 (SD=8%)	B(b) FLU	109 (SD=4%)	112 (SD=17%)
ANT	143 (SD=52%)	70 (SD=7%)	B(k) FLU	106 (SD=4%)	108 (SD=16%)
FLU	127 (SD=31%)	86 (SD=10%)	B(a) PYR	104 (SD=5%)	111 (SD=15%)
PYR	123 (SD=29%)	86 (SD=8%)	B(ghi) PER	103 (SD=4%)	108 (SD=13%)
B(a)ANT	112 (SD=9%)	103 (SD=13%)	Db (ah) ANT	104 (SD=2%)	109 (SD=12%)
CHR	113 (SD=12%)	102 (SD=14%)	Ind (123) PYR	97 (SD=5%)	101 (SD=3%)
B(e) PYR	107 (SD=8%)	115 (SD=20%)			

3. Log linear relationship of Log Kpom as the function of methanol volume fraction of 13 tested compounds

PHE

$y = -4.6731x + 4.5574$

ANT

$y = -3.8919x + 4.2878$

FLU

$y = -5.1564x + 5.1144$

PYR

$y = -5.0894x + 5.1321$

B(a)ANT

$y = -6.6932x + 6.2426$

CHR

$y = -6.5731x + 6.2084$

B(e)PYR

$y = -6.3993x + 6.4421$

B(b)FLU

$y = -6.7089x + 6.577$

B(k)FLU

Log Kpom (L/Kg) vs Methanol fraction (L/L)

y = -6.2127x + 6.4689

B(a)PYR

Log Kpom (L/Kg) vs Methanol fraction (L/L)

y = -6.391x + 6.5108

B(ghi)PER

Log Kpom (L/Kg) vs Methanol fraction (L/L)

y = -3.6505x + 5.4052

dB(ah)ANT

Log Kpom (L/Kg) vs Methanol fraction (L/L)

y = -3.7556x + 5.5678

Ind(123)PYR

Log Kpom (L/Kg) vs Methanol fraction (L/L)

y = -4.3463x + 5.9177

4. PAHs aqueous reduction for individual compounds
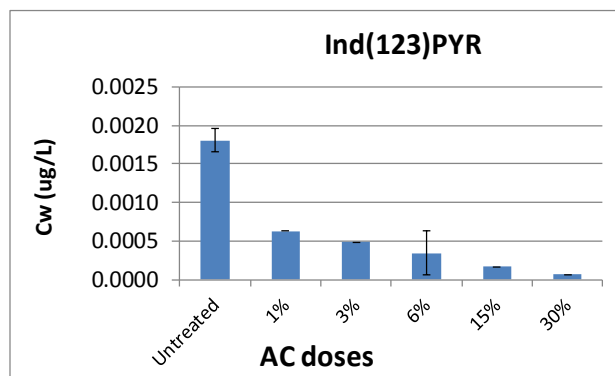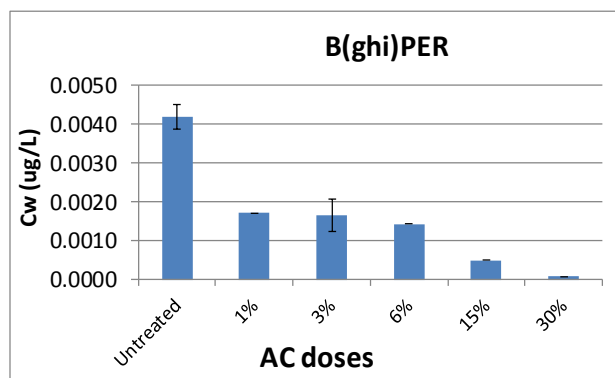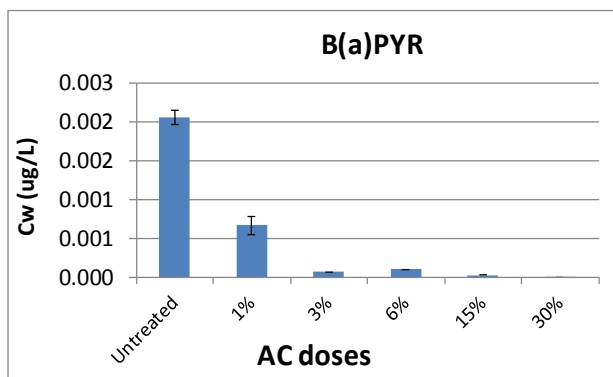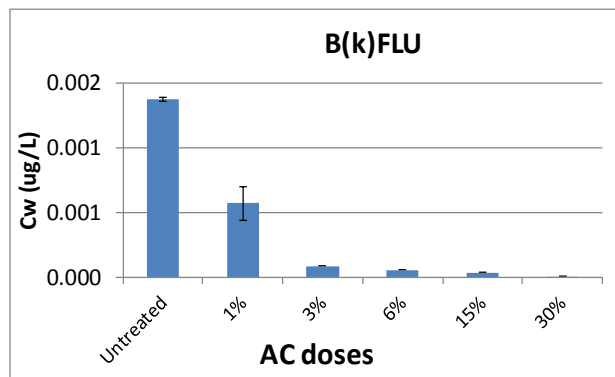
5. The table shows the comparison of CTO-375°C and WOM methods by basing on % of carbon quantified.

Samples	Methods	C analyzing (%)	Systems based on initial % AC				
			0	2	4	6	10
3m	CTO-375°C	TOC (%)	1.57	1.14	0.68	0.49	3.84
		%AC recovered	-	-	-	-	-
	WOM	TOC (%)	1.81	3.40	5.00	6.51	7.65
		%AC recovered	0	80	80	78	58
15	CTO-375°C	TOC (%)	0.23	1.05	1.19	2.02	4.07
		%AC recovered	-	-	-	-	-
	WOM	TOC (%)	2.08	3.64	5.38	5.27	5.51
		%AC recovered	0	78	82	53	34

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