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# DETERMINATION OF DISSOLVED CONCENTRATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN RIVER

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## ABSTRACT

This study shows the sensitivity of using silicone rubber passive sampler(SR-PS) andgas chromatography with mass spectrometer (GC-MS) detection for monitoring and identification of polycyclic aromatic hydrocarbons in surface water systems. The analysis was performed for eighteen PAHs compounds after pre-concentration using Soxhlet extraction method. By comparison, a total of 13 PAHs were detected in the spot water samples, of which none was quantifiable. The freely dissolved PAH concentrations were found to range from 0.17 ng/L to 0.76 ng/L at Ugieriver. The use of fluorine $d_{10}$ as Performance reference compound(PRC) gives a sampling rates of 8.14 (L/day) for silicone rubber passive samplers. Analysis of PAHs concentrations suggest the contaminants are mainly from pyrolytic sources. Overall it can be concluded that SR-PS are viable alternatives in the environmental monitoring of PAHs.

## 1. INTRODUCTION

The hydrosphere environment can be subjected to the input of dissolved organic and in-organic hazardous substances from a variety of sources, such as through atmospheric deposition, industrial and agricultural processes, sewage or industrial wastewater discharges, riverine inputs and poor environmental management (Emelogu et al 2013b). A great number of these pollutants tend to be persistent in the environment and are also often highly toxic to aquatic organisms and may ultimately be of concern to the consumer of these aquatic organisms (Emelogu et al 2012; Emelogu et al 2013a).

Sampling and analysis of surface waters for a broad range of environmentally relevant persistent pollutants like polycyclic aromatic hydrocarbons present significant analytical challenges, primarily as a result of low concentrations and incomplete phase separation between particle-bound and dissolved analytes (Smedes and Booij 2012). Until recently regulatory monitoring of water has generally relied on the collection and analysis of "spot" samples for total or dissolved pollutant concentrations. Such discrete sampling approaches can often provide an unrepresentative picture of temporal (e.g. seasonal variation) and spatial charges (point source discharges).Additionally environmental monitoring requires sensitive analytical methodologies that allow for detection of persistent pollutants in water biota and the water column itself.

Passive sampling (PS) is now internationally recognised as a promising technique in the area of contaminants analysis, where careful selection and deployment of appropriate passive sampling devices followed by targeted analysis can allow for the calculation of dissolved phase, time weighted, trace level water concentrations of a range of environmentally relevant pollutants (Vrana et al 2005; Kot-wasik et al 2005). Interest in passive sampling techniques for surface water monitoring to support legislative requirements, to track pollutant fate and to aid in toxicological/bioaccumulation studies continues to grow (Kot, Zabiegadla and Namiesnik 2000).

Water sampling for contaminant analysis can be completed by either direct or indirect means (with biomonitor/bioindicator organisms e.g. mussels). Currently, the most commonly used method for measuring levels of chemical pollutants in water is via the collection of discrete spot/grab/bottle samples, followed by extraction and instrumental analysis (Booij et al 2000). However the ongoing

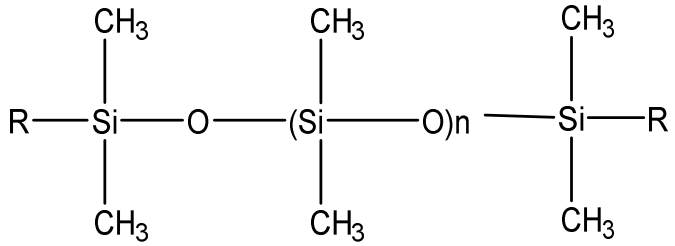
development of techniques such as passive sampling can provide a number of advantages over conventional techniques. According to Madrid and Zayas (2007), spot sampling can be carried out using three different options. Direct filling of sample bottle is applied to surface waters, dedicated water samplers are used for deep waters and use of peristaltic pumps for larger volume of water. Conventional sampling approaches often suffer from several limitations and are not appropriate for long-term monitoring of the presence of organic contaminants in water. This is because sample taken by snapshot may fail to identify temporal changes in contaminant and chemically liable volatile compounds can be altered during transport and storage of samples.

Passive sampling (PS) involves the measurement of analyte concentration as a weighted function of the time of sampling(the concentration of the analyte is integrated over the sampling period), as opposed to active sampling which involves the collection of samples at different time intervals using an external energy source (Kot, Zabiegba and Namiesnik 2000). Vrana et al (2005) defined PS in its broadest sense as any sampling technique based on free flow of analyte molecules from the sampled medium to a receiving phase in a sampling device. The main driving force and separation mechanism are based on the differences in analyte concentration between the two media. The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling period is completed (Gorecki and Namiesnik 2002).

In PS analytes are absorbed or adsorbed in/on a suitable medium within the passive sampler, known as a reference or receiving phase. This can be a solvent, chemical reagent or a porous adsorbent. The reference/receiving phase is then exposed to the water phase to "sample" the dissolved contaminants (Vrana et al. 2005). PS devices can be subsequently extracted in order to derive dissolved phase contaminant concentration information or "extracts" may be of use in biomarker exposure experiments.

Several passive sampling devices used for monitoring a range of substances have been developed. According to Smith and Booij (2012) water samplers for measuring hydrophobic pollutants are characterized into macro and micro ones. An example of micro samplers are solid-phase micro extractionextraction (SPME) and membrane enclosed sorptive coating (MESCO). Macro passive samplers are made from single organic polymer, for example; strips sampler made from low-density polyethylene (LDPE), polydimethylsiloxane (PDMS) or polyoxymethylene (POM). For monitoring of hydrophobic organic pollutants in water environment semi-permeable membrane devices (SPMDs), MESCO, Chemcatcher, Ceramic Dosimeters and Polar Organic Chemical Integrative Sampler (POCIS) are all documented (Hukins et al, 1993; Kingston et al, 2000; Vrana, Paschke and Popp, 2006).

Smedes (2007), suggested that any material with a non-polar structure can essentially function as a passive sampler (PS). Rusina et al (2007) also proposed that silicone rubbers can be used as reference phases for PS because of their high partition co-efficients and low transport resistances. Silicone rubber passive samplers consist of PDMS sheets, secured to a stainless steel frame. Figure 1 below shows the chemical structure of PDMS.




R= -OH or $CH_3$ and n= positive integer

**Figure 1: Chemical structure of the Polydimethylsiloxane (PDMS) polymer.**

Yates et al (2007) measured the silicone rubber-water partition co-efficients ($K_{sw}$) of a series of hydrophobic organic compounds (PCBs and PAHs), with octanol-water partition co-efficient (expressed as Log $K_{ow}$) values for the compounds studied ranging from 3.3 to 8.2 This confirmed that partitioning into the silicone rubber is strongly determined by compound hydrophobicity. This

in turn suggests that Log $K_{ow}$ is a good predictor of Log $K_{sw}$ and that absorption is the main mechanism for accumulation of analytes into the silicone rubber polymer.
The application of silicone rubber passive samplers for monitoring hydrophobic contaminants has been gaining importance in recent years. Freely dissolved concentration in environmental medium and sampling rates of added performance reference compounds (PRCs) can be determined using the sampler water partion co-efficient and concentration in the silicone rubber reference phase that equilibrates with the surrounding medium (Yates et al 2007; Meyer et al 2003; Huckins and Booij 2006).

## 2. MATERIALS AND METHODS

### 2.1 Materials

AlteSil$^{TM}$silicone rubber sheet manufactured from translucent, food grade silicone rubber (600 x 600 mm, 0.5 mm thick) obtained from Altec products, Ltd, Cornwall, UK. The analytical-reagent grade dichloromethane, methanol, ethyl acetate, acetone, Sodium sulphate, silica gel (all from Fischer scientific Ltd UK), *iso*-hexane (Rathburn chemicals Ltd, Scotland, UK) were chemicals used as solvents. A 200gmL$^{-1}$mixed PAH standard solution containing 16 PAHs compounds (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, benzo[*g,h,i*]perylene and dibenzo[*a,h*]anthracene) was purchased from sigma Aldrich, UK. PAH-Mix 31 containing five (5) deuteratedinternal standards (acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, naphthalene-$D_8$ chrysene-$d_{12}$ and perylene $d_{12}$) as well as Fluorene-$d_{10}$(usedas performance reference compounds during the spiking process) were obtained from QMX Laboratories, Essex, UK. A Gerhardt Soxtherm®system and Soxhlet® apparatus were used for the pre-extraction and deployed silicone strips extraction respectively whilst a Genevac evaporation unit was used for reducing the volumes of solvents.

### 2.2 Methods

#### 2.2.1 Preparation of Silicone rubber sampler

The silicone rubber sheet (0.5 mm thickness) was cut to the size of 6 x 4 cm pieces. Holes were made for mounting piece of sheet to the rim using a paper puncher. The prepared sheets were pre-extracted (Soxhlet extraction) with ethyl acetate using Gerhardt Soxtherm®system in order to remove any residues like oligomers, additives from silicone rubber production process or siloxanes which can be co-extracted with analyte and consequently interfere with the GC analysis either by coating the injection port or the liner or even the column leading to poor chromatographic separation.

150 mL ethyl acetate with anti-bumping granules in Gerhardt Soxhlet tubes was used to extract five (5) strips of silicone rubber sheets for four (4) hours. After cooling, the Silicone rubber strips were put in a wide mouth glass jar and 100 mL of methanol was added to the jar to rinse and remove the remains of ethyl acetate making it ready for spiking.

#### 2.2.2 Spiking of Silicone Rubber Sheets

The extracted silicone rubber strips were loaded with performance reference compounds (PRCs) according to the spiking method describes by Smedes and Booij et al (2012) and Yates et al (2007). Fluorene-$d_{10}$ and PCB mix90 were used as PRCs, although the PCB mix 90 was not analysed in this analysis due to time constraints. Consequently only fluorine-$d_{10}$will be taken as the PRC.

Briefly, 150 mL methanol was measured into a rinsed wide open mouth glass jar, and 1 mL of flourene-$d_{10}$ and PCB mix90 solution was added to the jar. Twenty seven (27) silicone rubber strips were added, the jar sealed and covered in foil to reduce PAH exposure to light, and placed on a shaker for two hours. After which, 37.5 mL water was added to obtain 80% methanol solution. The

strips were shaken for a further four hours and then 112.5 mL of water was added to obtain a 50% methanol solution. The strips were then shaken for twenty four hours before being transferred to a jar without any solution ready for site deployment.

### *2.2.3 Extraction of PAHs in Silicone Rubber Sampler*

The samplers were extracted following the procedure obtained from Booijet al 2012 and Yates et al 2013. Briefly the silicone rubber samplers were extracted using a soxhlet apparatus with 150 mL solvent of methanol in 500 mL round bottomed flasks; anti-bumping granules and 100 µL of deuterated PAHs-Mix 31 (100 ppm internal standard) were added to each flask. Both field and procedural blank silicone rubber strips were placed in separate Soxhlets column using long tweezers and the extraction process was allowed to proceed for six hours. The round bottom flasks were rinsed twice with *iso*-hexane to ensure all the extract was transferred. The extracts were subsequently stored in the fridge. The silicone rubber sheets were removed from extractor and weighed after cooling.

### *2.2.4 Extraction of PAHs in Water spot sample*

1 Litre of the sample collected from each site were measured and transferred to 1L separating funnel and then 50 mL and 100 µL of dichloromethane (DCM) and 100 ppm internal standard (deuterated PAHs) were added respectively and mixed. The mixture was allowed to settle on the stand for a while until two distinct layers were formed, and the bottom DCM layer collected. A further 50 mL of DCM was added to the water sample, extracted as before and the DCM fraction combined with the previous extract and stored at $4^0$C.

### *2.2.5 Clean-up procedure for extract*

The stored extracts obtained from spot water samples and silicone rubber samplers were removed from the fridge and allowed to warm to room temperature before being reduced to approximately 2 mL using the Genevac® evaporator.10 mL of *iso*-hexane was subsequently added to the extracts obtained from silicone rubber strips and reduced to about 2 mL by heating in water bath (repeated until no distinct layers), to evaporate or replace methanol. Approximately 2 mL of *iso*-hexane extract was obtained.

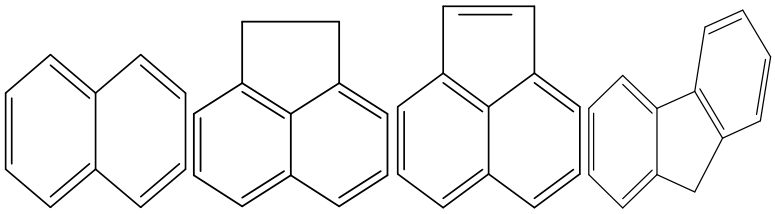
Both the water and silicone rubber sampler extracts were cleaned up by passing through a glass column containing silica gel using 1:3 v/v DCM :iso-hexane as elution solvent. 50 mL of eluent were collected and reduced to approximately 2 mL using the Genevac® evaporator syatem. The extract was transferred to a labelled GC vial and reduced to about 1 mL using the nitrogen blow-down apparatus ready for GCMS analysis.

## 2.3 Methods

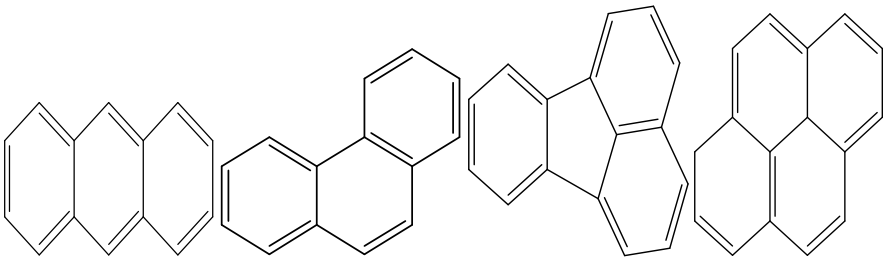
### *2.3.1 GC-MS Instrumentation*

The gas-chromatograph coupled with mass spectrometer (Shimadzu model GCMSQP2010) was used to carry out the PAHs analysis of the samples. The data obtained were acquired with instrument operating in selected ion monitoring (SIM) mode which allows quick identification and quantification of the selected ions.

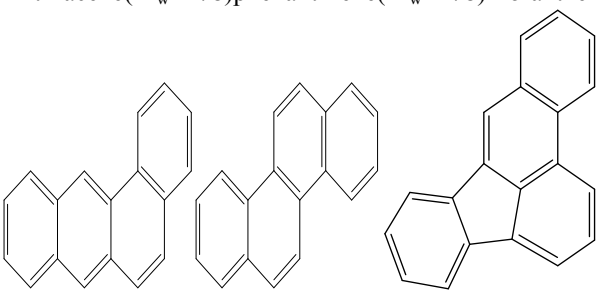
The GC used was equipped with a non-polar fused silica capillary column SLV - 5 MS (30m x 0.25 id x 0.25 µm) from Supelco (Milano, Italy). Ultra-pure (99.999%) helium is used as a carrier gas with column flow rate of 1.00 mL/min. The samples extracts are injected using the splitless mode. The injector and oven temperatures were maintained at 280 $^0$C and 40 $^0$C respectively. The GC oven temperature program was: $40^0$C (held for 12 min), ramped to $100^0$C at 35 $^0$Cmin$^{-1}$, followed by a ramp at $15^0$Cmin$^{-1}$ to $200^0$C (held for 3 min), and finally ramped at $10^0$Cmin$^{-1}$ to $300^0$C (held for 12min). The coupled mass spectrometer (quadrupole detector) operates with interface and ion source temperatures of $250^o$C and $200^0$C respectively. Apart from internal standards used the ions that will be monitored in this study were as follows:



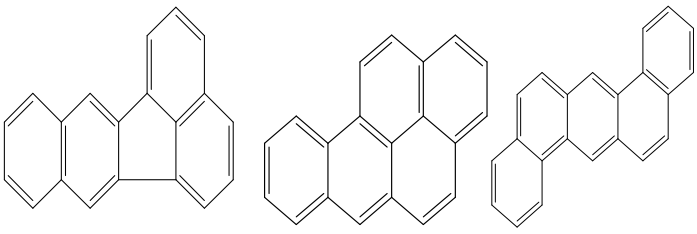
Naphthalene($M_w$=128)acenaphthene($M_w$=152) acenaphthylene($M_w$=153)Fluorine ($M_w$=166)



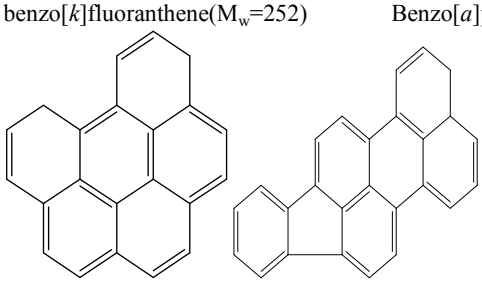
Anthracene($M_w$=178)phenanthrene($M_w$=178)Floranthene($M_w$=202)pyrene($M_w$=202)



benzo[*a*]anthracene($M_w$=228) Chrysene($M_w$=228) benzo[*b*]fluoranthene($M_w$=252)



benzo[*k*]fluoranthene($M_w$=252) Benzo[*a*]pyrene($M_w$ 252) dibenzo[*a,h*]anthracene($M_w$ 278)



benzo[*g,h,i*]peryrelene($M_w$ 276) Indeno[1,2,3-*c,d*]pyrene($M_w$ 276)

### 2.3.2 Sample Analysis (GC-MS)

The vials containing sample extractswere placedon GCMS auto-sampler tray for analysis. The instrument with instrumentation set-up described in section 2.3.1 above was set on to run the samples.

The GC-MS was calibrated using 0.5 – 10 ppm mixed PAH standards each containing 0.5 ppm of the PAH deuterated internal standard mix. Identification of the components of the standard and sample mixture was carried out by matching the specific mass to charge ion and retention time for each PAH component in the mixture with those of pure components analysed under the same experimental conditions**.** Also a calibration check was carried out to monitor the reliability of the calibration and confirm the retention time running any batch of samples.

## 2.4 Estimation of Freely Dissolved PAHs Concentrations

Three methodologies were utilised in order to convert analytical data to comparable basis i.e. PAH (ng/L).Dissolved water concentrations ($C_w$) were determined for sites using direct analysis of the water spot samples and Passive sampler derived $C_w$, using sampling rates ($R_S$).

### 2.4.1 Direct Analysis of the Water Spot Samples

Direct analysis of the concentrations of freely dissolved contaminants was performed on unfiltered spot water samples obtained from Bridge of Buthlaw, Bridge at Mill of Gaval and Bridge of Inverugie. Monthly collection of samples from the site was carried out for six (6) months and quantified for PAHs.

### 2.4.2 Analysis of Silicone Rubber sampler

In order to ultimately yield an estimate of the freely dissolved aqueous-phase concentrations ($C_w$) from the passive sampling membranes, a number of data conversions and calculations are required. This is achieved through the following stepwise process:-

- Assessment of appropriate PRCs.
- Calculation of the Passive Sampler Sampling Rate ($R_S$).
- Conversion of PS membrane data into water concentrations.

#### *2.4.2.1 Assessment of appropriate PRCs*

The sampling rate ($R_S$) can be simply described as the equivalent spot sample water volume that is sampled during a given time period. The sampling rate for each analyte was determined using the dissipation rate of a performance reference compound that was spiked onto the sampler prior to deployment. For the purpose of this work, the PRC elimination constant ($K_e$) was calculated using the dissipation rate of fluorene-$d_{10}$ using equation 1 below;

$$K_e(day^{-1}) = -\ln(C_t/C_o)/t \qquad \text{eqn.1}$$

Where$K_e$is the elimination constant of PRC, $C_t$ and $C_o$ are the concentrations of PRC at the time of retrieval and prior to deployment respectively and *t* is the deployment period (days).
On the basis of examination of the site specific datasets from James Huttons Institute and literature comparison, a number of PRCs were found to be suitable internal standard for PAHs use (Yates et al 2007 and Smedes et al 2007). In order to complete the process of the estimation of the sampling rate for this study, fluorine-$d_{10}$ was chosen as it is depleted to a measurable extent during the exposure period.

#### *2.4.2.2 Sampling Rates Estimation*

In order to determine freely dissolved concentrations of contaminants, the calculated PRC elimination constant ($K_e$) was used to estimate sampling rate for the specific compound. Estimation of the sampling rate is effectively a measure of the degree of similarity between the PRCs in the original membranes (100 %) and the remaining in the membranes after the exposure study. The sampling rate for the PRC in the sampler was calculated using the equation 2 below

$$R_{s\,(PRC)} = K_e * M_s * K_{sw}(L/day) \qquad \text{eqn. 2}$$

Where$K_{sw}$ is the sampler-water partition coefficient (L/kg) and $M_s$ (kg) is the mass of the sampler used.

#### *2.4.2.3 Conversion of Passive Sampling Membrane Data into Water Concentration*

For estimation of the freely dissolved concentration ($C_w$) in the water phase the full uptake model valid for equilibrium and non-equilibrium situations is applied. The uptake is described by the equation 3 obtained from Smedes et al (2009):

$$N^t=N^\infty(1-\exp(R_s*t/M_s*K_{sw})) \quad \text{eqn. 3}$$

Where:
$N^t$is the amount of compound (ng) in the sampler after deployment for time (in days), $N^\infty$ is the final amount taken up in the equilibrium situation,
$R_S$ the sampling rate (L/d), tthe exposure time (d), $M_s$the mass of the sampler (kg), and $K_{sw}$is the silicone rubber-water partition co-efficient.

The final amount taken up in the equilibrium situation ($N^\infty$) equals the equilibrium concentration ($Cs^\infty$) times the mass of the sampler ($M_s$) in kg. $C_s^\infty$ is related to $C_w$ by the partition coefficient $K_{sw}$ (L/kg) and consequently:

$$N^\infty=M_s*C_s^\infty=M_s*C_w*K_{sw} \quad \text{eqn. 4}$$

And therefore,

$$C_w=N^\infty/(M_s*K_{sw}) \quad \text{eqn.5}$$

By combining eqn.4and eqn.5, the freely dissolved water concentrations ($C_w$) in ng/L were determined by means of the following equation:

$$C_w = (N^t/(m*K_{sw}))*(1/(1-\exp-(R_s*t)/(m*K_{sw})) \ (ng/L) \quad \text{eqn. 6}$$

In order to calculate $C_w$, silicone membrane specific partition constants ($K_{sw}$) for PRC are required. These $K_{sw}$ co-efficient were obtained in either of two ways; that is by utilising the $K_{sw}$values available in the literature or by using the estimated (modelled) available literature data. $K_{sw}$value for the PRC used (fluorine-$d_{10}$) was obtained from Smedes (2007).

## 3. RESULTS AND DISCUSSION

### 3.1 Sampling Rates, $R_s$

The sampling rate of silicone rubber sampler deployed at Bridge of inverugie was calculated to be 8.41(L/day) using Fluorene-$d_{10}$ PRC dissipation (table 1). The data obtained from the PRC dissipation (a low $k_{sw}$ compound; fluorene-$d_{10}$) indicate that there is relatively slow kinetics transfer of the analytes during the exposure time. A minimum concentration of 32% was recovered when compared to un-deployed spiked silicone rubber sheets.

**Table 1: Showing the sampler weight, concentration and sampling rate of the site.**

| Site Name | Sampler weight (g) | Concentration of fluorene-$d_{10}$ (µg/g) | $R_s$ (L/day) |
|---|---|---|---|
| Bridge of Inverugie | 27.9030 | 0.52 | 8.14 |

### 3.2 Freely dissolved PAHs concentrations

#### 3.2.1 Spot water concentrations

The mean concentrations of PAHs analytes obtained from the analysis of spot water samples collected from the sites every 4 weeks covering the period from 03/12/2013 to 28/04/2014 was presented in table 2 below. The concentrations were found to be below the limit of detection and limit of quantification (see appendix for LODs and LOQs values).This shows that all the PAHs were below the limit of detection. Thus, the analysis of PAHs using spot sampling methodologies is not reliable.

**Table 2: Mean water concentrations of PAHs (pg/L) of six different spot water sampling of the sites.**

| | Concentration (pg/L) | | |
|---|---|---|---|
| **PAHs** | **Bridge of Buthlaw** | **Bridge at Mill of Gaval** | **Bridge of Inverugie** |
| Naphthalene | 38.1 | 1.8 | 27.4 |
| 1-Methyl Naphthalene | 6.0 | 2.1 | 3.6 |
| 2-Methyl Naphthalene | 6.1 | ND | 5.1 |
| Acenaphthylene | 0.9 | 0.7 | 5.9 |
| Acenaphthene | 11.4 | 10.6 | 12.1 |
| Fluorene | 8.4 | 4.9 | 8.7 |
| Phenanthrene | 5.6 | 3.7 | 4.1 |
| Anthracene | 8.1 | 5.6 | 6.0 |
| Fluoranthene | 5.4 | 4.4 | 5.1 |
| Pyrene | 3.0 | 2.8 | 3.4 |
| Benz[*a*]anthracene | 6.0 | 5.9 | 6.2 |
| Chrysene | ND | ND | ND |
| Benzo[*b*]fluoranthene | 7.5 | 7.8 | 7.9 |
| Benzo[*k*]fluoranthene | ND | ND | ND |
| Benzo[*a*]pyrene | 6.0 | 6.0 | 6.2 |
| Benzoperylene | ND | ND | ND |

ND= Not detected

### 3.2.2 Silicone rubber sampler derived water concentrations

The freely dissolved concentration of PAHs obtained from the sampler deployed at Bridge of Inverugie for period of 63 days is given in table 3 below. Due to the analytes lost that was encountered during evaporation step in the preparation stage, freely dissolved concentrations of PAHs analytes of site 1 (Bridge of Buthlaw) and site 8 (Bridge at Mill of Gaval) was not reported. Therefore, no comparison can be made with the spot sampling data of those sites.

**Table3.5: Showing the freely dissolved concentration of PAHs obtained from silicone rubber passive sampling of Bridge of Inverugie.**

| **PAHs** | **Cw (ng/L)** | |
|---|---|---|
| Naphthalene | 0.76 | BDL |
| 1-Methyl Naphthalene | 0.21 | BDL |
| 2-Methyl Naphthalene | 0.17 | BDL |
| Acenaphthylene | 0.11 | BDL |
| Acenaphthene | 0.26 | BDL |
| Fluorene | 0.33 | BDL |
| Phenanthrene | 0.61 | BDL |
| Anthracene | 0.08 | BDL |
| Fluoranthene | 0.49 | BDL |
| Pyrene | 0.40 | BDL |
| Benz[**a**]anthracene | 0.04 | BDL |
| Chrysene | 0.07 | BDL |
| Benzo[*b*]fluoranthene | 0.05 | BDL |
| Benzo[*k*]fluoranthene | 0.01 | BDL |
| Benzo[*a*]pyrene | 0.05 | BDL |
| Benzoperylene | ND | ND |

ND= not detected,
BDL= below detection limit

Table 3.5 shows that using silicone rubber passive sampling method, 15 of 16 US-EPA PAHs compounds were detected with concentration ranging from 0.01 to 0.76 ng/L with naphthalene having the highest concentration. Although the silicone rubber sampler gives concentrations of PAHs analytes higher than that obtained from spot water sampling method, the concentration of the analytes were below the detection limit both in water and silicone rubber sampler see appendix**.**
Generally, the dissolved concentration of PAHs found in Ugie catchment was very low. From the result obtained, it is evident that low molecular weight PAHs (2- and 3-rings) were the most abundant while the high molecular weight (4-6-ring) was very little or not present. Also, the results indicate that PAHs in Ugie water were within the allowableconcentration.
The likely source of these PAHs can be identified by plotting the concentrations of the PAH ratios (Webster et al 2004). When ratio of fluoranthene and pyrene was calculated; greater than 1(>1) is an indicative of pyrolytic source of PAHs while less than 1 (<1) indicates the petrogenic sources. From the silicone rubber passive sampler result, the fluoranthene/pyrene ratio was >1 and this give an insight that the source of PAHs found in Ugie catchment was most likely pyrolytic which may be from incomplete combustion of organic materials, combustion of fossil fuels, coal and peat, from incineration of agricultural, industrial or municipal waste.

## 4. CONCLUSION

Freely dissolved concentrations of PAHs in Ugie water were successfully determined using SR-PS devices. The study shows the sensitivity of silicone rubber passive sampling over conventional spot water sampling for identification of polycyclic aromatic hydrocarbons in surface water systems. The freely dissolved PAH concentrations of SR-PS were found to be higher than that found in spot samples.

The PRC derived in situ sampling rates of 8.14 (L/day) for silicone rubber passive samplers were observed. Analysis of PRC compound (fluorene-$d_{10}$) shows that there is slow kinetic exchange between the sampled analyte and PRC compound. Low kinetic exchange can be influenced by a number of variables including hydrodynamic, fouling, and salinity which suggest the sampling rates of the exposure site.

The result presented shows that the un-quantified PAHs entering the river of Ugie catchment may be as results of agricultural and related land use practices or atmospheric depletion of incomplete combustion of fuel. Due to the loss of internal standard in the processing stage, it becomes difficult to compare south and north Ugie water so as to identify the source of these PAHs compound detected.

Going by the EU water Framework Directive (2000/60/EC) on priority and hazardous substances the concentration of PAHs compound found by SR-PS device in this study was within the tolerable limit for short and long term exposure. Thus, it can be concluded that use of SR-PS devices in monitoring organic contaminant like PAHs was a viable alternative to conventional spot water sampling method.

### 4.2 Recommendation for Further Analysis

During this study it has become evident that there are a number of areas in which it could proceed. Future studies should focus on:

• Performing a larger study combining passive samplers (in appropriate areas) to further illustrate the effectiveness of the samplers as environmental monitors and begin a database for freely dissolved concentrations of contaminants of interest.
• Investigating which other contaminants may be taken up by the silicone rubber passive samplers; these might include other hydrophobic contaminants which have log $K_{ow}$ ranges between 3 and 8, such as pesticides and herbicides.
• Look at seasonal changes and how they affect freely dissolved contaminant concentrations.
• Investigate the effect of variables such as hydrodynamics and salinity on sampling rates.

## Appendix 1

**Table 3.2: Showing the equation of the line, $r^2$ value, and LOD & LOQ (ng/L) of 16 PAHs compounds.**

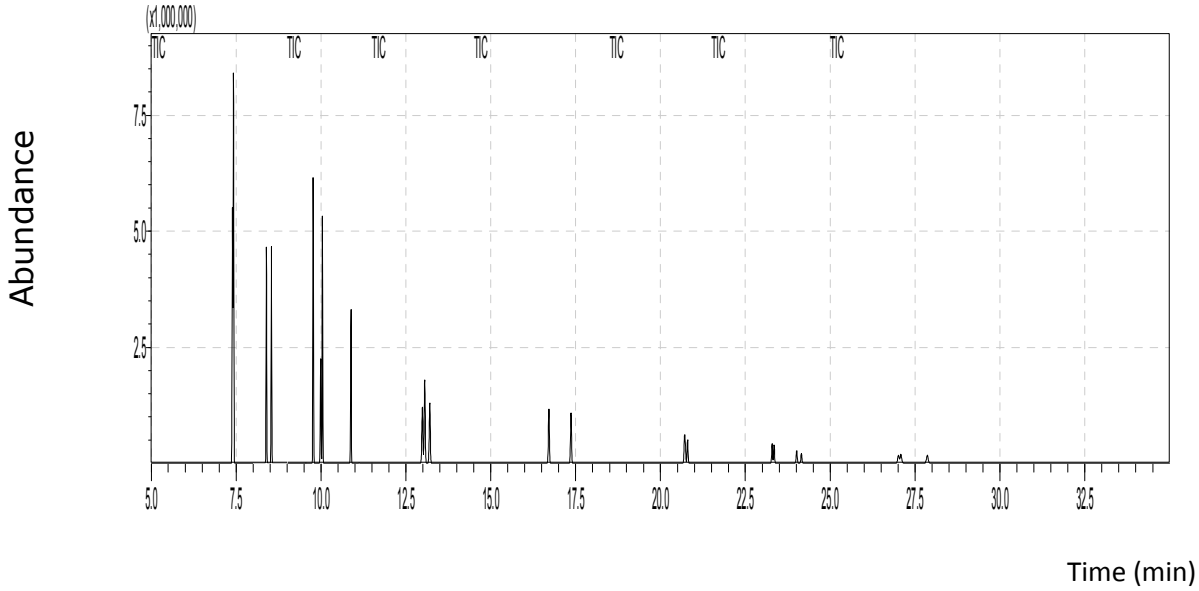
| PAHs | EQUATION OF LINE | R Square | LOD | LOQ | LOD SR sampler | No of point used | Int. std used |
|---|---|---|---|---|---|---|---|
| **Naphthalene** | Y = 0.1348X + 0.0601 | 0.9991 | 310 | 1040 | 3.29 | 5 | Naphthalene-$D_{10}$ |
| **2-Methylnaphthalene** | Y = 0.0713X - 0.0031 | 0.9999 | 120 | 410 | 0.51 | 5 | Naphthalene-$D_{10}$ |
| **1-Methylnaphthalene** | Y = 0.0731X + 0.0104 | 0.9999 | 120 | 410 | 0.46 | 5 | Naphthalene-$D_{10}$ |
| **Acenaphthylene** | Y = 0.2169X - 0.0185 | 0.9999 | 140 | 470 | 2.03 | 5 | Acenaphthene-$D_{10}$ |
| **Acenaphthene** | Y = 0.1482X - 0.1539 | 0.9935 | 1030 | 3420 | 5.69 | 4 | Acenaphthene-$D_{10}$ |
| **Fluorene** | Y = 0.1244X - 0.0511 | 0.9982 | 450 | 1500 | 2.28 | 5 | Acenaphthene-$D_{10}$ |
| **Phenanthrene** | Y = 0.1505X - 0.0280 | 0.9917 | 1200 | 4010 | 3.99 | 6 | Phenanthrene-$D_{10}$ |
| **Anthracene** | Y = 0.1098X - 0.0328 | 0.998 | 480 | 1590 | 1.39 | 5 | Phenanthrene-$D_{10}$ |
| **Fluoranthene** | Y = 0.0744X - 0.0259 | 0.9968 | 600 | 1980 | 1.55 | 5 | Phenanthrene-$D_{10}$ |
| **Pyrene** | Y = 0.0702X - 0.0190 | 0.9949 | 710 | 2380 | 1.79 | 6 | Phenanthrene-$D_{10}$ |
| **Benz[*a*]anthracene** | Y = 0.1174X - 0.0674 | 0.9983 | 440 | 1450 | 0.86 | 5 | Chrysene-$D_{12}$ |
| **Chrysene** | Y = 0.1331X + 0.0924 | 0.9992 | 370 | 1220 | 0.74 | 4 | Chrysene-$D_{12}$ |
| **Benzo[*b*]fluoranthene** | Y = 0.1504X - 0.1073 | 0.9937 | 1160 | 3110 | 2.20 | 5 | perylene-$D_{12}$ |
| **Benzo[*k*]fluoranthene** | Y = 0.1853X + 0.1757 | 0.9969 | 590 | 1960 | 1.12 | 5 | perylene-$D_{12}$ |
| **Benzo[*a*]pyrene** | Y = 0.1279X - 0.0731 | 0.9942 | 810 | 2690 | 1.54 | 5 | perylene-$D_{12}$ |
| **Benzo[*ghi*]perylene** | Y = 0.1153X + 0.0158 | 0.9982 | 530 | 1800 | 1.00 | 4 | perylene-$D_{12}$ |

indeno[1,2,3-*cd*]pyrene and dibenzo[*a,h*]anthracene were not reported because of their poor calibration observed during the analyses ($r^2 < 0.99$).

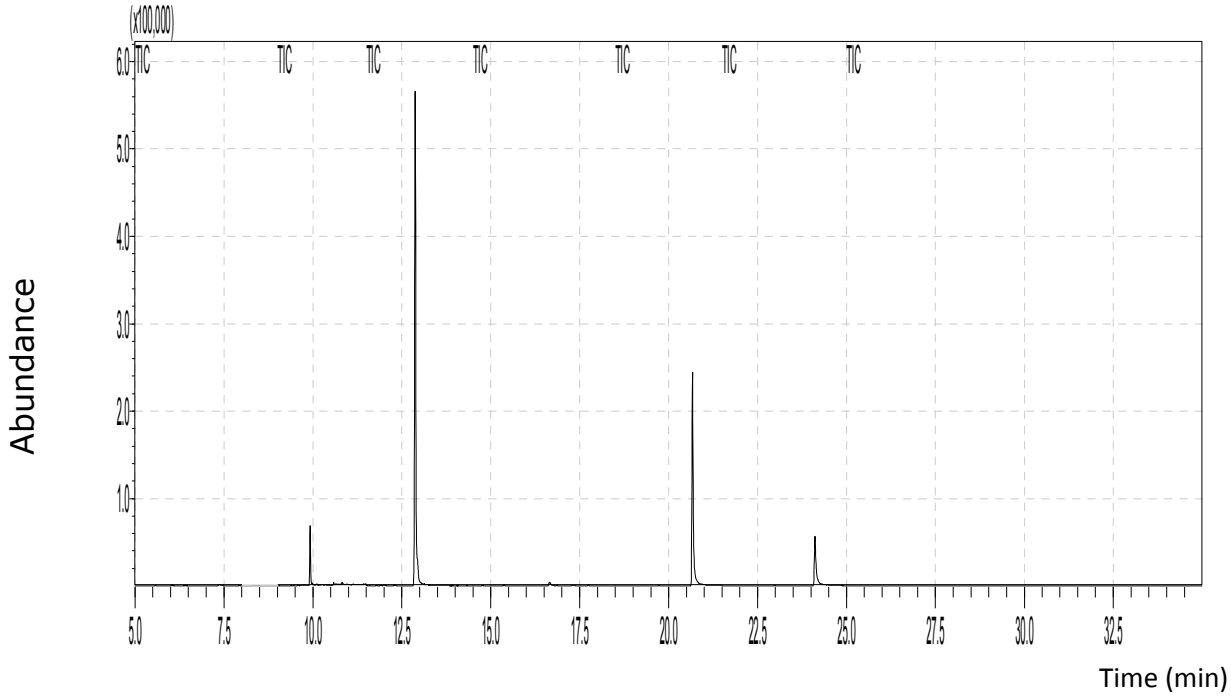
**Appendix 2**

Typical Chromatograms

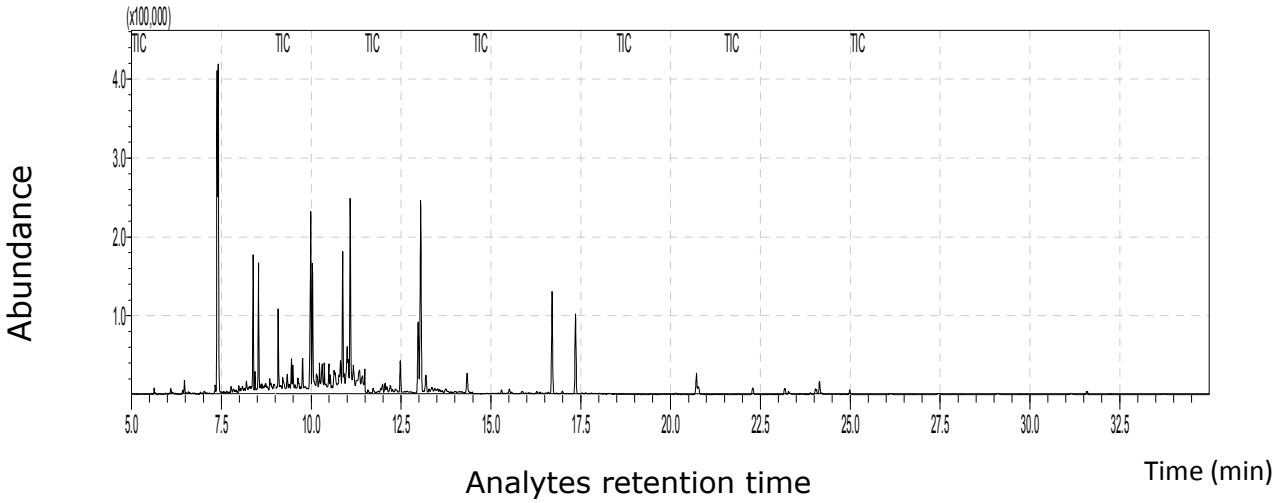
Calcheck Chromatogram (5ppm)




SAMPLE 1160748 (BRIDGE OF INVERUGIE WATER SAMPLE)




SR 1160748(BRIDGE OF INVERUGIE SILICONE RUBBER)




Analytes retention time

| Analyte | Ret. Time |
|---|---|
| Naphthalene-D8 | 7.38 |
| Naphthalene | 7.41 |
| 2-Methylnaphthalene | 8.38 |
| 1-Methylnaphthalene | 8.53 |
| Acenaphthylene | 9.76 |
| Acenaphthene-D10 | 9.98 |
| Acenaphthene | 10.04 |
| Fluorene-D10 | 10.82 |
| Fluorene | 10.87 |
| Phenanthrene-D10 | 12.98 |
| Phenanthrene | 13.05 |
| Anthracene | 13.19 |
| Fluoranthene | 16.70 |
| Fluoranthene-D10 | 16.91 |
| Pyrene | 17.36 |
| Benz[a]anthracene | 20.69 |
| Chrysene-D12 | 20.72 |
| Chrysene | 20.77 |
| Benzo[b]fluoranthene | 23.18 |
| Benzo[k]fluoranthene | 23.28 |
| Benzo[a]pyrene | 24.03 |
| Perylene-D12 | 24.14 |
| Indenopyrene | 27.01 |
| Dibenz[a,h]anthracene | 27.46 |
| Benzo[ghi]perylene | 27.86 |

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