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Surface Water Quality: Occurrence and Determination of Bisphenol A in Sungai Langat

J.Karim, M.A.M.Idrus, N.H.F.Hashim,, M.Abdullah,, S.S.Sharifuddin, M.F.Muhazeli, M.A.M.Yusof, R.T.Gunggang M.F.Abdullah, H.Jamaluddin, and N.S.Abdullah
Water Quality Laboratory, National Research Institute of Malaysia (NAHRIM),
Lot 5377, Jalan Putra Permai, 43300 Seri Kembangan, Selangor, Malaysia.

Abstract: Rivers as surface water in Malaysia are recipients of effluents and wastewater and yet it is important water source for daily uses of some villagers living along the river. Endocrine disruptors such as Bisphenol A (BPA) can be found in river due to continuous discharge into it. The objectives of this research is to find out the occurrence and concentration of BPA in Sungai Langat and also to see how water quality parameters such as temperature, pH, dissolved oxygen (DO), turbidity, Total Suspended Solid (TSS), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and ammonia nitrogen (AN) affecting the concentration of BPA. 12 stations in total including upstream to downstream of Sungai Langat and also tributary of Sungai Langat. The instrument used to find out concentration of BPA is Triple Quadrupole LC/MS. The source of BPA are mainly industrial effluents and also direct domestic discharges. The water quality parameters that will affect concentration of BPA are Ammonia Nitrogen (AN), turbidity, Biochemical Oxygen Demand (BOD), Total Suspended Solid (TSS), and Chemical Oxygen Demand (COD), Dissolved Oxygen (DO). While pH and water temperature are also factors that will affect concentration of BPA but the significance is not shown in the analysis. It can be concluded that upstream of Sungai Langat has lower concentration of BPA than downstream.

Key words: Endocrine disruptors, Surface water, Bisphenol A, water quality parameter,

INTRODUCTION

Emerging evidence from wildlife and laboratory studies indicates that some chemicals may interfere with the endocrine system. Compounds identified as endocrine-disrupting chemicals (EDCs) include pesticides, polychlorinated biphenyls (PCBs), dioxins, furans, alkyl phenols, and steroid hormones (natural and synthetic). The steroid hormones are of special concern due to their potency. The natural sex hormone estradiol and its metabolites (estrone and estriol) and the synthetic steroid ethinylestradiol are excreted in the urine of mammals and can be found in surface and ground waters. Other EDCs, such as the alkylphenols–nonylphenol, bisphenol A and pentachlorophenol are derived from industrial and domestic activities and also occur in environmental waters [1-7]. Bisphenol A (BPA) is a chemical that has been attracting increased attention because of its high potential for human exposure. Bisphenol A (BPA) is used as the base compound in the manufacture of plastics [1]. It is also used in multitude of products including food and beverage packaging, flame retardants, adhesives, building materials, electronic components, and paper coatings [8]. Worldwide, over 6 billion pounds of BPA are produced each year and over 100 tons are released into the air annually [1]. BPA has been shown to leach from food and beverage containers (via hydrolysis of polycarbonate plastics and epoxy resins) [9], dental sealants and composites [10] under normal conditions of use [5], these have been the major sources of human exposure. While the source for human exposure to BPA is food and liquid storage containers, BPA is released into the environment through either sewage treatment effluent (via human-ingested BPA being eliminated through sewage; [11]), landfill leachates (via hydrolysis of BPA from plastics; [12]), or natural degradation of

Corresponding Author: Jamilah Karim, Research Officer, Water Quality Laboratory, National Research Institute of Malaysia (NAHRIM), Lot 5377, Jalan Putra Permai, 43300 Seri Kembangan, Selangor, Malaysia., 603-89476482

polycarbonate plastics. While sewage effluent and landfill leachates are point sources of BPA in the environment, fragments of epoxy resins and polycarbonate plastic debris entering the watershed through runoff are non-point sources. The Sungai Langat Basin is one of the most populated river basins in Malaysia. As a result, it is surrounded by various environmental stresses of which agricultural activity is a dominant cause. For this study, concentration measurement and correlation of Bisphenol A and water quality index parameter were determined.

EXPERIMENT

Water Samplling

The Sungai Langat Basin occupies three distinct areas of the Putrajaya Federal Territory, the southern part of Selangor State and the northern part of Negeri Sembilan State. The basin catchment area is approximately 1815 square kilometres (km2) and lies between latitudes 2º40˙152''N–3º16'15''N and longitudes 101º19'10''E–102º1'10''E. The basin contains three topographical types: a lowland area, a hilly area and a mountainous area ([13],[14]). Swamps also exist along the river. In general, the topography of the basin is flat in the west, and from hilly to mountainous in the east and the north. More than half of the catchment is categorised as 'steepland'. The basin has three major tributaries: the Sungai Langat, the Semenyih River and the Labu River. The main river in the basin, the Sungai Langat, is 141 kilometres (km) long. It flows from the high hills in the north towards the flat west, turns westward towards the coast in the state of Selangor and ends in two estuaries: the Melacca Strait and Lumut Strait. The Melacca Strait is situated to the north of the Lumut Strait. The Sungai Langat Basin acts as a catchment area supporting approximately 1.2 million people. There are two major impoundments (the Langat Dam and Semenyih Dam) and eight water treatment plants that supply water to the entire basin.

The surface water samples from 12 locations were collected using 250 mL amber glass bottles and avoiding the immediate vicinity of wastewater (industrial/domestic) discharge point. Then they were immediately transported in cold condition to the laboratory and stored at 4^{O}C until chemical extraction. Water quality index parameter were also measured for all 12 locations as per Figure 1.

Quality Assurance and Quality Control

All analytical procedures were monitored under quality assurance and quality control measures. Duplicate and a standard quality control were measured to assure accurate result will be presented by the instrument.

Reagents and Solutions

BPA standard 4,4'-Isopropylidenediphenol 97% was pruchased from Acros Organics. Meanwhile HPLC grade ammonium acetate, methanol, acetonitrile were purchased from Fisher Scientific. Ultra pure water (UPW) used must be 18.2 MΩ resistivity.

Standard Preparation

The stock solutions of BPA were prepared by dissolving 10 mg of each chemical in 10 mL methanol. Working solutions for calibration and recovery check were prepared by diluting the stock solutions at required concentrations in methanol and water. All the standards were stored at -20ºC.

Sample Extraction

All surface water were centrifuged and filter. Sample were mix with methanol in 1ml vial before inject to the LC MS/MS.

Instrument

Identification of peak concentrations was made by means of a chromatogram of a standard solution of each compound. BPA was identified by respective retention time and peak area. Optimum condition to indentified and quantified Bisphenol A are as per Table 1.

Table 1.Chromatographic conditions for Bisphenol A

Instrument High-Performance Agilent 6470A Triple Quadrupole LC/MS	
Analytical Column:	Zorbax Eclipse Plus C18 2.1x50mm,1.8um
Guard Column	:Infinity In-line filter with 0.3um SS frit
Injection volume	:10 uL
Mobile phase	:A= UPW +5mM ammonium acetate B=(90% CAN + 10% UPW)+ 5mM ammonium acetate
Run time	: 6.4 min + 1.5 min post time
Flow rate	: 0.4 ml/min

Water Quality Analysis

All 12 locations were also measured for water quality analysis such as pH, Turbidity, Total Suspended Solids (TSS), Ammoniacal Nitrogen (AN), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO).

RESULT AND DISCUSSION

Bisphenol A in surface water

BPA compound precursor is 227 m/z. Meanwhile the product ion is 212 m/z and 133 m/z ion. Fragmentor voltage and collision energy used are 115 V and 25 V. BPA appear at the retention time around 6.5. as show in Figure 1. A calibration curve for each residue was constructed at six different concentrations of a mixed standard: 25.0, 20.0, 15.0, 10.0, 5.0, 1.0, 0.5 and 0.1 ppb. These curves show r value of 0.996 as Figure 2. The standard quality control gives 5.0 ppb with 100% accuracy. Detail of the sampling points and the concentration of BPA occurred is shown in Table 2.

Table 2: BPA mean concentration according to site sampling point

Station	Sampling Point	Site description	Mean concentration of BPA (ppb)
P1	Pangsun	Recreational area, receive water flow from Sungai Langat Dam	12.2395
P2	Sg.Semungkis	Recreational area and waste dumping area	14.1108
P3	Kampung Batu 13, Hulu	Residential area, crops and waste dumping area	19.6658
P4	Hulu Langat	Residential area, crops and waste dumping area	17.6361
P5	Sg. Semenyih upstream	Illegal waste dumping area, receives input from cattle farm and crops plantation	20.1396
P6	Budiman Industrial area	Construction site, paper mills, metal industries, illegal waste dumping area	23.8443
P7	Sungai Ramal	Residential area and waste dumping area. Receive input from sand mining, oil palm plantation and construction site	18.8837
P8	Dengkil	Residential area, waste dumping area, and crops plantation	16.6980
P9	STP effluent near Sg. Batang Nilai	Residential area, construction site, waste dumping area	20.6258
P10	Sungai Chincang	Residential area, poultry farm	12.3459
P11	Sungai Labu	Plantation area, receive plantation discharge and dopmestic waste	20.5508
P12	Sungai Changgang	Residential area and waste dumping area	16.5249

The levels of BPA in the Sungai Langat were the range of 2.2395 ppb to 23.8443 ppb respectively. BPA was detectable at all locations (Table 2 and Figure 3). The BPA distribution in Sungai Langat showed higher concentration in the middle stream than the upstream regions which may be due to the urban runoff. The highest concentration of 23.8443 ppb was detected at Budiman Industrial area (P6). Budiman Industrial area is coastal town with industrial activities, it is expected that local sewage disposal and runoff from upstream settlements may be the prime reasons. BPA is one of the ingredients used as a low cost image developer in the production of paper may therefore contribute as well. [15]. For upstream Sungai Langat, BPA shows value of 12.2395 ppb which may be due to many tourist attractions including waterfalls, dams and sanctuary in the upper reaches of the river, so contribution from human activities may not be ruled out. Among the phenolic compounds, BPA is the most documented chemical reported in surface waters around the world. It was reported at higher levels in the European rivers, i.e. up to 2970ng/L in Spain, 776 ng/L in Germany and up to 683 ng/L in Portugal, and also in China (up to 1040 ng/L), than observed in Sungai Langat in the present investigation [16-20].

Water Quality Index

Seven parameters were included to determine the quality of Sungai Langat; pH, Turbidity, Total Suspended Solids (TSS), Ammoniacal Nitrogen (NH3-N), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO). In-situ measurement of turbidity and dissolved oxygen (DO), and pH were obtained using YSI Model 556 Multi probe system (MPS). This instrument was calibrated and cleaned before being used for the sampling. Concentration of BOD, COD, TSS, and Ammoniacal Nitrogen were determined in the laboratory. The water samples for the parameters BOD, COD and Ammoniacal Nitrogen were stored in temporary ice box container before being transported to the laboratory for analysis. For BOD parameter, water samples were collected using dark glass bottles. Bottles were totally dipped into water with the lid on. The bottle mouth was directed downward in the water at a depth of 10-15 cm below the water surface. After all the bottles were filled with water sample and free from air bubbles, the bottle lids were closed. At the end of the five-day period, the remaining dissolved oxygen was 20 measured. The relationship between oxygen that was consumed during the five days and the volume of the sample increment were then used to calculate the BOD5. COD was analyzed in the laboratory using the reactor digestion method. The reactor was heated until the temperature reached 150 °C. 2 ml of water sample was added into the HACH COD vials using clean volumetric pipet. The second vial was added with 2 ml of deionized water. The vials were gently inverted to several times then, were placed in the reactor and heat for two hours. After that vials were cooled for about 20 min, the reading was obtained using HACH spectrophotometer. Total Suspension Solid (TSS) was analyzed using glass fiber filter paper Whatman with 0.45 um pore size and a diameter of 47 mm filtered with deionizer water to ensure that no dissolved salts and impurities present. Then, the filter paper was dried at temperature of 105°C in the oven for two hours and weighed. Then, filter papers were cooled in desiccators before being weighed to obtain a balanced weight with temperature. Difference weight of filter paper before and after filtration was calculated to obtain the weight of suspended solids.

Total Suspended Solids (mg/L) = (A-B) × 1000 / (Sample volume, mL)

Where:

A: Weight of filter paper before filtration in mg

B: Weight of filter paper after filtration in mg

Ammoniacal Nitrogen was measured using Nesslerization method. This analysis uses the principle of colorimetric. A total of 25 ml of water sample was filled into the measuring cylinder. 25 ml of deionized water blank was filled into another measuring cylinder respectively. Next, 3 drops of mineral stabilizer and solution of polyvinyl alcohol dispersant were added to both of cylinders and shaken for mixing to get the perfect solution. Then, 1 ml of Nessler reagent was added into each of measuring cylinder and shaken. Both of measuring cylinders were left 1 minute for the reaction to begin. Finally, each solution was poured into a round sample cell to be measured with HACH spectrophotometer. The result for all parameter are shown in Table 3.

Table 3: Water Quality Analysis and Water Quality Index for 12 sampling point

Station	COD (ppm)	BOD (ppm)	AN (ppm)	TSS (ppm)	DO (%)	pH	Turbidity (NTU)	WQI
P1	2.5	1.0	0.748	10	95.9	6.33	2.4	90
P2	2.5	1.0	0.114	13	102	6.6	73.4	95
P3	7.57	5.7	2.436	61	85.1	6.5	123.3	75
P4	38.93	10.4	3.705	24	25.3	6.16	19	49
P5	21.76	10.5	3.132	10	87.5	6.71	110.9	72
P6	7.05	5.4	1.964	25	87.8	6.92	236.1	80
P7	13.65	8.2	4.988	35	60.8	5.99	344.5	64
P8	11.82	5.3	3.353	56	57.9	6.48	387.5	66
P9	55.6	10.3	11.58	14	54.1	6.78	20.9	56
P10	16.31	10.5	1.746	66	87.4	6.87	78.4	72
P11	39.62	10.4	4.825	66	36.7	6.88	64.4	49
P12	10.03	5.2	3.186	10	92.8	6.81	171.8	79

Based on the findings, Sungai Langat was classified in class III based on the WQI classification. The water quality at Sungai Langat is highly affected by the surrounding human activities such as construction, manufacturing factories, sand mining and from domestic wastes.

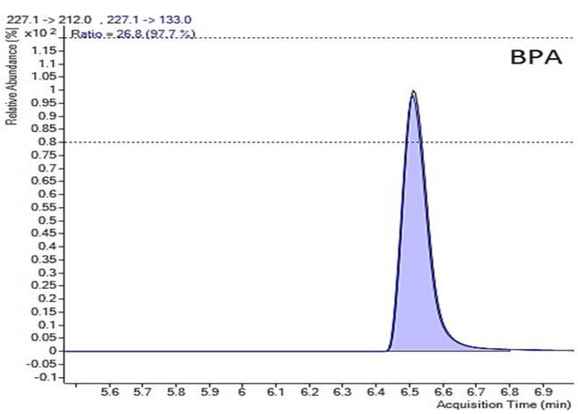

Figure 1: Relative abundance of BPA

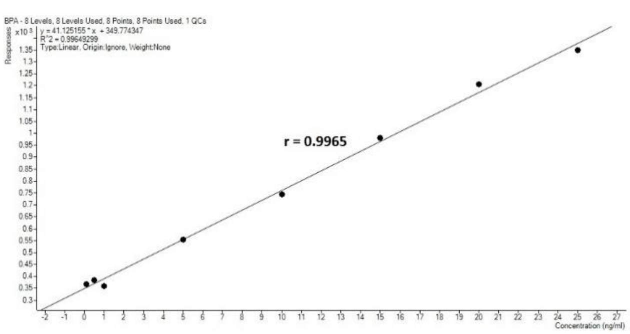

Figure 2: Calibration curve of BPA

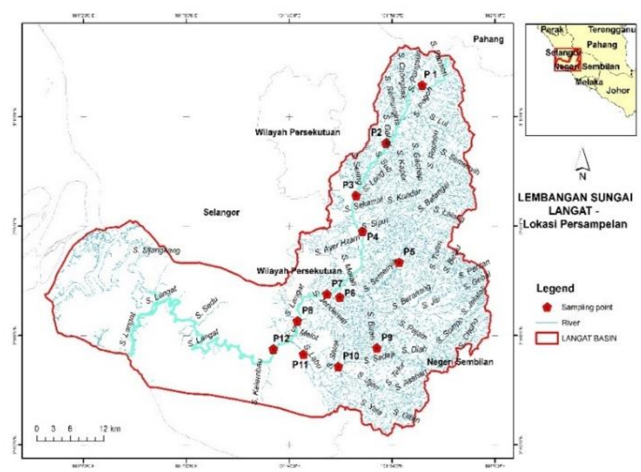

Figure 3: Map of sampling in the Sungai Langat basin

CONCLUSION

Water pollution due to various toxic solid wastes, effluents and emission are being discharged, resulting in an excessive amount of BPA in local ground water. Due to discharge of untreated industrial effluents in the sewage channels, the ground water quality is deteriorated to great extent, therefore, availability of healthy, clean and good quality drinking water is a matter of great concern especially in the urban areas. Increasing population and uncertain climatic change will pose heavy demands on water quality in the future. Therefore, the sources of fresh water supply especially Sungai Langat is needed to make sure it is clean for water supply and also well sustained from declining from the natural sources to be consumed by community within Langat watershed.

Therefore, it is very important to identify the pollutant sources through point source pollution based on the land use activities that took place around the Langat basin. Thus, in order to make sure the Sungai Langat is clean, the sources of pollutant discharge from the land use activities along the Sungai Langat basin must be identified and controlled.

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