Occurrence of Emerging Pollutants in Skudai River in Johor Bahru Region of Malaysia

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Abstract

Increase in landuse development and human activities have significant influence on the occurrence of emerging pollutants (EPs) in water bodies such as rivers. As rivers are the main source of water supply in Malaysia, a study was conducted to determine the occurrence of EPs in one of the drinking water sources, namely Skudai River. Samples were collected five times at eight sampling points from the upstream up to the water intake of the river. Sample pre-treatment was performed by solid-phase extraction (SPE), whereas the analyses of the EPs were performed by Liquid Chromatography-Mass Spectrometry (LCMS-MS QTOF). Results showed that about 50 compounds were detected and fall into categorise as pharmaceuticals, Personal Care Products (PCPs), and Endocrine Disrupting Chemical (EDC). The most prevalent (75-100%) compounds detected were of these categories, whereas the least (less than 40%) were mainly pharmaceuticals. The concentration of styrene, a health-hazards EPs ranged from 45.11 to 203.48 µg/L with increasing trend towards downstream of the river. Based on the landuse data of Skudai River Basin, the study concluded that human activity, landuse, and environmental factors could possibly contribute to the presence of the EPs in the river.

Keywords: *pharmaceutical, personal care products, styrene, endocrine disrupting chemical, Skudai River*

Introduction

Emerging pollutants (EPs) are defined as synthetic or naturally occurring compounds that are not often monitored but have the potential to enter the environment causing known or suspected adverse ecological and human health effects [(1–3)]. They are categorized into more than 20 classes based on their origin. The most important classes are pharmaceuticals, personal care products (PCPs), pesticides, by-products of disinfection, wood preservative and industrial based chemicals [(3,4)].

Emerging pollutants have been detected in surface water, groundwater, treated water and in effluent of wastewater treatment plants (WWTPs) [(5).] Several countries including UK, US, and Japan had reported the presence of PPCPs in concentrations ranging from ng/L to µg/L in WWTPs [(6)]. In addition, EPs are also released from diffuse sources through atmospheric deposition or from crop and animal production [(3,7,8]

One of the main concerns with regards to EPs is their ability to alter the normal function of endocrine systems and give adverse effect in animals and human. These EPs, known as Endocrine Disrupting Chemicals (EDCs), act by blocking, mimicking, development disorders and alter function systems of hormones in animals and human body [(9–11)].

Skudai River is an important river in the district of Johor Bahru as it is one of the sources of water supply in the area. The river originates from oil palm plantation and flows through several townships and industrial areas before it reaches the water intake point. As the river is exposed through various landuse and human activities, the river is anticipated to receive different types of pollutant including EPs. Being the source of water supply, it is of our interest to investigate the impact of the landuse and human activities on the occurrence of the EPs in the Skudai River. This paper reports the findings of the study on EPs conducted over a one-year period of 2016-2017 and quantifying the presence of styrene in Skudai River.

Methodology

The Study Area

The Skudai river is 46 km length with basin coverage area of 325 km^2. Skudai River is located in the southern part of Johor. The river starts from Sedenak area and flows down to the Straits of Johor. The average monthly rainfalls in the Skudai River basin is 169.5 mm with the highest rainfall occurring in October to November [(12)]. The upstream of the river is mainly covered by oil palm plantation while the central and downstream of the river are mainly urbanized.

Sampling

The water samples were taken at eight sampling points. The surrounding landuse of the sampling points is shown in Table 1. Five sampling exercises were conducted during the study. Grab samples were taken at about 0.5 m depth from the water surface. Samples were kept in clean amber glass bottles at temperature below 4°C prior to analysis. The collected samples were analysed within 48 hours of sampling.

Table 1: The location and landuse of the sampling stations

Station No.	Name of Location	Land Use Type
P1	Sedenak	Agriculture
P2	Kg. Sengkang	Oil palm plantation
P3	Taman Mewah	Residential & Agriculture
P4	Kg. Pertanian	Residential
P5	Saleng	Industrial
P6	Bridge to Airport Senai	Residential & Industrial
P7	Lee Rubber Plantation	Residential & Agriculture
P8	Skudai Water Intake	Residential

Chemicals

Methanol and acetonitrile were of gradient grade for liquid chromatography and purchased from Merck, Germany. Styrene standard solution was obtained from Sigma Aldrich, USA. Ultra-pure water was produced using Sartorius H_20PRO-UV-T Arium.

Analytical Method

Sample extraction procedure

Chromabond C18 (500 mg, MachereyNagel, Germany) was used for the SPE process. SPE cartridges were used on a 10-fold vacuum extraction box (Vacmaster10, MachereyNagel, Germany). The cartridge was first conditioned with 5.0 mL of methanol, followed by 5.0 mL acetonitrile, and finally, 5.0 mL of ultrapure water. Water sample of 500 mL was eluted at 10 mL/min. After the sample passed through the cartridge, 5.0 mL of ultrapure water was eluted from the cartridge followed by drying under vacuum conditions for about 30 min.

The analyte in the cartridge was eluted with 2.5 mL acetonitrile, followed by 2.5 mL methanol. The eluted part was collected in soda glass tubes (Samco, England) and air-dried until dryness. The residue was dissolved in 2.0 mL of the same solvent and capped with a poly stopper. The extract was transferred to a 2.0 mL glass vial (Agilent Technologies USA) with flexible stopper and injected into LCMS-MS QTOF.

Liquid Chromatography-Tandem Mass Spectrometry of Quadruple Time of Flight

After pre-treatment, the samples were analysed using Liquid Chromatography-Tandem Mass Spectrometry of Quadrupole Time of Flight (LC-MS-MS QTOF) (Agilent 6560 IM-QTOF). The capillary column used was Zorbax Extend-C18(2.1X50 mm/1.8 micron), equipped with a splitless injector. Purified helium (99.99%) was used at a flow rate of 1.6 mL/min as the carrier gas. The oven ramp was set to an initial temperature of 70°C, (and held for 2.0 min), followed by an increase to 100 °C at a rate of 5 °C per min (held for 2.0 min), to 200°C at 5°C/min (held for 2.0 min) to 250°C at 5 °C/min (held for 2.0 min) and increased stepwise up to 250°C with a total run time of 32 minutes.

Results and Discussion

Characterisation of EPs

The occurrences of EPs along with its percentage of detection during the sampling exercise are shown in Figures 1 to 3. About 50 compounds of different types were detected and they are categorized into three, namely pharmaceutical, PCPs and EDCs. The pharmaceutical group comprises of medicines, antibiotics, supplements, and steroids, while the PCPs comprised of soaps, surfactants, perfumes, lotions, toiletries and cosmetics. The EDCs are those related to manufacturing industries such as plasticizers, resin and polymers.

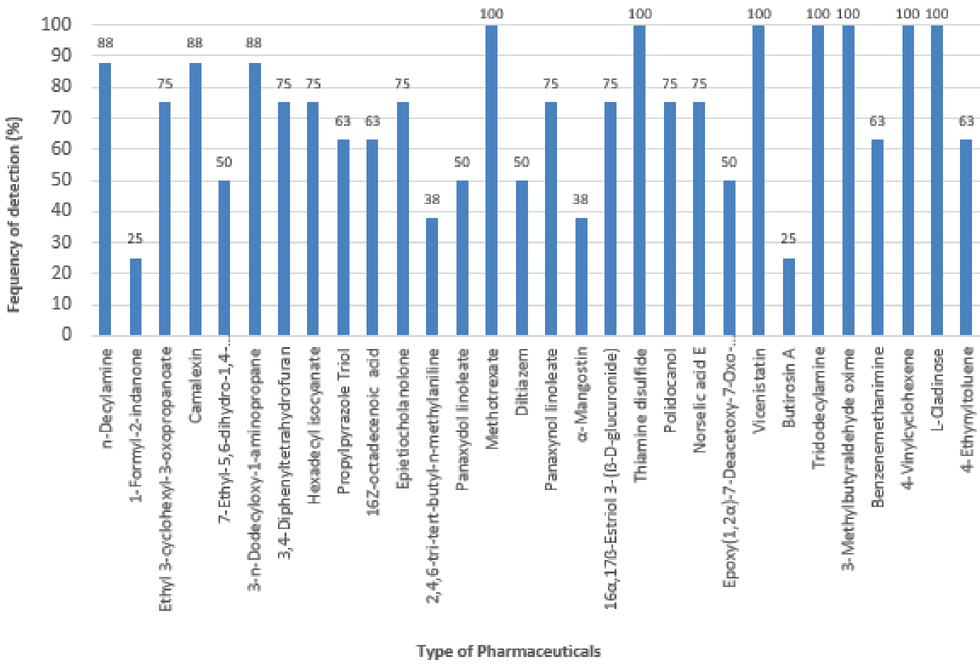

Figure 1: Frequency of detection of phaemaceutical compounds

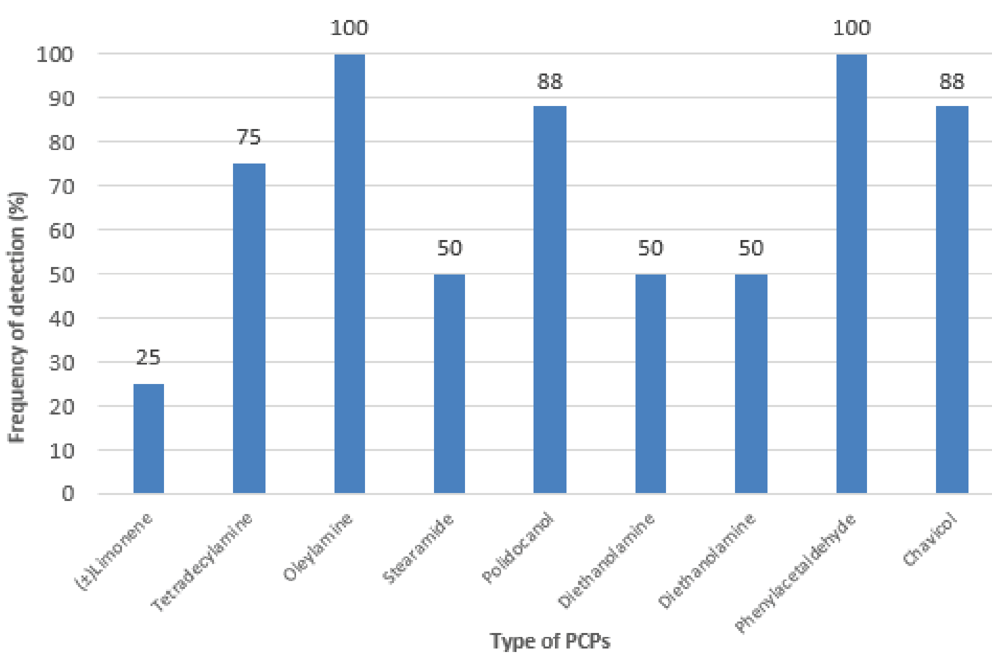

Figure 2: Frequency of detection of personal care product compounds

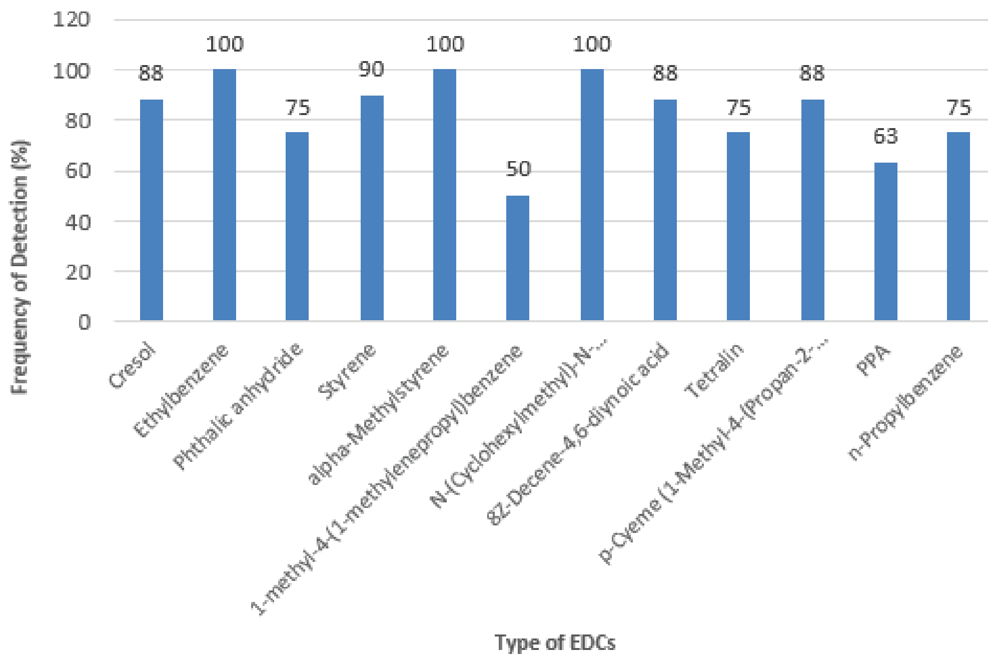

Figure 3: Frequency of detection of endocrine disrupting chemicals

Of the pharmaceutical compounds detected, majority of them are detected at a frequency of more than 50%. Eighteen compounds were detected at 75% and more, while only four compounds were detected less than 50%. Seven of these pharmaceutical compounds were detected at all samplings. As for the PCPs, only one of the eight compounds was detected less than 50% frequency, while five were detected at 75% and above, including two were detected at all samplings. All the EDCs were detected at 50% frequency and more with four of them detected at all samplings.

The findings of the study indicate that the water of Skudai River comprised of mixtures of EPs as it received effluent discharges from sewage treatment plants and industries which are located in Kulai and Senai areas. Additionally, sullage from the housing areas and shop houses, and urban runoff during rainy season contribute to the river pollution. The presence of the EPs in the river water suggest their poor biodegradability or resistence that results in their leaching into the environment. In the long run, these compounds, particularly EDCs, can exert adverse health effects to human and the environment due to accumulation even under exposure at low concentrations [13]. As Skudai River is used for the source of water supply, further study is therefore needed to determine the ability of the conventional water treatment process in removing these EPs.

Styrene

Styrene is a semi-volatile organic compound found in daily use and the industrial production of numerous chemicals and industrial products [14]. It is considered a carcinogenic compound with significant risk of cancer, as well as toxic and mutagenic effects on humans. Styrene is regarded as a potent toxin with potential adverse effects on the renal, respiratory, nervous, and gastro-intestine systems of humans [15,16]. As styrene was detected in Skudai River at a very high detection frequency (ie. 90%), and due to its health hazards, further study was carried out to determine the concentration of styrene in the water samples. Table 2 presents the concentration of styrene based on the five sampling exercises at the different sampling points. The concentration of styrene was determined using LC-MS-MS based on the calibration curve made using styrene standard solutions of 200, 250, 500, and 1000 µg/L.

Table 2: Concentration of styrene at different sampling points

Sampling Point	Sampling exercise				
	SB1	SB2	SB3	SB4	SB5
	Concentration (μg/L)+				
P1	ND	146.83	ND	78.72	ND
P2	ND	200.76	166.43	219.01	25.63
P3	87.78	188.44	159.39	106.00	176.89
P4	41.74	230.35	75.67	157.33	146.04
P5	207.12	150.57	152.32	197.15	310.25
P6	97.00	121.01	144.89	130.80	237.77
P7	161.10	46.05	82.27	149.95	282.37
P8	104.70	15.25	108.50	383.11	298.21

+ND – Not detected

Based on the average values of each sampling points, the concentration of styrene increased along the path of Skudai River from 45.11 to 203.48 μg/L. The highest and lowest concentrations were observed at P1 and P5, respectively, although P8 also recorded a relatively high concentration of styrene at 181.95 μg/L. The results reported for P1 can be ascribed to its location in a less densely populated but predominantly agricultural area compared to P5 which is located in the heart of the industrial belt. Styrene is an important raw material for the large-scale production of plasticisers, beverages, and PCPs [14]. Therefore, the high concentration observed at P5 is expected since numerous factories in the vicinity utilize styrene as their raw material. The presence of styrene in the water samples examined in this study suggests that the wastewater treatment in these areas requires further attention.

Conclusions

The study presented preliminary findings on the occurrence and detection of EPs in Skudai River in Johor Bahru region of Malaysia. The detection technique employed was LC/MS-QTOF. The selected method was based on the preliminary assessment of EPs in selected river water samples, which was found to be sensitive and selective for the characterisation of some pollutants. The results showed that the detected compounds could be broadly categorised as pharmaceuticals, PCPs and EDCs. Some of the compounds in these categories were detected at 100% frequency. Some of the pharmaceutical compounds, however, were detected, the least prevalent (Less than 40%). Furthermore, the concentration of styrene was examined and found to be present in the range 45.11 to 203.48 μg/L. The results highlight the urgency to examine the discharge of EPs such as styrene in Skudai River. It is envisaged that such measures will help to forestall future risks to human health, safety, and the environment.

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Ethical Clearance: Not needed as the study does not involve research on animal.

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Conflict of Interest: The authors confirmed that there is no conflict of interest in this study.

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