Evaluation of Acetaminophen as Chemical Marker for Wastewater Contamination

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Abstract - **Acetaminophen, an analgesic drug was evaluated as potential chemical marker for wastewater contamination. Water samples of various sources were analysed using online solid phase extraction liquid chromatography with diode array detector. Acetaminophen was detected in the range of 0.17-1.29 ng/mL in surface water samples contaminated with wastewater. Relatively high concentrations (16.7-74.61 ng/mL) of acetaminophen were observed in water samples from Universiti Teknologi MARA (UiTM) treatment plant monitored from March to August 2014. Positive correlation was obtained between the concentrations of acetaminophen with the students' population based on UiTM academic calendar.**

Keywords - acetaminophen, wastewater contamination, chemical marker

I. INTRODUCTION

Natural water, drinking water, and water used for recreational activities must be protected from sewage contamination. Suitable marker compound is therefore important in order to identify wastewater contamination. Microbial indicators such as coliform, E. coli and enterococci have been used as marker for fecal contamination. However, the method has several disadvantages including time consuming analysis (18-48 hours) [1] and short survival time of these microorganisms in water [2]. Hence, a more persistent compound, which is easily detected using analytical method, should be considered as marker for wastewater contamination.

A good chemical marker should be an anthropogenic compound, persistent and present at high (detectable) concentrations, do not undergo degradation/adsorption in wastewater/water, high solubility in water, low Kow and low volatility [3,4]. Therefore, in this study the mentioned characteristics were considered in the evaluation of chemical marker for wastewater contamination.

Several chemical markers have been proposed to distinguish pollution from sewage, animal and other sources. Fecal sterol such as cholesterol and coprostanol showed promising marker for fecal contamination [5,6]. Recent reviews on the occurrence of pharmaceuticals in aquatic environment suggested that these contaminants enter the aquatic environments via the effluents of wastewater treatment plants, discharges of sewage sludge and human and livestock wastes [7,8]. Therefore in this study, commonly used pharmaceuticals (acetaminophen, caffeine, carbamazepine and naproxen) in water samples of various sources were analysed for potential chemical marker for wastewater contamination.

II. EXPERIMENTAL

Standards and Solvents

Acetaminophen (ACT), caffeine (CAF), naproxen (NAP), carbamazepine (CBZ)

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were purchased from Sigma-Aldrich (purity assay in range of 98-101 %). Acetonitrile (HPLC grade) and methanol (HPLC grade) were purchased from Merck (Darmstadt, Germany). Individual stock solution (1 mg mL-1) was prepared for all pharmaceuticals in methanol and a series of working standard solution was prepared in ultrapure water (18 MΩ, Barnstead, USA) with proper dilution.

Sampling Sites

Wastewater, surface water and groundwater samples were collected for sampling sites tabulated in Table 1. Sampling of surface water and ground water was conducted from August 2014 to October 2014. Periodical sampling of wastewater from Mawar water treatment plant was done from March 2014 to August 2014.

Table 1: Water samples and sampling sites

Sample	Longitude	Latitude	Location (description)
Wastewater			
Mawar UiTM Wastewater Treatment Plant	E 101° 29.376’	N 03° 04.065’	Influent wastewater from Mawar College, UiTM Shah Alam, sewage
Surface water			
Klang River (sampling point 1)	E 101° 26.955’	N 03° 02.647	Discharge from socio-economic activities of Klang town, sewage
Klang River (sampling point 2)	E 101° 33.074’	N 03° 01.776’	Discharge from industrial area, Seksyen 26, Shah Alam, domestic sewage
Klang River (sampling point 3)	E 101° 35.829’	N 03° 01.234’	Discharge from domestic sewage of Puchong Weir
Klang River (sampling point 4)	E 101° 39.860’	N 03° 04.934’	Discharge from Petaling Bahagia, sewage
Damansara River (sampling point 1)	E 101° 33.156’	N 03° 04.823’	Discharge from TTDI Jaya, Seksyen 13 Shah Alam, IWK sewage
Damansara River (sampling point 2)	E 101° 33.495’	N 03° 06.156’	Discharge from TTDI Jaya, sewage
Damansara River (sampling point 3)	E 101° 32.583’	N 03° 08.815’	Discharge from Kampung Melayu Subang, socio-economic
Kuyoh River	E 101° 39.102	N 03° 04.008’	Discharge from Bandar Kinrara, mining
Kerayong River	E 101° 40.591’	N 03° 05.784’	Discharge from Klang Lama Road, industry area
Gabai River	E 101° 90.79’	N 03° 16.6’	Upstream river
Congkak River	E 101° 85.08’	N 03° 19.85’	Upstream river
Tekala River	E 101° 86.97’	N 03° 05.95’	Upstream river
Lui River	E 101° 87.93’	N 03° 16.65’	Upstream river
Groundwater			
Lenggeng	E 101° 53.512’	N 02° 52.010’	-
Puncak Alam	E 101° 47.779’	N 03° 14.829’	-

Sample Collection and Preparation

Influent wastewater and surface water samples were collected using the grab sampling technique (vertical grab sampler 5 L high-density polyethylene containers, Ocean test Equipment, Florida, USA) and transferred into a 1.0 L high-density polyethylene bottle. Water samples were collected in triplicates and acidified using hydrochloric acid (3M). The samples were vacuum filtered using Whatman 45 µm GF/A (Whatman International Ltd Maidstone, England). The filtered water samples were stored in the dark at 4 ºC.

Analysis of Pharmaceuticals

Pharmaceuticals in water samples were analysed using online solid phase extraction liquid chromatography system (Dionex

Ultimate 3000, Sunnyvale, CA, USA) [9]. The method showed good linear range, LOD, LOQ, accuracy and reproducibility [9].

III. RESULTS AND DISCUSSION

The Occurrence of Pharmaceuticals in Water Samples

The concentrations of selected pharmaceuticals in water samples from various sources are tabulated in Table 2. Acetaminophen and caffeine showed high detection frequency, while naproxen and carbamazepine showed low detection frequency. The selected pharmaceuticals were not detected in groundwater samples and surface water not contaminated with wastewater. The low detection frequency of naproxen and carbamazepine could be due to low consumption of these drugs in the communities and their low solubility in water.

The concentration of caffeine in surface water contaminated with wastewater ranged from 0.54-38.15 ng/mL. Caffeine was reported as a promising marker for urban fecal contamination due to its persistence, solubility in water and high occurrences [10].

The concentration of acetaminophen in surface water contaminated with wastewater ranged from 0.17-1.29 ng/mL. Acetaminophen was abundantly presence in surface water contaminated with wastewater, as it is a common painkiller. This compound is highly soluble in water with low Kow value (0.46). A comparable concentration for acetaminophen was reported in Malaysian rivers (maximum 0.35 ng/mL) [12] and Ebro River, Spain (n.d-0.71 ng/L) [12].

As acetaminophen and caffeine were frequently detected at high concentrations, these compounds fulfilled the criteria of chemical markers. However acetaminophen was selected for further study since it is more source specific compared to caffeine. The correlation between concentrations of acetaminophen and the population was assessed based on water samples of Mawar, UiTM Shah wastewater treatment plant.

Table 2: Concentrations of pharmaceuticals in various water samples

Sample		Caffeine	Acetaminophen	Naproxen	Carbamazepine
Wastewater	Frequency of detection % (n=4)	100	100	0	0
	Mean detected (ng/mL)	14.29	36.98	n.d	n.d
	Range (ng/mL)	4.66-26.7	11.6-74.6	-	-
Surface water contaminated with wastewater	Frequency of detection % (n=9)	100	100	67	11
	Mean detected (ng/mL)	9.88	0.7	3.07	2.48
	Range (ng/mL)	0.54-38.15	0.3-1.29	n.d-5.23	n.d-2.48
Surface water not contaminated with wastewater	Frequency of detection % (n=4)	0	0	0	0
	Mean detected (ng/mL)	n.d	n.d	n.d	n.d
	Range (ng/mL)	-	-	-	-
Ground water	Frequency of detection % (n=2)	0	0	0	0
	Mean detected (ng/mL)	n.d	n.d	n.d	n.d
	Range (ng/mL)	-	-	-	-

*n.d : non detected (below the detection limit)

Periodic Evaluation of Acetaminophen

Periodic samplings were conducted from March-August 2014 as this period covered one semester of UiTM academic calendar (Table 3). The concentrations of acetaminophen during the periodical sampling are shown in Figure 1.

Acetaminophen was frequently detected in influent wastewater samples, indicating high usage of this pharmaceutical among students. High concentration of acetaminophen was detected in March (24.8 ng/mL), possibly due the high population of student during the first month of the semester. The concentration of acetaminophen increased in May (35.15 ng/mL) and maximum concentration of acetaminophen was observed in June (74.94 ng/mL). A significant decreased in the concentration of acetaminophen was observed in August (16.7 ng/mL) due to low population during the semester break. Good correlation was observed between the concentrations of acetaminophen with the students' population based on UiTM academic calendar.

Table 3: UiTM academic calendar (Session 2: March – July 2014)

Activity	Date	Length of time
Lecture 1	3 March - 13 April 2014	6 weeks
Mid-semester break	14 - 20 April 2014	1 week
Lecture 2	21 April - 25 May 2014	5 weeks
Special break	26 May - 1 June 2014	1 week
Lecture 3	2 - 22 June 2014	3 weeks
Revision	23 - 24 June 2014	2 days
Examination	25 June - 13 July 2014	3 weeks
Intersession	12 July - 22 August 2014	5 weeks
Eid break	28 July - 3 August 2014	1 week
Special examination	27 - 29 August 2014	3 days
Semester break	14 July - 7 September 2014	8 weeks

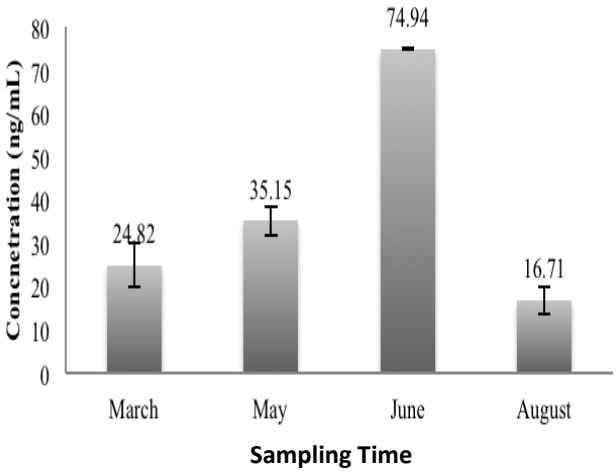

Figure 1: Concentration of acetaminophen from March to August 2014.

IV. CONCLUSION

This study showed that acetaminophen could be a good chemical marker for wastewater contamination as it was frequently detected at high concentration in water samples with input of wastewater. It was not detected in ground water samples. The use of acetaminophen as a chemical marker has the advantage of being source specific and can be correlated to its consumption in a community.

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