DISTRIBUTION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCP) IN SURFACE WATER OF LANGAT RIVER AND ITS BEHAVIOR IN WASTEWATER TREATMENT PLANT (WWTP): PPCP AS WATER SOLUBLE MOLECULAR MARKER OF SEWAGE POLLUTION

Tan Sin Sing*, Assoc. Prof. Dr. Mohamad Pauzi Zakaria, Assoc. Prof. Dr. Mohammad Ismail Yaziz, Dr. Nomala Halimoon

PhD (GS21923)
3rd Semester

INTRODUCTION

Personal-care products (PCPs) are synthetic organic chemicals derived from commercial products such as toiletries (soaps, lotions, toothpaste, etc.) cosmetics, household goods and many more. Together with pharmaceutical drugs, they constitute the chemical class termed as Pharmaceutical and Personal Care Products (PPCP). PPCP is the emerging class of pollutants in the past decade due to its ubiquitous nature, toxicity, and persistency in the environment.

The major contribution of pharmaceuticals into the environment is determined by the relationship between the quantities of drugs manufactured, the dosage prescribed and thereafter the release of unabsorbed drug from the human body. These residues after consumption are excreted via urine and feces. Meanwhile, personal care products can be directly administered into the environment from recreational waters and municipal wastewater.

Overall, the Wastewater Treatment Plant plays a key role in the removal of the PPCP. Two main mechanisms involved in the removal efficiency of PPCPs are (1) microbial biodegradation, and (2) sorption on sludge and particulate matter which is later removed by sludge. Other mechanisms of removal includes; filtration and chemical oxidation. However, not all PPCP can be efficiently removed by the WWTP.

Thus, their persistency in the environment renders them to be excellent water-soluble molecular markers for sewage pollution. They are useful for identifying the sources of pollution and their transport pathways.

The study area for this project is Langat River which is one of the four major river systems in the State of Selangor. It stretches within the latitudes of 2^{o} 40’ 152”E to 3^{o} 16’ 15” N and longitudes 101^{o} 19’ 20” E to 102^{o} 1’ 10” E with a total basin area of approximately 1815 km^2. This river basin located at southern part of Klang Valley, which is the most urbanised river basin in Malaysia, and it is believed that the Langat will compensate the virtue of ‘spill-over’ development from Klang Valley.

OBJECTIVES

- To quantify the distribution of PPCP in surface water of Langat River
- To analyze a wide range of PPCP in influents and effluents at WWTP as well as to evaluate its removal efficiencies
- To evaluate removal of PPCP by Chlorination and Powder Activated Carbon (PAW) in bench scale
- To propose selected PPCP as water soluble indicator of Sewage pollution

SIGNIFICANCE OF STUDY

PPCP is the new emergent pollutant in the past decade. The study of distribution and behavior of PPCP in the environment is crucial because large quantities of it is manufactured and administered in the Malaysia but yet extremely little is known about it.

Moreover, some PPCP particularly hormones, fragrances and detergent metabolites are known Endocrine Discrupting Compounds (EDC) responsible for feminization of male fishes through the production of vitellogenin. Owing to the negative effects of PPCP to environment, its fate needs to be studied and evaluated (Daughton and Ternes, 1999)

Developing PPCP as a chemical sewage indicator has several advantages over microbial sewage indicator which is currently used by our country such as total coliform and fecal coliform. These advantages are (1) shorter time of analysis compared to bacterial culture test and (2) anthropogenic source specificity. Microbial sewage indicator test would require 18-48 hours to complete. Although new microbial techniques such as Polymerase Chain Reaction (PCR) may reduce its time; the method is not widely comprehended.

On the other hand, microbial indicators lack source specificity as it is unable to differentiate between anthropogenic and non-anthropogenic sewage pollution. (Isobe et. al., 2002 and Glassmeyer et. al., 2005). The most frequently monitored *E.coli* for sources of non-anthropogenic fecal pollution is not suitable for tropical and subtropical climates due to its ability to replicate in contaminated soils (Petrisol et. al., 2006). Therefore, we are in need of a more relevant and efficient sewage indicator whose role can be replaced by PPCP.

LITERATURE REVIEW

The concern on the emergent contamination has lead to great increase on the study on its distribution and effects in the environment since the early nineties. A comprehensive study on the distribution of PPCP has been carried out U. S. Geological Survey (USGS) where 95 Organic Wastewater Contaminant (OCW) was studied in 139 streams across United States (Kolpin et. al., 2002). Other similar studies was also carried out elsewhere Wales (Kasprzyk-Horden et. al., 2007), Romania (Moldovan, 2006), German (Heberer, 2002) and many more.

In the Asian region, studies have been carried out in South Korea (Kim et. al.,2007), Japan (Nakada et. al., 2006), Taiwan (Lin et. al., 2008), South China (Peng et.

al., 2009). However, as to date, there are no data on the distribution of PPCP in the Southeast Asian Region. Overall, studies on the distribution, behavior and removal of PPCP in the environment are exponentially increasing and is deemed to gain much attention in Southeast Asian region in due time.

Owing to the persistency of PPCP several studies have been conducted to develop PPCP as sewage molecular indicator. Several PPCP compounds have been proposed such as tonalide, galaxolide, carbamazepine and caffeine due to human specificity (Glassmeyer et. al., 2005). Meanwhile in Japan crotamiton has been ruled to be the more efficient indicator than those previously listed due to its high usage in the region (Nakade et. al., 2008).

Overall, there is a huge gap of knowledge in the Southeast Asian Region for the distribution of PPCP as well as its behavior in the WWTP which can be fulfilled by this study. In addition, this will be a pioneering study to grasp the feasibility of this extensive range of PPCP as sewage indicator featuring oxybenzone, DEET, gemfibrozil and iopromide for the very first time.

METHODOLOGY

The samples for this study consist of river water, WWTP influent, inlets of various stages for WWTP and effluents of WWTP. All the samples are then subjected to the same laboratory extraction and analysis. Below is the flow chart of methodology:-

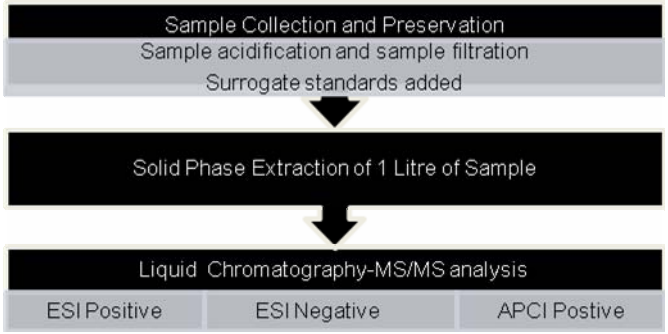

Figure 1: Simplified Flow Chart of Methodology

Sample collection and preservation

Two categories of samples are collected; (1) grab water samples are collected at Langat river and (2) WWTP influents, inlets of various WWTP process inlets (e.g. inlets of aeration, flocculation/coagulation and sedimentation) and WWTP effluents. All samples are stored in pre-silanized amber glass bottles.(Trenholm et. al., 2006). The samples are then transported back to the laboratory in cooler boxes. Upon receiving, the samples are immediately acidified to pH2 using sulfuric acid and stored at 4^{o}C until extraction. All samples are filtered prior to extraction using GF/F filters Whatman.

Solid Phrase Extraction

Samples are extracted using 500mg Hydrophilic-Lipophilic (HLB) catridges from Waters which has been pre-conditioned with 5ml of MTBE, 5ml of methanol and 5ml of reagent water. The samples were spiked with surrogate standards prior to extraction and loaded

into the cartridges at 15ml/min. Then the cartridge was dried under the stream of nitrogen for 60min. The analytes of interest were eluted with 5ml of 10/90 (v:v) methanol/MTBE followed by 5ml of methanol. The resulting extract was concentrated under the stream of nitrogen and spiked with internal standard before reconstituted to final volume of 1ml using methanol.

Liquid Chromatography-MS/MS analysis

The Liquid Chromatography method has been previously published (Vanderford et. al., 2003 and Trenholm et. al., 2006). Briefly, a binary gradient was achieved using 0.1% of formic acid and 100% methanol. Analytes were then detected in three different modes;(1) ESI positive, (2) ESI negative and (3) APCI positive.

REFERENCES

Daughton CG, Ternes TA. 1999. Pharmaceuticals and Personal care products in the environment: agents of subtle change? Environmental Health Perspectives, 107 (Suppl. 6):907-38.

Glassmeyer, S. T.; Furlong, E. T.; Kolpin, D. W.; Cahill, J. D.; Zaugg, S. D.; Werner, S. L.; Meyer, M. T.; Kryak, D. D., 2005. Transport of chemical and microbial compounds from known wastewater discharges: Potential for use as indicators of human fecal contamination. Environmental Science & Technology 39, 5157–5169.

Heberer T., 2002. Tracking persistent pharmaceutical residues from municipal sewage to drinking water. Journal of Hydrology , 266 , 175–189

Heberer, T., 2002.Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicology Letters 131, 5–17.

Isobe K. O., Tarao M., Zakaria M. P., Chiem N. H., Minh L. Takada H., 2002. Quantitative Application of Fecal Sterols Using Gas Chrotamatography- Mass Spectrometry To Investigate Fecal Pollution in Tropical Waters: Western Malaysia and Mekong Delta, Vietnam. Environmental Science & Technology, 36, 4497-4507

Kasprzyk-Hordern B., Dinsdale R.M., Guwy A.J., 2007. Multi-residue method for the determination of basic/neutral pharmaceuticals and illicit drugs in surface water by solid-phase extraction and ultra performance liquid chromatography–positive electrospray ionisation tandem mass spectrometry Journal of Chromatography A, 1161, 132–145

Kim S. D., Cho J., Kim I. S., Vanderford B. J., Snyder S. A., 2007. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking and waste waters. Water Research, 41, 1013-1021

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. Environmental Science & Technology 36, 1202–1211.

Lin A. Y., Yu T., Lin C., 2008. Pharmaceutical contamination in residential, industrial, and agricultural waste streams: Risk to aqueous environments in Taiwan. Chemosphere, 74, 131–141

Moldovan Z., 2006. Occurrences of pharmaceutical and personal care products as micropollutants in rivers from Romania Chemosphere, 64,1808–1817

Nakada N., Kiri K., Shinohara H., Harada A., Kuroda K., Takizawa S., Takada H., 2008. Evaluation of Pharmaceuticals and Personal Care Products as Water-soluble Molecular Markers of Sewage. Environmental Science & Technology 42, 6347–6353

Nakada, N.; Tanishima, T.; Shinohara, H.; Kiri, K.; Takada, H., 2006. Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Research 40, 3297–3303.

Peng X., Yu Y., Tang C., Tan J., Huang Q., Wang Z., 2008. Occurrence of steroid estrogens, endocrine-disrupting phenols, and acid pharmaceutical residues in urban riverine water of the Pearl River Delta, South China.Science of the Total Environment, 97, 158-166

Petrisor I. G., Parkinson R. A., Horswell H., Waters J.M., Burgoyne L. A., Catcheside D. E. A., Dejonghe W., Leys N, Vanbroekhoven K., Pattnaik P., Graves D, 2006. Microbial Forensics. In: Morison R.D., Murphy B.L. (Eds.), Environmental Forensic. Elsevier, USA, pp227-254.

Trenholm R. A., Vanderford B. J., Holady J. C., Rexing D. J., Snyder S. A., 2006. Broad range analysis of endocrine disruptors and pharmaceuticals using gas chromatography and liquid chromatography tandem mass spectrometry. Chemosphere, 65, 1990-1998

Vanderford B. J., Pearson R. A., Rexing D. J., Snyder S. A., 2003. Analysis of Endocrine Discruptors, Pharmaceuticals, and Personal Care Products in Water Using Liquid Chromatography/ Tandem mass Spectrometry. Analytical Chemistry, 75, 6265-6274