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Determination of Organochlorine Pesticides in Sembrong Barat Reservoir, Kluang

Nur Syahierah Johan and Razali Ismail*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
**Corresponding Author: zali@kimia.fs.utm.my*

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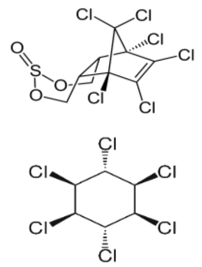
GRAPHICAL ABSTRACT



ABSTRACT

Sembrong Barat Reservoir, Kluang plays a major role in supplying raw water in the district of Kluang, Johor. However, the presence of any pollutants including organochlorine pesticides (OCPs) may affect the raw water quality and this may lead to the closing of water treatment plant operation that will ultimately affect the consumer. This study focused on determining the concentration of organochlorine pesticides namely lindane and endosulfan in raw water sample in Sembrong Barat Reservoir, Kluang. Liquid-Liquid Extraction (LLE) combined with Gas Chromatography-Electron Capture Detector (GC-ECD) was applied in the determination of selected organochlorine pesticides in the water sample. Water sample was extracted twice with dichloromethane and once with n-hexane. The final volume was made up to 1 mL and 1 μL sample was then injected into GC-ECD for analysis. The percent recovery (%) for lindane is 91.8 while for endosulfan is 94.7. The LOD and LOQ was calculated with the value obtained ranging from 0.002 ppm to 0.02 ppm. The real sample was analysed using the proposed method and concentration obtained for lindane and endosulfan are 0.0044 μg/mL and 0.0014 μg/mL respectively.

Keywords: Organochlorine pesticides, Sembrong Barat Reservoir, gas chromatography-electron capture detector, liquid-liquid extraction

1. INTRODUCTION

Water pollution is the changes that occurs to water in terms of content or colour as well as chemical properties caused by various pollutants due to human activity. The pollutants can be in various forms such as solids, liquids and also gases. Water pollution can lead to the destruction of aquatic ecosystems as well as health problems [1].

Agriculture is also a source of water pollution. Agricultural activities such as vegetable and rice farmers produce many liquid chemicals that are drained into rivers. Agricultural wastes such as organic fertilizer and chemical fertilizers (nitric fertilizers and phosphate fertilizers) can cause eutrophication and toxins (pesticides, herbicides) - this may cause toxic effects on the organisms that drink it [2]. Pesticides bring so many advantages to farmers because pesticides are widely used to protect crops against pest attacks. However, due to their properties, pesticides are very hazardous to aquatic system and especially to human being. Pesticides and insecticides or known pesticides are sprayed to kill pests and it has polluted water resources with the flow of pesticide residues into rivers when it rains.

In Johor, SAJ Ranhill Sdn. Bhd. is the authorized organization to monitor and ensure that the quality of water supplied to customers are within the guideline outlined by the Ministry of Health Malaysia (MOH) and World Health Organization (WHO). However, Water Quality Department of SAJR Sdn. Bhd. monitors the quality of drinking water and raw water based on the scheduled program according to all sampling stations. Thus, in this study, we are going to conduct a research on the quality of water intake and drinking water that is near on the agricultural and industrial area.

The objectives of this study are to:

1. To check the performance of the technique of extraction and determination of organochlorine pesticides in water sample.
2. To quantify the concentration of organochlorine pesticide present in raw water sample in Kluang, Johor by using GC-ECD.

Sembrong Barat Reservoir plays a major role in supporting the raw water to most of the places in Bandar Kluang. Thus, the water quality in Sembrong Barat Reservoir has to be monitored in order to avoid any pollutants coming in to reservoir. It is very important to monitor the water quality because if any violation occurs, the water treatment plant operation can be stopped for a while to handle this problem. Violation refers to any parameters (including pesticides) when tested, exceeds the permissible limit outlined by MOH. In such cases, reports have to be made and the operation of that particular water treatment plant has to be halted for a while.

Organochlorine pesticides chosen to be analysed were lindane and endosulfan because these compounds are famous for their high toxicity and are used in palm oil plantation. They are also widely used all over the world so it mostly can be found in water and soil. Liquid-liquid extraction technique is carried out as sample preparation and also to enrich the analyte in the sample. The prepared sample was then analysed using GC-ECD.

The study conducted will also help SAJ Ranhill to ensure that the water being supplied to the consumers are safe and do not bring harmful effects to them. Other than that, it will also help the authorized organisation to identify the areas that have a potential of being a threat to their water resources.

Generally, most of the organochlorine pesticides are volatile and strongly adsorbed on a particulate material such as soil. Therefore, it is not surprised to know that they are widespread in the marine environment. The most appropriate pathway for the entry of organochlorine pesticides is through the river [3].

In addition, organochlorine pesticides are mostly insoluble in water, for instance, the solubility of DDT in water is about 0.2 ng/l. On the other hand, they are readily soluble in organic solvents and in fats or lipids. So, once the pesticide enters the aquatic environment, it is unlikely to be found in the water, but it will be adsorbed on a particulate material, either organic or inorganic [4]. Soil adsorption is the tendency of materials to be in touch to the surface of soils particles. If a substance is adsorbed onto the surface of the soils, it remains in the soil and is more averse to move into the water system unless soil erosion occur. Pesticides have the ability of doing that, which means that the adsorbed pesticides may present in the sediment in the river or aquatic environment.

Once pesticides get into water, they substantially lower the quality of the surface waters and ground waters, which constitute sources of drinking water for the whole district of Kluang. Once they are in water, pesticides were subjected to a variety of processes. They can be accumulated, deposited, diffused and also diluted. Other than that, they will also undergo photochemical and biochemical processes such as photolysis, photo-degradation, biodegradation, biotransformation and bioaccumulation. These processes might give rise to substances of even greater toxicity.

The pesticides that are released to the environment have the possibility to be degraded or remain unchanged over a period of time. The released pesticides can move via the air, soil and water; however, their mobility depends on the properties of a particular pesticides. Pesticides with high solubility in water will easily be carried off with rainwater as a runoff, but if the pesticide is insoluble in water, it will stick to the soil and settle out with the sediment.

2. EXPERIMENTAL

2.1. Water sampling

In this study, the water sample will be collected into the Amber bottle (1,000 mL). Since pesticides are light sensitive, this darker bottle is used to ensure that the analytes do not break down or undergo photo degradation when exposed to ultraviolet radiation during transit to the lab. The bottle's head must be kept tightly so the analytes will stay dissolved in the water, and to prevent them from escaping into the air.

Before opening the J-pipe, make sure to remove any attachments that may fall into the sample bottle. Open the J-pipe and allow the water to flow about 5 minutes to flush. This is sufficient to remove any contaminants and to get a representative sample. Remove the cap from the Amber bottle and slowly collect the sample water. Make sure that the flow of water is slow enough to avoid overflowing. Remove the bottle from water flow and recap the bottle. Put the sample bottle in ice box, so that the temperature is maintained at 4°C.

2.2. Liquid-liquid extraction

25 mL water sample was extracted in a separatory funnel twice with dichloromethane (2×2.5 mL) and once with n-hexane (1.25 mL). The mixture was shaken for two minutes and was allowed to separate for 10 minutes. The combined organic extracts were dried over anhydrous sodium sulphate to absorb water left in the extracts. These extracts were evaporated just to the point of dryness in a rotary evaporator. The final volume was made up to 1 ml with acetone:n-hexane (1:9) v/v.

The sample was then injected into GC-ECD for analysis. Since the method used in this study is already established and is mostly used worldwide, the purpose of method performance is to check the performance the method of extraction and analysis done in this study. The parameters involved in the method performance study are limit of detection (LOD), limit of quantification (LOQ), repeatability, reproducibility, and percentage recovery.

Real sample was prepared with liquid-liquid extraction and was injected into GC-ECD. The quantification method was done by the single spiking addition and the concentrations of both analytes were calculated using respective formula.

2.3. GC-ECD conditions and settings

A gas chromatograph Agilent model 7890B equipped with a ^{63}Ni ECD, a split/spit-less injector operated in the split-less mode, a fused-silica capillary HP-1 column (60 m x 0.25 mm id. x 0.25 pm film thickness) (Hewlett-Packard). A HP 3365 Chemstation software was used for instrument control and data treatment. Nitrogen was the carrier and make up gas.

1 µL aliquot of the extract was injected manually in the injector with the split closed for 2 minutes. The temperature for injector was set at 250°C while for detector at 300°C. The temperature column was programmed from 130°C (hold a minute at 130°C) to 150°C at 14°C/min, then from 150°C to 200°C at 1°C/min and lastly, from 200°C to 260°C at 14°C/min (hold 20 minutes at 260°C). The carrier gas (N_2 gas) was set at 0.85 mL/min and the make-up gas (N_2 gas) flow rate was set at 60 mL/min at 150°C oven temperature [5].

3. RESULTS AND DISCUSSION

3.1. Peak identification of standard pesticides

The standard containing both analytes (lindane and endosulfan) were run using GC-ECD and the retention times of both analytes were detected. The retention time for lindane is at 4.4 minute while for endosulfan is at 6.9 minute. Figure 1 shows the chromatogram obtained by the conditions and settings stated above.

3.2. Method Performance

In this study, the repeatability and reproducibility of the method performance were expressed in the RSD value obtained. Generally, the accepted RSD value is 10% and below. For lindane, the RSD value obtained for repeatability parameter is 13% while 10% for reproducibility parameter. As for endosulfan, RSD value obtained for repeatability parameter is 10% while for reproducibility parameter is 12%. These results tell us that the data is tightly clustered around the mean and this would indicate that the data in this experiment is precise.

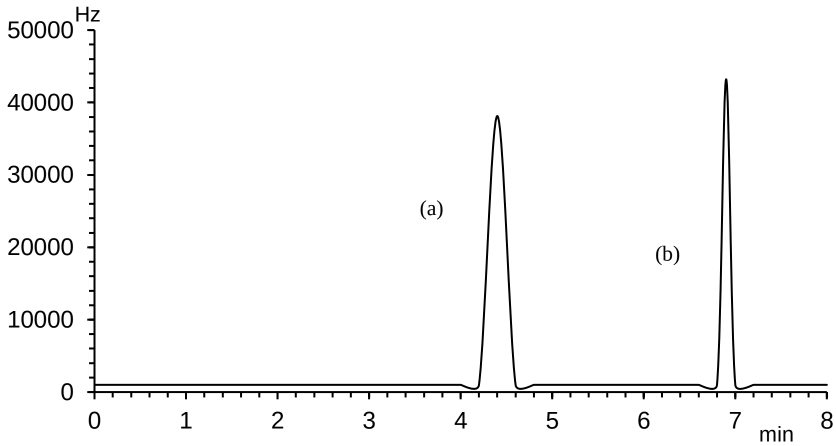
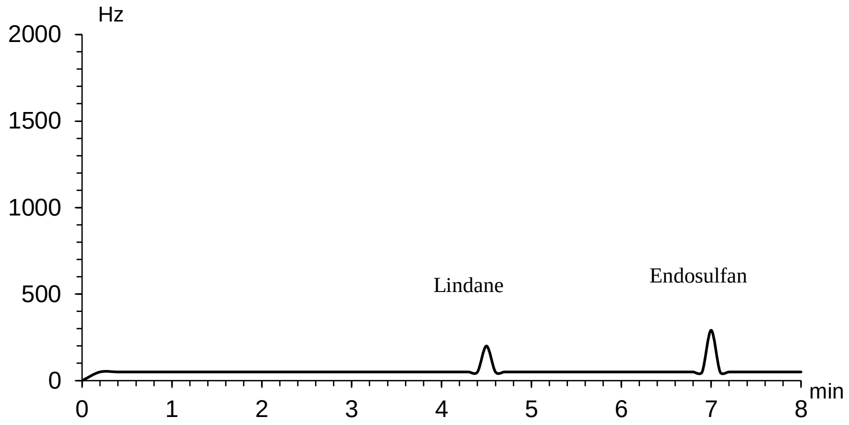


Figure 1. GC-ECD chromatogram of a standard solution in n-hexane at 200 µg/L for (a) lindane and (b) endosulfan. GC conditions: a fused-silica capillary HP-1 column (60 m x 0.25 mm id. x 0.25 pm film thickness). Temperature for injector and detector at 250°C and 300°C respectively. Temperature programming: from 130°C (hold a minute at 130°C) to 150°C at 14°C/min, then from 150°C to 200°C at 1°C/min and lastly, from 200°C to 260°C at 14°C/min (hold 20 minutes at 260°C). Carrier gas (N2 gas) is set at 0.85 mL/min and the make-up gas (N2 gas) flow rate is set at 60 mL/min at 150°C oven temperature.

(a)



(b)

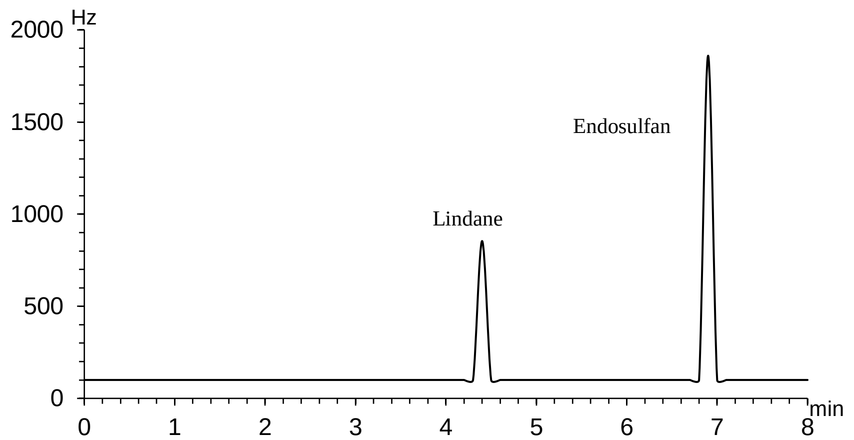


Figure 2. GC-ECD chromatogram obtained by solvent extraction for (a) **non-spiked sample** and (b) **spiked sample.** GC conditions: a fused-silica capillary HP-1 column (60 m x 0.25 mm id. x 0.25 pm film thickness). Temperature for injector and detector at 250°C and 300°C respectively. Temperature programming: from 130°C (hold a minute at 130°C) to 150°C at 14°C/min, then from 150°C to 200°C at 1°C/min and lastly, from 200°C to 260°C at 14°C/min (hold 20 minutes at 260°C). Carrier gas (N2 gas) is set at 0.85 mL/min and the make-up gas (N2 gas) flow rate is set at 60 mL/min at 150°C oven temperature.

By using the proposed method, the lowest concentration that this method can detect for both lindane and endosulfan are 2×10^{-3} ppm to 6.64×10^{-3} ppm respectively. As for limit of quantification, the lowest this method can quantify for both analytes lindane and endosulfan are 6.84×10^{-3} ppm and 0.022 ppm respectively. The proposed method gave an excellence percent recovery which indicates that no analyte loss during sample extraction. The percent recovery for lindane is 91.4% while for endosulfan is 94.7%. Figure 2 shows the chromatogram obtained by solvent extraction for non-spiked and spiked samples.

3.3. Real sample analysis

The extraction method was applied in the analysis of the raw water sample. The sample was treated according to the steps described in the sample preparation followed by analysis using GC-ECD. The unknown concentration of sample was determined using single addition spiking method. The concentration of lindane and endosulfan in the water sample is 0.0044 µg/mL and 0.0014 µg/mL respectively.

Based on the value obtained above, the concentration of lindane exceeds the permissible limit while the concentration of endosulfan does not exceed the permissible limit which is 0.002 µg/mL for both analytes. Endosulfan in detected at much lower concentration compared to lindane due to its low water solubility which is 0.53 mg/l while for lindane is 7.3 mg/l. Since lindane has higher solubility, it has higher potential to remain in in water for a long period of time compared to endosulfan.

The reservoir has been a significant water supply for the Kluang District since 30 years ago. About two million litre per day (MLD) raw water has been pumped directly from the reservoir to a nearby water treatment plant. Nonetheless, modern agricultural farming was initiated in the area since 2004 under the Malaysian Development Project. Since 1960s, rubber is the main agricultural activity, but was replaced with oil palm in the 1980s. As surveyed in 2014, more than 95% of the land use within the area is employed for agriculture [6].

With the concentration of each analytes detected, it indicates there is a possible use of lindane and endosulfan in the agriculture area near the reservoir. Lindane was frequently used to treat seed and fumigants in the agricultural area [7] [8].

3.4. Factors affecting real sample analysis

During sampling process done in March 2019, the weather is good, and it is not a rainy season. So, there is no effects of run off in the study done. There is no increase in volume of reservoir that resulted from raining, thus there is no dilution of pesticides in the sample. During rainy season, the pesticides that have been sprayed will be carried into the river by the rainwater. Consequently, the amount of pesticides inside the river water will increase. Surface water is often considered as a major pathway for pesticides to enter surface waters, especially for strongly adsorbing compounds, which are transported primarily in particulate-bound form.

However, there are two factors that will affect the concentration of pesticides during rainy season: loading of pesticides and volume of river water. Loading of pesticides refers to the amount of pesticides carried by the rainwater into the river water. Volume of water must be increasing during rainy season; thus these two factors are very important in the determination of concentration of pesticides in river water. When volume of river water is increased, there are two possibilities; the concentration of pesticides in river water is decreasing as the concentration is inversely proportional to the volume, and the amount of pesticides in the water is higher compared to non-rainy season because the volume of rain water that brings the pesticides into the river water is large, so there is a high amount of pesticides carried by the rain water into the river.

It is very important to know that organochlorine pesticides have the ability to adsorb onto the surface of a particulate, soil as example. Organochlorine pesticides might be adsorbed onto the surface of the soil in the river, so, the concentration obtained in this study is not including the residues of pesticides in the soil. With, it is better to carry out continuous analysis of pesticides and the effects of climate changes. During water treatment process, specifically in flocculation and sedimentation process, there is a possibility that pesticides are adsorbed onto the surface of the flocs or any particulate matter in the water. Thus, the adsorbed particulate is heavier than water, and it will be deposited at the bottom of the tank. In other words, total concentration of pesticides cannot be determined, only pesticides residue can be determined.

In the previous study done by Fosu-Mensah et al., (2016), they studied on the determination of organochlorine pesticides in soil and drinking water sources from Cocoa farms in Ghana. In their study, they found out that soil samples analysed showed the presence of organochlorine pesticide residue namely lindane, dieldrin, β-HCH and p,p'-DDT. In their findings, the concentration of organochlorine pesticide residue detected in both samples were below their respective US maximum residues limits (MRLs).

From the study mentioned above, it has been proven that organochlorine pesticides have the ability to adsorb onto the particulate material, which is soil resulting in the organochlorine pesticides to adsorb at much longer time at the soil. Sequentially, the soil will be brought into the river by the rain during rainy season.

In an almost similar study by Leena et al., (2012), the concentration levels and distribution pattern of persistent pesticides resides in water and bed sediments of the Ganga river showed the presence of both organochlorine and organophosphorus pesticides. The analysis applied liquid-liquid extraction using gas chromatography equipped with electron capture detector. They found out that the concentration of lindane in river water and sediments were low compared to other pesticides studied. The highest concentration of lindane detected in river water was 74.04 ng/L while the concentration of lindane detected in river sediments was in the range of 18.97 ng/g to 392.60 ng/g.

However, for endosulfan, high concentration was detected in both water as well as in sediment of river. The highest concentration detected was 739 ng/L in river sediments. A local survey of the market of this area reveals that endosulfan is overly used by the farmers of this area, which may be a reason for the presence of endosulfan in such a high concentration. Endosulfan is one of the most dangerous pesticides, resulting in many fatal pesticides poisoning incidents. Endosulfan is mostly known for its ability to disrupt endocrine and xenoestrogen, that caused damage in reproductive and development in humans [9].

In another study done by Okoya et al., (2013), the purpose of the study is to investigate levels of organochlorine pesticides residues in water and sediment samples from eleven rivers serving as drinking water sources and receiving run off from nearby cocoa plantations in Ondo State, Nigeria. Twenty-two composite samples of surface water and sediments (0-3 cm) were collected randomly using grab technique. He found out that low concentrations of organochlorine pesticides were observed for samples taken during the wet season relative to those for the dry season. This is expected due to the dilution at the former season and the fact that the transport and dispersion of pollutants in the aquatic environment is controlled by mass movement. In addition, he observed that the concentrations of the analytes were very low (almost all of the analyse were non detected) in water samples compared to the sediment samples in both dry and wet season. In his study, he concluded that organochlorine pesticides levels were significantly higher in dry season than wet season among the rivers [10].

4. CONCLUSION

The objective of this study has been achieved. This study has successfully showed a good method performance with RSD obtained is in a good range. Percent recoveries calculated also showed an excellence range which indicates that no analyte is loss during the method assay and no matrix interferes during analysis period. The concentration of each analytes has also been determined. The level of awareness among Malaysian society is not satisfying. The significant reason is the inadequate level of information distribution to address the problems of persistent organic pollutants. In Malaysia, no data about damages caused by persistent organic pollutants such as organochlorine pesticides are available for public viewing. The information gap could be due to our general population was unaware of the existence of persistence organic pollutants. Farmers especially are not aware of the hazard's pesticides could bring. Apart from awareness, lack of knowledge on proper pesticides applications and incentives to encourage farmers to have proper practice of pesticides use also contribute to the problems. Farmers are more concerned on getting higher yield and effectiveness in controlling pest compared to their health [11]. Academic institutions together with the Ministry of Health should organize a program or campaign among farmers about the dangers of persistent organic pollutants.

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