This is the authors' draft manuscript. Please cite the manuscript as Leong, K. H., Benjamin, T. L. L., Mustafa, M. A. (2007) Contamination levels of selected organochlorine and organophosphate pesticides in the Selangor river, Malaysia between 2002 to 2003. Chemosphere. 66: 1153- 1159. The full version of the paper is available at the publisher's website through the following link: http://www.sciencedirect.com/science/article/pii/S0045653506007466

Contamination levels of selected organochlorine and organophosphate pesticides in the Selangor River, Malaysia between 2002 to 2003

Leong Kok Hoong [1*], **Benjamin Tan L. L.** [2], **Mustafa Ali Mohd** [3] (Surnames underlined)

[1]Department of Pharmacy, Faculty of Medicine, University Malaya. 50603 Kuala Lumpur. Malaysia.

[2]Australian School of Environmental Studies, Griffith University , Nathan , Queensland 4111, Australia .

[3]Department of Pharmacology, Faculty of Medicine, University Malaya. 50603 Kuala Lumpur. Malaysia.

[*] Corresponding Author: **Leong Kok Hoong**

Tel: 603 – 7967 7519

Fax: 603 – 5638 5659

E – mail: leongkh@um.edu.my

Manuscript word count: 4,675

Abstract

In Malaysia, rivers are the main source of public water supplies. This study was conducted from 2002 to 2003 to determine the levels of selected organochlorine and organophosphate pesticides in the Selangor River in Malaysia. Surface water samples have been collected seasonally from nine sites along the river. A liquid-liquid extraction followed by gas chromatography-mass spectrometry technique was used to determine the trace levels of these pesticide residues. The organochlorine pesticides detected were lindane, heptachlor, endosulfan, dieldrin, endosulfan sulfate, o,p'-DDT, p,p'-DDT, o,p'-DDE and p,p'-DDE whereas for organophosphate pesticides, they were chlorpyrifos and diazinon. At the river upstream where a dam is located for public water supply, incidents of pesticide levels exceeding the European Economic Community Directive of water quality standards have occurred. Furthermore, the wetland ecosystems located at the downstream of the river which houses the fireflies community is being threatened by occasional pesticide levels above EPA limits for freshwater aquatic organisms. The occurrence of these residual pesticides in the Selangor River can be attributed to the intense agriculture and urban activity.

Keywords: Pesticides; River water; Agriculture; Urban; Southeast Asia.

Abstract word count: 172

1. Introduction

Pesticides were introduced after the World War II for their various benefits but general worldwide intensive usage now poses potential hazards to the environment and human health (Chambers et al., 2001). Organochlorine pesticide represents an important group of persistent organic pollutants (POPs), which are believed to be possible carcinogens or mutagens as well as endocrine disruptors (Thomas et al., 1998; Peter et al., 2002). The issue of POPs has given rise to a global campaign initiated by the United Nations Environmental Program (UNEP) to eliminate or reduce these health and environment threatening chemicals worldwide. The UNEP has listed 12 such chemicals that are chlorine containing organic compounds of which nine are pesticides (Peter et al., 2002). In an effort to substitute these persistent organochlorine pesticides, agricultural sectors have shifted towards organophosphate pesticides. However, organophosphate pesticides are generally much more toxic to vertebrates compared to other classes of insecticides even though they rapidly degrade in the environment (Chambers et al., 2001). The usage of these pesticides has brought about great concern in the scientific community on the possible toxic effects of these pesticide contaminations to both aquatic flora and fauna as well as to humans (Jorgenson, 2001).

Malaysia is experiencing a continuous rapid change in land use associated with government developmental policies. Among the states in Malaysia, Selangor is the most rapidly developing and densely populated with 3.9 million inhabitants in the year 2000 (Department of Statistics Malaysia, 2001). During the 1960s and 1970s the Malaysian economy was mainly based on agricultural activities. But from the 1980s onwards, there has been a major economic transformation focused on the manufacturing sector since the government has been aiming towards industrialization. During the period between 1981 and 1995, the land used for agriculture in the state of Selangor has increased from 46% to 49% due to an increase in oil palm plantations. The industrialization policy has brought about urbanization, commercial and infrastructure developments in the state. This is reflected in an increase in urban land usage from 5% in 1981 to 8% in 1995. The increase in land used for both urban and agricultural sector has brought about the clearing of natural and wetland forests. The forest coverage in the state has decreased from 49% in 1981 to 43% in 1995, with a higher decrease in wetland forest since the peat soil in wetlands is particularly good for oil palm plantations whereas mangrove areas are more suitable for aquaculture (Abdullah and Nakagoshi, 2005). Rapid changes in land use are recognized as bringing severe environmental degradation in various environmental compartments such as the forest, wetland and aquatic ecosystems.

In Malaysia, the riverine ecosystem is of particular interest since river water provides about 98% of the country's water requirements (Azhar, 2000). Therefore, contamination of river waters poses a serious health risk to the public. The monitoring of river water quality is under the responsibility of the Department of Environment (DOE), Malaysia. However, pesticide contaminations in rivers are not documented in the yearly environmental reports and information on pesticide contaminations is generally lacking (DOE, 1998). Despite the fact that the use of certain organochlorine insecticides in agriculture is prohibited in many countries, these compounds have been detected in the environment worldwide due to their persistency (Rajendran and Subramanian, 1997). The impacts of pesticide contaminations on aquatic ecosystems have been well studied in North America, Japan and many parts of Europe (Yamaguchi et al., 2003). In contrast, there is very little data on the levels of pesticide residues in developing countries (Albert, 1996). Therefore, monitoring data from developing countries is an important source of information portraying the state of environment in these countries as well as reflecting the effectiveness of environmental policies.

The objective of this study was to obtain systematic monitoring data on the contamination levels of selected organochlorine and organophosphate pesticide residues in the Selangor River, Malaysia. The selection of these insecticides was based on previous usage. Except for the organophosphate insecticides (chlorpyrifos and diazinon), the organochlorine insecticides have been either banned or restricted to only palm oil and coconut plantations since 1990. DDT and heptachlor were used to control malaria through fumigation. Chlorpyrifos and diazinon were used as household insecticides. Dieldrin, chlorpyrifos, endosulfan, heptachlor and lindane were used as wood preservatives against termites. Lindane was also used against lice. In agriculture; dieldrin and endosulfan were used as contact poisons for pests in vegetable, tea and cotton plantations. Heptachlor and lindane were used as seed and soil treatment against soil insects. Chlorpyrifos and diazinon are sprayed on rice, fruits, vegetables and horticultural plants to control leaf eating and suckling insects. Although most of the organochlorine insecticides have been banned, they can still be detected in the river water samples. This paper reports the contamination levels of these pollutants in the river water of selected sites where agricultural and urban activities are intense. It also examines the trends of pesticide residues over the two-year period (2002-2003) of the monitoring program for both the dry seasons

(February-March) and rainy seasons (September-October). This study gives an overall view of pesticide contaminations in a rapidly developing state and its effects on the surface water quality of the Selangor River.

2. Materials and methods

2.1. Reagents and materials

Pesticide standards lindane, dieldrin, heptachlor, o,p'-DDT, p,p'-DDT, o,p'-DDE, p,p'-DDE, diazinon and chlorpyrifos were purchased from Cerilliant Corporation, Texas,USA. Endosulfan (70% α-isomer: 30% β-isomer) and endosulfan sulfate were from Dr. Ehrenstorfer – Schäfers, Augsburg,Germany. All pesticide standards were above 99% purity. Diazepam as internal standard was purchased from Sigma Aldrich, Missouri, USA. Sodium chloride (NaCl) and sodium sulphate anhydrous (Na_2SO_4) were obtained from Asia Pacific Specialty Chemicals, New South Wales, Australia. Ethyl acetate, dichloromethane and concentrated hydrochloric acid were obtained from Fisher Scientific, Leicestershire, UK; all were of chromatographic purity.

2.2. Sample extractions and analysis

River water samples were filtered with glass fiber filters 0.1mm (Whatman, UK) to remove debris. A 500 mL river water sample was transferred into a 2 L glass-separating funnel and 100 μL of internal standard (diazepam at 2ug/mL) was added. It was thoroughly mixed by inverting the flask three to four times. Hydrochloric acid (2 N) was added to adjust the pH to about 2-3, checked by a pH meter (Mettler Toledo, Greifensee, Switzerland). Then, 30 g of NaCl was added to produce a salt out effect. The sample was extracted twice with 50 mL dichloromethane: ethyl acetate mixture (50:50); shaken for 10 min each time. The combined organic phase was dried by passing it through anhydrous Na_2SO_4. The organic phase was concentrated to 3-5 mL in a vacuum rotary evaporator (Eyela, Osaka, Japan) and further dried under a gentle stream of nitrogen. The sample was reconstituted in 100 μL of dichloromethane and 1 μL of the aliquot was analyzed by gas chromatography-mass spectrometry (GC-MS). A GC17A gas chromatograph coupled to a QP5050 mass spectrometer (Shimadzu Ltd., Tokyo, Japan) was used. It was operated using Class 500 GCMS Shimadzu software. The analytical column was a ValcoBond VB-1 (15 m x 0.25 mm I.D., 0.25 µm film thickness), coated with 5% biphenyl-95% dimethylsiloxane stationary phase (VICI Gig Harbor Group, Michigan, USA). The gas chromatograph was programmed from an initial temperature of 80 ^oC, held for 0.5 min, followed by a temperature increase at 12 ^oC min^{-1} up to 180 ^oC, held for 4 min, then increased to 220 ^oC at 8 ^oC min^{-1} and finally up to 300 ^oC at a rate of 45 ^oC min^{-1} and held for 2 min. The total run time was 22 min. The temperature of the injector and interface were 280 ^oC and 300 ^oC respectively. Helium was used as the carrier gas at a flow rate of 1.2 ml min^{-1}. The mass spectrometer was operated in the electron impact (70 eV) selected ion monitoring (SIM) mode. The mean recoveries of the pesticides were estimated at three concentration levels (Table 1). The limit of quantitation for these compounds, determined experimentally is presented in Table 1. Gas chromatogram of a blank and a spiked ultra-pure water sample are shown in Figure 1.

3. Study area and samplings

3.1. Site descriptions

The Selangor River originates at an altitude of 1,500 m in a naturally vegetated area and flows in a southwesterly direction before discharging into the Straits of Melaka. It is located in the northern part of the state of Selangor, which is the most developed state in the country with 3.9 million inhabitants. The river has a catchment basin of 1,743 km^2 and receives an annual mean rainfall of 2,670 mm. The Selangor River serves as a source of public water supply generating 2,500 million liters per day for 1.3 million inhabitants in the Selangor state and the country’s capital city, Kuala Lumpur. The Selangor River was chosen as the site of study because it is a source of raw water to the public water supplies. Along the river there are many areas of agricultural activities such as vegetable farms, oil palm and rubber plantations, as well as aquaculture farms cultivating freshwater fish for human consumption. It is also the recipient of industrial wastewater from paper manufacturing and rubber and oil palm refineries located near to the river. Downstream of this river is an ecotourism wetland area housing a vast number of species of flora and fauna, particularly fireflies. The sampling sites are shown on the sketch map in Figure 2 and the descriptions of each sampling site are as follows:

Site S1 (03°20’N, 101°15’E) is at an upstream part of the Selangor River where there are no agriculture or industrial activities present.

Site S2 (03°23’N, 101°24’E) was previously a recreation area but now a dam has been built there to provide water supply.

Site S3 (03°28’N, 101°38’E) receives wastewater discharges from a paper and furniture factory. There are ex-mining ponds downstream from the site whereas some agriculture and residences are located upstream of the site.

Site S4 (03°30’N, 101°38’E) is surrounded by oil palm plantations on both sides of the river. Upstream of this site are paint industries whereas downstream sand mining activities are in progress.

Site S5 (03°34’N, 101°41’E) is situated among an area of oil palm plantations and vegetable farms.

Site S6 (03°35’N, 101°36’E) is near to an area of aquaculture and vegetable farms. The river serves as a constant source of fresh water for the fishponds.

Site S7 (03°35’N, 101°36’E) is located in an area of rubber and oil palm plantations with housing estates along both sides of the river.

Site S8 (03°22’N, 101°36’E) is an ecotourism wetland area popular for its fireflies. This wetland is one of the three wetland forest reserves remaining in the state of Selangor.

Site S9 (03°22’N, 101°28’E) is the river’s estuary opening to the Straits of Melaka where fishing villages are found.

3.2. Sampling procedures

Seasonal field samplings were carried out during both the dry seasons (February-March) and rainy seasons (September-October) throughout the two-year period (2002-2003). Grab water samplings at 20 cm depth using a 1.2 L Kemmerer water sampler (Cole-Palmer, Minnesota, USA) were done in duplicate. In-situ measurements (pH, temperature, dissolved oxygen, salinity and conductivity) were taken prior to storing the samples in 1 L amber glass bottles. The containers were pre-rinsed with the river water sample before being filled just to overflowing. The samples were kept at 4 ^{o}C until extraction. These samples were extracted within 48 h together with spiked water samples (100, 200 and 400 ng l^{-1}) and blank ultra-pure water for quality control purposes.

4. Results and discussions

In the 2003 Global Report by Whylie et al. (2003) on Regional Based Assessment of Persistent Toxic Substances, it was pointed out that information on the importation, use and emission of pesticides is limited in the South East Asia region. Cheaper, outdated and broad-spectrum insecticides are often used in developing countries which have detrimental effects on both the environment and human health. Therefore, monitoring of these pesticide residues in developing countries is essential to determine its impacts on the environment. Furthermore, human health would be seriously threatened by drinking waters contaminated with these pollutants.

Our study has revealed that a significant number of pesticide residues were detected in the river. They were, in decreasing frequency of detection, chlorpyrifos, lindane, total DDEs, heptachlor, endosulfan, diazinon, total DDTs, endosulfan sulfate and dieldrin (Fig. 3). Fluxes in the detected pesticide levels in different parts of the Selangor River indicate local inputs of contaminants. There was no cumulative effect in contamination levels toward the downstream part of the river (Fig. 4) as compared to the trend found by Rovedatti et al., (2001) in the Reconquista river, Argentina where sampling sites downstream appears to be more polluted. This could be due to the evaporation of these volatile pesticides in tropical temperatures, dilution or adsorption of the pesticide residues into river sediments.

The concentration range of detected residual pesticides in the Selangor River, Malaysia during the dry season in the year 2002 were 23.4-92.9 ng L^{-1} for chlorpyrifos and 50.8-58.8 ng L^{-1} for lindane; whereas during the rainy season pesticide levels were from 87.0-100.2 ng L^{-1} for endosulfan, 182.1-202.1 ng L^{-1} for endosulfan sulfate, 39.5-270.7 ng L^{-1} for total DDEs, 29.3-147.0 ng L^{-1} for total DDTs, 16.9-90.3 ng L^{-1} for lindane and 31.5-55.8 ng L^{-1} for chlorpyrifos. For the year 2003, during the dry season, pesticide levels were 125.1-1,848.7 ng L^{-1} for endosulfan, 22.1-50.1 ng L^{-1} for dieldrin, 14.0-27.1 ng L^{-1} for total DDEs, 132.1-346.1 ng L^{-1} for heptachlor, 52.2-118.2 ng L^{-1} for chlorpyrifos and 116.1-510.0 ng L^{-1} for diazinon, whereas during the rainy season pesticide levels were 100.0-151.1 ng L^{-1} for endosulfan, 12.2-127.0 ng L^{-1} for total DDEs, 10.1-14.1 ng L^{-1} for lindane, 16.2-76.3 ng L^{-1} for heptachlor and 153.1-195.2 ng L^{-1} for chlorpyrifos.

Generally, chlorpyrifos was detected at all the nine sites during the dry season of 2002 whereas lindane was detected in all the sites during the rainy season of the same year (Fig. 4). The occurrence of chlorpyrifos in all the sites was due to its wide applications as a household insecticide, termite control agent as well as against agricultural insects. Although lindane usage is legally restricted to oil palms and coconut plantations (Quah, 1999) it has been detected in non-agricultural sites as well. Beside agricultural applications, lindane is also used to eradicate mites and lice in humans and animals. Detection of lindane during the rainy seasons could be attributed to surface runoff from oil palm plantations. The lindane level in this study (90.3 ng L^{-1}) is comparable to the level detected in the surface waters of Northern Greece (81.0 ng L^{-1}) (Golfinopoulos et al., 2003) but lower than the level detected in India, another tropical country (260.0 ng L^{-1}) (Sankararamakrishnan et al., 2005).

It is surprising to note that at site S1 which is located in the upstream part of the river where there are no agricultural or industrial activities, various pesticides were detected throughout the study period (Table 2 and 3). This could be due to fumigation activities to curb malaria in the area and household insecticide usage. In site S2 (Fig. 4) where a dam is located for public water supply the concentration of diazinon (510.0 ng L^{-1}) exceeded the EEC Council Directive 98/83/EC for water quality standard intended for human consumption as such that the total pesticide level of not more than 500.0 ng L^{-1} and individual pesticide levels of not greater than 100 ng L^{-1} (EECD, 1998). An exceptionally high concentration of endosulfan (1,848.7 ng L^{-1}) was detected in site S5 during the dry season of 2003 (Table 3). This could be due to leakage of pesticide storage tanks from the nearby oil palm plantations or vegetable farms. The heptachlor level (76.3 ng L^{-1}) detected in site S6 (Fig. 4) which is next to a fish aquaculture has exceeded the WHO guideline values (30.0 ng L^{-1}) for potentially carcinogenic pesticides (Hamilton et al., 2003). Heptachlor is a persistent organic pollutant capable of biomagnifying in the food chain (Perez-Ruzafa et al., 2000). The occurrence of heptachlor could originate from contaminated soil and wood of houses treated against termites. The wetlands in site S8 (Fig. 4) which are home to the fireflies community could be threatened by the chlorpyrifos levels (148.6 and 85.2 ng L^{-1}), which are above the EPA ambient water-quality levels for acute toxicity towards aquatic organisms (83.0 ng L^{-1}) (Hamilton et al., 2003).

The total DDTs detected in this study were present only during the rainy season of 2002 with concurrent detection of total DDEs as well (Fig. 4). During that period, there were heavy thunderstorms which caused occasional flash floods. DDT has been banned in Malaysia since 1990 (Quah, 1999), the presence of DDT in this study may be due to desorption of residual DDT from soil contaminated from previous fumigation activities. During these flash floods, rainwater could have washed off this soil and caused residual DDT to enter the river waters. DDT is a persistent pesticide that can remain in the soil for up to 30 years (Golfinopoulos et al., 2003).

This study has shown that agriculture, urban and industrial activities in the state of Selangor coupled with high population growth have caused deterioration in its river water quality. It has been previously observed by Dana et al. (2004) that an increase in urbanization can translate into a higher contamination levels in the streams of towns and cities. Whereas in the study of Kruawal *et. a*l. (2005), it was found that pesticides detected in raw river water intake were not removed by conventional water treatment process. Thus, residual endosulfan sulfate and atrazine detected in the raw water intake were at the same concentration range as detected in the tap water at the end of the treatment plant. That study was conducted in Thailand where water treatment involves sedimentation, clarification and disinfection process. These processes were not effective in removing these pesticides but with the incorporation of activated carbon, these pesticides can be removed from the water. Malaysia's water supply treatment also uses the conventional water treatment process with no activated carbon involved. Therefore, there are concerns that such pollution could result in potential health consequences associated with the occasional exposure of urban populations to contaminated drinking water. There is a need to undertake continuous monitoring of these pollutants in the Selangor River as rapid developments have caused deterioration in the water quality of the aquatic environment. Such monitoring programs would not only provide information on the levels of contamination but would also allow the assessment of the effectiveness of existing mitigation measures and policies, thus encouraging further improvements.

5. Conclusion

The occurrence of selected organochlorine and organophosphate pesticides was studied in the Selangor River, Malaysia over a period of two years. The pesticides detected were chlorpyrifos, lindane, heptachlor, endosulfan, endosulfan sulfate, diazinon, total DDTs, total DDEs and dieldrin. This study has shown the presence of organochlorine pesticides despite the fact that they have been banned for a considerable amount of time in Malaysia. The concentrations varied between sampling site and seasons. In some cases, the residual concentrations were higher than the limits set by the WHO or US EPA. Contamination of the Selangor River with these pesticide residues poses a significant health risk to the public from consuming contaminated drinking water and fish. The wetland ecosystems are also threatened by the presence of pesticides in its waters. The presence of pesticide residues is attributed to intense agriculture and urban activities due to rapid development over the past decade. While point sources of pollution are obvious and readily identifiable in the measurements, there is also a need to identify and control non-point sources of pollutions. This monitoring study is being continued to provide more information on the pesticide contaminations in the Selangor River, Malaysia which will further contribute to the information available on pesticide residues found in the surface waters of Malaysia.

Acknowledgements

This study was funded under the project of Environmental Monitoring and Governance in the East Asia Hydrosphere with the United Nation University (UNU), Tokyo, Japan. Field samplings were done with the assistance from WWF Malaysia and Alam Sekitar Malaysia Sdn. Bhd. (ASMA). Instrumentation was provided by Shimadzu Ltd., Tokyo, Japan. The authors would like to thank Dr. Michael Buckle from the Department of Pharmacy, University Malaya, Malaysia for editing this manuscript.

References

Abdullah, S.A., Nakagoshi, N., 2005. Changes in landscape spatial pattern in the highly developing state of Selangor, peninsular Malaysia. Landscape and urban planning. 52, 23-30.

Albert, L.A., 1996. Persistent pesticides in Mexico. Reviews of Environmental Contamination and Toxicology. 147, 1-44.

Azhar, M.G., 2000. Managing Malaysian Water Resources Development. Special Bulletin on Issues of Citizen's Health 2000. Corporate Development, Department of Irrigation and Drainage, Kuala Lumpur, Malaysia. 40-58.

Chambers, H.W., Boone, J.S., Carr, R.L., Chanbers, J.E., 2001. Chemistry of organophosphorus insecticides. In: Robert, I.K. (Eds.). Handbook of Pesticide Toxicology, 2nd ed. Academic Press, California, USA. 913-917.

Dana, W.K., Mary, S., Michael, T.M., Edward, T.F., Steven, D.Z., 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. Science of the Total Environment. 323, 119-130.

Department of Statistic Malaysia, 2001. Preliminary Count Report. Population and Housing Census. Department of Statistic Malaysia, Kuala Lumpur, Malaysia. 43-56.

DOE (Department of Environment), 1998. Malaysia Environment Quality Report 1998. Ministry of Science, Technology and Environment, Kuala Lumpur, Malaysia. 10-12.

EECD (European Economic Community Directive), 1998. EEC Council Directive 98/83/EC. Official Journal of European Communities, Brusells. L 330, 42.

Golfinopoulos, S.K., Nikolau, A.D., Kostopoulou, M.N., Xilourgidis, N.K., Vagi, M.C., Lekkas, D.T., 2003. Organochlorine pesticides in the surface waters of Northern Greece. Chemosphere. 50, 507-516.

Hamilton, D.J., Ambrus, A., Diterle, R.M., Felsot, A.S., Harris, C.A., Holland, P.T., 2003. Regulatory limits for pesticides in water-IUPAC Technical Report. Pure Applied Chemistry. 75, 1123-1155.

Jorgenson, J.L., 2001. Aldrin and Dieldrin: A review of research on their production, environmental deposition and fate, bioaccumulation, toxicology and epidemiology in the United States. Environmental Health Perspectives. 109, 113-139.

Kruawal, K., Sacher, F., Werner, A., Muller, J., Knepper T.P., 2005. Chemical water quality in Thailand and its impacts on the drinking water production in Thailand. Science of the Total Environment. 340, 57-70.

Perez-Ruzafa, A., Navarro, S., Barba, A., Marcos, C., Camara, M.A., Salas, F., Gutierrez, J.M., 2000. Presence of pesticides throughout trophic compartments of the food web in the Mar Menor lagoon (SE Spain). Marine Pollution Bulletin. 40, 140-151.

Peter, O., Lin, K.C., Karen, P., Joe, A., 2002. Persistent Organic Pollutants (POPs) and Human Health. World Federation of Public Health Association Publications, Washington D.C., USA. 1- 35.

Quah, S.H., 1999. Sustainable food production, income generation and consumer protection in Malaysia. Agro-chemical News in Brief Special Issue. Department of Agriculture, Kuala Lumpur, Malaysia. 39-46.

Rajendran, R.B., Subramanian, A., 1997. Pesticide residues in water from river Kaveri, South India. Chemistry Ecology. 13, 223 – 236.

Rovedatti, M.G., Castane, P.M., Topalian, M.L., Salibain, A., 2001. Monitoring of organochlorine and organophosphorus pesticides in the water of the Reconquista River (Buenos Aires, Argentina). Water Research. 35, 3457-3461.

Sankararamakrishnan, N., Sharma, A.K., Sanghi, R., 2005. Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Uttar Pradesh, India. Environment International. 31, 113-120.

Thomas, M.C., Eric, D.C., Ralph, L.C., William, P.W., David, G.A., Karl, P.B., Jennifer, L.H., Melba, S.M., Donald, J.R., John, E.S., Leslie, W.T., Maurice, G.Z., Yogendra, M.P., 1998. Environmental Endocrine Disruption: An Effects Assessment and Analysis. Environmental Health Perspectives. 106, 11-56.

Whylie, P., Albaiges, J., Barra, A., Bouwman, H., Dyke, P., Wania, F., Wong, M., 2003. Regionally based assessment of persistent toxic substances. Global Report 2003. UNEP Chemicals, Geneva, Switzerland. 35-156.

Yamaguchi, N., Gazzard, D., Scholey, G., Macdonald, D.W., 2003. Concentration and hazard assessment of PCBs, organochlorine pesticides and mercury in fish species from the upper Thames River pollution and its potential effects on top predators. Chemosphere. 50, 265-273.

List of tables and figures for manuscript

Table 1. Percentage mean recovery (n=6) with relative standard deviation (in parenthesis) of selected pesticides at three concentration levels and limit of quantitation.

Pesticides	Concentration levels (ng L^{-1})			Limit of quantitation (ng L^{-1})
	100	200	400	
Lindane	99.3 (7.3)	112.7 (3.8)	102.3 (7.6)	5
Diazinon	106.7 (9.3)	98.3 (10.5)	102.0 (10.3)	5
Heptachlor	96.7 (14.2)	100.6 (12.6)	104.8 (5.9)	10
Chlorpyrifos	101.5 (10.0)	97.8 (12.7)	108.4 (8.6)	5
o,p'-DDE	105.6 (11.6)	99.2 (6.0)	111.9 (4.7)	5
Dieldrin	104.1 (5.1)	98.5 (8.2)	111.4 (3.2)	10
p,p'-DDE	99.6 (8.6)	100.5 (5.3)	106.4 (9.8)	5
Endosulfan	98.1 (8.6)	100.7 (4.1)	103.6 (12.3)	10
Endosulfan Sulfate	99.1 (9.0)	105.4 (9.0)	101.6 (6.4)	10
o,p'-DDT	94.8 (10.1)	103.0 (9.8)	101.6 (14.2)	5
p,p'-DDT	93.0 (8.6)	89.3 (14.2)	107.2 (9.9)	5

Table 2. Mean concentration levels (ng L^{-1}) of detected pesticides for the year 2002 in Selangor river water samples, Malaysia.

Sampling sites	Chlorpyrifos	Lindane (2 μg L^{-1})[a]	Total DDEs	Heptachlor (50 ng L^{-1})[a]	Endosulfan (10 μg L^{-1})[a]	Diazinon	Total DDTs (100 ng L^{-1})[a]	Endosulfan sulfate	Dieldrin (20 ng L^{-1})[a]
(a) Dry season (February-March 2002)									
1	20.8								
2	54.0								
3	57.1								
4	92.9								
5	73.6								
6	55.6								
7	71.8	54.8							
8	92.8								
9	33.9								
(b) Rainy season (September-October 2002)									
1		90.3							
2	38.3	23.6	67.9						
3		16.9	174.8				30.0		
4	41.7	22.7	104.4				45.2		
5		45.1					25.1		
6	35.0	58.6	39.5				31.5		
7	31.5	52.1	270.7		93.6		147.0	192.1	
8	55.8	63.8							
9	49.2	79.6							

[a] Maximum concentration limit in Class IIA standard for pesticide levels in river waters suitable as water supply (DOE, 1998).

Table 3. Mean concentration levels (ng L^{-1}) of detected pesticides for the year 2003 in Selangor river water samples, Malaysia.

Sampling sites	Chlorpyrifos	Lindane (2 µg L^{-1})[a]	Total DDEs	Heptachlor (50 ng L^{-1})[a]	Endosulfan (10 µg L^{-1})[a]	Diazinon	Total DDTs (100 ng L^{-1})[a]	Endosulfan sulfate	Dieldrin (20 ng L^{-1})[a]
(a) Dry season (February-March 2003)									
1			27.1						36.1
2						510.0			
3						451.0			
4									
5				239.1	1848.7	211.1			
6						283.1			
7					125.1	116.1			
8	85.2		14.0						
9									
(b) Rainy season (September-October 2003)									
1	160.6			36.2					
2				16.2					
3	195.2			62.0	100.0				
4									
5	165.2			63.1					
6	177.1			76.3					
7	178.2				109.2				
8		12.1	12.2	57.1					
9			127.0		151.1				

[a] Maximum concentration limit in Class IIA standard for pesticide levels in river waters suitable as water supply (DOE, 1998).

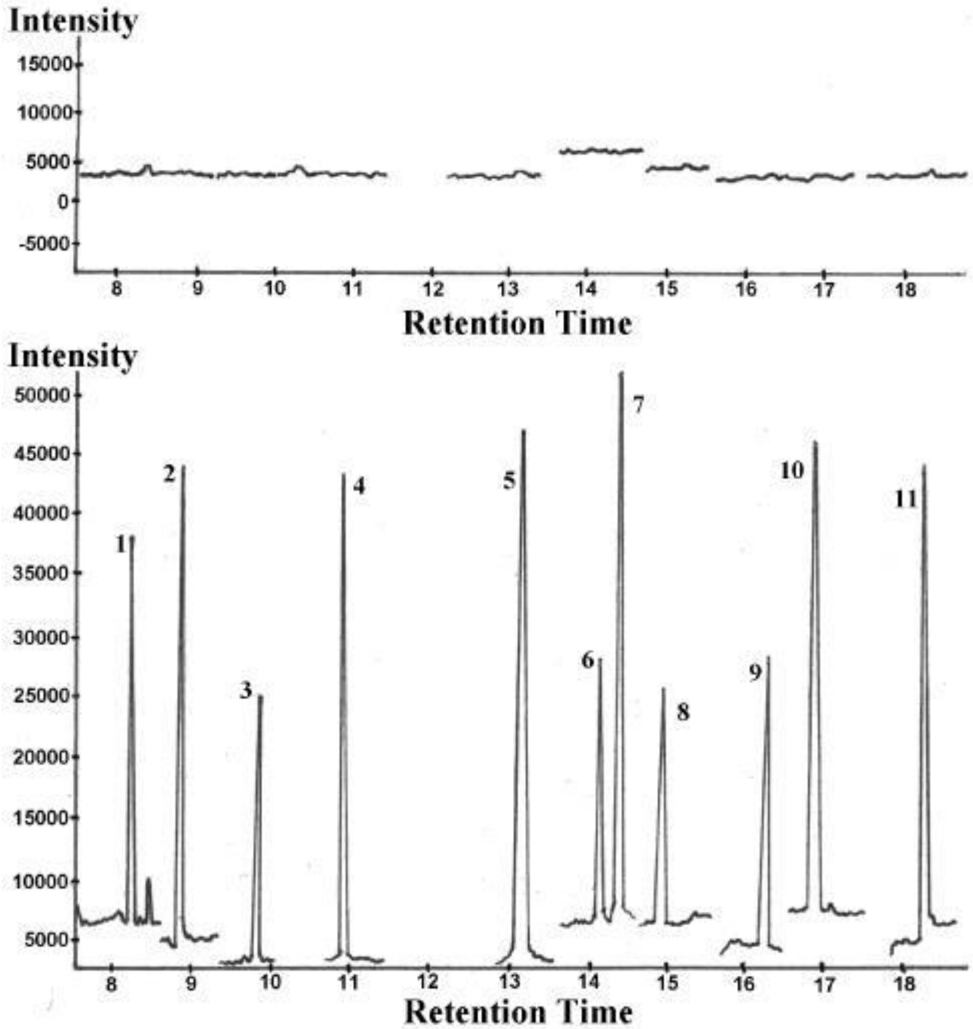

Fig. 1. Chromatogram of blank ultra-pure water and spiked water sample at 10 ngL^{-1} (LOQ). In the order of elution (1-11): lindane, diazinon, heptachlor, chlorpyrifos, o,p'-DDE, dieldrin, p,p'-DDE, endosulfan, endosulfan sulfate, o,p'-DDT and internal standard (diazepam).

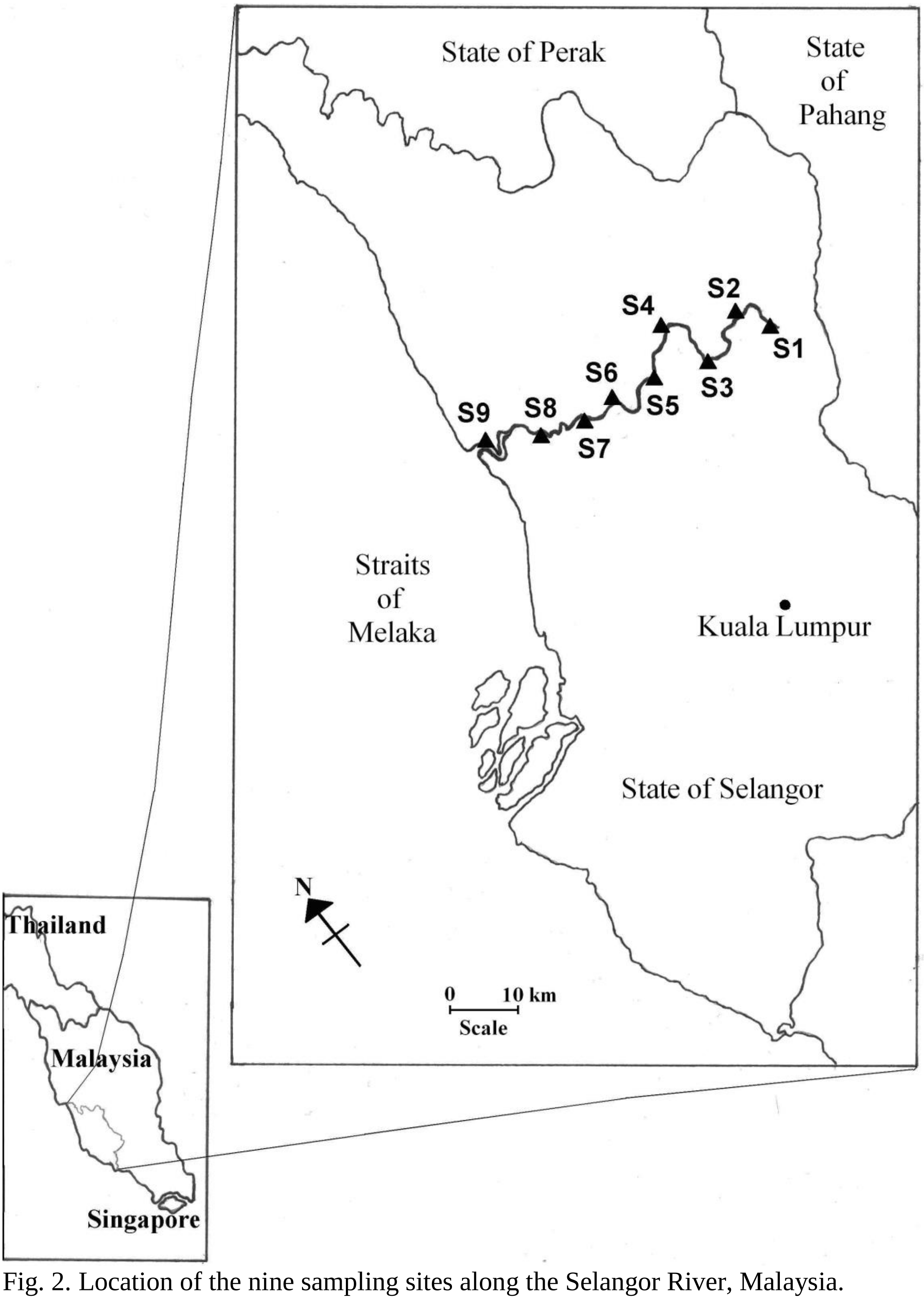

Fig. 2. Location of the nine sampling sites along the Selangor River, Malaysia.

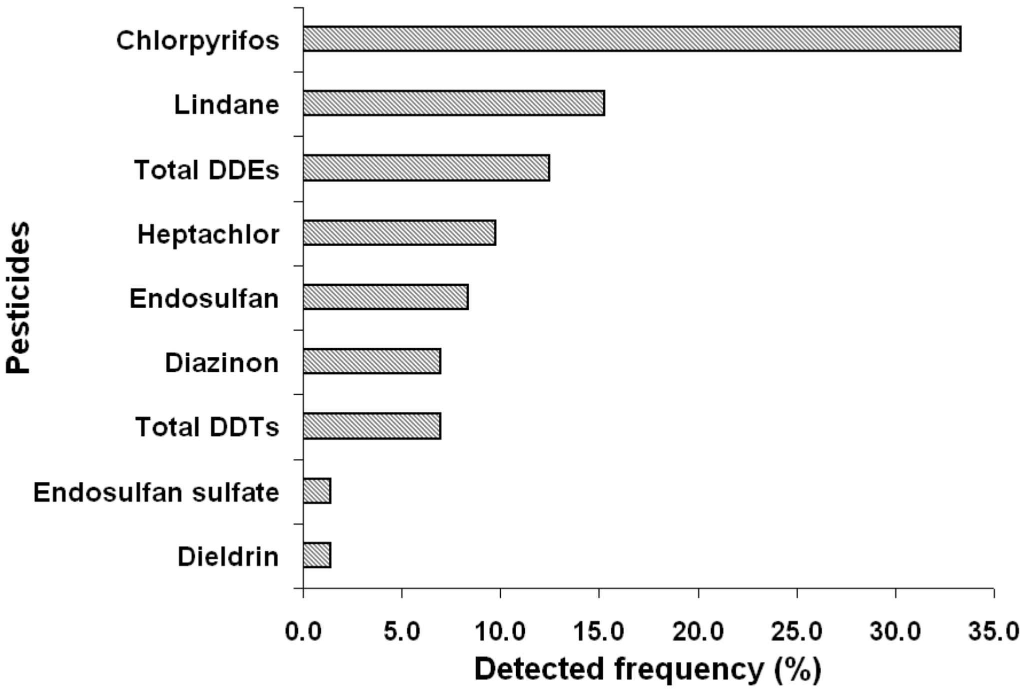

Fig. 3. Percentage detection frequency of pesticides in the Selangor River, Malaysia.

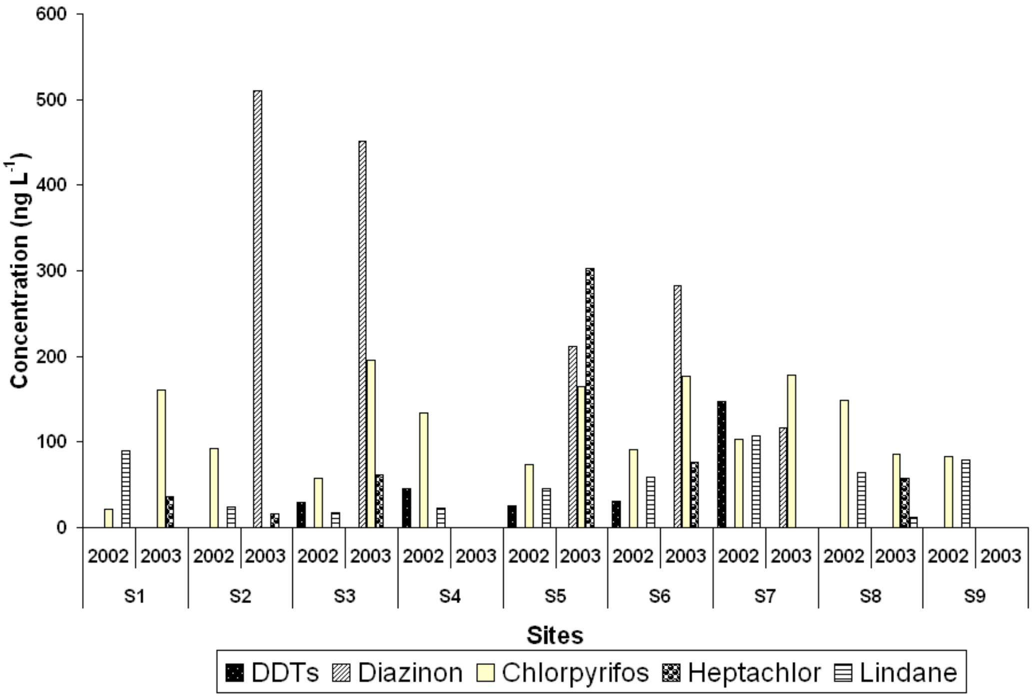

Fig. 4. Levels of pesticides detected at the nine sampling points (S1-S9) in Selangor River throughout the period of 2002 to 2003.