Cross-Sectional Assessment of *Chlorpyrifos* in a Small Stream Running Through a Densely Cultivated Area in Kandy District

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Introduction

Chlorpyrifos (*O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothionate*) is a highly active, non-systemic pesticide applied to control a wide range of soil pests and arthropods on various crops including vegetables, citrus, cereals, maize, potato and tobacco. *Chlorpyrifos* containing pesticides are commercially available as Durban, Lorsban, Syren, Commando, Judo, Bullet, Chlofos, Unifos, Loseban, Patas, Lidoband, Dhanwan, Dorson and Omexan in the local market. This chemical is moderately toxic following acute oral, dermal, and inhalation exposures (Zhao *et al.*, 2004). The embankment of Kiwullinda Oya (a small stream, 9.5 m wide and 1 m average depth), running through the Marassana area in Kandy District and feeding the Victoria reservoir, is densely cultivated with vegetables and paddy. *Chlorpyrifos*, with 40 days half-life in buffers at 30 °C (WHO, 2002), is one of the popular pesticides in use in Marassana. Therefore, the probable presence of *chlorpyrifos* in surface and ground water at Marassana, especially in the Kiwullinda Oya, has long been suspected. The objective of this research was to quantify *chlorpyrifos* concentrations (if present) in the water of Kiwullinda Oya stream basin. It is important because, according to the discharge water quality standards (CEA, 1990), no pesticide should be detected in surface water even in trace amounts.

Methodology

Five random water samples were collected from the Kiwullinda Oya in May 2007, which was during off-peak pesticide application period. On June 16th, 2007, which fell within the peak pesticide application period, 14 water samples were collected over a 3 km stretch of Kiwullinda Oya. The sampling locations are shown in the schematic diagram of Figure 1. From each sampling point, a 600 ml sample of water was collected in a 1-litre amber glass bottle with a glass lid, and the samples were transported to the Analytical Laboratory of the department within 4 hours of the sample collection. Samples were refrigerated below 5 °C until the time of analyses. Water samples were analyzed for the presence of *chlorpyrifos* using a High Performance Liquid Chromatograph (HPLC) method (CIPAC 1 C, 1985). In this method, the target compound, *chlorpyrifos*, was extracted using dichloromethane. The extract was then concentrated and dried by means of blowing ambient air, which is at 35 °C or below, over the extract. The residue was then dissolved in a mobile phase (acetonitrile). The solution so prepared was injected to the HPLC and the peak area readings were obtained. These readings were then converted to concentrations by use of calibration charts, which were generated in this study itself.

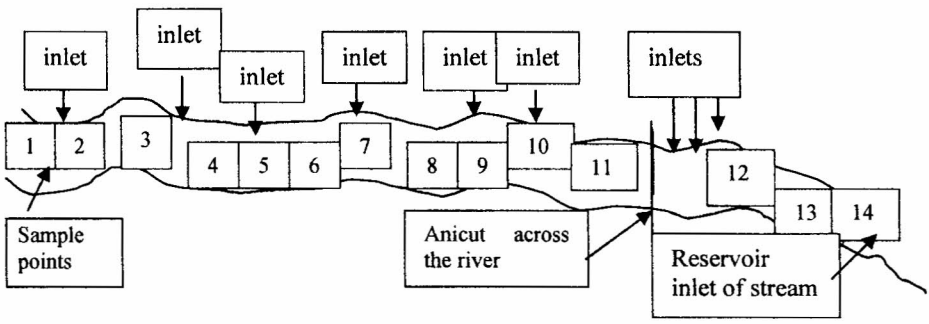

Figure 1. Schematic diagram of the 14 sampling points and the relative positions of inlets feeding significant amount of water to the investigated stream

Results

Chlorpyrifos in environmental wastewater samples were extracted using Dichloromethane for two reasons: (1) to prevent impurity contamination in HPLC column (2) to increase *chlorpyrifos* concentration in samples to HPLC measurable level. Figures 2(a) and 2(b) show charts used for HPLC calibration and extraction efficiency estimation, respectively. Both graphs exhibit linear relationships (regression coefficients are 0.9387 and 0.9913). The coefficients of linear regression shown in the figures were used in the conversions of HPLC peak area to *chlorpyrifos* concentration in wastewater samples. All measurements used for calibration curves were duplicated.

Chlorpyrifos concentrations of the 5 random samples collected from the stream during off-peak pesticide application period are 0.000, 0.017, 0.058, 0.116 and 0.118 μg/l. *Chlorpyrifos* concentrations of the 14 samples collected during peak pesticide application period are given in Figure 3.

Discussion

Significant amounts of the pesticide, *chlorpyrifos*, were detected in the water samples in the Marassana vegetable and paddy cultivation area during both the off-season and peak-season of pesticide application. The maximum detected concentration during off-season and peak-season were 0.12 μg/l and 2.48 μg/l, respectively.

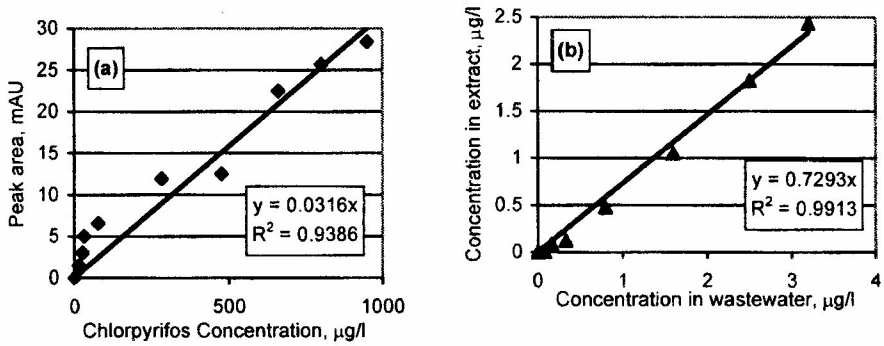

Figure 2. Calibration curves for (a) HPLC peak area versus *chlorpyrifos* concentration, (b) *chlorpyrifos* concentration in extract versus *chlorpyrifos* concentration in wastewater

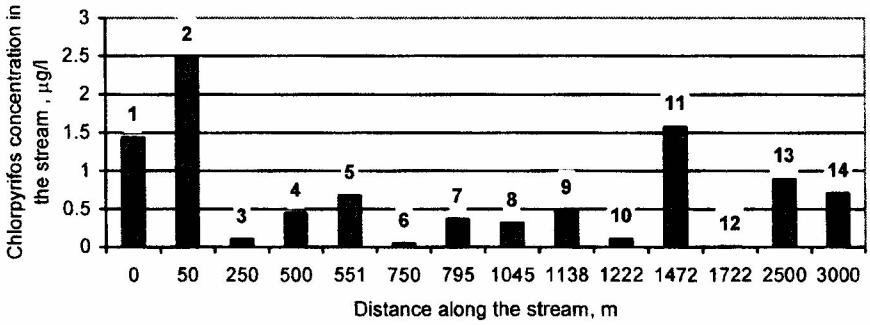

Figure 3. Variation of *chlorpyrifos* concentration along the stream on a day during peak pesticide application period

The *chlorpyrifos* concentration in the water sample collected from one of the community wells in this area was also as high as 0.79 µg/l. The highest *chlorpyrifos* concentration was detected at the sampling point 2 where several irrigated channels and field surface runoffs enter the stream. Comparison of concentration data (Figure 3) and the sampling locations (Figure 1) provides a telling relationship. Local peaks in concentrations are seen at points 2, 5, 7, 9 and 13, where main irrigated canals enter the Kiwullinda Oya. In the span of sampling points 13 to 14, surface runoffs from cultivated lands located at high elevations enter the stream water at no specific location, which keeps the *chlorpyrifos* concentration approximately a constant. Stream water at points 10 and 12 are diluted with large quantities of fresh water entering *via* channels, which are not running through cultivated land. It was observed that the both sides of stream banks between point 10 and 11 were cultivated with vegetables. The high peak at point 11 is therefore, attributed to accumulation of pesticide contaminated water seeping through the stream banks.

Conclusions

Though, according to Sri Lankan regulations, not even trace amounts of pesticides should be detected in discharge water from industrial and agricultural applications high concentrations of *chlorpyrifos* (up to 2.48 µg/l) have been observed along a 3 km stretch of Kiwullinda Oya, a small stream running through the cultivated lands in Marassana. It is apparent that *chlorpyrifos* entered the stream with the water from irrigation channels and surface runoffs. It is found that the presence of *chlorpyrifos* in surface waters is not limited only to the peak, but also to the off-peak pesticide application periods. The cross-sectional assessment of the *chlorpyrifos* reported in this paper is being repeated at present to study the variations in the concentration of *chlorpyrifos* in the stream with time.

Acknowledgements

RG/2006/33/E, University of Peradeniya, is acknowledged for funding. Special thanks are due to the Pesticide Registration Office of the Department of Agriculture and to the technical staff at the Department of Chemical and Process Engineering for the technical support provided.

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