MONITORING CHLORPYRIPHOS RESIDUES IN VEGETABLE GROWING AREA OF OTTANCHATHIRAM BLOCK, T.N., INDIA

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ABSTRACT

The presence of chlorpyrifos in water and soil creates serious threats to humans’ health due to major environmental concerns in terms of surface water, ground water and soil contamination. The study was taken in the Ottanchathiram in Dindigul district in the Indian state of Tamil Nadu. Ottanchathiram is a region in the southwest of Tamil Nadu. Five intensive vegetable growing villages namely Thasaraipatti, Veeralapatti, Ambilikai, Arasappapillaipatti and Vadakadu, were selected for chlorpyriphos residue analysis. Soil and water samples were collected from 0th day of spraying and residues in soil samples are continuously monitored at 15 days interval up to 120 days in Cauliflower, Brinjal, Bhindi and Chilli growing fields. Chlorpyriphos concentration ranged from 0.1 to 1.65 mg/kg in all the villages studied from 0th day to 120th days after application. The maximum concentration (1.65 mg/kg) of chlorpyriphos was observed in Cauliflower field of Ambilikai village and minimum (1.1 mg/kg) in Veeralapatti village. The concentration was reduced to 0.9mg/kg at 120th days after application in Ambilikai village. The reduction in concentration was observed at 120th days after application. The concentrations of chlorpyriphos in water samples ranged from 0.01 mg/l to 0.08mg/l. Most of the water samples collected at 45th day recorded 0.01-0.03 mg/l. The concentration was reduced to 0.01 mg/l at 75th day and then not detected in all the villages from 90 to 120th days after application.

KEY WORDS : Chlorpyriphos-soil-water-fate-Monitoring

INTRODUCTION

The term pesticide covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, plant growth regulators and others. These pesticides can be generally classified into four main chemical groups: organophosphate (OP), organochlorines (OC), carbamates/dithiocarbamates (EBDC), and synthetic pyrethroids. About 5.2 billion pounds of pesticides are used worldwide (EPA, 2013). In India, the production of pesticides started in 1952 with the establishment of a plant for the production of BHC near Calcutta, and India is now the second largest manufacturer of pesticides in Asia after China and ranks twelfth globally. In India, the Registration Committee (RC) has registered 299 technical grade pesticides and 589 pesticide formulations as on 1.7.2021. The total chemical pesticide consumption was 57353 MT in the year of 2014-2015. The use of synthetic chemicals for pest control is the most reliable and fastest method of pest management. Worldwide to overcome the problems of lower yields as well as culturally and biologically occurring pests mostly the pesticides are applied in agricultural fields (Hester and Harrison, 2016). On the contrary the substantial adverse effects on ecology and environment the use of such hazardous and toxic pesticide is increasing serious public concern (Pujeri et al., 2015).

The World Health Organization reports that every year there are 3 million pesticide poisonings, most of them were OP related, and 200,000 deaths worldwide that are attributed to either self-
poisoning or occupational exposure. Globally 4.6 million tonnes of pesticide are annually sprayed into the environment, out of which only 1% is effective to target plants and rest 99% is released in non-targeted ecosystem like soil, water bodies and atmosphere (Global pesticide pollution) (EPA, 2013). A vast majority of the population in India is engaged in agriculture and is therefore exposed to the pesticides used in agriculture. The rampant use of these chemicals, under the adage, “if little is good, a lot more will be better” has played havoc with human and other life forms.

The pesticide residues in soil and the environment have the tendency to pollute ground and surface water through leaching and surface run off, thereby increasing the risk of environmental contamination. Increased accumulation of pesticide residues in the food chain and drinking water have been reported to pose serious health hazards. There have been reports of delayed seedling emergence, fruit deformities and abnormal cell division upon prolonged exposure to chlorpyriphos (Liang et al. 2012). Although, solubility of chlorpyriphos is less in water, its toxicity is prevalent in aquatic ecosystem (Li et al., 2014).

Contamination of water by pesticides is widespread. Pesticides can reach surface water through runoff from treated plants and soil followed by groundwater pollution. According to the USGS at least 143 different pesticides and 21 transformation products have been found in ground water, including pesticides from every major chemical class. Increased accumulation of pesticide residues in the food chain and drinking water have been reported to pose serious human health hazards (Akan et al. 2013; Agbeve et al., 2014). For instance, exposure to pesticide residues through food and water are reported to affect thyroid function, cause low sperm count in males, birth defects, increase in testicular cancer, reproductive (Mesnager et al., 2010) and immune malfunction (Tanner et al. 2011), endocrine disruptions, cancers, immunotoxicity (Cocco et al. 2013), neuro behavioural and developmental disorders (Gill and Garg, 2014; Rathod and Garg, 2017). Therefore, the presence of chlorpyrifos in water and soil creates serious threats to humans’ health due to major environmental concerns in terms of surface water, ground water and soil contamination. This study therefore aims at assessing the levels of chlorpyriphos pesticide residues in soil and water from selected vegetable growing villages of Ottanchathiram Block, Dindigul District of Tamil Nadu.

**MATERIALS AND METHODS**

**Study area**

The study was taken in the Ottanchathirim in Dindigul district in the Indian state of Tamil Nadu. Oddanchatram is a region in the southwest of Tamil Nadu, famous for vegetable and cattle market. It is located at the base of the Western Ghats in South India. It is known as vegetable city of Tamil Nadu. Ottanchathiram vegetable market is the largest supplier of vegetables in Tamil Nadu and Kerala. Agriculture is the major economic support for the town region.

**Sampling design:**

Five intensive vegetable growing villages namely Thasaraipatti, Veeralapatti, Ambilikai, Arasappapillaipatti and Vadakadu, were selected for pesticide residue analysis. Soil samples were collected from 0th day of spraying and residues in soil samples are continuously monitored at 15 days interval up to 120 days. Samples were collected randomly at a depth of 0–20 cm with a soil auger and put together to form a composite sample. The composite soil samples were well mixed and three soil replicates were collected from each vegetable growing villages. The soil samples were air dried, sieved using 2 mm nylon mesh and taken for pesticide residues analysis and physico chemical characteristics.

**Water sampling and characterization**

Water samples were collected from the bore well sources located within and/or around five villages of intensive vegetable growing area (Chilli, Cauliflower, Brinjal and Bhendi) selected for the study. Wells were selected based on distance to vegetable growing field; 0–15 m. Three replicates were collected at 15 days interval from initial spray upto 120 days. Water sampler was used to collect water samples into 2.5l and 500 ml pre-cleaned polyethylene sample bottles with caps for pesticide residue and physico-chemical analysis, respectively. The sampling bottles were rinsed with well water before taking the water samples. The samples were labelled and transported to the laboratory within 24–48 h on ice in clean ice chests and stored in the refrigerator at 4 °C until they were analysed. The samples for pesticide residues analysis were extracted within 24 h of arrival at the laboratory.
Extraction of pesticide residues from soil samples

Ten gram (10 g) of the representative soil samples were weighed and quantitatively transferred into 250 ml separating flasks. A 10 ml of acetonitrile was added to each of the soil samples in the flasks and ultra-sonicated for 5 min. An additional 10 ml of acetonitrile was added, and the flasks were closed tightly. The samples were placed on a horizontal mechanical shaker and set to shake continuously for 30 min at 300 rpm. The contents were then allowed to stand for 10 min to sufficiently separate the phases or layers. A 10 ml of the supernatants was carefully taken by pipette and dried over 2 g anhydrous magnesium sulphate through filter paper into 50 mL round bottom flasks. The concentrates were then adjusted to about 2 mL using the rotary film evaporator at 35 °C, and made ready for silica clean up step.

Clean up procedure for soil samples

Clean up was done using polypropylene cartridge columns, packed with one-gram silica gel previously activated for 10 h in an oven at 130 °C, which have 1 cm thickness layer of anhydrous magnesium sulphate on top and conditioned with 6 ml acetonitrile. The concentrated extract was then loaded onto the cartridges, and 100 ml round bottom flask was placed under the column to collect the eluate. A 20 mL dichloromethane was then used to elute the column/cartridge afterwards, and the total filtrate (eluent) collected was concentrated just to dryness using the rotary evaporator set at 40 °C. The residues were re-dissolved in 1 ml ethyl acetate by pipetting and transferred to 2 ml GC vials prior to quantitation by gas chromatography (GC).

Extraction of pesticide residues from water samples

Water samples were filtered through 0.45 ml fiber glass filters to remove debris and suspended material, 1000 ml portions of the filtered water samples were transferred into 2 l capacity separating flasks. A 30 ml of saturated sodium chloride solution (NaCl) was added to each to produce a salt out effect in order to adjust the pH from 3.5 to 4. The samples were then thoroughly mixed by inverting the flask three to four times.

A 100 ml of dichloromethane as extraction solvent was then added to each sample and vigorously shaken manually for 2–3 min, while releasing the pressure intermittently. The phases were allowed to separate for 5 min and the dichloromethane extracts were separated from the aqueous layers. The extraction for each water sample was repeated twice with 100 ml of dichloromethane and the organic layers were added together and dried over anhydrous sodium sulphate through filter papers into 50 ml round bottom flask. The extracts from the water samples were then concentrated on a rotary vacuum evaporator to about 1 ml for GC-MS analysis.

Clean up procedure for water samples

Clean up was done, using polypropylene cartridge columns, packed with one-gram silica gel previously activated for 10 h in an oven at 130 °C, which have 2 g layer of anhydrous sodium sulphate on top and conditioned with 6 ml dichloromethane. The concentrated extract was then loaded onto the cartridges, and 100 ml round bottom flask was placed under the column to collect the eluate. A 20 mL dichloromethane was then used to elute the column/cartridge afterwards, and the total filtrate (eluent) collected was concentrated just to dryness using the rotary evaporator set at 40 °C. The residues were re-dissolved in 1 ml ethyl acetate by pipetting and transferred to 2 ml GC vials prior to quantitation by gas chromatography (GC).

GC-MS Analysis

The Gas Chromatography - Mass Spectrometer from Thermo fisher, Trace-1300 series, were engaged for analysis. The instrument was set as follows, Injector port temperature set to 220 °C, Interface temperature set as 250 °C, source kept at 220 °C. The oven temperature was programmed as available, 75 °C for 2 mins, 150 °C at 10 °C min⁻¹, up to 250 °C at 10 °C min⁻¹. Split ratio was set as 1:12 and the injector was set in splitless mode. The DB-5 MS capillary standard non - polar column with dimensions of 0.25mm OD x 0.25 μm ID x 30 m length (Agilent Co., USA) was used. Helium was used as the carrier gas at 1.5 ml min⁻¹. The MS was set to scan from 50 to 550 of ion source. The source was maintained at 220 °C and 4.5e⁻⁶ motor vacuum pressure. The ionization energy was -70eV. The inbuilt pre- filter of the MS reduced the neutral particles. The data system with inbuilt libraries are used for searching and matching the spectrum.

RESULTS AND DISCUSSION

Physico-chemical characteristics of soil samples

The soil samples were collected from different vegetable growing fields in five villages and
analysed for pH, EC (dSm$^{-1}$) and Organic carbon (%) (Table 1). The observed pH was in the ranges of 7.16 to 8.56 and highest pH was recorded in Cauliflower field soil sample (8.56) of Arasappappillaipatti. village and lowest in Veeralapatti brinjal field (7.16). Most of the samples showed pH above 7.5 and alkaline. The maximum EC (0.55 dSm$^{-1}$) was observed in the Bhendi field of Ambilikai village and lowest (0.11 dSm$^{-1}$) in the Chilli field soil samples from Thasarapatti village and highest (0.97%) in brinjal field of Arasappappillaipatti.

Table 1. Characterization of soil samples

<table>
<thead>
<tr>
<th>Villages</th>
<th>Vegetables</th>
<th>pH</th>
<th>EC</th>
<th>OC</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(dSm$^{-1}$)</td>
<td>(%)</td>
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<tr>
<td>Thasarapatti</td>
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<td>0.11</td>
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<td>0.12</td>
<td>0.96</td>
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Chlorpyriphos concentration in soils of Intensive vegetable growing area Ottanchathiram Block

The concentration of Chlorpyriphos is monitored in Cauliflower growing field from 0th day to 120th day in intensive vegetable growing villages of Thasarapatti, Veeralapatti, Ambilikai, Arasappappillaipatti and Vadakadu. The initial concentration at 0th day ranged from 1.52-1.65 mg/kg in all the soils of all the villages studied. After 60th days of application, the concentration of chlorpyriphos reduced to 0.9-1.38 mg/kg in Thasarapatti, Veeralapatti, and Arasappappillaipatti, but the Ambilikai village recorded highest concentration (1.38 mg/kg). At 120th day, Thasarapatti village recorded very low concentration (0.05 mg/kg). When compared to other villages, the village Ambilikai recorded maximum (0.9 mg/kg at 120 days after application. (Fig. 1).

The concentration of chlorpyriphos in Brinjal field ranged from 1.38 to 1.51 mg/kg. The maximum concentration at 0th day was observed in Ambilikai village 1.52 mg/kg and other villages Veeralapatti, Arasappappillaipatti and Vadakadu recorded 1.42 mg/kg of chlorpyriphos. At 60th day, the soils of Veeralapatti village recorded 1.13 mg/kg but the reduction in concentration at 120th day is 0.07mg/kg. In Ambilikai village the concentration of chlorpyriphos reduced from 1.13mg/kg to 0.88 mg/kg. The villages Vadakadu and Arasappappillaipatti also recorded highest concentration at 120th day (0.7mg/kg) (Fig. 2).

Soil samples collected from Bhindi field from 0th day to 120th days after application. The

![Fig. 1. Average Concentration of Chlorpyriphos in soils of Cauliflower field in Ottanchathiram Block](image-url)
concentrations of chlorpyriphos at 0th day ranged from 1.23 to 1.48 mg/kg. The maximum concentration was recorded in Ambilikai village and minimum in Thasaraiapatti village. From 0th day -120 days the maximum residues were observed in Ambilikai village. The reduction in concentration at 120th day is 0.70 mg/kg and next Ambilikai and Vadakadu, the village Arasappillaipatti recorded 0.6 mg/kg. The village Veeralapatti and Thasaraiapatti recorded very low concentration 0.03-0.05mg/kg at 120th days after application (Fig. 3).

The chlorpyriphos concentration from soils of Chilli field ranged from 1.1 to 1.2 mg/kg. The villages Ambilikai, Vadakadu and Thasaraiapatti recorded maximum of 1.2 mg/kg but in samples from Arasappapillaipatti village showed 1.08 mg/kg at 0th day. The highest concentrations were recorded in in soil samples of Ambilikai village at 120th day the concentration was 0.5 mg/kg. In Vadakadu village, from 75th days after application to 120th day, the concentration was 0.9 mg/kg. The minimum concentration at 120th day recorded in Thasarapatti village (Fig. 4). The half-lives of chlorpyrifos in soil were in the range of 3–7 days reported by Lu et al. (2014) and also observed that chlorpyrifos persisted in a low pH soil, i.e., less than 3% of the pesticide had degraded after 10 days and more than 50% of chlorpyrifos was dissipated at a higher pH soil (pH 8.5). Chai et al., 2013 reported that the half-lives in humid tropical soils from Malaysia were typically 7–120 days. However, Chai, et al. (2013) also reported that some half-lives were 257 days in the soils containing less soil microbial populations. In the literature, it was reported long environmental dissipation half-lives of chlorpyrifos, i.e., up to 4 years, depending on application rate, ecosystem, and pertinent environments (Lu et al., 2014). Since chlorpyrifos presented low water solubility and a higher log Kow, it had a strong tendency to sorb to organic matter and soil. Stability and effectiveness had made chlorpyrifos one of the most popular pesticides worldwide but on the other side its persistence had raised environmental concerns (Gebremarium et al., 2012).

Overall, observation showed the pesticide usage was maximum in Cauliflower field, when compared
to other crops. There won’t be any correlation observed between pH and EC of the soils and pesticide residues but the high organic carbon recorded in Cauliflower field of Thasarapatti village showed maximum chlorpyriphos. The reason may due to absorption of residues was maximum in high organic carbon content.

Chlorpyriphos concentration in water samples of Intensive vegetable growing area of Ottanchathiram Block

The water samples collected from borewells located at a distance of 0-15m from 0th day of application to 120th days after application near Cauliflower field. Initial concentration of chlorpyriphos were ranged from 0.05-0.09 mg/l and the highest concentration was observed in Vadakadu village (0.09 mg/l), at 75th day the concentration reduced to 0.03 mg/l and in other villages the reduction rate is 0.01-0.02 mg/l. After 90 days of application, the residues not detected in Thasaraipatti and Veeralapatti villages. The village Vadakadu recorded 0.01 mg/l of chlorpyriphos (Fig. 5).

The water samples collected near Brinjal field of different villages. Initial concentration of chlorpyriphos ranged from 0.04-0.05 mg/l. Most of the samples collected at 45th day recorded 0.01-0.03 mg/l. The concentration was reduced to 0.01 mg/l at 75th day and then not detected in all the villages from 90th to 120 days after application (Fig. 6). Water samples collected near Bhendi field recorded 0.03 to 0.08 mg/l of chlorpyriphos at 0th day and it was reduced to 0.01 to 0.03 mg/l at 75th day. Chlorpyriphos not detected in the samples collected after 75 days of after application (Fig. 7). The water sample collected near Chilli field showed concentration ranged from 0.01 to 0.06 mg/l. After 75 days all the samples collected showed no pesticide residues (Fig. 8). In case of water samples, in all the crops almost similar trend was observed.

Fig. 4. Average Concentration of Chlorpyriphos in soils of Chilli field in Ottanchathiram Block

Fig. 5. Average Concentration of Chlorpyriphos in water samples of Cauliflower field in Ottanchathiram Block
except near Cauliflower field samples. Water samples collected from Vadakadu village recorded 0.02 mg/l at 90-105 days after application. The highest concentration of chlorpyriphos at 0th day recorded in samples collected near Bhindi field. Arain et al. (2018) reported that the surface water collected from Union Council (KotriM.Kabir) showed the maximum concentration 79.7 μg/l of chlorpyriphos pesticide and the minimum concentration 43.46 μg/l. In all ground water samples, the values of pesticide residues were observed below the MRL guideline. The maximum concentration of chlorpyriphos pesticide 11.2 μg/l was observed in Union Council 5 (KotriM.Kabir) and minimum value 6.6 μg/L was found in the sample from Union Council 2 (Mehrabpur 2). Baride et al. (2015) reported that the ground water sample recorded more than 0.03 mg/l of chlorpyriphos. Chlorpyriphos was detected in high concentration (8.53 ± 0.53 mg/l) which is above the standard limits. The detected concentrations indicate that chlorpyriphos is mostly applied for treatment of crops.
in the agriculture activities near the canal. However, the application of pesticides treatment by aerial spraying which spreads the residues of the pesticides via air, leaching and runoffs after heavy rains was reported to result in supporting and increasing the presence of pesticides residues in the aquatic environment (Nadia Hanafy Metwally et al., 2016; Afifi et al. 2016).

REFERENCES


