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MONITORING MONOCROTOPHOS RESIDUES IN VEGETABLE GROWING AREA OF OTTANCHATHIRAM BLOCK, INDIA

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Abstract– The presence of Monocrotophos 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 undertaken 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 Monocrotophos residue analysis. Samples of Brinjal, Bhendi, Cauliflower and Chilli cultivated soil and water was collected periodically at 0, 15, 30, 45, 60, 75, 90, 105 and 120 days and analysed for monochrotophos residues in both water and soil samples usingGC-MS. The results revealed that average monochrotophos residues in the samples were in the range of 0.8 and 1.5 mg/kg in soil and 0.01-0.09 µg/l in water. Highest concentration was found in Arasappapillaipatti field, ranging from 1.5 mg/kg in Brinjal cultivated soil and in water the highest range was 0.09 µg/l. No residues were detected in samples that are not treated with pesticides. The study reveals reduction in concentration of monochrotophos residues in Ottanchathiram area.

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 3million 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

(Associate Professor- ENS)

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 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 (Mesnage *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 monocrotophos 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 monocrotophos 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 undertaken in the Ottanchathiram 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 0^{th} 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 sulphates 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 on to the column/ cartridge, and 50 ml pear shaped flask was placed under the column to collect the eluate. A 10 ml acetonitrile was used to elute the column/cartridge afterwards. The total filtrate (eluent) collected was concentrated to dryness using the rotary evaporator set at 40 °C. The residues were re-dissolved in 1 ml ethyl acetate by pipetting and transferred into 2 ml GC glass 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 sample

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 0.25 mm 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 4.5 e^{-6} motor vacuum pressure. The ionization energy was-70eV. The inbuiltpre- 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 charecteristics 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 pH level of the soil is a critical factor in vegetable farming, influencing nutrient availability, microbial activity, and overall plant health. The measured pH ranged from 7.16 to 8.56, resulting in the Veeralapatti brinjal field (7.16) recording the lowest pH and the Arasappapillaipatti village's cauliflower field soil sample (8.56) recording the highest pH. In most of the areas the pH ranges more than 7.5 which shows soil is Alkaline. Electrical Conductivity (EC) is an

Table 1. Characterization of soil samples

Villages	Vegetables	pH	EC (dSm^{-1})	OC (%)
Thasarapatti	Chilli	8.11	0.11	0.72
	Cauliflower	7.76	0.13	0.80
	Brinjal	7.90	0.23	0.62
	Bhindi	7.46	0.24	0.82
Veeralapatti	Chilli	8.20	0.13	0.85
	Cauliflower	8.03	0.18	0.35
	Brinjal	7.16	0.37	0.40
	Bhendi	7.75	0.62	0.70
Ambilikai	Chilli	8.11	0.25	0.92
	Cauliflower	7.70	0.12	0.88
	Brinjal	8.43	0.23	0.88
	Bhendi	8.28	0.55	0.86
Arasappapillaipatti	Chilli	8.44	0.15	0.76
	Cauliflower	8.56	0.17	0.50
	Brinjal	8.26	0.15	0.97
	Bhendi	7.67	0.14	0.90
Vadakadu	Chilli	7.80	0.16	0.90
	Cauliflower	7.43	0.25	0.70
	Brinjal	7.41	0.30	0.37
	Bhendi	8.27	0.12	0.96

important parameter in vegetable farming, especially when managing irrigation and nutrient levels in the soil. The soil samples from the Bhendi field in Ambilikkai village has the highest EC (0.55 dSm-1), lowest (0.11 dSm-1) at the Chilli field from Thasarapatti village, and highest (0.97%) in the brinjal field in Arasappapillaipatti.

Monocrotophos concentration in soils of Intensive vegetable growing area Ottanchathiram Block

The level of monocrotophos in the cauliflower fields in the very productive vegetable-growing villages of Thasaraipatti, Veeralapatti, Ambilikai, Arasappapillaipatti, and Vadakadu are tracked from the first to the 120th day. The initial concentration in all the soils of the villages under study at day 0 varied between 0.8 and 1.5 mg/kg. The amount of monochrotophos is highest in the Arasappapillaipatti field, ranging from 1.5 mg/kg, and lowest in Thasaraipatt (Brinjal and Chilli) were shown in Fig. 1 and 2, Ambilikai (Brinjal and Chilli), based on observations. The average concentration of monochrotophos reduced to 0.8-0.3 mg/kg in Thasaraipatti, Veeralapatti, and Arasappapillaipatti after 60 days of application; however, the highest concentration (0.8 mg/kg) was found in the Arasappapillaipatti area followed by Vadakadu, Ambilikai, Veeralapatti areas. Thasaraipatti area

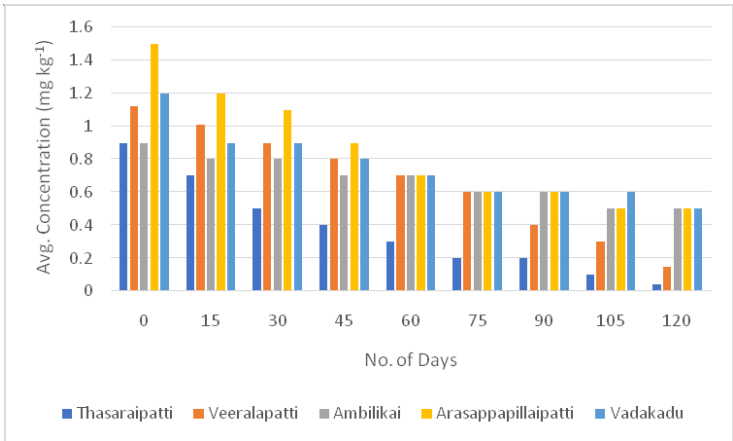

Fig. 1. Average Concentration of Monocrotophos in soils of brinjal field in Ottanchathiram Block

observed a very low concentration (0.3mg/kg) at day 60. The rural area of Arasappapillaipatti recorded the highest dose (0.9 mg/kg) at 60 days after application in comparison to other areas. The final observations were taken at the 120th day. The higher concentration of monochrotophos observed at the range, 0.50mg/kg in Arasappapillaipatti and Ambilikai areas. From the observed data, Thasaraipatti area observed a very low concentration (0.04 mg/kg) at day 120.

The soil sample collected from different areas are analysed further for the concentration of monochrotophos, there is high concentration (1.5 mg/kg) of monochrotophos in Brinjal shown in Fig.1. Followed by Bhendi cultivated soil shows 1.2 mg/kg at the day of 0 as shown in Fig. 2 followed by in Ambilikai area the Cauliflower cultivated soil shows 1.1 mg/kg of monochrotophos (Fig. 3). The samples were analysed further at different intervals, the level of monochrotophos has been reduced at 120th day (0.5 mg/kg) in both the crops, The lowest concentration was observed in Thasaraipatti area 0.9 mg/kg at day 0 in Brinjal cultivated field and wide range of reduction has been found at the 120th day (0.04 mg/kg) were found in Fig. 1.

The concentration of monochrotophos were also studied in Arasappapillaipatti field using Chilli crop at 0th day were 1.0 mg/kg later it reduced to 0.3 mg/kg at 120th day shown in Fig. 4. In Thasaraipatt area, the level of monochrotophos shows wide range reduction in Brinjal of 0.04 mg/kg. All pesticide residue MRL values, including those for methyl parathion, quinalphos, chlorpyrifos, and cypermethrin, were marginally exceeded in all

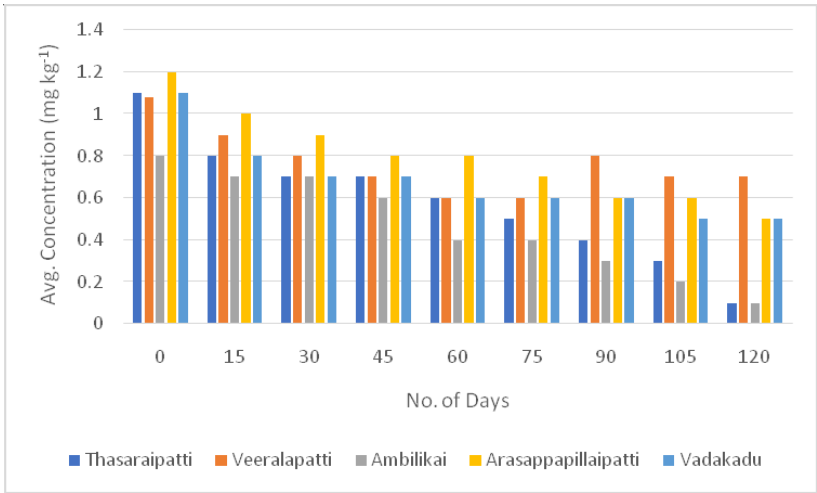

Fig. 2. Average Concentration of Monocrotophos in soils of Bhendi field in Ottanchathiram Block

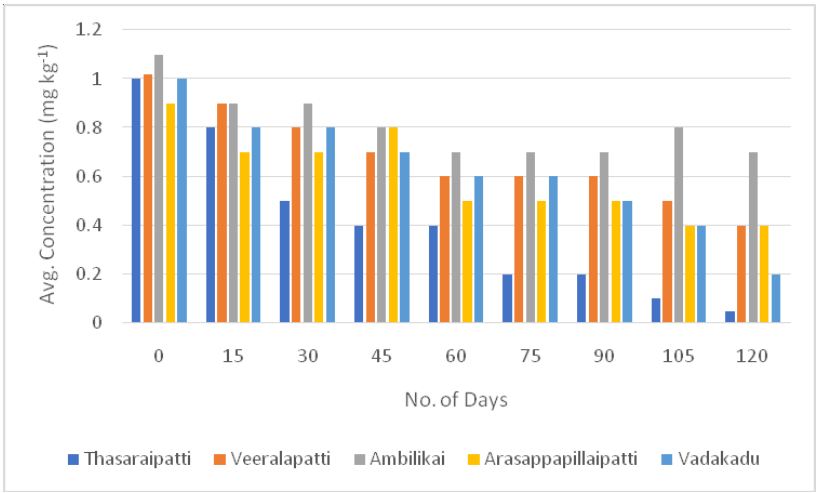

Fig. 3. Average Concentration of Monocrotophos in soils of Cauliflower field in Ottanchathiram Block

vegetables. The study's findings are consistent with those of other research projects (Madan *et al.* 1996; Chahal *et al.,* 1997).

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

Water samples were taken from borewells near a cauliflower field that were spaced 0–15 meters apart from the day of application to 120 days later. The samples were collected at 15 days of intervals. Monochrotophos initial concentrations varied from 0.01-0.09 µg/l, with village having the highest concentration (0.09 µg/l) followed by Arasappapillaipatti with the range of 0.08 µg/l. By the 60th day, the concentration had dropped to 0.03 µg/l in Veeralapatti area and 0.02 mg/l in Arasappapillaipatti area were found, while the other villages recorded a decline rate of 0.01-0.02 µg/l. The residues were not found in the villages of Thasaraipatti and Veeralapatti after 90 days of application. Vadakadu village registered 0.01µg/l of monochrotophos.

Different water samples were collected from different fields including crops like Cauliflower, Brinjal, Bhendi and Chilli were interpreted and are shown in Figure 5. The results were found different in between the crops. In Veeralapatti area, Cauliflower crop shows a higher concentration of monochrotophos of 0.09 µg/l followed by Brinjal at the range of 0.05 µg/l and chilli of 0.03 µg/l at the day of 0 (Fig. 5), later there was a reduction detected at 60th day. Least residue of monochrotophos were detected in Bhendi (Fig.6) in the range of 0.05 to 0.01 µg/l. The results were 0.03µg/l for Cauliflower (Fig.7) and 0.01 µg/l for Brinjal and Chilli. The results show a wide range of reduction of monochrotophos in the samples.

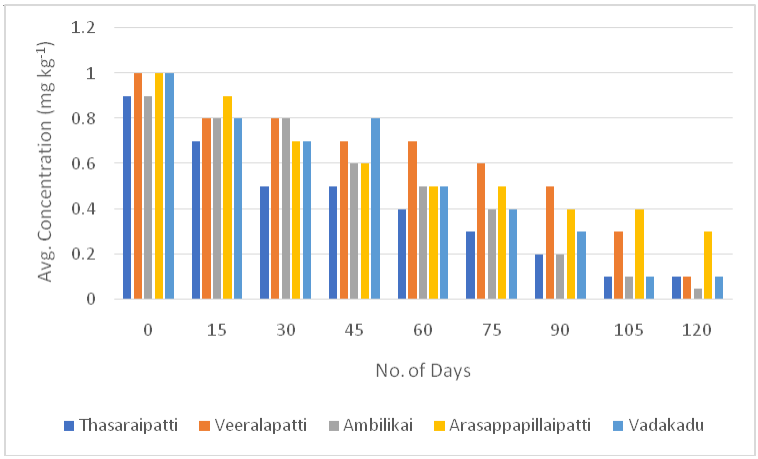

Fig. 4. Average Concentration of Monocrotophos in soils of Chilli field in Ottanchathiram Block

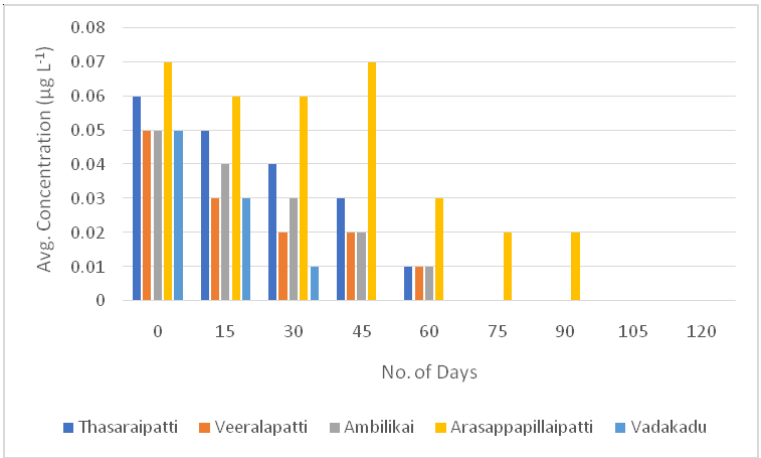

Fig. 5. Average Concentration of Monocrotophos in water samples of brinjal field in Ottanchathiram Block

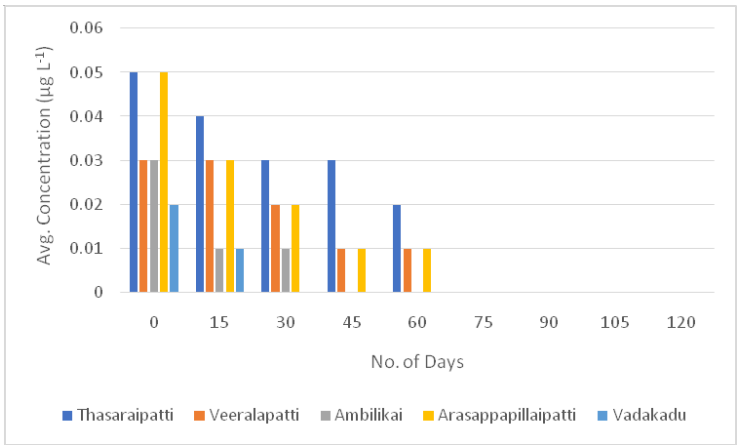

Fig. 6. Average Concentration of Monocrotophos in water samples of bhendi field in Ottanchathiram Block

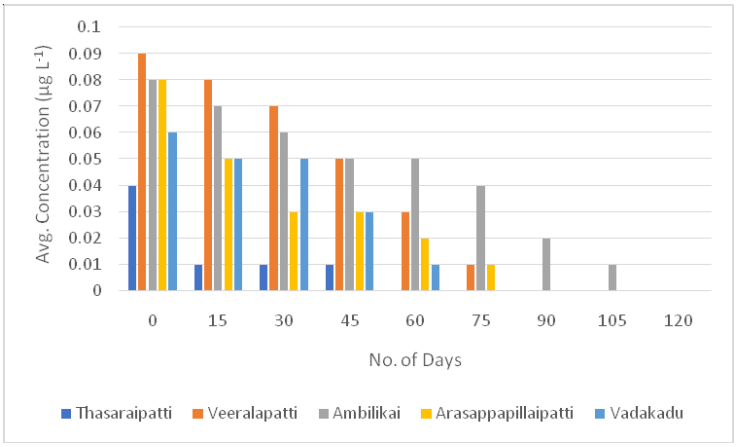

Fig. 7. Average Concentration of Monocrotophos in water samples of Cauliflower field in Ottanchathiram Block

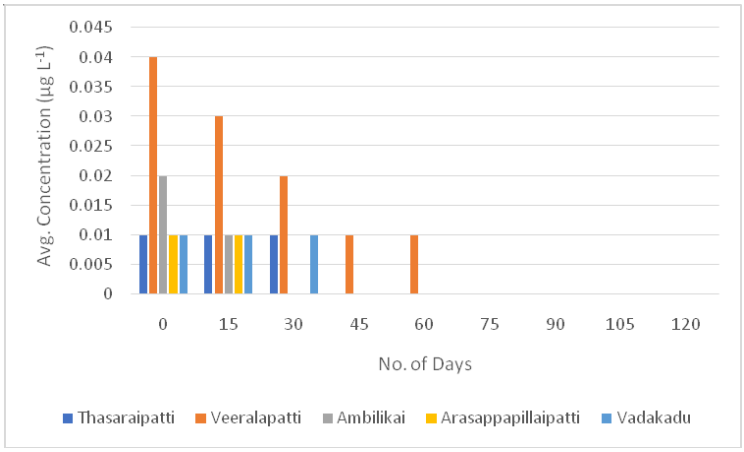

Fig. 8. Average Concentration of Monocrotophos in water samples of Chilli field in Ottanchathiram Block

Similarly, lower concentration of monochrotophos were observed in the samples collected from the field ranges 0.01 µg/l. Arasappapillaipatti filed soil shows a low concentration where chilli has been cultivated followed by chilli cultivated in the Thasaraipatt area were also observed 0.01 µg/l of monochrotophos were shown in Fig. 8. The reduction of concentration of monochrotophos were studied at different field with different vegetable crops.

Conflict of Interest: None

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