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In vitro evaluation of the leaching potentialand persistence of biocides used in the paddy fields of kuttanad, south west coast of India

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Abstract
The present study evaluated the leaching potential of biocides viz., Chlorpyrifos (organophosphate insecticide), Hexaconazole (triazole fungicide) and Imidacloprid (neonicotinoid insecticide) used in the paddy fields of kuttanad and their persistence in water. Leaching potential of biocides used in this experiment were in the order: Chlorpyrifos < Hexaconazole < Imidacloprid. All the three biocides used in this study viz., Chlorpyrifos, Hexaconazole and Imidacloprid were found to be persistent for more than 4 weeks. The results revealed that Chlorpyrifos, Hexaconazole and Imidacloprid used in the paddy fields of Kuttanad have potential to reach nearby aquatic systems and cause threat to a wide range of non-targeted organismsin the ecosystem including *M. rosenbergii*, prime species for export, earning overseas revenue for India.

Keywords: chlorpyrifos, hexaconazole, imidacloprid, kuttanad

Introduction

Pesticides play an important role in the success of modern farming and food production. However, residues of these compounds can be detected in different non-target sites such as soil, surface water and ground water. Despite the major role of pesticides in increasing productivity, there is a concern about the progressive pesticide contamination of aquatic ecosystem through leaching from soil. This can lead to severe impacts of pesticides on aquatic organisms and wildlife. When the water table is high, or close to the surface, water bodies are more prone to contamination. Kuttanad being situated 2.2 m below sea level is more vulnerable to contamination. Kuttanad, popularly known as "the rice bowl of Kerala", spans over 110,000 ha area. According to the data compiled by kuttanad water balance study project, 485 tonnes of pesticides were applied in kuttanad on an annual basis of which 370 tonnes were used in the punja crop alone (KWBSP, 1990).Chlorpyrifos, Hexaconazole and Imidacloprid are commonly used to control the pests attacking the paddy fields of Kuttanad. Chlorpyrifos (CPF) is the most toxic organophosphorus compound to fish and is more toxic than organo-chlorine compounds. CPF passes via air-drift or surface runoff into natural waters, where it is accumulated in different organisms living in water, especially in fish, thus making it vulnerable to several discernible effects (Varo *et al*., 2002) [15]. Hexaconazole is a systemic fungicide used for the control of many fungi particularly ascomycetes and basidiomycetes. It is a broad spectrum fungicide highly useful to prevent diseases on various crops. It is well suited for soil and seed borne diseases too (Kengar *et al*., 2014) [11]. It has been reported that hexaconazole is highly toxic to fish and aquatic species which killed 50% of rainbow trout within 24 and 96 h at concentrations of 0.57 and 0.38 mg L-1 respectively (Boran *et al*., 2012) [2].

Imidacloprid is used to control a variety of insect pests including plant and leafhoppers, aphids, termites, whiteflies and thrips (Jeschke *et al*., 2011) [7]. It is the most rapidly expanding chemical class of insecticides with a market share of 28.5% in 2011 (Jeschke *et al*., 2013) [8]. However, imidacloprid is highly toxic to many beneficial organisms (Cox, 2001) [4]. High leaching potential of pesticides create threat to a wide range of non-targeted organisms. Crustacean aquaculture has recently been facing severe crisis owing to massive setbacks due to rampant outbreak of diseases. Hence the present study aims to assess thepersistence and leaching potential of three biocides (Chlorpyrifos, Hexaconazoleand Imidacloprid) commonly used during paddy cultivation in laboratory condition.

Materials and Method

Description of study area

Kuttanad extending from 9° 17' to 9° 40' N latitude and 76° 19' to 76° 33' E longitude, is a unique ecosystem consisting of floodplains, coastal alluvial belt, river networks and backwaters. This region is in the deltaic formation of four rivers: Pampa, Achankovil, Meenachil and Manimala. The total geographic area of the region is around 1100 km^2 spread across three districts (Kottayam, Pathanamthitta and Alappuzha) of Kerala state (Sruthi *et al*., 2016).

Sediment texture and chemistry

Sediment sample from the paddy fields of Kuttanad, India (9° 17' – 9° 40' N and 76° 19' – 76° 33' E) were collected during the entire study period and used for the experiments. The sediment pH was determined by the use of electronic pH meter (model: Cyberscan pH 510 Meter, Aarkey Labtronix India). Sediment texture analysis was done based on the method followed by the Stokes law, where small particle in a liquid suspension tries to settle down due to its own weight under the action of gravity (Folk, 1964). Organic carbon content were determined using

Walkley-Black method which utilize the redox potentials of potassium dichromate ions ($K_2Cr_2O_7$) to determine the percentage of organic carbon in the sediment.

Description of biocides

Laboratory studies were conducted in order to determine the persistence and leaching potential of three biocides commonly used during paddy cultivation in Kuttanad. The tested compounds were Commercial-grade Chlorpyrifos by Cheminova India Ltd. (Classic 20 having active ingredient of 20% EC), Hexaconazole by Rallis India Ltd. (Contaf having active ingredient of 5% SC) and Imidacloprid by Bayer Crop Science Pty Ltd (Confidor having active ingredient of 17.8% SL).

Experimental set up

The experimental set up for the evaluation of leaching potential includes PVC cylinders (diameter of 15 cm and height of 35 cm), with a drainage outlet at their base, filled with 25 cm of the undisturbed soil collected from the paddy fields of Kuttanad using 15 cm i.d. PVC tubes (Begin *et al*., 2003). 2L each of Confidor (3ml/L), Chlorpyrifos (2.5ml/L) and Hexaconazole (1ml/L) (real concentrations sprayed in the paddy field) were allowed to pass through the soil column (Aslam *et al*., 2015 and Wenjuan *et al*., 2017). When the biocide solution applied leached out completely, leachates were collected and used for biocide detection using GC-MSMS, GC-MSMS and LC-MSMS respectively for Chlorpyrifos, Hexaconazoleand Imidacloprid (Interfield laboratories - NABL (ISO 17025)). Experimental set up run with distilled water instead of biocide solutions were considered as control. Triplicates were maintained for both control and test columns. The experimental set up to assess the persistence of biocides in water includes rectangular plastic troughs (60 cm x 40 cm x 28 cm), containingpaddy (Jyothy (PTB 39)) cultivated in polythene grow bags (24 cm x 24 cm x 40 cm) with water outlet pores at bottom and sides and filled with water up to soil surface in order to mimic the natural ecosystem of kuttanad. Biocides viz. Confidor (3ml/L), Chlorpyrifos (2.5ml/L) and Hexaconazole (1ml/L) (real concentrations sprayed in the paddy field) were applied to paddy. The simulation rain is applied at an intensity of 26.07 mm based on the average precipitation of the study area at daily scale. Water samples were collected from the trough twice at an interval of 2 weeksand used for biocide detection using GC-MSMS, GC-MSMS andLC-MSMS respectively for Chlorpyrifos, Hexaconazoleand Imidacloprid (Interfield laboratories - NABL (ISO 17025)). Experimental set up run with distilled water instead of biocide solutions were considered as control. Triplicates were maintained for both control and test troughs.

Result and Discussion

Granulometry and Textural facies: Sand, silt and clay contents in the sediment samples collected from the Kuttanad paddy fields are 43.7%, 51.2% and 7.5% respectively. Soil pH was 3.66 and organic carbon content of the sediment sample was 0.1209%

Result of the present study revealed that leaching potential of biocides used in this experiment were in the order Chlorpyrifos<Hexaconazole <Imidacloprid. Biocides used in the study were found to be persistent more than 4 weeks. Either their residues were detectable in water samples even after 28 days.

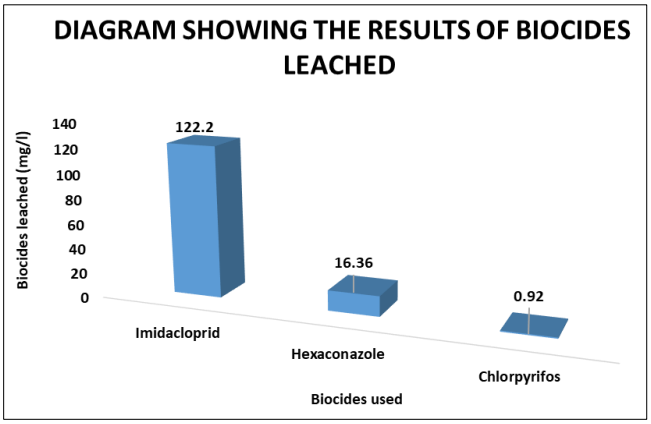

Fig 1

Table 1: showing the results of persistence of biocides in water

Sl No.	Biocide	After 2 weeks	After 4 weeks
1	Chlorpyrifos	0.333 mg/l	0.181 mg/l
2	Hexaconazole	2.47 mg/l	1.71 mg/l
3	Imidacloprid	55.1 mg/l	53.9 mg/l

It is found that Confidor transport in soil occurs much easier. The findings agreed with previous research on its transport in soils, where leaching and pollution is a high concern (Bonmatin *et al*., 2015, Flores *et al*., 2002, Leiva *et al*., 2015) [1, 5, 13]. Maznah *et al*., 2017 suggests water as a medium for hexaconazole residue dissipated through the soil profile. Only small amount of Chlorpyrifos washed off because of its lower desorption rate from soil. This agrees with the results of Correa Zuluaga *et al*., 2018 [3] whichsuggests that Chlorpyrifos can be mobilized to deeper horizons through preferential paths in spite of its high absorption coefficient. In this sense, the use of Chlorpyrifos should be more regulated. A higher pollution risk on water body of paddy field is due to the stronger preferential flow and better pore connectivity. These results can provide useful data and modeling approach for evaluating the risk of pesticide leaching.

Conclusion

Leaching is the movement of contaminants, such as water-soluble pesticides or fertilizers, carried by water downward through permeable soils. Soil protects the groundwater by providing an opportunity for pesticide adsorption and degradation, particularly in those layers at or near the soil surface. The greater the depth to the water table, the more protection the groundwater has from contamination. When the water table is high, or close to the surface, it is more vulnerable to contamination. Taking into account the quantity of biocide released into the Kuttanad waters, the problem of biocide toxicity needs to be addressed immediately.

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