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Study and prediction of persistent organochlorine and organophosphorous pesticide residue in soils of cardamom plantations in Idukki district (India)

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Abstract: *The indiscriminate use of toxic pesticides had created an environment that without this poison the plant life is unfruitful leading to the farmer's life miserable. For several years, this phenomenon was continuing and the ecosystem is protecting the environment and the life of human being from high risk of toxicity. But, how long it will continue or weather a paradigm change in the agricultural field is required? With this objective a field study was conducted in the cardamom plantations of Idukki district in South India to estimate and predict the persistence of pesticide residue in the soil environment. It is observed that residues of endosulfan, DDT and organophosphorous pesticides were present in soil samples at 31.6 %, 29 % and 21 % respectively. The present study gives a prediction of the concentration of persistent pesticide residues in the soil if the present dose and frequency of application is continued. The study also highlighted the adsorption capacity of soil in the study area and low water solubility of pesticides used in cardamom plantations which is referred as partition coefficient. The soil properties such as pH, organic content and microbial concentration which determine the fate of degradation of pesticides and formation of its metabolites are also been discussed in this context. Based on the observations and analysis, it is concluded that the formation of degradation products and bound residues decrease at higher concentration of pesticide applications but the concentration of persistent pesticides increases and the biodegradation reduced in such cases due to bound residues and reduced biological activity. The predicted values on multiple applications where the concentrations in soil may build up and reach a plateau, are 2.559,0.2559, 1.7324 and 0.659 mgKg^{-1} in the case of endosulfan, DDT, organophosphorous and total pesticides respectively.*
Keywords: *Cardamom plantations, , Organochlorine and Organophosphorous pesticide residues, Persistent pesticide residues in elevated levels, Prediction of pesticide residue.*

I. Introduction

Pesticides once applied to cropland, a number of changes will happen to the applied pesticide. It may be taken up by plants or ingested by animals, insects, worms, or microorganisms in the soil. It may move downward in the soil strata and either adhere to soil particles or dissolve in water. The pesticide can vaporize and enter the atmosphere or break down through microbial and chemical pathways into other less toxic compounds. Pesticides can also be leached out of the root zone through rain or irrigation water or wash off through surface runoff. All these changes that may happen on a pesticide applied to soil depend largely on two of its properties: persistence and solubility. [1]

Common pesticides used in Cardamom plantations are organophosphorous and organochlorine compounds. Although some organophosphorous compounds are highly toxic to humans, they generally break down rapidly and have been found rarely in the environment. Organochlorine compounds such as endosulfan are more toxic and its half life varies from weeks to months depending upon the physical and chemical properties of soil system such as moisture content, organic matter and clay contents.[2] Another group of pesticides are carbamate pesticides including aldicarb, carbofuran, and oxamyl. These compounds tend to be soluble in water and are weakly adsorbed to soil. The complex properties and the effects of pesticides in soil environment were discussed under the following headings viz. solubility and leaching, degradation and transformation products, bound residue formation in soils, repeat application and aging of pesticides in order to reach a reasonable conclusion to the problem of pesticide contamination in cardamom plantations.

II. Materials and Methods

Idukki town is located at $9^0$51N$76^0$58'N 76.97^{0}E coordinates. The project area is Idukki district in South India and sampling points were in Devikulam, Udumbanchola, Peermade and Thodupuzha Taluks. Soil samples collected from 38 locations covering both large and medium plantations across the district based on a random sampling technique and were marked with GIS coordinates for identification and modeling (Fig.1).

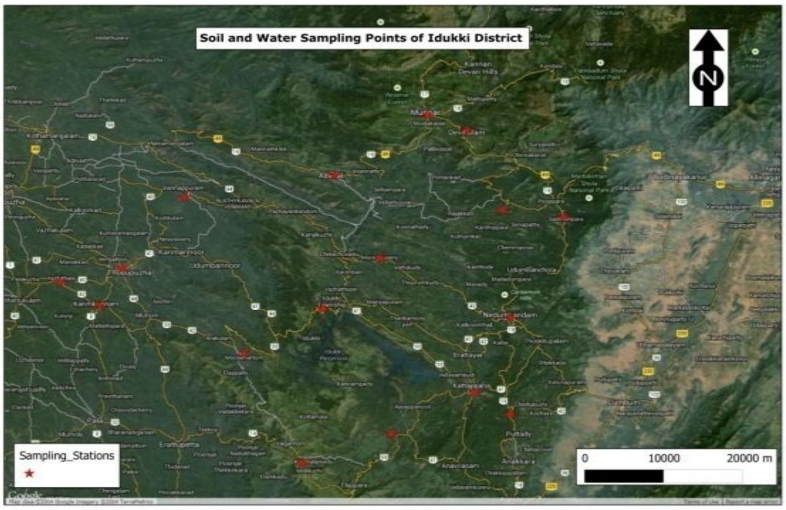

Figure.1 Sampling locations

The response of the pesticides applied to the environment depends on soil structure, geochemical parameters (mineralogical and chemical characteristics), soil-water interaction etc. [3] The grain size distribution of the soil samples collected from the project area were carried out as per IS: 2720 (part IV) to find out the particles size < 75 microns (% finer). The pH of soil and water content were also measured to study the soil parameters and to predict the fate of the pesticide residue and effectiveness in degradation. Soil samples collected from the study area covering all the seasons and following the standard protocols [4] were analysed through the NABL accredited laboratory to detect the present pesticide residue levels and the results (Table 1) are used for predicting the concentrations of persistent pesticide residues.

Table 1. Soil sample data for prediction of persistent pesticide residue analysis

Location code	Elevation(m)	Endosulfan-II	Endosulfan Sulfate	Total Endosulfan	P,P'- DDE	P,P' - DDD	Total DDT	Chlorpyriphos	Quinalphos	Total Organophosphorous
1010313	3890	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
2010313	3959	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
3010313	3947	BLQ	BLQ		BLQ	BLQ		BLQ	0.273	0.273
4010313	4003	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
5010313	3877	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
6010313	3014	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
7010313	3800	BLQ	0.09	0.09	BLQ	BLQ		0.069	BLQ	0.069
8020313	3656	BLQ	0.09	0.09	0.075	0.012	0.087	BLQ	BLQ	
9020313	3296	BLQ	0.09	0.09	0.017	0.01	0.027	BLQ	BLQ	
10020313	3264	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
11020313	3315	BLQ	0.09	0.09	0.01	BLQ	0.01	0.05	BLQ	0.05
12030313	4173	BLQ	0.137	0.137	BLQ	BLQ		BLQ	0.05	0.05
13030313	3708	BLQ	0.026	0.026	BLQ	BLQ		BLQ	0.098	0.098
14030313	3718	0.024	0.09	0.114	0.03	BLQ	0.03	BLQ	0.05	0.05
15030313	2850	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
16030313	2608	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
17030513	3607	BLQ	BLQ		BLQ	BLQ		0.01	BLQ	0.01
18030513	3563	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
19030513	3740	BLQ	BLQ		0.024	BLQ		BLQ	BLQ	
20030513	2390	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
21040513	3740	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
22040513	3133	BLQ	BLQ		BLQ	BLQ		0.589	BLQ	0.589
23040513	2365	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
24060513	3742	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
25060513	3270	BLQ	BLQ		BLQ	BLQ		0.069	BLQ	0.069
26060513	3254	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
27140114	3950	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
28140114	3805	BLQ	0.14	0.14	BLQ	BLQ		BLQ	BLQ	

29140114	3658	BLQ	BLQ		0.03	BLQ	0.03	BLQ	BLQ	
30140114	3335	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
31140114	3280	BLQ	BLQ		0.01	BLQ	0.01	BLQ	BLQ	
32150114	4167	BLQ	0.02	0.02	BLQ	BLQ		BLQ	BLQ	
33150114	3720	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
34150114	3720	0.09	0.78	0.87	0.01	0.07	0.08	BLQ	BLQ	
35150114	3609	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
36150114	3741	BLQ	BLQ		0.05	BLQ	0.05	0.05	BLQ	
37150114	3134	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	
38150114	3272	BLQ	BLQ		BLQ	BLQ		BLQ	BLQ	

Qualitative and quantitative analysis of pesticide residues in soil was carried out based on modified QuEChERS method for the extraction of pesticides from agricultural, ornamental and forestal soils[5] using GC—ECD, GC—FPD and GC-MS technology. The results of analysis for soil samples obtained are average water content -- 25 %, pH --6.02, and fine grained particles(<75 microns) were 40%. Endosulfan was present in 31.6 % of soil samples in the range of 0-0.87 mgKg^{-1} and a mean value of 0.093 mgkg^{-1} . Organophosphorous pesticides (Chlorpyriphos, Quinalphos and Ethion) were present in 21 % of the samples within a range of 0.01-0.589 mgkg^{-1} and a mean value of 0.1122 mgkg^{-1}. DDT was present in 29 % of the soil samples in the range of 0.01 - 0.087 mgkg^{-1} with a mean value of 0.0193 mgkg^{-1}. The largest value of Technical DDT is 0.087 mgKg^{-1}. It contains P, P'- DDE 0.075 mgkg^{-1} P, P'- DDD 0.012 mgKg^{-1}. As per the literatures if the ratio of P, P' – DDT/DDT metabolite is > 0.5, it indicate a recent usage[6-7] . In the present study P, P' – DDT was not detected in any of the samples and seems to be an earlier usage before it is restricted in agricultural sector.

2.1 Prediction of persistent pesticide residues in the plough layer of soils.

The residual concentration of pesticides in soil samples are very high and if the present situation and application strategy continued by the farmers then the environment would be at risk. In order to have a better control and monitoring, the future concentration is predicted using mathematical model developed by FOrum for the Co-ordination of pesticide fate models and their use(1997)[8] under various conditions as shown below.

Case 1. Multiple applications of pesticides for n times, the concentration in soil immediately after n applications (in mgkg^{-1}), spaced i days apart is given by the formula,

Initial PECS for n applications = $\frac{Initial\ PECS\ for\ 1\ application * (1-e^{-nki})}{(1-e^{-ki})}$ where k is the dissipation rate constant given by: k =$\frac{In2}{DT50}$ and DT50 = time for disappearance of half the chemical (days).

Case II. Time-weighted average concentrations
The time-weighted average concentration over a period of t days after application is given by,

Average PECS over t days = $\frac{Initil\ PECS * (1-e^{-kt})}{kt}$

Case III . Long-term concentrations and build-up

If a pesticide is relatively persistent then concentrations in soil may build up and reach a plateau. Once the plateau has been reached, concentrations fluctuate between a maximum when an application has just been made and a minimum just before the next application has been made. Assuming first order dissipation of residues, the time-weighted average concentration once the plateau has been reached is given by:

Plateau average PECS = $\frac{Initial\ PECS\ for\ 1\ application}{ki}$

Whilst the maximum concentration during the plateau period, immediately after an application is given by:

Plateau maximum PECS = $\frac{Initial\ PECS\ for\ 1\ application}{(1-e^{-ki})}$

The spread sheet model 'TWA' developed by R. Grau & H. Schäfer**[8]** is used to model the degradation pattern of pesticides against time interval and DT50 for multiple applications of pesticides at different concentrations. For single application the model form is

$$\frac{\bar{C}}{Co} = \frac{DT50}{\Delta t.\ln 2\{1-e^{(-DT50/\Delta t.\ln 2)}\}}.$$

Where $\bar{C}$ = time weighted average concentration, Co = Initial concentration, Δt = time interval.

III. Results and Discussions

3.1 Predicted environmental concentration of pesticide residue in soils of Idukki cardamom plantations.

The predicted values of pesticides on multiple applications of the pesticides concentration was carried out using the Mathematical equations as above and results tabulated in Table 2. The frequency of pesticide application per year commencing from February to December is 8 at an interval of 30-40 days. The predicted pesticide residues after 30 days of application are 0.714, 0.0711 , 0.4816 and 0.1832 mgKg^{-1}and the predicted values on multiple applications where the concentrations in soil may build up and reach a plateau, are 2.559,0.2559, 1.7324 and 0.659 mgKg^{-1} in the case of endosulfan, DDT, organophosphorous and total pesticides respectively. The initial degradation of pesticides is at a slow phase except in the case of repeat applications. The repeat applications will leads to a condition of plateau at which soil may lose all its properties and hence the presence of high concentrations of persistent residues.

Table 2. Mathematical model for maximum and mean concentrations of pesticides

Persistent pesticides present in the soils of Idukki District	max. endosulfan residue mgKg^{-1}	mean endosulfan residue mgKg^{-1}	max. DDT residue mgKg^{-1}	mean DDT residue mgKg^{-1}	max. organophosphorous residue mgKg^{-1}	mean organophosphorous residue mgKg^{-1}	mean total pesticides residue mgKg^{-1}
Observed values	0.87	0.0926	0.087	0.0193	0.589	0.1122	0.2241
For Multiple Applications , Initial PECS for n applications = Initial PECS for 1 application * (1 - e^{-nki}) / (1 - e^{-ki})	2.4670	0.2626	0.2467	0.0547	1.6702	0.3182	0.6355
Time-weighted average concentrations Average PECS over t days = Initial PECS x { 1 - e^{-kt}} / kt.	0.7114	0.0757	0.0711	0.0158	0.4816	0.0917	0.1832
Plateau average PECs = Initial PECs for 1 application /ki	2.0924	0.2227	0.2092	0.0464	1.4165	0.2698	0.5390
Plateau maximum PECS = Initial PECS for 1 application / { 1 – e^{-ki} }	2.5588	0.2724	0.2559	0.0568	1.7324	0.3300	0.6591

'TWA' spread sheet model for endosulfan and organophosphorous are shown in Figure. 2 and Figure.3 respectively. The DDT present in the samples proved to be of earlier application and hence future concentration not predicted.

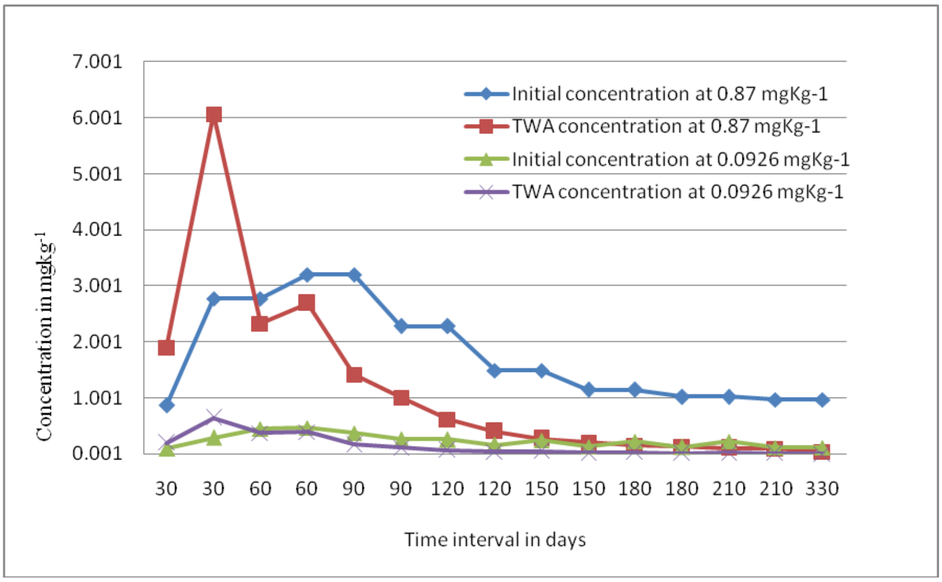

Figure 2.TWA model for Endosulfan at maximum and mean concentrations

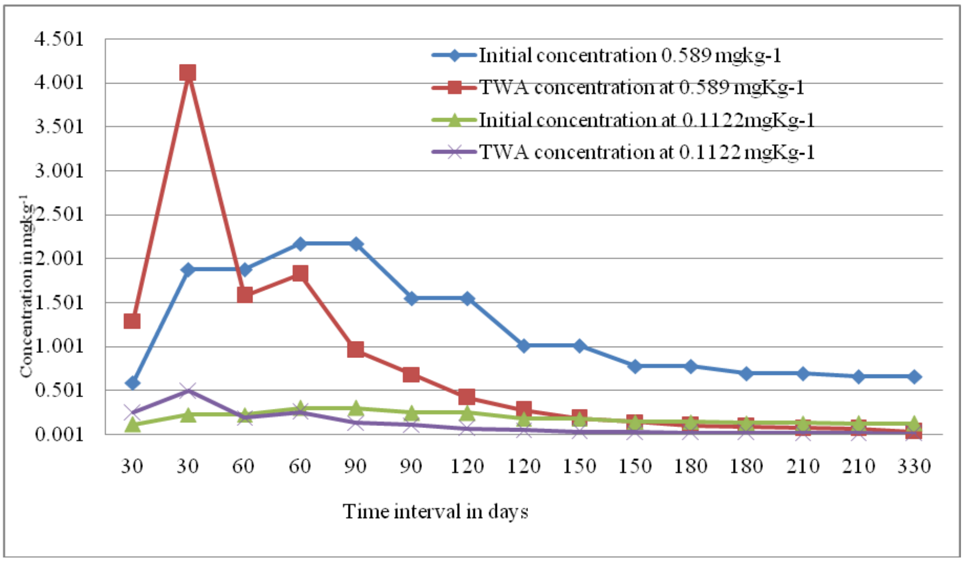

Figure 3. TWA model for Organophosphorous at maximum and mean concentrations

3.2 Soil environment and pesticide degradation

Persistence defines the lasting-power of a pesticide. Most pesticides break down or degrade with time as a result of chemical and micro-biological reactions in soils. The biological activity of these substances may also have environmental significance. Since population of microbes decrease rapidly below the root zone, pesticides leached beyond this depth are less likely to be degraded. However, some pesticides will continue to degrade by chemical reactions after they have left the root zone. [1] The single most important property influencing a pesticide's movement through water is its solubility. [6] One of the most useful indices for quantifying pesticide adsorption on soils is the partition coefficient (PC) [1] which is the ratio of pesticide concentration in the adsorbed-state (that is bound to soil particles) and the solution-phase (that is, dissolved in the soil-water). Persistence and movement of these pesticides and their Transformation Products (TPs) are determined by some parameters, such as soil-sorption constant (K_{oc}), the octanol/ water partition coefficient (K_{ow}), and half-life in soil (DT50). The partition coefficient is determined by a pesticide's chemical properties such as solubility and melting point and is independent of the soil type. [9] Similar index for sorption could be calculated for a given pesticide on a particular soil using equation, K = (PC) (%OM) (0.0058) where % OM is the percent of organic matter in the soil as determined by chemical analysis of the soil and PC is the partition coefficient of the pesticide. Thus, pesticides with PC or K = 0 will leach through run off. [1] Soil adsorption coefficient K_{oc} of pesticides used in cardamom plantations are shown in Table 3. The organic matter in soils of Idukki cardamom plantations are high [10] and more than 75 % of the samples contain an average 40% of its particles less than 75 microns. As part of this study, 100 water samples were collected across the project area and analysed for pesticide residues and confirm that the water sources are not contaminated with pesticide residues or the pesticides used are of large PC values. [11]

Table3. Pesticides adsorption coefficient and TPs characteristics

Pesticide	$K_{oc(ml/gOC}$	DT50	TPs	Characteristics
DDT,	635000	3000	DDD , DDE	Toxic persistent
Endosulfan	12400	50	Endosulfan sulfate	Persistent
Organophosphorous Malathion	1800	1	Oxidation product	More toxic
Carbofuran	14-160	30-117	3- Hydroxycarbofuran 3-Ketocarbofuran	Hydrolysis products, toxic, little persistent

3.3 Pesticide degradation and transformation products

Pesticides are degraded by chemical and microbiological processes. [1] Endosulfan, a highly persistent organochlorine pesticide degrade by microorganisms.[2] The bioavailability and the fraction of chemical that can be transformed by living organisms is unique for each species.[12] The organochlorine DDT and endosulfan pesticides present in the soil samples are hydrophobic which is more persistent and bio-accumulable. The organophosphorous pesticides – herbicides, carbamates and fungicides are polar pesticides that move along with runoff and leaching. [13] The extent of degradation ranges from the formation of metabolites (TPs) to the decomposition in inorganic products. [9] The studies on adsorption of pesticides and biodegraded products on soils particularly on clay minerals less than 75 microns observed that monmorillonite clay had considerable adsorption capacity. [14]

In this study a similar soil characteristic was observed in soils and point out high risk of contamination of persistent pesticide residues in the project area. Most of these pesticides are now banned in agriculture but they are still available in market with different trade names but with same chemical compositions and hence their residues were detected in the soil samples from the project area.

3.4 Analysis of the predicted values of pesticide residues, organochlorine and organophosphorous chemicals.

The accuracy in predicted models was evaluated based on the field data and its limitations in study. The degradation of pesticides and its residual concentration are compared with the results of earlier studies under similar conditions. However, there are limited studies in the literature which address the environmental behavior of pesticides at elevated levels. [15] The mathematical model gives realistic values of predicted concentrations within the limits of uncertainty. The TWA model (figure 2 &3) shows the degradation pattern and the predicted concentration at an interval of a crop period. The concentrations shows reasonably low value than the present field level concentrations due to reasons attributable to nature and limitations in the analysis.

The actual pesticide residue in soils shows only the free residue that is extractable and it is excluding the bound residue**. [15]** In contrast with the assumption that the kinetics is of first order and in all instances the degradation occurs in two phases. In the first phase the compound was being degraded so that its concentration progressively declined with time. The responsible organism was present in soil and conditions were suitable for metabolism even if the transformation was not overly rapid. In the second phase, the concentration did not fall detectably or it declined at a very low rate. The low phase indicate that the chemicals are intrinsically slowly transformed and hence liable to physical or chemical modifications that result in alterations in the availability to microorganisms which is represented as aging.[16] Ageing is thought to be the result of either a redistribution of the chemical from weaker to stronger adsorption sites, slow chemisorptions /sequestration, or covalent bond formation between the compounds and soil organic matter.[17] The predicted model (Fig.2 and 3) is agreeing with this arguments that the kinetics is not of first order but are in two phases and in the second phase the concentration declined at a very low rate.

A variety of agricultural and environmental factors viz. concentration , repeat applications, effect of aging of bound pesticides in soils, mode of application of pesticide in soil and effect of soil structure/texture with organic and inorganic fertilizers influences the fate and binding of xenobiotics in soil.[15] Persistence of pesticides in soils has been found to increase with increasing concentration whereas mineralization, formation of degradation products and bound residues decreases at higher concentrations. The formation of bound residues on a percentage basis have been found to vary inversely with increased initial application rates.[18] This argument agrees with the model and shows that the endosulfan and organophosphorous residues degraded at faster rate at higher initial concentrations of 0.87 $mgKg^{-1}$ than at a mean concentration of 0.0926 $mgKg^{-1}$. Similarly the Organophosphorous residue degraded at faster rate when the concentration is 0.589 $mgkg^{-1}$ than at the mean value, 0.1122 $mgkg^{-1}$. The initial hike in concentration is due to repeated applications within the half life period. The two effects of repeated applications on the fate of pesticides in soils are accelerated dissipation and decelerated binding, both of which are of profound significance in the context of transfer and retention processes of soil--applied pesticides [19] which decreases the pesticide persistence in soil and minimizes the potential environmental hazards.

The study reveals that optimum use of pesticides, maintaining soil moisture and organic contents in tandem with soil characteristics and microbial growth will reduce the contamination of soil and can improve degradation of bound pesticides so as to protect the environment from the formation of toxic metabolites. The use of banned pesticides which is available in the market should be completely seized by a random raid and continuous monitoring by authorized officials is necessary for a complete exit of highly toxic pesticides like endosulfan, DDT etc which is present in the soil at high concentrations. Intensive soil cultivation without applying agro-chemicals is a suitable method for a long-lasting soil decontamination of persistent organic chemicals like DDT. [7]

IV. Conclusions

- The study conducted in Idukki district, the Indian Cardamom Hills agrees with the earlier findings that formation of degradation products and bound residues decrease at higher concentration of pesticide applications and it is concluded that this findings are applicable to elevated levels also.
- The results of earlier studies [19-20-21] that, the fate of degradation of pesticides and formation of its metabolites is determined by the soil adsorption capacity and water solubility of pesticides which is quantified as partition coefficient and the properties of soil such as pH, organic content and microbiological concentration is in agreement with this study.

- The predicted environmental concentrations of pesticides using Time Weighted Average concentration based on mathematical model for multiple applications, when the concentrations in soil build up and reach a plateau, are 2.559, 0.2559, 1.7324 and 0.659 $mgKg^{-1}$ in the case of endosulfan, DDT, organophosphorous and total pesticides respectively which may be dreadful. The biodiversity in Western Ghats, the migrating bird's life, soil fertility and climatic changes, the flora and fauna and large water sources will be affected if the present scenario is continued further.[21]
- The 'TWA' spread sheet models show that the repeat application even at high dose increases the degradation of pesticides and reduce the residual concentration at a faster rate.
- Persistence of pesticides in soils has been found to increase with increasing concentration as found in the mathematical model which leads to aging on bound residues. As a result the bound pesticide residues tend to lose their biological activity and become even more resistant to degradation and extraction.

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