ECRONICON OPEN ACCESS

EC PHARMACOLOGY AND TOXICOLOGY
Research Article

Efficacy of Vermicompost as a Biostimulating Agent to Combat Residual Chlorpyrifos in Soil Matrix for Food Safety

Neeru Kadian[1]*, Santosh Satya[1], Anushree Malik[1] and Beena Kumari[2]

[1]Center for Rural Development and Technology, Indian Institute of Technology Delhi, New Delhi, India

[2]Department of Entomology, CCS Agriculture University, Hisar, Haryana, India

***Corresponding Author:** Neeru Kadian, Center for Rural Development and Technology, Indian Institute of Technology Delhi, New Delhi, India.

Received: December 11, 2017; **Published:** January 06, 2018

Abstract

A study was carried out to assess the effectiveness of vermicompost at 1, 3 and 5% doses for biostimulation of chlorpyrifos (CPF) contaminated soil at ambient environment. Different doses of vermicompost (1, 5 and 3% application) were found effective in CPF degradation with half-life period of 18.7, 19.5 and 20.1 days, respectively whereas in untreated soil CPF half-life period was found to be 23.6 days. As compared to control, vermicompost application shortened the half-life value ranging from 14 to 21% which signify good quality produce in next crop sowing. Findings clearly reveal the potential of vermicompost as suitable biostimulating agent to sustain the microbial activity for fast detoxification of CPF contaminated soil for achieving food safety.

Keywords: *Chlorpyrifos; Biostimulation; Vermicompost; Bioremediation; Soil*

Abbreviations

CPF: Chlorpyrifos; NCR: National Capital Region; EC: Emulsifiable concentrate

Introduction

Application of chemical pesticides as a pest control measure in agriculture has become common practice even though at the cost of food safety. However, overdose/irrational practice of these pesticides forms a foundation of endless detrimental effects in nature. Further, their persistence characteristics create a havoc even far away from the application sites. Persistence of chlorpyrifos (O, O-diethyl O-3, 5, 6-trichloropyridin-2-yl phosphorothioate) in environment is well documented [1-3]. It is a broad spectrum systemic organophosphate insecticide patented and introduced in 1965 by Dow Chemical Company in USA. Worldwide 900 products registered having this insecticide as active ingredients [4] and in India it is fourth highest consumed pesticide [5]. Even it was identified as most commonly applied pesticides in National Capital Region (NCR) of Delhi during a detailed NCR survey [6]. Approximately 50% of its consumption is in agricultural sector for plant protection and remaining is in non-agricultural sector including ~ 24% for termite control [7]. Not only on field crops but even for the post-harvest preservation of grain legumes it is used as prophylactic measures along with other insecticides [8].

Chlorpyrifos contamination has been found even up to 15 miles from the site of application, clearly showing that contamination can spread to long distances [9,10]. Being lipophilic (attracted to the fatty parts of body tissues) stretching its effect for longer duration as remain in a stored-release mode and transformed to chlorpyrifos-oxon [11]. This metabolite oxon has about 3000 times more neurotoxic potent as compared to parent molecule [12,13]. In chlorination process, commonly used for treatment of domestic water supplies; active chlorine dispersed in water, induces the rapid abiotic transformation of chlorpyrifos to oxon. Infact, it may lead to more life-threatening situation than the initial concentration of chlorpyrifos in the water [14]. Typical soil persistence is reported to be between 60 and 120 days [1], although it can be extended under conducive conditions. Even the repeated application does not favor the fast degradation rate of chlorpyrifos [15-17]. Due to its highly mammalian toxicity nature, EPA announced an agreement with chlorpyrifos registrants to eliminate certain uses of this pesticide [18,19], such as foods frequently eaten by children (apples, grapes, tomatoes), school premises and parks etc in June 2000. Hence, any method which helps in slight enhancement of CPF degradation can play a critical role in the removal of this neurotoxic pesticide and further lowering of buildup concentration in soil.

Organic manures are recognized as a valuable source of nutrients to improve conditioning of soil structure and further contribute to crop yields [20]. Additionally, bioprocessed materials like mushroom spent compost [21], dairy manure [22,23], vermicompost [24] and biogas slurry [25] have also been recently recognized as a good source of biostimulation process through a large number of pesticide degradative microorganisms along with soil/plant nutrients. Considering easy availability and accessibility of these materials for rural people' of India, four organic amendments (i.e. biogas slurry, farmyard manure, mushroom spent and vermicompost) were chosen for various biostimulation studies which have shown good potential for CPF degradation [24]. Hence, best proven biostimulating agent i.e. vermicompost from previous study [24] was reattempted to enhance the CPF degradation rate at 1% and two other doses i.e. 3 and 5% under the ambient environment. Above reported literature reveals that biostimulation is a potential technique but the same has not been systematically investigated in case of CPF. Moreover, the existing studies have been conducted with very high percentage of organic amendments or in pure organic matrix. In order to deliver a technology for degradation of CPF contaminated agricultural soils, there is a need to optimize the dose of organic amendments in such a way so that it will suit the current agronomic practices. It is highly significant point to note that bioremediation potential of such organic amendments according to agronomical practices for CPF degradation has not been studied earlier.

Hence, developing a pragmatic methodology for CPF removal from the source of origin (agricultural fields) assumes a great scientific significance along with a practical solution for the illiterate population of the country. In view of food safety for human consumption, if application of vermicompost doses can positively shorten the CPF half-life, it may be of great importance in terms of soil detoxification-an important parameter for amendment of biomagnification in the next sowing crop. In such a situation, residual CPF would be tackled at the pesticide application site resulting in fewer chances of biotransformation and biomagnification in soil ecosystem. In present agriculture scenario, bioremediation in term of biostimulation emerges as one of the most suitable strategy for remediation of the pesticide contaminated soil in terms of cost effectiveness and practical feasibility for farmers. Therefore, aim of present study is to find out the appropriate dose of vermicompost which can combat residual CPF on one hand and additionally become a source of nutrients to the soil.

Materials and Methods

Soil and organic amendment

Soil

For this study, same field soils were collected from a selected plot in IIT, New Delhi, as used in earlier studies by Kadian., *et al*. [24]. The sieved (2.0 mm sieve) soil samples were taken to investigate degradation of CPF in pot experiments under the ambient conditions.

Organic amendments

As well known, ambient environmental conditions are different and complex as compared to controlled conditions, hence out of biogas slurry, farmyard manure, mushroom spent and vermicompost, the proven best organic amendments [24], i.e. ability of 1, 3 and 5% vermicompost at three different doses was investigated in pot experiments under the ambient conditions for a period of 50 days.

Vermicompost obtained from Teri Gram, near Delhi (India) was procured for experiments, air dried and characterized as per method described earlier [25]. Physico-chemical characteristics of vermicompost reported earlier are as following: pH 7.4, EC 0.55 ds/m, OM 24.1%, phosphorus 0.11%, C/N ratio 10.85 [24].

Experimental setup

The experiments were conducted in 200g capacity plastic plantation pots. For this biostimulation study, calculated amount of commercially available CPF (Chlorpyrifos 20% EC of Insecticides Limited, Bhiwadi, Rajasthan, India) was added to soil samples, to make the final concentration of CPF at 7 mg kg^{-1}. Detailed investigation using vermicompost amendment at different doses i.e. 1, 3 and 5% was carried out. For these treatments calculated quantity of vermicompost amendments in 200g soil was added in respective pots having 7mg kg^{-1} spiked soil, mixed well and kept under the ambient conditions for a period of 50 days. No chemical nutrient supplement was added during the experimental period. These experiments were conducted during August-October months in Indian weather conditions (maximum temperature 30 - 37°C and minimum temperature 18 - 25°C; maximum relative humidity (R.H.) 96 - 69% and minimum R.H. 20 - 72%). The treatments were designed as: 7 mg kg^{-1} CPF contaminated soil as control (C), C + 1% VC termed as VC1, C + 3% VC as VC3 and C + 5% VC denoted as VC5. Soil samples at different time intervals (1, 3, 7, 12, 24, 38, 50th day) were drawn and analyzed for CPF degradation.

Extraction and analysis of chlorpyrifos residues

For residual CPF analysis, 15g soil samples were extracted according to method described by Kumari., *et al*. [26] and were analyzed by GC-ECD with a BP-5 capillary column (30 m x 0.59 mm ID) [24].

Results and Discussion

Chlorpyrifos degradation

The chemical behavior of CPF may be considerably different in artificially incubated soils, giving a false signal and thereby leading to over-optimistic assumptions. It is therefore, of paramount importance that biological and chemical processes inherent to biostimulation strategies are assessed in the ambient environment prior to undertaking the field scale ventures. The degradation of CPF in soil was assessed at three different doses (1% - VC1, 3%-VC3 and 5%-VC5) of vermicompost amendment under ambient environmental conditions.

The residues of CPF were monitored from 0 day to 50th day in all the four treatments (Table 1). Each data point in this study represents the average of three replicates (with standard deviation) as shown in table 1. The initial concentration of CPF (i.e. zero day) in C, VC1, VC3 and VC5 treatments were found to be 6.83, 6.55, 6.31 and 6.68 mg kg^{-1}, respectively which degraded by 53.13% (24th day) and 84.43% (50th day) in VC1. In VC3, the initial deposit was degraded by 50.22% on 24th day that progressively enhanced to 83.95% on 50th day and in case of VC5, degradation was reported slightly high i.e. 55.54% on 24th day but finally reached only to 83.68% on 50th day, whereas in control the corresponding values were low; 49.63 and 79.36% on 24th and 50th day, respectively. Hence, data clearly revealed that the unamended control (C) degraded the insecticide slowly as compared to the vermicompost applied soil. The degradation of CPF was accelerated from 79.36 (control) to 83.68 (VC5) and 83.95% (VC3) respectively, in case of higher doses of vermicompost in soils after 50 days (Table 1). The degradation trend was recorded as VC1 > VC3 ≈ VC5 > control. Highest degradation (84.43%) was observed in VC1 with 1% vermicompost application rate.

	Residual Chlorpyrifos							
	Control (C)		VC1		VC3		VC5	
Sampling days	Average* ± SD (mg kg^{-1})	Degradation (%)	Average* ± SD (mg kg^{-1})	Degradation (%)	Average* ± SD (mg kg^{-1})	Degradation (%)	Average* ± SD (mg kg^{-1})	Degradation (%)
0	6.83 ± 0.020	-	6.55 ± 0.035	-	6.31 ± 0.02	-	6.68 ± 0.044	-
1	5.73 ± 0.060	16.11	4.34 ± 0.070	33.74	5.96 ± 0.04	54.09	2.78 ± 0.053	58.38
3	5.57 ± 0.053	18.45	4.32^{d} ± 0.046	34.05	5.72 ± 0.03	26.00	5.53 ± 0.035	17.22
7	4.79 ± 0.031	29.87	4.28^{d} ± 0.044	34.66	5.2 ± 0.03	27.19	5.05 ± 0.040	24.40
12	4.36 ± 0.070	36.16	4.12 ± 0.036	37.10	4.71 ± 0.02	39.97	3.26 ± 0.026	51.20
24	3.44 ± 0.44	49.63	3.07 ± 0.066	53.13	3.87 ± 0.03	50.22	2.97 ± 0.010	55.54
38	2.11 ± 0.021	69.11	1.08 ± 0.044	83.51	3.43 ± 0.06	76.23	1.47 ± 0.053	77.99
50	1.41 ± 0.035	79.36	1.02^{f} ± 0.017	84.43	2.41 ± 0.01	83.95	1.09^{o} ± 0.026	83.68
$t_{1/2}$(days)	23.6		18.7		20.1		19.5	

Table 1: *Residual chlorpyrifos and its half-life with different doses of vermicompost in soil under ambient conditions. Where C = c (control), VC1 = o (1% vermicompost), VC3 = t (3%), VC5 = f (5%); insignificant denoted by c, o, t, f (superscript) respectively. Insignificant values day-wise denoted by superscript d. CD (p = 0.05) for treatments 0.038; for days = 0.27; for days × treatments = 0.076; * average of three replicates ± SD*

As shown in figure 1, there was a rapid loss of residual CPF in all the treatments (i.e. at varying doses of vermicompost) as compared to the control. On 1st day of sampling, there was very high i.e., 33.7, 54.1 and 58.4% degradation of CPF reported in VC1, VC3 and VC5, respectively whereas control showed only 16% degradation. In contrast to VC1, where a gradual decrease in CPF concentration was observed, there was remarkable decrease in residual CPF in VC3 and VC5 treatments on 1st sampling day (1st day after treatment); which again increased in the soil matrix on 3rd day and further there was a gradual decrease in CPF concentration.

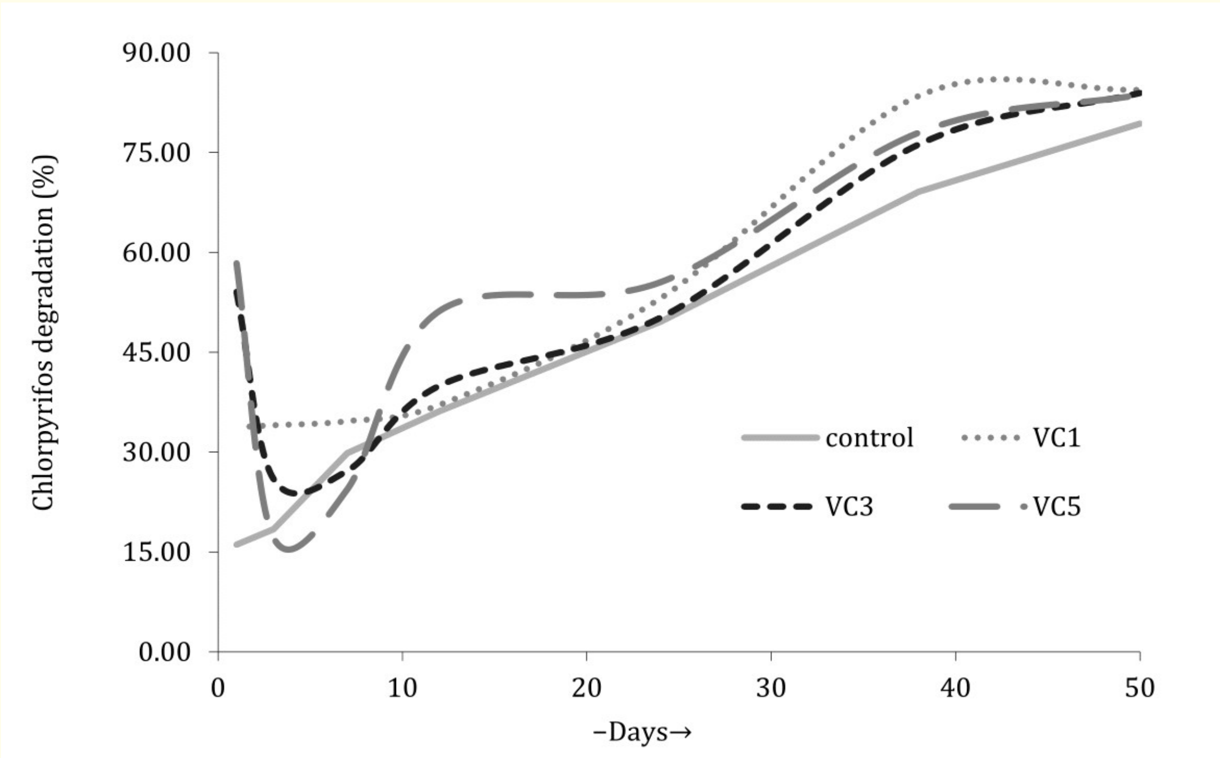

***Figure 1:** Degradation pattern of chlorpyrifos with dose dependent application of vermicompost (C -control, VC1-1%, VC3-3% and VC5-5%) in soil under ambient conditions.*

The disappearance and reappearance of CPF was correlated with the dose of vermicompost, both being higher at 5 and 3% as compared to 1% vermicompost application. But in case of VC1 such trend was not seen. It may be due to the phenomenon of adsorption-desorption in soil matrix with the vermicompost application. Such a sorption process has been previously reported to aid microbial degradation [27]. Possibly due to this reason, in initial few days (0 - 12), rapid dissipation was observed at higher doses of vermicompost, which may be due to sorption of CPF on vermicompost. Similar result was reported earlier, where vermicompost was found an effective sorbent at 5% application rate in sandy loam soil [28]. No such pattern was observed with 1% application (VC1) as there was a gradual increase in degradation with the passage of time. Due to this sorbent property of vermicompost, CPF degradation may take place according to the percentage of vermicompost applications. Enhanced degradation (i.e. 58.4%) was observed with the higher dose in 5% vermicompost treatment (VC5) as compared to 54% CPF degradation in 3% vermicompost treatment (VC3) on 1st day.

With the increased dose of vermicompost from 1% to 3% and 5%, there was an enhancement in CPF degradation on 12th day (2.59%, 10.53% and 41.57% respectively) as compared to the unamended soil. However, no clear trend with increase in VC dose was observed in the latter phase. On 50th day of sampling, there was almost same i.e.83.95 and 83.68% degradation observed irrespective of the dose of vermicompost i.e. 3 and 5%. To conclude, although increase of vermicompost dose can enhance the CPF disappearance in the initial phase (within 12 days' time period) but it doesn't influence overall degradation. Therefore, application of vermicompost at 1% dose may be recommended for decontamination of agricultural soil. Whereas high doses of vermicompost would be a good solution for rapid cleanup of industrial site in a short time duration (12 days) since higher doses (VC5 and VC3) on 12th day showed 51.2 and 39.97% degradation of CPF, respectively which is comparatively very high from VC1 i.e. 37.1%.

Rate Kinetics and half-life period of chlorpyrifos

Half-lives ($t_{1/2}$), i.e., the time required for any pesticide to undergo degradation to half of its initial concentration, were determined by the first-order kinetic models. The pesticide residue data were, therefore, statistically interpreted for computation of regression equation and half-life values. Half-life values in different treatments were derived by applying first order kinetics to residual CPF data (Figure 2; Table 1).

The degradation followed first order reaction as the log values of the residues of CPF when plotted against respective days gave $r^2 > 0.9$ for all the treatments (Figure 2). The degradation of CPF followed a first order kinetics in all the four treatments with r^2 values of 0.97 (C), 0.93 (VC1), 0.97 (VC3) and 0.97 (VC5) (Table 1). Present results corroborate with the general observation that CPF degradation in soil is often considered as first order reaction [29,30]. The results (including regression equation) are shown in figure 2. Degradation rates of CPF in all the VC dose treatments were significantly faster than in the unamended soil i.e. control. Half-life trends were found as shortest in VC1 (18.7) followed by VC5 (19.5) and VC3 (20.1). Without any vermicompost application, the contaminated soil showed longest half-life i.e. 23.6 days (C). Vermicompost application in contaminated soil reduced the half-life in case of VC1 (20.74%), VC3 (14.81%) and VC5 (17.35%), as compared to control (Table 1). From this half-life data, it is clear that 1% vermicompost is most suitable for the degradation of CPF, whereas sorption in case of 3 and 5% vermicompost doses may be the delaying factor due to which it finally showed somewhat longer half-life as compared to 1% dose treatment.

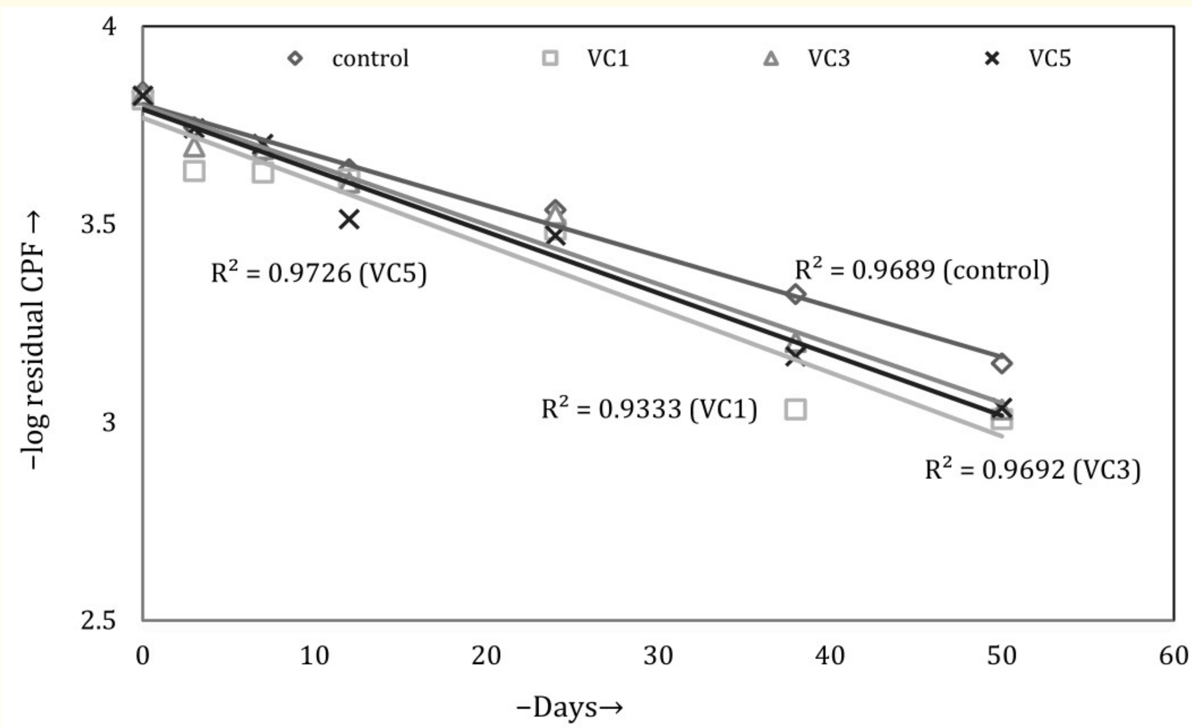

Figure 2: *Kinetics of CPF degradation with different doses of vermicompost in contaminated soil.*

Statistical interaction between days and treatments was found to be significant (p = 0.05). Critical difference calculated through two-way ANOVA revealed that the rate of degradation is at par between 3rd and 7th day in VC1 treatment. CPF degradation was found highly significant in case of all the vermicompost application on all days of treatments, as indicated by significant difference denoted by ANOVA (Table 1).

Conclusion

Since increased quantity of vermicompost can enhance the CPF degradation only in the initial phase (12 days period); it can be an effective way for remediation of CPF contaminated industrial sites in short life span. However, in case of agricultural soils, biostimulation through vermicompost amendment at 1% dose (which is accordance to normal agronomical practices i.e. 8.1 ton/acre in India) has a good potential as a cost-effective tool for CPF degradation in the sandy loam soil. It is noteworthy that bioremediation potential of such organic amendments according to agronomical practices for CPF degradation has not been studied earlier. Hence, this study makes a novel contribution in defining a new dimension regarding the role of organic manure in toxicity removal from soil, an effective way of safe food production. Nevertheless, it needs to be integrated with other effective techniques such as phytoremediation in order to enhance the CPF degradation rates more significantly. Vermicompost sorbent competence can be explored at highly contaminated industrial sites. Present study is a novel beginning towards harnessing the 'power of nature' for providing a pragmatic solution of a complex problem in modern agriculture system. This study would prove a milestone in promoting organic farming–a tough task in modern era. Further, extensive research work on Field Design for various crops in different agro-climatic regions needs to be carried out for recommending it at wider scale.

Acknowledgements

One of the authors (Dr. Neeru Kadian) is grateful to the Department of Science and Technology (Govt. of India) for Women Scientist Fellowship.

Conflict of Interest

The authors declare that there is no conflict of interest.

Bibliography

1. Howard Philip H. "Handbook of environmental fate and exposure data: for organic chemicals, volume III pesticides". *CRC Press* 3 (1991).

2. Jin Heng and G R B Webster. "Dissipation of chlorpyrifos, oxon, and 3, 5, 6-trichloro-2-pyridinol in litter and elm forest soil". *Journal of Environmental Science and Health Part B* 32.6 (1997): 879-900.

3. George Thomas Beevi S Naseema and Gowri Priya. "Persistence of chlorpyrifos in acid soils". *Pesticide Research Journal* 19.1 (2007): 113-115.

4. Josephson Julian. "Cancer: New Chlorpyrifos Link?". *Environmental Health Perspectives* 113.3 (2005): A158.

5. Pesticide Information Volume XXVIII, No. 3 (2002).

6. Kadian Neeru. "Bioremediation of chlorpyrifas contaminated soil using biostimulation and phytoremediation techniques" (2010).

7. Racke Kenneth D., *et al*. "Chlorpyrifos degradation in soil at termiticidal application rates". *Pest Management Science* 42.1 (1994): 43-51.

8. FCI Quality - Food Corporation of India (2016).

9. Glotfelty D E., *et al*. "Pesticides in fog". *Nature* 325 (1987): 602-605.

10. Seiber James N., *et al*. "Air and fog deposition residues of four organophosphate insecticides used on dormant orchards in the San Joaquin Valley, California". *Environmental Science and Technology* 27.10 (1993): 2236-2243.
11. Chambers Janice E., *et al*. "Inhibition patterns of brain acetylcholinesterase and hepatic and plasma aliesterases following exposures to three phosphorothionate insecticides and their oxons in rats". *Toxicological Sciences* 21.1 (1993): 111-119.
12. Sultatos, Lester G. "Metabolic activation of the organophosphorus insecticides chlorpyrifos and fenitrothion by perfused rat liver". *Toxicology* 68.1 (1991): 1-9.
13. Chambers Janice E., *et al*. "Bioactivation and detoxification of organophosphorus insecticides in rat brains". *Intermediary Xenobiotic Metabolism: Methodology, Mechanisms, and Significance* (1989): 99-115.
14. Wu Jigang and David A. Laird. "Abiotic transformation of chlorpyrifos to chlorpyrifos oxon in chlorinated water". *Environmental Toxicology and Chemistry* 22.2 (2003): 261-264.
15. Racke Kenneth D., *et al*. "Resistance of chlorpyrifos to enhanced biodegradation in soil". *Journal of Agricultural and Food Chemistry* 38.6 (1990): 1430-1436.
16. Mallick K., *et al*. "Bacterial degradation of chlorpyrifos in pure cultures and in soil". *Bulletin of Environmental Contamination and Toxicology* 62.1 (1999): 48-54.
17. Vischetti Costantino., *et al*. "The effect of initial concentration, co-application and repeated applications on pesticide degradation in a biobed mixture". *Chemosphere* 72.11 (2008): 1739-1743.
18. USEPA. Chlorpyrifos Revised Risk Assessments. US Environmental Protection Agency (2000).
19. United States Environmental Protection Agency (USEPA). "Chlorpyrifos Facts". US Environmental Protection Agency (2002).
20. Karlen D L., *et al*. "Crop rotations for the 21st century". *Advances in agronomy* 53.1 (1994): 45.
21. Kuo Wen-Shiuh and Raymond W Regan. "Aerobic carbamate bioremediation aided by compost residuals from the mushroom industry: laboratory studies". *Compost Science and Utilization* 6.1 (1998): 19-29.
22. Gaur A C., *et al*. "Note on detoxication of lindane by farmyard manure". *Indian Journal of Agricultural Sciences* (1975).
23. Gan J., *et al*. "Degradation of atrazine in two soils as a function of concentration". *Journal of Environmental Quality* 25.5 (1996): 1064-1072.
24. Kadian Neeru., *et al*. "Effect of organic amendments on microbial activity in chlorpyrifos contaminated soil". *Journal of Environmental Management 9*5 (2012): S199-S202.
25. Kadian Neeru., *et al*. "Biodegradation of herbicide (atrazine) in contaminated soil using various bioprocessed materials". *Bioresource Technology* 99.11 (2008): 4642-4647.
26. Kumari Beena., *et al*. "Status of insecticide contamination of soil and water in Haryana, India". *Environmental Monitoring and Assessment* 136.1 (2008): 239-244.
27. Romyen Siraprapa., *et al*. "Potential of agricultural by-product in reducing chlorpyrifos leaching through soil". *Journal of Applied Sciences* 7.18 (2007): 2686-2690.
28. Fernández-Bayo Jesús D., *et al*. "Improved retention of imidacloprid (Confidor®) in soils by adding vermicompost from spent grape marc". *Science of the Total Environment* 378.1 (2007): 95-100.
29. Walker Aiian., *et al*. "Influence of temperature, soil moisture and soil characteristics on the persistence of alachlor". *Pest Management Science* 35.2 (1992): 109-116.
30. Obrador Ana., *et al*. "Simulation of atrazine persistence in Spanish soils". *Pest Management Science* 37.3 (1993): 301-308.

Volume 6 Issue 1 January 2018