Journal of Environmental Protection, 2011, 2, 1207-1210
doi:10.4236/jep.2011.29138 Published Online November 2011 (http://www.scirp.org/journal/jep)

Degradation of Lindane (γ-HCH) in a Mollisol as Effected by Different Soil Amendments

Gunjan Bhatia[1], Anjana Srivastava[1*], Prakash Chandra Srivastava[2]

[1]Department of Chemistry, College of Basic Sciences & Humanities, Pantnagar, Udham Singh Nagar, India; [2]Department of Soil Science, College of Agriculture, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar, Udham Singh Nagar, India.
Email: *anj612003&yahoo.co.in

Received July 29th, 2011; revised September 7th, 2011; accepted October 8th, 2011.

ABSTRACT

Soil amendments play an important role in management of pesticide residues. In this study, incubation experiment was conducted using the surface (0 - 15 *cm*) *sample of a mollisol supplied with different soil amendments* (*farmyard manure*, *cow-dung slurry*, *pyrite and gypsum*) *to investigate the effect of amendments on the dissipation of lindane in mollisols. Dissipation of lindane in soil was studied at eight consecutive samplings* (0, 1, 3, 5, 7, 10, 15 *and* 30 *d*). *The results indicated that soil amendments could promote the degradation of lindane in soil. After* 30 *d of incubation* 79% *degradation was observed in the untreated soil* (*without any amendment*) *whereas*, *in the case of farmyard manure and cow-dung slurry amended soils*, 83% *and* 91% *degradation was observed*, *respectively. Gypsum also enhanced the degradation of lindane in soils*, *but the effect was less pronounced as compared to the organic amendments. Enhanced degradation in soil treated with organic amendments could be attributed to stimulated microbial activity after the addition of organic amendments. Application of organic amendments*, *under different soil management conditions*, *minimize the persistence of lindane and consequently the risk of leaching and seepage into aquifers*.

Keywords**:** *Lindane*, *Amendment*, *Soil*, *Residue*, *Degradation*

1. Introduction

Lindane, the 'γ' isomer of hexachlorocyclohexane (γ-HCH), is an organochlorine compound primarily used as an insecticide and fumigant against a wide range of soil dwelling and phytophagous insects. Other major uses are for personal hygiene as scabicide and pediculicide in the form of lotions, creams, or shampoos. However, agricultural uses are mainly responsible for the persistence of lindane residue in soil. Due to its worldwide use for more than 50 years, lindane-contaminated soil can be found in many parts of the world. Although many countries have restricted or eliminated its usage, obsolete stock piles continue to pose a threat to various ecosystems [1,2]. Once lindane enters the environment, it can distribute globally [3-6] and can persist in various environmental compartments [2,7-9]. Accumulation of OCPs in the lipid content of animals is also a common phenomenon due to their hydrophobic properties. Due to its continuous use and indiscriminate industrial production, lindane contaminated soils are widespread in the country.

Application of soil amendments has been a common agronomic practice followed in agriculture to increase the soil fertility and crop productivity. Soil amendments play an important role in the management of pesticides residues in agricultural fields. Supplemental soil amendments may be added to enrich the habitat for degrading organisms. MacRae *et al.* [10] showed a stimulated removal of α, β and δ -HCH by amendment of urea. Potassium chloride and potassium sulphate were also shown to enhance degradation of γ-HCH in cell suspensions of Clostridium sp. [11].

Since, lindane exerts adverse impacts on the environment, therefore, it is critically important to develop different methods to enhance it's degradation in polluted fields. These cost effective tools can help farmers to modify their farming practices and preserve soil and water quality. A laboratory investigation was, therefore, planned to evaluate different soil amendments for their efficacy to dissipate lindane in a mollisol.

2. Material and Methods

Lindane of 99.5% purity grade was obtained from Himedia Laboratories Pvt. Ltd., Mumbai and the solvents used in the study were of analytical grade and purchased from M/s Merck (India).

2.1. Preparation of Soil

The soil used in this study was collected from the Practical Crop production (PCP) Block located in G. B. Pant University of Agriculture and Technology, Pantnagar, India. Surface (0 - 15 cm) soil sample was collected and air-dried under shade and crushed by a wooden roller and sieved through a 2-mm sieve. The physico-chemical characteristics of the soil were determined using standard analytical procedures: pH measured at 1:2 soil-to-water ratio [12]; organic carbon content by Walkley and Black method [12]; soil mechanical fractions, sand, silt, clay by employing the Bouyoucos hydrometer method [13]. The physical and chemical properties of soil used in the study are presented in (**Table 1**). Two kg soil samples taken in different plastic bags were separately amended with farmyard manure @ 5 $t \cdot ha^{-1}$, cow dung slurry @ 0.5 $t \cdot ha^{-1}$, pyrite @ 5 $t \cdot ha^{-1}$ and gypsum @ 5 $t \cdot ha^{-1}$ while the unamended soil served as a control. Prior to addition of insecticide, the soils receiving different treatments were incubated for 15 d near field capacity moisture regime (26% on weight basis) and then lindane (2 $mg \cdot kg^{-1}$ soil) was added to each treatment. Soil moisture under each treatment was maintained near field capacity through out the incubation period by regularly adding the required amount of water.

2.2. Sampling

For determining the residue of lindane under different treatments, aliquots of treated soil (10 g) under different treatments were taken at 0, 1, 3, 5, 7, 10, 15 and 30 d after addition of lindane. Lindane residues were extracted from soil samples and determined by gas chromatography.

2.3. Extraction and Analyses

The insecticide residues from soil samples (10 g) were extracted using acetone (25 mL) by shaking on a shaker for 1 h. The acetone layer was separated and dried over anhydrous sodium sulphate. The solvent were concentrated and dissolved in 1 ml of hexane. The samples were quantified on a Chemito Gas chromatograph, Model series 800 plus, equipped with a ^{63}Ni electron capture detector (ECD) and fitted with packed column 10% SE 30 (8' length and 1.8' i.d). The GC operating conditions were: oven: 180˚C, injector: 230˚C, detector: 300˚C, carrier gas (nitrogen) flow rate: 30 $mL \cdot min^{-1}$. The detection limit for lindane was 0.01 μg and recovery from the soil at fortification levels of 0.1 - 10 $\mu g \cdot g^{-1}$ soil was more than 90%. Quantification of lindane was accomplished by using a standard curve prepared by injection of the standard solution in n-hexane.

Table 1. Some basic properties of the soil used.

Parameters	
Sand (%)	16.4
Silt (%)	44.0
Clay (%)	39.6
pH (1:2, soil water suspension)	8.16
Electrical conductivity ($dS \cdot m^{-1}$, 1:2 soil water suspension)	0.130
Organic carbon (%)	1.45
Free iron oxide (%)	0.97

3. Results and Discussion

Soil acts like an active filter, where pesticides are degraded by chemical, physical and biological means. The degradation of pesticides in the soil is a function of their availability to microorganisms or enzymatic systems which are capable to degrade them and also their population and activity [14-16]. The availability and degradability of a pesticide in the soil varies a lot from one pesticide to another and also depends upon the soil type [17]. Soil physicochemical properties play a determining role in the degradation of pollutants. These parameters affect both their equilibrium concentration in the soil system as well as possible adsorption onto various soil components [18]. The increase of organic carbon content in soil could increase the amount of microbial biomass and thus, induce the degradation [19]. As a result, total organic carbon (TOC) content could affect the residue levels of HCH in soils [20]. Soil pH can affect the concentration of HCH in soil by influencing the microbiological activity in the soil [21]. In the present study, however, no attempts were made to correlate the physico-chemical properties of lindane, soil and amendments with the degradation rate of lindane. It is assumed that pesticides generally dissipate in the soil in two phases; an initial period of rapid diminishing of residue followed by a longer period of slower reduction [22]. The relative importance of these phases depends on the availability of the pollutant, their hydrophobicity and affinity for organic matter [16].

Dissipation data for insecticide under 30 d incubation fitted well to a first-order kinetic equation: $\log(C/C_o) = -K_{obs}\, t$, where C_o is the initial concentration of insecticide (mg/kg); C is its concentration (mg/kg) after time t, t is time lapse (days) and K_{obs} is the rate constant of the reaction. **Figure 1** represents the dissipation behaviour of lindane under different amendment treatments of soil. In untreated natural soil (without amendment), lindane was found to be more persistent as compared to amended soils. After 30 d of incubation, 79% degradation was observed in natural soil but in the case of farmyard manure and cow-dung slurry amended soil, 83% and 91% degradation were observed, respectively. Gypsum amend-

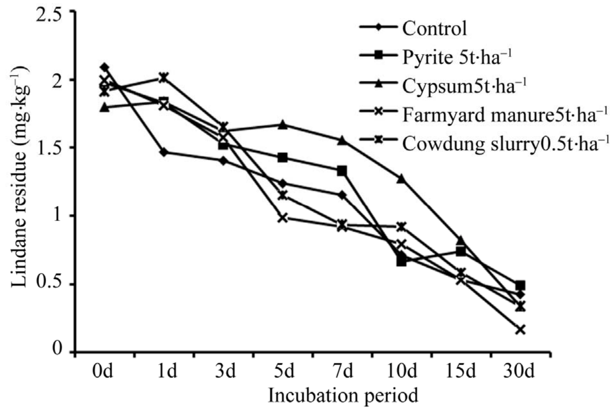

Figure 1. Dissipation of lindane in different treatments of soil with amendments.

ment also enhanced the degradation of lin- dane in soils, but the effect was less prominent as com- pared to the organic amendments. The computed values of simple correlation coefficient (r) between natural log residues and time for farmyard manure, cowdung slurry, pyrite and gypsum amendments were 0.981, 0.924, 0.826 and 0.973 (all significant at $p = 0.01$), respectively, indicating that the dissipation of lindane in different amended soil could also be accounted by the first order kinetics. The half life values ($t_{1/2}$) in farmyard manure and cow-dung slurry amended soils (**Table 2**) were found to be 8 and 11 d, which were lower than the value observed in the case of untreated natural soil ($t_{1/2}$ = 14 d). However, the $t_{1/2}$ values for lindane in pyrite and gypsum amended soils were 14 and 12 d, respectively. This indi- cated that organic amendment were more efficient in lindane deg- radation in soil as compared to other amendments. Or- ganic soil amendments, such as manure, biosolids and other organic residues, are commonly applied as soil amendments to improve soil productivity [23-26]. Addi- tion of organic amendments often changes the path- ways of pesticide movement and degradation in soils, depending on the reactivity of the organic amendments and their effect on microbial activity [27,28]. Organic amendments increase the soil organic carbon pool and soil microbial activity. These amendments not only serve as a nutrient source, but improve the aeration or water retention in the soil, reduce toxicity and create a suitable habitat for indigenous microorganisms. Earlier studies have also confirmed that organic amendments enhanced the degradation of lindane in soil [29-31]. Unlike organic amended soils, the inorganic amended soils did not bring much change in lindane degradation kinetics in the soil.

4. Conclusions

High lindane concentrations in soil from spills or dis- charges can result in point-source contamination of ground and surface waters. Cost effective technologies are needed for the on-site treatment that meet clean-up goals and restore soil function. Innovative treatments should be particularly, useful in country like India since lindane contaminated soils are widespread in the country. Study suggests that organic amendments like farmyard manure or fresh cowdung slurry certainly enhance the degrada- tion of lindane in soil. The addition of organic amend- ments means an increase in microbial activity to degrade lindane. These results have practical implications in ma- naging insecticide residues, especially that of lindane as it is reported to persist in different soil types.

Table 2. Degradation constants for lindane in different treatments of soil with amendments.

Parameter	Control	Farmyard manure	Cow-dung slurry	Gypsum	Pyrite
$K_{obs.}$	0.051	0.080	0.061	0.058	0.049
$T_{1/2}$ (day)	14	8	11	12	14
R^2-value	0.850**	0.980**	0.924**	0.972**	0.826**

** Significant at $p \le 0.01$.

5. Acknowledgements

Authors gratefully acknowledge the financial support from Ministry of Environment and Forests, New Delhi, India.

REFERENCES

[1] WHO, "Environmental Program on Chemical Safety," Environmental Health Criteria.124, Lindane, Geneva, Switzerland, 1991.

[2] World Wildlife Fund (WWF), "Lindane—A Review of Toxicity and Nvironmental Fate," Canada, 1999.

[3] S. L. Simonich and R. A. Hitéis, "Organic Pollutants Accumulation in Vegetation," *Environmental Science & Technology*, Vol. 29, No. 12, 1995, 2905-2914. doi:10.1021/es00012a004

[4] K. L. Willet, E. M. Utrich and R. A. Hites, "Differential Toxicity and Environmental Facts of Hexachlorocyclo- hexane Isomers," *Environmental Science & Technology*, Vol. 32, 1998, pp. 2197-2207. doi:10.1021/es9708530

[5] Y. F. Li, "Global Technical Hexachlorocyclohexane (HCH) Usage and Its Contamination Consequences in the Environment: From 1948 to 1997," *Science of the Total Environment*, Vol. 232, No. 3, 1999, pp. 121-158. doi:10.1016/S0048-9697(99)00114-X

[6] K. Walker, D. A. Vallero and R. G. Lewis, "Factors In- fluencing the Distribution of Lindane and Other Hexa- chlorocyclohexanes in the Environment," *Environmental Science & Technology*, Vol. 33, No. 24, 1999, pp. 4373- 4378.

[7] P. C. Abhilash, S. Jamil, V. Singh, A. Singh, N. Singh and S. C. Srivastava, "Occurrence and Distribution of Hexachlorocyclohexane Isomers in Vegetation Samples

from a Contaminated Area," *Chemosphere*, Vol. 72, No. 1, 2008, pp. 79-86. doi:10.1016/j.chemosphere.2008.01.056

[8] P. C. Abhilash and N. Singh, "Distribution of Hexachlorocyclohexane Isomers in Soil Samples from a Small Scale Industrial Area of Lucknow, North India, associated with lindane production," *Chemosphere*, Vol. 73, No. 6, 2008, pp. 1011-1015. doi:10.1016/j.chemosphere.2008.07.037

[9] P. C. Abhilash, "Monitoring of Organochlorine Pesticide (Lindane) in Soil-Plant System of a Contaminated Environment and Its Phytoremediation/Bioremediation," PhD Thesis, University of Lucknow, India, 2009.

[10] I. C. MacRae, Y. Yamaya and T. Yoshida, "Persistence of Hexachlorocyclohexane Isomers in Soil Suspensions," *Soil Biology and Biochemistry*, Vol. 16, 1984, pp. 285-286. doi:10.1016/0038-0717(84)90018-X

[11] N. Sethunathan, E. M. Bautista and T. Yoshida, "Degradation of Benzene Hexachloride by a Soil Bacterium," *Canadian Journal of Microbiology*, Vol. 15, No. 12, 1969, pp. 1349-1354. doi:10.1139/m69-245

[12] M. L. Jackson, "Soil Chemical Analysis," Prentice Hall Inc., New Delhi, 1967.

[13] C. A. Black, D. D. Evans, J. L. White, L. E. Ensminger and F. E. Clark, "Methods of Soil Analysis," 2nd Edition, Agronomy monograph 9. Agronomy Society of America and Soil Science Society of America, Madison, 1965.

[14] H. Hams and A. J. B. Zehnder, "Bioavailability of Sorbed 3-Chlorodibenzofuran," *Applied and Environmental Microbiology*, Vol. 61, 1995, pp. 27-33.

[15] T. N. Bosma, P. J. M. Middeldrop, G. Schraa and A. J. B. Zehnder, "Mass Transfer Limitation of Biotransformation: Quantifying Bioavailability," *Environmental Science & Technology*, Vol. 31, No. 1, 1997, pp. 248-252. doi:10.1021/es960383u

[16] M. E. Sanchez, I. B. Estrada, O. Martinez, V. Martin, A. Aller and A. Moran, "Influence of the Application of Sewage Sludge on the Degradation of Pesticides in the Soil," *Chemosphere*, Vol. 57, No. 7, 2004, pp. 673-679. doi:10.1016/j.chemosphere.2004.07.023

[17] N. Chung and M. Alexander, "Differences in Sequestration and Bioavailability of Organic Compounds Aged in Dissimilar Soils," *Environmental Science & Technology*, Vol. 32, No. 7, 1998, pp. 855-860. doi:10.1021/es970740g

[18] H. Zhang, Y. L. Lu, R. W. Dawson, Y. J. Shi and T. Y. Wang, "Classification and Ordination of DDT and HCH in Soil Samples from the Guanting Reservoir, China," *Chemosphere*, Vol. 60, No. 6, 2005, pp. 762-769. doi:10.1016/j.chemosphere.2005.04.023

[19] H. Z. Wang, M. C. He, C. Lin, X. C. Quan, W. Guo, and Z. F. Yang, "Monitoring and Assessment of Persistent Organochlorine Residues in Sediments from the Daliaohe River Watershed, Northeast of China," *Environmental Monitoring and Assessment*, Vol. 133, No. 1-3, 2007, pp. 231-242. doi:10.1007/s10661-006-9576-z

[20] H. B. Zhang, Y. M. Luo, Q. G. Zhao, M. H. Wong and G. L. Zhang, "Residues of Organochlorine Pesticides in Hong Kong Soils," *Chemosphere*, Vol. 63, No. 4, 2006, pp. 633-641. doi:10.1016/j.chemosphere.2005.08.006

[21] K. D. Wenzel, M. Manz, A. Hubert and G. Schuurman, "Fate of POPs (DDX, HCHs, PCBs) in Upper Soil Layers of Pine Forests," *The Science of the Total Environment*, Vol. 286, No. 1-3, 2002, pp. 143-154. doi:10.1016/S0048-9697(01)00972-X

[22] K. C. Jones, R. E. Alcock, D. L. Johnson, G. L. Nothcott, K. T. Semple and P. J. Woolgar, "Organic Chemicals in Contaminated Land: Analysis, Significance and Research Priorities," *Land Contamination Reclamation*, Vol. 4, No. 3, 1996, pp. 189-197.

[23] J. F. Power and W. A. Dick (Eds.), "Land Application of Agricultural, Industrial, and Municipal By-Products, Vol. 6, Soil Science Society of America Book Series," Soil Science Society of America, Inc., Madison, 2000.

[24] F. Laturnus, K. von Arnold and C. Grøn, "Organic Contaminants from Sewage Sludge Applied to Agricultural Soils, False Alarm Regarding Possible Problems for Food Safety?" *Environmental Science & Pollution Research*, Vol. 14, 2007, pp. 53-60. doi:10.1065/espr2006.12.365

[25] H. Wang, S. L. Brown, G. N. Magesan, A. H. Slade, M. Quintern, P. W. Clinton, *et al.*, "Technological Options for the Management of Biosolids," *Environmental Science & Pollution Research*, Vol. 15, No. 4, 2008, pp. 308-317. doi:10.1007/s11356-008-0012-5

[26] T. Natal-da-Luz, S. Tidona, B. Jesus, P. V. Morais and J. P. Sousa, "The Use of Sewage Sludge as Soil Amendment. The Need for an Ecotoxicological Evaluation," *Journal of Soils Sediments*, Vol. 9, No. 3, 2009, pp. 246-260.

[27] S. Alvey and D. E. Crowley, "Influence of Organic Amendments on Biodegradation of Atrazine as Nitrogen Source," *Journal of Environmental Quality*, Vol. 24, 1995, pp. 1156-1162. doi:10.2134/jeq1995.00472425002400060015x

[28] B. Pan, P. Ning and B. Xing, "Sorption of Hydrophobic Organic Contaminants," *Environmental Science & Pollution Research*, Vol. 15, No. 7, 2008, pp. 554-564. doi:10.1007/s11356-008-0051-y

[29] T. F. Castro and T. Yoshida, "Effect of Organic Matter on the Biodegradation of Some Organochlorine Insecticides in Submerged Soils," *Soil Science and Plant Nutrition*, Vol. 20, No. 4, 1974, pp. 363-370.

[30] R. Siddaramappa and N. Sethunathan, "Persistence of γ-BHC and β-BHC in Indian Rice Soils under Flooded Conditions," *CRC Critical Reviews in Microbiology*, Vol. 10, 1975, pp. 125-172.

[31] S. K. Sahu, K. K. Patnaik, S. Bhuyan and N. Sethunathan, "Degradation of Soilapplied Isomers of Hexachlorocyclohexane by a Pseudomonas sp," *Soil Biology & Biochemistry*, Vol. 25, 1993, pp. 387-391. doi:10.1016/0038-0717(93)90139-3

