The Ecoscan 8 (1&2): 27-32, 2014
AN INTERNATIONAL BIANNUAL JOURNAL OF ENVIRONMENTAL SCIENCES

STUDIES THE MECHANISM OF VERTICLE MOVEMENT AND DISTRIBUTION OF LINDANE IN DIFFERENT SOIL TYPES OF UTTAR PRADESH, INDIA

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ABSTRACT

Downward movement and distribution of Lindane, was investigated in some selected agricultural soils of Uttar Pradesh, India. Thus, six composite soil samples were collected from selected sites of Uttar Pradesh, India having diversified phycio-chemical properties were analyzed. The pH of soil observed that from neutral to slightly alkaline in nature considering sandy loam, sandy clay loam and loamy sand in texture respectively. In the present study, Lindane downward movement was performed in the packed soil column; the distribution of lindane was obtained throughout the column and even showed presence in the lower most soil core. The recovered amount of Lindane was detected on Varanasi soil in 0-10cm depth (83.77%) followed by Banda soil (78.17%) and the lowest residues was detected on Azamgarh soil (74.88%) in 0-10cm depth respectively. Downward movement of lindane in each soils and its observed scanty move beyond the 10 cm soil depth except in the Azamgarh soil because of reduce amount of organic matter. Percentage Lindane in upper layer was varied from72.36 to 83.77 whereas, less though leachate (11.33%) was obtained. The degree of adsorption of Lindane on soils

KEY WORDS
Pesticide, Sandy clay loam
Organic matter, Column
Soil characteristics
Gas Chromatograph

Received : 23.02.2013
Revised : 06.04.2014
Accepted : 07.05.2014

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INTRODUCTION

Pesticides and herbicides have been extensively used for agricultural purpose during the last five decades to protect against wide range of pests and herbs. Pesticides in soil may be taken by plants or downward move possibly to ground water. Lindane or γ-HCH is a broad spectrum insecticide used for control of insect pests in agriculture, vector control in public health programme and also for control of termite. It is a non-ionic sparingly water soluble organochlorine pesticides (Weber, 1994) used consistently more than 50 years in India. Lindane consisting of almost pure γ-hexachlorocyclohexane (-HCH) is a persistent organochlorine insecticide which has been used for decades throughout the world (Li *et al.,* 2004). It can retain for a long period of time in soils matrix due to its interaction with organic matter and its poor solubility in water. The most persistent pesticides are of greatest concern because they can be bio-accumulated and biomagnified through the food chain and ingested by humans. Pesticides dissolved in soil solution are leached downward through the soil by gravitational forces and upward through the soil by capillary action. This has been thoroughly reviewed by Lately and Oddson (1972); Hartely and graham-Bryce (1980) and Leistra (1980). The movement of a slug of an organic solute in an aqueous mobile phase through a homogeneous sorbet stationary phase normally follows chromatographic principles (Miller, 1975). The organic solute diffusion through the soil matrix was strongly affected by the moisture content of the soil (Ryan and Cohen, 1990). Zaman *et al*. (2007) observed that the vertical movement of pesticide like DDT, soil particles and organic matter with soil fluid in lower horizons will be very limited, although lateral movement of soil occurs in the soil naturally. The potential for leaching is the greatest when highly soluble chemicals are used in well-drained sandy soils with low organic matter content (Reddy and Singh, 1993).

The adsorption rate and adsorption capacity of lindane exhibited highest in compost soil that retarded the downward movement whereas, it was the least for sandy soil (Rama Krishna and Philip, 2008). Lindane distribution in soil column is great important pertaining to its influence on crops and ground water contamination. The chemical characteristics of the pesticides are largely responsible for their adsorption and consequent movement and distribution through soil. Information on movement and distribution of pesticide in soil is useful in order to product the probable effectiveness of the chemical and their influence on quality of ground water. Recently, frequent detection of organochlorine insecticides in surface and ground water and different other

Table 1: Properties of the pesticide used in movement study

Pesticide	Chemical Name	Formula	M.W	m.p.(0C)	Ionizability	Solubility K_{sp} (mg/L)	Volatility VP (mm Hg x 10^{-6})	Longevity $T_{½}$ (days)
Lindane.γ-HCH	1,2,3,4,5,6-Hexachlorocyclohexane (a,a,a,e,e,e confugration of chlorine atom in HCH)	$C_6H_6Cl_6$	290.85	112.5	Non-ionic	7.3	95	180

Source: Weber, J. B. (1994).

Table 2: Physico-chemical properties of soil used for mobility study

SoilProperties	Soil Locations Varanasi	Chandauli	Basti	Azamgarh	Mirzapur	Banda
Soil Texture	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy clay loam	Loamy sand
Sand (%)	60.2	62.7	69.1	72.5	48.8	76.5
Silt (%)	22.8	23.7	12.4	20.0	28.6	13.5
Clay (%)	17.0	13.0	18.5	7.5	21.6	10.0
Organic matter (g kg^{-1})	3.5	7.0	4.3	1.8	2.8	8.3
CEC[C mol(P^+) kg^{-1}]	9.3	17.1	16.6	7.5	9.5	13.8
$CaCO_3$ (%)	0.98	2.0	2.3	40.0	1.0	15.5
Free iron oxide (%)	2.1	4.3	3.7	5.3	7.5	0.83
Free aluminium oxide (%)	1.4	3.8	2.2	3.4	3.1	0.27
Surface area (m^2 g^{-1})	178.75	163.37	187.61	102.71	157.15	163.54
EC (d S m^{-1})	0.11	0.34	0.41	1.08	0.20	0.21
pH	7.7	6.6	8.2	9.8	7.6	8.4
Bulk density (Mg/m^3)	1.39	1.28	1.47	1.32	1.43	1.41
Particle density (Mg/m^3)	2.53	2.41	2.43	2.67	2.31	2.56
Water holding capacity (%)	44.25	40.67	47.96	40.51	39.94	40.83

environmental components in Uttar Pradesh (Nayak *et al.*, 1995; Raha *et al.*, 1999; Raha *et al.*, 2003) has increased interest in the studies of vertical movement of Lindane in six different types of soil of Uttar Pradesh with a view to ascertain the probability of its potential polluting the ground and surface water.

MATERIALS AND METHODS

The state of Uttar Pradesh lying between 23°52′-31°28′N latitude and 70°04′-84°38′E longitude logged with international border Nepal to the north alongwith state border includes Uttarakhand, Haryana and Delhi to north to north-east, Rajasthan on the west, Madhya Pradesh on the south and Bihar on east. The total geographical area of the state is 24.3 m ha. Covers a large part of highly populated (820/km^2) upper gangatic plain. There are four well defined (Pathak and Sharma, 1985) broad soil groups in Uttar Pradesh viz. (i) Alluvial soil (ii) Bundelkhand soil (iii) Vindhyan soil and (iv) Aravali soil. The percent coverage of Aravali soil in Uttar Pradesh is comparatively very low. Thus, six soils from different physiographic and agro climatic zones of Uttar Pradesh varying widely in their physico-chemical properties were selected for this study. Location of soil samples are given in (Fig. 1).

An area of diversified agricultural activity was selected in Uttar Pradesh for sampling. Six composite surface soil samples (0-15 cm) were collected from different locations of the state having diversified soil characteristics. Standard procedure was followed to collect representative soil samples from each site. Collected soil samples were air-dried at room temperature, powdered, passed through 2 mm sieve, mixed homogeneously and stored at 4°C for analysis. The soil samples were analyzed various physico-chemical properties by standard procedure (Jackson, 1973) given in Table 2.

The analytical grade (98.9%) lindane was obtained from Kanoria Chemicals Ltd., Renukut, Uttar Pradesh, India. The properties and chemical structure of lindane is summarized in (Table 1 and Fig. 2).

Stock solution of lindane of concentration 500 mg mL^{-1} was prepared by dissolving requisite quantity in methanol and stored solution at -20°C in deep freezer. Vertical movement of pesticides in the six different soils was determined by using packed soil column as per method described by Saeed *et al.* (1997). Pesticide from soil samples used for movement studied were extracted using standard solvent with liquid-liquid. Samples were transferred into seperatory funnel to which added n-hexane and shaken for one minute, allowed to separate sufficient de-ionized distilled water was added to facilitate partitioning of residues into hexane portion. The hexane portion was collected and passed through anhydrous sodium sulfate. The process was repeated twice in same manner and pooled n-hexane was concentrated to appropriate volume (5mL) using rotary evaporator. The clean organic samples were taken and analyzed by Gas Liquid Chromatography equipped with electron capture detector.

The concentration of Lindane in n-hexane extract was analyzed using Nickel 63 Electron Capture Detector of Gas Liquid Chromatography; Hewlett Packard 5890 a gas chromatograph equipped with a HP 3392 A integrator. n-hexane was evaporated to dryness and residues were re-dissolved in spectral grade n-hexane. Operating parameters for analysis of Lindane were as follows: 1.8 m ´ 2 mm I.D. glass packed with 1.5% OV-17 + 1.95% OV-210 of W.H.P. (80-100 mesh)

Figure 1: Location map of the study area

column; oven temp.190°C, injector temp.210°C, detector temp. 300°C and N_2 as carrier gas; flow rate 70mL min^{-1}. The compounds were identified on the basis of their retention time compared with technical grade reference standard.

RESULTS AND DISCUSSION

Soil samples were collected from six different sites of Uttar Pradesh varied widely with respect to their physico-chemical properties (Table 2). The soil pH varied from 6.6 to 9.8; highest recorded with Azamgarh soil. The organic matter and clay content was lowest in these soils however, its $CaCO_3$ content was highest among all six soil samples. Organic matter content ranges from 1.8 to 8.3 g kg^{-1}, lower organic matter content indicate that higher the pH and $CaCO_3$ (Bhattacharya *et al.*, 2004). Based on the mechanical analysis, the Varanasi, Chandauli, Basti and Azamgarh soils were classified as sandy loam where the clay content was maximum 18.5 and minimum 7.5 percent whereas, Mirzapur and Banda soils, the clay content was 21.6 and 10.0 were classified as sandy clay loam and loamy sand respectively. The Banda and Chandauli soils were noted to be richer in organic matter and moisture content and neutral to slightly alkaline in nature. High clay content established in Mirzapur (21.6%) and Basti (18.5%) compared to other soils. The organic matter and clay content attributed a major concern to permit the movement of Lindane in the lower depth as well. Cation Exchange Capacity of soil was also influence by clay and organic matter content. Soils of Chakia and Basti reflected high CEC (17.1 and 16.6 [C mol (P^+) kg^{-1}]) followed by other types of examined soils. The properties of soils are summarized in (Table 2).

Soil organic matter is the principal adsorbent for many non-ionic organic compounds (Chiou *et al.*, 1979; Mader *et al.*, 1977; Xing and Pignatello, 1996). It has been suggested that the retention mechanism of nonionic organic chemicals in soil is a partitioning of the chemical between the aqueous phase and the hydrophobic organic matter. Lindane is nonionic, non-polar hydrophobic compound and thus, weak attractive interaction such as Vander Waals forces is the dominant forces of attraction in case of the adsorption of Lindane on soil surface and there is reason to believe that the exchange complex of inorganic clays in soils played little in Lindane adsorption.

Downward movement of pesticide through soil column is important to determine their efficacy as well as their potential for crop damage and environmental pollution (Mersie and Foy, 1986). Lindane is less soluble, its absorption in soil is relatively high that inhibit the possible mobility in soil. In the present study Lindane movement was performed with soil containing diversifies physic-chemical properties in the packed soil column, the distribution of Lindane was obtained throughout the column and even showed presence in the lower most soil core. Few of Lindane residues were also detected in leachate fractions in types of soil (Table 4) which depicted much of the chemical was noted within the 10 cm depth of soil layer of the packed column where complete movement of the chemical through the soil column was not observed in tested soils in the present study, as the Lindane was detected rather less in leachates. The highest quantity of Lindane leachates was associated with Azamgarh and Mirzapur soil due to low organic matter content. Sinnakkannu *et al.*, (2005) observed that significance adsorption and limited leaching of pesticides particularly in soil with high organic matter content is indicative of potential of the chemical to undergo limited leaching through soil profile hence reducing the risk of ground water contamination. Very significant quantity of Lindane percentage in leachate was detected as follows in Azamgarh > Mirzapur > Banda > Basti > Chandauli > Varanasi soil respectively. The trend of in leaching could be explained more on the basis of texture of soil than organic matter content. Texture of soil was predominant factors in leaching study and its playing an important role in leaching. The recovered amount of Lindane was detected on Varanasi soil with depth 0-10cm (83.77%) followed by Banda soil (78.17%) and the lowest residues was detected on Azamgarh soil (74.88%) in 0-10cm (Table 4). Results revealed lower downward movement of Lindane in all soils and its observed scanty move beyond the 10 cm soil depth except in the Azamgarh soil which was containing reduce amount of organic matter.

Reduced leaching of Lindane in different soils could be explained in terms of higher sorption coefficients of pesticides (Lin *et al.*, 2009). Leaching behavior of pure grade Lindane were studied in various textural group of soil in pact columns which was drenched 100mL of water when Lindane incorporated into the surface of soil, the mobility of Lindane behaved differently in different soils due to significant interaction between soil and elution contents. Result showed

Table 3: Study the movement of Lindane in soil column

Soil	Depth of column (cm)	Lindane Mobility in Soil column (μ g^{-1}) 0 - 2 (cm)	2 - 4 (cm)	4 - 6 (cm)	6 - 8 (cm)	8 - 10 (cm)	10 - 12 (cm)	12 - 14 (cm)	14 - 16 (cm)
Varanasi	13.8	9.205 (0.211)	8.127 (0.186)	8.352 (0.191)	7.216 (0.165)	3.594 (0.082)	1.258 (0.028)	0.863 (0.019)	
Basti	13.0	10.174 (0.232)	11.293 (2.58)	7.484 (0.171)	2.202 (0.050)	1.278 (0.029)	1.137 (0.026)	0.945 (0.021)	
Chandauli	15.2	9.241 (0.213)	8.806 (0.203)	5.444 (0.125)	4.101 (0.094)	3.739 (0.086)	2.682 (0.062)	2.063 (0.047)	1.908 (0.044)
Azamgarh	15.0	9.252 (0.211)	8.056 (0.184)	6.728 (0.153)	5.137 (0.117)	3.551 (0.081)	1.257 (0.028)	1.060 (0.024)	0.174 (0.003)
Mirzapur	13.3	9.217 (0.206)	8.037 (0.180)	7.166 (0.160)	5.421 (0.121)	3.058 (0.068)	1.948 (0.043)	1.445 (0.032)	
Banda	13.5	8.288 (0.193)	9.915 (0.230)	6.524 (0.151)	6.430 (0.149)	2.405 (0.056)	1.985 (0.046)	0.862 (0.020)	

Figures in parentheses denote the fraction of Lindane

Table 4: Distribution (%) of Lindane in soil column (Uttar Pradesh)

Soil	Depth of column (cm)	Lindane distribution (%) in Soil 0-2(cm)	2-4(cm)	4-6(cm)	6-8(cm)	8-10(cm)	10-12(cm)	12-14(cm)	14-16(cm)	Leachate fractions
Varanasi	13.8	21.13	18.66	19.17	16.56	8.25	2.88	1.98		11.33
Basti	13.0	23.3	25.87	17.12	5.04	2.92	2.60	2.16		14.13
Chandauli	15.2	21.37	20.37	12.50	9.48	8.64	6.20	4.77	4.41	12.13
Azamgarh	15.0	21.17	18.43	15.39	11.75	8.12	2.87	2.42	0.39	19.39
Mirzapur	13.3	20.66	18.01	16.06	12.15	6.85	4.36	3.23		18.64
Banda	13.5	19.30	23.09	15.19	14.97	5.62	4.62	2.00		15.17

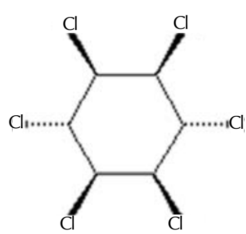

Figure 2: Chemical Structure of Lindane

that the distribution of Lindane was recovered throughout the soil column related to the behavior of soil. The relative mobility of pesticides through soil and its longevity are key indicators of the potential for contamination of drainage effluent and ground water by that chemical (Weber and Keller, 1994). Movement of a pesticide is regulated by the properties of the chemical, soil and hydro geologic, application conditions and climatic conditions (Hartly and Graham-Bryce, 1980). Vertical soil leaching column studies are normally carried out by applying a pesticide to a soil followed by 50 cm of water representing the amount of rainfall needed to produce a crop. A comparison of the relative amount of given pesticide leached through the soil and the soil distribution of the pesticide retained in the soil with standard reference compounds can they be made. In present experiment, vertical leaching loss was carried out of high persistence organochlorine insecticides, viz. Lindane in six soils of Uttar Pradesh, India. The recoveries of Lindane from fortified six soils of Uttar Pradesh and were 87.1, 87.4, 86.4, 87.3, 89.2 and 85.8 % in Varanasi, Basti, Chakia, Azamgarh, Mirzapur and Banda soils respectively. The highest concentration of Lindane was found in Basti soil with 2cm (10.174 mg^{-1}) and 11.293 mg^{-1} with 2 to 4cm column depth and lowest trend was observed with each soil column layer in Banda soil. Studies showed that the content of pesticides was associated maximum in surface soil and decreasing gradually with depth (Table 3). Similar trends with regard to fraction of Lindane (Table 3 in parentheses) were identified in all types of soils which retained in experimental soil due less solubility to non-ionic nature of chemicals (Table 1) having strong affinity with organics and clay content in soil texture.

Several study of pesticide movement in soil columns have been carried out by Dousset and Mouvet (1997); Mouvet *et al.,* (1997); Vereeken *et al*. (1995). However, there have been no studies on the vertical migration of Lindane, because it decomposes rapidly in soil. Downward movement increases with frequency of irrigation, increasing temperature accelerates the degradation of pesticides slowing their migration and large amount of clay and organic matter in the soil diminish pesticide mobility (Martinez Vidal *et al*., 1994).

Distribution of Lindane is also affected by properties of pesticides and soils indicated in Table 1 and 2 respectively was studies using six different types of soil considering the textural group sandy loam, sandy clay and loamy sand of alluvium region. Lindane showed 'C' type isotherm curve in all types of soil, indicating affinity of it towards soils. The distribution coefficient, Kd, for the soil in batch adsorption as well as in columns were calculated. Vertical distributions of lindane in six sampling sites, similar pattern were seen in most sites. The highest concentration were found at the surface and near surface horizons and decreased with depth in Table 3. A large amount of water is needed for leaching the Lindane as well to receive into ground water (Om Prakash *et al*., 2004). Percentage Lindane in upper layer was varied from 72.36 to 83.77 (Table 4). The maximum distribution percent was recorded with the Varanasi soil (sandy loam) (83.77%) whereas, less though leachate (11.33%) was obtained and 19.39% leachate measured in Azamgarh sandy loam soil might be due to less clay and organic matter content (Singh *et* *al*., 2010). Priya and George (2010) reported that movement and adsorption of pesticides regulated by both chemical and soil properties. The inverse relationship between mobility of Lindane and the mobility is affected by solubility and sorption of insecticide.

Other worker (Helling, 1971) had also reported high inverse correlation between pesticide mobility and organic matter in soil. It is revealed that the more than 70% Lindane was retained in surface soil and approx. 30% entered into the sub-surface region of the soil. This observation might be caused by the strong adsorption between pesticides and the test soils (Gua *et al.,* 2003 and Gibson, 2001). But halogenated aliphatic compounds are often considered to be relatively recalcitrant in many sub-surface environments, such as soils, sediments, and ground water, due in part to their chemical stability and in part to the lack of appropriate microbial activity for their degradation (Bewich, 1994). Moreover, the lack of selective pressure, which is related to the compound concentration and availability, might also play a role in their relative recalcitrant. The soil properties primarily soil organic matter and clay content and half life of chemicals that regulate their persistence and residence period in the soil. Above results supported our finding that no soil type will guarantee to save the ground water contamination of highly persistence pesticides in the future that could not be ignored.

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