

## Simulation of Persistence of Pesticide Residues in Groundwater of Ludhiana and Muktsar Districts, Punjab

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**Abstract :-** Groundwater quality analyses carried out for pesticide residues in Ludhiana and Muktsar districts of Punjab have shown the persistence of Organo-Chlorine pesticides of BHC (Lindane), Heptachlor, Heptachlor Epoxide, Endosulfan I, 4,4 - DDT, Methoxychlor and Organo-Phosphorous pesticides of Methyl Parathion, Dimethoate and Malathion. It has been found that in general persistence of organo-chlorine pesticide residues in groundwater of Muktsar district is 6-8 times higher than Ludhiana district during July 2003. The use of pesticides depends on crops grown in the area. The cotton crop grown over large areas in Muktsar district is contributing more pesticide residues to the groundwater as compared with predominantly paddy grown areas of Ludhiana district. Further, shallow water table condition in the Muktsar district adds to the problem as pesticides leach fast to the shallow water table when compared with the deep water table condition in Ludhiana district. Compared to cotton crop, paddy crop requires more irrigation water and thereby more dilution of pesticide residues may take place during leaching to the groundwater table. Persistence of a typical organo-chlorine pesticide residue has been illustrated through PESTAN Model for the prevailing groundwater conditions in Muktsar and Ludhiana districts. Suggested regular monitoring of pesticide residues to provide secured potable water supply to the people in these districts.

### INTRODUCTION

Agriculture is the back-bone of Indian economy. Up to 70% of the population is engaged in farm sector directly or indirectly. Growing Indian population needs sufficient farm produce. Farming and the agriculture crops are susceptible to attacks by various kinds of pests in form of insects, fungus, bacteria or virus or weeds and control of these has become necessary to reduce losses to a minimum. A study of the pesticides-use pattern in the country has revealed that cotton, which accounts for just 5 per cent of the cropped area, consumes about 52 to 55 percent of the pesticides. Rice grown over 24 per cent of the cropped area uses about 18 per cent, vegetables raised over 3 per cent area, about 14 per cent plantation crops covering 2 per cent of the area, 8 per cent and cereals, millets and oilseeds extending over 58 per cent of the area, 7 per cent. Sugarcane uses 2 per cent of pesticides and other crops grown over 6 per cent of the cropped area account for another 2 per cent. The per hectare consumption

of pesticides in the country is far lower than that in some of the developed countries. But the number of chemicals that are sold in the country and the indiscriminate use of plant protection chemicals are matter of grave concern. The groundwater conditions in Ludhiana district central part and Muktsar district in the southern part of Punjab state represent over exploited zone and water logging condition respectively.

### LUDHIANA DISTRICT

Intensive agriculture in Ludhiana district has caused deep water table conditions. The climate is characterized by dryness except in the brief monsoon season, a very hot summer and bracing winter. July, August and the first half of September constitute the southwest monsoon. About 70 % of rainfall is received during the July – September. The rainfall during December to March accounts for 16% and remaining received during other months. The district is plain region with flatness and featureless topography. The alluvial plain is

a result of agrarrational work of Sutlej River. Agriculture provides single largest source of employment and livelihood. There are two principal crop seasons kharif and Rabi. Area under food crops is 88% covers about 530000 hectares. The crops grown during kharif season are: Paddy, maize, groundnut, sugarcane, cotton, pulses chillies etc., whereas wheat, gram, barley, potatoes, oilseeds are grown during Rabi season (Census of Ludhiana, 1991). In addition to the use of green and organic manure, chemical fertilizers are increasingly being used. The percentage of net irrigated area to net sowed area stands at 99.5%. The texture of the soils varies from loam to sandy loam.

### **MUKTSAR DISTRICT**

Muksar district in south western part of Punjab is almost flat and is underlain by alluvial soil of low permeability. Introduction of canal irrigation involved in high losses through percolation to groundwater. In flat alluvial areas with little slope, the natural drainage is insufficient to discharge the recharged water and hence level of groundwater rose in few years resulting in very shallow water table condition. Further clays form major part of alluvium, resulted in water logging conditions. Desert soils are formed through wind action in Malout and Lambi blocks. Sierozen soils of calcareous with a knakar layer at 0.75 – 1.25 m have formed in northern part of the district include Muktsar, Kotbhai blocks. Gram, wheat, barley, cotton, rape and mustard are grown under low annual rainfall conditions of about 370 mm. Irrigated agriculture is practiced in 95% of the area through canals and bore wells. Farmers are protecting the crops by using lot of pesticides.

### **PESTICIDES AND RESIDUES**

“Pesticide” means any substance intended for preventing, destroying, attracting, repelling, or controlling any pest including unwanted species of plants or animals during the production, storage, transport, distribution, and processing of food,

agricultural commodities, or animal feeds or which may be administered to animals for the control of eco-parasites. The term includes substances intended for use as a plant-growth regulator, defoliant, desiccant, fruit-thinning agent, or sprouting inhibitor and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport. The term normally excludes fertilizers, plant and animal nutrients, food additives and animal drugs.

“Pesticide residue” means any specified substances in food, agricultural commodities, or animal feed resulting from the use of a pesticide. The term includes any derivatives of a pesticide, such as conversion products, metabolites, reaction products, and impurities considered to be of toxicological significance.

Groundwater samples for pesticide residue analysis have been collected from Ludhiana and Muktsar districts during August 2003. The representative groundwater samples have been collected in 40 observation wells in both Muktsar and Ludhiana districts (Fig. 1). Generally the samples collected in Ludhiana district are fall under paddy and wheat crop areas whereas the most of the samples collected in Muktsar district represent the areas covered by Cotton crop. The pesticide residue concentrations (mg/l) in groundwater in the above study areas have been presented in Table 1& 2 during July 2003. The data indicate that BHC residue is present in all the samples tested.

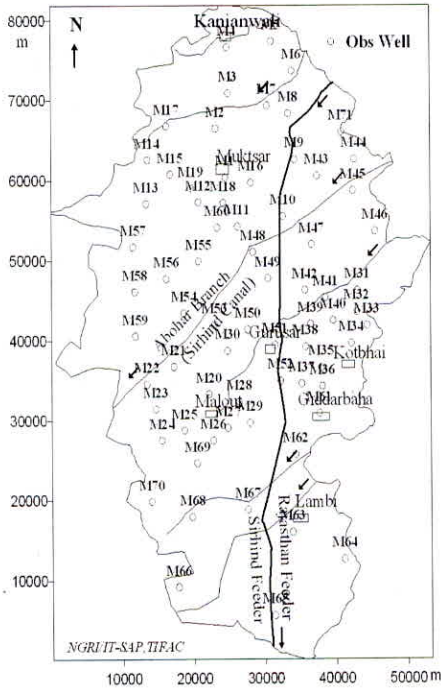
### **Importance of pesticide residues and Environmental Fate**

#### **DDT (Dichlorodiphenyltrichloroethane)**

DDT is an organo-chlorinated insecticide used mainly to control mosquito-borne malaria; use on crops has generally been replaced by less persistent insecticides. DDT is very highly persistent in the environment, with a reported half

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Location of Observation Wells, Muktsar District, Punjab



Location of Observation Wells in Ludhiana District, Punjab

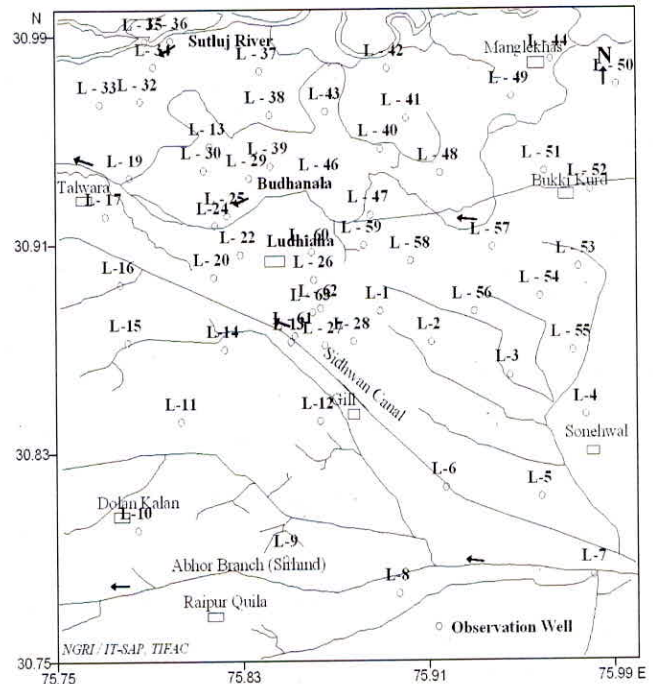


Fig. 1 : Observation Wells for Pesticide Residue Analyzes in Muktsar & Ludhiana districts

Table 1 : Persistence of Pesticide Residues in groundwater ( in ig/l) Muktsar District, Punjab, July 2003

Sample No.	$\alpha$ -BHC	$\beta$ -BHC	$\gamma$ -BHC	$\delta$ -BHC	Heptachlor	Aldrin	Heptachlor-epoxide	Endosulfan I	4,4-DDE
MK-7A	<0.01	0.33	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MK-15	<0.01	0.04	0.13	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MK-24A	<0.01	0.21	0.09	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
MK-33	<0.01	0.38	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MK-43	<0.01	0.26	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MK-51	<0.01	0.28	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MK-58	<0.01	0.26	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01
MK-64	<0.01	0.16	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01
MK-67	<0.01	0.22	0.25	<0.01	0.21	0.01	0.03	<0.01	<0.01

**Table 2 :** Persistence of Pesticide Residues in groundwater (in  $\mu\text{g/l}$ ) Ludhiana District, Punjab, July 2003

Sample No.	$\alpha$ -BHC	$\beta$ -BHC	$\gamma$ -BHC	$\delta$ -BHC	Heptachlor	Aldrin	Heptachlor-epoxide	Endosulfan I	4,4-DDE
L-5	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
L-9	<0.01	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
L-11	<0.01	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
L-32	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
L-48	<0.01	0.05	0.04	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
L-49	<0.01	0.02	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
L-53	<0.01	0.02	0.03	<0.01	<0.01	<0.01	0.01	<0.01	<0.01

life of between 2-15 years and is immobile in most soils. Routes of loss and degradation include runoff, volatilization, photolysis and biodegradation (aerobic and anaerobic). These processes generally occur only very slowly. Breakdown products in the soil environment are DDE and DDD, which are also highly persistent and have similar chemical and physical properties. Due to its extremely low solubility in water, DDT will be retained to a greater degree by soils and soil fractions with higher proportions of soil organic matter. It may accumulate in the top soil layer in situations where heavy applications are (or were) made annually; e.g., for apples. Generally soil organic matter tightly sorbs DDT, but it (along with its metabolites) has been detected in many locations in soil and groundwater where it may be available to organisms. This is probably due to its high persistence; although it is immobile or only very slightly mobile, over very long periods of time it may be able to eventually leach into groundwater, especially in soils with little soil organic matter.

The reported half-life for DDT in the water environment is 56 days in lake water and approximately 28 days in river water. The main pathways for loss are volatilization, photodegradation, adsorption to water-borne particulates and sedimentation. DDT does not appear to be taken up or stored by plants to a great extent.

### Lindane

Lindane is an organochlorinated insecticide and fumigant, which has been used on a wide range of soil-dwelling and plant-eating (phytophagous) insects. It is commonly used on a wide variety of crops, in warehouses, in public health to control insect-borne diseases, and (with fungicides) as a seed treatment. Lindane is also presently used in lotions, creams, and shampoos for the control of lice and mites (scabies) in humans. Technical lindane is comprised of the gamma-isomer of hexachlorocyclohexane, HCH. Trade or other names Gammexane, Gamasan, Gexane, hexachlorocyclohexane, HCH, Isotox, Jacutin and Lorexane.

Lindane is highly persistent in most soils, with a field half-life of approximately 15 months. When sprayed on the surface, the half-life was typically much shorter than when incorporated into the soil. It shows a low affinity for soil binding, and may be mobile in soils with especially low organic matter content or subject to high rainfall. It may pose a risk of groundwater contamination. Plants may pick up residues from not only direct application, but through water and vapor phases. The metabolism in plants is not well understood, but carrots are estimated to metabolize lindane with a half-life of just over 10 weeks (based on plant uptake) whereas it may have a half-life in lettuce of only 3 to 4 days.

## **Heptachlor**

Heptachlor is an organochlorinated cyclodiene insecticide, first isolated from technical chlordane in 1946. During the 1960s and 1970s, primarily farmers to kill termites, ants, and soil insects in seed grains and on crops, as well as by exterminators and home owners to kill termites used it. Before heptachlor was banned, formulations available included dusts, wettable powders, emulsifiable concentrates, and oil solutions. It acts as a non-systemic stomach and contact insecticide. An important metabolite of heptachlor is heptachlor epoxide, which is an oxidation product formed from heptachlor by many plant and animal species. Heptachlor and heptachlor epoxide are highly persistent in soils, with a reported representative field half-life of 250 days. This compound has sometimes been detected in soil in trace amounts 14 to 16 years after application. Heptachlor and its epoxide are moderately bound to soils and should not be highly mobile. Over their long residence times, even low mobility may result in appreciable movement and so heptachlor and its metabolite (heptachlor epoxide) may be considered to pose a risk of groundwater contamination over time. Very low levels of heptachlor have been found in well water. Heptachlor epoxide is not very susceptible to biodegradation, photolysis, oxidation, or hydrolysis in the environment. Heptachlor is almost insoluble in water, and will enter surface waters primarily through drift and surface run-off. In water, heptachlor readily undergoes hydrolysis to a compound, which is then readily processed (preferentially under anaerobic conditions) by micro-organisms into heptachlor epoxide. After hydrolysis, volatilization, adsorption to sediments, and photodegradation may be significant routes for disappearance of heptachlor from aquatic environments. In plants, the major breakdown product of heptachlor is the epoxide. Heptachlor is nonphyto-toxic when used as directed.

## **Endosulfan**

Endosulfan is a chlorinated hydrocarbon insecticide and acaricide of the cyclodiene subgroup, which acts as a poison to a wide variety of insects and mites on contact. Although it may also be used as a wood preservative, it is used primarily on a wide variety of food crops including tea, coffee, fruits, and vegetables, as well as on rice, cereals, maize, sorghum, or other grains. Formulations of endosulfan include emulsifiable concentrate, wettable powder, ultra-low volume (ULV) liquid, and smoke tablets. It is compatible with many other pesticides and may be found in formulations with dimethoate, Malathion, methomyl, monocrotophos, pirimicarb, triazophos, fenoprop, parathion, petroleum oils, and oxine - copper. It is not compatible with alkaline materials. Technical endosulfan is made up of a mixture of two molecular forms (isomers) of endosulfan, the alpha- and beta-isomers. Trade or other names for the product include Afidan, Beosit, Cyclodan, Devisulfan, Endocel, Endocide, Endosol, FMC 5462, Hexasulfan, Hildan, Hoe 2671, Insectophene, Malix, Phaser, Thiodan, Thimul, Thifor, and Thionex. Endosulfan is a highly toxic pesticide.

Endosulfan is moderately persistent in the soil environment with a reported average field half-life of 50 days. The two isomers have different degradation times in soil. The half-life for the alpha-isomer is 35 days, and is 150 days for the beta-isomer under neutral conditions. These two isomers will persist longer under more acidic conditions. The compound is broken down in soil by fungi and bacteria. Endosulfan does not easily dissolve in water, and has a very low solubility. It has a moderate capacity to adhere or adsorb to soils. Transport of this pesticide is most likely to occur if endosulfan is adsorbed to soil particles in surface runoff. It is not likely to be very mobile or to pose a threat to groundwater. It has, however, been detected in California well water. In raw river water at room temperature and exposed to light,

both isomers disappeared in 4 weeks. In plants, endosulfan is rapidly broken down to the corresponding sulfate. On most fruits and vegetables, 50% of the parent residue is lost within 3 to 7 days. Endosulfan and its breakdown products have been detected in vegetables (0.0005-0.013 ppm), in tobacco, in various sea foods (0.2 ppt-1.7 ppb), and in milk. The pesticide residue analyses of groundwater in Muktsar and Ludhiana districts during July 2003 have been presented in Table 1 & 2. Comparison of depth to water level and persistence of pesticide residues shows that shallow water table of Muktsar district shows more pesticide residues compared to the deep water table condition of Ludhiana district.

### PESTAN ( PESTicide Analytical) Model

PESTAN model uses an analytical solution to predict the transport of organic solutes through the unsaturated zone to the groundwater table. The model is commonly used for initial screening assessments to evaluate the potential for groundwater contamination by pesticides used in agricultural applications. However, it is also quite useful for determining potential groundwater impacts from any organic solutes migrating through the unsaturated zone. The model is based on a close -form analytical solution of the advection -dispersive reactive transport equation. It assumes a one-layer homogeneous profile. Simulates the processes of constant recharge rate, agricultural application of pesticides in the surface condition. In the subsurface the process simulated are flow and transport of pesticides through the soil with constant velocity, sorption and decay of pesticide, leaking of pesticide to groundwater. The vertical transport of dissolved pollutant through the vadose zone is simulated in the model as a slug of contaminated water that migrates in homogeneous partly saturated soil. Movement of pesticides in environment is presented in Figure 2.

A maximum of ten applications of the active ingredients can be applied in a single calculation and for each application, the time of application

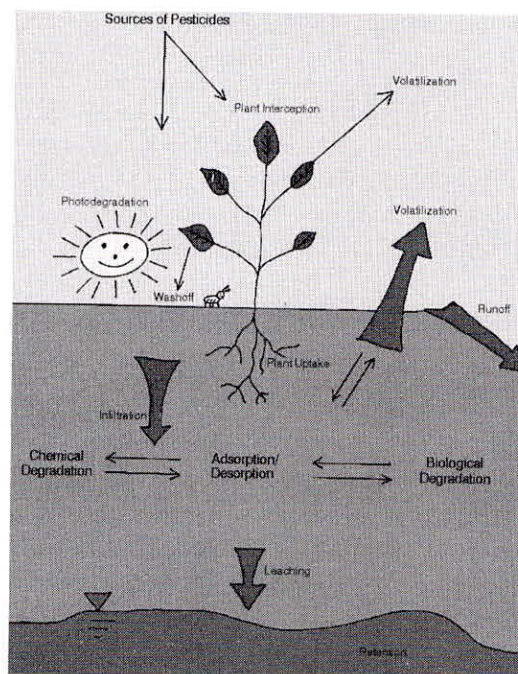
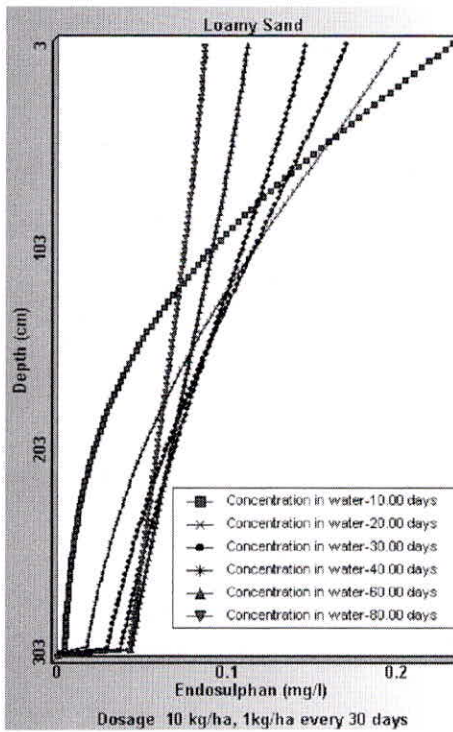
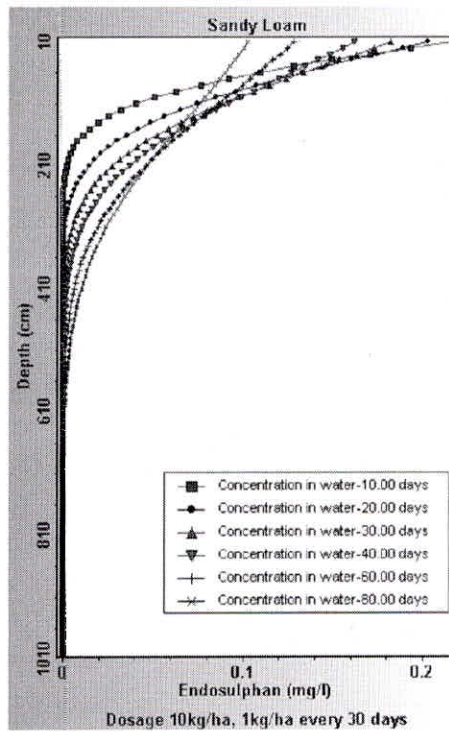


Fig. 2 : Movement of Pesticides in Environment

prior to recharge needs to be provided. The slug begins to enter the soil at the first precipitation and irrigation event at a rate equal to the pore water velocity. The pollutants stored at the soil surface before the recharge is subject for solid phase decay. Once the recharge starts, the remaining pollutant is considered dissolved and starts to enter the soil. In the soil the pollutant is influenced by liquid phase decay, sorption and dispersion. The flow of the pollutant slug occurs with the constant velocity. The hydraulic conductivity of the soil accounts for partly saturated conditions using the Campbell's equation. The persistence of Endosulphan in shallow water table conditions of loamy sand of Muktsar District under various phases has been depicted its persistence (Fig. 3) whereas the least persistence in sandy loam of Ludhiana district under deep water table condition could be seen in Figure 4. The preliminary results of PESTAN indicate that solubility of applied pesticide,



**Fig. 3 :** Persistence of Endosulphan in Loamy sand of Muktsar district



**Fig. 4 :** Persistence of Endosulphan in Sandy Loam of Ludhiana district

partition coefficients between liquid phase and solid phase determine the movement in vadose zone.

**CONCLUSIONS**

The pesticide residue analyzes in groundwater of Ludhiana and Muktsar districts show the persistence of BHC, Endrin, Heptachlor, Heptachlor Epoxide, DDT, Methyl parathion, Malathion, Dimethoate and Endosulfan. Pesticide residue persistence is about 10 times higher in groundwater of Muktsar district compared to the Ludhiana district. The reasons attributable to higher concentration of pesticide residues could be due to cropping pattern and usage of pesticides on crops.

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