

CHEMICAL ANALYSIS OF PESTICIDES AND THEIR IMPACT ON LIVING ORGANISMS

Kaushal Kishor Singh¹, Ph. D. & Dev Prakash², Ph. D.

¹Department of Chemistry, Sarswati (P.G.). College, HATHRAS, U.P.

²Department of Chemistry, S.V. College ALIGARH, U.P.

Abstract

The available reports from various investigations from different parts of the world including India, recommend the need for continues survey and monitoring programs for pesticide in all food commodities in order to protect the end user for the indiscriminate exposure of pesticides. Based on limited knowledge with direct and indirect and/or inferential information on pesticides, there is a certain ambiguity of a situation in which people are undergoing life-long exposure. A multidisciplinary integrated approach involving toxicology, epidemiology, physiology and behavioral sciences may realize the hazards and sketch the preventive strategies need to be developed. Pesticide means any substance intended for preventing, destroying, attracting, repelling or controlling any pest including unwanted species of plants or animals during production, storage, transport, distribution and processing of food, agricultural commodities or animal feeds or which may be administered to the animals for the control of ectoparasites (FAO). The term includes substances intended for use as a plant growth regulator, defoliant, desiccant, fruit thinning agent and substances applied to the 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.

Keywords: Pesticide, fertilizer, Living Organisms, Unwanted species.



Scholarly Research Journal's is licensed Based on a work at www.srjis.com

Discussion and Results:

Pesticide and fertilizer use has been recorded since ancient times, suggesting that ecosystem management is not a recent cultural attribute. In the context of modern agriculture, the objectives of pesticide use are to increase production efficiency and yields; reduce the cost of food and, especially, to increase the availability of grains, fruits, and vegetables; improve food quality and losses during transport and storage; improve soil conservation; and ensure a stable and predictable food supply (NRC 2000).

Indian Council of Agricultural Research, New Delhi, monitored Residues of pesticides from food commodities through their centers located in different parts of the country. It was found that 51 % of food commodities were contaminated with pesticide residues and out of these 20% had pesticide residues above the MRL values, as compared to 21 % contamination with only 2% above the MRL on worldwide basis (Agnihotri, 1999). The analysis of bottled water, colas and other soft drinks carried out by the Centre for Science and Environment, New Delhi, revealed very high content of pesticide residues in the samples (Anonymous, 2003 a, b and c).

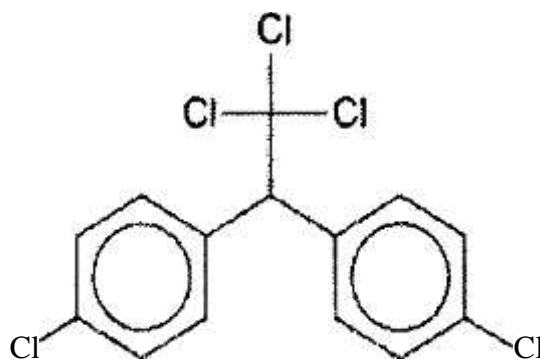
CHEMICAL CLASSIFICATION BASED ON STRUCTURE: Based on the chemical structure and properties they are mainly classified as given below.

- (i) **Organochlorines (OCPs)**
- (ii) **Organophosphates (OPs)**
- (iii) **Carbamates**
- (iv) **Synthetic Pyrethroids**

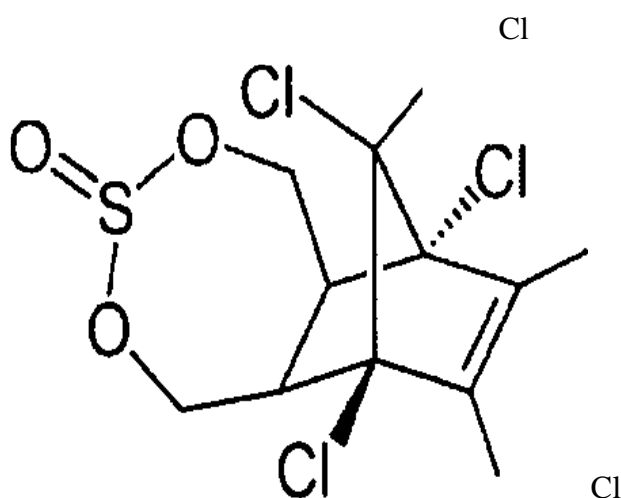
- a) Cyclodienes, aldrin, dieldrin, endrin, heptachlore, endosulfan, and endosulfan sulfate
- b) Diphenyl aliphatic such as DDT
- c) Hexachlorocyclohexanes α HCH, β PHCH, γ XHCH, and δ HCH

Organochlorine Pesticides are chlorinated organic compounds used predominantly as insecticides. They are mainly classified into three categories; namely **diphenyl aliphatics** such as DDT and its metabolites, **cyclodienes** which includes aldrin, dieldrin, endrin, heptachlore, endosulfan, and endosulfan sulfate. **Hexachlorocyclohexanes** exist in several structural isomers such as α HCH, β PHCH, γ HCH, and δ HCH are the most known common organochlorine insecticides (Banu and Semra, 2004). These pesticides are typically very persistent in the environment, and are known for accumulating in sediments, plants and animals. Most of them break down slowly and can remain in the environment long after application and in organisms long after exposure (Hodgson, 2004). Organochlorine pesticides are broad spectrum insecticides active against a great variety of pests. They vary in their chemical structures. The OCPs and their metabolites are mainly classified into three categories; namely diphenyl aliphatics, cyclodienes and hexachloro- cyclohexanes (Banu and Semra, 2004).

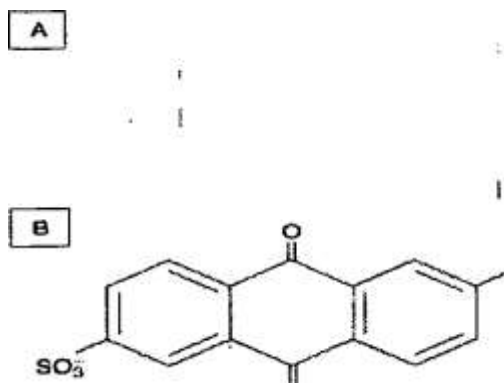
Diphenyl aliphatics include p, p' -DDT (Fig. I. I), p, p' -DDE, p, p' -DDD and methoxychlor. DDT successfully controlled spreading of malaria, a disease still plaguing large parts of the human population in Africa, and crop destroying insects (Ahmed, 2007).



Cyclodiene compounds are collective group of synthetic cyclic hydrocarbons, which includes aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, heptachlore, heptachlor epoxide, aendosulfan, endosulfan, and endosulfan sulfate. They are particularly effective where contact action and long persistence is required; for example endosulfan acts as a contact poison on sucking, chewing and boring insects of field crops (Ahmed, 2007).

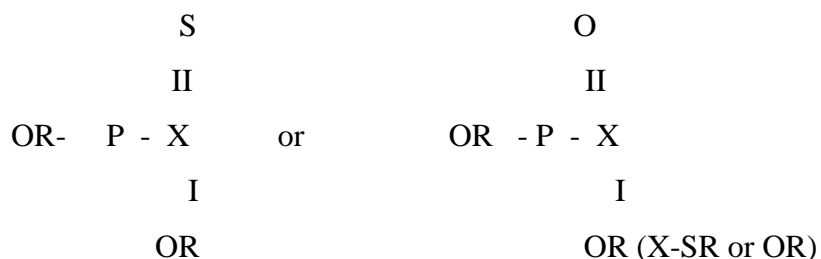


Hexachlorocyclohexanes (HCH) are manufactured chemicals that exist in several structural isomers such as α HCH, β HCH, γ HCH, and δ HCH. Only one of these forms, α HCH (commonly called lindane) has insecticidal activity and used as an insecticide on fruits, vegetables, in forestry and animal husbandry.



Organophosphates (OP)

Organophosphorus compounds include all chemicals which contain both carbon and phosphorus. Many of these do not inhibit the enzyme acetylcholine- esterase and are not used as pesticides. OP insecticides are, in general, characterised by their low mammalian toxicity and high acute insect toxicity. This selective toxicity has been designed into the molecule and exploits differences in the metabolism of OPs between mammals and insect pests. Monocrotophos, phorate, phosphamidon, methyl parathion and dimethoate are some of highly hazardous pesticides that are continually and indiscriminately used in India.



Structure of organophosphates

Pyrethroids

Pyrethrins are derived from the naturally occurring pyrethrum, which in turn are the oleo-resin extracts of dried chrysanthemum flowers. These pyrethrins owe their insecticidal activity to the keto alcoholic esters of chrysanthemic and pyrethroic acids. Pyrethroids are synthetic analogues of Pyrethrins modified by introducing a biphenoxy moiety and substituting some hydrogens with halogens in order to confer stability at the same time retaining the basic properties. Of pyrethrins. The insecticidal components of pyrethrum flowers are the optically active esters derived from (+)-trans chrysanthemic acid and (+)-trans-pyrethroic acid. Pyrethroids are acknowledged of their fast knocking down effect against insect pests, low mammalian toxicity and facile biodegradation. Their persistence in

the environment is in the order of weeks, unlike organochlorines, which persist for years (Elliot, 2006).

Type I "T" pyrethroids are contact poisons that produce restlessness, incoordination, prostration, hyperexcitement, aggressiveness, body tremors and paralysis in both insects and mammals (Klaassen, 2006). Type I "T" pyrethroids do not contain an alpha cyano group (R-C=O, O-R), as do Type II "CS" pyrethroids. Type I pyrethroids include: Allethrin, Permethrin, Resmethrin Bifenthrin etc. Type II "CS" synthetic pyrethroids contain an alpha cyano group (RC=O, C=CN, R). These pyrethroids have a powerful capacity to disable or "knockdown" many insect species. Type II "CS" pyrethroids are used in household, veterinary and agricultural pesticides (Klaassen 2006). Type II pyrethroids have a higher insecticide activity meaning that they are more toxic to insects than type I pyrethroids. Type II "CS" pyrethroids include: Cypermethrin, Cyfluthrin, Deltamethrin, Fenvalerate and Fipronil.

Carbamates

Carbamates are organic pesticides derived from carbamic acid. They are used in agriculture as insecticides, fungicides, herbicides, nematocides, or sprout inhibitors. In addition, they are used as biocides for industrial or other applications and in household products. A potential use is in public health vectorcontrol. The figure 1.5 denotes the structure where R1 is an alcohol group, R2 is a methyl group and R3 is usually hydrogen. The cholinesterase inhibitions of carbamates differ from that of organophosphorous in that, it is species specific and it is reversible (Drum, 1980). Included in this group are aldicarb, carbofuran (Furadan), carbaryl (Sevin), ethienocarb, fenobucarb, oxamyl and methomyl.

Pesticide Usage:

Agriculture is a critical sector of the Indian economy. Even if its contribution to the overall Gross Domestic Product (GDP) of the country has fallen from about 30 percent in 1990-91 to less than 15 percent in 2011-12, a trend that is expected in the development process of any economy, agriculture yet forms the backbone of development. An average Indian still spends almost half of total expenditure on food, while roughly half of India's work force is still engaged in agriculture for its livelihood. One of the strategies to increase crop productivity is effective pest management because more than 45% of annual food production is lost to pest infestation. Availability of safe and efficacious pesticides their judicious use by the farming community is critical to a sustained increase in agricultural production and

productivity. In tropical countries, crop loss is even more severe because the prevailing high temperature and humidity are highly conducive to rapid multiplication of pests (Kannan, 2002; Lakshmi, 2003).

Accordingly, the application of a wide variety of pesticides on crop plants is necessary in the tropics to combat pests and vector borne diseases. However, the sporadic use has been leading to awful consequences not only to public health but also to food quality resulting in an impact load on the environment and hence the development of pest resistance (Agnihotri, 1999). The extensive use of these chemicals, under the adage, "if little is good, a lot more will be better" has become

Direct impact on Living Organisms:

If the credits of pesticides include enhanced economic potential in terms of increased production of food and fibre, and amelioration of vector-borne diseases, then their debits have resulted in serious health implications to man and his environment. There is now overwhelming evidence that some of these chemicals do pose a potential risk to humans and other life forms and unwanted side effects to the environment (Forget, 2003; Igbedioh, 2001; Jeyaratnam, 2001; WHO, 2010). The world-wide deaths and chronic diseases due to pesticide poisoning number about 1 million per year. Overall fatality ranges from 10% to 20% and the WHO has estimated that 200000 people die each year from pesticide poisoning (Phillips, 2002). The high risk groups exposed to pesticides include production workers, formulators, sprayers, mixers, loaders and agricultural farm workers. The effects of pesticides on human health are based on the toxicity of the chemical and the length and magnitude of exposure.

Certain environmental chemicals, including pesticides termed as endocrine disruptors, are known to elicit their adverse effects by mimicking or antagonizing natural hormones in the body and it has been postulated that their long-term, low dose exposure is increasingly linked to human health effects such as immune Supper SSI On, hormone disruption, diminished intelligence, reproductive abnormalities and cancer. A study on 356 workers in four units manufacturing HCH in India revealed neurological symptoms (21 %) which were related to the intensity of exposure (Nigam, 2003). The magnitude of the toxicity risk involved in the spraying of methomyl, a carbamate insecticide, in field conditions was assessed by the National Institute of Occupational Health (NIOH) (Ahmed, 2006).

Significant changes were noticed in the ECG, the serum LDH levels, and cholinesterase (ChE) activities in the spraymen, indicating cardiotoxic effects of methomyl.

Observations confined to health surveillance in male formulators engaged in production of dust and liquid formulations of various pesticides (malathion, methyl parathion, DDT and lindane) revealed a high occurrence of generalised symptoms (headache, nausea, vomiting, fatigue, irritation of skin and eyes) besides psychological, neurological, cardiorespiratory and gastrointestinal symptoms coupled with low plasma ChE activity (Gupta G K., 1984). Data on reproductive toxicity were collected from 1,106 couples when the males were associated with the spraying of pesticides (OC, OP and carbamates) in cotton fields (Rupa D 2011).

Short term human health hazards from the misapplication of pesticides include mild headaches, flu, skin rashes, blurred vision and other neurological disorders while rare, but severe human health hazards include paralysis, blindness and even death (ICAR 2007). Increasing incidence of cancer, chronic kidney diseases, suppression of the immune system, sterility among males and females, endocrine disorders, neurological and behavioral disorders, especially among children, have also been attributed to chronic pesticide poisoning (Jadon S P,2009).

Pesticide consumption is reported as the major method of suicides and deaths in India. A report of poisoning was from U P which caused deaths of 162 people due to careless handling and storage of wheat. Subsequently, several cases of human and animal poisonings, besides deaths of birds and fishes, have been reported. In general, it has been observed that organophosphorus pesticides are responsible for death in more than 70% cases. On the night of December 2 and 3, 1984, a Union Carbide plant in Bhopal, began leaking 27 tons of the deadly gas methyl isocyanate (MIC). Half a million people were exposed to the gas and 20,000 have died to date as a result of their exposure. More than 120,000 people still suffer from ailments caused by the accident and the subsequent pollution at the plant site. The economic impact of pesticides in non-target species (including humans) has been estimated at approximately \$8 billion annually in developing countries (Gupta G K 2006).

Impact through food commodities:

For determining the extent of pesticide contamination in the food stuffs, programs entitled 'Monitoring of Pesticide Residues in Products of Plant Origin in the European Union' started to be established in the European Union since 1996. An average of about 9700 samples has been analysed out of which 5.2% of the samples were found to contain residues and 0.31% had residues higher than the respective MRL for that specific pesticide. In 2007, 13 pesticides were analysed in five commodities (mandarins, pears, bananas, beans, and

potatoes) for some 6000 samples. Residues of chlorpyrifos exceeded MRLs most often (0.24%), followed by methamidophos (0.18%), and iprodione (0.13%). With regard to the commodities investigated, around 34% contained pesticide residues at or below the MRL, and 1% contained residues at levels above the MRL. With regard to four commodities investigated in 1998 (oranges, peaches, carrots, spinach), about 32% contained residues of pesticides at or below MRL, and 2% above the MRL.

In 2009, 4700 samples of four commodities (cauliflower, peppers, wheat grains, and melon) were analysed for the same 20 pesticides as in the 2008 study (European Commission, 2009). With regard to all the commodities investigated, around 22% of samples contained residues of pesticides at or below the MRL and 8.7% above the MRL. The exposure ranged between 0.43% of the ADI for methamidophos and 1.4% of the ADI for endosulfan.

In a multi-centric study to assess the pesticide residues in selected food commodities collected from different states of India (Surveillance of Food Contaminants in India, 2003), DDT residues were found in about 82% of the 2205 samples of bovine milk collected from 12 states. About 37% of the samples contained DDT residues above the tolerance limit of 0.05 mg/kg (whole milk basis). The highest level of DDT residues found was 2.2 mg/kg. The proportion of the samples with residues above the tolerance limit was highest in Maharashtra (74%), followed by Gujarat (70%), Andhra Pradesh (57%), Himachal Pradesh (56%), and Punjab (51%). In the remaining states, this proportion was less than 10%. Data on 186 samples of 20 commercial brands of infant formulae showed the presence of residues of DDT and HCH isomers in about 70 and 94% of the samples with their maximum level of 4.3 and 5.7 mg/kg (fat basis) respectively.

The average total DDT and BHC consumed by an adult were 19.24 mg/day and 77.15 mg/day respectively (Kashyap A., 2004). In another study, the average daily intake of HCH and DDT by Indians was reported to be 115 and 48 mg per person respectively, which were higher than those observed in most of the developed countries (Varsha P 2004). In a study at Hyderabad, analyzed fruit and vegetable samples before and after washing treatments and detected values above MRL for most commodities using liquid chromatography tandem mass spectrometry.

Environmental Impacts of Pesticides:

Pesticides can contaminate soil, water, turf, and other vegetation. In addition to killing insects or weeds, pesticides can be toxic to a host of other organisms including birds, fishes,

beneficial insects, and non-target plants. Insecticides are generally the most acutely toxic class of pesticides, but herbicides, can also pose risks to non-target organisms. Pesticides can reach surface water through runoff from treated plants and soil. The results of a comprehensive set of studies done by the U.S. Geological Survey (USGS) on major river basins across the country in the early to mid- 90s yielded startling results. More than 90 percent of water and fish samples from all streams contained one, or more often, several pesticides (Desai P 2005).

The pesticides were found in all samples from major rivers with mixed agricultural and urban land use influences and 99 percent of samples of urban . Trifluralin and 2,4-D were found in water samples collected in 19 out of the 20 rivers.

According to USGS (U.S. Geological Survey & Washington State Department of Ecology), "in general more pesticides were detected in urban streams than in agricultural streams"

Hydrophobic, persistent, and bioaccumulable pesticides that are strongly bound to soil include the organochlorines DDT, endosulfan, endrin, heptachlor, lindane and their metabolites. Most of them are now banned in agriculture but their residues still. Heavy treatment of soil with pesticides can cause populations of beneficial soil microorganisms to decline. According to the soil scientist Dr. Elaine Ingham, "If we lose both bacteria and fungi, then the soil degrades. Overuse of chemical fertilizers and pesticides have effects on the soil organisms that are similar to human overuse of antibiotics.

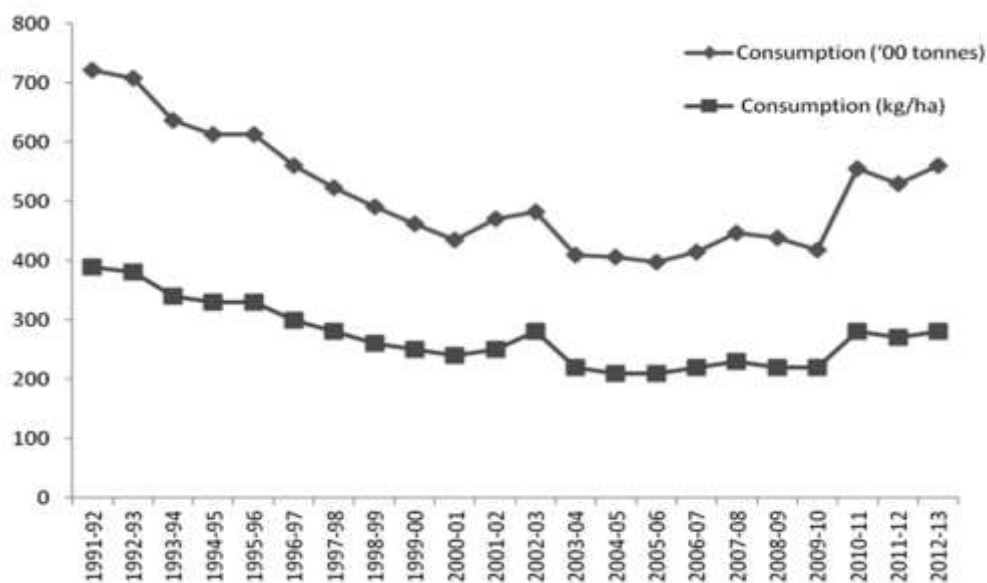
Pesticide sprays can directly hit non-target vegetation, or can drift or volatilize from the treated area and contaminate air, soil, and non-target plants. Some pesticide drift occurs during every application, even from ground equipment. Drift can account for a loss of 2 to 25% of the chemical being applied, which can spread over a distance of a few yards to several hundred miles. As much as 80-90% of an applied pesticide can be volatilised within a few days of application.

Phenoxy herbicides, including 2, 4-D, can injure nearby trees and shrubs if they drift or volatilise onto leaves. Exposure to the herbicide glyphosate can severely reduce seed quality. It can also increase the susceptibility of certain plants to disease.(Singh A 2006)

Herbicides are also toxic to birds. Exposure of eggs to 2, 4-D reduced successful hatching of chicken eggs and caused feminization or sterility in pheasant. Glyphosate treatment obviously caused dramatic decreases in the populations of birds that lived there

(Goel M 2006). Among the countries that continue to use Organo chlorine pesticides, India has become one of the major producers and consumers in recent years. As a consequence, wild birds in India are exposed to great amounts of OC pesticides.

Chlorpyrifos, a common contaminant of urban streams, is highly toxic to fish, and has caused fish, kills in waterways near treated fields or buildings. The weed-killers Ronstar and Roundup are also acutely toxic to fish (Pandya K 2005). Aquatic mammals such as dolphins accumulate increased concentrations of persistent organic pollutants because of their high trophic level in the food chain and relatively low activities of drug-metabolising enzymes, and are thereby vulnerable to toxic effects from contaminant exposures. In addition to habitat degradation such as construction of dams), boat traffic, fishing, incidental and intentional killings, and chemical pollution have been threats to the health of river dolphins. The Ganges river basin is densely populated and heavily polluted by fertilizers, pesticides, and industrial and domestic effluents (Kavita , 2006). Exposure to great concentrations of persistent, bioaccumulative, and toxic contaminants such as DDT (1, 1, I-trichloro-2,2-bis[p-chlorophenyl] ethane) and PCBs has been shown to elicit adverse effects on reproductive and immunological functions in captive or wild aquatic. Non-target birds may also be killed if they ingest poisoned grains set out as bait for pigeons and rodents. Avitrol, a commonly used pigeon bait, poses a large potential for ingestion by non target grain feeding birds. It can be lethal to small seed-eating birds. Brodifacoum, a common rodenticide, is highly toxic to birds. It also poses a secondary poisoning hazard to birds that may feed on poisoned rodents (USEPA, 2008).



(MINISTRY OF AGRICULTURE - GOVERNMENT OF INDIA & FARMERS WELFARE DEPARTMENT OF AGRICULTURE & DIRECTORATE OF PLANT PROTECTION, QUARANTINE AND STORAGE)

References:

- Jadon S S (2010), *Diffuse agricultural water pollution in India*, *Water Sci. Technol.* 39; 33-47.
- Varshney Suresh (2010), *Pesticide Safety and Monitoring*, *All India Coordinated Research Project on Pesticides Residues*, Indian Council of Agricultural Research, New Delhi, India.
- Saraswat P K(2009), *Organochlorine insecticide residue in River Ganga, water at KANPUR UP*, *Environmental monitoring and assessment*, 30(2);12-105.
- Modi S (2009), *Determination of residual contents of pesticides in rice (Oriza sativa L.) Crop from different regions of Punjab* 40(3); (2008)1253-1257.
- Singh V P (2008) "*Pesticide Residues in Water, Soil, Fruits and Vegetable Samples in Aligarh UP India*," *Experimental Publication*, New Delhi, India. p- 73
- Bansal OP(2006), Gupta R *Groundwater Quality of Aligarh district of Uttar Pradesh. Pesticide Research Journal* 12 (2): 188-194.
- Chauhan SS (2006), *A Monitoring of pesticides residues in farm gate vegetables Uttarakhand, India. Wudpecker Journal of Agricultural Research.* 1 (7); 250 - 256.
- Chowdhury MTI (2006), Razzaque MA, Khan MSI *Chlorinated Pesticide Residue Status in Tomato, Potato and Carrot Journal of Experimental Sciences* 2, (1), 01-05