American-Eurasian J. Agric. & Environ. Sci., 15 (1): 24-28, 2015
ISSN 1818-6769

DOI: 10.5829/idosi.aejaes.2015.15.1.12475

Analysis of Pesticides in Vegetables, Degradation and its Side Effects: A Review Paper

Salma Shad, Nadia Bashir and Quratul Ain Jadoon

Department of Chemistry, Hazara University, Mansehra, Pakistan

Abstract: The lack of irrigation facilities and poor irrigation system and due to the deficiency of agricultural knowledge, farmers introduce new brands of pesticides for their better production. Unaware of all the facts and health hazards, aim of farmers is only better productivity. Many pesticides are used in the homes, industries, hospitals, for killing pests like mosquitoes, mites, cockroaches, ants, aphids, worms, snails, etc. which are the source of spreading various diseases like mosquito causing malaria, yellow fever and west Neil virus and bees, wasps and ants spreading allergy. The data in part however, has been based on the side effects of pesticides used and one question that should come to our mind is "how much do we really know about pesticides? Keeping these facts in view, the literatures on the excess used of pesticides are reviewed in this paper.

Key words: Pesticides · Determination · Degradation · Effects

INTRODUCTION

Pesticide is a chemical or biological agent which seduce, kill, destroy, deter, attract or mitigate the pests which are harmful for the humans, animals and crops. They belong to the class of biocides whose targeted pests are insects, plant pathogens, birds, weeds, molluscs, birds, mammals, fish,microbes and nematodes which are the vector for diseases, cause nuisance and destroy property. Many pesticides are used in the homes, industries, hospitals, for killing pests like mosquitoes, mites, cockroaches, ants, aphids, worms, snails, etc which are the source of spreading various diseases like mosquito causing malaria,yellow fever and west Neil virus and bees, wasps and ants spreading allergy.

Insects and weeds are the main factors which are responsible for low yield of crops and annual loss is estimated more than 10 billion rupees. As the pesticides are beneficial for crop productivity but their extensive use may cause many health risks and environmental threats. All this happens due to the awareness and information about new modern methods of agriculture, Lack of knowledge and misuse of pesticides.

In 2006-2007, the world used approximately 5-2 billion pounds of pesticides including insecticides, herbicides and fungicides while U.S consumes 1.1 billion pounds from which 80% are used in agricultural sector and 20% are used in the house hold sprays. According to the report of WHO every year pesticides cause 3.5 to 5 million acute poisonings.While a rough estimate show that 20,000 workers dying from exposure every year and most of them from developing countries.

The lack of irrigation facilities and poor irrigation system and due to the deficiency of agricultural knowledge, farmers introduce new brands of pesticides for their better production. Unaware of all the facts and health hazards, aim of farmers is only better productivity. They are introducing varieties of pesticides including insecticides, herbicides and weedicides to protect their vegetables and crops from foreign invaders and those who are destroying their land. The main weeds of vegetables are *Aanagallis arvensis, Rumex crispus, Euphorbia helioscopia, Convolvulus arvensis, Chenophodium album, Carthamus oxyacantha , Fumaria indica , Alhagi, maurorum, Avenafatua, Euphorbia helioscopia,* etc. On these weeds of crops and vegetables many herbicides and weedicides are applied without knowing their merits and demerits.

From the above knowledge the review was plane to discuss the methodology of Part per million for the determination of pesticides residue level in fruit and vegetables.

Determination of Pesticides: Dhundhel and Rai [1] developed a new methodology for the insecticide cypermethrin determination on part per million levels.

Corresponding Author: Salma Shad, Department of Chemistry, Hazara University, Mansehra, Pakistan.
E-mail: salma.chemist9@hotmail.com.

Cypermethrin is worldwide use as insecticide. The method developed was based on hydrolysis of cypermethrin to cyanide ion, which further react with bromine water to cyanogen bromide. For the removal of excess bromine potassium iodide was added which react with p-aminoacetophenon reagent.The maximum absorption were found at 400nm in acidic medium. Beer's law was obeyed at 10 to 60µl/25ml in final solution, while lowest limit of detection was 0.4µg/ml. The used method was very rapid, sensitive and simple for determination and analysis of cypermethrin insecticide from different vegetables.

Prasannaand Surendra [2] describe a newly and highly sensitive spectrophotometric method for the determination of cypermethrin insecticide on part per million levels. Methodology was based on cypermethrin hydrolysis (Popff's reaction) further which reacts with potassium iodide-iodate to liberate iodine under acidic condition. The leucomalachite green was used as indicator which is oxidized to malachite green dye by liberating iodine. The absorption maxima were found at 610nm, while the Beer's law was obeyed over the concentration range of 2.0 to 16µg/25mL. The developed method was adequately applied for the determination of insecticides in different environmental and biological samples because of its precision and accuracy.

Akinloye and Adamson [3] investigated the constituents and residue level, antioxidant enzyme were detected spectrophotometerically which shows presence of paraquat in commonly consuming vegetables. Residue level of paraquat was found in range of 0.04 to 0.27ppm. In an increase in paraquat concentration it directly affects the chlorophyll of the herb so chlorophyll contents. It is directly affect the chlorophyll of the herbs so the chlorophyll content decreases. Paraquat diverts photosynthetic electron transport from reducing NADPH to reduce the PQ ion. The presence of oxygen help the univalent reduced PQ radical to re-oxidize and produces superoxide radical, which is normally present in the chloroplast and scavenged by superoxide dismutase enzyme.

Rai *et al.* [4] described a sensitive and simple spectrophotometric methodology for the detection of broad spectrum herbicide Paraquat using a versatile reducing agent sodium borohybride. In an alkaline medium it reacts with reducing agent to give a blue radical ion with absorbance maxima at 600 nm. Beer's law was obeyed in the range of 0.05-0.5 μgml^{-1} respectively. The molar absorbtivity and Sandell's sensitivity was found to be 2.9×10^5 $mol^{-1}cm^{-1}$ and 0.0006µg cm^{-2}.

Ouyang *et al.* [5] developed a simple high performance liquid chromatography method for analyzing paraquat in soil. In this method UV detection was developed to analyze paraquat herbicide content in soil solution samples. The analytical method was compared with the Liquid scintillation counting (LSC) method using ^{14}C-paraquat.Agreement obtained between the two methods was reasonable. However, the detection limit for paraquat analysis was 0.5mg L^{-1} by HPLC method and 0.05mg L^{-1} by the LSC method. The LSC method was, therefore, 10 times more precise than the HPLC method for solution concentrations less than 1mg L^{-1}. In spite of the high detection limit, the ^{12}C (non-radioactive) HPLC method provide an inexpensive and environmentally safe means for determining paraquat concentration in soil solution compared with the ^{14}C-LSC method.

Subhash *et al.* [6] defined the methodology of GC-ECD for the detection of chlorpyrifos and Cypermethrin from different vegetables like brinjal, cauliflower. The vegetables were bought from the local market of India. The residues pesticides from vegetables were analyzed which were extracted with ethyl acetate and n-hexane (3:7 v/v) mixture using charcoal and florisil column. The total residue recovery was 90% with coefficient of variation below 5%. This method was suitable for the detection and analysis of pesticide.

Arrebola-*et al.* [7] applied the gas chromatography and tandem mass spectrometry for the determination of pesticide residues from fresh vegetables. By using single injection method for detection and confirmation, 54 multiclass pesticides were analyzed and quantified. The applied method rapidly extracts 15g of vegetable samples with dichloromethane. Clean up step was not necessary when injecting 10µL extract.MS/MS detection mode provide additional selectivity. Same method was applied and validate in a routine laboratory to 1300 samples. Recovery % ranged between 70.2 to 110.8% at two different fortified levels. Relative standard deviation was found to be lower than 16.7%. Important parameters were also studied for the influence of method.

Sadia *et al.* [8] analyzed the residues of pesticides, cypermethrin, dichlorvos, deltamethrin and chlorpyrifos by extraction method of reverse phase high performance liquid chromatography from potato, apple and peach. Pesticides were extracted from vegetables and fruits by using small volumes of anhydrous sodium sulfate, sodium chloride and ethyl acetate. While activated charcoal is used for cleaning of extract and these extracted samples were analyzed by using reverse phase high performance liquid chromatography with an ultra –violet detector in an

isocratic mode. Maximum residue levels (MRL) 0.283 µg/g for dichlorvos was found in apple samples while 0.924, 1.630 and 0.454 µg/g for chlorpyrifos, cypermethrin and deltamethrin were found in peach respectively. It was concluded that cypermethrin and chlorpyrifos residues level were greater than codex maximum residue levels, so that their spray on vegetables and fruits should be made limited due to their resistance to degradation.

Josem *et al.* [9] studied the organophosphorus pesticide residues in vegetables by using Oven Transfer Adsorption Desorption (TOTAD) interface method. The analysis was made by large volume GC injection using (TOTAD) interface. The limit of detection calculated using NPD is lower than 0.35µg/kg which considerable lower than MRLs established by European legislation. The defined method reduced the amount of solvent used, numbers of analytical step essential, avoiding time consumption and laborious step by providing good repeatability and linearity.

Hui-Ping and Sarah [10] used capillary electrophoresis for the extraction of paraquat and diquat. For extraction of herbicides from aqueous solution before capillary electrophoretic analysis, the silica nanoparticle tubes (SiNPs) were used as concentrating probes. With rinsing of acetic acid solution the analytes were eluted from the surface of SiNPs. After the centrifugation and extraction process, the extract was checked with UV absorption detection where limit of detection (LOD) was 0.03µM for Paraquat and 0.05µM for diquat, respectively.

Degradation of Pesticides: Nilesh *et al.* [11] degraded cypermethrin through microrganisms. Four types of microrganisms were assessed for degradation of insecticide by using scale up technique. *Alcaligenes faecalis, Pseudomonas aeruginosa, Rhizopus stolonifer* and *Trichoderma viride* were used under controlled environmental condition and were isolated from cypermethrin treated field soil of cotton crop. These insecticides are used as a source of carbon and energy by microorganisms. Gas chromatography- mass spectroscopy (GC-MS) and Gas chromatography-Electron capture detector (GC-ECD) techniques were used for metabolite detection while analysis was done on bioremediation of cypermethrin of different ppm solutions. The result of GC-ECD showed that microorganism *Pseudomonas aeruginose* had potential to degrade cypermethrin while other two show moderate degradation. GC-MS results two metabolite Proponic acids and Pathalic acid.

Anissa and Nafaa [12] reported degradation of Paraquat by electrochemical advanced oxidation methods (EAOPs) including photoelectron-fenton (PEF), electro-fenton (EF) anodic oxidation (Ao) and by utilizing aqueous acidic solution at pH 3.0. Comparison of EAOPs and GFT was done on the basis of their effectiveness at mineralizing the herbicidal solution. Chemical oxygen demand (COD), parent compound and degradation intermediates were analyzed over the treatment of time. AO and CFT were least efficient methods, while EF and PEF displayed most efficient behavior due to the additional effect of UV-irradiation. Paraquat decay kinetics were found to obey the pseudo-first order model and second order rate constant with hydroxyl radicals were determined as($k_{PQ} = 2.55 - {}^{1}09\ M^{-1}\ s^{-1}$). From the above it was concluded that EF and PEF are effective and powerful detoxification process in which three aromatic degradation intermediates were formed and degraded.

Effects of Pesticides on Living Organisms: Lessenger [13] stated that exposure of human to cypermethrin cause, itching of skin, experienced shortness of breath, cough and congestion at the time of exposure, ocular irritation of eyes. Also CNS effects may occur after large ingestions.

Grzenda *et al.*;[14] stated the ecological effects of paraquat in water have been studied in relation to its use as an aquatic herbicide at a normal concentration of 1 mg/litre. Following this use, the concentration present in water decreased to about half of the initial 1 mg/litre level within 36 h and, in less than 2 weeks, the concentration was below 0.01 mg/litre. Weed-sample analysis, 4 days after paraquat application, showed a residue of approximately 25 mg/kg, suggesting that absorption by the weed was mainly responsible for paraquat removal. Mud-residue analysis 5 1/2 months after treatment showed that 36% of the applied paraquat remained in the mud and 70% of that was found in the top 2.5 cm. In the mud, paraquat had been adsorbed on to the mineral material. Since bottom mud often has organic components, the residues may be more accessible to bacterial degradation. Compared to other products, paraquat appears to be the herbicide of choice for future use in water supplies because of its rapid disappearance from water (6 - 14 days after treatment). The residues were not desorbed from the bottom sediments and mud taken from the bottom of a paraquat-treated lake carrying inactivated residues, showed no toxic effects on barley seedlings that germinated on it.

George [15] stated the environmental impact of pesticides consist of their effect on the non-targeted species where they are sprayed on the insects, herbs, weeds, etc. but they put direct impact on soil, food and beneficial herbs and insects like honey bees. When pesticides are sprayed, about 98% of insecticides and 95% of herbicides reach the destination other than their target areas as they are sprayed widely [13]. Due to water runoff they enter into the aquatic water while wind carries it to atmosphere, other fields, grazing areas and human residence areas. As their use increase the production of crops but also play a vital role in the hazardous health effects like DDT which is carcinogenic and causes endocrinal disruptor while atrazine disturbs the immune system of vertebrates and herbicides reduces the food availability and adverse secondary effect on the life of butterflies and soil invertebrates.Animals which interacts with targeted pest can also be effected by the chemical application. The reduction in these other organisms can result in changes in the biodiversity of an area and effect natural biological balances. It also contaminated the underground water reservoirs by drifting into soil when it rains it come out and enter into the rivers by killing fish and other aquatic animals.

Nafeesand Jan [16] studied insecticide cypermethrin and endosulfan widely used in swat valley. 63 soil samples were collected from 27 different villages of swat valley. Extract of pesticide were carried out in n-hexane and identified and quantified by GC-ECD system. Residue level of endosulfan was 0.24-1.51 mg/kg^{-1} and 0.13-12.67^{-1} mg/kg in rainy and irrigated areas, while the level of cypermethrin was high 0.14 to 27.62 mg/kg^{-1} and 0.05 to 73.75 mg/kg^{-1}. The main reason of high level of residue of pesticides in soil was that in swat people use cypermethrin for fishing and same water of Swat River is used for irrigation and other purposes. So in the all above the trend of pesticides use in swat valley is increase and this may lead to negative effect on aquatic flora and fauna of river swat and also on human being.

Sonia and Saksham [17] reported the effects of bio-pesticides and pesticides on soil microbial biomass carbon. Microorganism play primly role in the decomposition of plant and plant material. Microbial activities are essential to the global cycling of nutrients in soil. Pesticides are known as biocides which have effects on micro flora of the soil which may leads to soil infertility. Effect of five pesticides contributing Cypermethrin, victor, Malathion, Tafgor and Monocil while five biopesticides containing B*acillus subtilis, Paeciliomyceslilacinus, Beauveria bassiana, Folicon* and *Pseudomonas fluorescens* on soil biomass was assessed under laboratory conditions. With application of bio-pesticide the toxic effect on soil microbial biomass carbon content which increases with time in bio-pesticide, while drastic decrease was observed in victor treated soil.

Kamal *et al.* [18] observed hematological and clinical changes in the female rabbits by giving treatment with cypermethrin. 24 female rabbit were grouped in A, B, C and D groups. The A, B, C, were injected with cypermethrin 25, 50 and 75 mg.kg, while the group D was kept as controlled and received normal saline. After two days of each treatment the blood samples collected with ETDA and were checked for hematological studies. The animals were checked twice daily for symptoms and signs. Signs like licking of legs, ataxia, increase urination, jerky moments in coordination, dizziness persisted and staggering giant for 30 to 90 minutes after each dose. Pyrethroid modifies the gating characteristics of voltage sensitive sodium channels in mammalians neuronal membranes. The blood samples were analyzed for hematological parameters like red blood cells (RBCs) and hemoglobin. The clinical symptoms of cypermethrin in rabbit started 5-10 mints and were persisted 30-90 minutes in all groups. Irritation of skin has also been reported.

CONCLUSION

In the respect of above review it can be concluded and suggested that excessive use of pesticide leads to contamination of the environment. Control measure should be made to the agriculture fields. Former should be aware of the excess use of the pesticide and must also know its divers effect on soil organism, human and main thing the environment.

REFERENCES

1. Dhundhe, R.S. and M.K. Rai, 2011. A newly sensitive method for the determination of cypermethrin in various samples. A. J. Biochem and Pharma Res., 3: 2231-2560.
2. Prasanna Kumar Sharma1 and Surendra K. Rajput, 2012. ModifiedPopoff's Reaction for indirect spectrophotometric determination of cypermethrin. J.App. Chem, 1(4): 490-499
3. Akinloye, O.A, I. Adamson, O. Ademuyiwa and T.A. Arowolo, 2013. Paraquat toxicity and its mode of action in some commonly consumed vegetables in Abeokuta, Nigeria, Adv.Res. J. Biochem, 4: 70-77.

4. Rai, M.K., V.D. Joyce and V.K. Gupta 1998. A sensitive determination of Paraquat by spectrophotometry".
5. Ouyang, Y., R.S. Mansell and P.A. Nkedi-Kizza, 2004. simple high performance liquid chromatography method for analyzing paraquat in soil solution samples.Journal of environmental quality, 1: 406-408.
6. Subhash, C., N. Anil, Mahindrakar and L.P. Shinde, 2010. determination of cypermethrin and chlorpyrifos in vegetables by GC-ECD, Internet. J. Chem Tech Res., 2: 908-911.
7. Arrebola, F.J., V. Martınez, 2003. Mateu-Sánchez JLM, and Álvarez-Castellón, FJ. Determination of 81 multiclass pesticides in fresh foodstuffs by a single injection analysis using gas chromatography–chemical ionization and electron ionization tandem mass spectrometry.Analytica ChimicaActa, 2: 167-180.
8. Sadia, A., H.W. Feroza, F. Momina, H.S.W. Muhammad, A.T. Syed and J.A. Muhammad, 2013. Ethiopian Journal of Environmental Studies and Management, 2013. 6: 4.
9. Josem, Corteas, S. Raquel, Evam, P. Diaaz, V. Jesuas and V.Z. Ana Large, 2006. Volume GC Injection for the Analysis of Organophosphorus Pesticides in Vegetables Using the Through Oven Transfer Adsorption Desorption (TOTAD) Interface. ;J. Agric. Food Chem. 54(1997-2002): 1997.
10. Hui-Ping C. and Y.C. Sarah, 2011. Determination of Paraquat and Diquat by Combination of Nanoparticles-Based Extraction with Capillary Electrophoresis. J. Chine. Chem. S., 58: 793-797.
11. Nilesh, P., S. Bhosle, Zafar, Khan and N. Sahera, 2013. In-vitro degradation of Cypermethrin through microorganisms by scale up technique Inter. J. Adv. Res., pp: 229-238.
12. Anissa, D. and A. Nafaâ, 2009. Degradation of paraquat herbicide by electrochemical advanced oxidation methods;;. J- . Electroanaly Chem, pp: 33-42.
13. Lessenger, J.E., 1992. Five office workers inadvertently exposed to cypermethrin. J. Tox Environ Health, 35: 261-267.
14. Grzenda, A.R., H.P. Nicholson and W.S.J. Cox, 1966. Water Works Assoc., 3: 326-332.
15. George, T.M., 2004. Sustaining the Earth: An Integrated Approach. Thomson/Brooks/Cole. pp: 211-216.
16. Nafees, M. and M.R. Jan, 2009. Residues of cypermethrin and endosulfan in soils of Swat valley, Soil and Environ, 2: 113-118.
17. Sonia, S. and G. Saksham, 2013. Impact of Pesticides and Biopesticides on Soil Microbial Biomass Carbon, Uni. J. of Environ Res and Tech, 3: 326-330.
18. Kamal, S.M., A. Khan, F. Rizvi, M. Sididdue and Sadeeq-ur-Rehman, 2007. Effect of cypermethrin on clinico-haematological parameters in rabbits, Pakistan Vet. J. , 4: 171-175.