MONITORING THE BEHAVIOUR OF SOME PESTICIDE RESIDUES AND HEAVY METALS IN CERTAIN WATER RESOURCES AND THEIR DEGRADATION BY MICROORGANISMS

BY

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M.Sc. Agric. Sc. (Pesticides), Ain Shams University, 2000

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ABSTRACT

Sherif Hussein Abd El-Rahman. Monitoring the behavior of some pesticide residues and heavy metals in certain water resources and their degradation by microorganisms. Unpublished Doctor of Philosophy Dissertation, Ain Shams University, Faculty of Agriculture, Department of Plant Protection, Egypt, 2005.

Twenty-one different pesticide residues and heavy metals were investigated in variety of water samples collected from different locations during 2002-2003.

The obtained results showed that most of the analyzed water contained different residues level of pesticides and heavy metals, according to sampling location and the time during which the samples were examined. Also, laboratory experiments were carried out at Faculty of Agricultural, Ain Shams University, Egypt, to study the bioaccumulation of butachlor and fenitrothion in *Tilapia nilotica* fish. Moreover, biodegradation of the two studied pesticides by certain microorganisms was also studied. The effects of temperature and UV on the degradation of these pesticides were investigated.

Key words: Monitoring, Contamination, Pollution, Pesticides, Heavy Metals, Residues, Water, Bioaccumulation, Biodegradation, Thermal and photodegradation.

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I- INTRODUCTION

Chemicals for many years have been an important means of controlling pests afflicting man, his animals, and food crisis. Informed opinion is a consensus that with the growing world crisis, chemicals for pest control will continue to be vital in production of food. This does not minimize other non-chemicals approaches, or integrated pest managem-ent approaches, but rather recognize that pesticides remain in many insects our sole weapon of defense. Beneficial use of pesticides without attendant problems. One of these problems is that not all of the chemical will remain in the area of treatment. The physico-chemicals properties of the substance, together with environmental transport processes result in a portion of the chemical released, moving elsewhere in the environment. Indeed this has been one of the puzzling and even troubles some questions of our time. Traces of certain of the more persistent pesticides have been found well removed from areas of treatment, that is quite common to find water bodies near to, but not necessarily adjacent to treated areas contaminated with the pesticides. Instance of long distance; i.e., several hundred miles, aerial transport have been reported.

The finding that pesticides were being transported from areas of treatment confronts us with a number of challenging scientific questions; among them:

1-what amount of the pesticides that has been used and what is the distribution of these pesticides in the environment.

2-what is the fate and behavior of pesticides during the transport process in the environment.

When considering accumulation of pesticides in the environment, among the first things that usually come into our minds are the concentrations and accumulation of various pesticides in aquatic food chains with subsequent detrimental effects on some species of birds and elevated of pesticides in fish which are to be used for food by humans.

Elaboration of the knowledge of the dynamics of pesticides will lead not only to better understanding of the fate and behavior of pesticides in environment, but will point the development of improvement of our technology of the use of these compounds. This can mean safer, less environmentally contaminating practices, greater effectiveness, both of which should contribute to the production of food and the protection of man's health.

With increasing population in Egypt, industrialization and food production, the amounts of this pollutants entering River Nile water are continuously increasing, so the monitoring programs should be carried out along the River Nile. Monitoring program should be carried out to identified and determined the pollutants in sources of pollution and in the target to know what is the type of pollutants in the environmental risk cup.

The present investigation aimed to throw light on the followings:

1- Monitoring and identification of various chemical contaminants as pesticide residues and heavy metals in water
2- Bioaccumulation of investigated pesticides in fish
3- Biodegradation of investigated pesticides by certain microorganisms
4- Photo and thermal decomposition of investigated pesticides

II- REVIEW OF LITERATURE

1– Methods for determination of pesticides residues and heavy metals in water.

Millet, *et al.* (1996) described a multiresidue analytical method for the analysis of 13 pesticides in fog, rainwater, gas and particles. The pesticides were p,p'DDT, p,p'DDD, p,p'DDE, aldrin, dieldrin, HCB [hexachlorobenzene], lindane, mecoprop, fenpropathrin, methyl-parathion [parathion-methyl], atrazine, isoproturon and aldicarb. This method is based upon solid-liquid extraction using Sep-PakTM tC18 light cartridges for aqueous samples, soxhlet for gas (adsorbed on XAD-2 R) and particles (on glass fibre filters), HPLC-based fractionation of the extracted residues using a silica column, and a linear gradient of n-hexane/tert butyl methyl ether followed by GC-ECD and HPLC-UV analyses of each fraction. Prior to analysis with GC-ECD, a methylation procedure using BF3/methanol was developed for the analysis of the fraction which contains chlorophenoxy acid herbicides. The recoveries of the extraction procedure of liquid samples and of the methylation were greater than 92 and 97% with a standard deviation lower than 8 and 5%, respectively. The detection limits varied between 0.1 and 0.01 µg ml-1 for the 13 pesticides studied with a standard deviation of less than 9%. This method was used for the determination of pesticides in 18 fog water samples (soluble + insoluble), 31 rainwater samples and 17 air (gas + particles) samples collected during 1991-93 in Colmar (eastern France).

Lagana, *et al.* (1997) developed a multiresidue method for the analysis of 28 common organophosphorus pesticides and 3 of their main metabolites (paraoxon-ethyl, paraoxon-methyl and malaoxon) in a variety of crop samples. An aliquot of the chopped sample was homogenized with an organic solvent. The efficiency of extraction methods using methanol, acetone and acetonitryl was evaluated. Acetonitryl gave higher recoveries and minimized co -extractives from the sample matrix. The

resulting aqueous acetonitryl extract was filtered and cleaned by solid phase extraction (SPE). For SPE, three different types of adsorption materials (Carbograph, LiChrolut-EN and Amberchrom CG-161m) were compared. The cleaned-up extract was injected into the LC system. Three different analytical columns were tested in conjunction with two mobile phase compositions of different polarity. The use of LC-DAD techniques allowed the identification of both organophosphorus pesticides and metabolites by means of standard and spectral comparison, respectively. The accuracy of the quantitative determination measured in terms of average percentage recovery of 31 compounds in crop samples was 61-96% with a relative standard deviation of 5-10%.

Miliadis (1998) described a multiresidue analytical method which is suitable for the simultaneous extraction and determination of approximately 60 pesticides in water samples. Extraction is performed by a previously described solid phase extraction method. The chromato-graphic separation and determination steps described here were developed using 2 chromatographic systems running simultaneously.

Yoshii, *et al.* (1999) studied the simultaneous determination of 71 pesticides in cereals by HPLC and GC. The pesticides were extracted by SFE (super critical fluid extraction) with collection using Extrelut R, defatted with Extrelut R+C18 and cleaned up using gas permeation chromatography and a Sep-Pak R Florisil cartridge. The test solution was subjected to HPLC with UV and FL detection, GC with FPD, ECD and GC/MS. Surveillance of wheat and corn [maize] imported into Japan was carried out by these methods. Malathion, fenitrothion, chlorpyrifos-methyl and cyfluthrin were determined by GC and confirmed by GC/MS.

Garrido-Frenich, *et al.* (2000) stated that gas chromatography (GC) with nitrogen-phosphorus detection (NPD) and mass spectrometry (MS), in full scan and tandem (MS-MS) modes were used to determine 11 pesticides (methamidophos, heptenophos, dimethoate, metalaxyl,