DETERMINATION OF PESTICIDE RESIDUES IN CROPS PRODUCED BY BIOLOGICAL METHODS: (1) CEREAL CROPS.

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ABSTRACT

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Biological cultivations are now well known,all over the world as a method to decrease the agrochemical residues (i.e. pesticides and heavy metals) in cereal, vegetable and fruit crops. Samples of wheat produced in the old valley, where extensive use of pesticides and chemical fertilizers are evidents, and another samples of wheat which were produced through the biological cultivations were analyzed to determine their contents from pesticide residues. Results indicated that soil samples, green parts of the plants and grains produced from the old valley contained about eleven pesticide residues. The major residues were Endrin, Dieldrin, Lindane and ∑DDT. Level of these residues varied from traces to 0.52 ppm, while the same samples from the biological cultivations were nearly free from pesticide residues.

INTRODUCTION

Agrochemicals (i.e. fertilizers, pesticides plant growth regulators ... etc.) are widely misused most seriously in Egypt where pesticide regulation and their enforcement are less restrict and products that have been banned or restricted in developed countries are still widely available.

There is increasing public concern about the safety of food from toxic chemicals.

Abbott et al., 1969 found that cereal grains contained BHC, Dieldrin and DDT in the following mean levels: 0.003; 0.0025 and 0.0085 respectively.

Barrentine and Cain, 1969 indicated that the soils contained Endrin at range from 0.04 to 1.12 ppm produced soyabeans contained 0.17 to 0.54 ppm. Also, wheat grains cultivated in the same soils contained 0.086, 0.138, 0.032 and 0.338 ppm of Endrin, ∑DDT, Dieldein and Lindane respectively. Van Middelen, 1969 reported that it is well established that root crops absorb chlorinated insecticides from soils. The most significant pesticide residues detected were ∑DDT and Dieldrin in levels more than 1.0 ppm in peanut hulls and dried forage definitely constituting an excessive residue potential in milk. Total ∑DDT residues in peanut meats were found to be from 0.04 to 0.13 ppm. Dieldrin residues were detected at levels from 0.35 to 0.83 ppm. Also, Endrin residues found in soyabeans at level from 0.02 to 0.11 ppm.

Polizu et al., 1972 indicated that the residues of organochlorine insecticides in wheat varied between 0.01 and 0.83 ppm and in maize between 0.1 and 0.33 ppm. The accumulation of organochlorine residues in the crops was proportional to the amounts present in the

soil,but showed an increase of up to two folds over the soil residues.

Rowlands and Bramball, 1977 reported that wheat bran was very rich in pesticide residues. Endrin, ∑DDT, Dieldrin and Lindane residues levels in bran were 0.102, 0.252; 0.120 and 0.536 ppm respectively. Insecticide residues levels in fresh bread were 0.002, 0.007, 0.010 and 0.016 ppm respectively.

Sullivan, 1980 reported that DDT and BHC were detected in all analyzed samples of wheat collected from 28 producing countries at levels less than 0.5 ppm while other chlorinated hydrocarbons such as Dieldrin, Endrin and HCB were detected sporadically at very low level.

Bengston, et al., 1983 indicated that residues of Deltamethrin, Fenvalerate, Permethrin and Phenothrin were highly persistent on stored wheat. Mean residue levels often 10 months storage were 1.82; 0.70; 0.82 and 1.21 mg/kg respectively.

In Egypt Khaled, 1989 detected the residues of Lindane, ∑HCH, ∑DDT and Malathion in wheat, rice and maize samples collected from 16 governorates. The detected residues exceeded the acceptable limits in Germany in 54.8% of wheat grain samples and 63% of wheat flour samples. The residues in wheat grains ranged from 0.002 to 1.205 ppm Lindane; 0.001 to 4.396 ppm ∑HCH; 0.005 to 0.535 ppm ∑DDT and 0.039 to 3.302 ppm Malathion. Also, Abdel Gawaad and Shams El-Dine, 1990 reported that most of imported wheat samples contained organochlorine insecticide such as Endrin, Dieldrin, DDT, Lindane and some traces of unidentified compounds.

Ezz, et al., 1991 detected Dieldrin, ∑DDT, Endrin and Lindane in samples of cereals analysed to determine the enfant daily intake of pesticide. The average of detected residues were 0.13; 0.2; 0.2 and 1.1 mg/kg respectively.

No date are available about the pesticide residues in the biological cultivation products. We will try in this paper to through light about the pesticide residues in wheat crop produced by biological methods.

MATERIALS AND METHODS

Experiments:

Experiments were conducted in two separate fields. The first one is in Moshtohor research station. In this field all the normal agricultural practice (i.e. irrigation, fertilizers; chemical control ... etc.) were conducted without any interfer. In these fields pesticides and chemical fertilizers were extensively used, and we considered these fields as best example for old valey fields. Samples from soil, green plants were taken 60 days after cultivation. While grain samples were taken at the end of yield.

The second one is a private field in El-Shalhia Area. In this field no pesticides or chemical fertilizers were used since 10 years ago. Irrigation was carried out by underground water, from 65 m in depth.

Organic fertilizers produced in the same field or produced out side were used as fertilizer at the rate of 16 cubic meter/feddan. The normal agricultural practice were conducted as normal. The samples were taken in the same time as in the first experiment.

Samples:

A. Soil Samples:

Ten samples from each field were taken. Each soil core 8.1 cm in diameter and 15 cm in deepth was taken by randam. Samples were composited, seived and reserved in deep freezer for the time of analysis.

B. Plant Samples:

One killogram of plants was collected at randam from the hole area after 60 days of cultivation in both area. Samples were kept in deep freezer for the time of analysis.

C. Wheat grains:

Ten samples from the wheat yield were taken from the both areas. Every sample weight was 50 grams. The samples were kept in deep freezer until analysis.

The Analysis of Samples:

Extraction:

a) Soil samples: A 100 gram subsamples of air-dried soil were weighted and mixed with 200 ml of propylene carbonate on a mechanical shaker for 2 hours. The mixture was vacuum-filtered through a fritted glass Buchner funnel containing glass wool and a $^1/_2$ inch layer of granular sodium sulfate. The filtered exctract is dried over approximately 20 grams of sodium sulfate for a minimum of 10 minutes.

b) Samples of wheat plants and grains: Representative samples were chopped and mixed prior to subsampling. A subsample is then macerated for 1 minute with 2 ml of propylene carbonate per gram of sample. A 50-gram sample was used. The macerate is Vacuum-filtered as described in extraction of soil samples.

Clean up:

The deactivated florisil was prepared according to the procedure described by Langlois et al., 1964. Thirty grams were added to a chromatographic column (25-mm o.d. x 400 mm length) containing 5 grams of sodium sulfate. An additional 5 grams of sodium sulfate was added on top of the florisil. The column was prewashed with 50 ml of petroleum ether, and the washings were discarded. Five milliliters of extract, representing 2.5 grams of sample, were transferred to the column and allowed to penetrate the upper portion of the Florisil. The sample was eluted with successive and separate 200 ml of petroleum ether followed by 7% diethyl ether in petroleum ether. The eluate was concentrated in the Rotavapor apparatus to less than 1 ml but not to dryness. The remaining solvent was removed by means of an air current. The whole interior of the flask was washed repeatedly with small portions of petroleum ether, the washings quantitatively transfered to a 5 ml volumetric flask. The volume adjusted and the flask shaked well to mix.

Determination:

Analysis were performed on gas chromatograph equipped (Pye Unicam, 304-PM 8251 single beam recorder) with electron capture detector under the following conditions:

Column: 183 cm long pyrex glass column with an inside diameter 4 mm and outside diameter 6 mm, with DC-30 or OV-17 stationary phase.

Carrier Gas: Pure nitrogen at a flow rate of 30 ml/min.

Operating temperature: Injection port : 250 °C.
Column : 230 °C
Detector : 250 °C

Rate of Recovery determination:

Samples from every tested material were fortified with some chlorinated hydrocarbon pesticides at the level of one ppm and then extracted, cleaned-up and concentrated with the same above procedure. The recovery rate was calculated.

RESULTS AND DISCUSSION

Data in table (1) indicated that the used procedure; which was a modified for the universal method reported by Schnorbus and Philips, 1967 and Abdel Gawaad and Shams El-Din, 1985 was applicable for the residue analysis of the chlorinated hydrocarbon pesticides.

Data in table 2 show that Moshtohor soil contained agregate ∑DDT and Endrin at levels varied from 0.02 to 0.52 ppm ∑DDT and from traces to 0.08 ppm Endrin. While the maximum levels of ∑DDT and Endrin in El-Salhia (a new reclaimed land) reached to 0.02 and 0.01 ppm respectively while no residues of Dieldrin and Lindane were detected in the samples of the new reclaimed area.

The non-point source of pesticide residues in Salhia fields could be from rain water or from the organic fertilizers which were produced for other fields. No other source of pesticide residues are available because no pesticide were used in this area from a very long time.

The source of pollutants was not only the direct or indirect application of pesticides but also from the rain water (Edwards, 1974 and Abdel-Gawaad, 1980). Also, the organic fertilizers and the under ground water can be considered as the major source of soil pollution in new reclaimed lands.

Many authors studied the persistance of pesticide residues in soils. They reported that organochlorine pesticide persisted in soil for several years, i.e. Endrin and Isodrin for 15 years and DDT for 10 years (Nash and Woolson, 1967); Aldrin and Dieldrin (John, 1975 and Richardson, 1975) and Lindane (Fuhremann and Lichtenstein, 1980). Edwards (1966) showed that although DDT was the most persistent residue in soil, it was only slightly more persistent than Dieldrin. The larger persistance of residues of DDT in soil may be due to the longer period of usage than Aldrin and Dieldrin (Edwards, 1974).

Many authors confirmed the presence of pesticide residues in different parts of the plants. They tried to know how these residues reached to these parts (Abd-El Gawaad, 1980). Bradbury and Whitaker, 1956 detected the Lindane in the aerial parts of the wheat plants, and Haines (1956) in corn seedlings. Also, Anderson, 1955 and Lichtenstein, 1959 indicated that DDT, Lindane, Aldrin and Endrin were absorbed into crops. Leahey and Carpenter (1980) reported that permenthrin and its metabolites were detected in wheat plants for 120 days after soil treatment.

Data in table 3 showed that the green parts of wheat plants contained some residues which were translocated from the soil. These data well agreed with these reported in the above studies. The maximum translocated residue showed in lindane (about 33% from soil residues) while the greatest residue level was ∑DDT (0.12 ppm) because of the larger level in old valley soil. The plants cultivated by biological method had no detectable residues except DDT at mean level less than 0.005 ppm.

Data in Table 4 indicated that wheat grains from the old valley contained some pesticide residues such as DDT, Dieldrin, Endrin, Lindane and another 7 undetected compounds. While the wheat grain taken from the new reclaimed area had'nt residues except traces of ∑DDT.

In general the residues in both grains were less than the ERL; which is the maximum concentration of a pesticide residue that is recommended by the Codex (FAO/WHO, 1986). These results indicated that the biological cultivation or the clean food production methods decreased the levels of pesticide residues to very large extent. The non point source of pesticide in this case is the traces of pesticide which find its way to the field through the organic fertilizers which imported outside this field or from rain water.

Table (1): Recovery of pesticides added to wheat plants, grains and soils.

Compound	Material	Amount added ppm.	Residue found ppm.	Rate of recovery
$\sum$ DDT	Soil	1.00	0.99	99%
	wheat plants	1.00	0.89	89%
	wheat grains	1.00	1.00	100%
Lindane	Soil	1.00	0.91	91%
	wheat plant	1.00	0.93	93%
	Wheat grains	1.00	0.89	89%
Endrin	Soil	0.1	0.90	90%
	wheat plant	0.1	0.88	88%
	wheat grains	0.1	0.83	83%
Dieldrin	Soil	0.1	0.93	93%
	wheat plant	0.1	0.88	88%
	wheat grains	0.1	0.91	91%

Table (2): Pesticide Residues in soil.

Detected Residue Region		$\sum$ DDT ppm	Dieldrin ppm	Endrin ppm	Lindane ppm
Old Valley lands	min.	0.02	T	T	0.01
(Moshtohor)	mean.	0.10	0.04	0.03	0.03
	max.	0.52	0.06	0.08	0.05
Reclaimed lands	min.	N.D	N.D	N.D	N.D
(El-Salheia area)	mean.	T	N.D	T	N.D
	max.	0.02	N.D	0.01	N.D

N.D = No detectable residue

T = Traces, Less than 0.005 ppm.

Table (3): Pesticide residues in green parts of wheat plants.

Detected residue region		DDT ppm.	Dieldrin ppm.	Endrin ppm.	Lindane ppm.
Old Valley (Moshtohor)	min.	T	T	T	T
	mean.	0.03	0.01	0.01	0.02
	max.	0.12	0.03	0.02	0.03
Reclaimed land (El-Salhia area)	min.	N.D	N.D	N.D	N.D
	mean	T	N.D	N.D	N.D
	max.	0.005	N.D	N.D	N.D

Table (4): Pestciides detected in wheat grains.

Pesticide residues		Old Valley "Moshtohor" ppm.	Reclaimed land "El-Salhia" ppm.	ERL ppm.
DDT	min.	T	N.D	100
	mean.	0.020	T	
	max.	0.060	0.005	
Dieldrin	min.	T	N.D	20
	mean.	0.005	N.D	
	max.	0.020	N.D	
Endrin	min.	T	N.D	20
	mean.	0.010	N.D	
	max.	0.020	N.D	
Lindane	min.	T	N.D	500
	mean.	0.010	N.D	
	max.	0.030	N.D	

N.D.= No Detectable residues T= Traces, less than 0.005 ppm. ERL= Etraneous Residue Limit = Refers to a pesticide residues arising from environmental sources other than the use of pesticide directly or indirectly on the

Abdel-Gawaad and Shams El-Din, 1985 detected residues in imported wheat exceeded the ERL whereas the mean detected residues were 86, 20, 226 and 202 mg/kg for Endrin, Dieldrin, ∑DDT and Lindane respectively. This is improved that our production from cereals were more healthy than the imported one..

Finnaly the relation between the ecotoxicological impact of pesticide and the environment is very clear in Egypt. The increase of death cases by cancer, kidney failure and liver failure in many countries is found to be related to the impact of agriculture chemicals in the environment. For that, countries tried to minimize the use of agrochemicals through a new developed method of cultivation which is called, clean food production or biological cultivation. Our results improved that our country can share in this field if the uses of agrochemical are restricted and the pesticide regulations take their enforcement in the new reclaimed areas.

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