INTRODUCTION

Measurable amounts of pesticidal residues in our food present a variety of problems. If a chemical is nontoxic to human and causes no harm to living cells, residual amounts in food could be tolerated. However, the lack of detailed knowledge concerning the potential effects of agricultural chemicals on human and animals has necessitated the establishment of legal limits.

One major problem concerning the food supply emerged when several crops grown in pesticide treated soil were found to contain within their edible parts measurable amounts of some pesticide residues. These pesticide residues were usually chlorinated hydrocarbons. The amounts that penetrated into plant parts were dependant on the nature of the chemical , soil type, temperature, moisture content, organic matter, pH, porosity, chemical contents, clay minerals etc. The availability of these chemicals for penetration into the plant root system is also

dependent on many factors.

Egypt used 617507 metric tons of pesticides between 1952 and 1984. Nearly 50 % of this quantity found its way to the soil. In the soil they persisted for a long time and have many side effects on soil fertility, soil pollution, water pollution and also food contamination., Abdel - Gawaad 1985.

A study of the feeding habits and behaviour of the people in Egypt showed that they used a large quantity of bread in their meals. However little information about pesticide residue levels in grain are available. The limits of these residue levels under Egyptian conditions are not known.

In this work the author is interested in throwing light on the pesticides residue levels in grain (wheat) and their levels after bread processing.
The levels of these residues in the local samples were also determined.

The absorption and translocation of pesticide residues through the root system of the plant was also studied.

REVIEW OF LITERATURE

Pesticide residues in cereal grains.

Winteringham et al. 1955 reported that the chemical fate of methyl bromide absorbed by wheat under the conditions of fumigation has been studied. Whole-wheat flour was exposed to 14C-labelled methyl bromide. The fat, starch, gluten and water-soluble fractions were prepared from the exposed flour and their 14C-content assayed. The gluten or protein fraction was responsible for some 80% of the decomposition of the absorbed fumigant. By measuring the 14C of the volatile products obtained on treating the gluten with sodium hydroxide or hydriodic acid under different conditions, it was shown that the decomposition of methyl bromide in gluten was due almost entirely to methylation with the formation of 50% of N-methyl derivatives, 30% of dimethyl sulphonium derivatives, and of 20% of methoxyl and thiomethoxyl derivatives in about equal proportions. Similar results were obtained when gluten alone was exposed to the labelled fumigant. The production of free methanol in the flour by

hydrolysis of the absorbed fumigant was about 10% or less. The rate of spontaneous decomposition of the dimethyl sulphonium compounds formed as a result of fumigation was estimated by using wheat which had been grown of ^{35}S-labelled sulphate.

Sinclair et al. (1962) reported that wheat and wheat products were fumigated with ethylene dibromide at dosages of 0.5 and 1.0 pound per 1,000 cubic feet for a 24-hour exposure period at 70°F in a gas-tight fumatorium equipped with a recirculating system. The data presented in these experiments show that more than 95% of the added ethylene dibromide was recovered from whole and ground wheat samples after 10 days, reaction time at approximately 70°F. At a treatment dosage of 1.0 pound for a 24-hour exposure, fumigated wheat at 9% moisture content contained 5.8 ppm ethylene dibromide at the end of the 10-day aeration period. The bran fraction of wheat initially sorbed the greatest amount of ethylene dibromide, followed by shorts, flour and middlings. These milled fractions, on the 35th day after fumigation, had, on the average, 4.5ppm of ethylene dibromide. The wheat samples containing 15% moisture not only sorbed the greater initial amount of ethylene dibromide during the exposure, but

retained several times more fumigant than the 9% moisture sample after 15 days of aeration. The total bromine residues that resulted from fumigation are reported as the sums of the ionized bromine (salt form) and the bromine equivalent to the ethylene dibromide in the samples at the time of analysis.

Polizu et al. (1972) indicated that the residues of organochlorine insecticides in wheat varied between 0.06 and 0.83 ppm (average 0.21 ppm) and in maize between 0.1 and 0.33 ppm (average 0.2 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 fold over the soil residues.

Lahue and Dicke (1977) showed that candidate insecticides were tested on high moisture sorghum as protectants against several species of stored-grain insects. Pirimiphos methyl and chlorpyriphos methyl prevented the establishment of insect infestation during 12 months' storage and prevented appreciable test weight loss and kernel damage. Average residues concentrations (ppm) after 12 months' storage were (concentration applied in parentheses) : malathion spray 0.8

(16.7), pirimiphos methyl spray 3.7 (8.4), fenitrothion spray 1.1 (8.9), chlorpyriphos methyl spray 1.6 (6.7) and malathion dust 0.1 (11.2).

Lahue (1977) indicated that pirimiphos methyl degraded more slowly, leaving 83.1% of the initial residue after 12 months, compared with 16.3% for malathion.

Rowlands and Bramhall (1977) reported that malathion residues are found chiefly in regions of high lipid content in the individual wheat grain; mainly in the germ and scutellum and seldom in the starchy endosperm. Malathion applied directly to the endosperm is rapidly transported to other regions.

Some grains have an enhanced affinity for malathion, and this property is not related to the size or weight of the grain. The current methods for calculating and applying safe limitsfor pesticide residual levels in grain are criticised in the light of these results.

Isshiki et al. (1978) reported that residual levels of

piperonyl butoxide were determined in 531 samples of 10 species (unhulled and hulled rice, wheat, barley, buckwheat, rye, oats, milo, corn, soybean and red bean) using a high speed liquid chromatography equipped with a fluorometric detector. The detection limit of piperonyl butoxide was 0.1 ppm. Piperonyl butoxide was detected in 3 of 65 wheat samples (all 3 from USA) and in 3 of 39 barley samples (1 from USA and 2 from Australia). The range of residual concentrations was from 0.2 to 1.4 ppm.

Abu-Elamayem et al. (1979) reported that leptophos (phosvel), an insecticide with delayed neurotoxic effects, was added to milk and wheat at 100 ppm prior to processing. Residues of leptophos, its oxygen analogue and the phenol derivative (2,5-dichloro-4-bromophenol)were determined at each stage of the cheesemaking process and the milling process using the spiked samples. Washing of wheat was not very effective in removing leptophos; the finished flour contained 0.99 ppm and the bran 11.95 ppm but the degradation products were not detected in either fraction.

Alnaji and Kadoum (1979) showed that methyl phoxim

[phenylglyoxylonitrile oxime (0,0-dimethyl phosphorothioate)] was applied to separate batches of cleaned, soft red winter wheat as water emulsions at 10 ppm active ingredient. Samples of the treated wheat were stored for periods up to 365 days to determine residues on the whole wheat and on milled fractions. The residue degraded rapidly during the first month after the wheat was treated; thereafter it degraded gradually. The higher residues of methyl phoxim were found in the bran and shorts and very small amounts of the residues were in the flour. The losses during milling were 8-10% in methyl phoxim residues

Alnaji and Kadoum (1979 reported that soft red winter wheat(12,5% moisture) was sprayed with an emulsion of the insecticide methyl phoxin (phenylglycoxylnitrile oxime 0-(0,0-dimethyl phosphothioate)] at 10 ppm active ingredient. Grain was then stored in covered drums at 26 °C and 60 % relative humidity for 365 days, with samples being removed for determination of residues in whole wheat and fractions produced by laboratory milling. Before milling, moisture content was adjusted to 14% to ensure uniform milling. Average milling yields were bran 16%, shorts 10% and flour

72%. Residues (ppm) of methyl phoxim after 1 and 365 days of storage were : whole wheat 9.86±0.24, 1.12±0.04; bran 32.78±0.46, 4.26±0.06; shorts 18.41±0.36, 2.83±0.08 and flour1.71±0.08, 0.19±0.02.

Extensive laboratory and field studies were conducted by Mensah (1979) to examine the effects of various factors (type of insecticide formulation, type of substrate and conditions after treatment) on the uptake and persistence of malathion, bromophos, iodofenphos and pirimiphos-methyl on the structural surfaces of granaries (e.g. wood, concrete, galvanized steel) and on stored grain(e.g. corn, wheat, barley); uptake and persistence were measured by GLC methods and by bioessay with Cryptolestes ferrugineus and Tribolium castaneum. On the basis of the results obtained, it is concluded that bromophos and iodofenphos are suitable alternatives to malathion for short-term protection of stored grain, advantages of these 2 compounds being their residual effectiveness, relatively short persistence and low mammalian toxicities.

Mensah et al. (1979) reported that water-based emulsions of (i) malathion, (ii) bromophos, (iii) iodofenphos, and (iv) pirimiphos-methyl were applied at 2 dosage rated to No. 2 C.W. red spring wheat of 12 and 16 % moisture content to compare residue distribution in fractions milled from wheat samples stored over a period of 6 months. High levels of insecticide residues were contained in the bran and middlings. Significantly less ($P<0.05$) (i) than (ii), (iii) or (iv) was found in the bran and middlings after 6 months of storage of treated wheat. Comparatively smaller amounts of insecticide residues were found in the flour than in the bran or middlings. Less (iii) than (i), (ii) or (iv) occurred in the flour. Pirimiphos-methyl degraded at a comparatively slower rate than (i), (ii) or (iii). Residues recovered from fractions of wheat of 16% moisture content were generally lower than residues found in wheat fractions of 12 % moisture content.

Rajukannu et al. (1979) showed that pesticide residues in sorghum grain following application to the crop 30, 45 and 60 days after sowing of phosalone (dust), phosalone (spray), quinalphos (spray) and malathion (spray) at rates of 0.60, 0.44, 0.50 and 1.0 kg active ingredient/ha respectively per

application were not detectable with phosalone, 0.32 ppm with quinalphos and 1.21 ppm. with malathion. All residues were below the tolerance level.

Abdel-Kader and Webster (1980) reported that studies were conducted on (i) the effect of Canadian storage temperature on rate of malathion and fenitrothion degradation in stored wheat, and (ii) the translocation of both insecticides in stored wheat kernels under Canadian storage conditions. <3% degradation occurred in wheat stored at -35 or -20 °C for 72 weeks. As temperature increased, residue decreased, the rate depending on the age of the insecticide deposit.

Fenitrothion residues were slightly more stable at colder temperature than malathion. Highest residues of fenitrothion and malathion were found in bran and middlings of milled wheat and very little in flour.

Dumas (1980) reported that the sorption and desorption of PH3 from wheat treated with concentrations of 0.5-5 mg/kg of wheat was determined at 25, 45 and 85°C. The desorbed PH3 was extracted from the air by passing through a cold trap; here

sufficient quantities of the gas could be accumulated for accurate analysis by GLC. Most of the PH3 was desorbed in the first 2-3 days but small amounts continued to desorb for many weeks following treatment. After 220 days of aeration, PH3 was still present in the grain and desorbing at the rate of ppt (10-12 g). For a wide range of concentrations, about 10% of the PH3 applied was found to be adsorbed. The amount of physically sorbed PH3 increased with the fumigant concentration applied and with the length of exposure. Because of reduced reactivity even when the temperature was increased to 85°C for several days, unreacted PH3 still desorbed slowly from wheat. Corn aerated 26 days desorbed 0.004 ng/g in 2 days.

Lee et al. (1980) used GLC to determine organochlorine pesticide residues extracted from refined vegetable oils, including rapeseed, rice bran, sesame, perilla and corn. Mean levels were generally below the tolerance levels, absolute values varying with type of soil and pesticide. Aldrin, dieldrin and endrin were still detectable in some samples (despite the ban on their use, the maximum level being 0.112 ppm of endrin in perilla oil. DDT was also detected in most oil samples, up to a maximum in 0.134 ppm in a sesame oil sample. Mean

concentration of BHC and heptachlor and its epoxide were up to 0.01 ppm (below the tolerance levels). Since sesame and perilla oils are mechanically pressed, whereas rapeseed, rice bran and corm are processed in modern mills, they had 2-10 times as much residual pesticide.

Sullivan (1980) reported that pesticide analyses for residues of chlorinated hydrocarbons were performed on 28 spices from 25 producing countries. Several shipments were examined during several crop years. In all, 226 samples were analyzed. Low levels of DDT and BHC were detected consistently, the level being generally below 0.5 ppm. Residues of other chlorinated hydrocarbons such as Dieldrin, Endrin and HCB were detected sporadically at a very low level. Except for oregano from Mexico, some of which is grown in an area where DDT is actively used, there is no relationship between pesticide residues and country of origin or individual spice.

Webley and Kilminster (1980) showed that the persistence and biological activity of insecticide spray deposits on jute and woven polypropylene (PP) sheets were compared and the build-up of residues in thin layers of maize under the sprayed

sheets was measured over 12 weeks. Results showed that the insecticides (bromophos, fenitrothion, malathion, pirimiphos-methyl at 1 g/m2, permethrin at 0.1 or 1 g/m2) had a much shorter persistence on PP than on jute, coupled with higher residues on the grain.

Abdel-Kader (1982) reported that malathion and fenitrothion were applied as water-based emulsions at 0.8 ml/kg to provide a deposit of 8 ppm on hard red spring wheat. The treated grain was then stored in the dark at -35, -20, -5, 5, 10, 20 and 27 °C for ≤ 72 weeks. The level of insecticide residues was generally found to decrease with increasing temperature and duration of storage, fenitrothion being somewhat more persistent than malathion, particularly at low temperatures.

Kumar et al. (1983) indicated that pirimiphos-methyl was sprayed at 0.15, 0.30 and 0.45 g active ingredient/m2 on bags of wheat (10% moisture) and rice (9.5% moisture). From each crop a 500 g sample was drawn and stored in a refrigerator for residue analysis by TLC. Average residues in wheat were

(according to location of test) 0.7-3.0 ppm, and in rice 0.8-1.95 ppm.

Bengston et al. (1983) indicated that residues of deltamethrin, fenvalerate, permethrin and pheonthrin were highly persistent on stored wheat. During milling, residues accumulated in the bran fractions and were reduced in white flour (54.1-68.5% of residues in bran, 8.5-14.1% in flour, 23.0-31.8% in pollard). They were not significantly reduced during baking. Mean residue levels of deltamethrin, fenvalerate, permethrin and phenothrin after 10 months storage were 1.82, 0.70, 0.82 and 1.21 mg/kg respectively in wheat, 1.3, 0.49, 0.67 and 0.81 in wholemeal bread, 0.25, 0.08, 0.13 and 0.23 in white flour, and 0.20, 0.06, 0.13 and 0.20 in white bread. Apparent reduction of residue levels in bread was attributed to its greater moisture content.

Viljoen et al. (1984) reported that dichlorvos was applied weekly (on non-working days) at 2 corn mills using different application systems: (i) installed high-pressure system

comprising tanks (pressurized to 5000 kPa with CO2) and nozzles delivering 35 mg active ingredient (a.i.)/m3; and (ii) aerosol cans at 93 mg a.i./m3.

Concentration of the insecticide in air, residues in milling materials and effects on insects were studied, and efficacy was compared with that of pyrethrin in a wheat flour mill as control. (ii) gave very good insect control but at high cost. Poorer (though satisfactory) control by (i) was due to nozzle blockages giving irregular application not to the lower dose rate, and would be overcome by use of steel piping and nozzles. (i) gave better distribution of dichlorvos. (i) has high installation costs, but low operating costs. Using (i) and (ii), insecticide concentration in air declined to relatively low levels within 6 h, and there was no hazard to workers after 48 h. Residues in food materials varied widely and were often over the tolerance limit of 0.5 mg/kg, but dichlorvos use in mills is safe provided that food products are stored unexposed to insecticide for 7 days following application.

Joia et al. (1985) indicated that cypermethrin and fenvalerate were applied at 8 and 12 mg/kg to wheat of 13.3

and 15.0% moisture content. Treated wheat was stored at 25 and -5°C for 60 weeks and sampled at six 12-week intervals. Residues were determined in wheat and milled fractions, viz., bran, middlings, and flour (endosperm). It was observed that highest amounts of insecticides were present in bran and least in endosperm. Both the insecticides degraded in treated wheat at slow rates. Half-lives of fenvalerate on grain ranged from 385.1 weeks on wheat of 13.3% moisture content stored at -5°C to 69.3 weeks on wheat of 15% moisture stored at 25°C. Reduction of residues in flour through bread baking was low and 79-84% of cypermethrin and 82-88% of fenvalerate were present in bread made from flour (white and wholemeal) containing cypermethrin and fenvalerate residues.

The extent and the pattern of desorption of PH_3 residue in wheat, raw polished rice, raw unpolished rice and parboild rice were followed at laboratory level for 60 days by 14. The PH_3 residue on each day of storage was computed by knowing the total amount of PH_3 desorbed over 60 days. The PH_3 desorption patterns from four types of cereals are discussed under three stages: up to 19 days, 20-49 days, and 50-60 days of storage. The relationship between the logarithm of such residues vs.

storage in days is linear over the first 19 days, except in the case of residue from raw polished rice, which is only up to the first 9 days. During the period of linearity the desorption follows first-order kinetics. Between days 20 and 49 there is a waxing and waning in the amount of PH3 desorbed. Between days 50 and 60 there is a regular fall in PH3 desorbed. Between days 50 and 60 there is a regular fall in pH3 residues due to uniform decreased desorption except in raw unpolished rice in which desorption is a bit sluggish up to 56 days

Duplicate field trials were carried out by Bengston et al. (1983) on bulk wheat in commercial silos in Queensland and New South Wales. Laboratory bioassays on samples of treated grain at intervals over 8 or 9 months storage using malathion-resistant strains of insects established that treatments were generally effective.

Mean residues of cyfluthrin and cypermethrin after 9 months storage were 58% and 52% of the calculated application rates, respectively. Compared with overall concentrations in the wheat, residue levels were higher in bran and pollard and lower in white flour. During baking, residues decreased by up to

29 %. Operators experienced respiratory irritation associated with exposure to both combinations and alternative formulations would be required for use of these materials in grain storage.

White (1986) indicated that rye, wheat and triticale were stored for 8 months at 22°C in PVC cylinders placed on panels of plywood or galvanized steel which had either been untreated or treated with 0.5 g (active ingredient)/m2 of malathion or pirimiphos-methyl. Grain samples were taken from the top and bottom of the cylinders at regular intervals.

Insecticide residues were 0.8 in top samples and generally declined during storage ,while residues in bottom samples usually increased during storage . Maximum insecticide residues in bottom samples were :in rye „14.3 ppm malathion from wood and 13.5 ppm pirimiphos-methyl from steel ; in wheat , 8.3 ppm malthion from steel and 5.3 ppm pirimophos-methyl from steel ; in triticale 8.4 ppm malthion from steel and 7.2 ppm pirimophos-methyl from steel. Insecticide levels were highest in rye and lowest in wheat.

Laboratory studies were conducted by Mensah (1987) to determine whether insecticides applied to storage structures are able to move past a single layer of grain kernels to give adequate control of stored-grain insects. The extent of uptake of insecticides was assessed on three layers of wheat in contact with wood surfaces treated with malathion 8.36 g/litre e.c. at 1.0 g a.i. m-2 using chemical and biological methods at predetermined time intervals. There was a progressive uptake of malathion beyond the layer directly in contact with the treated surfaces and the uptake depended on the duration of storage.

The sorption of 1,1,1-trichloroethane on wheat, barley and oats during fumigation and its subsequent loss during airing has been studied by Scudamore (1987) after treatment with 1,1,1-trichloroethane alone or in a mixture with bromomethane. The extent of sorption of bromomethane and the amount of inorganic bromide formed from reaction of bromomethane with constituents of the grain samples were not affected by the presence of 1,1,1-trichloroethane. The sorption of 1,1,1-trichloroethane on cereal grains and the amount of inorganic bromide formed increased with commodity moisture

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content. Bromide formation also increased with temperature and varied both with the cereal and with different varieties of wheat tested. At low dosage levels, residues of 1,1,1-trichloroethane were proportional to concentration X time (CT product) but at the highest dosage used residues were disproportionately higher than expected, owing to vapour concentration approaching saturation pressure. The rate of loss of 1,1,1-tichloroethane from wheat, barley and oats under controlled conditions was found to be more dependent on the storage time than on the residue remaining or the original level of treatment. For wheat, initial sorption of 1,1,1-trichloroethane varied with variety and to a lesser extent also varied between different samples of a single variety tested. However, the rate of airing appeared to be similar for all samples of wheat tested. Results are also described showing the effects on airing rated induce in wheat in which the moisture content was also changing. These results suggest that, in wheat in which moisture content increases during storage, the residue at a specific time after treatment would not be particularly dependent on the interim conditions while in wheat of falling moisture content, residues would very much depend on the conditions prevailing.