THE UNIVERSITY OF MANITOBA

PERSISTENCE AND TRANSLOCATION OF ORGANOPHOSPHORUS INSECTICIDES ON STRUCTURAL SURFACES AND IN STORED GRAIN

BY

GEORGE WILLIE KEN MENSAH

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF ENTOMOLOGY

WINNIPEG, MANITOBA

FEBRUARY, 1979

PERSISTENCE AND TRANSLOCATION OF ORGANOPHOSPHORUS INSECTICIDES ON STRUCTURAL SURFACES AND IN STORED GRAIN

BY

GEORGE WILLIE KEN MENSAH

A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

ABSTRACT
BY
GEORGE WILLIE KEN MENSAH

PERSISTENCE AND TRANSLOCATION OF ORGANOPHOSPHORUS INSECTICIDES ON STRUCTURAL SURFACES AND IN STORED GRAIN

Insecticides used to protect stored grain from insect infestation may be applied to the structural surfaces of granaries or to the grain itself. The degree of protection afforded by an insecticide depends on its rate of degradation or change after application. Various factors such as the type of formulation, type of substrate and conditions after treatment influence the behaviour and toxicity of insecticides. Laboratory and field studies were therefore conducted to investigate the effects of these factors on the persistence of malathion, bromophos, iodofenphos, and pirimiphos-methyl on structural surfaces and on stored grain using both chemical analysis with gas-liquid chromatography and bioassay.

Malathion, bromophos (EC and WP), and iodofenphos (EC) were applied as water-based solutions at 0.05 litre/m^2 to provide a deposit of 1.0g AI/m^2 on wood and concrete surfaces. Persistence was assessed in the laboratory at different times after treatment by bioassay and chemical assay of 30 g wheat, barley, and corn after the grains had been in contact for one week with the treated surfaces. The grains were bioassayed with susceptible *Cryptolestes ferrugineus* (Stephens) and *Tribolium castaneum* (Herbst) adults. Significantly higher ($P < 0.01$) mortalities of *C. ferrugineus* and *T. castaneum* were obtained on cereals in contact with treated wood surfaces than on cereals in contact with treated concrete surfaces. Malathion EC provided better control of the beetles on grains in contact with wood surfaces whilst bromophos formulations gave better control than malathion formulations or iodofenphos on grains in contact with concrete surfaces. Lower mortalities were obtained

on corn stored on treated structural surfaces than on wheat or barley. Reproduction of test beetles was significantly greater ($P < 0.01$) in grains previously stored on treated concrete surfaces than in grains stored on treated wood surfaces. Significantly more ($P < 0.01$) of each insecticide translocated into grain samples in contact with wood than with concrete surfaces. Smaller amounts of iodofenphos translocated into grain samples in contact with treated structural surfaces than malathion or bromophos. Lower amounts of insecticide residues were recovered from corn than from wheat or barley. Persistence of the insecticides on structural surfaces and their uptake into stored grains was found to decrease as the age of deposit increased.

The first field test was conducted with bromophos WP applied at 1.0g AI/m^2 to the concrete floor of a farm granary. Persistence and uptake of bromophos into wheat, enclosed by open-ends of plywood boxes on the treated floor, were determined by bioassay with _C. ferrugineus_ and by chemical analysis of wheat samples. Complete mortality was obtained on the bottom 8.3-cm layers of grain in contact with the treated floor. Higher residues were also found in these layers. In the second field test, bromophos WP was applied at 1.0g AI/m^2 to the concrete floor and galvanized steel sides of a farm granary to determine the uptake of bromophos into wheat during seven months' storage of 1093 bushels of wheat in the treated granary. Bromophos residues of less than 1.0 ppm were detected in the peripheral layers of grain in contact with treated floor and walls.

Uptake of malathion and bromophos in wheat stored for one week on wood surfaces treated at 1.0g AI/m^2 was independent of wheat moisture content.

Studies of uptake of malathion by three layers of wheat in contact with wood surfaces treated at 1.0g AI/m^2 showed that the extent of progressive uptake of malathion past the bottom layer depended on the duration of storage.

The persistence of malathion, bromophos (EC and WP), and iodofenphos (EC) applied at 250 mg AI/m^2 to wood surfaces was enhanced by sweeping the surfaces one week after treatment. By contrast, treated surfaces that were abraded by the movement of wheat lost their effectiveness: after one day for iodofenphos, and after three weeks for malathion and bromophos.

Malathion, bromophos, iodofenphos, and pirimiphos-methyl in liquid formulations were applied to dry (12.0% mc) and tough (16.0% mc) wheat at initial doses equivalent to their tolerance levels and at 1.5 times these levels to examine the residual effects on susceptible and malathion-resistant strains of *T. castaneum* on 50 g wheat at certain intervals after treatment. Pirimiphos-methyl, at the dosages tested, was the most persistent and effective compound against both strains. Malathion at both dosages was ineffective against resistant *T. castaneum*. Pirimiphos-methyl at both rates prevented reproduction of both *T. castaneum* strains. Residue analysis of stored grain over a 24-week period revealed that pirimiphos-methyl was the most stable compound followed by bromophos, malathion, and iodofenphos. The bulk of insecticide residues in milled fractions of wheat were found in the bran and middlings, with very small amounts in the flour.

The residual effectiveness of bromophos and iodofenphos on structural surfaces and in stored grain coupled with their relatively short persistence and low mammalian toxicities demonstrate that these compounds are suitable alternatives to malathion for short-term protection of stored grain against insect infestations. Pirimiphos-methyl will be a very useful grain-protectant for long-term storage against susceptible and resistant strains of stored-grain insects.

ACKNOWLEDGEMENT

This study was undertaken at the suggestion of my advisor, Dr. F.L. Watters of the Agriculture Canada, Research Station, Winnipeg, and Professor of the Faculty of Graduate Studies and Research, University of Manitoba, Winnipeg, Manitoba, Canada. I wish, therefore, to express my deep sense of gratitude to him for his expert advice, constant encouragement, and helpful criticisms which were all invaluable to me for the success of the study.

My sincere gratitude is extended to Professor A.G. Robinson, Head, Department of Entomology, University of Manitoba, Winnipeg, for the interest he showed in my academic program at the Entomology Department, and also for his constructive criticism of the manuscript.

I am deeply indebted to Dr. G.R. Barrie Webster, Pesticide Research Laboratory, Department of Soil Science, University of Manitoba, Winnipeg, for making facilities available to me to carry out the chemical residue analyses. His understanding, willingness to help and all valuable suggestions concerning residue analysis at all stages of the study as well as his helpful comments on the manuscript are greatly appreciated.

It is a pleasure to express my great indebtedness to Mr. Fred Switzer, former Stored Product Entomology Technician at the Agriculture Canada, Research Station, Winnipeg, Messrs. Len Sarna and Jim Rogers of the Pesticide Research Laboratory, Department of Soil Science, University of Manitoba, Winnipeg, for their devoted technical assistance they rendered to me at all phases of this study. I am appreciative for all the helpful suggestions received during the analysis of the chemical residues in grain samples from Mr. Tom W. Nowicki, Grain Research

Laboratory, Canadian Grain Commission, Winnipeg.

My sincere thanks go to Dr. R.J. Baker, formerly of the Agriculture Canada, Research Station, Winnipeg, for carrying out the statistical analysis of the data. I wish to express my sincere appreciation to Dr. W.C. McDonald, Director, Agriculture Canada, Research Station, Winnipeg, for permission to use all available facilities at the station to undertake the study. I am also thankful to Mr. Ross Jones and his staff at the Ciba-Geigy's Research Farm, Elm River near Portage La Prairie, for their assistance during the field studies. Special thanks are extended to Mr. Reggie W. Sims for the preparation of photographs and illustrations, and to Mrs. Connie Ashdown, who willingly and effectively typed the thesis. Thanks are also due to all the staff at the Agriculture Canada, Research Station and Department of Entomology for their kindness and help during the period of the study.

I owe much gratitude to Miss Clara Fagan for her encouragement and help in many ways, including some laboratory assistance. Thanks are also due to all friends for their help.

During the entire period of my academic training and preparation of this thesis, I was supported by funds from CIDA and the University of Science and Technology, Kumasi, Ghana, and for which I am most grateful.

George Willie Ken Mensah

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Insect pests have always demonstrated amazing plasticity in their abilities to overcome man's best efforts to control them. Thus, storage of grain and grain products always involves risk of infestation. It is therefore abundantly clear that continued research in insect pest control during storage of grain and grain products is essential to ensure abundant supplies of high quality food for the expanding populations of the world.

Protecting our cereal crops during storage on the farm and in warehouses is often more difficult than during the growing season. This is especially true where insect infestation starts in the field and continues throughout the duration of storage of both grain and grain products.

Among the numerous insect pests which cause losses and deterioration to stored food grains and cereal products are the rusty grain beetle, *Cryptolestes ferrugineus* (Stephens) and the red flour beetle, *Tribolium castaneum* (Herbst). These two species have been known in the Canadian grain industry as major biotic factors responsible for grain heating, spoilage, and grade losses (Sinha, 1971). These pest species can, if left unchecked, cause a substantial loss of food grains during storage.

Although thorough sanitation practices are the essential tools in maintaining quality and abundance of stored grain and grain products, prestorage treatment of granaries and food warehouses with contact insecticides is generally the most effective management method available to reduce insect populations to tolerable levels.

Malathion and pyrethrins are the major contact insecticides most widely used by the grain industry for the treatment of structural surfaces for the control of rusty grain beetle and red flour beetle infestations but information is also needed on other insecticides that may be more effective.

Scope and objectives of study

Treatments of structural surfaces with contact insecticides, in many instances, have been used effectively to confer long-term protection on insect-free commodities against infestation. Although persistent residues of contact insecticides on surfaces may be useful from the standpoint of insect pest control, tolerance levels established by international committees (FAO/WHO, 1967, 1968a,b, 1969a,b, 1973a,b, 1976a,b) and accepted by national regulatory agencies, e.g., Agriculture Canada (Anon., 1977), coupled with increasing consumer demands have necessitated determination of microquantities of residues of pesticides and their metabolites in stored products. Thus, the need for detailed checks on persistence of insecticide residues in stored products after treatment and, particularly, prior to consumption cannot be overstressed.

Various factors govern the persistence and biological effectiveness of stored product insecticides applied on granary surfaces and on stored grain. Under a wide range of environmental conditions in which the insecticide applications are made, the effects of grain moisture and temperature are well known, but other variable factors affecting persistence and effectiveness are not well understood. The objectives of the study were therefore to determine in the laboratory and during a limited field study:

(1) the persistence of malathion and bromophos both as emulsifiable concentrate (EC) and as wettable powder (WP) formulations, and iodofenphos as an EC applied to concrete and wood surfaces;

(2) the translocation of these insecticides into wheat, barley, and corn stored on treated concrete and wood surfaces;

(3) the effect of grain moisture content on uptake of malathion and bromophos residues from treated wood surfaces into wheat;

(4) the distribution of malathion residues in layers of grain kernels stored on treated wood surfaces;

(5) the effects of physical disruption on persistence of insecticide deposits on structural surfaces;

(6) the persistence of malathion, bromophos, iodofenphos, and pirimiphos-methyl residues in dry and tough stored wheat.

The above studies were done by both bioassay and chemical assay methods. The bioassay of cereal grains and structural surfaces was done with adults of the rusty grain beetle, *Cryptolestes ferrugineus* (Stephens) and the red flour beetle, *Tribolium castaneum* (Herbst) at different intervals after treatment. Chemical analysis using gas-liquid chromatography was carried out to supplement the bioassays, and to compare the residue levels with internationally approved tolerance limits.

The importance of study

Substantial quantities of food grains are often lost through damage caused by insect pests in the absence of efficient storage management systems. The increasing demand for food as a result of expanding human populations therefore underlines the need to conserve both the quality and quantity of food grains during storage.

Although even today there are few reliable estimates of losses resulting from the various causative factors, pre- and post- harvest losses of food grains due to insect pests havebeen stated as 14 percent of potential production (Walker, 1975). An FAO report has given the value of stored grain lost annually through damage and feeding by insect pests as 10 percent of the total production in the world (Hall, 1970) or 100 million tons due to failure to store properly (Wolpert, 1966). The heaviest losses are considered to occur at the rural level in tropical and subtropical countries where 60 to 80 percent of total production in developing countries is consumed. It has been estimated that postharvest losses can, in specific instances, be as high as 35 to 50 percent (Prevett, 1975) and in some cases higher (Hall, 1970).

Though recent trends in food production emphasize less dependence on chemicals to control infestation in growing crops, there are few alternatives to the use of pesticides to control infestations in stored products. Fumigants are applied to eliminate insect infestations already present while the treatment of structural surfaces of storage houses with insecticides or the admixture of approved insecticides with stored grains are the main methods of protecting the quality and abundance of stored foods. Regardless of the kind and type of formulation used, pesticide applications are intended to create an environment unsuitable for the continued growth of pest populations.

Malathion and pyrethrins are the two major contact insecticides most widely used in practice as postharvest residual protectants against infestations of a wide variety of stored-product insects. Malathion, for instance, has been the stored-grain insecticide of choice in several countries over the past decade because of its high toxicity to several stored-product insects and its low mammalian toxicity [LD_{50} rat = 2800 mg/kg body weight (Martin and Worthing, 1977)]. There is, however, a need for alternative insecticides which are effective on concrete surfaces or under conditions of high alkalinity (e.g., new concrete) or grain moisture content which render malathion unstable (Watters, 1959; Strong and Sbur, 1960; Parkin, 1966; Lemon, 1967). The need for newer or alternative insecticides for use in stored products becomes even more apparent by the increasing number of malathion-resistant strains of *T. castaneum* which have been reported from Nigeria (Hayward, 1962; Parkin *et al.*, 1969), the U.S.A. (Speirs *et al.*, 1967; Zettler, 1974, 1975), Australia (Champ and Campbell-Brown, 1970), and the United Kingdom (Dyte and Blackman, 1970); and now becoming widespread mostly through international trade (Dyte and Blackman, 1970)

Bromophos, iodofenphos, and pirimiphos-methyl may be used as grain protectants as well as for the treatment of structural surfaces of granaries and are promising alternatives to malathion. Bromophos is used in some countries to control malathion-resistant strains of *T. castaneum* (Dyte and Forstescue, 1967; Dyte and Rowlands, 1968; Champ and Campbell-Brown, 1970). The effectiveness of pirimiphos-methyl against both malathion-specific and malathion-non-specific resistant strains of *T. castaneum*, and also in areas where *T. castaneum* has shown cross-tolerance to bromophos have been demonstrated (Pierterse *et al.*, 1972; Anon., 1974a). Iodofenphos, on the other hand, has been proved to be more toxic to *T. castaneum* and *C. ferrugineus* adults than malathion (Blackman, 1969; Girish *et al.*, 1970; Anon., 1974b; Tauthong and Watters, 1978). Though these organophosphorus insecticides are relatively new in the grain industry for protection of stored products against insect infestation, bioassay data on their residual effectiveness on different structural surfaces are well documentated (Immel and Geisthardt, 1964; Lemon, 1967; Hansens et al., 1968; Mathis and Schoof, 1968; Nawrot, 1969; Riley and Cornes, 1969; Tyler et al., 1969; Gradidge et al., 1970; Hope et al., 1970; Watters, 1970, 1976; Slominski et al., 1971; Slominski and Gojmerac, 1972; Green, 1973; Tauthong, 1975). Also, much data are available in the literature on the amounts of initial malathion deposits in grain and cereal products as well as the quantities of residues remaining at different time intervals after application. There is, however, very little or no adequate information on the rates of uptake of these potential grain protectants by food grains stored on treated structural surfaces as well as the amounts and nature of insecticide residues remaining in grains of different moisture contents, and in cereal products.

As an essential prerequisite for regulating the proper use of agricultural chemicals, determination of residue levels in treated commodities intended for human or animal consumption is necessary to assess both the efficacy of pest control measures and adherence to established tolerances. The persistence of these organophosphorus insecticide residues on storage structures and their translocation in stored grain and grain products is therefore an important subject which requires investigation. The results obtained from such a study would be of value from the point of view of practical insect pest control in stored grain, of determining the extent of contamination of the stored grain, and of safety to consumers.

CHAPTER II

LITERATURE REVIEW

Organophosphorus chemicals comprise an increasingly important class of insecticides that have gained wide acceptance for protecting stored products against insect infestations. Their rapid degradation under certain environmental conditions poses much less of a residue hazard than the organochlorine insecticides. Apart from their chemical nature and type of formulation, the persistence and biological effectiveness of residual insecticides used for the protection of stored products are influenced by the type of surfaces on which they are applied, the moisture content and temperature of the stored commodity being protected, the rate of penetration of insecticides within grains and on structural surfaces, and environmental factors such as temperature and relative humidity.

1. Persistence of malathion, bromophos, and iodofenphos on structural surfaces

Residual insecticides may be used for spraying walls, floors and ceilings of warehouses or storage rooms in order to control an insect infestation or to confer long-term protection on insect-free commodities against infestation. The surface on which an insecticide is applied influences the persistence and therefore the toxicity of the deposit. This phenomenon has been observed for a number of building materials commonly present in the interior surfaces of processing plants, granaries, storage bins or warehouses.

Malathion, bromophos, and iodofenphos are considered safe for use as residual protectants applied on infested stored grain (Rowlands, 1967, 1975) but little use seems to have been made of iodofenphos in storage practices. However, various research reports have shown that the practical insecticidal value of these compounds is modified significantly by the type of surfaces on which they are applied. Though bromophos is reported to be less effective than malathion against *Tribolium confusum* Jacquelin duVal and *T. castaneum* (Lemon, 1966), Immel and Geisthardt (1964) claimed that it is very stable under alkaline conditions and has a long residual effectiveness on lime-washed walls.

Parkin (1966) used bioassay to study the persistence over eight months of malathion, fenthion, chlorthion, and diazinon on surfaces of the type commonly found in warehouses when applied as water-dispersible powders. He found that malathion had a very poor stability on cement, whitewash and tile, but it persisted for up to four months on wood and sacking. Burkholder and Dicke (1966) also stated that malathion treatments on concrete blocks were effective for less than one week against larvae of black carpet beetle, *Attagenus megatoma* (F.).

In a laboratory experiment, bromophos gave a longer residual life than either malathion or fenitrothion when applied as a WP on concrete surfaces (Lemon, 1967). The toxicity of malathion applied at 0.75 g/m^2 on concrete was negligible after one week against *T. confusum*, whereas bromophos, at the same deposit, produced 96.8 percent mortality after 24 weeks. At 1.5 g/m^2, bromophos showed almost complete control up to 40 weeks after treatment. This laboratory result was confirmed by field experiments showing that malathion at 1 g/m^2 provided complete control of *C. ferrugineus* on wood floors but inadequate control on concrete floors, whereas bromophos was effective on both wood and concrete floors (Anon., 1974b). Again, observations in a granary treated with bromophos WP showed a fall in residual effectiveness after 16 weeks against *T. castaneum* exposed for 3 hours to treated surfaces while even after 46 weeks there was good control of wandering saw-toothed grain beetle, *Oryzaephilus surinamensis* (L.), and granary weevil, *Sitophilus granarius* (L.), which were originating in large numbers from the under-floor residue of infested barley intentionally left untreated (Hope *et al*., 1970). Cogburn (1972), however, reported that at 1.26 g/m^2, malathion was over 90 percent effective for two weeks and at 2.5 g/m^2 it was 95 percent effective for five weeks against *T. confusum* on concrete floors in a Gulf of Mexico port warehouse.

In a test similar to that of Lemon (1967), Erakay and Ozar (1975) carried out laboratory tests on the effectiveness of malathion WP and bromophos WP applied at 1 g active insecticide (AI)/m^2 on concrete, plaster and wood surfaces against adults of *S. granarius*, *Rhyzopertha dominica* (F.), and *T. confusum*. Both insecticides were equally effective against all the test insects on wood surfaces. On concrete, malathion remained 100 percent effective against all species for up to 21 days but bromophos began to lose its effectiveness against *T. confusum* after the 7th day and had lost much of it by the 28th day. Both chemicals were found equally effective on plaster against *S. granarius* and *R. dominica* but bromophos was again less effective than malathion against *T. confusum*.

Watters (1976) studied the persistence of malathion (EC) and bromophos (WP) applied at the rate of 1 g/m^2 AI on concrete, metal, fir plywood, and maple hardwood floor surfaces under granary conditions. The results of insecticide persistence on the treated surfaces assessed by 24-hour exposures of *T. castaneum* adults showed both insecticides as being fully effective (100% mortality) on metal surfaces for 40 weeks. Malathion was again effective on fir plywood surface for 40 weeks but on maple hardwood floor it provided 100 percent mortality up to four weeks. It lost its residual toxicity against the test insects on concrete surfaces at one week after treatment. Bromophos remained effective on fir plywood for 18 weeks and on the concrete and maple hardwood floor for four weeks. Its persistence on concrete surfaces and maple hardwood floor was longer than malathion.

Iodofenphos has shown considerable promise for control of endemic populations of insects under various situations. In tests in which laboratory-reared *Trogoderma* larvae and *Tribolium* adults were exposed for 48 hours to concrete blocks sprayed at 0.5 g/m^2 in a warehouse with iodofenphos, the treatment remained toxic to the insects for about seven weeks, whereas the standard DDT treatment lost its effectiveness against *Tribolium* after four weeks and against *Trogoderma* after two weeks (Riley and Cornes, 1969).

Iodofenphos has been used both as an EC and as a WP for the control of *O. surinamensis* and other stored-product insects in granaries (Gradidge *et al.*, 1970). When applied as WP spray at the rate of 80 mg AI/ft^2 (0.86 g AI/m^2) to the internal surfaces comprising of brick and plaster of an old wooden barn, the insecticidal deposit remained active for the entire 6-week period against a heavy endemic population of *O. surinamensis* and a smaller number of other insect species. This surface treatment was also highly effective against the yellow mealworm, *Tenebrio molitor* (L.). The application of iodofenphos EC at 75 mg AI/ft^2 (0.81 g AI/m^2) to surfaces that included brick, concrete, wood, asbestos, and galvanized metal of a clean modern granary, showed that the residual deposit was again highly effective against O. surinamensis, and by the 5th week had almost eliminated the pest population. At this rate of application, the deposit protected newly harvested, uninfested grain stored in a granary for the 14-week period of observation.

Girish et al. (1970) studied the efficacy and residual toxicity of iodofenphos and malathion against adults of S. oryzae, T. castaneum, R. dominica, and larvae of Trogoderma granarium Everts using doses of 0.25, 0.5, 1.0, and 1.5 g AI/m^2 on cement concrete slabs and jute bags. The studies showed that iodofenphos was comparatively more persistent on both concrete slabs and jute bags than malathion, and it exhibited a fairly high contact toxicity to the four species at all dosages tested. Malathion, on the other hand, showed slightly higher toxicity on jute bags than on concrete slabs.

Tauthong (1975) in his laboratory evaluation determined the persistence of malathion, bromophos, and iodofenphos on fir plywood surfaces for protection against five species of stored-product insects. At the rate of 1.0 g/m^2, there was complete control of C. ferrugineus exposed 24 hours on surfaces treated with both insecticides 52 weeks after treatment. Bromophos was, however, less effective against T. castaneum than malathion and iodofenphos. Bromophos and iodofenphos gave 100 percent mortality of C. ferrugineus over 80 weeks but against T. castaneum, malathion and iodofenphos were the most effective compounds. Bromophos lost its residual toxicity to T. castaneum after 80 weeks. Iodofenphos was the most persistent insecticide against all species tested, and although bromophos was the least effective of the three insecticides, its persistence over a 52-week period was enhanced when dosage was increased to 2.5 g/m^2.

Iordanou (1976) also found that iodofenphos applied at the rate of 1 g toxicant/m^2 a week before grain was introduced into a storehouse heavily infested with *Trogoderma* larvae gave good protection to the grain.

Malathion, bromophos, and iodofenphos appear to be more stable on surfaces that are almost neutral. Using filter paper as a substrate malathion, applied at 0.86 g/m^2, persisted for 16 months against *S. granarius*, *T. castaneum*, and *O. surinamensis* (Parkin and Scott, 1960). Similarly, high mortalities of *T. confusum* were obtained for 16 weeks on filter papers treated with malathion and bromophos at 0.75 g/m^2 (Lemon, 1967). Iodofenphos applied as an EC to filter papers at doses of 0.01 - 0.15 percent showed effectiveness against a wide range of stored-grain insects (Nawrot, 1969). Parkin (1966) reported that malathion applied on wood and sacking at 0.43 g/m^2 persisted up to four months; El - Rafie *et al*. (1975) found that when applied to whole wheat flour in cotton bags at 684 ppm, it appeared to be a promising treatment for protecting the flour for more than three months against *T. castaneum* infestation. In a small scale trial in which bromophos and lindane/malathion were sprayed at the rate of 3 g AI/m^2 either directly on the bags or on a hessian sheet which covered the stacks, bromophos was more effective against the tropical warehouse moth, *Ephestia cautella* Walker, during a two-month storage period than the standard treatment with lindane/malathion (Schulten, 1970). In a large scale trial where bromophos was applied to bagged maize at a rate of 0.75 g AI/m^2 at monthly intervals, the control of *E. cautella* on bromophos treated stacks was again superior to the lindane/malathion treatment at weekly intervals. However, bromophos treatment of bags or hessian sheets at 0.5 g AI/m^2 was less effective in protecting the stored maize against this insect pest than the routine lindane/malathion treatment (Schulten, 1973). Malathion has also been found to be stable on glass, masonite and plywood (Anon., 1973).

Parkin and Hewlett (1946) showed that films of pyrethrum or DDT in Shell Oil P_{31} deposited on certain common building materials rapidly lost their toxicity to *T. castaneum*. They also reported preliminary tests which showed that the persistence of toxicity could be greatly increased by pretreating the surface of such materials with a suitable substance such as starch paste before application of the insecticides. This phenomenon of mixing additives to insecticides to prolong the insecticidal activity had been tried with some success by several workers. Malathion residues on unpainted concrete surfaces were effective for less than one week but when the concrete surfaces were painted with "Sher-gide" the residues of both EC and WP formulations were effective against dermestid larvae for 17-20 weeks longer than when concrete surfaces were not painted (Burkholder and Dicke, 1966). The silicone waterproofing material applied to concrete bricks, however, was not completely effective in extending the effective time of toxicity for the malathion EC but it did extend the time for the WP formulation to two weeks. Tyler and Rowlands (1967) used sodium carboxymethyl cellulose as a stabilizer and found that by incorporating 0.5 percent of this compound in malathion, the effective residual life of the sprays improved from less than one week for the EC and four weeks for the WP to 14 weeks. They attributed this improvement in persistence partly to the absorption of both malathion and hydroxyl ions by the cellulose, thus preventing their interaction and consequent breakdown of malathion, and also partly to a reduction in absorption into the porous substrate. Slominski and Gojmerac (1972) using larvae of black carpet beetle, A. megatoma as the test insect also noted that pretreating concrete and other alkaline surfaces with certain materials minimized malathion detoxification. Their research indicates that malathion, which is unstable on concrete, remains toxic for a month or two on painted surfaces or those treated with talc or calcium carbonate.

Recent evidence has shown that concrete surfaces become less alkaline with age; washing the surfaces and the accumulation of dust and other debris tend to stabilize the insecticide and prolong the effectiveness of deposits. Thus, Okwelogu (1968) attributed the loss of toxicity of malathion on concrete to high pH, and showed with bioassay tests that the residual toxicity of malathion on concrete can be enhanced by decreasing the alkalinity of the concrete through washing with water. Watters (1970) also presents evidence from bioassay that the accumulation of successive layers of grain dust on the concrete floor of a terminal grain elevator prolonged the residual toxicity of bromophos and malathion for over 10 weeks. The author relates the unexpected prolonged effectiveness of the insecticides to the low pH (5.9 - 6.2) of the concrete surface and by cool floor temperature of 10 - 12°C. He also noted that after 33 weeks bromophos treatment on painted areas exhibited more toxicity than malathion treatment which was, however, superior to bromophos on unpainted areas.

In tropical and subtropical areas of the world outbreaks of stored-grain insects occur frequently because of high temperatures and the lack of effective means of control. In some cases above-average harvests force farmers and traders to use unsuitable buildings and containers for temporary storage. A combination of treatment of building surfaces and the admixture of grain with approved insecticides have been found as effective methods of controlling insect infestation. In Cyprus, Iordanou (1976) found that iodofenphos applied as a wall treatment at the rate of 1 g/m^2 supplemented by grain treatment with malathion dust at 10 ppm considerably reduced existing insect infestation during storage of the grain. It was also found that wall treatment with malathion or bromophos was inadequate for stored grain protection unless supplemented by malathion grain treatment. The combination of admixture treatment of maize with a bag impregnation technique using pirimiphos-methyl has also been observed to effectively protect the grain from further insect damage for 12 months (Morallo-Rejesus and Eroles, 1976).

2. Persistence of insecticide residues in grain and grain products

Insecticides are often mixed with the produce to provide protection for a long period and to kill insect pests which have already infested the stored produce. Malathion has been the insecticide of choice in several countries over the past decade for admixture treatment of stored grain, but the use of bromophos, iodofenphos or pirimiphos-methyl is becoming more prevalent in certain countries for the control of malathion-resistant strains of stored-product insects since the mammalian toxicities of these insecticides are comparable with that of malathion.

Insecticide applied as a dust or spray for post-harvest protection of stored product against insect infestations is relied on for residual effectiveness and, depending upon storage conditions, protection may last from several months to an entire season. Lindgren *et al.* (1954) thus reported from laboratory experiment that malathion applied at 2 ppm to wheat containing 10.0 percent moisture was effective against *S. granarius*, *S. oryzae*, and *R. dominica* for two months, and when applied at 8 and 16 ppm it remained effective for six to seven months. Malathion applied at 2 ppm to wheat of 13.5 percent moisture content also provided complete control of *C. ferrugineus* for eight months (Watters, 1959).

Bang and Floyd (1962) reported that malathion applied as a dust or spray at 8 ppm gave excellent control of *S. oryzae* for five months in stored polished rice. Four ppm also gave complete protection from *C. pusillus* (Schonh) but was less effective against *T. castaneum*.

Wheat grains having 13.0 percent moisture content were mixed with malathion at rates of 8, 16, and 24 ppm, stored at 78°F (25.6°C) and sampled for chemical analysis immediately after treatment and at four successive monthly intervals (Lal and Beri, 1964). The initial average residues measured 6.36, 13.40 and 21.23 ppm in the 8, 16 and 24 ppm treatments, respectively, and declined to 0, 0.45 and 0.78 ppm after four months of storage.

Teotia and Singh (1966) carried out tests in India on the immediate and residual action of malathion dust at 1 - 5 ppm against *S. oryzae* in stored maize and rice grain, and in maize on the cob. The results of bioassay in which adults of *S. oryzae* were confined in the grain for 48 hours in batches of 25 per 100 g, immediately after treatment and at monthly intervals thereafter, showed that the minimum amounts of insecticide initially giving total mortality of the weevils were

2 and 3 ppm in maize and rice, respectively. The effectiveness of malathion was found to decline more rapidly in rice than in maize but it lost much of its toxicity after one month. In a further experimental study, malathion applied at 4 ppm to freshly harvested maize ears afforded complete control of S. oryzae to the end of the experiment.

An evaluation made in small-bin laboratory tests of the protectant properties of malathion applied at two rates to insect-infested sorghum grain showed that malathion was not able to give adequate protection against insect damage for the whole 12-month storage period (LaHue, 1967). It was found that the residues degraded rapidly and, as determined by insect infestations in the bins, became non-toxic in 3 - 6 months, at which times the residue levels were about 1.5 ppm. The non-toxicity of malathion residues of less than 1.5 ppm was also indicated in special toxicity tests with S. oryzae.

In a test of malathion as a possible alternative to the use of BHC, a 1 percent malathion dust was incorporated at the rate of 10 ppm into the top six inches of maize in a silo previously fumigated with phosphine (Adesuyi, 1969). Samples of maize grains taken at intervals after treatment, both for detection of naturally occurring insect infestations and for exposure to laboratory-reared adults of S. zeamais and T. castaneum revealed that the residues were effective for 15 weeks against S. zeamais but only for one to two weeks against T. castaneum. It was also observed that infestation from outside by T. castaneum and Cryptolestes sp., but not S. zeamais, occurred from the ninth week after malathion treatment.

El-Rafie et al. (1969a) carried out studies to evaluate the effectiveness of four insecticides in dusts for controlling insect pests of stored wheat and maize. The results judged by the average percentage infestation during storage indicated that the malathion treatment gave good protection during the 10-month period. In a similar study, El-Rafie _et al_. (1969b) found that the rate of degradation of malathion was faster on maize than on wheat, and in grains stored in bags than those stored in silos.

In an investigation on the effectiveness of malathion and lindane as protectants for stored wheat against damage by _C. pusillus_, groups of 100 adults of this species were confined in 150 g samples of grain treated with malathion at 2, 4, 8, 16 and 24 ppm, and 2, 4 and 6 ppm of lindane immediatley after treatment and at monthly intervals thereafter (Srivasta and Srivasta, 1970). Malathion at 16 - 24 ppm was found to cause complete mortality for three months, and at 8, 16 and 24 ppm caused 25, 40 and 36 percent mortality, respectively, after six months. Lindane at 4 - 6 ppm produced complete mortality up to 10 months and 94 - 98 percent after 12 months.

In laboratory tests the effectiveness of malathion dust applied at 3 and 5 ppm to wheat was evaluated against dust of phoxim and phenthoate at 5 and 10 ppm for the protection of stored grain against damage by _S. granarius_, _S. oryzae_, _T. castaneum_ and _T. confusum_ (Quintanilla _et al_., 1970). Observation from the bioassay results indicated that malathion at 5 ppm afforded good control of _Sitophilus_ spp. for about 10 months and of _Tribolium_ spp. for about three months.

McGaughey (1971) tested residual effectiveness of aqueous dilutions of malathion as a 57% EC at 11, 17 and 20 ppm in protecting milling fractions of three varieties of rough rice for up to 12 months against infestation by _T. confusum_, _R. dominica_, and _S. oryzae_ in a warehouse by means of bin and jar tests under the commercial storage conditions found along the Gulf coast in Texas. Generally, it was found that malathion at the three concentrations gave protection for 6 - 12 months, the protection lasting slightly longer in the bin tests than in the jar tests. Malathion residues of 8, 4 and 2 ppm were required to kill the three pests, respectively. The author also noticed from residual analysis that after applications to give 20 ppm, residues on rough rice were initially 20 ppm but decreased to below 8 ppm after three months, and those on hulls were initially 80 ppm but decreased to below 8 ppm after 11 months. The residues on bran, initially at 20 ppm, increased for three months, reaching peak of 30 ppm, and then decreased to below 8 ppm after 10 months; malathion residues on milled rice, initially at 0.2 ppm, increased to a peak of 0.32 ppm after three months and then decreased to 0.1 ppm after nine months. The retention of malathion residues on the three varieties of rice tested was found to be dependent on the relative surface area and thickness of the covering hull. Udeaan and Bindra (1971) also studied the malathion residues in different fractions of cereals and their finished derivatives by treating paddy, wheat, maize, and pearl-millet grains with 50% premium grade malathion EC at 20, 30 and 50 ppm. They found that in the case of wheat and maize treated at the above dosages, a major portion of residues remained in the bran, while the flour contained residues below 8 ppm.

On wheat of 12.0 percent moisture content, in storage, malathion had an average residual half-life of 5.6 months (Gunther _et al._, 1958). Schesser _et al._ (1958) also found half-life of malathion applied to wheat at a rate of 2.5 - 7.5 ppm as 5.5 months whilst Gunther and Jeppson (1960) calculated half-life of malathion residues in stored wheat from the investigation of several workers as 150 to 190 days.

Lemon (1967) carried out studies on the persistence of dust formulations of malathion, fenitrothion and bromophos on wheat at 12.0 percent moisture content using S. granarius as the test insects. Bromophos was found to be the least effective of the three compounds over a period of eight weeks at all dosages tested.

Joubert and De Beer (1968) in their comparative studies on persistence of two dosage levels of bromophos with pyrethrum and malathion on maize, reported that bromophos at 5 and 10 ppm AI afforded excellent control against S. oryzae, T. castaneum, O. surinamensis, and E. cautella over a storage period of 50 weeks under the subtropical conditions of South Africa. R. dominica was, however, not completely controlled by the 5 ppm rate. The authors also found bromophos treatments survived a 50-week bulk storage period without an appreciable infestation or increase in the percentage of internal damage.

Green et al. (1970) in assessing bromophos for the protection of wheat and barley, applied bromophos in water-based emulsion at 8, 16 and 24 ppm to clean bagged wheat and barley of 14.0 and 13.0 percent moisture content, respectively, which were exposed to heavy infestations of O. surinamensis and S. granarius, and at 9 or 20 ppm to infested wheat containing 15.0 percent moisture stored in bulk on a farm. Biological and chemical assays showed that bromophos residues broke down more quickly on infested bagged wheat and barley stored at 25°C than on cooled wheat stored during the winter on the farm. The bioassay on samples from bagged grains showed that the bromophos residues were effective against the test insects at lower concentrations on barley than on wheat. There was, however, a sharp decline in biological effectiveness after 16 weeks in 8 ppm treatment and after 24 weeks in the 16 ppm treatment. The 24 ppm treatment was fully effective against O. surinamensis for 36 weeks and against S. granarius for 24 weeks. The farm grain treated at 9 ppm remained effective against O. surinamensis for up to 12 months.

Large-scale laboratory studies on wheat treated with bromophos at 8 or 12 ppm and stored at temperatures usual in grain kept in bulk storage over a period of a year in temperate regions showed a degradation rate of 40 to 50 percent after 12 months (Eichler and Knoll, 1974). The metabolism studies which were limited to the analysis of bromoxon (the oxygen analogue) and 2,5-dichloro-4-bromophenol in wheat revealed that the second compound was the only one that could be detected, and was found at rates below 1.0 ppm. On examination of milled products, it was established that bromophos penetrates into the inner layers of the grains, causing higher residues in the coarse bran and semolina bran. The flour was only slightly contaminated.

Adesuyi and Adeyemi (1973) compared the residual effectiveness of malathion, bromophos, and iodofenphos for the control of insect infestations on maize stored in cribs with a view to finding a substitute for BHC dust which is mostly used. Malathion, bromophos, and iodofenphos applied at 30, 20 and 20 ppm, respectively, to stored maize were used. Monthly samples from each treatment analyzed for percentage insect damage showed that malathion and iodofenphos were effective for nine months and bromophos for seven months. None of the insecticides was found to give complete control but each was more effective than BHC at 10 ppm when compared with the results of past trials.

Iodofenphos at 10 ppm was found to give complete protection of bagged wheat and barley for about 20 weeks against O. surinamensis and S. granarius (Kane et al., 1973).

LaHue (1975) also estimated the relative effectiveness of iodofenphos applied to hard winter wheat, shelled corn, and sorghum grain, containing 12.5 percent moisture, at rates of 5, 10 and 20 ppm AI against the standard malathion treatment at a dose of 10 ppm AI for protection against S. oryzae, an internal feeding insect. Iodofenphos applied at a rate of 10 ppm gave excellent protection to corn for 12 months even though an F_1 progeny did emerge. Sorghum was better protected also by the 10 ppm iodofenphos than by the 10 ppm standard malathion, but the residual effectiveness decreased gradually during the 12-month storage. Wheat was not well protected by the 10 ppm treatment of both insecticides but iodofenphos at 20 ppm protected it for 12 months.

Krishnaiah et al. (1976) in their studies on relative efficacy of fenitrothion, malathion, gardona, and iodofenphos observed the latter compound was least effective and slow in killing the insects. It was further observed that 2 ppm of malathion was quite effective to protect grains for quite a long period as against 5 ppm of iodofenphos.

Chawla and Bindra (1971) evaluated the suitability of several organophosphorus insecticides as grain protectants against three major insect pests of stored wheat. The results of the six months of analysis revealed that pirimiphos-methyl was the most persistent compound. The residues of bromophos and iodofenphos were, however, observed to dissipate at a faster rate like those of malathion.

Field trials conducted in the United Kingdom showed that pirimiphos-methyl at 4 ppm gave good control of O. surinamensis, S. granarius and T. castaneum in wheat stored in small sacks in a building in which severe infestation pressure was artificially sustained over the six months duration of the experiment (Anon., 1974a). In laboratory tests in Australia, pirimiphos-methyl at 5 ppm AI gave complete control of S. granarius and T. confusum in wheat for five months and was superior to the 103% malathion EC normally used by bulk handlers. Similar laboratory tests showing greater efficacy of pirimiphos-methyl than the conventional insecticides approved for use against stored-product insect infestations have been demonstrated in Argentina, Cyprus, Guyana, Malaysia, Indonesia and the United States. Mixture of pirimiphos-methyl with rice at 4 ppm controlled any pests already present and protected the grain stored in sacks from other insects for up to six months (Seth, 1974).

Cogburn (1976) compared the control of stored-product insects with pirimiphos-methyl applied at 5, 10 or 15 ppm directly to rough rice with the control obtained with 14 ppm malathion when the treated rice was stored in fibreboard drums and subjected to constant, heavy infestation pressure for 12 months. Pirimiphos-methyl at 10 and 15 ppm protected the rice from infestation by T. castaneum, S. oryzae, R. dominica and S. cerealella for 12 months but malathion was ineffective in protecting the grain from a malathion-resistant strain of S. cerealella.

Redlinger (1976) reported that residues of pirimiphos-methyl degraded at a rate approximately 33 percent less than malathion during a 12-month period when the effectiveness of pirimiphos-methyl applied to unshelled groundnuts was assessed against the standard malathion treatment for the control of 10 species of stored-product insects.

LaHue (1977a) evaluated the relative effectiveness of pirimiphos-methyl residues applied to hard winter wheat as a water emulsion at gradient doses from 1 to 10 ppm AI to determine the minimum effective dosage required to kill the adults of *T. castaneum*, *T. confusum*, *S. oryzae* and *R. dominica*. Doses of 3 ppm or greater caused complete mortality of *S. oryzae* while 4 ppm or more gave excellent control of *T. castaneum* for 12 months. Residues of 6 ppm caused 97.0 percent mortality of *R. dominica* for six months but 8 ppm or more were required to give 90.0 percent or greater control at 12 months after treatment; for *T. confusum* doses of 8 ppm or more were required to give an effective control for 12 months. LaHue and Dicke (1977) and LaHue (1977b) again reported that after 12 months' storage about 50 and 83 percent of pirimiphos-methyl residues remained on sorghum grain and wheat, respectively, when applied to the grains at the rates of 8.4 and 7.8 ppm AI.

Various workers have observed that the efficacy and persistence of insecticides used for admixture treatment of stored grain to protect it against insect infestation are closely related to the distribution of insecticide amongst the grain (Tyler *et al*., 1969; Green, 1969; Green *et al*., 1970; Rowlands, 1971). The biological and chemical assays of single grains from practical trials with bromophos indicated that complete control of *O. surinamensis* was achieved when only four percent of the grain carried an effective dose (Green *et al*., 1970); Minett and Williams (1971, 1976) in their laboratory and field trials also indicated that treatment of a small proportion of wheat bulk with a high concentration of malathion was a more effective method of treatment for control of stored-grain insects than the conventional method of treating all grains uniformly with the same overall level of insecticide. In a laboratory experiment, the authors showed from results of bioassay that treating 1 or 2 percent of grains in a bulk with malathion gave protection against _S. oryzae_ and _T. confusum_, when an overall level of insecticide of about 10 ppm was applied to the grain. In a large-scale field trial, they again showed that grain pretreated with malathion at 750 - 800 ppm and added to untreated grain to obtain overall one percent of pretreated grain in the bulk remained effective against _T. castaneum_ and _S. oryzae_ throughout the 10-month storage period of grain in silos. The conventional method of treatment failed to prevent infestation by _S. oryzae_ after six months of storage.

Quinlan (1972) attempted to apply malathion uniformly as a thermally generated aerosol to insect-infested corn in storage and found that the uniform treatment of malathion to all grains was less effective than treatment of a small proportion of grain bulk with a high concentration of malathion.

3. <u>Uptake and/or translocation of malathion, bromophos and iodofenphos into stored products</u>

The main reason for using residual contact insecticides for spraying storage premises is to control existing insect infestations and to protect the stored produce from damage by insects. Beri and Lal (1965) studied the extent of uptake of malathion by stored grains from surface dusting of the bags with malathion at the rate of 1.68 g/ft^2 (18.08 g/m^2) and stored under room conditions. It was found that 1.65 ppm of malathion residues translocated into the peripheral layer of the stored grain after 15 days but the residue was only 0.88 ppm one month after dusting.

Cereals in contact with surfaces treated with lindane and methoxychlor vary in the rates of insecticide uptake according to the type of cereal, type and formulation of insecticide applied and the type of surface (Watters and Grussendorf, 1969). Their study over a 24-week period showed that the uptake of lindane into cereals stored on concrete, wood and metal surfaces was higher than that of methoxychlor. The uptake of lindane by barley was higher than by wheat or oats and also lindane applied to surfaces as dispersible powders tended to move rapidly and in greater amounts into cereals than from lindane applied as oil solution. More methoxychlor was also recovered from barley and oats than wheat. There was a similarity in the rates of uptake of lindane by wheat stored on wood and metal, whereas greater amounts of methoxychlor were taken up by wheat stored on metal surfaces than on wood and concrete.

In a similar study, Watters (1976) examined the rate of uptake into wheat of malathion EC and bromophos WP applied at 1.0 g/m^2 to hardwood floor surfaces in a farm granary. The rates of uptake of insecticide residues were determined by analysis of core wheat samples 8-cm deep and weighing 125 g. The results of the study over a period of 40 weeks indicate an increase in the uptake of bromophos from 0.28 ppm after 18-week storage to 0.47 ppm after 40 weeks but malathion showed no increased uptake after the 4th week. The author also noticed that the greatest amounts of insecticide residues were recovered in the bottom 8-cm layer of wheat in contact with the treated surface. There was however, negligible uptake of bromophos or malathion by wheat beyond the 8-cm layer of grain.

4. Factors affecting persistence of residues in stored products and on surfaces

The persistence and toxicity of insecticide residues in stored products and of the deposits on structural surfaces are governed by many factors such as storage temperature, moisture, nature of the surface, type of formulation,and method and rate of application.

Higher moisture and storage temperatures generally result in more rapid breakdown of grain protectants, particularly organophosphorus compounds, largely by stimulation of enzyme activity (Rowlands, 1967) in which the major mode of degradation is hydrolysis (Orth and Minett, 1975). Watters (1959) found that malathion in wheat lost its insecticidal properties more quickly when the grain moisture content exceeded 13.5 percent. Malathion applied to wheat of 13.5 percent moisture content at 2 ppm, was as effective as malathion applied at 16 ppm to wheat of 15.5 percent moisture content against C. ferrugineus; malathion was ineffective when applied at 16 ppm to wheat at 18.0 percent moisture content. This is thought to be due to the more rapid decomposition of malathion under conditions of higher moisture content (Malathion Panel, 1960).

Strong and Sbur (1960) working on the effect of moisture content, storage temperature and the interrelation of moisture and dosage on the effectiveness of malathion in protecting stored wheat against S. granarius, S. oryzae and T. confusum observed that the residual effectiveness of malathion was much reduced by high grain moisture and storage temperature. They reported that the residual effectiveness of malathion applied to wheat at 10 ppm was higher at 10°C than at 50°C, and it would remain effective against insect infestations for at least 12 months when storage temperature was not higher than 15.6°C and moisture content of wheat did not exceed 14.0 percent at this initial dosage. Koivistoinen (1961) also noted that the temperature of storage had a marked effect on malathion disappearance, with greater losses occurring at about 20°C than at about 4.0°C when apples and beans were treated with malathion after harvest. Godavari Bai (1964) in his studies on the persistence of malathion residues on treated food grains under different conditions of storage and processing found that both high temperature and relative humidity result in loss of malathion on the grains and milled materials during storage. The results also revealed that moisture content of the materials play a major role in the decomposition of malathion. Tests carried out in France on the effect of grain humidity on the control of *S. granarius* afforded by sprays of malathion applied at 0.80 g toxicant per quintal to wheat stored with moisture contents of 13.5, 14.0, 15.6 or 17.1 percent, revealed that the rapidity with which malathion spray lost its effectiveness during a 13-week period was in direct relation to the moisture content of the grain, and that artificial drying of damp grain improved the persistence of the chemical (Coulon, 1966).

Using data from chemical assay, Minett *et al*. (1968) demonstrated temperature and moisture dependence of malathion breakdown on wheat. They showed from residue analysis the critical moisture content for malathion breakdown on wheat of about 11.5 - 12.0 percent, above which the loss of malathion increased more rapidly with increasing moisture content. At increasing storage temperature, degradation of malathion was found to increase, particularly at high moisture levels. Storage of treated wheat at low temperature and low moisture levels, on the other hand, resulted in conservation of the malathion applied as grain protectant and consequently insect damage was limited. Orth and Minett (1975) also observed that when increased storage temperature and moisture were simultaneously involved their effects on malathion breakdown were additive.

Champ et al. (1969) in their comparative studies of four organophosphorus insecticides for control of S. oryzae and R. dominica in wheat reported that an increase of temperature from 25 to 30°C effected a 1.5 potency increase for malathion at grain moisture contents from 11 to 13 percent. Biological assessment of the residual activity of malathion using S. oryzae showed malathion residues dropping to lowest levels with a marked and uniform rate of depletion of the toxicant with increase in time, temperature and moisture content. Higher storage temperature and increased moisture content causing a rapid breakdown of malathion residues in grain sorghum has also been reported by Kadoum and LaHue (1969).

Bromophos, although less frequently used than malathion as an admixture for protection of stored grain, is relatively stable on damp grain (Rowlands, 1967). At 16.5 percent moisture content, the residual life of bromophos is longer than that of malathion and fenitrothion. Green et al. (1970) also assessed the influence of moisture content of the grain on persistence of bromophos and malathion by comparing their effectiveness when applied at 10 and 20 ppm to warm moist grain in the laboratory against O. surinamensis. Applied to wheat of 18.5 percent moisture content and stored at 30°C, bromophos lost effectiveness after six weeks to the same extent as malathion after two weeks. The high dosage rate did not give longer protection with either compound. Eichler and Knoll (1974), in studying the degradation of bromophos in stored wheat, observed that the type of formulation and the degree of moisture content of the stored grain have no significant influence on the degradation of the compound when the treated wheat was stored at an average temperature of 15.0°C. However, by increasing the storage temperature to 26.0°C, the rate of decomposition is significantly increased.

In laboratory studies, Wilkin et al. (1973) compared the periods of effectiveness of malathion and iodofenphos at 10 ppm on English wheat, with initial moisture contents of 14, 16 or 18 percent, and stored at 17.5°, 30° or 35°C. The results of the experiment over a 20-week period showed that iodofenphos applied to the wheat has a longer effective life than malathion against O. surinamensis even on warm moist grain. In comparison with malathion, residual effectiveness of iodofenphos on wheat of 16 and 18 percent moisture content stored at 30°C was 9 and 7 weeks respectively, as against 4 and 2 weeks for malathion under the same conditions. The authors explained that the longer persistence of iodofenphos is associated with much slower rate of breakdown of the compound.

Analytical studies have shown that residues of pirimiphos-methyl on wheat grains are degraded and detoxified by hydrolysis of the phosphorus ester side chain (Anon., 1974a). It was observed from such studies that at a given temperature, the rate of breakdown of the insecticide depended on the moisture content of the grains. When the moisture content was 14.0 percent or less, only 20 percent of the chemical was hydrolyzed in eight months, while at 18.0 percent moisture the extent of degradation was 70 - 80 percent.

When treated grain was stored at 95% relative humidity for two weeks, resulting in a moisture content 16 - 20 percent in the grain, malathion was unstable and consequently ineffective against S. granarius, S. zeamais and S. cerealella even at 20 ppm, whilst under the same storage conditions pirimiphos-methyl showed effectiveness against these species after two weeks with its activity beginning to decline after four weeks (Anon., 1974a). In treated grain stored at a relative humidity of 55% or more, pirimiphos-methyl was again found to be effective against Sitophilus spp., S. cerealella and Plodia interpunctella over 8-week storage period. Malathion at 20 ppm failed to control the Sitophilus spp. in grain stored for eight weeks at the same relative humidity.

The rate at which insecticides penetrate into stored grain can affect the ultimate persistence of their residues. The moisture content of the grain is one of the factors discussed by Rowlands (1967) affecting penetration of insecticide into stored grain. He observed that malathion tends to enter more rapidly into stored grain with moisture content exceeding 14.0 percent, whereas bromophos is taken up faster below this level.

Temperature has a significant effect on the usefulness of many insecticides against most species of stored-product insects. The influence of temperature on insecticide toxicity was determined on impregnated filter papers by Iordanou and Watters (1969). At temperature levels of 26.7°, 15.5° and 10.0°C five species of common stored-product beetles were exposed to deposits of DDT, methoxychlor, lindane, malathion and bromophos for 24 hours, assessing mortality 72 hours after the insects had been returned to flour and kept at the same temperature. Malathion and bromophos showed positive temperature coefficients against all the species. Malathion was the most effective insecticide at all the three temperatures used. Bromophos exhibited minimum activity at 10.0°C; activity increased at 15.5°C level and reached the maximum at the higher temperature. The toxicity-temperature gradient of the insecticide parallelled the biological activities of the insects. At low temperatures, the toxicity of bromophos on Tribolium spp. decreased more than on C. ferrugineus and O. mercator.

Okwelogu (1968) attributed the loss of toxicity of malathion on concrete to high pH. To assess further the extent of alkalinity on the effectiveness of insecticide deposits, the rate of breakdown of malathion and bromophos on concrete surfaces that had various pH levels was determined by bioassay with C. ferrugineus and T. castaneum exposed for 24-hour periods (Anon., 1975). When applied to concrete with a pH 7.0 or 8.5, effectiveness of bromophos WP persisted for 32 days against C. ferrugineus but only for four days against T. castaneum. Bromophos EC was less effective than the WP formulation and persisted for only four days against C. ferrugineus. Application of malathion EC at 2.5 g/m^2 was superior to application rate of 1.0 g/m^2 but the effects lasted for only two days at pH 8.5 and one day at pH 10.0 when tested against C. ferrugineus.

CHAPTER III

MATERIALS AND METHODS

The investigation on the persistence and translocation of malathion, bromophos, iodofenphos and pirimiphos-methyl on structural surfaces and in stored grain was undertaken at the Canada Agriculture Research Station, Winnipeg, and at the Pesticide Research Laboratory of the Department of Soil Science, University of Manitoba, Winnipeg.

MATERIALS

(1) Test insects: The test insects used for the biological assay of the study were adults of susceptible rusty grain beetle, *Cryptolestes ferrugineus* (Stephens) (Coleoptera; Cucujidae) and susceptible and malathion-resistant strains of red flour beetle, *Tribolium castaneum* (Herbst)(Coleoptera: Tenebrionidae) (Figs. 1 and 2).

Source and culturing of insects: The test insects were obtained from standard laboratory cultures of the Cereal Crop Protection Section of the Canada Agriculture Research Station, Winnipeg. These stock cultures have been maintained at the Research Station for more than three years and as far as is known, none of the susceptible strains of insects had any history of exposure to insecticides. The malathion-resistant strain was established from *T. castaneum* collected from an empty bulk carrier cargo ship during an inspection at the port of Vancouver, B.C. on November 19, 1975. The resistance and susceptibility of the test insects were confirmed by discrimination dose tests according to the FAO (1970) methods.

The insect cultures were raised in temperature controlled cabinets maintained at 27.5°C and in which the relative humidity of 63 - 75% was maintained by introducing an open try filled with water.

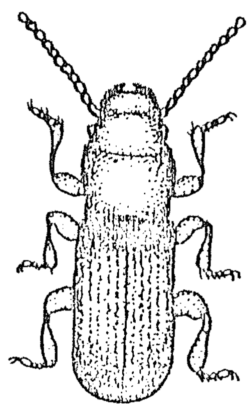


Fig. 1: Cryptolestes ferrugineus
Rusty grain beetle

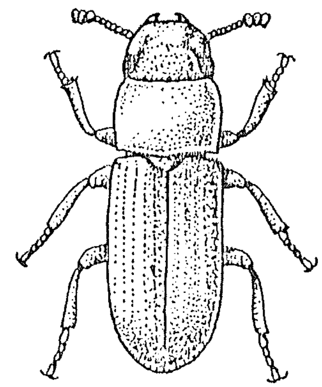


Fig 2: Tribolium castaneum
Red flour beetle

For *C. ferrugineus*, the breeding medium consisted of wheat grains (16.0% moisture content) fortified with 5 percent wheat germ. For breeding, 300 adult beetles (no sexing) were introduced into the breeding medium contained in 2.6 liter (128 fl. oz.) jars and sealed with Whatman No. 3 filter paper (9 cm diameter) and paraffin wax to prevent cross infestation from mites and other insects. The beetles were removed by sifting after 7 days from the culture medium and the culture allowed to stand until adults of new progeny emerged. Successive cultures were raised from the new stock and these were used as the test insects.

T. castaneum was cultured in whole wheat flour under the same conditions used for the rusty grain beetle. Cultures of 200 beetles (no sexing) per culture medium were set up and after 7 days of egg laying the beetles were sifted from the medium and the culture allowed to stand until new adult beetles had emerged. Similar new cultures were raised from the new stock for the study.

A summary of the culturing media, temperature and adult age at test for the two test species is given in Table 1.

Groups of 500 adults of each test insect were maintained in culture media until they were about 3 - 5 weeks old at which age they were used for the study. As far as possible this age was kept constant throughout the experimental period.

TABLE 1. Culturing media, temperature and approximate age for the test species

Species	Source	Resistant type	Culturing medium	Rearing temperature (°C)	Adult age at test (weeks)
C. ferrugineus	Canada Agric. Research Station, Laboratory stock, Winnipeg	Susceptible	Whole wheat grains + 5% wheat germ	27.5	3-5
T. castaneum	Canada Agric. Research Station, Laboratory stock, Winnipeg	Susceptible	Whole wheat flour	27.5	3-5
T. castaneum	M.V. 'Sun Chong', Vancouver	Malathion-specific resistance	Whole wheat flour	27.5	3-5

TABLE 2. Details of insecticides used.

Compound	Alternative name(s)	Chemical designation	Type of formulation	Source of availability
Bromophos	Brofene Cela S-1942 Nexion	O-(4-bromo-2,5-dichlorophenyl) O,O-dimethyl phosphorothioate	(a) 40% w/v emulsifiable concentrate (E.C.) (b) 25% w/w wettable powder (W.P.)	Green Cross Insecticides, Winnipeg
Iodofenphos	Alfacron C-9491 Nuvanol N USDA ENT 27408	O-(2,5-dichloro-4-iodophenyl) O,O-dimethyl phosphorothioate	20% w/v E.C.	Ciba-Geigy of Canada Ltd., Montreal
Malathion	Chemathion Cythion	O,O-dimethyl S-1,2 di (ethoxycarbonyl) ethyl phosphorodithioate	(a) 83.6% w/v E.C. (b) 25% w/v W.P.	Cyanamid of Canada Ltd., Montreal
Pirimiphos-methyl	Actellic 7E PP 511	O-[2-(diethylamino)-6-methyl-4-pyrimidinyl] O,O-dimethyl phosphorothioate	84% w/v E.C.	ICI United States Inc., Goldsboro, North Carolina

(2) Test insecticides: The insecticides given in Table 2 were evaluated for their persistence and translocation on structural surfaces and in stored grain.

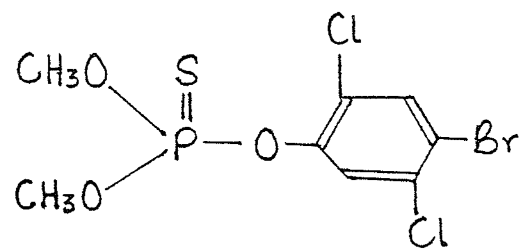
The formulations were diluted with distilled water to provide the required initial deposit (g active ingredient) of the insecticide per square meter when applied to test surfaces at the rate of 0.05 litre/m^2 or when applied directly to the grain as an admixture treatment.

Some chemical and toxicological properties of the insecticides

Bromophos

Chemical name: O-(4-bromo-2,5-dichlorophenyl) O,O-dimethyl phosphorothioate.

Structural formula:



Solubility: Soluble in most organic solvents; in water 40 ppm at room temperature.

Acute toxicity: Acute oral LD_{50} rats = 3750 - 7700 mg/kg body weight;
Acute dermal LD_{50} rabbit = 2181 mg/kg body weight;
Relatively harmless to fish and aquatic life;
Bees have some tolerance.

Chronic toxicity: No clinical symptoms (except cholinesterase inhibition) up to 350 mg/kg/day on rats, and up to 87.5 mg/kg/day on dogs.

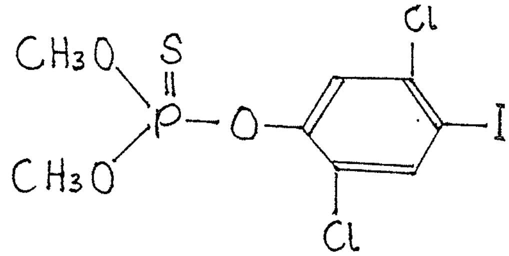
Tolerance in cereals: 10 ppm (Rowlands, 1975; FAO/WHO, 1976a).

Formulations: EC - 25, 35 and 40% A.I. Dusts - 2.3% A.I.
WP - 25% A.I. Granules - 5% A.I.

Iodofenphos:

Chemical name: O-(2,5-dichloro-4-iodophenyl) O,O-dimethyl phosphorothioate.

Structural formula:



Solubility: Soluble in methylene chloride, benzene and acetone; slightly soluble in hexane and isopropanol; its solubility in water is less than 2 ppm.

Stability: Relatively stable in neutral or weakly acidic or alkaline media; unstable to strong acids or alkalies.

Acute toxicity: Acute oral LD_{50} rats = 2100 mg/kg body weight;

Acute dermal LD_{50} rats = 2000 mg/kg body weight;

Low toxicity to birds but toxic to bees.

Chronic toxicity: To hens, applications of 2000 mg/kg twice at intervals of 3 weeks caused no neurotic symptoms.

Tolerance in cereals: 10 ppm (Rowlands, 1975).

Formulations: EC - 20% A.I.

WP - 5, 50% A.I.

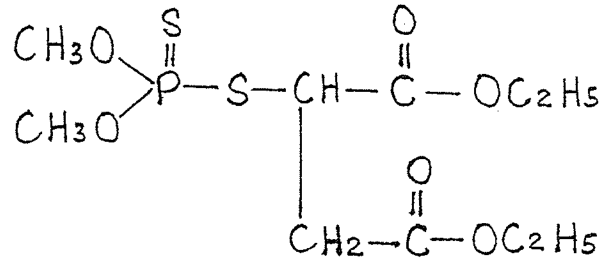
Dusts - 5% A.I.

Others - 20% A.I. dip concentrate, 1% A.I. kerosine spray.

Malathion

Chemical name: O,O-dimethyl-S-1,2 di(ethoxycarbonyl) ethyl phosphorodithioate.

Structural formula:



Solubility: Miscible with most organic solvents and highly aromatic commercial oils; of limited solubility in petroleum oils; solubility in water 145 ppm at 25°C.

Stability: Highly unstable in aqueous solution at pH above 7.0.

Acute toxicity: Acute oral LD_{50} rats = 2800 mg/kg body weight;

Acute oral LD_{50} chickens = 200 - 400 mg/kg body weight;

Acute dermal LD_{50} rats = $>$ 4400 mg/kg body weight.

Chronic toxicity: No cholinesterase inhibition up to 100 ppm in diets of rats.

Tolerance in cereals: 8 ppm

Formulation: EC - 50, 83.6 and 95% A.I.

WP - 25, 50% A.I.

Dusts - 4, 5% A.I.

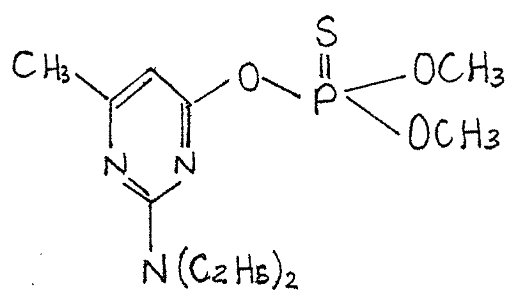
Aerosols - 95% A.I.

Many additional formulations.

Pirimiphos-methyl

Chemical name: O-[2-(diethylamino)-6-methyl-4-pyrimidinyl]O,O-dimethyl phosphorothioate

Structural formula:



Solubility: Miscible with most organic solvents; solubility in water approximately 5 ppm at 30°C.

Stability: Hydrolysed by strong acid or base.

Acute toxicity: Acute oral LD_{50} rats = 2050 mg/kg body weight;
Acute dermal LD_{50} rats = 2000 mg/kg body weight.

Chronic toxicity: Symptoms of poisoning are typical of cholinesterase inhibition.
No toxic effects observed when fed to hens up to 4 ppm in the diet, and pigeons up to 5 ppm in the diet for 28 days.

Tolerance in cereals: 4 ppm (Anon., 1974a; Rowlands, 1975).

Formulations: EC - 25, 50 and 84% A.I.
Dusts - 2% A.I.
Others - smoke generator, diluent-free formulations.

(3) Experimental surfaces

(i) Wood panels: Fir plywood sheets, original 2.44m x 1.42m x 0.6cm (8' x 4' x ½"), good one side, were obtained from a local source. The sheets were cut into square panels which measured 12.2 x 12.2 x 0.6 cm providing a top surface area of $148.84 cm^2$.

(ii) Concrete slabs: Concrete slabs of approximately similar dimensions were cast in plastic moulds from a 3:1 mixture of coarse sand and Normal Portland cement. The initial pH of concrete slabs after preparation was 11.2 to 11.3 and this pH was lowered to the average pH 8.26 (range pH 8.20 to 8.30) at test to simulate aged concrete in granaries. The pH 8.26 was attained by soaking the slabs in 2 percent glacial acetic acid solution for 20 hours followed by washing under running tap water for 18 hours, and leaving to dry overnight. Batches of two concrete slabs were soaked in 1.4 litre of distilled water for two hours and the pH of the resultant solution determined with Corning Model 610A Expand Portable pH meter. Whenever the pH of the concretes was found below 8, these were further washed under running tap water and the pH again determined by the same procedure. Concrete slabs which were above pH 8.5 were soaked further in 0.5 percent glacial acetic acid solution for 18 hours, washed under running tap water and the pH determined as outlined above.

(4) Test cereal grain: The cereal grains used for the study were samples of hard red spring wheat, Neepawa variety, barley of Fergus variety and hybrid corn of W9 x ND203 variety. The moisture content of each test grain variety was tempered either by aeration or by addition of calculated volume of distilled water and tumbled on a Norton rotary mixer for one hour and then left for three days to equilibrate to the desired moisture content for tests. The moisture content was determined at room temperature with Moisture Master 101 A (CAE Industries Ltd., Canada) with a precision of $\pm$ 0.05%.

(5) Copper and glass rings of dimensions 5 x 2.5cm and 8 x 4cm, respectively, with open ends were used to confine the grains and test insects on the treated surfaces.

(6) Apparatus, solvents and reagents for residue analysis:

(i) Extraction apparatus: 50ml round-bottom stainless steel centrifuge tubes (International Equipment Co. No. 613), stainless steel caps fitted with Teflon-O-ring gaskets, stainless steel balls of approximately 1.75cm diameter (Fig. 3).

(ii) Reciprocating shaker capable of delivering a stroke of at least 7cm at 350 cycles/min (Fig. 4).

(iii) Rotary grinder - GS Iona high speed coffee grinder, Model CG8 (General Signal Appliances Ltd., Canada).

(iv) Erlenmeyer flasks - Graduated 250ml, with 24/40 ground joint.

(v) Vacuum flasks - 250ml (Hysl Reg., England).

(vi) Filter funnels - 7cm short stem, 60ml capacity, medium porosity fritted disk (ASTM, 10-15M).

(vii) Repipets - 1, 5, 10, 20 and 30ml, with reservoirs.

(viii) Evaporator - Rotavapor-R (Rinco Instrument Co., Inc. Greenville, Ill.).

(ix) Dispopipets (Fisher Scientific Co., Pittsburgh, Pa.).

(x) Gas chromatographic equipment and operating conditions: Tracor Micro-Tek 220 gas chromatograph equipped with Melpar flame photometric detector (Tracor, Inc., Austin, Texas) operated with interference filter for spectral isolation of phosphorus emission at 526nm was used.

Operating conditions - 60cm x 4mm o.d. silanized Pyrex glass column packed with 3% OV-17 on Chromosorb W HP, 80/100 mesh (Chromatographic Specialities, Brockville, Ont., Canada). The column was conditioned overnight at 245°C before use.

Temperature: Column temperature (isothermal) 200°C, detector temperature 210°C, inlet temperature 220°C.

Gas flow rates (ml/min); Nitrogen (carrier gas) 60, oxygen 20, air 100, hydrogen 160.

FIGURE 3. - Assembly of the ball-milling extraction apparatus.

FIGURE 4. - The reciprocating (wrist-action) shaker.

Chart speed - 3mm/min.

A 10.2cm long removable glass sleeve liner containing about 2.5cm silane-treated glass wool (Applied Science Laboratories Inc., State College,Penna.) was inserted in the injection port of the column. This glass sleeve liner was changed periodically, usually after 12 - 30 injections of the sample extract. Before reuse, it was thoroughly rinsed with acetone followed by hexane and dried under a stream of nitrogen.

(xi) Soxhlet extraction apparatus (Fisher Scientific Co.).

(xii) Solvents and reagents: acetone, chloroform, ethyl ether, hexane, isopropanol, methanol (pesticide quality and distilled in glass; Caledon Laboratories Ltd., Georgetown, Ont., Canada).

(xiii) Test insecticide standards were analytical grade samples kindly supplied by the manufacturers.

METHODS

Application of insecticides to test surfaces

The test insecticides were prepared as water-base emulsions just before use at various dosage levels. A Paasche Type H airbrush sprayer fitted with a No. 5 nozzle (Paasche Airbrush Co., Chicago, Ill.; Toronto, Ont., Canada), operating at a constant pressure of 0.70 kg/cm^2 (10 lb/in^2) was used to apply each dosage level of the prepared insecticide dilution on one surface of plywood panel and concrete slab under a fume hood at room conditions. The sprayer is a continuous action mist sprayer which releases the spray by continuous action on compression. The prepared insecticide solutions were applied to the test surfaces at the rate of 0.05 $litre/m^2$. At this rate of application, the initial insecticide deposit was 1g AI/m^2.

Scattering of spray droplets at the periphery of the target surface accounts for the losses of the actual amount of insecticide deposit intended for a target surface. Losses due to scattering of droplets at the periphery of the target during application of various types of insecticide formulations have been estimated by Parkin (1966), Lemon (1967), and Watters and Grussendorf (1969). Watters and Grussendorf (1969) using Shell Risella oil, found that the amount of oil applied onto Whatman No. 1 filter paper targets with Paasche airbrush was 92 $\pm$ 1 percent of the total amount intended for deposition. Thus, to compensate for the loss through drift of spray droplets, it is necessary to adjust the amount of insecticide deposited on the target by increasing the volume of spray applied from 0.046 litre/m^2 to 0.05 litre/m^2.

Control surfaces were sprayed with distilled water prior to the insecticide treatments.

After treating the surfaces, the wood panels and concrete slabs were held on horizontal shelves in a room at 21° - 25°C and 40 - 60% relative humidity for seven days after which the surfaces were used for the tests at pre-determined intervals. The control surfaces were stored apart from the treated surfaces.

1. Persistence of insecticides applied to concrete and wood surfaces

The persistence of bromophos, iodofenphos and malathion on concrete and wood surfaces was determined by bioassay of the cereals exposed to treated surfaces 1, 2, 4, 8, 16 and 32 weeks after treatment. Thirty grams of hard red spring wheat, Fergus barley and hybrid corn at 14.0 percent moisture content were stored on each surface in three open-end copper rings, 5cm high and 2.5cm diameter

(Fig. 5), and left on the treated surfaces for seven days. In this way, the insecticide would be more likely to be absorbed into the grain and therefore would correspond more closely to a treatment of a storage structure for postharvest protection against infestation. After seven days the cereals were removed into 227ml (8 fl. oz.) mason jars and two 30g portions were used for bioassay. Each insecticide treatment and control was set up in triplicate.

The test insects, C. ferrugineus and susceptible T. castaneum after collection from the culture medium were grouped together and mixed in kilner jars to have a homogeneous population for each species. The insects were placed in batches of 20 adults held in small plastic vials and starved for 5 hours prior to placing them on the grain. The batches of test insects were then released randomly onto the grains contained in mason jars closed with cheesecloth secured with a rubber band. The grain samples thus infested with insects were stored at 27.5°C and 60 - 70% relative humidity for another seven days.

Following exposure, the beetles were separated from the grain kernels with a 2.4mm sieve. For assessing the toxic effects of the insecticides and hence their persistence on the concrete and wood surfaces, the test insects were classified as dead or alive by the method used by Hewlett (1947). Those insects that were not able to more spontaneously or respond to reflex action from a slight mechanical pressure or heat stimulation for three minutes were considered as dead. Percent mortality was corrected by Abbott's (1925) formula.

After recording the response, the kernels were returned to the mason jars for progeny assessment. The jars were kept in temperature controlled cabinets maintained at 27.5°C and 65 - 70% relative

FIGURE 5. - Exposure of wheat, barley, and corn, confined by open ends of copper rings to treated concrete and wood surfaces.

humidity. Estimates of progeny were based on those insects which emerged 42 days after they had been removed from the grain samples. All results were assessed by analysis of variance using split-plot in time.

2. The translocation of bromophos, iodofenphos and malathion into wheat, barley and corn

The chemical residue analysis to measure the translocation of bromophos, iodofenphos and malathion into grain samples stored on treated and controlled surfaces was conducted through a 4-step method:

(a) Selection of extraction solvent.

(b) Recovery efficiency of the insecticides by ball-milling method.

(c) Extraction efficiency.

(d) Chemical residue analysis of the grain samples stored on test surfaces.

Selection of extraction solvent

The first step in the preparation of a sample, whether from crop material, animal tissue, soil, water, food product or other environmental compartment for pesticide residue analysis is to extract the pesticide into a suitable, relatively pure solvent. The choice of solvent for extracting pesticide from any type of sample is therefore critical especially in the hands of workers not already familiar with laboratory methods found in the literature.

A review of the literature shows reference to many extraction procedures used for determining organophosphorus pesticide residues in food and crop materials. The use of hexane as an extractant for determining malathion residues in wheat has been reported (Elms, 1967; Minett and Belcher, 1969; Grussendorf et al., 1970). Other extraction techniques describe the use of other extraction solvents for stripping organophosphorus insecticide residues from crop materials

(Watts and Storherr, 1965; Thornburg, 1965; Thornton and Anderson, 1968; American Cyanamid Co., 1973). Acetone has been described as the best and most suitable solvent for the extraction of bromophos and bromophos-ethyl from all crops having a low fat content (Leber and Deckers, 1967). However, crops containing large quantities of fat are better extracted with acetonitrile or methanol. Crisp and Tarrant (1971) reported methanol as the best solvent for extracting malathion and dichlorvos from wheat for gas-liquid chromatographic determination. They found that between concentrations of 0.25 and 10 ppm, both malathion and dichlorvos were recovered from spiked wheat samples with between 87 and 99 percent efficiency. The malathion Panel (1973) in their investigation on the choice of solvent for the extraction of malathion and dichlorvos residues for gas-liquid chromatographic determination found that ethyl acetate, acetonitrile, dichloromethane-water and acetone were not as effective as methanol without clean-up. Levi and Nowicki (1974) also reported a good recovery of malathion from ground wheat by ball-milling extraction technique with ethyl ether - hexane (3:97) mixture as extractant without cleanup.

Hexane, ethyl ether-hexane (3:97), and methanol were therefore tested as to their suitability for extraction of malathion, bromophos and iodofenphos residues in wheat using Soxhlet apparatus.

Fifty grams of uncontaminated hard red spring wheat of 13.8 percent moisture content were ground for 30 seconds in an Iona high-speed coffee grinder and was fortified with insecticide-acetone standard solution at a level of 4 ppm. The solvent was evaporated in a fume hood by a gentle stream of air for one hour, and subsequently left to stand for 24 hours after which the insecticide residues were extracted with the test solvents using Soxhlet extraction apparatus. Ten-gram aliquots of fortified wheat sample were weighed and transferred to Soxhlet thimbles, and topped with small plugs of glass wool. The extraction thimbles were then inserted into the Soxhlet apparatus and the wheat exhaustively extracted with 200ml of each test solvent for six hours under water reflux. The Soxhlet solvent cycled six times per hour at 65°C. The extracts were concentrated in a Rinco rotavapor evaporator to about 40ml and the final volume adjusted to 50ml with each solvent. The extracts were then analyzed by injecting 5µl into the gas-liquid chromatograph with flame photometric detector. Duplicate samples of fortified wheat were prepared for each solvent tested.

The average of four determinations for recovery of the insecticide residues from fortified wheat with the test solvents are shown in Table 3.

TABLE 3. Comparison of solvents for extraction of malathion, bromophos and iodofenphos residues from fortified wheat using Soxhlet extraction method.

Solvent	Percent recovery[a]		
	Malathion	Bromophos	Iodofenphos
Hexane	97.47 ± 2.51	96.12 ± 1.36	84.84 ± 4.69
Ethyl ether-hexane	99.98 ± 1.03	100 ± 0.85	94.74 ± 1.71
Methanol	97.84 ± 1.05	97.75 ± 1.01	91.23 ± 1.57

[a] ± standard deviation

All the solvents tested were suitable for the removal of insecticide residues from fortified ground wheat. Methanol was chosen, however, as the extraction solvent because of its relative cheapness and its reported suitability for the extraction of pesticide residues from cereals containing high moisture content and lipids.

Recovery efficiency of insecticides by ball-milling method

The recovery efficiency of the ball-milling method of extraction using methanol as an extractant was determined for recovery of malathion from ground wheat analyzed 24 hours after fortification.

Fifty grams of uncontaminated wheat were ground and 10g portions were weighed into four clean plastic vials. Using malathion-acetone standard solution, each sample was fortified to 1.00 ppm by adding the solution dropwise and spreading it over the surface of the sample. The plastic vials were then put in a fume hood of a gentle stream of air for one hour to allow the solvent to evaporate. The vials were then stoppered, agitated by hand for five minutes, and stored in a deep-freeze (-25°C) for 24 hours after which the malathion residue was extracted with methanol.

The fortified wheat was transferred to an extraction tube and two stainless steel balls added. Using a 50ml repipet, 30ml methanol was added. The cap was sealed in place and the extraction tube mounted horizontally on a wrist-action shaker and agitated for one hour. Using a partial vacuum, the extract was filtered through a medium porosity fritted disk filter funnel and collected in 250ml vacuum flask. The extraction tube was washed three times with 2ml methanol, filtering the washing on each occasion. Five ml of the filtrate was then transferred to a 5ml volumetric flask. Four samples were prepared for the residue analysis. Parallel tests of analysis of unfortified samples were run alongside the recovery test.

The residue analysis determined by injecting 5µl of the methanolic extract into the glc column connected to flame photometric detector, showed an average percent recovery of 99.17 by the ball-milling method of extraction, with a standard deviation of 0.45%.

Extraction efficiency

Extraction efficiency of the ball-milling extraction technique using methanol was compared with efficiency of Soxhlet extraction with methanol-chloroform (10:90) as extractant. Sets of 50g uncontaminated ground wheat (12.5% mc) samples were weighed into 125ml Erlenmeyer flasks. Each wheat sample was fortified with malathion, bromophos, iodofenphos and pirimiphos-methyl at levels of 1.00 and 5.00 ppm, using insecticide-acetone standard solutions. The acetone was evaporated under a gentle stream of air in a fume hood. The flasks were stoppered, agitated by hand, and stored in a dark room for seven days before analysis. Triplicate samples of each residue level were analyzed by both extraction methods. Ten-gram aliquots of each fortified wheat sample were used for the extraction. The details of the extraction procedures and residue analysis by glc were as described previously.

The results of the residue analysis for the recovery of the test insecticides are shown in Table 4.

The mean of triplicate determinations for the recovery of the test insecticides by the ball-milling method appeared to be as efficient as the Soxhlet extraction method. The ball-milling extraction has an added advantage of being rapid and thereby

TABLE 4. Mean percent recovery of insecticides by ball-milling and Soxhlet extraction methods

Insecticide	Residue level (ppm)	Percent recovery[a]	
		Ball-milling	Soxhlet
Malathion	1.00	99.04 ± 3.47	97.84 ± 1.55
	5.00	99.33 ± 3.94	97.75 ± 1.21
Bromophos	1.00	100.68 ± 3.87	96.02 ± 3.90
	5.00	98.62 ± 3.40	99.44 ± 2.72
Iodofenphos	1.00	85.73 ± 4.30	89.93 ± 4.00
	5.00	91.60 ± 3.69	91.69 ± 3.45
Pirimiphos-methyl	1.00	96.00 ± 2.64	93.44 ± 2.30
	5.00	96.11 ± 2.58	95.43 ± 1.87

[a] ± standard deviation.

enabling a large number of samples to be handled economically both in terms of solvent and time.

As a further check on the extraction efficiency of the ball-milling technique, a sample of uncontaminated ground wheat was spiked with malathion-acetone standard solution to 1.00 ppm and kept in a dark room for seven days after which the insecticide residue was extracted with 30ml methanol by the ball-milling method. Following the ball-milling extraction, the filter cake was exhaustively extracted with 100ml methanol-chloroform (10:90) in a Soxhlet apparatus for 10 hours. Two ml of isopropanol was added as a keeper and the extract was concentrated to about 1ml, and the final volume adjusted to 5ml with methanol-chloroform. The samples for glc determination in both extraction procedures were prepared in quadruplicates, and analyzed by injecting 5µl into the glc.

The mean percent malathion residue recovered by the ball-milling method was 99.10 (range 98.85 to 100.87). No malathion residue was recovered from the Soxhlet extraction method, indicating either an almost complete removal of the insecticide residue by the ball-milling procedure or a residue that was below the limit of detection of the glc method used.

Residue analysis of grain stored on concrete and wood surfaces

Thirty g of hard red spring wheat, Fergus barley, and hybrid corn stored for seven days on test surfaces 1, 2, 4, 8, 16 and 32 weeks after treatment were removed and ground for 20 seconds in an Iona high-speed coffee grinder. The ground grain was thoroughly mixed and 10g portions were weighed into extraction tubes, and the insecticide residues extracted by the ball-milling method using methanol. Twelve tubes could be mounted on the wrist-action shaker simultaneously (Fig. 6) and these were agitated for one hour.

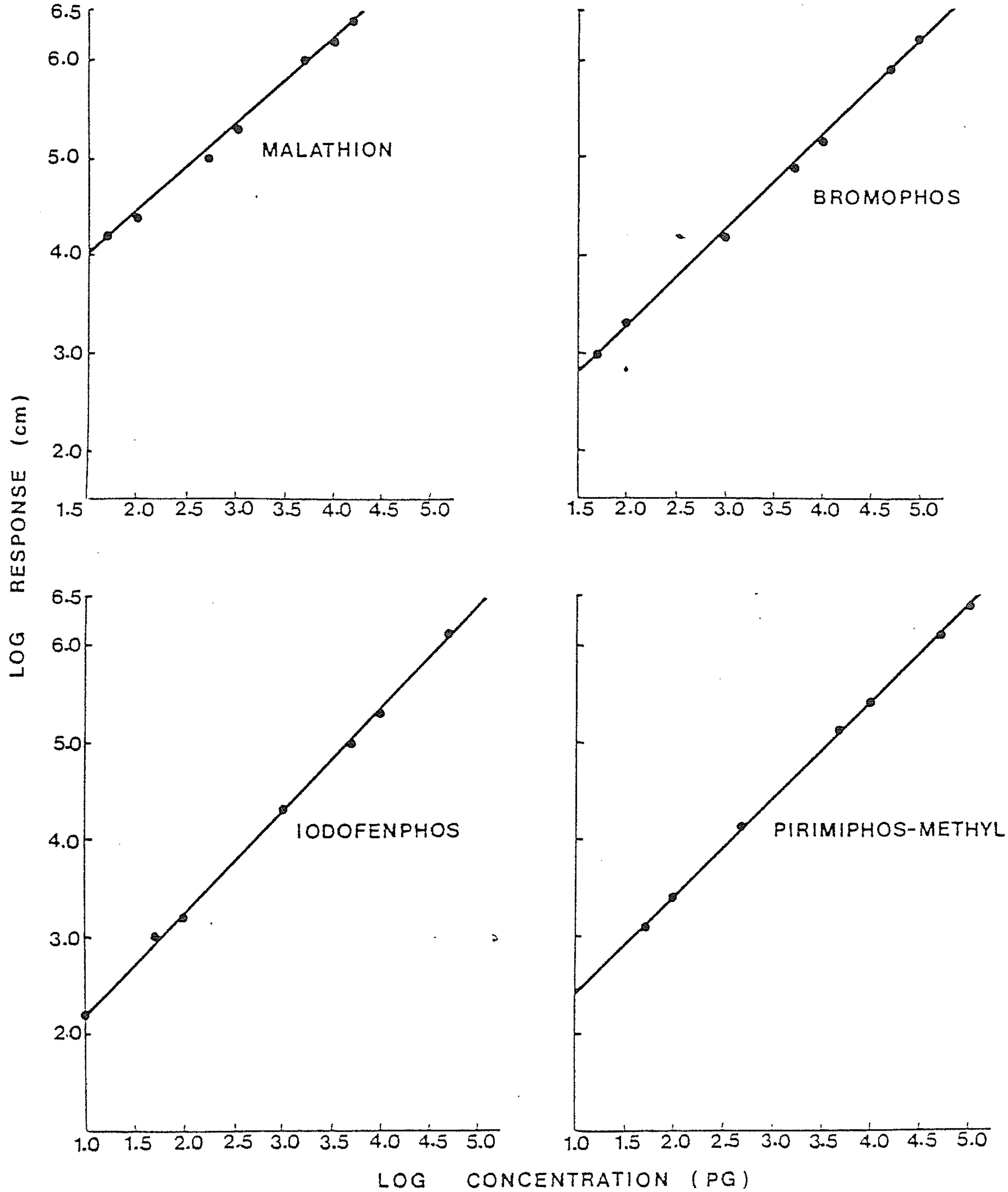
The analytical determinations of the methanolic extracts were conducted by injecting 2µl and 5µl of extracts from cereals stored on wood and concrete surfaces, respectively, into the gas chromatograph equipped with Melpar flame photometric detector, and operated in the phosphorus mode at 526nm. The amounts of insecticide residue in all the analytical determinations were obtained by means of standard calibration curves. The data were statistically analysed.

Preparation of standard calibration curves

Standard calibration curves for test insecticides were prepared from analytical grade chemicals kindly supplied by the manufacturers. In preparing the standard calibration curves 99.3 - 99.6 percent AI of analytical insecticides were diluted with methanol to provide a range of standard concentrations for each insecticide. The standard calibration curve obtained for each insecticide was a straight line, as shown in Fig. 7. It is seen from all the test insecticides that the curve does not pass through the origin, but slightly above it, intersecting the ordinate at points representing approximately the limits of detection for the insecticides (Table 5).

FIGURE 6. - Twelve sets of extraction tubes mounted simultaneously on reciprocating (wrist-action) shaker.

FIGURE 7. The standard calibration curves for glc analysis of malathion, bromophos, iodofenphos, and pirimiphos-methyl.



MALATHION
BROMOPHOS
IODOFENPHOS
PIRIMIPHOS-METHYL
LOG RESPONSE (cm)
LOG CONCENTRATION (PG)
6.5
6.0
5.0
4.0
3.0
2.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
1.0

TABLE 5. Retention time and limit of detectability of analytical standards of insecticides in methanol.

Insecticide	Retention time (min.)	Limit of detectability (ng)[1]
Malathion	2.52	0.05
Bromophos	2.78	0.04
Iodofenphos	4.59	0.01
Pirimiphos-methyl	4.05	0.05

[1] ng = 10^{-9}g.

3. <u>Field tests with bromophos 25% WP as a residual protectant against rusty grain beetle infestations</u>

Bromophos has been approved in Canada for use against insect infestations in stored grain. Following its promising effectiveness in comparision with malathion and iodofenphos on concrete surfaces for the control of *C. ferrugineus*, field studies were conducted for further evaluation.

An empty galvanized steel bin with concrete floor (pH 8.0), 4.27m (14 ft) diameter and 2.44m (8 ft) high was selected for the study at the Ciba-Geigy's Research Farm at the Elm River, Portage La Prairie. One-half of the floor area was treated with bromophos 25% WP at 1g toxicant/m^2 as water-based solution, and the other half was left untreated as a control.

One week after treatment, the treated and control areas were enclosed by a plywood box 25 x 35cm and 25cm high, open at the top and bottom, and filled with 15.3kg of hard red spring wheat of 12.6 percent moisture content. Three plywood boxes were placed at random on both treated and control floor areas.

The wheat was sampled 1, 2, 4 and 8 weeks after storage from randomized locations in each box by inserting an open copper cylinder 25 x 5cm i.d. into the wheat surface to the concrete floor. Three equal layers of wheat, 134g each, were removed by suction with a vacuum cleaner from the cylinder and designated as the top, middle and bottom layers. These core samples of wheat were used for bioassay with adults of C. ferrugineus and for insecticide residue analysis. The bioassay was determined by exposing 20 adult beetles on 50g wheat for seven days in 227ml (8 fl. oz.) glass jars covered with a cheesecloth. After assessing the mortality, the insects were discarded and the grains returned to the glass jars which were then held for 42 days at 27.5°C and 60 - 70 percent RH for F_1 adult beetles. The residue analysis was conducted as previously described for the translocation of insecticides into wheat from treated structural surfaces.

At each sampling period, temperature and relative humidity of the bin, and temperature and moisture content of the stored wheat were recorded (Table 59).

In another field test, a galvanized steel bin of dimensions 4.27m (14 ft) diameter and 2.44m (8ft) high with concrete floor of pH 8.0 was sprayed in mid August, 1976, with bromophos 25% WP at the rate of 1g AI/m^2 at the Ciba-Geigy's Elm River Research Farm. About 14 days after treatment, the treated bin was filled with 1093 bushels of hard red spring wheat, Neepawa variety, (m.c. 12.4%) as it came from the field. The bin was then closed and left undisturbed until unloading in mid March, 1977. Control sample of grain was stored in an area separate from the treated bin.

As the grain was being augered from the bin at the end of the storage period, samples of grain weighing approximately 500g were withdrawn at the following intervals:

Sample No.	Bushels removed from bin when sample was taken
1	150
2	300
3	450
4	600
5	750
6	875
7	950
8	1000
9	1050
10	1075
11	1090 including swept grain
Control	----

During the unloading of the grain, the auger was pushed into the bin at the bottom, thereby ensuring mixing of grain strata as the grain ran down into the auger.

Bioassay and residue analysis of the grain samples stored in the treated and control bins were determined as in the previous experiment. F_1 adult beetles resulting from infestation of the grain with _C. ferrugineus_ were also assessed.

4. <u>The effect of moisture content on uptake of malathion and bromophos from wood surfaces into wheat</u>.

Fir plywood panels, 30 x 30cm (surface area 900 cm^2), were sprayed with malathion and bromophos as water-based solutions of emulsifiable concentrate at the rate of 1g AI/m^2. Control wood surfaces were sprayed with distilled water. Treated wood surfaces were then stored for one week on shelves in a room maintained at 21.0°C and 70% RH, after which they were used for the tests of insecticide uptake into wheat.

Wheat of Neepawa variety was tempered to a moisture content of 12, 14 and 16%. Three 30-g samples of grain were exposed to the treated wood surface in copper rings for seven days. Four replicates were set for each insecticide and moisture content treatment. The treatments were held in temperature and humidity controlled cabinets (Table 6).

TABLE 6. Conditions under which grains were stored on treated surfaces to maintain moisture content.

Storage temp. (°C)	Relative humidity (%)	M.C. before exposure	M.C. after exposure
23.9	49	12.0	11.9
19.9	65	14.0	14.0
18.9	75	16.0	15.8

After seven days of continuous exposure to treated surfaces, the grains were removed into 227ml (8 fl. oz.) glass jars. One set of grain samples was used for bioassay with adults of *C. ferrugineus* and *T. castaneum*. Mortality was assessed seven days after continuous exposure of the insects to the grain.

Residue analysis was conducted on the other set of grain samples to determine the amounts of insecticide picked up by the kernels.

5. The distribution of malathion residues in layers of grain kernels stored on wood surfaces

This experiment was conducted to determine whether insecticides applied to storage structures are able to move past a single layer of kernels.

Oil Red O dye and Methylene Blue dye solutions were prepared by dissolving 0.10g of dye in 20ml acetone and methanol, respectively. Five ml of each prepared dye solution were sprayed onto 350g of cleaned, uninfested hard red spring wheat (13.8% m.c.) with a Paasche airbrush. Another 350g sample of wheat was left unsprayed.

Preliminary studies on the use of these dye solutions on wheat grain showed no adverse effects on adults of *T. castaneum* and produced no interference with glc determinations of the extracted dyes from the sprayed wheat.

The colored kernels were set in single layers up to three layers deep, enclosed by open glass rings, 8cm high and 4cm diameter on wood surfaces treated at 1g AI/m^2 (Fig. 8). Each layer of kernels was 3mm deep and weighed approximately 10g.

The translocation of malathion into the various layers of grain kernels was assessed after 1, 3 and 7 days, and 1 and 2 months of continuous exposure to the treated surfaces by bioassay with susceptible adults of *T. castaneum* and also by chemical residue analysis. The experiment was replicated four times for each exposure period. Controls consisting of four replicates were also prepared.

FIGURE 8. - Set-up of three single layers of wheat enclosed by open glass rings on treated wood surface.

6. Effect of physical disruption on the persistence of insecticide residues on structural surfaces

Plywood panels (12.2 x 12.2cm) were treated at 250mg AI/m^2 with malathion, bromophos (EC and WP) and iodofenphos (EC). One week after treatment, the surfaces were physically disrupted by subjecting them to twelve unidirectional sweepings and by mechanical shaking of the surfaces for two hours with 600g of cleaned wheat to simulate the abrasion of surfaces caused by the pouring of grain into a treated bin or granary.

The effect of the physical disruption of the treated surfaces on the persistence of insecticide resdiues was determined by bioassay with adults of T. castaneum 1 day and 1, 3, 6, 12 and 24 weeks after treatment. Twenty susceptible beetles were exposed on the surface for 5 hours and then removed and placed in plastic vials, 5cm high and 2.4cm diameter, containing about 2g of crushed wheat. The vials were stored in a cabinet at 27.5°C and 65 - 70% RH for three days after which mortality was assessed. Wood surfaces treated with insecticides were prepared as checks to compare by bioassay the impact on the persistence of the insecticides on surfaces that were disturbed by physical disruption.

7. Persistence of malathion, bromophos, iodofenphos and pirimiphos-methyl residues in dry and damp stored wheat

Hard red spring wheat, Neepawa variety, stored in a temporary wooden bin for three months was collected into 27.2kg capacity jute bags and stored under cold conditions (-16° to -23°C) for 2½ weeks to kill any existing insect infestations. Following this cold treatment the wheat was thoroughly cleaned of weeds and other foreign materials with a Clipper M-2B (A.T. Ferrel and Co., Saginaw, Michigan) to give uniform grain kernels, and divided into 10kg lot samples. These cleaned, uninfested wheat samples were then tempered to 12 and 16 percent moisture content by adding a calculated volume of distilled water and then mechanically tumbled for one hour on a rotating machine. The tempered wheat lots were kept in tied polythene bags for seven days to equilibrate before the application of insecticides. Prior to the insecticide treatments, the moisture content of each sample lot (12.0 ± 0.1% and 16.0 ± 0.1%) was determined with Moisture Master 101A.

Water-based sprays of premium grade malathion, bromophos, iodofenphos and pirimiphos-methyl were applied to the wheat lots as the grain was augered. The insecticide concentrates were diluted with distilled water as necessary to obtain the amount of insecticide (AI) needed in 8ml of spray for the desired deposit of residue (Table 7) when applied to the 10kg samples of wheat.

TABLE 7. Insecticide dosages applied to the wheat.

Insecticide	Formulation	Aimed dosage
Malathion	83.6% EC	8 ppm and 12 ppm
Bromophos	40% EC	10 ppm and 15 ppm
Iodofenphos	20% EC	10 ppm and 15 ppm
Pirimiphos-methyl	84% EC.	4 ppm and 6 ppm

A 10-ml glass syringe, held approximately at 15cm from the open-end of the auger, was used to dispense the insecticide spray. The rotating screw at the bottom of the filling hopper turned at a sufficient speed to allow a uniform flow of grain from the spout to coincide with the application of the spray. The treated wheat was collected in plastic pails and was then mixed thoroughly for about three minutes with a clean metal rod. Samples weighing 50g were drawn from each lot of treated wheat into 0.45kg (1-lb) capacity polythene bags and kept in a deep-freeze at -25°C for the estimation of the applied insecticide dosage. The remaining lots of treated wheat were put into 27.2kg (60-lb) jute bags, tied and stored on horizontal shelves in humidity controlled rooms to maintain the moisture content of the treated wheat. Control wheat samples were passed through the auger without being treated and were stored under similar conditions. Three replicates were allocated for each insecticide dosage and control and for each moisture content.

At intervals of 1, 3, 6, 12 and 24 weeks after treatment, samples of 100g were drawn from five different locations from each bag with a 18.5cm long, 2cm diameter, copper sampling spear and composited into a 500g lot of grain. Three 50g subsamples were used for bioassay and chemical analysis of residues. The test insects were susceptible and malathion-resistant strains of _T. castaneum_ (Table 1). Fifty g samples of wheat were transferred into 227ml (8 fl. oz.) glass jars and infested with 20 adult species of susceptible and resistant strains of _T. castaneum_. The insects were held in the jars by covering the latter with cheesecloth secured with a rubber band and stored at 27.5°C and 65 - 70% RH for seven days. After the desired period of exposure to the wheat, mortality counts were recorded as described in the previous experiments. Percent mortality was corrected by Abbott's (1925) formula.

After recording the response to the toxicants, the insects were discarded and the grains returned to the glass jars. About five percent of the treated wheat was ground and added to the grains in the jars. The jars containing the treated kernels were then stored at 27.5°C and 60 - 70% RH for a further 42 days to assess the F_1 adult beetles produced from oviposition during the 7-day exposure period.

The chemical analysis of insecticide residues was based on the method previously described for determination of pesticide residues in wheat, barley and corn stored on treated concrete and wood surfaces.

At intervals of 1, 3 and 6 months after treatment 20g wheat were drawn with the sampling spear from five different locations and composited into 100g lots of samples. These samples were milled into bran, middlings and flour for determination of insecticide residues in the milled fractions. Residues in whole grain (ground grain) were also determined.

At weekly intervals and at any time of sampling, temperature and relative humidity of the storage rooms were recorded as well as the temperature and moisture content of the stored wheat (Table 69). Samples that could not be analyzed immediately were stored in a deep-freeze at -25°C in 0.45kg capacity polythene bags until they were analyzed.

CHAPTER IV

RESULTS

1. Persistence of insecticides applied to concrete and wood surfaces

The persistence of malathion, bromophos (EC and WP), and iodofenphos (EC) on wood and concrete surfaces was determined at 1, 2, 4, 8, 16 and 32 weeks after treatment by bioassay of wheat, barley and corn with susceptible strains of *C. ferrugineus* and *T. castaneum* after the cereals had been removed from contact for one week with treated surfaces.

Bioassay of cereals - The statistical analysis of the data showed that insect mortality was influenced by the type of surface used for storing the grain, the type and formulation of the insecticide, the type of cereal grain, the age of insecticide deposit and the interactions between these factors (Tables 8-25 and Figs. 9 and 10). Significantly higher mortalities ($P < 0.01$) of *C. ferrugineus* were obtained on all grains stored on treated wood surfaces than on those grains stored on treated concrete surfaces at each period of assessment (Tables 8, 10, 11, 13 and 16). Regardless of the type and formulation of insecticide used, more than 80 percent mortality was obtained on grains stored on treated wood surfaces (Tables 8 and 10).

There were significant differences ($P < 0.01$) between the insecticide treatments on the two types of structural surfaces (Tables 8-10, 13 and 16). Generally, higher mortalities were obtained from bromophos-treated surfaces than from malathion- and iodofenphos-treated surfaces (Tables 8 and 10) but on wood surfaces, malathion EC persisted longer and therefore provided better control of *C. ferrugineus* on the stored grains (Tables 8, 10, 13 and 16).

On concrete surfaces, bromophos WP appeared to be more persistent than the other insecticide treatments (Tables 10 and 13). It provided more than 60 percent mortality on wheat and barley for eight weeks, and on corn for two weeks (Table 16). Iodofenphos deposits on concrete surfaces persisted significantly longer ($P < 0.05$) than either of the malathion formulations (Table 13). Comparing the insect mortality on the grains stored on concrete surfaces for all insecticide treatments, the order of increasing persistence was bromophos WP > bromophos EC > iodofenphos EC > malathion EC = malathion WP.

There were no significant differences in mortality between wheat and barley stored on treated structural surfaces ($P > 0.05$) but there were significant differences between the two types of grain and corn ($P < 0.01$). Significantly lower mortalities were obtained on corn stored on treated structural surfaces at each assessment period (Tables 9, 10, 14 and 15). On treated wood surfaces, however, the slight differences between corn and the two cereal grains (wheat and barley) became significant ($P < 0.05$) either at 16 or 32 weeks after treatment, whereas on treated concrete surfaces the differences were apparent either at one week or two weeks after treatment (Table 16). Generally, malathion EC afforded better control of C. ferrugineus on grains stored on treated wood surfaces and bromophos WP provided relatively good control on grains stored on treated concrete surfaces.

The percent mortality of C. ferrugineus on grains stored on treated structural surfaces generally decreased with age of insecticide deposit (Tables 11-13, 15 and 16). The persistence of insecticide deposits on both surfaces declined sharply after 16 weeks for

TABLE 8. Mean percent mortality of <u>C. ferrugineus</u> adults exposed for one week on grains removed after contact for one week on wood and concrete surfaces treated with insecticides at 1.0 g AI/m^2.

Insecticide	Wood surface	Concrete surface	Insecticide means
Malathion EC	97.5	16.8	57.1
Malathion WP	89.0	14.7	51.9
Bromophos EC	88.3	41.3	64.8
Bromophos WP	92.0	51.0	71.5
Iodofenphos EC	82.3	28.1	55.2
Surface type means	89.8	30.4	60.1

L.S.D. between	5%	1%
(i) means of type of surface	2.3	3.2
(ii) any two means of insecticide treatment	3.7	5.1
(iii) any two means of surfaces for the same insecticide or vice versa	5.2	7.2

TABLE 9. Mean percent mortality of *C. ferrugineus* adults exposed for one week on wheat, barley and corn removed after contact for one week on structural surfaces (wood and concrete) treated with insecticides at 1.0 g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
Malathion EC	58.6	61.0	51.8	57.1
Malathion WP	56.3	53.8	45.6	51.9
Bromophos EC	70.7	71.4	52.4	64.8
Bromophos WP	75.8	78.6	60.1	71.5
Iodofenphos EC	59.3	63.2	43.2	55.2
Grain means	64.1	65.6	50.6	60.1

L.S.D. between any	5%	1%
(i) two means of stored grain type	1.8	2.3
(ii) two means of grain type for the same insecticide or vice versa.	3.9	5.2

TABLE 10. Mean percent mortality of *C. ferrugineus* adults exposed for one week on wheat, barley and corn removed after contact for one week on wood and concrete surfaces treated with insecticides at 1.0 g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
		Wood		
Malathion EC	99.4	99.4	93.6	97.5
Malathion WP	90.6	90.6	85.8	89.0
Bromophos EC	93.3	92.5	79.2	88.3
Bromophos WP	96.1	93.1	86.9	92.0
Iodofenphos EC	85.0	87.2	77.2	82.3
		Concrete		
Malathion EC	17.8	22.5	10.0	16.8
Malathion WP	21.9	16.9	5.3	14.7
Bromophos EC	48.1	50.3	25.6	41.3
Bromophos WP	55.6	64.2	33.3	51.0
Iodofenphos EC	33.6	41.7	9.2	28.1
Grain means	64.1	65.6	50.6	60.1

	5%	1%
L.S.D. between any two means of surface type/ insecticide/grain type interaction.	5.5	7.4

TABLE 11. Mean percent mortality of C. ferrugineus adults exposed for one week on grains removed after contact for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Surface type	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Surface type means
Wood	99.9	100	99.9	99.3	92.9	47.0	89.8
Concrete	64.8	50.8	38.2	23.3	4.9	0.3	30.4
Age of insecticide deposit means	82.4	75.4	69.1	61.3	48.9	23.7	60.1

L.S.D. between any	5%	1%
(i) two means of age of insecticide deposit	1.9	2.6
(ii) two means of age of insecticide deposit for the same surface type or vice versa	2.8	3.6

TABLE 12. Mean percent mortality of _C. ferrugineus_ adults exposed for one week on grains removed after contact for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
Malathion EC	74.7	61.7	57.8	54.4	49.2	45.0	57.1
Malathion WP	71.4	63.1	57.8	51.7	48.3	18.9	51.9
Bromophos EC	94.2	90.0	77.8	60.6	43.3	23.1	64.8
Bromophos WP	93.9	91.1	84.2	76.9	56.9	26.1	71.5
Iodofenphos EC	77.5	71.1	76.9	63.1	46.7	5.3	55.2
Age of insecticide deposit means	82.4	75.4	69.1	61.3	48.9	23.7	60.1

	5%	1%
L.S.D. between any two means of age on insecticide deposit for the same type of insecticide or vice versa.	2.8	3.6

TABLE 13. Mean percent mortality of *C. ferrugineus* adults exposed for one week on grains removed after contact for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Insecticide	1	2	4	8	16	32	Insecticide means
	Age on insecticide deposit (weeks)						
			Wood				
Malathion EC	100	100	100	100	96.7	88.3	97.5
Malathion WP	100	100	100	100	96.1	37.8	89.0
Bromophos EC	100	100	100	98.9	85.0	46.1	88.3
Bromophos WP	100	100	100	100	100	52.2	92.0
Iodofenphos EC	99.4	100	99.4	97.8	86.7	10.6	82.3
			Concrete				
Malathion EC	49.4	23.3	15.6	8.9	1.7	1.7	16.8
Malathion WP	42.8	26.1	15.6	3.3	0.6	0	14.7
Bromophos EC	88.3	80.0	55.6	22.2	1.7	0	41.3
Bromophos WP	87.8	82.2	68.3	53.9	13.9	0	51.0
Iodofenphos EC	55.6	42.2	36.1	28.3	6.7	0	28.1
Age of insecticide deposit means	82.4	75.4	69.1	61.3	48.9	23.7	60.1

	5%	1%
L.S.D. between any two means of surface type/insecticide/age of insecticide deposit interaction.	6.2	8.1

TABLE 14. Mean percent mortality of *C. ferrugineus* adults exposed for one week on wheat, barley and corn removed after contact for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Grain type	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Grain means
Wheat	87.2	81.2	71.0	63.8	52.7	29.0	64.1
Barley	87.8	80.7	76.8	67.0	54.2	27.0	65.6
Corn	72.0	64.3	59.3	53.2	39.8	15.0	50.6
Age of insecticide deposit means	82.4	75.4	69.1	61.3	48.9	23.7	60.1

L.S.D. between any	5%	1%
(i) two means of stored grain type	1.8	2.3
(ii) two means of age of insecticide deposit	1.9	2.6
(iii) two means of stored grain type for the same age of insecticide deposit or vice versa	3.4	4.5

TABLE 15. Mean percent mortality of C. ferrugineus adults exposed for one week on wheat, barley and corn removed after contact for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

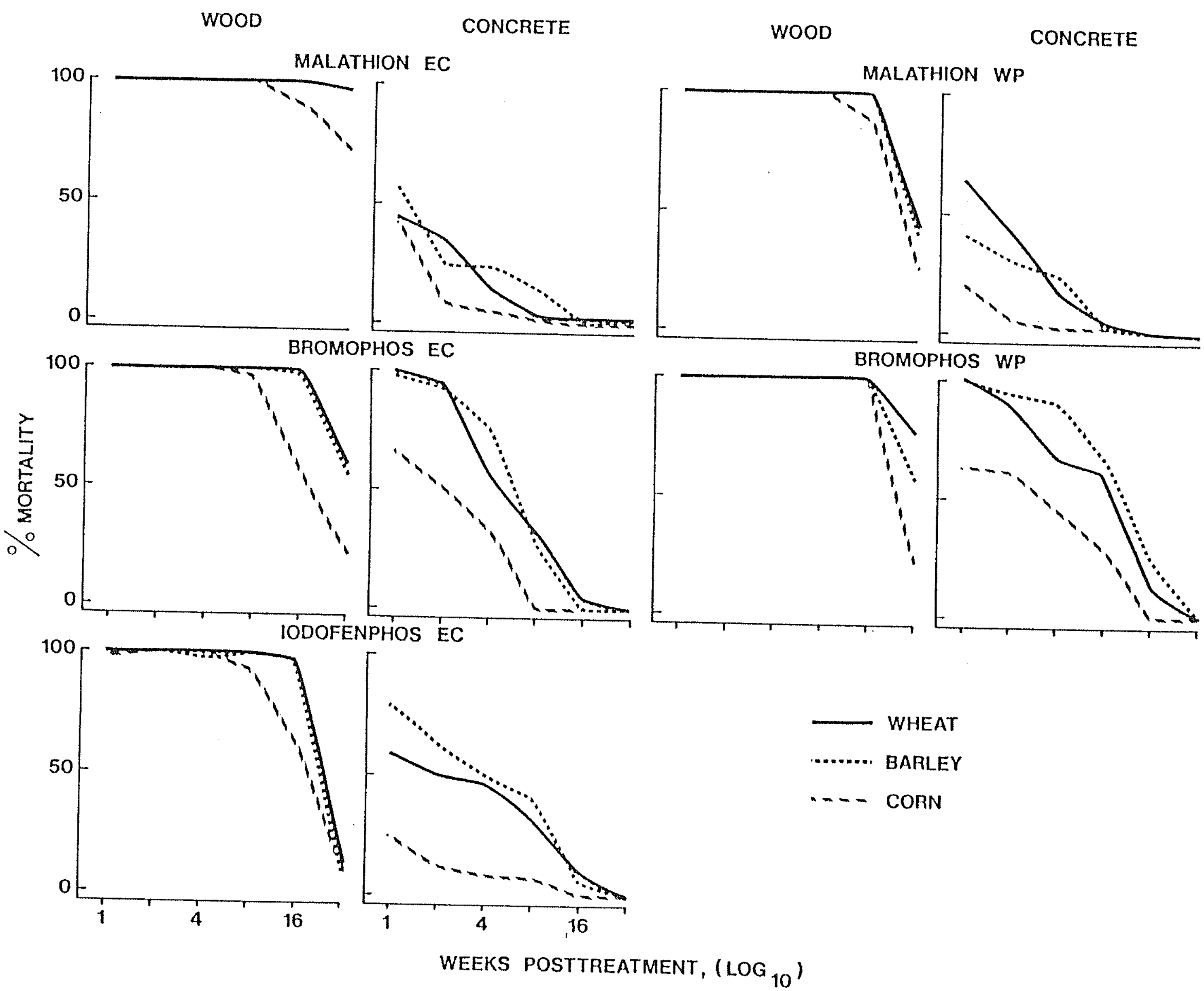
Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
			Wheat				
Malathion EC	73.3	67.5	58.3	52.5	50.8	49.2	58.6
Malathion WP	82.5	70.8	60.0	52.5	50.0	21.7	56.3
Bromophos EC	100	97.5	78.3	66.7	51.7	30.0	70.7
Bromophos WP	100	95.0	84.2	80.8	56.7	38.3	75.8
Iodofenphos EC	80.0	75.0	74.2	66.7	54.2	5.8	59.3
			Barley				
Malathion EC	79.2	62.5	62.5	60.0	51.7	50.0	61.0
Malathion WP	70.8	65.0	62.5	51.7	50.8	21.7	53.8
Bromophos EC	99.2	96.7	88.3	65.8	50.0	28.3	71.4
Bromophos WP	100	97.5	95.8	85.0	64.2	29.2	78.6
Iodofenphos EC	90.0	81.7	75.0	72.5	54.2	5.8	63.2
			Corn				
Malathion EC	71.7	55.0	52.5	50.8	45.0	35.8	51.8
Malathion WP	60.8	53.3	50.8	50.8	44.2	13.3	45.6
Bromophos EC	83.3	75.8	66.7	49.2	28.3	10.8	52.4
Bromophos WP	81.7	80.8	72.5	65.0	50.0	10.8	60.1
Iodofenphos EC	62.5	56.7	54.2	50.0	31.7	4.2	43.2
Age of insecticide deposit means	82.4	75.4	69.1	61.3	48.9	23.7	60.1

	5%	1%
L.S.D. between any two means of stored grain type/ insecticide/age of insecticide deposit interaction.	7.5	10.0

TABLE 16. Mean percent mortality of *C. ferrugineus* adults exposed for one week on wheat, barley and corn removed after contact for one week on wood and concrete surfaces treated with insecticides at 1.0 g AI/m^2.

Insecticide	Time (weeks)	Wood			Concrete		
		Wheat	Barley	Corn	Wheat	Barley	Corn
Malathion EC	1	100	100	100	44.9	57.6	42.4
	2	100	100	100	35.0	25.0	8.4
	4	100	100	100	13.9	23.5	5.0
	8	100	100	100	3.3	14.2	1.7
	16	100	100	90	1.7	0	0
	32	96.7	96.7	71.7	1.7	1.8	0
Malathion WP	1	100	100	100	63.8	40.5	20.3
	2	100	100	100	41.7	30.0	5.1
	4	100	100	100	17.4	23.6	1.7
	8	100	100	100	3.3	1.8	1.7
	16	100	100	88.3	0	0	0
	32	43.3	41.4	26.7	0	0	0
Bromophos EC	1	100	100	100	100	98.3	66.0
	2	100	100	100	95.0	93.3	51.0
	4	100	100	100	55.5	76.2	33.3
	8	100	100	96.6	32.3	26.7	0
	16	100	98.1	56.7	3.3	0	0
	32	60.0	55.1	21.7	0	0	0
Bromophos WP	1	100	100	100	100	100	62.6
	2	100	100	100	90.0	95.0	61.3
	4	100	100	100	67.4	91.4	45.0
	8	100	100	100	61.0	66.7	28.5
	16	100	100	100	13.3	25.3	0
	32	76.7	56.8	21.7	0	0	0
Iodofenphos EC	1	100	100	98.3	58.8	79.3	25.3
	2	100	100	100	50.0	63.3	11.9
	4	100	98.3	100	46.8	50.4	8.3
	8	100	100	93.1	32.4	41.4	6.7
	16	98.3	98.3	63.3	10.0	5.3	0
	32	11.7	8.7	8.3	0	0	0
L.S.D. between any two means of surface type/insecticide/grain type/age of insecticide deposit interaction						5% 10.7	1% 14.1

FIGURE 9. - Persistence of insecticides taken up in wheat, barley, and corn stored for one week on surfaces treated at 1.0 g AI/m^2 against *C. ferrugineus*.


WOOD
CONCRETE
MALATHION EC
WOOD
CONCRETE
MALATHION WP
BROMOPHOS EC
BROMOPHOS WP
IODOFENPHOS EC
100
50
0
% MORTALITY
1
4
16
WEEKS POSTTREATMENT, (LOG 10)
WHEAT
BARLEY
CORN

wood surfaces and two weeks for concrete surfaces (Tables 13 and 16). Bromophos WP appeared to have longer persistence on structural surfaces but its effectiveness declined sharply after 32 weeks (26.1%) whilst more than 40 percent mortality was obtained on grains stored on malathion EC-treated surfaces after 32 weeks (Table 12). By contrast there was no significant difference ($P > 0.05$) in persistence between the malathion formulations until 32 weeks after treatment whereas a significant difference ($P < 0.05$) was apparent between the bromophos formulations on structural surfaces after four weeks (Table 12).

Percent mortality of _T. castaneum_ exposed on cereals in contact with treated wood and concrete surfaces is presented in Tables 17-25 and Fig. 10. These results are similar to those reported for _C. ferrugineus_.

Bromophos EC and iodofenphos produced 67 percent or more mortality of _T. castaneum_ for eight weeks on all grains stored on wood surfaces whilst malathion EC and WP formulations and bromophos WP were effective (89-100%) against _T. castaneum_ for 16 weeks on grains stored on wood surfaces (Table 25). The malathion formulations and iodofenphos lost their effectiveness against _T. castaneum_ on grains stored on concrete surfaces after one week. More than 80 percent mortality was, however, obtained on wheat and barley stored on concrete surfaces treated with bromophos EC for two weeks but on corn it was ineffective (Table 25). Bromophos WP gave 50 percent or more mortality of _T. castaneum_ for two weeks on wheat stored on concrete surfaces and for one week on barley and corn.

TABLE 17. Mean percent mortality of *T. castaneum* adults exposed for one week on grains removed after contact for one week on wood and concrete surfaces treated with insecticides at 1.0 g AI/m^2.

Insecticide	Wood surface	Concrete surface	Insecticide means
Malathion EC	94.0	7.2	50.4
Malathion WP	86.9	5.6	46.3
Bromophos EC	73.7	26.8	50.3
Bromophos WP	85.4	19.9	52.7
Iodofenphos EC	66.5	7.7	37.1
Surface type means	81.3	13.4	47.4

L.S.D. between	5%	1%
(i) Means of type of surface	2.1	3.8
(ii) Any two means of insecticide	3.3	4.5
(iii) Any two means of surfaces for the same insecticide or vice versa.	4.6	6.3

TABLE 18. Mean percent mortality of _T. castaneum_ adults exposed for one week on wheat, barley, and corn removed after contact for one week on structural surfaces (wood and concrete) treated with insecticides at 1.0 g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
Malathion EC	50.4	53.8	47.6	50.6
Malathion WP	47.4	47.1	44.2	46.3
Bromophos EC	57.6	56.0	37.1	50.3
Bromophos WP	54.6	53.8	49.6	52.7
Iodofenphos EC	40.6	38.5	32.2	37.1
Grain means	50.1	49.8	42.1	47.4

L.S.D. between any	5%	1%
(i) Two means of stored grain type	1.2	1.6
(ii) Two means of grain type for the same insecticide or vice versa.	2.7	3.6

TABLE 19. Mean percent mortality of *T. castaneum* adults exposed for one week on wheat, barley, and corn removed after contact for one week on wood and concrete surfaces treated with insecticides at 1.0 g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
		Wood		
Malathion EC	95.6	95.3	91.1	94.0
Malathion WP	85.8	88.1	86.7	86.9
Bromophos EC	77.8	76.4	66.9	73.7
Bromophos WP	85.6	86.1	84.4	85.4
Iodofenphos EC	72.8	65.6	66.1	66.5
		Concrete		
Malathion EC	5.3	12.2	4.2	7.2
Malathion WP	8.9	6.1	1.7	5.6
Bromophos EC	37.5	35.5	7.2	26.8
Bromophos WP	23.6	21.4	14.7	19.9
Iodofenphos EC	8.3	11.4	3.3	7.7
Grain means	50.1	49.8	42.1	47.4

	5%	1%
L.S.D. between any two means of surface type/ insecticide/grain type interaction.	3.8	5.1

TABLE 20. Mean percent mortality of *T. castaneum* adults exposed for one week on grains removed after contact for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

	Age of insecticide deposit (weeks)						
Surface type	1	2	4	8	16	32	Surface type means
Wood	99.9	100	99.9	93.9	73.2	20.8	81.3
Concrete	39.0	24.7	11.7	4.8	0.2	0.2	13.4
Age of insecticide deposit means	69.5	62.4	55.8	49.4	36.7	10.5	47.4

L.S.D. between any	5%	1%
(i) Two means of age of insecticide deposit	1.9	2.6
(ii) Two means of age of insecticide deposit for the same surface type or vice versa.	2.7	3.6

TABLE 21. Mean percent mortality of *T. castaneum* adults exposed for one week on grains removed after contact for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
Malathion EC	64.2	53.1	51.7	51.7	48.9	34.2	50.6
Malathion WP	59.4	53.3	52.8	51.1	49.7	10.8	46.3
Bromophos EC	85.0	81.4	62.8	45.8	26.1	0.3	50.3
Bromophos WP	79.2	68.6	56.7	55.3	50.0	6.1	52.7
Iodofenphos EC	59.4	55.3	55.0	42.8	8.9	1.1	37.1
Age of insecticide deposit means	69.5	62.4	55.8	49.4	36.7	10.5	47.4

	5%	1%
L.S.D. between any two means of age of insecticide deposit for the same insecticide or vice versa.	4.3	5.7

TABLE 22. Mean percent mortality of *T. castaneum* adults exposed for one week on grains removed after contact for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Insecticide	1	2	4	8	16	32	Insecticide means
	Age of insecticide deposit (weeks)						
			Wood				
Malathion EC	100	100	100	100	96.7	67.2	94.0
Malathion WP	100	100	100	100	99.4	21.7	86.9
Bromophos EC	100	100	100	89.4	52.2	0.6	73.7
Bromophos WP	100	100	100	100	100	12.2	85.4
Iodofenphos EC	99.4	100	99.4	80.0	17.8	2.2	66.5
			Concrete				
Malathion EC	28.3	6.1	3.3	3.3	1.1	1.1	7.2
Malathion WP	18.9	6.7	5.6	2.2	0	0	5.6
Bromophos EC	70.0	62.8	25.6	2.2	0	0	26.8
Bromophos WP	58.3	37.2	13.3	10.6	0	0	19.9
Iodofenphos EC	19.4	10.6	10.6	5.6	0	0	7.7
Age of insecticide deposit means	69.5	62.4	55.8	49.4	36.7	10.5	47.4

	5%	1%
L.S.D. between any two means of surface type/insecticide/age of insecticide deposit interaction.	6.1	8.1

TABLE 23. Mean percent mortality of T. castaneum adults exposed for one week on wheat, barley, and corn removed after contact for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Grain type	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Grain means
Wheat	73.3	66.5	57.3	52.2	40.0	11.3	50.1
Barley	74.8	65.7	57.5	51.3	37.8	11.7	49.8
Corn	60.2	54.8	52.5	44.5	32.3	8.5	42.1
Age of insecticide deposit means	69.5	62.4	55.8	49.4	36.7	10.5	47.4

L.S.D. between any two means of stored grain type for the same age of insecticide deposit or vice versa.	5%	1%
	3.4	4.4

TABLE 24. Mean percent mortality of <u>T. castaneum</u> adults exposed for one week on wheat, barley, and corn removed after contact for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

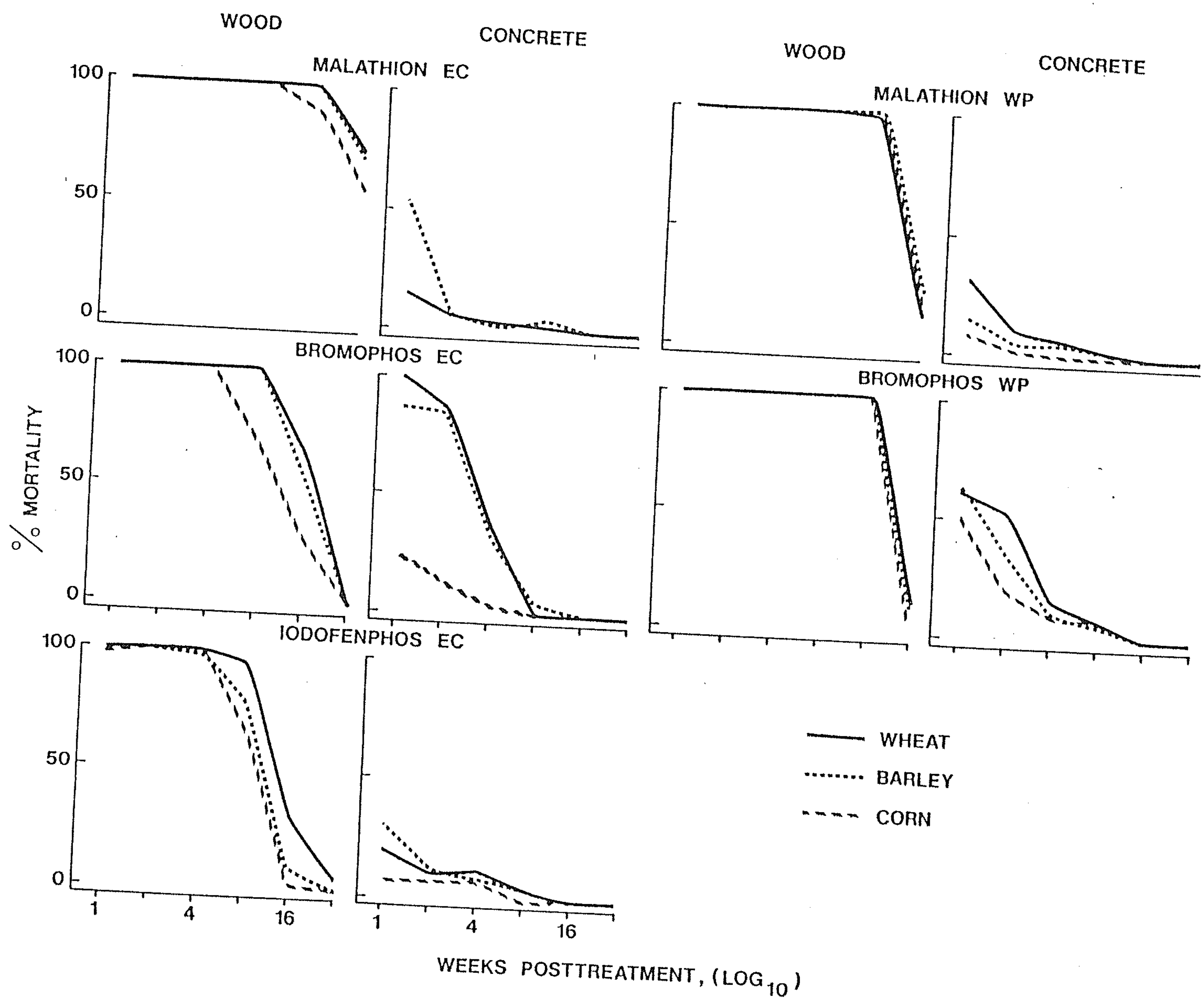
Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
			Wheat				
Malathion EC	58.3	52.5	51.7	51.7	50.0	38.3	50.4
Malathion WP	66.7	55.0	53.3	51.7	49.2	8.3	47.4
Bromophos EC	100	93.3	68.3	50.8	33.3	0	57.6
Bromophos WP	80.8	76.7	57.5	55.8	50.0	6.7	54.6
Iodofenphos EC	60.8	55.0	55.8	50.8	17.5	3.3	40.6
			Barley				
Malathion EC	76.7	54.2	51.7	52.5	51.7	35.8	53.8
Malathion WP	57.5	54.2	55.0	51.7	50.0	14.2	47.1
Bromophos EC	93.3	93.3	67.5	52.5	29.2	0	56.0
Bromophos WP	81.7	69.2	57.5	55.8	50.0	8.3	53.8
Iodofenphos EC	65.0	57.5	55.8	44.2	8.3	0	38.5
			Corn				
Malathion EC	57.5	52.5	51.7	50.8	45.0	28.3	47.6
Malathion WP	54.2	50.8	50.0	50.0	50.0	10.0	44.2
Bromophos EC	61.2	57.5	52.5	34.2	15.8	0.8	37.1
Bromophos WP	75.0	60.0	55.0	54.2	50.0	3.3	49.6
Iodofenphos EC	52.5	53.3	53.3	33.3	0.8	0	32.2
Age of insecticide deposit means	69.5	62.4	55.8	49.4	36.7	10.5	47.4
L.S.D. between any two means of stored grain type/insecticide/age of insecticide deposit interaction						5% 7.5	1% 9.9

TABLE 25. Mean percent mortality of T. castaneum adults exposed for one week on wheat, barley, and corn removed after contact for one week on wood and concrete surfaces treated with insecticides at 1.0 g AI/m^2.

Insecticide	Time (weeks)	Wood			Concrete		
		Wheat	Barley	Corn	Wheat	Barley	Corn
Malathion EC	1	100	100	100	15.1	53.3	15.0
	2	100	100	100	5.0	5.0	5.0
	4	100	100	100	3.3	1.8	3.3
	8	100	100	100	1.8	5.0	1.7
	16	100	100	89.3	0	0	0
	32	72.5	69.8	56.2	0	0	0
Malathion WP	1	100	100	100	32.2	15.0	8.3
	2	100	100	100	10.0	5.0	1.7
	4	100	100	100	6.7	5.2	0
	8	100	100	100	1.8	1.7	0
	16	98.2	100	100	0	0	0
	32	15.2	23.1	18.3	0	0	0
Bromophos EC	1	100	100	100	100	86.7	23.3
	2	100	100	100	86.7	84.6	15.0
	4	100	100	100	36.7	31.6	5.0
	8	100	100	68.3	0	5.0	0
	16	64.2	54.6	29.3	0	0	0
	32	0	0	1.7	0	0	0
Bromophos WP	1	100	100	100	61.0	63.3	50.0
	2	100	100	100	53.3	35.9	20.0
	4	100	100	100	15.0	10.5	10.0
	8	100	100	100	8.7	6.9	8.4
	16	100	100	100	0	0	0
	32	11.8	10.4	5.0	0	0	0
Iodofenphos EC	1	100	100	98.3	20.3	30.0	6.7
	2	100	100	100	10.0	11.9	6.7
	4	100	98.1	100	11.7	8.8	6.7
	8	94.7	78.2	66.7	3.5	5.1	0
	16	30.1	9.0	1.7	0	0	0
	32	5.0	0	0	0	0	0

	5%	1%
L.S.D. between any two means of surface type/insecticide grain type/age of insecticide deposit interaction.	10.6	14.0

FIGURE 10. - Persistence of insecticides taken up in wheat, barley, and corn stored for one week on surfaces treated at 1.0 g AI/m^2 against *T. castaneum*.



WOOD
CONCRETE
MALATHION EC
WOOD
CONCRETE
MALATHION WP
BROMOPHOS EC
BROMOPHOS WP
IODOFENPHOS EC
100
50
0
% MORTALITY
1
4
16
WEEKS POSTTREATMENT, (LOG10)
WHEAT
BARLEY
CORN

926

F_1 progeny - Tables 26-43 show the mean number of F_1 adults produced by 20 adults exposed for seven days in the grains previously stored for one week on untreated and treated wood and concrete surfaces at different times after treatment.

Significantly fewer progeny ($P < 0.01$) were produced in grains stored on wood surfaces than in grains stored on concrete surfaces with both *C. ferrugineus* and *T. castaneum*; also, the number of F_1 beetles resulting from grains stored on untreated structural surfaces was significantly greater than the number obtained from grains stored on treated structural surfaces (Tables 26-28, 31, 34-37, 40, and 43). There was, generally, no significant difference ($P > 0.05$) in the number of F_1 adults produced in grains stored on untreated wood and concrete surfaces with both test insects (Tables 28, 33, 34, 37, 42, and 43).

The differences in the number of F_1 adult *C. ferrugineus* produced in grains stored on treated structural surfaces were not significant at the 5 percent level of probability (Tables 26-28 and 32), but for *T. castaneum*, there were significant differences ($P < 0.01$) in the numbers of F_1 beetles produced in the different grains stored on malathion WP-treated structural surfaces (Tables 35-37 and 41). The insecticide deposits nearly prevented reproduction of both test beetles in grains stored on wood surfaces (Tables 33 and 42), and on malathion EC-treated wood surfaces, there was no progeny production by either species throughout the experimental period (Tables 34 and 43). In contrast, bromophos EC applied to concrete surfaces prevented reproduction of test beetles on grains for two weeks, and bromophos WP gave zero progeny of *C. ferrugineus* for four weeks (Tables 33 and 42). The insecticide deposits transferred to stored grains from treated concrete surfaces inhibited reproduction of adults in the grains at one or more weeks after treatment (Tables 34 and 43).

Comparing insect reproduction on grains stored on treated structural surfaces, significantly fewer ($P < 0.01$) numbers of adults were produced in barley than in wheat or corn (Tables 27, 28, 30, 31, 34, 36, 37, 39, 40, and 43). Very few or no progeny were produced in barley stored on both untreated and treated concrete surfaces despite a high percentage of survivors (Tables 34 and 43). There was no significant difference ($P > 0.05$) in the number of F_1 adult *C. ferrugineus* produced in wheat and corn stored on treated structural surfaces (Tables 27 and 28), but the number of F_1 adult *T. castaneum* produced in corn was significantly greater ($P < 0.01$) than the number obtained in wheat (Tables 36 and 37). On both treated wood and concrete surfaces, corn appeared to be the least protected against *C. ferrugineus* and *T. castaneum* apparently because of the relatively lower mortality obtained on corn (Tables 34 and 43).

The emergence of adult beetles in stored grain was directly related to the age of insecticide deposits on the structural surfaces; as with the increase in age of insecticide deposit there was a corresponding increase in emergence (Tables 29-36 and 38-43). The maximum adult beetle emergence in wheat and corn took place at 32 weeks after treatment (Tables 30-33 and 39-42).

TABLE 26. Mean number of *C. ferrugineus* F_1 adults produced in grains after one week of infestation of grain previously stored for one week on wood and concrete surfaces treated with insecticides at 1.0 g AI/m^2.

Insecticide	Wood	Concrete	Insecticide means
Control	14.2	13.1	13.7
Malathion EC	0.0	5.9	3.0
Malathion WP	0.2	7.1	3.7
Bromophos EC	1.7	3.6	2.7
Bromophos WP	1.2	4.3	2.8
Iodofenphos EC	2.2	4.3	3.3
Surface type means	3.3	6.4	4.8

L.S.D. between	5%	1%
(i) Means of type of surface	0.4	0.6
(ii) Any two means of insecticide treatment	0.7	1.0
(iii) Any two means of surface type for the same insecticide or vice versa.	1.0	1.4

TABLE 27. Mean number of C. ferrugineus F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on structural surfaces (wood and concrete) treated with insecticides at 1.0g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
Control	22.9	0.2	17.7	13.7
Malathion EC	4.3	0	4.6	3.0
Malathion WP	5.7	0.1	5.2	3.7
Bromophos EC	3.4	0	4.6	2.7
Bromophos WP	2.4	0	5.9	2.8
Iodofenphos EC	4.0	0	5.8	3.3
Grain means	7.1	0.1	7.3	4.8

L.S.D. between any	5%	1%
(i) Two means of stored grain type	0.5	0.7
(ii) Two means of stored grain type for the same insecticide or vice versa.	1.3	1.7

TABLE 28. Mean number of C. ferrugineus F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on wood and concrete surfaces treated with insecticides at 1.0g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
		Wood		
Control	24.6	0.3	17.6	14.2
Malathion EC	0	0	0	0
Malathion WP	0	0	0.7	0.2
Bromophos EC	2.7	0	2.6	1.7
Bromophos WP	1.0	0	2.7	1.2
Iodofenphos EC	3.0	0	3.6	2.2
		Concrete		
Control	21.3	0.1	17.8	13.1
Malathion EC	8.6	0	9.2	5.9
Malathion WP	11.4	0.2	9.7	7.1
Bromophos EC	4.2	0	6.6	3.6
Bromophos WP	3.8	0	9.0	4.3
Iodofenphos EC	4.9	0	8.1	4.3
Grain means	7.1	0.1	7.3	4.8

	5%	1%
L.S.D. between any two means of surface type/insecticide/grain type interaction.	1.8	2.4

TABLE 29. Mean number of _C. ferrugineus_ F_1 adults produced in grains after one week of infestation of grain previously stored for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Surface type	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Surface type means
Wood	2.7	2.2	2.0	2.4	2.8	7.5	3.3
Concrete	2.3	2.9	3.7	6.9	9.7	12.9	6.4
Age of insecticide deposit means	2.5	2.6	2.8	4.6	6.2	10.2	4.8

L.S.D. between any	5%	1
(i) Two means of age of insecticide deposit	0.6	0.8
(ii) Two means of age of insecticide deposit for the same surface type or vice versa.	0.9	1.2

TABLE 30. Mean number of *C. ferrugineus* F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Grain	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Grain means
Wheat	4.8	4.1	4.2	6.9	8.3	14.4	7.1
Barley	0.1	0	0.1	0.1	0	0	0.1
Corn	2.7	3.6	4.2	6.9	10.4	16.1	7.3
Age of insecticide deposit means	2.5	2.6	2.8	4.6	6.2	10.2	4.8

	5%	1%
L.S.D. between any two means of stored grain type for the same age of insecticide deposit or vice versa.	1.1	1.4

TABLE 31. Mean number of C. ferrugineus F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Grain	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Grain means
			Wood				
Wheat	5.6	4.6	3.5	3.5	3.7	10.5	5.2
Barley	0.1	0.1	0.2	0	0	0	0.1
Corn	2.6	2.1	2.1	3.7	4.7	12.0	4.5
			Concrete				
Wheat	4.1	3.6	4.9	10.3	12.8	18.4	9.0
Barley	0.1	0	0	0.1	0.1	0.1	0.1
Corn	2.7	5.1	6.2	10.2	16.2	20.1	10.1
Age of insecticide deposit means	2.5	2.6	2.8	4.6	6.2	10.2	4.8

	5%	1%
L.S.D. between any two means of surface type/grain type/age of insecticide deposit interaction.	1.5	2.0

TABLE 32. Mean number of _C. ferrugineus_ F_1 adults produced in grains after one week of infestation of grain previously stored for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
Control	14.6	12.5	12.3	13.8	15.0	13.6	13.7
Malathion EC	0	0.8	1.8	3.5	4.8	6.9	3.0
Malathion WP	0.5	0.9	0.9	5.7	5.6	8.3	3.7
Bromophos EC	0	0	0.8	1.9	3.7	9.6	2.7
Bromophos WP	0	0	0	0.7	5.1	10.8	2.8
Iodofenphos EC	0	1.1	1.2	2.1	3.3	11.9	3.3
Age of insecticide deposit means	2.5	2.6	2.8	4.6	6.2	10.2	4.8

	5%	1%
L.S.D. between any two means of insecticide for the same age of insecticide deposit or vice versa.	1.5	2.0

TABLE 33. Mean number of C. ferrugineus F_1 adults produced in grains after one week of infestation of grain previously stored for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Insecticide	1	2	4	8	16	32	Insecticide means
	Age of insecticide deposit (weeks)						
			Wood				
Control	16.4	13.3	11.8	14.3	15.0	14.2	14.2
Malathion EC	0	0	0	0	0	0	0
Malathion WP	0	0	0	0	0	1.4	0.2
Bromophos EC	0	0	0	0	1.3	9.1	1.7
Bromophos WP	0	0	0	0	0	7.4	1.2
Iodofenphos EC	0	0	0	0	0.4	12.7	2.2
			Concrete				
Control	12.8	11.7	12.8	13.2	15.0	12.9	13.1
Malathion EC	0	1.7	3.6	7.0	9.6	13.8	5.9
Malathion WP	1.0	1.9	1.9	11.4	11.2	15.2	7.1
Bromophos EC	0	0	1.7	3.9	6.0	10.0	3.6
Bromophos WP	0	0	0	1.3	10.1	14.1	4.3
Iodofenphos EC	0	2.1	2.3	4.2	6.2	11.1	4.3
Age of insecticide deposit means	2.5	2.6	2.8	4.6	6.2	10.2	4.8

	5%	1%
L.S.D. between any two means of surface type/insecticide/age of insecticide deposit interaction.	2.2	2.8

TABLE 34. Mean number of C. ferrugineus F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on wood and concrete surfaces treated with insecticides at 1.0g AI/m^2.

		Wood			Concrete		
Insecticide	Time (weeks)	Wheat	Barley	Corn	Wheat	Barley	Corn
Control	1	33.3	0.3	15.7	24.7	0.3	13.3
	2	27.3	0.3	12.3	20.3	0.3	14.7
	4	21.0	1.3	13.0	24.3	0	14.0
	8	21.0	0	22.0	19.7	0	20.0
	16	21.7	0	23.0	21.0	0	24.0
	32	23.3	0	19.3	17.7	0	21.0
Malathion EC	1	0	0	0	0	0	0
	2	0	0	0	1.3	0	3.7
	4	0	0	0	3.7	0	7.0
	8	0	0	0	12.3	0	8.7
	16	0	0	0	16.7	0	12.0
	32	0	0	0	17.7	0	23.7
Malathion WP	1	0	0	0	0	0	3.0
	2	0	0	0	0	0	5.7
	4	0	0	0	1.7	0	4.0
	8	0	0	0	19.7	0.7	14.0
	16	0	0	0	16.7	0.3	16.3
	32	0	0	4.3	30.3	0.3	15.0
Bromophos EC	1	0	0	0	0	0	0
	2	0	0	0	0	0	0
	4	0	0	0	0	0	5.0
	8	0	0	0	3.3	0	7.7
	16	0.3	0	3.7	5.0	0	13.0
	32	15.7	0	11.7	16.0	0	14.0
Bromophos WP	1	0	0	0	0	0	0
	2	0	0	0	0	0	0
	4	0	0	0	0	0	0
	8	0	0	0	1.3	0	2.7
	16	0	0	0	10.0	0	20.3
	32	6.0	0	16.3	11.3	0	31.0

(Continued)

TABLE 34 (Continued)

Insecticide	Time (weeks)	Wood			Concrete		
		Wheat	Barley	Corn	Wheat	Barley	Corn
Iodofenphos EC	1	0	0	0	0	0	0
	2	0	0	0	0	0	6.3
	4	0	0	0	0	0	7.0
	8	0	0	0	4.7	0	8.0
	16	0	0	1.3	7.7	0	11.0
	32	18.0	0	20.0	17.3	0	16.0

L.S.D. between any two means of surface type/ insecticide/grain type/age of insecticide deposit interaction (0.05) = 3.7

(0.01) = 4.9

TABLE 35. Mean number of T. castaneum F_1 adults produced in grains after one week of infestation of grain previously stored for one week on wood and concrete surfaces treated with insecticides at 1.0g AI/m^2.

Insecticide	Wood	Concrete	Insecticide means
Control	16.8	19.0	17.9
Malathion EC	0	8.9	4.5
Malathion WP	0.1	13.6	6.9
Bromophos EC	0.5	5.6	3.1
Bromophos WP	0.5	5.6	3.1
Iodofenphos EC	2.3	5.8	4.0
Surface type means	3.4	9.8	6.6

L.S.D. between	5%	1%
(i) Means of type of surface	0.6	0.9
(ii) Any two means of insecticide treatment	1.1	1.5
(iii) Any two means of surface type for the same insecticide or vice versa.	1.6	2.2

TABLE 36. Mean number of _T. castaneum_ F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on structural surfaces (wood and concrete) treated with insecticides at 1.0g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
Control	16.4	0.2	37.1	17.9
Malathion EC	3.9	0	9.5	4.5
Malathion WP	5.6	0	15.0	6.9
Bromophos EC	3.2	0	6.1	3.1
Bromophos WP	2.8	0	6.4	3.1
Iodofenphos EC	3.1	0	8.9	4.0
Grain means	5.8	0	13.8	6.6

L.S.D. between any	5%	1%
(i) Two means of stored grain type	0.7	1.0
(ii) Two means of stored grain type for the same insecticide or vice versa.	1.8	2.4

TABLE 37. Mean number of T. castaneum F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on wood and concrete surfaces treated with insecticides at 1.0g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
		Wood		
Control	12.9	0.2	37.3	16.8
Malathion EC	0	0	0	0
Malathion WP	0.1	0	0.2	0.1
Bromophos EC	0.6	0	1.1	0.5
Bromophos WP	0.1	0	1.3	0.5
Iodofenphos EC	1.9	0	5.0	2.3
		Concrete		
Control	19.9	0.3	36.9	19.0
Malathion EC	7.8	0	18.9	8.9
Malathion WP	11.2	0	29.8	13.6
Bromophos EC	5.9	0	11.1	5.6
Bromophos WP	5.4	0	11.4	5.6
Iodofenphos EC	4.4	0	12.9	5.8
Grain means	5.8	0	13.8	6.6

	5%	1%
L.S.D. between any two means of surface type/ insecticide/grain type interaction.	2.5	3.3

TABLE 38. Mean number of T. castaneum F_1 adults produced in grains after one week of infestation of grain previously stored for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Surface type	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Surface type means
Wood	3.1	2.9	3.9	2.5	2.8	5.0	3.4
Concrete	4.4	4.1	8.6	11.5	14.7	15.3	9.8
Age of insecticide deposit means	3.7	3.5	6.2	7.0	8.8	10.2	6.6

L.S.D. between any	5%	1%
(i) Two means of age of insecticide deposit	1.9	2.5
(ii) Two means of age of insecticide deposit for the same surface type or vice versa.	2.7	3.5

TABLE 39. Mean number of *T. castaneum* F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Grain	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Grain means
Wheat	4.5	2.5	3.3	6.5	8.7	9.6	5.8
Barley	0.1	0.1	0	0	0	0	0
Corn	6.6	7.8	15.4	14.6	17.6	20.9	13.8
Age of insecticide deposit means	3.7	3.5	6.2	7.0	8.8	10.2	6.6

	5%	1%
L.S.D. between any two means of stored grain type for the same age of insecticide deposit or vice versa.	3.3	4.4

TABLE 40. Mean number of *T. castaneum* F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Grain	1	2	4	8	16	32	Grain means
	Age of insecticide deposit (weeks)						
			Wood				
Wheat	3.0	2.4	2.2	1.7	1.7	4.5	2.6
Barley	0.1	0.1	0	0	0	0	0
Corn	6.1	6.2	9.4	5.9	6.7	10.5	7.5
			Concrete				
Wheat	6.0	2.5	4.4	11.3	15.7	14.7	9.1
Barley	0	0	0	0	0	0	0
Corn	7.2	9.4	21.4	23.2	28.5	31.3	20.2
Age of insecticide deposit means	3.7	3.5	6.2	7.0	8.8	10.2	6.6

	5%	1%
L.S.D. between any two means of surface type/grain type/age of insecticide deposit interaction.	4.6	6.1

TABLE 41. Mean number of *T. castaneum* F_1 adults produced in grains after one week of infestation of grain previously stored for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
Control	21.1	16.4	24.1	15.7	17.4	12.8	17.9
Malathion EC	0.8	0.9	1.9	7.0	8.0	8.1	4.5
Malathion WP	0	2.4	5.9	8.8	10.8	13.2	6.9
Bromophos EC	0	0	1.1	4.3	5.7	7.5	3.1
Bromophos WP	0	0.1	2.9	4.2	4.8	6.3	3.1
Iodofenphos EC	0.6	0.9	1.4	2.1	5.9	13.2	4.0
Age of insecticide deposit means	3.7	3.5	6.2	7.0	8.8	10.2	6.6

	5%	1%
L.S.D. between any two means of insecticide for the same age of insecticide deposit or vice versa.	4.6	6.1

TABLE 42. Mean number of T. castaneum F_1 adults produced in grains after one week of infestation of grain previously stored for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
			Wood				
Control	18.4	17.3	23.1	15.0	14.9	12.0	16.8
Malathion EC	0	0	0	0	0	0	0
Malathion WP	0	0	0	0	0	0.4	0.1
Bromophos EC	0	0	0	0	0.4	2.8	0.5
Bromophos WP	0	0	0	0	0	2.8	0.5
Iodofenphos EC	0	0	0	0.2	1.6	12.0	2.3
			Concrete				
Control	23.7	15.6	25.0	16.4	19.9	13.6	19.0
Malathion EC	1.6	1.9	3.9	14.0	16.0	16.1	8.9
Malathion WP	0	4.9	11.9	17.6	21.7	25.9	13.6
Bromophos EC	0	0	2.1	8.7	10.9	12.2	5.6
Bromophos WP	0	0.2	5.8	8.3	9.7	9.8	5.6
Iodofenphos EC	1.2	1.8	2.9	4.0	10.2	14.4	5.8
Age of insecticide deposit means	3.7	3.5	6.2	7.0	8.8	10.2	6.6

	5%	1%
L.S.D. between any two means of surface type/ insecticide/age of insecticide deposit interaction.	6.5	8.6

TABLE 43. Mean number of *T. castaneum* F_1 adults produced in wheat, barley, and corn after one week of infestation of grain previously stored for one week on wood and concrete surfaces treated with insecticides at 1.0g AI/m^2.

Insecticide	Time (weeks)	Wood			Concrete		
		Wheat	Barley	Corn	Wheat	Barley	Corn
Control	1	18.0	0.7	36.7	32.7	0.3	34.7
	2	14.7	0.3	37.0	14.0	1.3	43.3
	4	13.0	0	56.3	17.3	0	57.7
	8	10.3	0	34.7	17.3	0	32.0
	16	10.3	0	34.3	21.3	0	38.3
	32	11.3	0	24.7	13.3	0	27.3
Malathion EC	1	0	0	0	0	0	4.7
	2	0	0	0	1.0	0	4.7
	4	0	0	0	3.7	0	8.0
	8	0	0	0	12.3	0	29.7
	16	0	0	0	15.3	0	32.7
	32	0	0	0	14.3	0	34.0
Malathion WP	1	0	0	0	0	0	0
	2	0	0	0	0	0	14.7
	4	0	0	0	1.3	0	34.3
	8	0	0	0	19.7	0	33.0
	16	0	0	0	24.7	0	40.3
	32	0.3	0	1.0	21.3	0	56.3
Bromophos EC	1	0	0	0	0	0	0
	2	0	0	0	0	0	0
	4	0	0	0	0	0	6.3
	8	0	0	0	11.0	0	15.0
	16	0	0	1.3	11.3	0	21.3
	32	3.3	0	5.0	13.0	0	23.7
Bromophos WP	1	0	0	0	0	0	0
	2	0	0	0	0	0	0.7
	4	0	0	0	3.7	0	10.3
	8	0	0	0	6.7	0	18.3
	16	0	0	0	11.7	0	17.3
	32	0.7	0	7.7	10.7	0	18.7

(Continued)

TABLE 43 (Continued)

Insecticide	Time (weeks)	Wood			Concrete		
		Wheat	Barley	Corn	Wheat	Barley	Corn
Iodofenphos EC	1	0	0	0	0	0	3.7
	2	0	0	0	0	0	5.3
	4	0	0	0	0.3	0	8.3
	8	0	0	0.7	0.7	0	11.3
	16	0	0	4.7	9.7	0	21.0
	32	11.3	0	24.7	15.7	0	27.7

L.S.D. between any two means of surface type/insecticide/grain type/age of insecticide deposit interaction (0.05) = 11.3

(0.01) = 14.9

2. <u>The translocation of bromophos, iodofenphos, and malathion deposits into wheat, barley, and corn</u>.

The statistical analysis of the data from the chemical assay performed at 1, 2, 4, 8, 16, and 32 weeks after treatment on 30 g of stored grain also showed a significant difference between the two structural surfaces in the amount of toxic material picked up by the cereal grains. Significantly more insecticide residues ($P < 0.01$) were recovered from all grain samples stored on treated wood surfaces than from grain samples stored on treated concrete surfaces (Tables 44, 46, 47, 49, and 52). The mean insecticide residue recovered from grains stored on wood surfaces during the 32-week period of the study ranged from 4.46 ppm for iodofenphos EC to 14.95 ppm for bromophos EC, in contrast to 0.38 ppm iodofenphos to 1.21 ppm bromophos EC on concrete surfaces (Table 44).

The translocation of the insecticides into stored grains from treated surfaces was found to be dependent upon the type and formulation of insecticide, the kind of grain in contact with the treated surfaces, the age of insecticide deposit and the interactions between these factors. Significantly higher amounts of insecticide residues ($P < 0.01$) were recovered from the bromophos EC treatment (Table 44) but the insecticide transferred to the stored grain samples decreased sharply after eight weeks on both structural surfaces (Tables 48, 49, and 52). Although less iodofenphos was transferred to the stored grain samples from both structural surfaces in comparison with other insecticide treatments (Tables 46, 48, 49, 51, and 52), it appeared to have a relatively good stability. A comparison of the EC and WP formulations of malathion and bromophos showed higher residue recoveries from the EC on both structural surfaces than from the WP formulation (Tables 44 and 46) but with age of insecticide deposit, bromophos WP persisted longer than its EC formulation whereas the reverse was true for the malathion treatments (Tables 48 and 52). According to the residual amounts of insecticide recovered from the grain samples stored on structural surfaces, malathion formulations were generally more stable on wood surfaces than bromophos and iodofenphos (Table 52). On concrete surfaces, however, both insecticide treatments had shorter persistence but bromophos EC was recovered in relatively higher amounts in stored grain samples for four weeks (Table 52).

The kind of cereal grain in contact with treated surface also influenced the amount of insecticide transferred to the stored grain. Lower amounts of insecticides ($P < 0.01$) were transferred to corn stored on treated structural surfaces than to wheat and barley (Tables 45, 49, and 50) and the differences were more apparent in grain samples stored on treated wood surfaces (Tables 46 and 52). There was generally no significant difference ($P > 0.05$) in the uptake of insecticides by wheat and barley stored on treated structural surfaces (Tables 45, 46, 50, and 51). The uptake of iodofenphos by wheat from treated wood surfaces significantly ($P > 0.05$) exceeded that of barley only at two weeks after treatment (Table 52).

Generally, the translocation of insecticides into stored grain from wood and concrete surfaces decreased progressively with age of the insecticide deposit (Tables 47-52). Initially, the insecticide residues recovered from stored wheat and barley in direct contact with wood surfaces were high but when they were mixed with the upper layers of grain the residues decreased sharply to within tolerable limits (FAO/WHO, 1973a, 1976a).

TABLE 44. Mean uptake of insecticides (ppm) by grains stored for one week on wood and concrete surfaces treated at 1.0g AI/m^2.

Insecticide	Wood	Concrete	Insecticide means
Malathion EC	12.29	0.91	6.60
Malathion WP	10.65	0.86	5.76
Bromophos EC	14.95	1.21	8.08
Bromophos WP	8.44	0.72	4.58
Iodofenphos EC	4.46	0.38	2.42
Surface type means	10.16	0.82	5.49

L.S.D. between	5%	1%
(i) Means of type of surface	0.33	0.45
(ii) Any two means of insecticide	0.53	0.72
(iii) Any two means of surface type for the same insecticide or vice versa.	0.75	1.02

TABLE 45. Mean uptake of insecticides (ppm) by wheat, barley, and corn stored for one week on structural surfaces (wood and concrete) treated at 1.0g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
Malathion EC	7.31	8.40	4.09	6.60
Malathion WP	6.76	7.22	3.29	5.76
Bromophos EC	10.18	10.03	4.02	8.08
Bromophos WP	6.07	5.51	2.16	4.58
Iodofenphos EC	3.38	2.55	1.33	2.42
Grain means	6.74	6.74	2.98	5.49

L.S.D. between any	5%	1%
(i) Two means of stored grain	0.37	0.49
(ii) Two means of stored grain for the same insecticide or vice versa.	0.82	1.10

TABLE 46. Mean uptake of insecticides (ppm) by wheat, barley, and corn stored for one week on wood and concrete surfaces treated at 1.0g AI/m^2.

Insecticide	Wheat	Barley	Corn	Insecticide means
		Wood		
Malathion EC	13.75	15.60	7.53	12.29
Malathion WP	12.38	13.46	6.11	10.65
Bromophos EC	18.68	18.69	7.48	14.95
Bromophos WP	11.22	10.10	3.99	8.44
Iodofenphos EC	6.31	4.65	2.41	4.46
		Concrete		
Malathion EC	0.88	1.21	0.65	0.91
Malathion WP	1.13	0.98	0.48	0.86
Bromophos EC	1.69	1.37	0.57	1.21
Bromophos WP	0.93	0.91	0.33	0.72
Iodofenphos EC	0.45	0.45	0.24	0.38
Grain means	6.74	6.74	2.98	5.49

L.S.D. between any two means of surface	5%	1%
type/insecticide/grain type interaction	1.16	1.55

TABLE 47. Mean uptake of insecticides (ppm) by grains stored for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Surface type	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Surface type means
Wood	17.41	15.62	12.39	8.95	5.09	1.47	10.16
Concrete	2.02	1.29	0.96	0.50	0.10	0.04	0.82
Age of insecticide deposit means	9.71	8.45	6.68	4.72	2.59	0.76	5.49

L.S.D. between any	5%	1%
(i) Two means of age of insecticide deposit	0.34	0.45
(ii) Two means of age of insecticide deposit for the same surface type or vice versa.	0.48	0.64

TABLE 48. Mean uptake of insecticides (ppm) by grains stored for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
Malathion EC	10.65	8.07	7.19	6.98	4.48	2.24	6.60
Malathion WP	8.82	8.10	7.68	5.47	3.51	0.95	5.76
Bromophos EC	17.81	15.71	10.23	3.42	1.14	0.17	8.08
Bromophos WP	6.70	6.46	5.69	5.30	3.00	0.33	4.58
Iodofenphos EC	4.60	3.93	2.60	2.44	0.84	0.09	2.42
Age of insecticide deposit means	9.71	8.45	6.68	4.72	2.59	0.76	5.49

	5%	1%
L.S.D. between any two means of age of insecticide deposit for the same insecticide or vice versa.	0.77	1.01

TABLE 49. Mean uptake of insecticides (ppm) by grains stored for one week on treated wood and concrete surfaces at different ages of insecticide deposit.

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
			Wood				
Malathion EC	18.81	14.98	13.42	13.30	8.85	4.39	12.29
Malathion WP	15.51	15.04	14.31	10.35	6.87	1.82	10.65
Bromophos EC	32.43	29.14	18.93	6.60	2.25	0.34	14.95
Bromophos WP	11.75	11.59	10.61	10.08	5.93	0.66	8.44
Iodofenphos EC	8.56	7.34	4.71	4.42	1.55	0.15	4.46
			Concrete				
Malathion EC	2.50	1.15	0.95	0.66	0.12	0.08	0.91
Malathion WP	2.13	1.17	1.06	0.60	0.15	0.09	0.86
Bromophos EC	3.18	2.29	1.52	0.24	0.04	0.0	1.21
Bromophos WP	1.64	1.32	0.78	0.52	0.06	0.01	0.72
Iodofenphos EC	0.64	0.52	0.49	0.45	0.13	0.03	0.38
Age of insecticide deposit means	9.71	8.45	6.68	4.72	2.59	0.76	5.49

	5%	1%
L.S.D. between any two means of surface type/insecticide/age of insecticide deposit interaction.	1.08	1.43

TABLE 50. Mean uptake of insecticides (ppm) by wheat, barley, and corn stored for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Grain	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Grain means
Wheat	11.93	10.46	8.39	5.82	3.00	0.84	6.74
Barley	11.74	10.60	7.84	5.95	3.37	0.95	6.74
Corn	5.47	4.30	3.80	2.41	1.41	0.48	2.98
Age of insecticide deposit means	9.71	8.45	6.68	4.72	2.59	0.76	5.49

L.S.D. between any two means of stored grain for the same age of insecticide deposit or vice versa.	5%	1%
	0.59	0.78

TABLE 51. Mean uptake of various insecticides (ppm) by wheat, barley, and corn stored for one week on treated structural surfaces (wood and concrete) at different ages of insecticide deposit.

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
			Wheat				
Malathion EC	11.55	9.08	7.85	8.14	4.54	2.73	7.31
Malathion WP	10.67	10.13	9.01	6.36	3.44	0.93	6.76
Bromophos EC	21.71	19.16	13.74	4.64	1.68	0.16	10.18
Bromophos WP	8.90	8.45	7.88	6.72	4.19	0.29	6.07
Iodofenphos EC	6.82	5.50	3.47	3.22	1.14	0.11	3.38
			Barley				
Malathion EC	13.52	9.72	9.32	9.15	6.05	2.66	8.40
Malathion WP	10.29	9.60	9.83	7.06	5.27	1.27	7.22
Bromophos EC	21.90	21.39	11.21	4.27	1.27	0.15	10.03
Bromophos WP	8.06	7.92	6.38	6.68	3.47	0.53	5.51
Iodofenphos EC	4.94	4.38	2.48	2.57	0.81	0.11	2.55

(Continued)

TABLE 51 (Continued)

Insecticide	Age of insecticide deposit (weeks) 1	2	4	8	16	32	Insecticide means
			Corn				
Malathion EC	6.89	5.41	4.40	3.65	2.86	1.32	4.09
Malathion WP	5.49	4.58	4.21	3.00	1.82	0.67	3.29
Bromophos EC	9.80	6.59	5.72	1.35	0.48	0.21	4.02
Bromophos WP	3.12	3.00	2.82	2.52	1.33	0.18	2.16
Iodofenphos EC	2.05	1.92	1.85	1.52	0.57	0.04	1.33
Age of insecticide deposit means	9.71	8.45	6.68	4.72	2.59	0.76	5.49

L.S.D. between any two means of insecticide/stored grain type/age of insecticide deposit interaction

(0.05) = 1.33

(0.01) = 1.75

TABLE 52. Mean uptake of insecticides (ppm) by wheat, barley, and corn stored for one week on wood and concrete surfaces treated at 1.0g AI/m^2.

Insecticide	Time (weeks)	Wood			Concrete		
		Wheat	Barley	Corn	Wheat	Barley	Corn
Malathion EC	1	20.96	23.68	11.78	2.13	3.36	2.00
	2	16.78	18.13	10.04	1.38	1.30	0.77
	4	14.71	17.48	8.08	0.99	1.16	0.71
	8	15.73	17.26	6.90	0.56	1.04	0.41
	16	8.96	11.86	5.71	0.11	0.24	0.0
	32	5.33	5.19	2.64	0.12	0.13	0.0
Malathion WP	1	18.31	18.49	9.72	3.03	2.09	1.26
	2	18.81	17.76	7.88	1.46	1.43	0.62
	4	16.83	18.21	8.54	1.19	1.44	0.55
	8	11.97	13.53	5.53	0.75	0.59	0.46
	16	6.66	10.32	3.64	0.22	0.22	0.0
	32	1.72	2.41	1.34	0.13	0.13	0.0

(Continued)

TABLE 52 (Continued)

Insecticide	Time (weeks)	Wood			Concrete		
		Wheat	Barley	Corn	Wheat	Barley	Corn
Bromophos EC	1	38.50	40.50	18.30	4.93	3.31	1.30
	2	35.59	39.91	11.06	2.73	2.88	1.22
	4	25.34	20.76	11.55	2.15	1.66	0.76
	8	9.02	8.21	2.58	0.25	0.33	0.13
	16	3.29	2.48	0.97	0.06	0.05	0.0
	32	0.32	0.30	0.42	0.0	0.0	0.0
Bromophos WP	1	15.74	13.93	5.59	1.70	2.20	0.65
	2	15.20	14.12	5.45	2.07	1.72	0.55
	4	14.71	11.88	5.23	0.58	0.60	0.41
	8	12.86	12.76	4.64	1.05	0.87	0.39
	16	8.26	6.87	2.66	0.11	0.07	0.0
	32	0.54	1.07	0.36	0.04	0.0	0.0
Iodofenphos EC	1	12.93	9.00	3.75	0.70	0.87	0.34
	2	10.38	8.13	3.50	0.61	0.63	0.34
	4	6.28	4.48	3.37	0.66	0.48	0.33
	8	5.90	4.63	2.72	0.54	0.51	0.32
	16	2.16	1.45	1.03	0.12	0.16	0.15
	32	0.19	0.18	0.09	0.04	0.05	0.0

L.S.D. between any two means of surface type/insecticide/grain type/age of insecticide deposit interaction (0.05) = 1.87

(0.01) = 2.47

3. Field tests with bromophos 25% WP as a residual protectant against rusty grain beetle infestations

The data in Tables 53-56 give the experimental conditions during storage of wheat on the treated, concrete floor of a granary, the percent mortality of *C. ferrugineus* exposed for seven days on wheat stored previously on the treated floor, F_1 progeny development, and residues (ppm) recovered from the stored wheat.

There was an unusually high insect mortality in wheat stored on the control surface, especially on the bottom 8.3-cm layer of stored wheat (Table 54). Bromophos taken up by the bottom layer of wheat provided complete control of *C. ferrugineus* for eight weeks, whereas the residues on the middle and top layers gave very low or no mortality of *C. ferrugineus*. The residues in the bottom layer completely prevented reproduction of *C. ferrugineus* in contrast to the middle and top layers (Table 55). Significantly higher ($P < 0.01$) numbers of F_1 adult beetles were produced in the middle layer of stored wheat compared with the bottom layer but there was similar ($P > 0.01$) development of F_1 progeny on layers of wheat from the control surface.

Significantly higher amounts of bromophos residues ($P < 0.01$) were recovered in the bottom layers of stored wheat in contact with the treated floor (Table 56). The insecticide transferred to the bottom layer of wheat increased from 0.62 ppm after one week to 0.68 ppm after two weeks and then decreased to 0.32 ppm eight weeks after treatment. There was very little uptake of bromophos by the middle and top layers of the stored wheat. No bromophos residues were found in the layers of wheat stored on the control surface.

In studies conducted to determine bromophos residues in grain stored in a granary whose structural surfaces were treated with

TABLE 53. The experimental conditions during storage of wheat on the treated concrete floor of a farm granary.

	Granary conditions			Wheat	
Post-treatment period (weeks)	Floor temp. (°C)	Air temp. (°C)	R.H. (%)	Grain temp. (°C)	Moisture content (%)
0	16.0	17.0	70	17.0	12.6
1	18.0	23.0	60	17.0	–
2	19.0	22.0	71	20.0	–
4	18.0	19.4	69	17.0	–
8	18.0	20.0	70	18.0	12.8

TABLE 54. Mean percent mortality of *C. ferrugineus* adults exposed for one week on wheat previously stored on a concrete floor of a farm granary treated with bromophos WP at 1.0g AI/m^2.

Treatment	Column layer[a]	Time after treatment (weeks) 1	2	4	8
Control	Top	1.7	0.7	0	0.7
	Middle	1.7	0	0	1.7
	Bottom	18.3	0	10.0	11.7
Bromophos WP	Top	3.3	10.0	1.7	3.3
	Middle	3.3	1.7	1.7	0
	Bottom	100	100	100	100

[a]Each layer was 8.3cm deep.

TABLE 55. Mean number of *C. ferrugineus* F_1 adults produced in 50g wheat after seven days of infestation of the grain with 20 adult beetles.

Treatment	Column layer[a]	Time after treatment (weeks) 1	2	4	8	Column layer means
Control	Top	36.0	51.0	45.7	33.3	41.5
	Middle	45.7	55.0	39.3	44.7	46.2
	Bottom	39.0	50.0	41.3	30.0	40.1
Bromophos WP	Top	38.7	35.7	42.7	27.0	36.0
	Middle	44.0	47.7	55.7	40.7	47.0
	Bottom	0	0	0	0	0
Time means		33.9	39.9	37.5	29.3	35.2

[a]Each layer was 8.3cm deep

L.S.D. between any	5%	1%
(i) Two column layer means	7.3	9.7
(ii) Two post-treatment period means	5.9	7.9
(iii) Two column layer means for the same post-treatment period or vice versa.	14.5	19.4

TABLE 56. Uptake of bromophos WP into stored wheat from a concrete floor of a farm granary[a].

Column layer[b]	Time after treatment (week)[c] 1	2	4	8
Top	0.08	0.07	0.04	0.09
Middle	0.05	<0.04	<0.04	0.04
Bottom	0.62	0.68	0.52	0.32

[a]Mean residue (ppm) of 3 replicates

[b]Each layer was 8.3cm deep

[c]S.E. ± 0.05

bromophos WP at 1.0g AI/m^2 prior to storage of wheat, the following results were obtained. Table 57 shows the mean bromophos residue recovered from wheat, the percent mortality of *C. ferrugineus*, and the F_1 progeny produced in wheat samples taken at different levels (bushels) during unloading of the grain from the treated bin.

No bromophos residues were detected in the upper 450 bushels of wheat stored in the treated bin. There was negligible uptake of bromophos at the 600-bushel level. The uptake of bromophos by wheat was found to increase considerably as the bin was emptied. The greatest amount of bromophos residue (0.68 ppm) was recovered in wheat close to the treated walls and floor.

There was a close relationship between the bromophos residues detected at the various bushel levels of wheat, percent mortality, and development of *C. ferrugineus* in the wheat samples taken at these levels. Complete control of *C. ferrugineus* was obtained on wheat samples with 0.51 ppm or higher, and these residue levels prevented reproduction of *C. ferrugineus*. Although 0.29 and 0.38 ppm bromophos gave 87.5 and 95.3 percent mortality, respectively, F_1 adult beetles were able to develop at these concentration levels.

TABLE 57. Mean residue (ppm), percent mortality, and numbers of *C. ferrugineus* F_1 adults in wheat stored in a bin treated with bromophos WP at 1.0 g AI/m^2.[1]

Bushel level at which sample was taken	Residue (ppm)	% mortality	F_1 progeny
Control	0	-	85.3
150	0	0	91.7
300	0	0	88.3
450	0	0	81.7
600	0.07	0	70.0
750	0.09	0	54.7
875	0.10	2.3	42.7
950	0.16	18.4	45.0
1000	0.29	87.5	8.3
1050	0.38	95.3	4.3
1075	0.51	100.0	0
1090 + swept grain	0.68	100.0	0

[1] Based on 3 determinations from the same sample.

4. <u>The effect of moisture content on uptake of malathion and bromophos from wood surface into wheat</u>.

Bioassay of the grain with adults of *C. ferrugineus* and *T. castaneum* exposed for one week showed 100 percent mortality in both insecticide treatments.

Significantly more bromophos residues ($P < 0.01$) were recovered from wheat than malathion (Table 58). The mean bromophos residue recovered from the grain stored on the wood surface was 34.06 ppm whereas the mean malathion residue was 18.22 ppm (Table 58). However, with each insecticide treatment, there was no significant difference ($P > 0.05$) between the various moisture contents on the uptake of insecticide into the grain from the treated surface. The uptake of insecticide from treated surfaces into stored grain appeared to be independent of the moisture content of the grain.

TABLE 58. Uptake of malathion and bromophos (EC) from wood surface treated at 1.0g AI/m^2 into wheat of varying moisture content stored for one week.[1]

	Moisture Content (%)			
Insecticide	12	14	16	Insecticide means
Malathion	18.33	17.48	18.84	18.22
Bromophos	33.88	33.16	35.15	34.06
M.C. means	26.11	25.32	27.00	

[1]Mean residue (ppm) of 4 replicates.

5. <u>The distribution of malathion residues in layers of grain kernels stored on wood surfaces.</u>

The results of this experiment conducted to determine whether the insecticide moves up past a single layer of kernels are shown in Tables 59 and 60, and Fig. 11.

TABLE 59. Uptake of malathion by each of three single layers of wheat stored on wood surfaces treated at 1.0g AI/m^2.

Column layer[a]	Residues (ppm) recovered after: Days 1	Days 3	Days 7	Months 1	Months 2	Column layer means
Top	0.25	0.41	1.56	6.30	9.07	3.52
Middle	0.79	3.06	5.22	17.73	21.59	9.68
Bottom	7.05	13.08	18.21	41.49	42.85	24.54
Storage period means	2.70	5.52	8.33	21.84	24.50	

[a]Each layer was 3mm deep

L.S.D. between any	5%	1%
(i) Two column layer means	1.71	2.28
(ii) Two storage period means	2.20	2.95
(iii) Two column layer means for the same storage period or vice versa.	3.82	5.10

Significantly ($P < 0.01$) more malathion translocated to the bottom layer of wheat than to the middle or top layers. The malathion picked up by the bottom layer ranged from 7.05 ppm, after a day of storage of the grain on the treated surface, to 42.85 ppm after two months of storage (Table 59). At the end of the storage period, malathion transferred to the middle and top layers were 21.59 and 9.07 ppm, respectively.

The amount of malathion transferred to the layers of wheat increased progressively with the duration of storage. There was a marked increase in the uptake of insecticide into the layers between the first and the fourth week of storage (Table 59 and Fig. 11). A significant difference ($P < 0.05$) in the amount of malathion residue recovered from the top layer occurred after one month of storage whereas in the middle and bottom layers, the differences were apparent after the seventh and the first day of storage, respectively.

The results of the bioassay of the layers of wheat stored on the treated surfaces showed a pattern similar to the results obtained for the residue analysis of the grain. Complete mortality of *T. castaneum* was obtained on the bottom layer of wheat at each assessment period in comparision with complete mortality which occurred on the middle and top layers of grain after seven days and one month of storage, respectively (Table 60 and Fig. 11). There was a progressive increase in mortality with the duration of storage of the top and middle layers of grain on the treated surface. The mortality of *T. castaneum* on the layers of wheat reflects the amount of toxicant that was transferred to the layers from the treated surface.

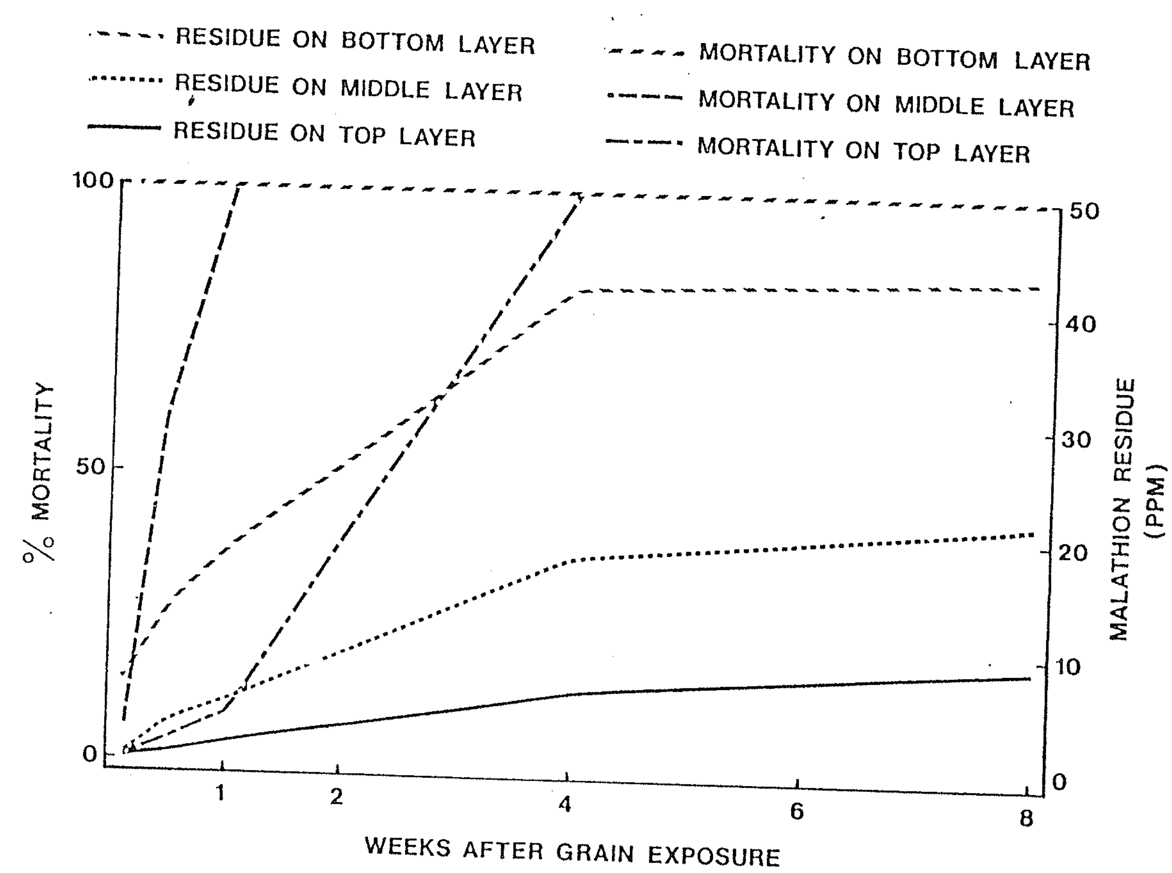
TABLE 60. Mean percent mortality of *T. castaneum* exposed for one week on layers of wheat column stored on treated wood surfaces for 1 day to two months.

Column layer[a]	Percent mortality after: Days 1	3	7	Months 1	2	Column layer means
Top	0.0	2.5	7.6	100	100	42.0
Middle	6.3	58.8	100	100	100	73.0
Bottom	100	100	100	100	100	100.0
Storage period means	35.4	53.8	69.2	100	100	

[a]Each layer was 3mm deep

L.S.D. between any	5%	1%
(i) Two column layer means	3.7	5.0
(ii) Two storage period means	4.9	6.5
(iii) Two column layer means for the same storage period or vice versa.	8.6	11.4

FIGURE 11. - Mean malathion residue (ppm) recovered from layers of wheat, and percent mortality of _T. castaneum_ on the layers of wheat stored on wood surface treated at 1.0 g AI/m^2.



RESIDUE ON BOTTOM LAYER
RESIDUE ON MIDDLE LAYER
RESIDUE ON TOP LAYER
MORTALITY ON BOTTOM LAYER
MORTALITY ON MIDDLE LAYER
MORTALITY ON TOP LAYER
100
50
0
% MORTALITY
50
40
30
20
10
0
MALATHION RESIDUE (PPM)
1
2
4
6
8
WEEKS AFTER GRAIN EXPOSURE

6. Effect of physical disruption on the persistence of insecticide deposits on structural surfaces.

The effect of physical disturbances on the persistence of malathion, bromophos (EC and WP), and iodofenphos (EC) on wood surfaces as determined by bioassay of the treated surfaces with adults of *T. castaneum* exposed for five hours are shown in Tables 61-63 and Fig. 12.

There were significant differences ($P < 0.01$) between the treated surfaces that were variously disturbed, the type of insecticide, the age of insecticide deposit, and their interactions.

The type of physical disruption used on the treated surfaces significantly ($P < 0.01$) affected the persistence of insecticide deposit. The mean percent mortality obtained on surfaces that were swept was significantly higher ($P < 0.01$) than the mean percent mortality on undisturbed surfaces and on the surfaces subjected to mechanical shaking with wheat (Table 61). Generally, more than 50 percent mortality was obtained, at each assessment period, on the surfaces that were swept 12 weeks after treatment (Table 61). There was a complete mortality of *T. castaneum* for 12 weeks on malathion- and iodofenphos-treated surfaces that were swept (Table 63 and Fig. 12). The type of physical disturbance on the effectiveness of insecticide deposit was more apparent on the surfaces that were mechanically shaken with wheat (Table 63 and Fig. 12). In the iodofenphos-treated surfaces, about 29 percent mortality was obtained one day after treatment in contrast to 99 percent mortality from other disturbed surfaces treated with the same insecticide.

Generally, the effectiveness of the insecticides decreased with the age of the deposit after the disturbance of the treated surfaces

(Tables 61 and 62). The effectiveness of the insecticide deposit with age was greatly affected on surfaces that were disturbed by abrasion (mechanical shaking) with wheat (Table 63 and Fig. 12).

There were significant differences in effectiveness of the insecticide deposits on the various disturbed surfaces. Significantly higher ($P < 0.01$) mortality was obtained on malathion-treated surfaces (Table 62), and according to the order of increasing effectiveness at the 5% level of probability malathion EC = malathion WP > iodofenphos EC > bromophos EC > bromophos WP.

TABLE 61. Mean percent mortality of T. castaneum adults exposed for 5 hours to various disturbed treated surfaces at different ages of insecticide deposit.

Type of physical disturbance	Time after treatment: Day 1	Weeks 1	3	6	12	24	Physical disturbance means
No physical disruption	97.7	99.0	89.8	71.5	42.5	1.8	67.1
Sweeping	99.5	97.5	99.5	90.0	67.3	9.5	77.2
Abrasion (with grain)	77.0	73.5	29.3	11.3	2.0	1.3	32.4
Age of insecticide deposit means	91.4	90.0	72.9	57.6	37.3	4.2	58.9

L.S.D. between any	5%	1%
(i) Two means of disturbed treated surface	2.7	3.3
(ii) Two means of age of insecticide deposit	3.6	4.4
(iii) Two means of disturbed treated surface for the same age of insecticide deposit or vice versa.	6.6	8.0

TABLE 62. Mean percent mortality of *T. castaneum* adults exposed for 5 hours to disturbed insecticide deposits on wood surfaces at different times after treatment.

	Time after treatment						
	Day	Weeks					
Insecticide	1	1	3	6	12	24	Insecticide means
Malathion EC	95.4	98.8	86.3	73.3	56.3	10.0	70.0
Malathion WP	98.8	99.6	83.3	68.8	50.8	1.7	67.2
Bromophos EC	96.3	92.5	68.3	40.0	2.5	0.4	50.0
Bromophos WP	91.3	84.6	53.8	35.4	12.5	0.0	46.3
Iodofenphos EC	75.4	75.0	72.1	70.4	64.2	8.8	61.0
Age of insecticide deposit means	91.4	90.0	72.9	57.6	37.3	4.2	58.9

L.S.D. between any	5%	1%
(i) Two means of insecticide deposit	3.4	4.1
(ii) Two means of insecticide deposit for the same age or vice versa.	8.4	10.2

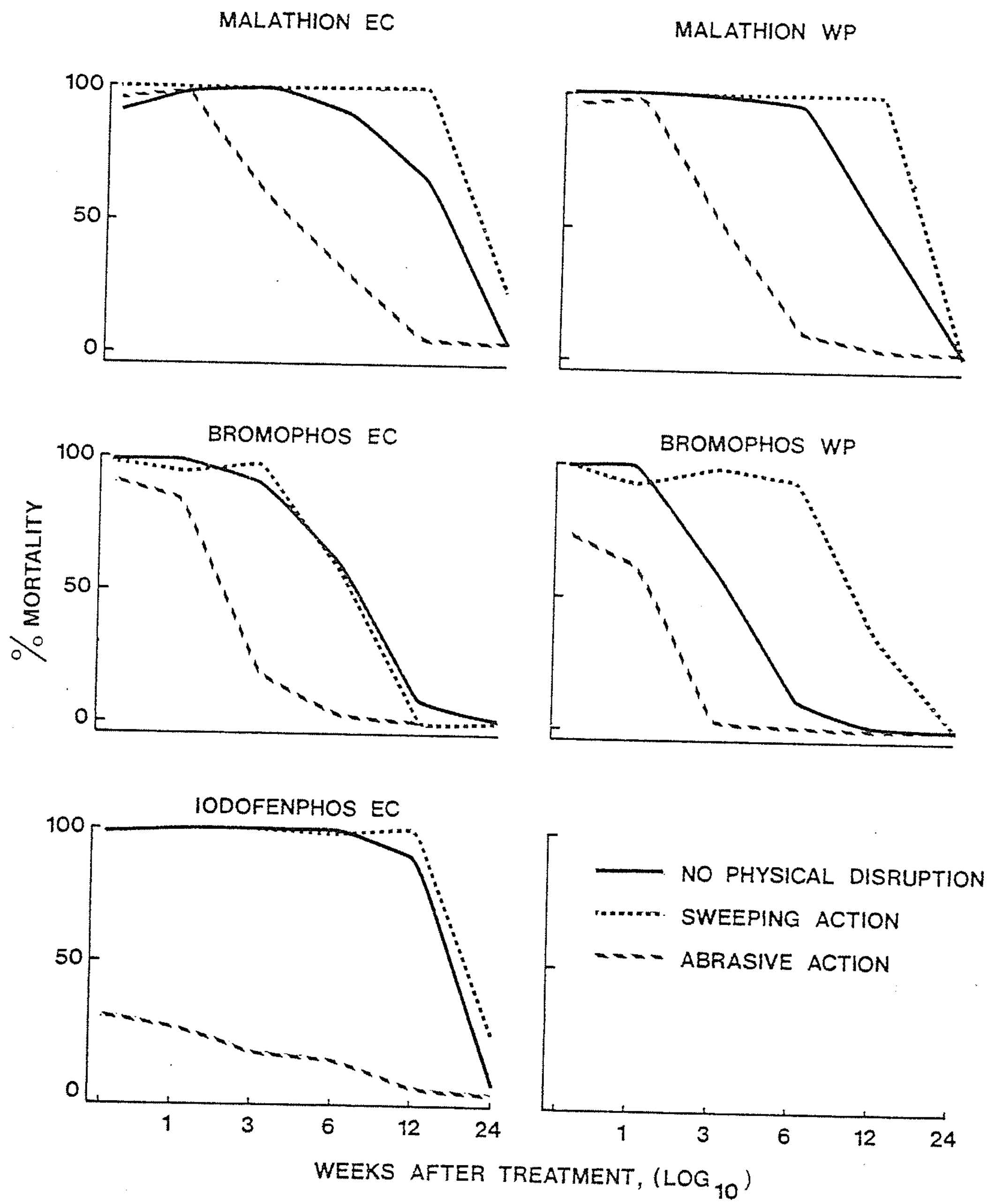
TABLE 63. Mean percent mortality of *T. castaneum* adults exposed for 5 hours to various disturbed insecticide deposits on wood surfaces at different times after treatment.

Physical disturbance	Insecticide	Time after treatment: Day 1	Weeks 1	3	6	12	24	Insecticide means
No physical disruption	Malathion EC	91.3	97.5	100	90.0	65.0	2.5	74.4
	Malathion WP	100	100	98.8	96.3	48.8	1.3	74.2
	Bromophos EC	98.8	98.8	90.0	60.0	7.5	1.3	59.4
	Bromophos WP	100	100	60.0	11.3	1.3	0	45.4
	Iodofenphos EC	98.8	100	100	100	90.0	3.8	82.1
Sweeping	Malathion EC	100	100	100	100	100	23.8	87.3
	Malathion WP	100	100	100	100	100	1.3	83.6
	Bromophos EC	98.8	95.0	97.5	57.5	0	0	58.1
	Bromophos WP	100	92.5	98.8	93.8	36.3	0	70.2
	Iodofenphos EC	98.8	100	100	98.8	100	22.5	86.6
Abrasion	Malathion EC	95.0	98.8	58.8	30.0	3.8	3.8	48.4
	Malathion WP	96.3	98.8	51.3	10.0	3.8	2.5	43.8
	Bromophos EC	91.3	83.8	17.5	2.5	0	0	32.5
	Bromophos WP	73.8	61.3	2.5	1.3	0	0	23.2
	Iodofenphos EC	28.8	25.0	16.3	12.5	2.5	0	14.2
Age of insecticide deposit means		91.4	90.0	72.9	57.6	37.3	4.2	58.9

L.S.D. between any two means of disturbed surface/insecticide/age of insecticide deposit interaction

(0.05) = 14.6 (0.01) = 17.6

FIGURE 12. - Physical disturbances on persistence of malathion, bromophos, and iodofenphos on wood surface against T. castaneum.


MALATHION EC
MALATHION WP
BROMOPHOS EC
BROMOPHOS WP
IODOFENPHOS EC
100
50
0
% MORTALITY
NO PHYSICAL DISRUPTION
SWEEPING ACTION
ABRASIVE ACTION
1
3
6
12
24
WEEKS AFTER TREATMENT, (LOG 10)

7. Persistence of malathion, bromophos, iodofenphos, and pirimiphos-methyl residues in dry and tough stored wheat.

Storage conditions - The conditions under which the treated wheat grains were stored are presented in Table 64. At the termination of the study, wheat of 12.0 and 16.0 percent moisture content has dropped to 11.0 and 14.0 percent, respectively. The slight variations in temperature of bagged wheat were found to be closely dependent upon the temperature of the storage rooms. The highest temperature in both storage rooms and in bagged wheat occurred in July. Cold temperatures were recorded in the 12.0 percent moisture content treatments in November.

Bioassay of the treated wheat - The biological effectiveness to determine the persistence of malathion, bromophos, iodofenphos, and pirimiphos-methyl on dry (12.0% mc) and tough (16.0% mc) stored wheat was done by bioassay with susceptible and malathion-resistant strains of *T. castaneum* exposed continuously for seven days on treated wheat at 1, 3, 6, 12, and 24 weeks. Percent mortality was corrected by Abbott's (1925) formula.

Tables 65 and 67, and Fig. 13 show that significantly higher ($P < 0.01$) mortalities of susceptible and malathion-resistant strains of *T. castaneum* were obtained on treated dry wheat than on treated tough wheat. Percent mortality with both strains increased significantly ($P < 0.05$) with increasing dose of each insecticide applied. However, in the pirimiphos-methyl treatments, both dosage rates applied to wheat gave 100 percent mortality of susceptible *T. castaneum* (Table 65). In dry and tough wheat treated at 4.0 and 6.0 ppm with pirimiphos-methyl, complete mortality of susceptible

T. castaneum was obtained for 24 weeks (Table 66) whilst 6.0 ppm was required to give complete mortality of the resistant strain for the same 24-week period (Table 68). Pirimiphos-methyl at 4.0 ppm produced 93.3 and 78.3 percent mortality of the resistant *T. castaneum* on dry and tough wheat, respectively, 24 weeks after treatment.

Under the conditions of storage of the treated wheat (Table 64), the effectiveness of malathion at 8.0 ppm on dry and tough wheat against susceptible *T. castaneum* lasted for six weeks, but at 12.0 ppm it was effective (85% mortality) for 24 weeks on dry wheat and 12 weeks on tough wheat (Table 66). The ineffectiveness of malathion at the dosages tested against resistant *T. castaneum* is shown in Table 68. Only 52 percent mortality was obtained with 12.0 ppm malathion on dry wheat one week after treatment.

Bromophos and iodofenphos at the dosages applied to wheat were equally effective ($P > 0.05$) on both dry and tough wheat against susceptible *T. castaneum* (Table 65) but as the age of the insecticide deposit increased, iodofenphos treatments persisted longer on wheat at the dosages tested (Table 66). Iodofenphos at 10.0 ppm on dry wheat gave equal protection against susceptible *T. castaneum* as malathion at 12.0 ppm (Tables 65 and 66). Against resistant *T. castaneum*, bromophos treatments on dry and tough wheat provided significantly better ($P < 0.01$) protection than the iodofenphos treatments (Tables 67 and 68). Dry and tough wheat treated at 15.0 ppm with bromophos gave 100 percent mortality of resistant *T. castaneum* for 12 weeks whereas iodofenphos at equivalent dosage produced 100 percent mortality for three weeks (Table 68).

TABLE 64a. Storage conditions of treated wheat of 12.0% moisture content during the experimental period.

Month of the year (1977)	Storage room[1]		Bagged wheat[1]	
	Temp. (°C)	RH (%)	Temp. (°C)	Moisture Content (%)
April	20.1 ± 2.1	50.3 ± 1.5	18.8 ± 0.7	12.0 ± 0.1
May	23.0 ± 2.5	51.0 ± 0.8	21.4 ± 1.6	12.0 ± 0.1
June	26.0 ± 1.9	50.4 ± 2.4	25.9 ± 2.0	11.9 ± 0.2
July	27.2 ± 0.6	50.5 ± 0.5	26.8 ± 1.0	11.8 ± 0.3
August	25.0 ± 1.1	50.0 ± 1.0	24.7 ± 1.9	11.8 ± 0.1
September	22.8 ± 0.5	47.5 ± 2.9	20.9 ± 0.4	11.6 ± 0.1
October	22.8 ± 4.7	41.5 ± 1.3	19.7 ± 0.4	11.2 ± 0.4
November	11.4 ± 7.2	41.0 ± 1.0	10.2 ± 7.4	11.0 ± 0.4

[1] ± Standard deviation

TABLE 64b. Storage conditions of treated wheat of 16.0% moisture content during the experimental period.

Month of the year (1977)	Storage room[1]		Bagged wheat[1]	
	Temp. (°C)	RH (%)	Temp. (°C)	Moisture content (%)
April	23.0 ± 1.8	78.4 ± 3.3	21.4 ± 0.7	16.0 ± 0.1
May	22.8 ± 2.1	78.0 ± 2.1	20.0 ± 1.2	16.1 ± 0.2
June	22.4 ± 1.4	78.9 ± 7.9	21.3 ± 1.8	16.0 ± 0.2
July	23.6 ± 0.7	78.0 ± 8.5	24.0 ± 0.6	15.9 ± 0.4
August	22.2 ± 0.5	76.0 ± 7.5	23.3 ± 0.7	15.8 ± 0.2
September	20.9 ± 0.9	76.7 ± 3.5	20.2 ± 0.7	15.6 ± 0.6
October	23.7 ± 2.3	80.0 ± 6.5	23.6 ± 2.4	15.3 ± 0.3
November	22.7 ± 3.0	78.2 ± 2.6	21.2 ± 2.1	14.0 ± 0.3

[1] ± Standard deviation

TABLE 65. Mean percent mortality of susceptible *T. castaneum* adults exposed for seven days on treated stored wheat of different moisture contents.

Insecticide	Dosage applied (ppm)	Wheat moisture content (%) 12.0	16.0	Insecticide treatment means
Malathion	8.0	76.3	67.7	72.0
	12.0	97.0	80.7	88.9
Bromophos	10.0	93.0	78.0	85.5
	15.0	100	89.0	94.5
Iodophenphos	10.0	97.0	80.3	88.7
	15.0	100	93.7	96.9
Pirimiphos-methyl	4.0	100	100	100
	6.0	100	100	100
Moisture content means		95.4	86.2	90.8

L.S.D. between	5%	1%
(i) Any two means of insecticide treatment	3.3	4.3
(ii) Means of wheat moisture content	1.6	2.2
(iii) Any two means of moisture content for the same insecticide dosage applied or vice versa.	4.7	6.2

TABLE 66. Mean percent mortality of susceptible *T. castaneum* adults exposed for seven days on treated dry (12.0% mc) and tough (16.0% mc) stored wheat at various times after application.

Treatment		Weeks after treatment				
Insecticide	Applied dosage (ppm)	1	3	6	12	24
				12.0% mc		
Malathion	8.0	100	100	100	56.7	25.0
	12.0	100	100	100	100	85.0
Bromophos	10.0	100	100	100	100	65.0
	15.0	100	100	100	100	100
Iodofenphos	10.0	100	100	100	100	85.0
	15.0	100	100	100	100	100
Pirimiphos-methyl	4.0	100	100	100	100	100
	6.0	100	100	100	100	100
				16.0% mc		
Malathion	8.0	100	100	100	38.3	0
	12.0	100	100	100	100	3.3
Bromophos	10.0	100	100	100	83.3	6.7
	15.0	100	100	100	100	45.0
Iodofenphos	10.0	100	100	100	70.0	31.7
	15.0	100	100	100	100	68.3
Pirimiphos-methyl	4.0	100	100	100	100	100
	6.0	100	100	100	100	100

L.S.D. between any two means of insecticide treatment/moisture content/time after insecticide application interaction (0.05) = 10.4

(0.01) = 13.8

TABLE 67. Mean percent mortality of malathion-resistant *T. castaneum* adults exposed for seven days on treated stored wheat of different moisture contents.

Treatment		Wheat moisture content (%)		
Insecticide	Applied dosage (ppm)	12.0	16.0	Insecticide treatment means
Malathion	8.0	18.3	10.0	14.2
	12.0	27.3	18.3	22.8
Bromophos	10.0	66.3	58.7	62.5
	15.0	95.7	81.3	88.5
Iodofenphos	10.0	57.7	40.7	49.2
	15.0	74.7	63.3	69.0
Pirimiphos-methyl	4.0	98.0	95.0	96.5
	6.0	100	100	100
Moisture content means		67.3	58.4	62.9

L.S.D. between	5%	1%
(i) Any two means of insecticide treatment	3.0	4.0
(ii) Means of wheat moisture content	1.5	2.0
(iii) Any two means of moisture content for the same insecticide dosage applied or vice versa.	4.2	5.6

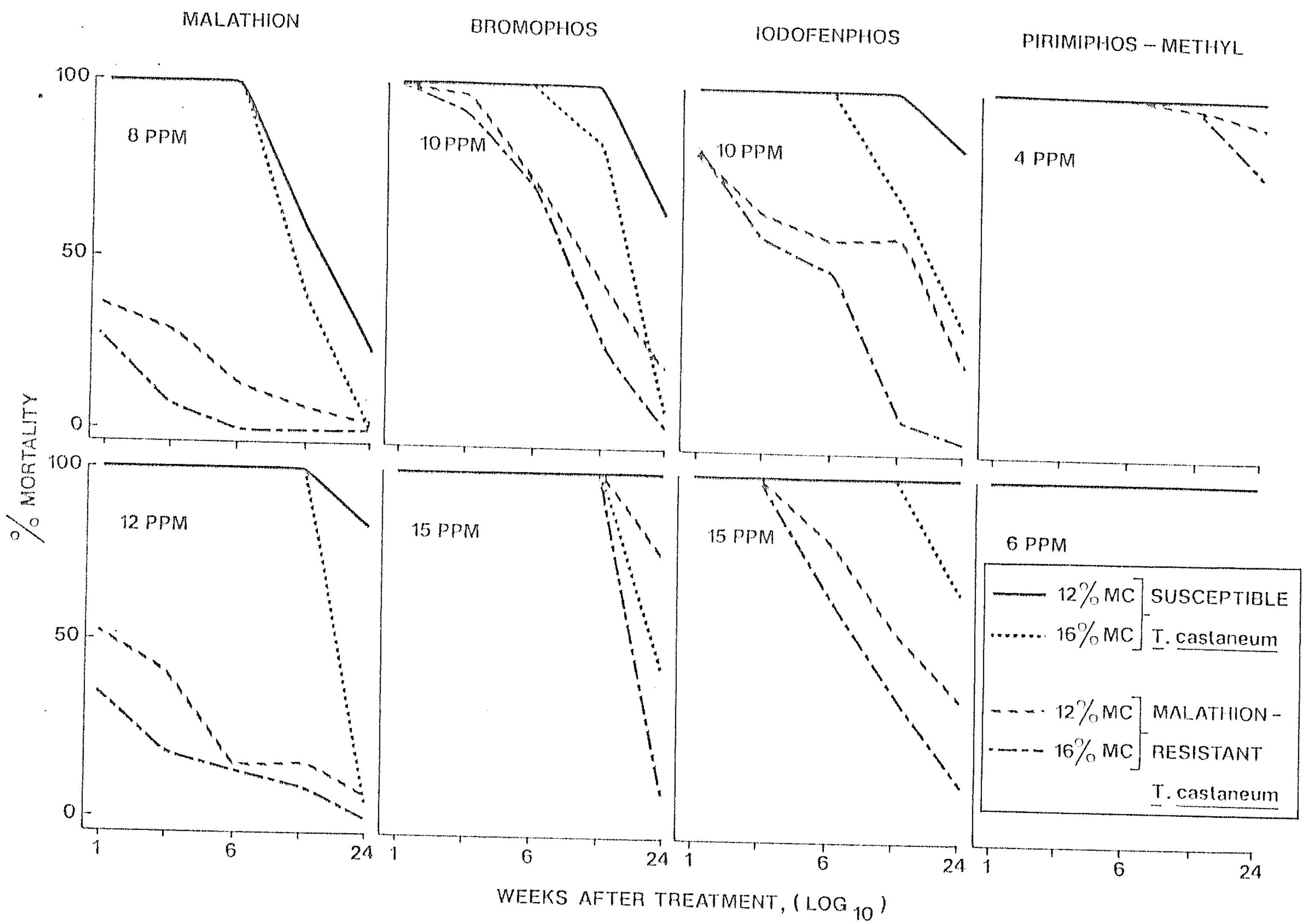
TABLE 68. Mean percent mortality of malathion-resistant *T. castaneum* adults exposed for seven days on treated dry (12.0% mc) and tough (16.0% mc) stored wheat at various times after application.

Treatment		Weeks after treatment				
Insecticide	Applied dosage (ppm)	1	3	6	12	24
				12.0% mc		
Malathion	8.0	38.3	30.0	13.3	8.3	1.7
	12.0	51.7	41.7	18.3	18.3	6.7
Bromophos	10.0	100	98.3	71.7	41.7	20.0
	15.0	100	100	100	100	78.3
Iodofenphos	10.0	82.2	66.8	55.9	56.7	21.7
	15.0	100	100	81.4	53.3	38.3
Pirimiphos-methyl	4.0	100	100	100	96.7	93.3
	6.0	100	100	100	100	100
				16.0% mc		
Malathion	8.0	29.3	9.2	0	0	0
	12.0	36.1	20.2	15.3	8.3	0
Bromophos	10.0	100	94.1	71.1	25.0	1.7
	15.0	100	100	100	100	6.7
Iodofenphos	10.0	84.3	59.3	49.2	5.0	0
	15.0	100	100	67.7	36.7	11.7
Pirimiphos-methyl	4.0	100	100	100	96.7	78.3
	6.0	100	100	100	100	100

L.S.D. between any two means of insecticide treatment/moisture content/ time after insecticide application interaction (0.05) = 9.5

(0.01) = 12.5

FIGURE 13. - Percent mortality of susceptible and malathion-resistant strains of *T. castaneum* adults exposed for seven days to treated dry (12% mc) and tough (16% mc) stored wheat.



MALATHION
BROMOPHOS
IODOFENPHOS
PIRIMIPHOS – METHYL
100
50
0
% MORTALITY
8 PPM
10 PPM
10 PPM
4 PPM
12 PPM
15 PPM
15 PPM
6 PPM
1
6
24
WEEKS AFTER TREATMENT, (LOG 10)
12% MC
16% MC
SUSCEPTIBLE
T. castaneum
12% MC
16% MC
MALATHION -
RESISTANT
T. castaneum

From the treated means of the dosages applied, the order of persistence of insecticide treatments on dry wheat:

(i) against susceptible *T. castaneum*, was pirimiphos-methyl = iodofenphos = bromophos $>$ malathion; ($P = 0.05$).

(ii) against malathion-resistant *T. castaneum*, the order of persistence was pirimiphos-methyl $>$ bromophos $>$ iodofenphos $>$ malathion ($P = 0.01$); and on tough wheat

(i) against susceptible *T. castaneum*, the order of persistence was pirimiphos-methyl $>$ iodofenphos $>$ bromophos $>$ malathion ($P = 0.05$);

(ii) against malathion-resistant *T. castaneum*, the order of persistence was pirimiphos-methyl $>$ bromophos $>$ iodofenphos $>$ malathion ($P = 0.01$).

Determination of persistence by production of F_1 progeny - The data (Tables 69 and 70) show the persistence of the test insecticides on dry and tough wheat as determined by F_1 progeny production after incubation of treated wheat samples at 27.5°C and 60-70 RH for 42 days.

The test strains of *T. castaneum* produced more progeny in untreated wheat than in treated wheat at each assessment period.

Pirimiphos-methyl at 4.0 and 6.0 ppm completely prevented reproduction of both strains of *T. castaneum* in dry and tough wheat throughout the 24-week period of the study.

On tough wheat treated at 8.0 ppm with malathion, 14 adult susceptible *T. castaneum* emerged after 24 weeks and 13 adults of the resistant strain were produced after six weeks. In dry wheat, malathion at 8.0 ppm prevented reproduction of the susceptible strain but six beetles of the resistant strain emerged 24 weeks after treatment.

TABLE 69. Mean number of susceptible *T. castaneum* F_1 adults produced in dry (12.0% mc) and tough (16.0% mc) wheat after seven days of infestation of the grain at various times after insecticide application.

Treatment		Weeks after treatment				
Insecticide	Applied dosage (ppm)	1	3	6	12	24
				12.0% mc		
Control	0	56	48	73	39	107
Malathion	8.0	0	0	0	0	0
	12.0	0	0	0	0	0
Bromophos	10.0	0	0	0	0	0
	15.0	0	0	0	0	0
Iodofenphos	10.0	0	0	0	0	0
	15.0	0	0	0	0	0
Pirimiphos-methyl	4.0	0	0	0	0	0
	6.0	0	0	0	0	0
				16.0% mc		
Control	0	50	54	79	62	97
Malathion	8.0	0	0	0	0	14
	12.0	0	0	0	0	0
Bromophos	10.0	0	0	0	0	3
	15.0	0	0	0	0	0
Iodofenphos	10.0	0	0	0	0	3
	15.0	0	0	0	0	30
Pirimiphos-methyl	4.0	0	0	0	0	0
	6.0	0	0	0	0	0

TABLE 70. Mean number of malathion-resistant *T. castaneum* F_1 adults produced in dry (12.0% mc) and tough (16.0% mc) wheat after seven days of infestation of the grain at various times after insecticide application.

Treatment		Weeks after treatment				
Insecticide	Applied dosage (ppm)	1	3	6	12	24
				12.0% mc		
Control	0	40	58	44	34	81
Malathion	8.0	0	0	0	0	0
	12.0	0	0	0	0	0
Bromophos	10.0	0	0	0	0	0
	15.0	0	0	0	0	0
Iodofenphos	10.0	0	0	0	0	0
	15.0	0	0	0	0	0
Pirimiphos-methyl	4.0	0	0	0	0	0
	6.0	0	0	0	0	0
				16.0% mc		
Control	0	35	54	48	49	49
Malathion	8.0	0	0	13	18	22
	12.0	0	0	1	9	12
Bromophos	10.0	0	0	0	0	1
	15.0	0	0	0	0	0
Iodofenphos	10.0	0	0	0	0	30
	15.0	0	0	0	0	21
Pirimiphos-methyl	4.0	0	0	0	0	0
	6.0	0	0	0	0	0

No susceptible strain of T. castaneum was produced in the dry and tough wheat treated at 12.0 ppm with malathion. However, progeny of the resistant strain started to emerge from the tough wheat treated with an equivalent dose after six weeks.

Bromophos at 10.0 ppm on dry wheat inhibited reproduction of both strains of T. castaneum but on tough wheat there was production of progeny of both strains after 24 weeks. Fifteen ppm of bromophos on dry and tough wheat prevented reproduction of both T. castaneum strains throughout the study.

No progeny of susceptible T. castaneum emerged in dry wheat treated at 10.0 or 15.0 ppm with iodofenphos but on tough wheat treated at the same concentrations, progeny emerged 24 weeks after treatment. Similarly, emergence of the resistent strain occurred in the tough wheat treated at 10.0 and 15.0 ppm after 24 weeks.

Analysis of the residues - The initial deposits of the insecticides were close to the dosages intended for application except for bromophos and iodofenphos at 10.0 and 15.0 ppm, respectively (Table 72). The data (Tables 71 and 73, and Fig. 14) showed that generally the rate of breakdown of the insecticides was significantly greater ($P < 0.01$) on tough wheat (16.0% mc) than on dry wheat (12.0% mc). There was, however, no significant difference ($P > 0.05$) in the rate of breakdown of pirimiphos-methyl applied to the dry and tough wheat (Tables 71 and 72).

A significant difference ($P < 0.05$) in the amount of malathion residue recovered from dry and tough wheat occurred after three weeks of storage, and for bromophos after 12 weeks (Table 72). The residue of iodofenphos recovered from the dry wheat treated at 10.0 ppm was significantly greater ($P < 0.05$) than the residue from the tough wheat after six weeks whilst the differences in the recovery of iodofenphos residues from the dry and tough wheat treated at 15.0 ppm were significant ($P < 0.01$) three weeks after the insecticide application.

Tables 73 and 74, and Fig. 14 show the mean percent residue degradation of malathion, bromophos, iodofenphos, and pirimiphos-methyl applied to dry and tough wheat. Pirimiphos-methyl was comparatively more stable on both dry and tough wheat under the same conditions of storage, and iodofenphos degraded faster among the test insecticides. The rate of breakdown of iodofenphos and pirimiphos-methyl residues on dry and tough wheat was not dependent upon the level of insecticide concentration ($P > 0.05$) but the lower concentrations of malathion and bromophos degraded at a faster rate ($P < 0.01$) than the higher concentrations (Table 73). However, at the termination of the study (24 weeks) the differences in the percent degradation of insecticide residues between the concentrations were not significant at the 5 percent level of probability (Table 74). There was very little difference in the persistence of malathion 8.0 ppm and iodofenphos 10.0 ppm on dry and tough wheat.

The percent degradation of insecticide residues on dry and tough wheat increased with age of insecticide deposit, with marked percent degradation in residual amounts of malathion, bromophos, and pirimiphos-methyl occurring at 12 weeks after treatment, and for iodofenphos at six weeks after treatment (Table 74).

TABLE 71. Mean insecticide residues (ppm) recovered from stored wheat of different moisture contents during 24 weeks.

Treatment		Wheat moisture content (%)		
Insecticide	Applied dosage (ppm)	12.0	16.0	Treatment means
Malathion	8.0	4.97	3.77	4.37
	12.0	8.60	6.98	7.79
Bromophos	10.0	5.98	5.36	5.67
	15.0	10.96	9.67	10.32
Iodofenphos	10.0	5.23	4.31	4.78
	15.0	7.62	6.50	7.06
Pirimiphos-methyl	4.0	3.11	3.03	3.07
	6.0	4.68	4.65	4.67
Moisture content means		6.40	5.53	5.97

L.S.D. between	5%	1%
(i) Means of moisture content	0.12	0.15
(ii) Any two means of moisture content for the same insecticide dosage applied	0.33	0.43

TABLE 72. Mean insecticide residues (ppm) recovered from dry (12.0% mc) and tough (16.0% mc) stored wheat at various times after application.

Treatment		Weeks after treatment[1]					
Insecticide	Aimed dosage (ppm)	0	1	3	6	12	24
				12.0% mc			
Malathion	8.0	7.91	6.57	6.41	6.06	3.19	2.62
	12.0	11.81	11.62	10.88	9.30	6.59	4.52
Bromophos	10.0	8.31	7.86	7.44	6.08	4.76	3.76
	15.0	13.99	13.70	13.10	12.02	9.02	6.99
Iodofenphos	10.0	8.97	8.51	7.18	5.12	3.20	2.17
	15.0	13.14	12.47	11.51	6.32	4.28	3.55
Pirimiphos-methyl	4.0	3.56	3.48	3.35	3.22	2.92	2.54
	6.0	5.47	5.32	5.01	4.85	4.54	3.66
				16.0% mc			
Malathion	8.0	7.76	5.73	5.64	4.30	1.97	1.19
	12.0	11.62	11.37	9.85	7.64	4.57	1.45
Bromophos	10.0	8.65	7.84	7.07	6.00	3.79	2.12
	15.0	14.26	13.32	12.89	11.39	6.69	4.06
Iodofenphos	10.0	8.88	7.95	6.61	3.30	2.37	1.34
	15.0	13.03	11.87	9.59	4.87	3.60	2.54
Pirimiphos-methyl	4.0	3.47	3.37	3.30	3.18	3.04	2.26
	6.0	5.51	5.11	5.06	4.78	4.44	3.86

[1] 0 week residue is the actual applied dosage determined immediately after insecticide application to the wheat.

L.S.D. between any two means of insecticide treatment/moisture content/time after insecticide application interaction (0.05) = 0.73

(0.01) = 0.95

TABLE 73. Mean percent residue degradation of malathion, bromophos, iodofenphos, and pirimiphos-methyl in stored wheat of different moisture contents during 24 weeks.

Treatment		Wheat moisture content (%)		
Insecticide	Dosage applied (ppm)	12.0	16.0	Treatment means
Malathion	8.0	37.15	51.48	44.32
	12.0	28.63	40.29	34.46
Bromophos	10.0	28.08	37.89	32.99
	15.0	21.56	32.14	26.85
Iodofenphos	10.0	41.58	51.35	46.47
	15.0	41.98	50.21	46.10
Pirimiphos-methyl	4.0	12.58	12.56	12.57
	6.0	14.46	15.61	15.03
Moisture content means		28.25	36.44	32.35

L.S.D. between	5%	1%
(i) Any two means of insecticide treatment	2.27	3.0
(ii) Means of moisture content	1.14	1.50
(iii) Any two means of moisture content for the same insecticide dosage applied or vice versa.	3.21	4.24

TABLE 74. Mean percent residue degradation during 24-week period of storage of dry (12.0% mc) and tough (16.0% mc) wheat treated with malathion, bromophos, iodofenphos, and pirimiphos-methyl, with reference to initial deposits.

Treatment		Weeks after treatment				
Insecticide	Dosage applied (ppm)	1	3	6	12	24
				12.0% mc		
Malathion	8.0	16.88	18.97	23.35	59.66	66.87
	12.0	1.54	14.87	20.84	44.15	61.77
Bromophos	10.0	5.22	11.07	26.80	42.67	54.63
	15.0	2.10	6.42	14.06	35.27	49.95
Iodofenphos	10.0	5.08	19.86	42.83	64.37	75.76
	15.0	5.12	12.43	51.94	67.41	72.99
Pirimiphos-methyl	4.0	2.14	5.99	9.57	16.42	28.76
	6.0	2.68	8.36	11.29	16.90	33.06
				16.0% mc		
Malathion	8.0	25.31	28.26	44.63	74.58	84.64
	12.0	2.69	15.65	34.64	60.86	87.60
Bromophos	10.0	9.34	18.26	30.53	55.85	75.49
	15.0	6.53	9.38	20.24	52.97	71.58
Iodofenphos	10.0	10.53	25.35	62.74	73.36	84.79
	15.0	9.31	26.36	62.55	72.36	80.48
Pirimiphos-methyl	4.0	2.70	4.90	8.36	12.21	34.64
	6.0	7.26	8.17	13.19	19.48	29.94

L.S.D. between any two means of insecticide treatment/moisture content/storage period interaction (0.05) = 7.18

(0.01) = 9.48

FIGURE 14. - Percent residue degradation of malathion, bromophos, iodofenphos, and pirimiphos-methyl applied to dry (12% mc) and tough (16% mc) wheat.

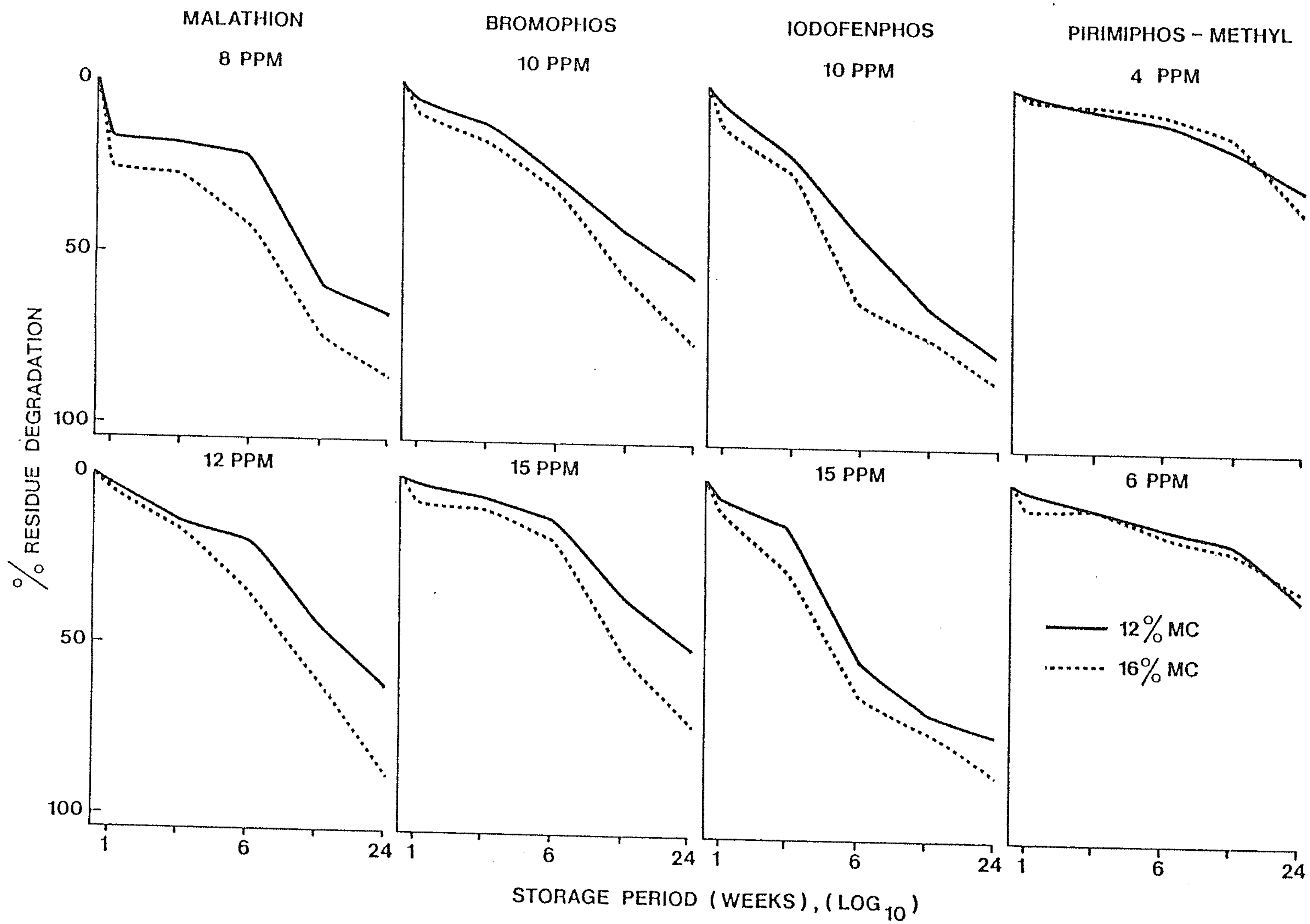

MALATHION
8 PPM
12 PPM
BROMOPHOS
10 PPM
15 PPM
IODOFENPHOS
10 PPM
15 PPM
PIRIMIPHOS - METHYL
4 PPM
6 PPM
% RESIDUE DEGRADATION
0
50
100
1
6
24
12% MC
16% MC
STORAGE PERIOD (WEEKS), (LOG 10)

Table 75 shows the estimated period during which 50 percent (half-life, $t\frac{1}{2}$) of the applied insecticide is lost under the conditions of storage of the treated wheat. These half-life values were estimated from the regression of the logarithm of percent residue degradation on time after treatment. The half-life of the insecticide deposits was generally longer on dry wheat than on tough wheat, and pirimiphos-methyl treatments, by extrapolation, had the longest half-life. The half-life of the insecticides increased with an increase in concentration level except iodofenphos treatments on dry wheat. Also, high concentrations did not increase the half-life of bromophos and iodofenphos on tough wheat.

Residues in milled fractions of stored wheat

The milling of the dry wheat yielded percent by weight 16.5 percent bran, 12.5 percent middlings, and 71.0 percent flour; the tough wheat on milling produced 20.0 percent bran, 15.0 percent middlings, and 65.0 percent flour.

The amounts of insecticide recovered from treated whole wheat and milled fractions of dry and tough wheat are presented in Table 76. The highest residues were found in the bran and middlings. There were slight differences in residual amounts of insecticide recovered from the bran and middlings. Very small amounts of residue were found in the flour. Insecticide residues recovered from the milled fractions decreased with age of insecticide deposits. The residues recovered from milled fractions of tough wheat were generally slightly lower than the residues recovered from dry wheat fractions.

TABLE 75. Half-life ($t_{1/2}$) of malathion, bromophos, iodofenphos, and pirimiphos-methyl in stored wheat expressed as time (weeks) required for disappearance of 50% of the actual amount applied.

Treatment		Time (weeks)[1]	
Insecticide	Aimed dosage (ppm)	12.0% mc	16.0% mc
Malathion	8.0	10.9	7.3
	12.0	16.5	9.8
Bromophos	10.0	20.4	11.6
	15.0	22.1	11.7
Iodofenphos	10.0	7.6	5.2
	15.0	6.1	5.2
Pirimiphos-methyl	4.0	37.8	33.3
	6.0	42.4	43.4

[1] Based on mean of 3 replicates of the actual dosage applied.

TABLE 76a. Mean insecticide residues (ppm) on dry wheat (12.0% mc) and milled fractions after 1, 3, and 6 months of storage of wheat.

Insecticide	Dosage applied (ppm)	Whole wheat[a] Storage period (months)			Bran Storage period (months)			Middlings[b] Storage period (months)			Flour Storage period (months)		
		1	3	6	1	3	6	1	3	6	1	3	6
Malathion	8.0	6.24	3.19	2.62	19.42	15.57	6.59	19.01	14.33	8.55	1.35	1.39	1.42
	12.0	10.06	6.59	4.52	29.01	25.42	9.34	24.79	22.06	12.70	2.52	1.73	1.50
Bromophos	10.0	6.76	4.96	3.76	18.39	15.58	10.95	21.37	17.92	9.13	2.34	1.89	1.42
	15.0	12.56	9.02	6.99	27.32	24.59	21.98	37.76	26.88	17.80	3.40	2.38	1.88
Iodofenphos	10.0	6.15	3.20	2.17	20.08	20.13	13.35	20.13	14.13	12.17	0.71	0.76	0.65
	15.0	8.91	4.28	3.55	30.43	27.15	21.33	30.36	19.15	14.87	1.02	0.75	0.69
Pirimiphos-methyl	4.0	3.29	2.98	2.54	15.66	13.93	13.16	21.44	15.10	13.80	1.94	1.93	1.56
	6.0	4.93	4.54	3.66	20.87	20.54	19.32	23.15	19.34	16.05	2.86	2.42	2.23

[a] Ground wheat

[b] Wheat germ and finer parts of the bran

TABLE 76b. Mean insecticide residues (ppm) on tough wheat (16.0% mc) and milled fractions after 1, 3, and 6 months of storage of wheat.

Treatment		Whole wheat[a] Storage period (months)			Bran Storage period (months)			Middlings[b] Storage period (months)			Flour Storage period (months)		
Insecticide	Dosage applied (ppm)	1	3	6	1	3	6	1	3	6	1	3	6
Malathion	8.0	4.97	1.97	1.19	15.58	14.78	2.99	9.35	6.68	3.07	0.62	0.41	0.30
	12.0	8.50	4.57	1.45	23.34	19.95	3.99	13.45	11.31	3.45	1.36	0.51	0.34
Bromophos	10.0	6.54	3.97	2.12	17.13	13.78	9.50	12.07	9.66	5.58	0.57	0.65	0.47
	15.0	12.14	6.69	4.06	22.73	21.77	18.42	22.68	14.14	9.52	1.57	1.04	0.60
Iodofenphos	10.0	4.96	2.37	1.34	19.92	19.55	10.79	19.77	10.97	6.26	0.50	0.36	0.31
	15.0	7.23	3.60	2.54	29.30	25.21	18.93	28.92	14.30	12.22	0.52	0.40	0.34
Pirimiphos-methyl	4.0	3.24	3.04	2.26	19.81	13.45	11.98	15.35	13.51	10.68	1.57	1.16	0.81
	6.0	4.92	4.44	3.86	27.33	20.90	18.60	21.83	17.89	16.89	1.91	1.50	1.33

[a] Ground wheat

[b] Wheat germ and finer parts of the bran

CHAPTER V

DISCUSSION

1. Persistence of insecticides applied to concrete and wood surfaces.

The results of persistence of malathion, bromophos (EC and WP), and iodofenphos (EC) on wood and concrete surfaces determined by bioassay with C. ferrugineus and T. castaneum adults of known age on wheat, barley, and corn stored for seven days on structural surfaces are presented in Tables 8-25 and Figs. 9 and 10.

There were significant differences ($P < 0.01$) in the persistence of the insecticide deposits on wood and concrete surfaces as determined by the toxicity of the insecticide residues in wheat, barley, and corn infested for seven days with adults of C. ferrugineus and T. castaneum. Significantly higher ($P < 0.01$) mortalities of C. ferrugineus and T. castaneum were obtained on all grains stored on treated wood surfaces than on grains stored on treated concrete surfaces (Tables 8, 16, 17, and 25). The high mortality counts on grains stored on treated wood surfaces, indicating greater persistence of the insecticides on wood than on concrete, agree with the results of bioassay of treated surfaces reported by other workers (Burkholder and Dicke, 1966; Parkin, 1966; Erakay and Ozar, 1975; Watters, 1976). Parkin (1966) found that malathion applied as an aqueous suspension of WP at 0.43 g/m^2 persisted for up to four months on wood and sacking against T. castaneum but was very unstable on cement, whitewash and tile. Watters (1976) also recorded complete control of T. castaneum with 40- and 18-week old deposits of malathion and bromophos, respectively, at 1.0g AI/m^2 on wood surfaces. Bromophos was effective on concrete surfaces for four weeks and malathion for one week. Alkaline surfaces are known to hydrolyse and detoxify insecticides (Lemon, 1967; Okwelogu, 1968; Anon., 1975). The low mortalities of *C. ferrugineus* and *T. castaneum* observed on grains stored on treated concrete surfaces therefore indicate the rapid breakdown or strong adsorption of the insecticides on this type of structural surface.

Significant differences ($P < 0.01$) were observed between the insecticide treatments on the two types of structural surfaces. Most granaries are constructed of either wood or concrete or both materials. Taking combined treatment of wood and concrete, higher mortalities of *C. ferrugineus* were obtained on grains stored on bromophos-treated surfaces than on grains stored on malathion- and iodofenphos-treated surfaces (Tables 8 and 15). However, on wood surfaces, malathion EC provided a better control ($P < 0.01$) of *C. ferrugineus* on stored grains for 32 weeks (Table 16). Malathion WP, bromophos formulations, and iodofenphos EC produced equivalent control of *C. ferrugineus* on grains stored on wood surfaces for 16 weeks. In contrast with this study, Tauthong (1975) recorded 100 percent mortality with a 52-week old deposit of malathion EC at 1.0 g/m^2 against *C. ferrugineus* exposed for 24 hours. Tauthong and Watters (1978) also reported complete control of *C. ferrugineus* at an exposure period of 24 hours on wood surfaces treated at the rate of 1.0 g/m^2 with emulsions of bromophos and iodofenphos 80 weeks after treatment. The difference in persistence of insecticide deposits on wood surfaces observed in the present investigation and those reported by Tauthong (1975), and Tauthong and Watters (1978) is probably due to the methods of bioassay used for the determination of insecticide persistence. In this study, the persistence was determined by the protection afforded by the insecticide residues transferred to food grains stored on treated surfaces. On concrete surfaces, bromophos WP was the most persistent chemical (Tables 10 and 13), providing more than 60 percent mortality of C. ferrugineus on wheat and barley for eight weeks and on corn for two weeks (Table 16). The residual effectiveness of bromophos WP on concrete surfaces against C. ferrugineus and Tribolium spp. have also been reported by other workers (Lemon, 1967; Anon., 1975; Watters, 1976). Pinniger (1975) noted that the physical nature of wettable powder makes the insecticide more readily available on porous surfaces and therefore WP formulations tend to be more persistent than EC formulations. Iodofenphos deposit on concrete surfaces persisted significantly ($P < 0.05$) longer than malathion formulations against C. ferrugineus (Table 13). This result is in agreement with the studies of Girish et al. (1970) who showed that the efficacy and residual toxicity of iodofenphos at 1.0 g/m^2 on concrete slabs and jute bags against adults of S. oryzae, T. castaneum, R. dominica, and larvae of T. granarium were comparatively better than malathion deposits on the same surfaces.

The persistence of the insecticide treatments on wood and concrete surfaces against T. castaneum on grains stored on these structural surfaces are summarized in Tables 22 and 25. Complete mortality of T. castaneum was obtained on grains stored on wood surfaces treated with bromophos WP for 16 weeks but effectiveness decreased sharply (5-11.8% mortality) after 32 weeks (Tables 22 and 25). The malathion formulations also produced almost complete control for 16 weeks, with the EC formulation giving 50 percent mortality or more of *T. castaneum* on test grains stored on treated wood surfaces for 32 weeks. Bromophos EC and iodofenphos gave more than 67 percent mortality on all grains stored on wood surface for eight weeks. This result is confirmed by the data on bioassay of treated surfaces with *T. castaneum* reported by Watters (1976), and Tauthong and Watters (1978) that malathion deposit on wood surfaces persisted longer than the deposit of bromophos. The result obtained in this study is further confirmed by the laboratory studies conducted by Lemon (1966) that bromophos is less toxic than malathion against *T. castaneum*. The shorter persistence of iodofenphos deposit on wood surfaces is rather contrary to the findings recorded by Tauthong and Watters (1978) that 97 percent mortality of *T. castaneum* was obtained with an 80-week old iodofenphos deposit of 1.0 g/m^2. The difference is probably due to the procedure used to determine the persistence of iodofenphos deposit on this type of structural surface.

The malathion formulations and iodofenphos were completely ineffective against *T. castaneum* on grains stored on concrete surfaces one week after treatment whereas more than 80 percent mortality was obtained on wheat and barley stored on concrete surfaces treated with bromophos EC for two weeks (Table 25). Bromophos WP, on the other hand, gave 50 percent mortality or more for two weeks on wheat and for one week on barley and corn stored on concrete surfaces. The ineffectiveness of malathion deposits on concrete surfaces or surfaces of high alkalinity against stored-product insects has been demonstrated by various workers (Burkholder and Dicke, 1966; Parkin, 1966; Lemon, 1967; Girish *et al*., 1970; Watters, 1976). However, evidence presented from bioassay tests has shown that concrete surfaces that become less alkaline with age or washing of the surfaces, and the accumulation of dust and other debris tend to stabilize malathion and prolong the effectiveness of the deposits (Okwelogu, 1968; Watters, 1970). Slominski and Gojmerac (1972) also demonstrated by bioassay with larvae of *A. megatoma* that malathion remains toxic for a month or two on painted concrete surfaces or those treated with talc or calcium carbonate.

The loss of effectiveness of iodofenphos on grains stored on concrete surfaces demonstrates the rapid breakdown of the compound on alkaline surfaces. This fact is supported by the results of the residue analysis of the grains stored on wood and concrete surfaces (Table 52) as well as by the results of bioassay of surfaces obtained by Blackman (1969), Gradidge *et al*. (1970), and Girish *et al*. (1970). Blackman (1969) found that iodofenphos was more toxic to adults of *T. castaneum* than malathion. Gradidge *et al*. (1970) also showed from field tests that iodofenphos applied as an emulsion at 0.8g AI/m^2 to the structural surfaces of a granary was generally more effective than malathion deposits of 1.2g AI/m^2 when the surfaces were compared by bioassay against *T. castaneum* at 10 and 28 days after treatment. The studies by Girish *et al*. (1970) also indicated that iodofenphos applied at 1.0g AI/m^2 was comparatively more persistent on concrete slabs than malathion when the surfaces were tested against *T. castaneum*.

Lemon (1967) reported that bromophos WP applied to concrete at the rate of 0.75 g/m^2 provided complete protection against *T. confusum* adults exposed for six days on the treated surfaces for 16 weeks. The rather shorter persistence of bromophos treatments on concrete surfaces obtained in this study in contrast with the results reported by Lemon (1967) might be due to the differences in the level of the toxicant available on the surfaces of test materials to the test insects as well as the differences in toxicity of the insect species used for the studies.

Comparison of insect mortality on grains stored on concrete surfaces for all insecticide treatments showed that significantly lower ($P < 0.01$) mortality of C. ferrugineus was obtained on corn than on wheat or barley eight weeks after treatment for bromophos and iodofenphos and two to four weeks for the malathion formulations (Table 16). However, against T. castaneum the differences in mortality between the stored grains were only apparent in the bromophos formulations at two to four weeks after treatment (Table 25). On wood surfaces, significantly lower ($P < 0.05$) mortalities of C. ferrugineus and T. castaneum obtained on corn than on wheat or barley were apparent with age of insecticide deposit (Tables 16 and 25). The low mortality obtained on corn may be due to a smaller surface area of the kernels in contact with the treated surface in comparison with that of wheat or barley, but it may also be due to the fact that there is less surface area of corn to adsorb residues translocated in the gas phase.

The percent mortality of C. ferrugineus and T. castaneum on grains stored on treated structural surfaces generally decreased with age of insecticide deposit (Tables 16 and 25). The persistence of deposits on wood surfaces against both beetles declined sharply after 16 weeks except C. ferrugineus on wheat and barley stored on malathion EC-treated wood surfaces which provided about 97 percent mortality after 32 weeks (Table 16). On concrete surfaces there was a sharp decline in persistence of the insecticide deposits against the beetles one to two weeks after treatment (Tables 16 and 25). Bromophos WP, however, appeared to have a slightly longer persistence against *C. ferrugineus*. Its effectiveness decreased sharply after eight weeks.

From the bioassay of the grains stored on the treated surfaces, the effectiveness and persistence of the insecticide deposits against the test beetles can be summarized as follows: *C. ferrugineus* on grains stored on (i) wood surface - malathion EC $>$ bromophos WP = malathion WP = bromophos EC $>$ iodofenphos EC ($P = 0.05$); (ii) concrete surface - bromophos WP $>$ bromophos EC $>$ iodofenphos EC $>$ malathion EC = malathion WP ($P = 0.05$). *T. castaneum* on grains stored on (i) wood surface - malathion EC $>$ malathion WP = bromophos WP $>$ bromophos EC $>$ iodofenphos EC ($P = 0.05$); (ii) concrete surface - bromophos EC $>$ bromophos WP $>$ iodofenphos EC = malathion EC = malathion WP ($P = 0.05$).

F_1 progeny - In assessing the production of F_1 adult beetles in the grains which had been previously stored on wood and concrete surfaces, only adult counts were made because Sinha and Muir (1977) have shown that assessment of eggs and first instar larvae usually introduce unacceptable levels of errors.

The effectiveness of insecticides transferred to the grains from wood and concrete surfaces on the emergence of F_1 adults of *C. ferrugineus* and *T. castaneum* are summarized in Tables 34 and 43. Significantly fewer ($P < 0.01$) progeny were produced in grains stored on treated structural surfaces than in grains stored on untreated surfaces for both *C. ferrugineus* and *T. castaneum*. There was no significant difference ($P > 0.01$) in the number of F_1 adult beetles produced in grains stored on untreated wood and concrete surfaces in both test insects. It is, however, interesting to note that the number of progeny produced in the grains stored on untreated structural surfaces were lower than that reported by other workers. Smith (1965) reported that the mean number of eggs produced in a week by a female _C. ferrugineus_ at 30°C and 70 percent relative humidity ranged from 19.8 to 33.7. The author again suggested that _C. ferrugineus_ developed faster in finely divided food medium such as whole wheat flour than in sliced wheat kernels, and that it could breed under a wide range of physical conditions when food is finely divided. Park and Frank (1968) observed that the rate of oviposition per female _T. castaneum_ in a whole wheat flour-yeast culture medium at 29°C and 75 percent relative humidity was 17 eggs per day. The lower number of F_1 adult beetles produced in grains stored on untreated structural surfaces in comparison with the numbers reported by earlier workers might possibly be due to physical differences in food media as well as to low moisture content (14.0%) of the grains used for the study. Smith (1962) recorded low oviposition rates of _C. ferrugineus_ on moist wheat kernels (18 - 20% mc) in comparison with cracked dry kernels which had larger numbers of oviposition sites. The zero progeny or very low number of F_1 beetles in barley stored on untreated and treated structural surfaces seemed to be due to lack of kernels of sufficiently high moisture content, and the absence of finely divided food particles or suitable cracks and crevices for oviposition.

Significantly higher ($P < 0.01$) numbers of F_1 adult beetles were produced in grain samples stored on treated concrete surfaces than in grains stored on treated wood surfaces, apparently because of the high rate of survival of test insects in grains stored on concrete surfaces. Insecticides transferred to grain samples stored on wood surfaces nearly prevented reproduction of the beetles, and there was zero progeny in all grains stored on wood surfaces treated with malathion EC (Tables 34 and 43). Most of the insecticide deposits on concrete surfaces were able to impart sufficient residues to the stored grain samples that inhibited reproduction of the beetles for one or more weeks even though the percentage of survivors of the test beetles were quite high (Tables 34 and 43).

There was no significant difference ($P > 0.05$) in the reproduction of F_1 adult C. ferrugineus in wheat and corn stored on treated structural surfaces. However, the number of T. castaneum adults produced in corn was slightly greater than the number obtained in wheat with increase in age of insecticide deposit (Table 43). This might probably be due to the relatively lower mortality obtained on corn.

The mean number of adult beetles from wheat and corn samples stored on untreated structural surfaces is, however, an indication of the potential population levels that could have emerged from the grain samples if the insecticide deposits were not effective in killing the insects or inhibiting reproduction.

From the present study, it can be inferred that application of insecticides on the interior surfaces of store houses coupled with storage of grain of adequately low moisture content can retard the reproduction of the beetles and so preserve the quality of food grains.

2. <u>The translocation of bromophos, iodofenphos, and malathion deposits into wheat, barley, and corn.</u>

The analytical procedure for the determination of bromophos, iodofenphos, malathion, and pirimiphos-methyl residues on stored grains was based on recoveries from fortified wheat samples aged one to seven days. The accuracy and reproducibility of the ball-milling extraction with methanol and analysis by glc equipped with flame photometric detector without clean-up gave satisfactory recoveries for the four organophosphorus compounds used for the study. The residue recoveries were estimated entirely on the parent compounds of the insecticides.

The translocation of insecticide into stored grain from structural surfaces was chemically assayed on 30 g grain 1, 2, 4, 8, 16, and 32 weeks after ageing of the insecticide deposit. There was a significant difference between wood and concrete surfaces on the amount of insecticides that was picked up by grain samples stored on the surfaces. Significantly higher ($P < 0.01$) levels of insecticide residue were transferred to all grain samples stored on wood surfaces than grain samples stored on concrete surfaces (Tables 44 and 52). The insecticide residue recovered from grains stored on wood surfaces ranged from 0.09 ppm after 32 weeks to 40.50 ppm after one week of storage in contrast to zero ppm after 32 weeks to 4.93 ppm after initial storage of grain samples on concrete surfaces (Table 52). Alkaline surfaces have been known to hydrolyse and detoxify insecticides (Okwelogu, 1968) but the stability of bromophos on concrete surfaces has been reported by Immel and Geisthardt (1964) and Lemon (1967). The physical differences between the two structural surfaces such as pH and porosity probably influenced the persistence of insecticide deposits, which therefore accounted for the difference in uptake of toxic materials in grain in contact with the surfaces. The low amounts of residue recovered from grain samples stored on concrete surfaces may be partly due to the more porous nature of the concrete which resulted in a lower actual concentration of the insecticide per unit surface area than that obtained for the wood surface. Furthermore, the alkalinity of the concrete may have caused more rapid breakdown of the insecticide than did the neutral surface such as wood. A result obtained by Watters and Grussendorf (1969) on lindane and methoxychlor in wheat, barley, and oats in contact with treated wood and concrete surfaces also indicated a greater uptake of insecticides into stored cereals from wood than concrete.

The rate of uptake of the insecticides into stored grain samples from treated surfaces varied with the type and formulation of insecticide, the kind of grain in contact with the treated surfaces, the age of insecticide deposit, and the interactions between these factors. Significantly higher ($P < 0.01$) insecticide residues were recovered from the bromophos EC treatment but the uptake of the insecticide decreased sharply after eight weeks on both structural surfaces (Table 52). The residual amounts of iodofenphos recovered from grain samples stored on wood and concrete surfaces were lower than residues recovered from malathion and bromophos formulations on the structural surfaces. Rowlands (1967) observed that malathion tends to enter more rapidly into stored grain with moisture content exceeding 14.0 percent, whereas bromophos is taken up faster below this level. This phenomenon probably accounts for the initially high recovery of bromophos residues in the stored grain. There is no similar explanation for low recoveries of iodofenphos which is an iodo-analogue of bromophos. Comparatively, higher residue recoveries were obtained from grains stored on surfaces treated with EC formulations of malathion and bromophos than from the WP treatments, and the malathion formulations were generally more stable on wood surfaces than bromophos and iodofenphos (Table 52).

The translocation of insecticides into the grains varied with the kind of cereal grain in contact with the treated surfaces. Significantly less ($P < 0.01$) insecticide residues were recovered from corn stored on treated structural surfaces than from wheat and barley, the differences being more pronounced in the grain samples that were stored on treated wood surfaces. There was no significant difference ($P > 0.05$) in the rates of uptake of insecticide in wheat and barley stored on treated surfaces. Watters and Grussendorf (1969) also observed differences in the rates of uptake of insecticide in cereals in contact with surfaces treated with lindane and methoxychlor at 1.0g AI/m^2. The low residues recovered from corn in comparison with residues from wheat or barley agree with the results of the bioassay of the grain samples.

The persistence of the insecticides on wood surfaces is useful from the standpoint of control of stored-grain insects. Tolerance levels of 8 ppm for malathion and 10 ppm for bromophos in raw cereals have been set by the Joint FAO/WHO Committee on Insecticide Residues (1973a, 1976a), and 10 ppm has been suggested for iodofenphos (Rowlands, 1975). From the initial insecticide deposits on wood surfaces, a tolerance limit was reached for the malathion treatments and bromophos EC in corn eight weeks after treatment. The tolerance limit was reached for wheat and barley in contact with malathion-treated surfaces generally after 32 weeks, and for grain samples stored on surfaces treated with bromophos after eight to 16 weeks. Iodofenphos residues recovered from barley and corn were within the tolerance level one week after treatment, and four weeks after treatment for wheat in contact with the treated surface. Insecticides that translocated into stored grains from treated concrete surfaces never exceeded the tolerance limits (Table 52). This observation was consistent with the low actual concentrations of the insecticides per unit surface area.

The high residues, which exceeded the tolerance limits, obtained in grain from insecticide-treated surfaces can be reduced to recommended tolerance limits if the grain is thoroughly mixed with other layers of grain not in contact with the treated floors and walls of bins or granaries. The low insect mortalities due to the low levels of insecticide residue found in grain samples stored on concrete surfaces indicate that concrete structures will require more frequent application of insecticides than wooden structures for the control of insect infestations in stored grains or the amount of insecticide deposit on concrete surfaces will have to be increased to give better control of infestations during grain storage. Another approach to overcome the shortcoming of insecticide deposit on alkaline surfaces to control stored-grain insects may be to supplement the treatment of floor and walls by admixture of grain with approved insecticides.

The biological effectiveness of bromophos and iodofenphos on structural surfaces coupled with their relatively short persistence in relation to health hazards show that both compounds are good alternatives to malathion as residual grain-protectants.

3. Field tests with bromophos 25% WP as a residual protectant against rusty grain beetle infestations.

The data (Table 54) showed high insect mortality on the bottom layer of wheat in contact with the control surface. This may possibly be due to abrasion caused by pieces of broken concrete which were sampled together with the bottom layer of the wheat kernels since it was found later that when samples of the bottom layer of wheat were sieved to eliminate these foreign materials there was minimal or zero mortality. Complete mortality was obtained on samples from the bottom layer of wheat in contact with the treated surface when infested for seven days with adults of C. ferrugineus at each assessment period. In contrast, wheat samples from the top and the middle layers provided negligible control of C. ferrugineus. It has been reported that 0.25 ppm bromophos is the minimum effective dose required to give complete mortality of C. ferrugineus exposed continuously for seven days to treated wheat of 13.5 percent moisture content (Anon., 1974a). The residues recovered from the bottom layer at each period of assessment (Table 56) were above the level of the minimum effective dose (0.25 ppm) and, as expected, provided complete control of C. ferrugineus exposed for seven days on the wheat samples.

No F_1 adult progeny were produced in the bottom layer of wheat in contact with the treated surface after samples had been incubated for 42 days at 27.5°C and 60-70% RH (Table 55). Few F_1 adult progeny developed in the top and middle layers of core samples from the treated surface despite the high rate of insect survival. The low F_1 adult counts recorded were in contrast to observations made by Smith (1965), probably because of the low moisture content of the wheat (12.6-12.8%). This indicates the potential level of insect infestation that can easily develop in layers of grain far from the treated surfaces.

Bromophos residues recovered from the core samples were significantly higher ($P < 0.01$) in the bottom 8.3-cm layer of stored wheat (Table 56). The highest residue recovery was 0.68 ppm after two weeks, decreasing to 0.32 ppm after eight. There was very little uptake of bromophos by the middle and top layers of wheat. Similar rates of uptake of bromophos by wheat stored on maple hardwood floor of a granary treated at 1.0g AI/m^2 had been reported by Watters (1976).

Though the residue level in the bottom 8.3-cm layer of wheat in contact with the treated surface provided complete control of C. ferrugineus for the eight weeks of study, it is doubtful that these residues can sufficiently form a toxic barrier to C. ferrugineus to prevent insects from reaching the inner layers of the bulk grain, and thus preventing them from building up a high population level.

In the whole bin treatment, no bromophos residues were detected in the upper 450 bushels of wheat nor in the wheat stored in the control bin. The highest residue (0.68 ppm) was recovered in the layer of wheat close to the treated walls and floor, and this decreased considerably in the grain bulk towards the grain surface (Table 57).

Complete control of C. ferrugineus was achieved on wheat samples with doses of 0.51 ppm or higher, and which prevented reproduction of C. ferrugineus. Bromophos residues of 0.29 and 0.38 ppm provided 88 and 95 percent mortality, respectively, but few F_1 adult counts were recorded at these concentration levels. F_1 adult beetles produced in the wheat samples decreased with increase in bromophos residue. More than 80 adult beetles per sample were produced in wheat taken at the upper 450 bushels.

This study indicates that it is only a small portion of the grain bulk in contact with the treated surface that can be adequately protected from an infestation. The grain layers far from treated walls and floor are likely to be damaged by insects from outside the bin if treatment of the interior surfaces of the bin is not supported by other storage practices such as periodic turning of the grain bulk as well as thorough sanitation.

4. The effect of moisture content on uptake of malathion and bromophos from wood surface into wheat.

At the prevailing temperature and relative humidity under which grains were stored on treated surfaces, no appreciable moisture losses occurred (Table 6).

There was a complete mortality of *C. ferrugineus* and *T. castaneum* on grain samples stored on wood surfaces treated at 1.0g AI/m^2 with malathion and bromophos.

Significantly more ($P < 0.01$) bromophos residues were translocated into wheat at each moisture content than malathion. However, with each insecticide treatment, there was no significant difference ($P > 0.05$) between the grain moisture contents on the rate of uptake of insecticide into the grain from treated surfaces. This is contrary to the observation made by Rowlands (1967) that malathion moves rapidly into stored grain with the moisture content above 14.0 percent whilst bromophos enters the grain at a faster rate below 14.0 percent moisture. It appears that factors other than moisture content also play a role in the uptake of the insecticides. Probably, lipophilic affinity of the insecticides may also be a contributing factor in the rates of uptake of malathion and bromophos into grain in contact with treated surfaces. Thorough study on this possibility, however, is required for a firm conclusion to be drawn.

5. The distribution of malathion residues in layers of grain kernels stored on wood surface.

Significant differences were observed on the rates of uptake of the insecticide by the layers of grain kernels in contact with the treated surface, between the duration of storage of the grain on the treated surface, and their interaction.

Malathion transferred to the bottom layer of wheat was significantly greater ($P < 0.01$) than the amounts picked up by the middle and top layers. The malathion residue recovered from the bottom layer of wheat in contact with the treated surface increased from 7.05 ppm after the first day of storage of grain to 42.85 ppm after two months. In contrast, malathion residues in the middle and top layers increased, respectively, from 0.79 to 21.59 ppm and 0.25 to 9.07 ppm during the same period of storage.

The uptake of malathion by the layers of wheat increased progressively with the duration of storage of the grain kernels. A marked increase in the uptake of malathion by the layers occurred after one month of storage but there was no significant increase ($P > 0.05$) in the bottom and top layers after two months.

The detection of malathion in layers of grain kernels not directly in contact with the treated surface may be due to diffusion in the vapour phase of the insecticide from the wood surface which then became adsorbed on the kernels in the middle and top layers. Watters (1976) detected about 0.02 to 0.03 ppm malathion in a layer of wheat

24 cm from a maple hardwood floor of a granary treated at 1.0g AI/m^2. Evidence also exists indicating that pesticides can become airborne as a vapour or adsorbed onto dust particles and translocated far from the treated area (Hindin, 1967). Cohen and Pinkerton (1966) reported that on several occasions rain water collected in Cincinnati, Ohio, contained large amounts of chlorinated hydrocarbon insecticides and an organophosphate (ronnel). The work of Acree et al. (1963) revealed that DDT "co-distils" with water at ambient temperatures from the soil surface, and it was shown graphically that the co-distillation rate of DDT below 100 μg/1 at three different temperatures is a straight line function of the log of DDT per gram of water vaporized when plotted against the log concentration of DDT in solution. It is probable that some amount of malathion deposit evaporated through volatilization at the ambient temperature of the storage room (23 $\pm$ 2°C) and therefore accounted for the movement of the insecticide in the layers of kernels stored on the treated surface. Much work, however, remains to be done to determine the factors and the phenomenon involved in the movement of malathion through a grain bulk.

The bioassay of the layers of wheat showed a pattern similar to the results obtained for the residue analysis of the grain. A complete control of T. castaneum on the bottom layer of wheat was obtained at each storage period whilst a progressive increase in mortality with the duration of storage of the grain layers was observed in the middle and top layers (Table 60 and Fig. 11). The mortality of T. castaneum on the layers of wheat depicts the amount of toxicant picked up by the layers from the treated wood surface.

The study demonstrates an extent of contamination of about a 1-cm layer of grain in contact with treated wood when stored for less than three months. However, this high residue should not pose any toxicological hazard to consumers if the peripheral layer of grain is thoroughly mixed with the rest of the grain in storage.

6. Effect of physical disruption on the persistence of insecticide deposits on structural surfaces.

The type of physical disturbance applied on the treated wood surface affected the persistence of insecticide deposits as shown by bioassay of the treated surfaces with adults of *T. castaneum* exposed for five hours.

The mean percent mortality obtained on surfaces that were swept was significantly higher ($P < 0.01$) than the mean percent mortality on undisturbed surfaces and on the surfaces that were abraded by mechanical shaking with wheat for two hours (Table 61). Malathion formulations and iodofenphos EC provided an almost complete control of *T. castaneum* for 12 weeks on surfaces that were swept (Table 63 and Fig. 12). In contrast, iodofenphos was completely ineffective against *T. castaneum* one day after the surfaces had been subjected to abrasion, and malathion lost its effectiveness after three weeks. Bromophos deposits on surfaces abraded with wheat failed to control *T. castaneum* after one week but the effectiveness persisted for about six weeks on surfaces that were swept. On treated surfaces prepared as checks to compare by bioassay the impact on the persistence of the insecticidies on surfaces that were disturbed, iodofenphos virtually provided complete control of *T. castaneum* for 12 weeks compared with malathion WP and EC which provided 48 and 65 percent mortality for the same post-treatment period. This agrees with the result obtained by Blackman (1969) that iodofenphos was more toxic to *T. castaneum* adults than malathion. Bromophos WP and EC sharply declined in effectiveness on the undisturbed surfaces three and six weeks, respectively, after treatment probably because of the slow-acting nature of the insecticide to control stored-product insects which has been reported by Green *et al*. (1970), Tauthong and Watters (1978); and also by the fact that *T. castaneum* is more susceptible to malathion than bromophos (Lemon, 1967; Iordanou and Watters, 1969).

The short persistence of insecticides on surfaces disturbed by abrasion with wheat compared with other treated surfaces indicates that much of the insecticide residues were removed from the surfaces by the abrasive action of the wheat kernels, and that measurable amounts of insecticide residue would have been recovered if residue analysis of the grain had been made. Smallman (1948) noted that the use of a heavy, stiff-bristled broom for sweeping a warehouse treated with a gamma benzene hexachloride-oil solution for the control of spider beetles, and the number of times the shed was swept reduced the effectiveness of the treatment through abrasion in comparison with other treated warehouses. The relatively long persistence of insecticides on surfaces that were swept in contrast to observation made by Smallman (1948) was probably due to the use of soft-bristled broom which caused the residues to effloresce on the surfaces.

7. Persistence of malathion, bromophos, iodofenphos, and pirimiphos-methyl residues in dry and tough stored wheat.

Bioassay of the treated wheat - The persistence of the insecticides on dry (12.0% mc) and tough (16.0% mc) wheat showed that significantly higher ($P < 0.01$) mortalities of susceptible and malathion-resistant strains of *T. castaneum* occurred on dry wheat than on tough wheat (Tables 65 and 67, and Fig. 13). The percent mortality in both strains increased significantly ($P < 0.05$) with increasing dose of each insecticide applied.

Pirimiphos-methyl admixed with dry and tough wheat at 4.0 and 6.0 ppm provided complete control of susceptible *T. castaneum* for 24 weeks (Table 66) but 6.0 ppm was required to give complete mortality of the malathion-resistant strain for the same period (Table 68). Pirimiphos-methyl applied at 4.0 ppm produced 93.3 and 78.3 percent mortality of the malathion-resistant *T. castaneum* on dry and tough wheat, respectively, 24 weeks after the insecticide application. The demonstrated high toxicity and long residual effectiveness of pirimiphos-methyl against stored-product insects under practical storage conditions have been shown by various workers (Anon., 1974a; Cogburn, 1976; Redlinger, 1976; LaHue, 1977a; Kadoum *et al*., 1978). Pirimiphos-methyl at 4.0 ppm provided good control of *T. castaneum* in wheat stored in small sacks in a building in which severe infestation pressure was artificially sustained for six months (Anon., 1974a). Cogburn (1976) reported that pirimiphos-methyl at 10 and 15 ppm protected rice from infestation by *T. castaneum* for 12 months, and LaHue (1977a) showed that 4.0 ppm pirimiphos-methyl applied to wheat containing 12.5 percent moisture produced complete control of *T. castaneum* for 12 months. The efficacy and relatively long persistence of pirimiphos-methyl on wheat against strains of *T. castaneum* was also demonstrated in this study. The relative effectiveness of pirimiphos-methyl at 4.0 ppm on dry and tough wheat against both strains of *T. castaneum* correlated with the residual amounts found in whole grain and milled fractions (Tables 72 and 76) as well as its low mammalian toxicity [the acute oral LD_{50} rats is 2050 mg/kg (Martin and Worthing, 1977)] amply justifies its potential for use at this dosage rate to control *T. castaneum* in stored grain.

The effectiveness of malathion at 8.0 ppm applied to dry and tough wheat against susceptible *T. castaneum* lasted for six weeks, but at 12.0 ppm, it gave effective control for 24 weeks on dry wheat and 12 weeks on tough wheat (Table 66). It was ineffective at the dosages tested against the resistant strain (Table 68). Malathion at 12.0 ppm on dry wheat produced about 52 percent mortality one week after treatment. Malathion is known to lose its biological effectiveness against stored-product insects at higher moisture and storage temperatures (Watters, 1959; Strong and Sbur, 1960; Koivistoinen, 1961; Kadoum and LaHue, 1969). Watters (1959) found from bioassay with *C. ferrugineus* that malathion in wheat lost its insecticidal properties more quickly when the grain moisture content exceeded 13.5 percent. Similarly, Strong and Sbur (1960) reported that the residual effectiveness of malathion applied to wheat at 10 ppm to control *S. granarius*, *S. oryzae*, and *T. confusum* was much reduced at 50°C than at 10°C, and it would remain effective against insect infestations for at least 12 months as long as the storage temperature was not higher than 15.6°C and the moisture content of wheat did not exceed 14.0 percent at this initial dosage. Koivistoinen (1961) also observed that greater losses of malathion occurred at about

20°C than at 4°C when apples and beans were treated with malathion after harvest. The high storage temperature and grain moisture content under which the treated wheat was stored (Table 64) therefore explains the rather short residual effectiveness of malathion against T. castaneum. The result obtained in this investigation is therefore comparable with the observations reported by the earlier workers that malathion degrades faster under conditions of high storage temperature and relative humidity or high grain moisture content. The result is further validated by observations made by Quantanilla et al. (1970) that malathion at 5.0 ppm afforded good control of T. castaneum for about three months, and at 2.0 ppm to wheat of 13.5 percent moisture content, it provided complete control of C. ferrugineus for eight months (Watters, 1959). Lindgren et al. (1954) also reported from laboratory experiments that malathion applied to wheat containing 10 percent moisture at 8 and 16 ppm remained effective against S. granarius, S. oryzae, and R. dominica for six to seven months. More than 20 ppm malathion is the minimum effective dose required to give complete mortality of malathion-resistant T. castaneum exposed for seven days on treated wheat of 13.5 percent moisture content (Anon., 1974a). It was therefore not surprising that malathion at the doses tested failed to control resistant T. castaneum.

Bromophos and iodofenphos applied to wheat at 10 and 15 ppm were all effective ($P > 0.05$) on both dry and tough wheat against susceptible T. castaneum (Table 65) but with age of insecticide deposit, iodofenphos treatments provided better control ($P < 0.01$) of T. castaneum than bromophos (Table 66). Iodofenphos at 10 ppm on dry wheat gave equal protection against susceptible T. castaneum as 12 ppm malathion. The bromophos treatments on dry and tough wheat significantly ($P < 0.01$) afforded better control of malathion-resistant T. castaneum than the iodofenphos treatments. Bromophos and iodofenphos, applied at the rate of 15 ppm to dry and tough wheat, provided complete control of the resistant strain for 12 and three weeks, respectively.

The results of the relative effectiveness of bromophos on dry and tough wheat against insect infestation are in line with those of Green et al. (1970). The authors reported that bromophos applied as water-based emulsion at 8, 16, and 24 ppm to clean bagged wheat and barley of 14.0 and 13.0 percent moisture content, respectively, sharply declined in biological effectiveness against O. surinamensis and S. granarius after 16 weeks in the 8 ppm treatment, and after 24 weeks in the 16 ppm treatment. The 24 ppm treatment remained fully effective against O. surinamensis for 36 weeks and S. granarius for 24 weeks. The persistence of bromophos is, however, contrary to the findings of Joubert and De Beer (1968) who claimed that bromophos applied to maize at 5 and 10 ppm AI afforded excellent control against S. oryzae, T. castaneum, O. surinamensis, and E. cautella over a storage period of 50 weeks under the subtropical conditions of South Africa. The differences in the persistence of bromophos might possibly be due to the use of different types of formulation, type and physical conditions of the grains, and the environmental conditions under which the studies were made. Green et al. (1970) noted that bromophos, applied to infested wheat containing 15 percent moisture, at 9 ppm and stored in bulk on the farm during winter, remained effective against O. surinamensis for up to 12 months. Malathion is more toxic to T. castaneum than bromophos (Lemon, 1966; Iordanou and Watters, 1969). In the present study, bromophos at 10 ppm was about equal in effectiveness as 12 ppm malathion (Table 65), which demonstrates that bromophos was more stable on wheat under the conditions of the storage.

The biological effectiveness of iodofenphos against susceptible _T. castaneum_ and its relative persistence on wheat in comparison with malathion are similar to those reported by other workers. Adesuyi and Adeyemi (1973) found that iodofenphos applied at 20 ppm to stored maize to protect against insect damage was as effective for nine months as malathion applied at 30 ppm. Bromophos at 20 ppm was effective for seven months. Kane _et al_. (1973) also reported that iodofenphos at 10 ppm gave complete protection of bagged wheat and barley for about 20 weeks against _O. surinamensis_ and _S. granarius_, and LaHue (1975) observed that 10 and 20 ppm iodofenphos gave excellent protection to corn and wheat, respectively, for 12 months. Wilkin _et al_. (1973) showed from laboratory studies that iodofenphos at 10 ppm on English wheat had longer effective life than an equivalent dose of malathion against _O. surinamensis_ on warm moist grain.

The effectiveness of pirimiphos-methyl and bromophos, and to some extent, iodofenphos against malathion-resistant _T. castaneum_ indicates the absence of any significant cross-tolerance to these compounds, thus ensuring their potential as suitable compounds against stored-product insects resistant to malathion.

_F_1 progeny_ - The F_1 adult counts of the test strains of _T. castaneum_ from incubated samples were higher in the untreated wheat than in the treated wheat at each time interval after treatment.

Pirimiphos-methyl at the rates of 4.0 and 6.0 ppm prevented reproduction of both resistant and susceptible strains of _T. castaneum_ in dry and tough wheat for 24 weeks. This was possibly due to the high mortality rate.

There was emergence of F_1 adults of susceptible _T. castaneum_ and malathion-resistant _T. castaneum_ in tough wheat treated with malathion at 8 ppm after 24 and six weeks, respectively. In dry wheat, malathion at 8 ppm prevented reproduction of the susceptible strain but F_1 adults of the resistant strain were recovered 24 weeks after treatment. No susceptible _T. castaneum_ were produced in the dry and tough wheat treated with malathion at the rate of 12 ppm, but the efficacy on tough wheat against the resistant strain lasted for only three weeks. Godavari Bai (1964) showed that the breeding of _T. castaneum_ could be inhibited by malathion even at a concentration of 2.0 ppm. More than 2.0 ppm malathion (2.62-4.52 ppm) was recovered from the dry wheat samples and less than 2.0 ppm (1.19-1.45 ppm) from the tough wheat samples after 24 weeks (Table 72). The high grain moisture and temperature, and low malathion concentration as well as the high survival rate of resistant _T. castaneum_ possibly contributed to the rate of emergence of adult beetles in the treated tough wheat.

Bromophos at 10 ppm on dry wheat prevented reproduction of both strains of _T. castaneum_ but on tough wheat emergence of both strains occurred at 24 weeks after treatment. Bromophos, applied to dry and tough wheat at 15 ppm, inhibited breeding of both test strains for 24 weeks.

No F_1 adults of either strain emerged from the dry wheat treated with iodofenphos at 10 and 15 ppm. In contrast, counts of F_1 adults from tough wheat treated at the same concentrations were recorded after 24 weeks.

Analysis of the residues - At the prevailing temperature and relative humidity at the time of tests, appreciable moisture losses during the 24-week storage period were confined to grain of 16.0 percent moisture content but these did not exceed two percent 24 weeks after insecticide applications.

The chemical analysis of the treated wheat for insecticide residues immediately after treatment showed that the amounts applied were close to the dosage rates intended for application (Table 72). As the tests progressed, residues of each insecticide showed a general trend of degradation (Table 74 and Fig. 14).

The oxygen-analogue of organophosphorus insecticides usually makes up only a small fraction of the residue on crops (Coffin, 1966; Rowlands, 1966a; Anon., 1974a). It was therefore considered adequate to measure only the parent compounds of the test insecticides for assessing the residue burden of the stored grain. No attempts were made to detect, identify or measure the hydrolytic degradation products of the insecticides or their metabolites even though the possibility exists that some metabolic products of the originally applied insecticides may be present. The analytical data presented in Tables 71-75 and Fig. 14 were based strictly on residues of the parent compounds.

General comparisons on the persistence of the insecticides based on the residual amounts recovered from the treated wheat are difficult because of widely differing concentration levels applied to the wheat. However, the rate of loss of the insecticides generally was significantly greater ($P < 0.01$) on tough wheat than on dry wheat. There was no significant difference ($P > 0.05$) in the rate of loss of pirimiphos-methyl applied to dry and tough wheat. The mean loss of pirimiphos-methyl applied to dry and tough wheat at 4.0 ppm was about 29 and 35 percent, respectively, after 24 weeks; at 6.0 ppm on dry and tough wheat, the residue losses were 33 and 30 percent, respectively, for the same duration of storage. This confirms the data obtained from the bioassay that pirimiphos-methyl was comparatively the most stable compound among the insecticides tested. The results of this study agree with the findings of Chawla and Bindra (1971) who reported that pirimiphos-methyl dissipated at a slower rate on wheat than bromophos or iodofenphos. Redlinger (1976) also observed that residues of pirimiphos-methyl degraded at a rate approximately 33 percent less than malathion over 12 months. LaHue and Dicke (1977) and LaHue (1977b) found that after 12 months' storage about 50 and 83 percent of pirimiphos-methyl residues remained on sorghum grain and wheat, respectively, when admixed with grains at 8.4 and 7.8 ppm AI.

Significantly higher ($P < 0.05$) malathion residues were recovered from the dry wheat treated at both concentration levels than from the tough wheat after three weeks. About 67 percent malathion was lost after 24 weeks in the 8 ppm treatment and 62 percent in the 12 ppm treatment on dry wheat. In contrast, the loss of malathion on tough wheat was 85 percent in the 8 ppm treatment and 88 percent in the 12 ppm treatment. A similarity in the pattern of malathion degradation on wheat of varying moisture content or relative humidity and storage temperatures had been reported by Lal and Beri (1964), Kadoum and LaHue (1969), and Minett _et al_. (1968). There was no significant difference ($P > 0.05$) in the percent rate of loss of malathion at 8 and 12 ppm on dry wheat and on tough wheat 24 weeks after treatment (Table 74).

Bromophos and iodofenphos were recovered in significant amounts ($P < 0.01$) from dry wheat than from tough wheat after 12 and 3-6 weeks, respectively. The percent rate of loss of iodofenphos on both dry and tough wheat was significantly greater ($P < 0.01$) than the rate of loss of bromophos. Bromophos became more stable on dry wheat than on tough wheat after 12 weeks, and for iodofenphos, after six weeks. On dry wheat 50-55 percent bromophos was lost 24 weeks after treatment in comparison to a loss of 72-75 percent of residue on tough wheat for the same duration of storage. In contrast, 73-76 and 80-85 percent iodofenphos residue degraded on dry and tough wheat, respectively, after 24 weeks. On dry wheat, iodofenphos was lost at a faster rate than malathion, bromophos or pirimiphos-methyl but on tough wheat malathion and iodofenphos broke down at almost equal rates. Chawla and Bindra (1971) observed that loss of iodofenphos residue on wheat at an initial moisture content of 8.6 percent, stored under a wide range of temperatures and relative humidities, was similar to the rate of loss of malathion residue. The relative stability of bromophos residue on wheat had also been demonstrated by Eichler and Knoll (1974). The authors showed from large-scale laboratory studies on wheat treated at 8 or 12 ppm that 40 to 50 percent of the residues was degraded after 12 months under temperate conditions.

The present analytical studies indicate a very slow rate of loss of pirimiphos-methyl residues on wheat compared with bromophos, malathion, and iodofenphos residues. Iodofenphos was lost at a faster rate than bromophos, which also was lost at a comparatively slower rate than malathion.

The insecticidal activity is determined by the residual life of the chemical and the toxicity of any metabolites produced. The estimated half-life, $t\frac{1}{2}$, of the insecticide residues obtained from the study and presented in Table 75 shows variations in half-life values between insecticides and grain moisture content, and between dosage levels of the same insecticide except when bromophos or iodofenphos were applied to the tough wheat. Gunther et al. (1958) observed that on wheat of 12 percent moisture content, at storage conditions of 23.9°C and low relative humidity, malathion had an average half-life of 5.6 months. The authors also noted variations in half-life of malathion applied at different dosages; malathion applied to wheat at 8 and 16 ppm had residual half-life values of five and six months, respectively. Gunther and Jeppson (1960) calculated half-life of malathion residues in stored wheat from the investigations of several workers as 150 to 190 days. Schesser et al. (1958) also found half-life of malathion applied to wheat at a rate of 2.5 to 7.5 ppm as 5.5 months. The data of Green et al. (1970) indicated that 50 percent of bromophos was degraded in three to four months on wheat stored at 24-25°C and under 50 percent relative humidity. The limited study made by Horler and Clark (1970) in which iodofenphos was applied to barley stored at a high moisture content (14-22%) and under severe temperature conditions indicated that 50 percent of iodofenphos residues were lost in about two weeks. Chawla and Bindra (1971) noted that the half-life value of malathion, bromophos, and iodofenphos applied to wheat of 8.6 percent initial moisture content and stored under a wide range of environmental conditions (18.1-31.5°C and 44 - 76.5% RH) was two to three months, and for pirimiphos-methyl three to four months.

The half-life of the insecticides was generally longer on dry wheat than on tough wheat. Pirimiphos-methyl treatments had the longest residual half-life, ranging from 33.3 to 43.4 weeks, and iodofenphos treatments had the shortest residual half-life of 5.2 to 7.6 weeks (Table 75). Bromophos, applied to wheat at either grain moisture content, showed a longer residual half-life than malathion. The longer residual half-life value of pirimiphos-methyl on wheat than malathion, bromophos, or iodofenphos agrees with the findings reported by Chawla and Bindra (1971). The half-life of bromophos, being relatively more stable on tough wheat than malathion, has also been reported (Rowlands, 1967; Green et al., 1970).

The effect of grain moisture content, storage temperature, type of formulation, and the method and rate of application affecting persistence of insecticides have been shown by other workers. Minett et al. (1968) demonstrated from chemical assay data the temperature and moisture dependence on malathion breakdown on wheat. Bromophos and pirimiphos-methyl are relatively stable on damp grain (Rowlands, 1967; Anon., 1974a) but Eichler and Knoll (1974) observed that the rate of decomposition of bromophos was significantly increased when the storage temperature of treated wheat was raised from 15°C to 26°C. The differences in residual half-life values of the insecticides estimated from the present investigation and those reported in the literature is due to the wide range of environmental conditions under which the treated wheat used for individual studies was stored, as well as the grain moisture content, which either enhanced or retarded the loss of the insecticides.

Residues in milled fractions of stored wheat

Table 76 shows the mean insecticide residues found on whole wheat just before milling, and residues recovered from the milled fractions of dry and tough wheat during the six months' storage of the grain. High insecticide residues were recovered from bran and middlings (wheat germ plus the finer parts of the bran) with very slight differences in residual amounts occurring between these fractions. Comparatively small amounts of insecticide residue were found in the flour. The insecticide residues recovered from the milled fractions decreased with the duration of storage of the treated grain. The largest amounts of insecticide residue contained in the milled fractions were found after a month of storage, which indicate a rapid penetration of the insecticide deposits through the pericarp of the grain, small amounts being carried over into the endosperm or aleurone layer. The penetration of insecticide deposits through the pericarp into other tissues of stored grain has already been described by Rowlands (1966b,c; 1967, 1970), Horler and Rowlands (1968), and confirmed by other workers (Eichler and Knoll, 1974). The results of other workers (Schesser et al., 1958; Strong et al., 1961; Eichler and Knoll, 1974; Kadoum and LaHue, 1977; Kadoum et al., 1978) were similar to the present study and have shown that the bran and middlings contain the largest insecticide residues; very small amounts of residues were found in the flour at various time intervals after the insecticide application.

The insecticide residues recovered from milled fractions of tough wheat were generally lower than the residues found in the dry wheat fractions. This observation indicates that the levels of insecticide residue on wheat of low moisture content can markedly be reduced when the moisture content of the grain is increased to the required moisture level prior to milling of the treated wheat. Kadoum and LaHue (1977) also found that there was a marked reduction of malathion residues on wheat when the moisture content of the treated wheat was raised to 15 percent for milling.

The data presented in Table 76 (a and b) indicate that the use of malathion, bromophos, iodofenphos or pirimiphos-methyl at any of the dosages tested present less of a residue problem to consumers who store treated grain for relatively long periods. The bran and middlings contain higher residues than flour. Therefore, there is the possibility that animal feeds pose more of a toxicological hazard than human foods. However, bran is often mixed with other ingredients for animal feeds, thus reducing the actual concentrations consumed.

CHAPTER VI

SUMMARY AND CONCLUSION

Treatment of the interior surfaces of storage structures with residual contact insecticides is a recommended farm practice to protect stored grain and cereal products from spoilage by insects. Persistence of malathion, bromophos, and iodofenphos applied as water-based emulsions (EC) or wettable powders (WP) at 1.0g AI/m^2 to wood and concrete (pH 8.26) surfaces was therefore determined in the laboratory at various times after treatment by bioassay of 30 g of wheat, barley, and hybrid corn with susceptible strains of *C. ferrugineus* and *T. castaneum* after the cereals had been removed from contact for one week with the surfaces. Residue analysis using glc was also carried out to supplement the bioassay, and to compare the residue levels with internationally approved tolerance limits.

Significantly higher mortalities ($P < 0.01$) of *C. ferrugineus* and *T. castaneum* were obtained on cereals stored on treated wood surfaces than on cereals that were stored on treated concrete surfaces. On wood surfaces, malathion EC provided better control of the insects on stored grains for 32 weeks. Bromophos WP gave complete mortality of both beetles for 16 weeks but its effectiveness against *T. castaneum* declined sharply after 32 weeks. Malathion WP, bromophos and iodofenphos (EC) were effective on stored grains against *C. ferrugineus* for 16 weeks but their residual effectiveness against *T. castaneum* varied from eight to 16 weeks after treatment. On concrete surfaces, bromophos WP provided relatively good control on grains against *C. ferrugineus* than other insecticide treatments. Iodofenphos deposit on concrete surfaces persisted significantly longer ($P < 0.05$) than the malathion formulations but it was less effective than bromophos EC. Insecticide deposits on concrete surfaces transferred to stored grains generally lost their effectiveness against T. castaneum one week after treatment. Significantly lower mortalities ($P < 0.01$) were obtained on corn stored on treated structural surfaces than on wheat or barley.

The mean number of F_1 adults produced by 20 adult beetles exposed for one week on the grains previously stored for one week on untreated structural surfaces was significantly greater ($P < 0.01$) than the number recorded from grains stored on treated structural surfaces. On treated structural surfaces, significantly fewer progeny ($P < 0.01$) were produced in grains previously stored on wood surfaces than in grains stored on concrete surfaces with both C. ferrugineus and T. castaneum. The reproduction of test beetles was nearly prevented in grain samples stored on treated wood surfaces, and no progeny of either species were produced in grains stored on wood surfaces treated with malathion EC. Insecticides translocated into stored grains from concrete surfaces inhibited reproduction of the adult beetles in the grains at one or more weeks after treatment. Very few or no progeny were produced in barley stored on untreated or treated structural surfaces. Corn samples stored on treated structural surfaces were the least protected against C. ferrugineus and T. castaneum infestations.

Residue analysis showed that significantly more insecticide ($P < 0.01$) translocated into grain samples stored on treated wood surfaces than into grain samples stored on treated concrete surfaces. Insecticide residues recovered from grain samples stored on treated structural surfaces depended on the type and formulation of insecticide, the kind of cereal grain in contact with the treated surfaces, and the age of insecticide deposit. Initially, more insecticide residues were recovered from grains stored on structural surfaces treated with bromophos EC but the residual amounts decreased sharply after eight weeks. The malathion formulations were generally more stable on wood surfaces than bromophos and iodofenphos. Iodofenphos residues were recovered in less amounts from grain samples stored on wood and concrete surfaces. Insecticides translocated into stored grains from structural surfaces treated with malathion or bromophos EC were higher than the WP formulations but with age of deposit bromophos WP showed longer persistence than its EC formulation. Significantly, the uptake of insecticides into wheat and barley was greater than the rate of uptake into corn from treated structural surfaces. Also, with an increase in age of deposit, less insecticide translocated into stored grain samples from the surfaces.

The low insect mortalities due to the low levels of insecticides that translocated into cereals stored on concrete surfaces indicate that concrete structures will require more frequent application of insecticides than wooden structures to protect stored grain from insect infestations. For long-term protection of stored grain in wooden bins or granaries or storage surfaces that are near neutral against C. ferrugineus and T. castaneum infestations, the use of malathion EC is preferable. Bromophos WP is recommended for treating concrete floors and walls. The application of insecticides to concrete surfaces may also have to be supplemented with admixture of approved insecticides with stored grain.

The biological effectiveness of bromophos on both structural surfaces and iodofenphos on wood coupled with their relatively short persistence in relation to health hazards show that both compounds are promising alternatives to malathion as residual grain-protectants.

Field tests with bromophos WP applied at 1.0g AI/m^2 to the concrete floor of a farm granary and to a galvanized steel bin with a concrete floor prior to storage of wheat were conducted to assess persistence and effectiveness of the deposit as a residual protectant against C. ferrugineus infestation. Bioassay of wheat samples previously stored on the treated, concrete floor of the granary showed 100 percent mortality of C. ferrugineus for eight weeks on bottom 8.3-cm layer of wheat. Bromophos taken up by the middle and top layers of stored wheat was ineffective. Significantly higher ($P < 0.01$) numbers of C. ferrugineus F_1 adults were produced in the middle and top layers of wheat samples but the residues in the bottom layer completely prevented reproduction of C. ferrugineus. There was negligible uptake of bromophos beyond 8.3 cm of stored wheat. High bromophos residues were recovered in the bottom layers of wheat, ranging from 0.62 ppm after one week to 0.32 ppm eight weeks after treatment.

In the whole bin treatment, bromophos residues detected at the various bushel levels of stored wheat determined the percent mortality and development of C. ferrugineus in the wheat sampled at these levels. Bromophos residues were recovered in greatest amount in samples of wheat close to the treated walls and floor, and the residue levels of bromophos increased as the bin was emptied. Wheat samples with 0.5 ppm or higher provided 100 percent mortality and also prevented reproduction of C. ferrugineus. F_1 progeny developed in all wheat samples with residues of 0.38 ppm or less. This field study has demonstrated that only the layers of grain stored in direct contact with treated structural surfaces are adequately protected from insect infestation. The main bulk of the grain will be unprotected unless it is admixed with a suitable insecticide at the beginning of the storage period.

Wheat of different moisture contents stored for one week on wood surfaces treated with malathion and bromophos (EC) at 1.0g AI/m^2, showed that moisture content of grain had no effect on the uptake of these chemicals into stored wheat.

Residue recoveries from each of the three single layers of grain kernels in contact with wood surfaces treated with malathion at 1.0g AI/m^2 showed that insecticide moved up past a single layer of grain kernels. The uptake of malathion by the layers of grain kernels increased progressively with the duration of storage. Bioassay of the layers of wheat stored on the treated surfaces also indicated that mortality of T. castaneum depended upon the time the layers of wheat had been in contact with the treated surfaces, thus reflecting the amount of toxicant that translocated into the three layers of grain kernels. The accumulation of residue in about 1 cm layer of grain in contact with the treated surface shows the extent of toxicological contamination that can be expected from the peripheral layers of grain bulk directly in contact with treated wood surface.

The type of physical disturbance applied to treated surfaces affected the persistence of malathion, bromophos (EC and WP), and iodofenphos (EC) applied at 250mg AI/m^2 on wood surfaces when the insecticide deposits were assessed with susceptible T. castaneum adults at exposure periods of five hours for 24 weeks. Insecticide deposits on surfaces that were swept persisted significantly longer than the deposits on undisturbed surfaces and surfaces disturbed by abrasion caused by wheat kernels. Deposits on surfaces disturbed by abrasion with wheat lost their effectiveness one day after treatment for iodofenphos and after three weeks for malathion and bromophos formulations. Malathion and iodofenphos deposits on surfaces that were swept were equally effective against T. castaneum but bromophos lost its effectiveness after 12 weeks. The study indicates that the effectiveness and persistence of insecticide deposit on wood surface can be enhanced when treated surfaces are slightly disturbed,but prolonged, heavy abrasion of surfaces as to be expected during loading of harvested grain into a treated bin or granary can markedly reduce the biological effectiveness of insecticide deposits on surfaces.

Wheat of 12.0 and 16.0% mc (dry and tough wheat, respectively) were treated with malathion, bromophos, iodofenphos, and pirimiphos-methyl in liquid formulations at initial doses equivalent to their tolerance levels and 1.5 times these levels to examine the residual effects on susceptible and malathion-resistant strains of T. castaneum. Mortality counts were examined over a 24-week period by placing 20 adult beetles on 50 g samples of treated wheat for seven days, at certain intervals after treatment. Pirimiphos-methyl at dosages tested provided complete control of susceptible T. castaneum on dry and tough wheat for 24 weeks but 6.0 ppm was required to give 100 percent mortality of the resistant strain on dry and tough wheat 24 weeks after treatment. Malathion at the dosages applied to wheat was not effective against the resistant T. castaneum but the higher dosage on dry and tough wheat was quite effective against the susceptible strain. Bromophos and iodofenphos showed equal effectiveness on dry and tough wheat against susceptible T. castaneum but bromophos was more effective than iodofenphos against the resistant strain.

Effects of the treatments on the production of F_1 progeny in wheat were examined by counting adult emergence in the wheat samples 42 days after each assessment period. No F_1 progeny of both strains of T. castaneum were produced in wheat treated with pirimiphos-methyl. Dry wheat treated with malathion, bromophos, and iodofenphos prevented reproduction of susceptible T. castaneum but F_1 adult emergence was observed in tough wheat treated with lower dosage rates of malathion and bromophos and at both dosages of iodofenphos. F_1 adult emergence of the resistant T. castaneum occurred in the tough wheat treated with malathion after six weeks and after 24 weeks for 10.0 ppm bromophos treatment and both iodofenphos treatments.

Residue analysis of stored grain showed that generally the rate of loss of the insecticides was significantly faster ($P < 0.01$) on tough wheat than on dry wheat, except pirimiphos-methyl in which the rate of loss was equal ($P > 0.05$) on both dry and tough wheat At the dosages tested, pirimiphos-methyl showed greater stability followed by bromophos, malathion, and iodofenphos according to the order of their percent residue degradation and the estimated half-life values on wheat.

The studies on the distribution of insecticide residues in milled fractions of wheat showed that high amounts of residue were concentrated in the bran and middlings. Comparatively, very small residues were detected in the flour. Insecticide residue found in the milled fractions decreased with age of deposit.

The efficacy of bromophos and iodofenphos on wheat against both strains of _T. castaneum_ as well as their relatively short persistence and low mammalian toxicities indicated that these compounds are good alternatives to malathion as short-term residual grain-protectants for use against malathion-resistant strains of stored-grain pests. Pirimiphos-methyl would be a very useful grain-protectant for long-term storage. It would also be useful against malathion-resistant strains and strains of stored-product insects which have shown cross-tolerance to bromophos and iodofenphos provided it is cleared from the point of view of health hazards and approved dosage rates are established for use on stored products.

REFERENCES CITED

Abbott, W.S. 1925. A method of computing the effectiveness of an insecticide. J. Econ. Ent. 18: 265-267.

Acree, Jr., F., M. Beroza, and M.C. Bowman. 1963. Codistillation of DDT with water. J. Agr. Food Chem. 11: 278-280.

Adesuyi, S.A. 1969. Post-fumigation protection of maize in aluminium silo with one percent malathion dust. Nigerian stored Prod. Res. Inst. Ann. Rep. 1969: 45-48.

Adesuyi, S.A. and S.A.O. Adeyemi. 1973. A comparison of malathion, iodofenphos and bromophos for the control of insect infestation on maize in cribs. Nigerian stored Prod. Res. Inst. Tech. Rep. 1970-1973. No. 5: 39-46.

American Cyanamid Company. 1973. Recommended method of analysis: Malathion. American Cyanamid Co., Agric. Div., Prod. Develop. Paper. 9p.

Anonymous. 1973. Paint the surfaces before using insecticides. Agr. Chem. 28: 6.

Anonymous. 1974a. 'Actellic' containing pirimiphos-methyl: An insecticide for stored products. ICI Technical Data Sheet, March 1974. 27p.

Anonymous. 1974b. Field control of stored-product insects. Canada Dept. Agr., Res. Branch Rep. 1973: 230-231.

Anonymous. 1975. Control of stored-product insects. Canada Dept. Agr., Res. Branch Rep. 1974: 244.

Anonymous. 1977. Canada Dept. of National Health and Welfare. Office of Consolidation of the Food and Drugs Act and of the Food and Drug Regulations with Amendments to Oct. 7, 1977. Ottawa.

Bang, Y.H. and E.H. Floyd. 1962. Effectiveness of malathion in protecting stored polished rice from damage by several species of stored grain insects. J. Econ. Ent. 55: 188-190.

Beri, Y.P. and R. Lal. 1965. Studies on the insecticide residues in and on plants as well as on contamination of wheat contained in bags treated with insecticides or fumigated. Insect. Toxicol. Inform. Serv. 8: 124-125.

Blackman, D.G. 1969. Tests of newer insecticides. Pest Infest. Res. Rep. 1968: 46.

Burkholder, W.E. and R.J. Dicke. 1966. The toxicity of malathion and fenthion to dermestid larvae as influenced by various surfaces. J. Econ. Ent. 59: 253-254.

Champ, B.R. and M.J. Campbell-Brown. 1970. Insecticide resistance in Australian Tribolium castaneum (Herbst) (Coleoptera, Tenebrionidae) - II. Malathion resistance in Eastern Australia. J. stored Prod. Res. 6: 111-131.

Champ, B.R., R.W. Steele, B.G. Genn, and K.D. Elms. 1969. A comparison of malathion, diazinon, fenitrothion and dichlorvos for control of Sitophilus oryzae (L.) and Rhyzopertha dominica (F.) in wheat. J. stored Prod. Res. 5: 21-48.

Chawla, R.P. and O.S. Bindra. 1971. Residues of some promising grain-protectants on stored wheat. Proc. 1st All-India Symp. Progress and Problems in Pesticide Residue Analysis. Nov. 18-19, 1971. Ludhiana, India. p. 68-74.

Coffin, D.E. 1966. Oxidative metabolism and persistence of parathion and malathion on field-sprayed lettuce. J. Assoc. Offic. Anal. Chemists 49: 1018-1021.

Cogburn, R.R. 1972. Natural surfaces in a Gulf port warehouse: influence on the toxicity of malathion and Gardona to confused flour beetles. J. Econ. Ent. 65: 1706-1709.

Cogburn, R.R. 1976. Pirimiphos-methyl as a protectant for stored rough rice: small bin tests. J. Econ. Ent. 69: 369-373.

Cohen, J.M. and C. Pinkerton. 1966. Organic pesticides in the environment - Widespread translocation of pesticides by air transport and rain-out. Adv. Chem. Ser. 60: 163-176.

Coulon, J. 1966. Influence of grain humidity on the effectiveness of some insecticides used for the treatment of stored cereals. Phytiat. Phytopharm. 15: 269-275. In Rev. appl. Entomol. Ser. A, 57: 349.

Crisp, S. and K.R. Tarrant. 1971. Determination of residues of dichlorvos and malathion in wheat grain by gas-liquid chromatography. Analyst 96: 310-313.

Dyte, C.E. and D.G. Blackman. 1970. The spread of insecticide resistance in Tribolium castaneum (Herbst) (Coleoptera, Tenebrionidae). J. stored Prod. Res. 6: 255-261.

Dyte, C.E. and F.H. Fortescue. 1967. Toxicity studies on organophosphorus compounds. Pest Infest. Res. Rep. 1966: 36-37.

Dyte, C.E. and D.G. Rowlands. 1968. The metabolism and synergism of malathion in resistant and susceptible strains of Tribolium castaneum (Herbst) (Coleoptera, Tenebrionidae). J. stored Prod. Res. 4: 157-173.

Eichler, D. and H.A. Knoll. 1974. Degradation of bromophos in stored wheat. Proc. 1st internat. Working Conf. stored Prod. Entomol. Oct. 7-11, 1974. Savannah, Ga., USA. p. 582-590.

Elms, K.D. 1967. Determination of malathion residues in wheat by gas-liquid chromatography. J. stored Prod. Res. 3: 393-395.

El-Rafie, M.S., M.R.A. El-Ghar, and F.A. Metwally. 1969a. Evaluation of certain grain protectants under common methods of storage in Egypt. Bull. Entomol. Soc. Egypt, Econ. Ser. 3: 135-148.

El-Rafie, M.S., M.R.A. El-Ghar, and F.A. Metwally. 1969b. The rate of degradation of certain grain protectants under common methods of storage in Egypt. Bull. Entomol. Soc. Egypt, Econ. Ser. 3: 17-28.

El-Rafie, M.S., A. Badawi, and M.M. Zewar. 1975. Effect of surface treatment of jute and cotton bags with DDT and malathion on the protection of stored wheat grain and flour from infestation with certain pests. Agr. Res. Review 53: 99-104. In Rev. appl. Entomol. Ser. A, 65: 1528.

Erakay, S. and A.I. Ozar. 1975. Bromophos (Nexion)'lu preparatlarm malathion'la mukayaseli olarak bazi ambar böceklerine etkileri üzerinde arastirmalar. (Investigation on the effectiveness of bromophos (Nexion) preparations compared with malathion ones on some stored-product insects). Bitki Koruma Bulteni 15: 107-123. In Rev. appl. Entomol. Ser. A, 64: 1906.

FAO. 1970. Recommended methods for the detection and measurement of resistance of agricultural pests to pesticides: Tentative method for adults of the red flour beetle, Tribolium castaneum (Herbst) - FAO Method No. 6. FAO Plant Prot. Bull. 18: 107-113.

FAO/WHO. 1967. Evaluation of some pesticide residues in food. FAO/PL:CP/15; WHO/Food Add./67.32. 237p.

FAO/WHO. 1968a. Pesticide residues. Report of the 1967 Joint Meeting of the FAO Working Party and the WHO Expert Committee. FAO/PL: 1967/M/11; WHO Techn. Rep. Ser. 391. 43p.

FAO/WHO. 1968b. 1967 evaluation of some pesticide residues in food. FAO/PL: 1967/M/11/1; WHO/Food Add./68.30. 242p.

FAO/WHO. 1969a. Pesticide residues in food. Report of the 1968 Joint Meeting of the FAO Working Party of Experts on Pesticide Residues and WHO Expert Committee on Pesticide Residues. FAO Agr. Studies No. 78; WHO Techn. Rep. Ser. 417. 40p.

FAO/WHO. 1969b. 1968 evaluations of some pesticide residues in food. FAO/PL: 1968/M/9/1; WHO/Food Add./69.35. 293 p.

FAO/WHO. 1973a. Pesticide residues in food. Report of the 1972 Joint Meeting of the FAO Working Party of Experts on Pesticide Residues and the WHO Expert Committee on Pesticide Residues. FAO Agr. Studies No. 90; WHO Techn. Rep. Ser. No. 525. 47p.

FAO/WHO. 1973b. 1972 evaluations of some pesticide residues in food. FAO/AGP/1972/M/9/1; WHO Pesticide Residues Ser. No. 2. 587p.

FAO/WHO. 1976a. Pesticide residues in food. Report of the 1975 Joint Meeting of the FAO Working Party of Experts on Pesticide Residues and the WHO Expert Committee on Pesticide Residues. FAO Plant Prodn. Protect. Ser. No. 1; WHO Techn. Rep. Ser. No. 592. 45p.

FAO/WHO. 1976b. 1975 evaluations of some pesticide residues in food. FAO/AGP:1975/M/13; WHO Pesticide Residues Ser. No. 5. 409p.

Girish, G.K., R.K. Goyal, and K. Krishnamurthy. 1970. Studies on stored grain pests and their control. I. Efficacy and residual toxicity of iodofenphos and malathion. Bull. Grain Technol. 8: 103-106.

Godavari Bai, S. 1964. Persistence of malathion residues on treated food grains under different conditions of storage and processing. Pesticides (Symp. on Pesticides, Dec. 21-22, 1964, Mysore). Academy of Pest Control Sciences, Mysore, India. 1968. p. 310-315.

Gradidge, J.M.G., D.R. Wilkin, and V.K. Bharadwaj. 1970. Treatment of granaries with iodofenphos. Pest Infest. Res. Rep. 1969: 28.

Green, A.A. 1969. The use of insecticides. Chemy. Indy. 41: 1452-1454.

Green, A.A. 1973. Control of insects infesting groundnuts in the Gambia. Pest Infest. Res. Rep. 1970: 108.

Green, A.A., P.S. Tyler, J. Kane, and D.G. Rowlands. 1970. An assessment of bromophos for the protection of wheat and barley. J. stored Prod. Res. 6: 217-228.

Grussendorf, O.W., A.J. McGinnis, and J. Solomon. 1970. Rapid sample preparation for gas-liquid chromatography of pesticide residues by ball-grinding extraction, freeze-out and semimicro column cleanup. J. Assoc. Offic. Anal. Chemists 53: 1048-1054.

Gunther, F.A. and L.R. Jeppson. 1960. Modern insecticides and world food production. London. Chapman and Hall. Chapt. 6. p. 76-104.

Gunther, F.A., D.L. Lindgren, and R.C. Blinn. 1958. Biological effectiveness and persistence of malathion and lindane used for protection of stored wheat. J. Econ. Ent. 51: 843-844.

Hall, D.W. 1970. Handling and storage of food grains in tropical and subtropical areas. FAO Agr. Development Paper 90, FAO, Rome. 350p.

Hansens, E.J., E.S. Evans, Jr., and D.B. Shibles. 1968. Tests of bromophos for housefly control in New Jersey. J. Econ. Ent. 61: 833-836.

Hayward, L.A.W. 1962. Groundnuts. Rep. W. Afr. stored Prod. Res. Unit 1961: 12-15.

Hewlett, P.S. 1947. A direct-spray technique for the biological evaluation of pyrethrum-in-oil insecticides for use against stored product insects in warehouses. Ann. appl. Biol. 34: 357-375.

Hindin, E. 1967. Residue analysis in water resources. In G. Zweig (ed.): Analytical methods for pesticides, plant growth regulators, and food additives. Volume 5. Academic Press, New York and London. p. 83-114.

Hope, J.A., D.R. Wilkin, and B. Robbins. 1970. Treatment of a granary with bromophos. Pest Infest. Res. Rep. 1969: 28.

Horler, D.F. and J.S. Clark. 1970. Treatment of grain - admixture of iodofenphos. Pest Infest. Res. Rep. 1969: 31-32.

Horler, D.F. and D.G. Rowlands. 1968. Metabolism of insecticides in stored cereals. Pest Infest. Res. Rep. 1967: 29-30.

Immel, R. and G. Geisthardt. 1964. Bromophos, ein neues Insektizid mit geringer Toxizitat. Meded.LandbHoogesch Opzockstns Gent 29: 1242-1251.

Iordanou, N. 1976. Control of stored grain insects in Cyprus. Tech. Bull., Cyprus Agr. Res. Inst. No. 20. 20p.

Iordanou, N.T. and F.L. Watters. 1969. Temperature effects on the toxicity of five insecticides against five species of stored-product insects. J. Econ. Ent. 62: 130-135.

Joubert, P.C. and P.R. De Beer. 1968. The toxicity of contact insecticides to seed-infesting insects: Tests with bromophos on maize. Tech. Commun., Dept. Agr. Tech. Serv. 84. Pretoria. 9p.

Kadoum, A.M. and D.W. LaHue. 1969. Effect of hybrid, moisture content, foreign material and storage temperature on the degradation of malathion residue in grain sorghum. J. Econ. Ent. 62: 1161-1164.

Kadoum, A.M. and D.W. LaHue. 1977. Degradation of malathion in wheat and milling fractions. J. Econ. Ent. 70: 109-110.

Kadoum, A.M., D.W. LaHue, and L. Alnaji. 1978. Efficacy and fate of pirimiphos-methyl residue applied at two dosage rates to wheat for milling. J. Econ. Ent. 71: 50-52.

Kane, M.J., A.A. Green, S.L. Aggarwal, M.E. King, and K.P. Thomas. 1973. Protective treatment of bagged grain. Pest Infest. Res. Rep. 1970: 111-112.

Koivistoinen, P. 1961. Studies on the appearance of malathion from plant materials. Ann. Acad. Sci. Fennicae Ser. A. IV. Biol. 51. 91p.

Krishnaiah, N.V., B.P. Khare, and V.K. Sharma. 1976. Relative efficacy of some safer organophosphate insecticides used as grain protectants. Pesticides 10: 39-41.

LaHue, D.W. 1967. Evaluation of malathion, synergized pryethrum, and a diatomaceous earth as protectants against insects in sorghum grain in small bins. U.S. Dept. Agr., Agr. Res. Serv., Mktg. Res. Rep. No. 781. 11p.

LaHue, D.W. 1975. Iodofenphos as a protectant of grain against the rice weevil. Proc. North Centr. Branch Ent. Soc. Amer. 30: 40-43.

LaHue, D.W. 1977a. Pirimiphos-methyl: gradient of effective doses on hard winter wheat against attack of four species of adult insects. J. Econ. Ent. 70: 295-297.

LaHue, D.W. 1977b. Pirimiphos-methyl: effect on populations of *Tribolium confusum* and *T. castaneum* in wheat. J. Econ. Ent. 70: 135-137.

LaHue, D.W. and E.B. Dicke. 1977. Evaluation of selected insecticides applied to high moisture sorghum grain to prevent stored grain insect attack. U.S. Dept. Agr., Agr. Res. Serv., Mktg. Res. Rep. No. 1063. 10p.

Lal, R. and Y.P. Beri. 1964. Studies on the persistence of malathion residues in wheat grains. Insect. Toxicol. Inform. Serv. 7: 114.

Leber, G. and W. Deckers. 1967. Determination of residues of bromophos and bromophos-ethyl. Proc. 4th British Insectic. Fungic. Conf. 2: 570-576.

Lemon, R.W. 1966. Laboratory evaluation of some organophosphorus insecticides against *Tribolium confusum* Duv. and *T. castaneum* (Hbst) (Coleoptera, Tenebrionidae). J. stored Prod. Res. 1: 247-253.

Lemon, R.W. 1967. Laboratory evaluation of malathion, bromophos and fenitrothion for use against beetles infesting stored products. J. stored Prod. Res. 2: 197-210.

Levi, I. and T.W. Nowicki. 1974. Rapid screening method for simultaneous determination of organochlorine and organophosphate pesticide residues in wheat by gas-liquid chromatography. J. Assoc. Offic. Anal. Chemists 57: 924-929.

Lindgren, D.L., H.E. Krohne, and L.E. Vincent. 1954. Malathion and chlorthion for control of insects infesting stored grain. J. Econ. Ent. 47: 705-706.

Malathion Panel. 1960. The determination of malathion in cereals and oilseeds. Analyst 85: 915-921.

Malathion Panel. 1973. The determination of malathion and dichlorvos residues in grain. Analyst 98: 19-24.

Martin, H. and C.R. Worthing. 1977. Pesticide manual. 5th edn. British Crop Protection Council. 593p.

Mathis, W. and H.F. Schoof. 1968. Chemical control of houseflies in dairy barns and chicken ranches. J. Econ. Ent. 61: 1071-1073.

McGaughey, W.H. 1971. Malathion on milling fractions of three varieties of rough rice: Duration of protection and residue degradation. J. Econ. Ent. 64: 1200-1205.

Minett, W. and R.S. Belcher. 1969. Determination of malathion and dichlorvos residues in wheat grains by gas-liquid chromatography. J. stored Prod. Res. 5: 417-421.

Minett, W. and P. Williams. 1971. Influence of malathion distribution on the protection of wheat grains against insect infestation. J. stored Prod. Res. 7: 233-242.

Minett, W. and P. Williams. 1976. Assessment of non-uniform malathion distribution for insect control in a commercial wheat silo. J. stored Prod. Res. 12: 27-33.

Minett, W., R.S. Belcher, and E.J. O'Brien. 1968. A critical moisture level for malathion breakdown in stored wheat. J. stored Prod. Res. 4: 179-181.

Morallo-Rejesus, B. and D.C. Eroles. 1976. Direct grain treatment and sack impregnation with insecticides to control corn storage pests. Phillippine Agriculturalist 59: 356-363.

Nawrot, J. 1969. The effectiveness of the preparation of Sumitox, Dusturan Kornkafer Puder and C 9491 against some storehouse pests. Biul. Inst. Ochr. Rosl. 45: 157-169. In Rev. appl. Entomol. Ser. A, 61: 241-242.

Okwelogu, T.N. 1968. The toxicity of malathion applied to washed concrete. J. stored Prod. Res. 4: 259-260.

Orth, R.A. and W. Minett. 1975. Iodometric analysis and shelf life of malathion in formulations. Pestic. Sci. 6: 217-221.

Park, T. and M.B. Frank. 1948. The fecundity and development of the flour beetles, *Tribolium confusum* and *Tribolium castaneum* at three constant temperatures. Ecology 29: 368-374.

Parkin, E.A. 1965. The onset of insecticide resistance among field populations of stored product insects. J. stored Prod. Res. 1: 3-8.

Parkin, E.A. 1966. The relative toxicity and persistence of insecticides applied as water-dispersible powders against stored-product beetles. Ann. appl. Biol. 57: 1-14.

Parkin, E.A. and P.S. Hewlett. 1946. The formation of insecticidal films on building materials. I. Preliminary experiments with films of pyrethrum and DDT in a heavy oil. Ann. appl. Biol. 33: 381-386.

Parkin, E.A. and E.I.C. Scott. 1960. Persistent tests. Pest Infest.

Res. Rep. 1959: 24.

Parkin, E.A., E.I.C. Scott, and R. Forster. 1962. The resistance of field strains of beetles. Pest Infest. Res. Rep. 1961: 34-35.

Pieterse, A.H., G.G.M. Schulten, and W. Kuyken. 1972. A study on insecticide resistance in <u>Tribolium castaneum</u> (Herbst) (Coleoptera, Tenebrionidae) in Malawi (Central Africa). J. stored Prod. Res. 8: 183-191.

Pinniger, D.B. 1975. An assessment of residual insecticide treatments for the control of the saw-toothed grain beetle (<u>Oryzaephilus surinamensis</u>) in farm grain stores. Proc. 8th British Insectic. Fungic. Conf. (1975) 1: 365-372.

Prevett, P.F. 1975. Stored product pests causing losses of stored food. FAO Plant Prot. Bull. 23: 115-117.

Quinlan, J.K. 1972. Malathion aerosols applied in conjunction with aeration to corn stored in a flat storage structure. Proc. North Centr. Branch Ent. Soc. Amer. 27: 63-65.

Quintanilla, R.H., H.E.S. De Gonzalez, and A.M. De Haro. 1970. New evaluations of insecticides for the protection of stored grains. Revta Fac. Agron. Vet. B. Aires 18: 113-119. <u>In</u> Rev. Appl. Entomol. Ser. A, 60: 767.

Redlinger, L.M. 1976. Pirimiphos-methyl as a protectant for farmers' stock peanuts. J. Econ. Ent. 69: 377-379.

Riley, J. and M.A. Cornes. 1969. Tests of two organophosphorus insecticides and DDT on concrete blocks against <u>Trogoderma granarium</u> Everts larvae and <u>Tribolium castaneum</u> (Herbst) adults. Nigerian Stored Prod. Res. Inst., Ann. Rep. 1969: 27-29.

Rowlands, D.G. 1966a. The activation and detoxification of three organic phosphorothionate insecticides applied to stored wheat grains. J. stored Prod. Res. 2: 105-116.

Rowlands, D.G. 1966b. Metabolism of insecticides on stored cereals. Pest Infest. Res. Rep. 1965: 37-39.

Rowlands, D.G. 1966c. The metabolism of bromophos in stored wheat grains. J. stored. Prod. Res. 2:1-12.

Rowlands, D.G. 1967. The metabolism of contact insecticides in stored grains. Residue Reviews 17: 105-177.

Rowlands, D.G. 1970. Metabolism of insecticides on stored cereals. Pest Infest. Res. Rep. 1969: 36-37.

Rowlands, D.G. 1971. The metabolism of contact insecticides in stored grains - II. 1966-1969. Residue Reviews 34: 91-161

Rowlands, D.G. 1975. The metabolism of contact insecticides in stored grains. III. 1970-1974. Residue Reviews 58: 113-155.

Schesser, J.H., W.E. Priddle, and E.P. Farrell. 1958. Insecticidal residue in milling fractions from wheat treated with methoxychlor, malathion and lindane. J. Econ. Ent. 51: 516-518.

Schulten, G.G.M. 1970. Preliminary results of field trials on the control of *Ephestia cautella* as a pest of bagged maize in Malawi. PANS 16: 709-713.

Schulten, G.G.M. 1973. Further insecticide trials on the control of *Ephestia cautella* on stacks of bagged maize in Malawi. Intern. Pest Control 15: 18-21.

Seth, A.K. 1974. Use of pirimiphos-methyl for the control of stored rice insect pests in S.E. Asia. Proc. 1st. Internat. Working Conf. stored Prod. Entomol. Oct. 7-11, 1974. Savannah, Ga., USA. p. 656-658.

Sinha, R.N. 1971. Spoilage of farm-stored grain by molds, insects and mites in Western Canada. Canada Dept. Agr. Publ. No. 1437. 8p.

Sinha, R.N. and W.E. Muir. 1977. Susceptibility of Faba beans to infestation by insects and mites during storage. Trans. ASAE 20: 567-570.

Slominski, J.W. and W.L. Gojmerac. 1972. The effect of surfaces on the activity of insecticides. College Agr. Life Sci., Univ. Wisconsin Res. Rep. No. 2376. Madison, Wisconsin. 8p.

Slominski, J.W., W.L. Gojmerac, and W.E. Burkholder. 1971. Toxicity of residues of bromophos and ronnel to houseflies as influenced by several surfaces. J. Econ. Ent. 64: 550-551.

Smallman, B.N. 1948. Residual insecticides for the control of spider beetles in cereal warehouses. J. Econ. Ent. 41: 869-874.

Smith, L.B. 1962. Observations on the oviposition rate of the rusty grain beetle, *Cryptolestes ferrugineus* (Steph.) (Coleoptera: Cucujidae). Ann. Ent. Soc. Amer. 55: 77-82.

Smith, L.B. 1965. The intrinsic rate of natural increase of *Cryptolestes ferrugineus* (Stephens) (Coleoptera, Cucujidae). J. stored Prod. Res. 1: 35-49.

Spiers, R.D., L.M. Redlinger, and H.P. Boles. 1967. Malathion resistance in the red flour beetle. J. Econ. Ent. 60: 1373-1374.

Srivastava, A.S. and J.L. Srivastava. 1970. Residual toxicity of lindane and malathion against *Laemophloeus minutus* Oliv. Z. angew. Entomol. 66: 100-102.

Strong, R.G. and D.E. Sbur. 1960. Influence of grain moisture and storage temperature on the effectiveness of malathion as a grain protectant. J. Econ. Ent. 53: 341-349.

Strong, R.G., D.E. Sbur, and R.G. Arndt. 1961. Influence of formulation on the effectiveness of malathion, methoxychlor, and synergized pyrethrum protective sprays for stored wheat. J. Econ. Ent. 54: 489-501.

Tauthong, S. 1975. Persistence on structural surfaces of residues of organophosphorus and pyrethroid insecticides against five species of stored-product insects. M.Sc. Thesis, Univ. Manitoba, Winnipeg, Canada.

Tauthong, S. and F.L. Watters. 1978. Persistence of three organophosphorus insecticides on plywood surfaces against five species of stored-product insects. J. Econ. Ent. 71: 115-121.

Teotia, T.P.S. and R. Singh. 1966. Preliminary studies on the residual effectiveness of BHC, malathion and Sevin for the protection of stored grains against Sitophilus oryzae Linn. Bull. Grain Technol. 4: 67-72.

Thornburg, W.W. 1965. Preparation and extraction of samples prior to pesticide residue analysis. J. Assoc. Offic. Anal. Chemists 48: 1023-1026.

Thornton, J.S. and C.A. Anderson. 1968. Determination of residues of Di-Syston and metabolites by thermionic emission flame gas chromatography. J. Agr. Food Chem. 16: 895-898.

Tyler, P.S. and D.G. Rowlands. 1967. Sodium carboxymethyl cellulose as a stabilizer for malathion formulations. J. stored Prod. Res. 3: 109-115.

Tyler, P.S., A.A. Green, J.A. Hope, and B. Robbins. 1969. Insects infesting farm stores: Treatment of granaries. Pest Infest. Res. Rep. 1968: 30-31.

Tyler, P.S., D.F. Horler, D.G. Rowlands, and B. Robbins. 1969. The distribution of insecticides amongst grains. Pest Infest. Res. Rep. 1968: 33-34.

Udeaan, A.S. and O.S. Bindra. 1971. Malathion residues in different fractions of treated food grains and their finished derivatives. Proc. 1st All-India Symp. Progress and Problems in Pesticide Residue Analysis. Nov. 18-19, 1971. Ludhiana, India. p. 61-67.

Walker, P.T. 1975. Pest control problems (pre-harvest) causing major losses in world food supplies. FAO Plant Prot. Bull. 23: 70-77.

Watters, F.L. 1959. Effects of grain moisture content on residual toxicity and repellency of malathion. J. Econ. Ent. 52: 131-134.

Watters, F.L. 1970. Toxicity to the confused flour beetle of malathion and bromophos on concrete floors. J. Econ. Ent. 63: 1000-1001.

Watters, F.L. 1976. Persistence and uptake in wheat of malathion and bromophos applied on granary surfaces to control the red flour beetle. J. Econ. Ent. 69: 353-356.

Watters, F.L. and O.W. Grussendorf. 1969. Toxicity and persistence of lindane and methoxychlor on building surfaces for stored-grain insect control. J. Econ. Ent. 62: 1101-1106.

Watts, R.R. and R.W. Storherr. 1965. A sweep co-distillation cleanup method for organophosphate pesticides. I. Recoveries from fortified crops. J. Assoc. Offic. Anal. Chemists 48: 1158-1160.

Wilkin, D.R., S.L. Aggarwal, and K.P. Thomas. 1973. Treatment of grain: admixture of iodofenphos. Pest Infest. Res. Rep. 1970: 110-111.

Wolpert, V. 1966. Rats in store, India. Far Eastern Econ. Rev. 53(10): 439. In D.W. Hall. Handling and storage of food grains in tropical and subtropical areas. FAO Agr. Development Paper 90, FAO, Rome 350p.

Zettler, J.L. 1974. Malathion resistance in Tribolium castaneum collected from stored peanuts. J. Econ. Ent. 67: 339-340.

Zettler, J.L. 1975. Malathion resistance in strains of Tribolium castaneum collected from rice in the U.S.A. J. stored Prod. Res. 11: 115-117.