THE RESIDUAL BEHAVIOUR OF CHEMICALS ON STORED GRAIN

J. M. DESMARCHELIER and M. BENGSTON

CSIRO, Division of Entomology, P.O. Box 1700
Canberra, A.C.T., 2601, AUSTRALIA

and

Department of Primary Industries
Meirs Road, Indooroopilly,
Queensland, 4068, AUSTRALIA

INTRODUCTION: In this paper are summarized results of a continuing programme to evaluate grain protectants suitable for use in Australia. The peculiar Australian requirements are caused by local patterns of insecticide resistance and local climates. These are briefly summarized so that individual countries can more easily judge the extent to which Australian requirements are similar to their own.

In addition to widespread specific resistance to malathion there is general resistance to organophosphorus insecticides in *Tribolium castaneum, Rhyzopertha dominica, Ephestia cautella,* and *Sitophilus oryzae,* and general resistance to pyrethroids in *Tribolium castaneum* and *Sitophilus oryzae*. Nevertheless, the potency of the newer compounds is such that they provide effective grain protection despite the occurrence of appreciable levels of resistance.

Australia's grain is grown over a range of latitudes from 12 degrees south to 38 degrees south and this is the range of latitude from Lake Nyara to Cape Town or equivalent to the range from Nicaragua to Washington, D.C., or Bangkok to Seoul. Some crops, especially peanuts, sorghum, and some wheat, are grown in tropical regions characterized by summer, monsoon rainfall whereas most of the wheat, barley, oats, and rice are grown in regions of Mediterranean climates, characterized by dry summers and winter rainfall. Wheat temperatures at receival are typically between 30 and 40°C, though the moisture content is restricted by strict administration to less than 12%. Wheat is harvested in spring to early summer, and, in the most unfavourable climates must be stored over a hot humid summer and autumn before ambient temperatures fall. Sorghum is harvested in the autumn or winter at higher humidities than wheat but usually at lower temperatures.

METHODOLOGY: The methods used to evaluate protectants suitable for any given set of conditions can be summarized as follows:

1. Laboratory tests on effectiveness, resistance patterns, etc.;
2. Laboratory tests on period of protection, under a range of conditions, against artificial re-infestations;
3. Development of methods of analysis of residues;
4. Trials in two commercial storages, one in a summer rainfall climate, one in a winter rainfall climate. Chemical assays by up to ten residue chemists, and biological assays, against up to twenty strains in 8 species, are performed on samples of stored grain at intervals of 6 weeks for a period of nine months;
5. Extensive pilot usage trials in 20 commercial storages. In such trials, residues are monitored at regular intervals and the storages are regularly examined for possible insect infestation;
6. Development of a predictive model of loss of residues, and comparison of laboratory predictions with commercial results;
7. Organoleptic and residue tests on grain products such as cooked rice, malt, and bread.

BIOLOGICAL RESULTS: Candidate protectants are eliminated at various stages of the trials and application rates are altered in the light of new knowledge. The trials are aimed at finding protectants that give nine months protection against re-infestation. Interestingly, malathion failed to do this not only against resistant strains but also against strains of four species susceptible to malathion. These species were *Tribolium castaneum, Rhyzopertha dominica, Ephestia cautella,* and *Sitophilus oryzae.*

From the list of chemical applications judged as effective (Table 1) it can be seen that many applications are mixtures, with a pyrethroid or carbaryl for control of *Rhyzopertha dominica,* especially resistant strains, and an organophosphorus insecticide to control other species.

Following appropriate approval by Codex Alimentarius Commission, a number of these treatments have been successfully used in full scale commercial applications.

CHEMICAL RESULTS AND PREDICTIVE MODELS: We have developed predictive models for loss of residues of twelve protectants on grains and from these models one can calculate the persistence of a chemical on any grain at any constant or varying condition of temperature and moisture content. The models are discussed fully elsewhere (1), but can be briefly summarized as follows (see also Appendix):

1. At constant temperature and grain equilibrium relative humidity (e.r.h.) a fixed proportion of insecticide is lost over a given interval of time. Thus the time for residues to halve from say 20 to 10 g/t is the same as that from 2 to 1 g/t and we speak of the half life ($t1/2$). This type of loss is conveniently shown by a plot of log residues against time (Figure 1).

Table I. Grain protectants for 9 months' storage in Australia

Compounds approved at least Codex stage 4:
- For Species Excepting *Rhyzopertha:*
  - Fenitrothion 12 ppm
  - Pirimiphos-methyl 4 ppm
- For *Rhyzopertha*:
  - Bioresmethrin 1 ppm + Piperonyl butoxide 10 ppm
  - Carbaryl 8 ppm (aerated storage 5 ppm)

Compounds under development:
- For Species Excepting *Rhyzopertha*:
  - Chlorpyrifos-methyl 10 ppm
- For *Rhyzopertha:*
  - Fenvalerate 1 ppm + Piperonyl butoxide 10 ppm
  - Permethrin 1 ppm + Piperonyl butoxide 10 ppm
  - Phenothrin 2 ppm + Piperonyl butoxide 10 ppm
- For All Species:
  - Decamethrin 2 ppm + Piperonyl butoxide 10 ppm
  - Methacrifos 22.5 ppm (aerated storage 15 ppm)

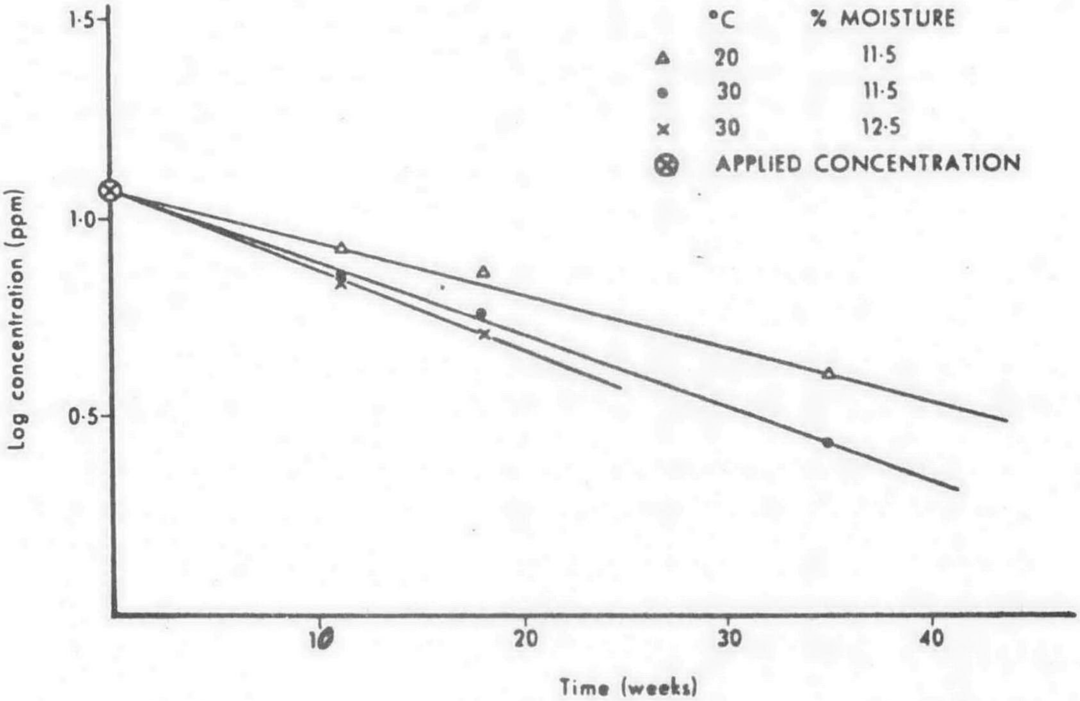

Figure 1. Plot of logarithm of malathion concentration, under 3 fixed conditions, versus time after application

By estimating the slope of such plots, one can calculate the rate constant, k. (The slope equals k/2.3 since we are using logarithms to base 10.) Alternatively one can estimate $t_{1/2}$ from such plots and then calculate k from $k = 0.7/t_{1/2}$.

2. In figure 2 it can be seen that k is proportional, at a fixed temperature, to e.r.h., or, more correctly, to water activity, a_{H_2O} which is proportional to e.r.h. Rate constant does not depend on type of grain. Therefore, at a fixed temperature, if one knows the half-life on wheat at one e.r.h., one can calculate half-life on barley, sorghum, etc. at any e.r.h.

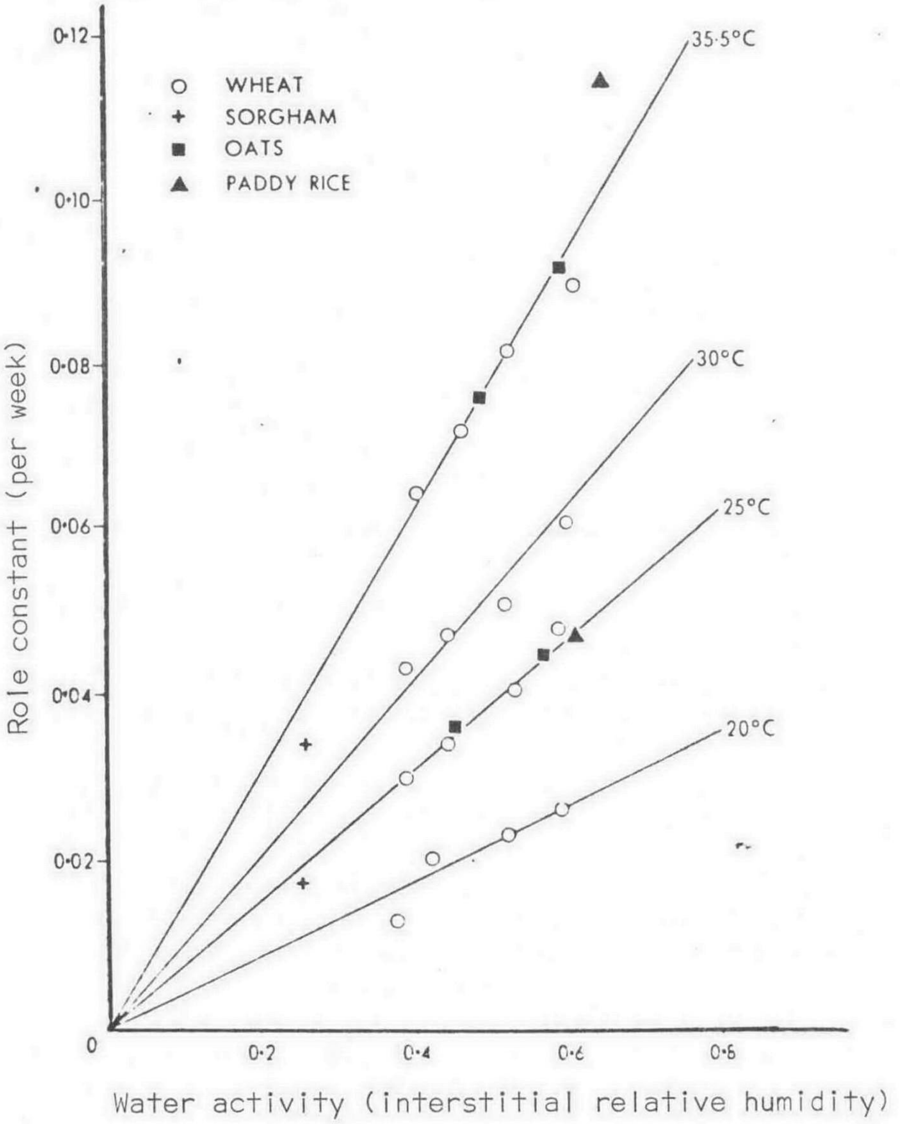

Figure 2. Rate constants for fenitrothion on whole grains as a function of water activity and temperature

3. The effect of temperature on rate constants is of the form of the Arrhenius equation, which has been approximated in Figure 3 as a plot of log k against temperature.

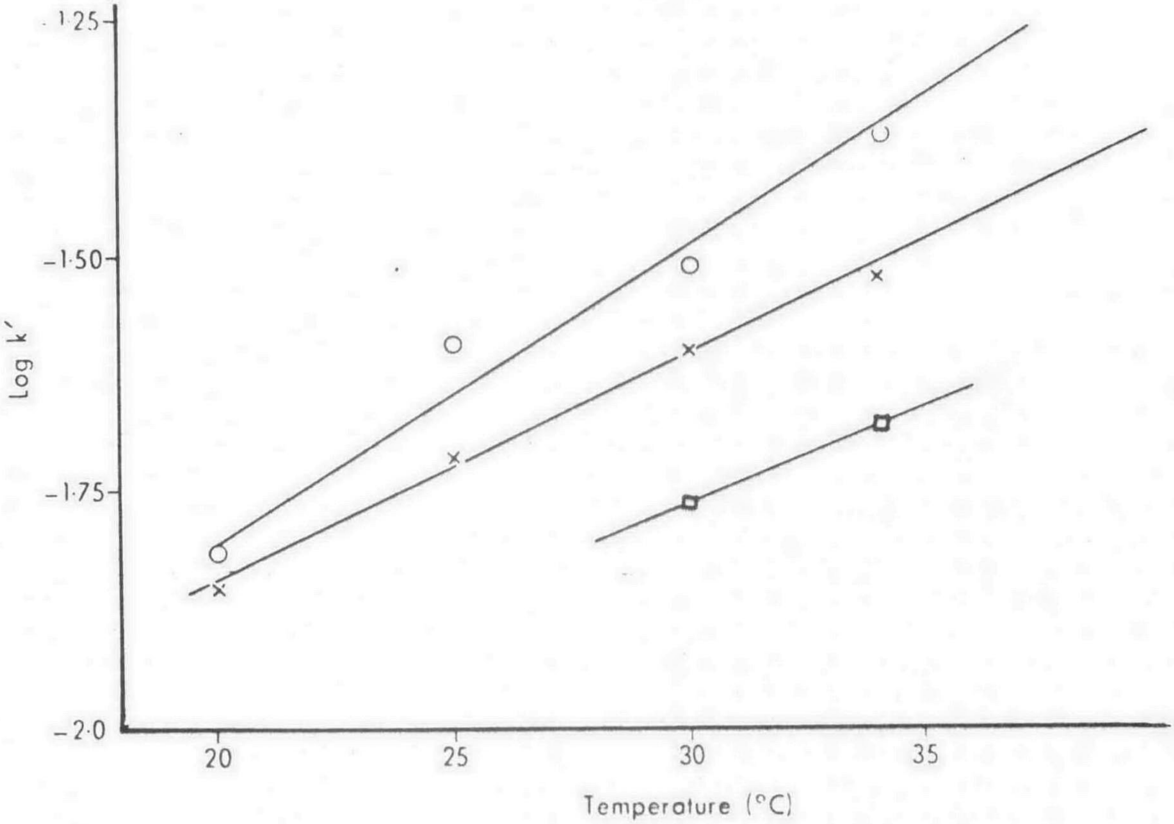

Figure 3. Plots of log of rate constants, k', against T, °C for carbaryl (O), bioresmethrin (x) and d-phenothrin (◻)

It is possible to summarize the above in a chart (Figure 4) from which one reads off the half-life at any temperature and e.r.h.

In Table II are general predictive models for twelve protectants. A reference half-life is used, evaluated at 30°C, 50% e.r.h., and the relative persistence of the protectants can be seen from the tables. Thus one can select a protectant with the appropriate degree of persistence.

From the data in Table II one can derive charts (Figure 4) relating half-life to temperature and e.r.h. as follows:

1. Obtain semilog paper, which is convenient for plotting half-life, log scale, against temperature;
2. At 30°C, 50% e.r.h., insert value for reference half-life (e.g. 12 weeks for malathion);

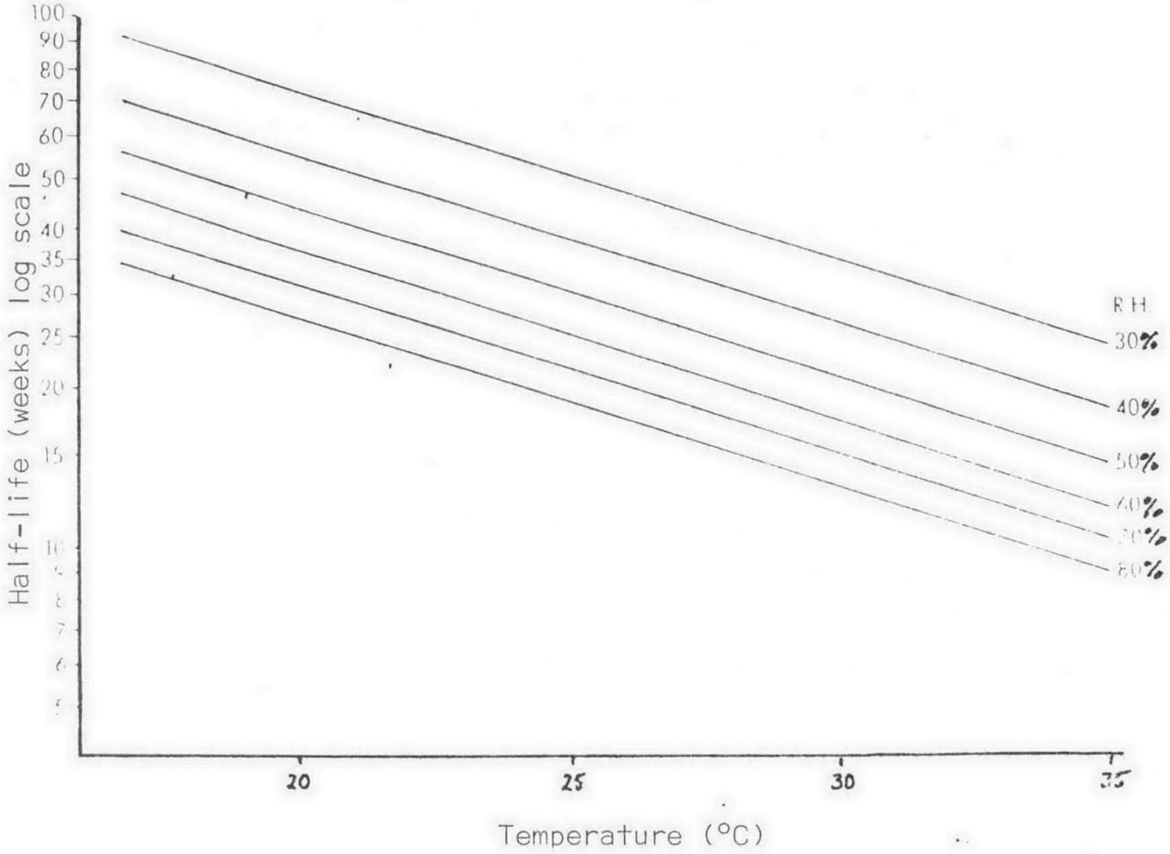

Figure 4. Chart relating half-life (log scale of carbaryl) on grains to equilibrium R.H. and temperature, °C

Table II. General rate expressions for 12 protectants, plotted to the equation: $\log t_{1/2} = \log (t_{1/2})_0 - B.T.^*$, where $t_{1/2}$ is half-life, $(t_{1/2})_0$ is the half-life at 30°C, 50% relative humidity, B is the temperature co-efficient per week, and T* is the temperature in °C less 30.

Protectant	$(t_{1/2})_0$	B
Fenitrothion	14	.036
Bioresmethrin	24	.033
Bioresmethrin+	38	.031
d-Phenothrin	38	.029
d-Phenothrin+	40	.029
Pyrethrum+	55	.022
Methacrifos	8	.055
Malathion	12	.05
Chlorpyrifos-methyl	19	.04
Carbaryl	21	.031
Pirimiphos-methyl	70	small
Pyrethrum	34	-

+ plus piperonyl butoxide at 20 mg/kg.

3: Calculate the temperature drop, dT, required to double the half-life from the formula dT = 0.30/B. For malathion, the half-life will be doubled at a temperature equal to 30-0.30/.05 = 24°C;

4. Insert this point on the graph, and draw a line through it and the previous point;

5. Calculate the half-life at 30°C, x% e.r.h., from the formula $t_{1/2} = (t_{1/2})o \times \frac{50}{x}$. For example, the half-life is 8 weeks at 75% e.r.h.

6. Through such points, draw lines parallel to the first line.

TESTS OF PREDICTIONS: Figure 5 summarizes observed values, and predicted lines, for losses of methacrifos on grain in a commercial storage at temperatures which decreased throughout the experiment. Cooling occurred most rapidly at the grain surface. Initial residues in the bulk (6 m) were greater than those near the surface (0.6 m) but those in the bulk decayed more rapidly and in time became less than those at the surface. By the time surface temperatures had fallen to 15°C, rate of loss of methacrifos had become very slow.

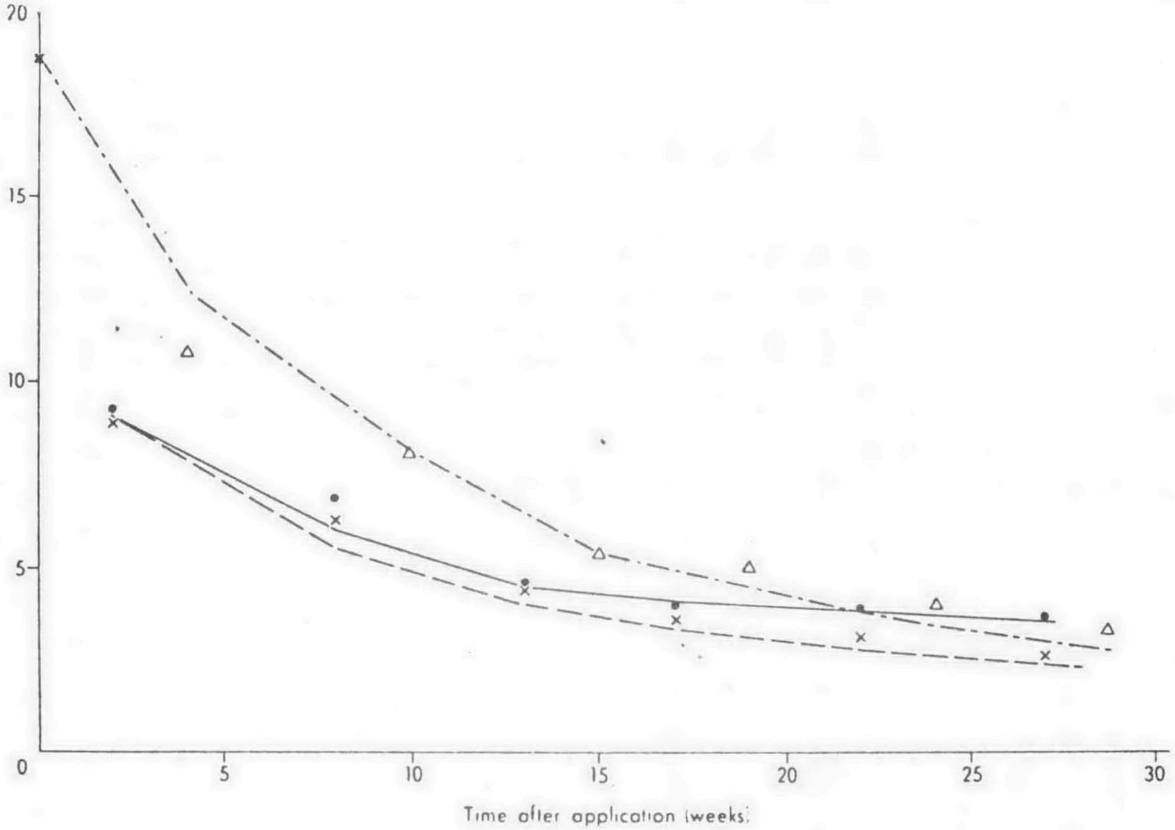

Figure 5. Predicted curves for, and measured values of, residues during storage of methacrifos on wheat stored at Wattamondara (●, 0.6 m; X, 1.5 m; Δ, 6.0 m; x nominal applied residue).

We find, and we are talking of about 2000 separate tests, that the mean predicted residue is very close to the mean observed residue, typically to within a few percent. However, individual results often vary from individual predictions, partly because of errors in application, sampling, and analysis.

Finally in predicting residues in commercial applications we take the actual applied residue to be 85% of the calculated residue. Thus 15% of applied protectant is taken to be lost by vapour losses, missing of target, and other processes.

USE OF PREDICTIVE MODELS: The main use of our predictive models is to enable the grain industries to select rates appropriate for given circumstances. As an example, there are three applications to sorghum, one used above the Tropic of Capricorn, one used near the Tropic of Capricorn, and one used where sorghum is typically cool, that is, below 25°C, at intake. Also, reduced rates are used in storages equipped with grain aeration facilities. Clearly the effect of partial cooling on increasing the residual life of protectants is most pronounced for protectants with high temperature co-efficients (B in Table II) and short half-lives. Thus, for nine months protection with methacrifos, to leave a residue of 1 g/t to control *Tribolium* and *Sitophilus* species, one would apply at 50% e.r.h., 22.5 g/t at temperatures of 30°C, 4.6 g/t at temperatures of 25°C, and 2.2 g/t at temperatures of 19-20°C. There are clearly enormous advantages in achieving even partial cooling; this cooling also reduces potential numbers of insects and enhances grain quality. Australia is increasingly using ambient-air aeration in sub-tropical regions to achieve, with the use of protectants, an integrated control, even though conditions are not suitable to control insects by cold alone. We hope, also, to use mobile grain coolers to cool grain at intake to 20-30°C, depending on moisture content, and thereby reduce rates of applied protectant. It is worth recalling that high moisture grain is more easily and cheaply cooled than dry grain.

An interesting example of cooling in the tropics (Tropic of Capricorn) is in the peanut industry, where malathion is still effective, despite widespread resistance to it, and is effective because used in conjunction with cooling. One device used for cooling is a hinge door on the bottom of silos, which is opened and closed by the chimney effect. There are a large number of low cost measures that achieve partial cooling or drying, and these include the chimney effect on stacked bags, which is used in India, shading of storages, use of small storages, and painting storages white. Such measures are often inadequate in themselves as control measures, but would greatly enhance the effect of grain protectants. Even the very old method of turning grain is extensively used in Australia to achieve, among other things, partial cooling.

THE NEED FOR COMMERCIAL TRIALS: The work briefly described above has been extensive, and it has been frequently suggested that much of the work load could have been reduced by elimination of the commerical trials. There were, and are, a number of practical reasons for such trials, principally that they are required by Codex Alimentarius Commission and desired by commercial organizations. We feel that these organizations are correct to require such trials because they bring to light many aspects that one does not think of in the laboratory. For example, it was only in the pilot usage studies that we experienced trouble with formulations of carbaryl, especially problems associated with nozzle blocking after continued use. Similarly, we have found anomalies in the rate at which temperatures fall in storages, and this was a subject we thought was well understood. Similarly, our findings that protectants were more stable on the surfaces of storages than in the bulk of the store was exactly the opposite of what we expected to find. The trials also illustrated the vital importance of the practical side of pest control, such as correct size of nozzle, correct type of measuring cylinder and correct type of book-keeping. Success or failure depend largely on such "trivia," the attitudes and education of personnel, and management procedures. Such considerations are seldom published in scientific journals.

Finally, in any scientific study, there is a need for replication and the device of laboratory studies followed by field trials ensures complete replication.

FUTURE DEVELOPMENTS: Rates of loss of insecticides are sufficiently understood to enable an educated guess at the stability of protectants on grain (2). Given the desire, we should be able to develop other persistent protectants, such as pirimiphos-methyl, or labile protectants, such as dichlorvos. We already have one protectant - methacrifos - which is persistent on cool grain but almost entirely degraded even by the simple process of cooking rice in a mimimum amount of water. In this context, fenitrothion is not so degraded, and simple extrapolation of data on half-lives in Table II relating to 30°C to values for 100°C predicts both results. The important difference is not the reference half-life but the temperature co-efficient. Thus methacrifos is predicted to have a half-life of less than one hundredth the half life of fenitrothion at 100°C and, although the extrapolations to 100°C have not been demonstrated to be valid, they are consistent with the observed results. Possibly such considerations will influence development of new protectants.

The use of grain protectants with partial cooling and drying will undoubtedly increase. We have concentrated on use of cooling to prolong the effectiveness of protectants, as illustrated by examples. The effects of partial cooling or drying can be summarized by Eq. I for all protectants, where $t_{1/2}$ is half-life, R_0 is applied concentration, and t is the time at which a residue has reached the minimum effective level (R) for complete control. It is obvious that increasing $t_{1/2}$ by partial cooling can enormously increase t, or reduce R_0.

$$t = 3.3 \log \left(\frac{R_0}{R}\right) . t_{1/2} \qquad \text{Eq. 1}$$

Similarly, in cases where an insecticide gives less than 100% mortality, insects can be controlled by incomplete mortality plus reductions in rate of increase, r_m, achieved by partial drying and cooling. From Eq. 2 it can be seen that there are two points of attack on insect numbers, T, after time t, namely reduction in initial numbers. N_0 and reduction in rate of increase, r_m,

$$2.3 \log N = 2.3 \log N_0 + r_m . t \qquad \text{Eq. 2}$$

For example, if, under a given set of conditions, insects increase by a factor of 33 every 6 weeks, and it is desired to keep insect number below the initial low number, N_0, for 6 months, the following strategies may be used:

1. One may cool grain such that $r_m < 1$. This approach requires insulation and cooling units in the tropics.
2. One may kill all insects with a labile chemical. This approach is successful only if less than one insect in a million survive, and if there is no re-infestation.
3. One may cool grain so that development time increases and apply a labile chemical. This approach will be successful if development time increases to 3 months and if no more than one insect survives out of a thousand.
4. One may cool grain by ambient cooling so that r_m becomes less than one some time after application. If r_m becomes less than one after 3 months the initial kill by the chemical only needs to be about 99%.
5. One may apply a protectant and cool grain such that development time is increased to 3 months. This approach will be successful with mortalities as low as 90% per generation.
6. One may apply a protectant. This will be successful if the average control per generation is 97%.

While the above approach is theoretical, all systems 1-6 have been successfully used in Australia. The use of protectants and the integrated programmes, especially number 5, leave the most margin for errors of under application, etc., and require neither the expansive structural modifications required by number 1 nor the very high standards of commercial performance required by number 2.

The results outlined in Table 1 were obtained under condition 6, with a level of control per generation approaching 100%. This is a requirement considerably above the 97% control per generation outlined above, and it might be sometimes appropriate to aim at the lower control level.

Costs per tonne range from about 8 cents per tonne for fenitrothion or chlorpyrifos-methyl, in the absence of generally resistant *Rhyzopertha dominica*, or for pirimiphos-methyl, where low levels of that insect can be tolerated, to about 15 cents per tonne for any of these protectants plus carbaryl. Substituting permethrin and synergised bioresmethrin for carbaryl raises the price per tonne to about 25 and 50 cents respectively and we give no figures for chemicals not currently available.

ACKNOWLEDGEMENTS: The authors thank the Australian Wheat Board and the Australian Wheat Industry Research Council for financial assistance.

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(1) Desmarchelier, J. M. Loss of fenitrothion on grains in storage. Pestic. Sci. 9: (1978), 33.
(2) Briggs, G. C. Degradation in soils. (Proc. BCPC Symposium Persistence of Insecticides and Herbicides). London, 1976, 41.

SUMMARY: There are protectants available that are able to protect grain from insects under harsh storage conditions. Models are available to assist in correct choice of a protectant for a given set of storage conditions. Protectants can be greatly assisted by partial drying and cooling, even by the type of cooling that can be achieved in the tropics without consumption of energy.

APPENDIX

DERIVATION OF MATHEMATICAL EXPRESSION

4.1 Fixed Proportional Decay

Fixed proportional decay with time t of a residue R, from an initial residue, R_0, is described mathematically by:

$$\frac{dR}{dt} = -k.R \qquad (a)$$

integrating, one obtains:

$$\ln R = \ln R_0 - k.t \qquad (b)$$

or

$$2.3 \log R = 2.3 \log R_0 - k.t \qquad (c)$$

For t equal to half-life, $t_{1/2}$, R equals $\frac{1}{2} R_0$, and by numerical substitution in (c) one obtains:

$$k = 0.7 / t_{1/2} \qquad (d)$$

4.2 Effect of Water

Decay of R proportional to both R and water is described by:

$$\frac{dR}{dt} = -k^{*}.R.\ a_{H_2O} \qquad (e)$$

Because water is vastly in excess of R, one can integrate (e) to:

$$\ln R = \ln R_0 - k^{*}.a_{H_2O}.t \qquad (f)$$

Equation (f) is of the same form as equation (b) provided that water activity is constant. Thus, plots of rate constants k (from b) against a_{H_2O} will be linear (*cf*. Fig. 2) if water participates in the rate expression.

4.3 Effect of Temperature

Equations of the form of the Arrhenius equation are of the form of (g), where k_1 and k_2 are rate constants at two temperatures K_1 and K_2, in kelvins (a kelvin K = 273 + T, the temperature on the Celsius scale).

$$2.3 \log k_1 = 2.3 \log k_2 + \frac{H}{R} \cdot \frac{(K_1 - K_2)}{K_1 \cdot K_2} \qquad (g)$$

For small changes in temperature, changes in $K_1 . K_2$ are much less than changes in $K_1 - K_2$, and may be regarded as constant to give (h) and (i)

$$\log k_1 = \log k_2 + B(K_1 - K_2) \qquad (h)$$

$$= \log k_2 + B(T_1 - T_2) \qquad (i)$$

Note that the expression "equations of the form of the Arrhenius equation" is used in preference to "the Arrhenius equation" because equations of the form of (g) can be derived from assumptions other than those used by Arrhenius.

4.4 Charts

Half-lives are substituted from (d), into (i) to give the equation used in Table 2 and in charts such as the one in Fig. 4.

The formula $dT = 0.30/B$ is obtained from this equation for

$$t_{1/2} = 2.(t_{1/2})0$$

Eq. 1

By substituting $t_{1/2}$ for k from (d) into (c) one obtains (j).

$$2.3 \log R = 2.3 \log R_0 - \frac{0.7}{t_{1/2}} . t \qquad (j)$$

By re-arrangement of (j) one obtains (k), or, by further re-arrangement, Eq. 1.

$$t = 2.3 . t_{1/2} . \log \frac{R_0}{R} \qquad (k)$$

Eq. 2

Fixed proportional, that is, exponential, increase of insect numbers N is the same form as fixed proportional decrease of residues. Substitution in (a) of N for R and r_m for -k gives Eq. 2, which is formally equivalent to (c).