

Grain Protectants and Fumigants: assumptions, refutations, proposals and opportunities

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Abstract

Grain protectants have been, and remain, useful in protecting the world's foodstuffs. However, since the introduction of malathion, a number of erroneous assumptions have been made concerning grain protectants. These are discussed. It is suggested that some errors can be traced back to false assumptions, which are sometimes explicit and sometimes implicit. However, false assumptions are not restricted to grain protectants: very similar assumptions, based on similar errors, have been made for fumigants. In most cases, errors arise from uncritical use of useful, but simplistic, theories. If these are regarded as limiting cases of more realistic theories, the chance of errors is reduced and new insights are obtained, leading to new opportunities. A similar comment can be made regarding toxicological theories.

Identification of some of the errors in our understanding of chemicals used on grain is a useful step in improving food safety and food protection. A better theoretical understanding has resulted in improved use of chemicals, in the context of integrated pest management. The potential for further improvement is considerable.

The points made above are illustrated with reference to chemicals currently classified as grain protectants, fumigants, structural sprays, natural products, inert dusts and insecticidal formulations. It is argued that the traditional division between 'protectants' and 'fumigants' is more misleading than helpful. There is enormous potential in the areas of new and existing 'protectants', 'fumigants', 'natural products', etc, but only if each is judged according to the same, or at least similar, criteria and subjected to the highest degrees of critical evaluation.

Introduction and Aims

As grain protectants (Arthur, 1996) and inert dusts (Golob, 1997) have been recently reviewed, there is no need for me to review recent literature, as I did previously

(Desmarchelier, 1994)

Rather, I shall discuss some general issues. I wish to make five main points:

1. in both chemistry and insect toxicology, there are general theories in stored products which are useful.
2. however, these theories are based on simplistic assumptions. We should regard them as limiting cases of more general theories.
3. if we think in terms of these more general theories, even where they are only semi-quantitative.
4. we can retain the good points of existing theories, but avoid the mistakes that arise from their uncritical use.
5. we also develop new insights, leading to new experiments.

The theories, and the mistakes, with protectants and fumigants and, to some extent, with inert dusts are very similar, and there appears to be little interaction between the various chemical branches of stored products. The sharp distinction, in work areas of individual scientists and in conferences, between 'fumigant' and 'protectants' creates more harm, I believe, than good. I argue that it would be better to think more in terms of 'chemicals' than in terms of 'fumigants', 'protectants' and 'inert dusts'.

Assumptions, Refutations, Proposals and Opportunities in 'Chemistry'

General theory

Since the work of Gibbs (Campbell and Smith, 1951; Denbigh, 1966), most of the basic laws of chemistry used in study of grain chemicals form part of a 'unified theory' based on a few postulates of 'continuum chemistry'. 'Continuum chemistry' means that energy levels, such as binding energies, are distributed evenly, and not into divisions separated by large gaps of quanta. A basic hypothesis of 'continuum chemistry' is an energy distribution in a group of molecules that is governed by the Maxwell-Boltzmann distribution. This is shown by the large normal distribution in Figure 1, where the mean energy per molecule is given by $kT/2$. (The term kT is an energy term, where T is the absolute temperature, and k equals R/N , where R is the universal gas constant and N is Avogadro's number. Thus an energy of kT per molecule corresponds to an energy of RT per mole, as in the ideal gas

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law of $PV = nRT$, where n is the number of moles of gas
The term k is written in dark print to distinguish it from the

k used in chemistry and Section 2c to refer to rate constants)

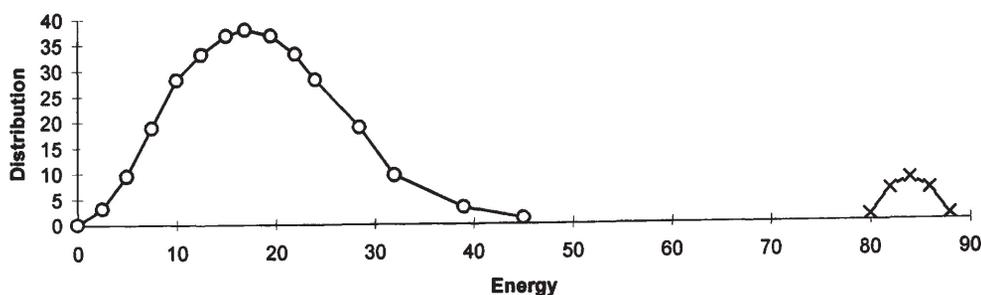


Fig. 1. Distribution with mean 'continuum' energy per molecule of $kT/2$ (○) and with quantum energies(×).

The following are examples of important models used in stored products that form part of a general framework and which are based on continuum chemistry:

- phase rule and water activity;
- constant kinetics, e.g., first-order kinetics;
- predictable effects of temperature on rates (e.g., Arrhenius equation, diffusion);
- ideal gas laws;
- constant sorption (e.g., Freundlich isotherm);
- even distribution (homogeneity);

equilibrium, at least in the sense that the behaviour of chemicals is independent of the pathway used to attain a given situation, in the same way that 20°C is the same whether one cools or heats to attain that 'function of state'.

Figure 1 also shows another distribution of some molecules which have a higher energy, e.g., a higher binding energy to grain molecules. In a homogeneous phase (i.e., in an 'ideal gas' or 'an infinitely dilute solution', distribution of molecules will follow the Maxwell-Boltzmann distribution. In a heterogeneous substrate, some molecules may follow a similar distribution, but others may have stronger binding energies. Such a scenario is illustrated by the two functions shown in Fig. 1. There is a major problem with this distribution, which is that we do not know either its shape or its mean value. However, if we recognise that it exists, we can avoid errors and conduct experiments to assess its effect on parameters such as residue breakdown and desorption. If the distributions shown in Fig. 1 are accepted as a schematic model, the laws of 'continuum chemistry' become the limiting case of a more general theory.

My contention is that Figure 1, showing two types of energy distribution, is more realistic than a single distribution. Basically, molecules with total energies, including binding energies, described by the Maxwell-Boltzmann distribution with a mean energy of $kT/2$ are described by continuum chemistry. Those with higher binding energies (or 'quanta') are not necessarily described by continuum chemistry. Moreover, during breakdown and

desorption, chemicals with low binding energies disappear preferentially, with the result that the proportion of molecules with higher energies increases. At this point, errors arising from assuming continuum chemistry become increasingly more important.

I shall illustrate this point with reference to methods of analysis, rates of loss of residues, equilibrium sorption isotherms determined chemically and biologically and temperature effects on loss of residues.

Analytical chemistry

In many methods of analysis, chemists make 'stock solutions' and, subject to certain qualifications, it makes little difference whether one adds water to, e.g., acid, or acid to water, or how long the stock solution is held. In thermodynamic terms, molarity is a function of state, that is, it is independent of its history. However, if one spills wine on a carpet and tries to remove it with water, history becomes important, because it is much easier to remove wine soon after spilling than after it has been on the carpet for a considerable period. Yet many methods of analysis of protectants and fumigants use a methodology that assumes that residues are functions of state, and that the history of their formation is unimportant.

The editor of *Residue Review*, Francis Gunther, made this point in 1962 (Gunther, 1962): it has been a practice in some residue laboratories to add a known amount of the compound of interest ('fortification') to a portion of the control sample, then to process and analyse this fortified sub-sample, and to claim that the per cent recovery so obtained represents the efficiency of the processing and subsequent operations. This practice is illusory except in a few instances, permissible examples being a pesticide dissolved in olive oil or in a clarified fruit juice. 'Gunther is drawing a distinction between homogeneous substrates (e.g., olive oil) and heterogeneous substrates (e.g., grains) and this distinction implicitly assumes that solutions approach the ideal of 'infinitely dilute solutions', which is a form of continuum chemistry. Thus Gunther makes the

point that recoveries of fortified levels of chemicals is a necessary but insufficient condition for validating a methodology.

The practice of bad methodologies leading to 'illusory' residue determinations of dichlorvos and malathion was recognised by the Codex Expert Committee on Pesticide Residues soon after the introduction of organophosphorus protectants (JMPR, 1968). Protocols developed for determination of residues in field crops in the immediate post-war era were applied to grain protectants in the nineteen seventies (e.g., Desmarchelier et al., 1977). By application of existing protocols, it was shown that residue determinations of organophosphorus insecticides were not merely 'illusory', but wrong. Despite this, procedures for determination of fumigants, especially of phosphine, rely entirely on fortification studies (Bruce, Robbins and Tuft, 1962; Nowicki, 1978; Brockwell 1978). Nowicki (1978) showed that procedures that relied on fortification of phosphine in a solution were not only illusory for determination of phosphide residue, but were also wrong. In a similar manner, Allen et al. (1998) showed that a method that relied on fortification studies from phosphine introduced as a gas (Brockwell, 1978) was wrong. Nowicki's method, which is based on recoveries of phosphine from phosphide, is used to determine phosphine residues, which involves the assumption that 'aged' residues of phosphine are recovered to the same degree as phosphide residues. This is not self-evident, and the assumption requires empirical testing. In addition, there is some doubt about the technique because percentage recoveries of phosphide from commodities vary with amount of phosphide.

It has been demonstrated (Gunther, 1962; Desmarchelier et al., 1977; Allen et al., 1998) that percentage recovery from certain methods of analysis varies with age of deposit. This indicates that the amount of residue is not function of state in the way that, e.g., the amount of AgNO_3 in a solution is a function of state. Such results are understandable, if one considers Fig. 1. Molecules with low binding energies would be lost preferentially during desorption, such that most of the molecules forming residues would have high binding energies. However, methodologies that rely on percentage recovery of fortified samples assume that the molecules of high binding energies behave like those of low binding energies.

The discussion on methods of analyses illustrates my points that 'fumigants' and 'protectants' have much in common and, I believe, that several methods of analysis of fumigant residues have ignored general protocols long developed for less volatile chemicals, both inside and outside of stored products. In each case, the errors could have been avoided if one had considered the schematic distributions shown in Fig. 1. For both protectants and fumigants, errors

in methodology resulted in an underestimation of residues.

On Gunther's assessment, which I share, many residue determinations remain 'illusory' because, I believe, of an implicit assumption that residues are described by continuum chemistry. My proposal is that those protocols developed to determine 'aged' residues should be used in development of methods of analysis. Furthermore, results not shown to be based on adequately-validated methods should be simply discarded. They are 'illusory' and there is no need to base our pest control on illusions.

Loss of residues of protectants and fumigants

In 1978 I proposed that loss of grain protectants (except for very stable ones) could be described by 'first order kinetics' (Eq. 1) (Desmarchelier, 1978a). This assumption is that the 'half life', $(t_{0.5})$, i.e., the time for any residue to decay to half its former value, is constant, and equal to $\log(2)/k$. It was postulated that $(t_{0.5})$ was proportional to temperature (Eq. 2). Eqs. 1 and 2 describe the model, for constant moisture content.

$$\log(R/R_0) = -k \cdot t \quad \text{Eq. 1}$$

$$\log(t_{0.5}) = a + b \cdot T, \text{ where } a \text{ and } b \text{ are constants}$$

Eq. 2

In Fig. 2 the logarithm of residues is plotted against time after application for 3 cases, namely dichlorvos on wheat (Minett and Belcher, 1970), methacrifos on sunflowers (Sharp, 1989) and phosphine on hazelnuts (Noack et al., 1984). The graph illustrates the type of decay that is found, but is not a comparison between the 3 chemicals because the conditions studied differ (Fig. 2). A linear plot (Eq. 1) describes the loss of methacrifos and the loss of about 90% of dichlorvos. It is inappropriate for phosphine, as the proportional loss of this fumigant declines continuously with period after fumigation (Noack et al., 1984). A large amount of work on loss of grain protectants on paddy, maize, sunflowers and peas was performed by two Ph. D. students (Brayan, 1989; Sharp, 1989) and, in broad terms, the types of breakdown shown in Fig. 2 occur with other chemicals, in a manner that varies with chemical and commodity.

Morton et al. (1998) modelled the data of Sharp and Brayan, using six literature models for pesticide decay. They developed a new model, in which the constant 'k' in Eq. 1 is replaced by K, which is derived from the lambda function. Statistically, the new model gave a better fit of the data than any existing model. The model is also consistent with a 'quantum' framework, in which molecules are gradually being concentrated in a number of states with different binding energies. This corresponds to Fig. 1 with a number of distributions of binding energies, rather than the two shown in Fig. 1.

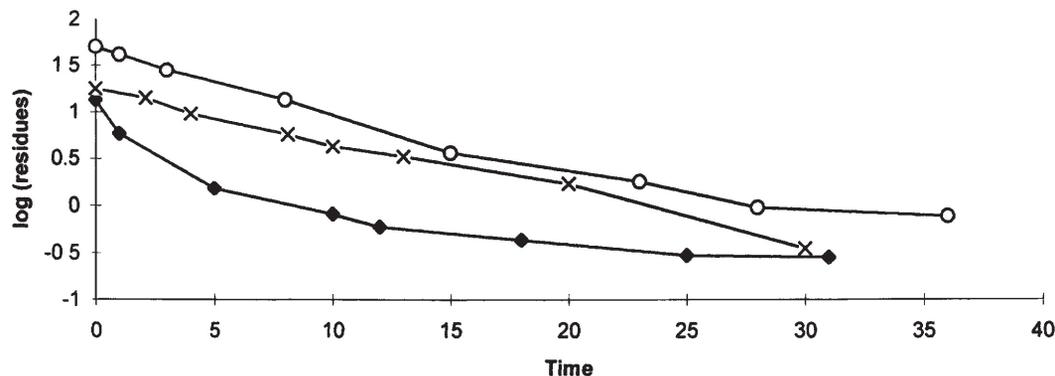


Fig.2. Plot of log(residues) against time after application (days, except for methacrifos, in weeks) for phosphine on hazelnuts at 5°C (◆), dichlorvos on wheat at 35°C (○) and methacrifos on sunflowers at 30°C (×).

In the limiting case, $K = k$, and Eq. 1 applies. Thus my models (Desmarchelier, 1978a) are the limiting case of a more general model, which incorporates different binding energies that result in rate of loss that varies with the age of the deposit. In many cases, Eqs 1 and 2 remain useful in predicting residues over the range of applied amount (i. e. , initial deposit) down to 5 – 20% of applied amount. This is useful if one wishes to know the storage period in which residues are below the Maximum Residue Limit but above the amount needed to control insects, or the reduction in application that can be achieved by cooling the commodity. However, Eqs 1 and 2 generally underestimate the residues after some 80 – 95% of residues has been lost. In some cases, e. g. carbaryl on paddy rice or maize (Sharp, 1989; Brayan, 1989) or phosphine on hazelnuts (Fig. 2), Eq 1 is a poor description of residue loss.

Eq. 1 and Fig. 2, like all semi-logarithmic models, give equal space in the graph to the ratio 10 : 1 as to the ratio 1 to 0.1 or even 0.1 to 0.01, though this does not oblige us to give equal emphasis to each ratio. For example, in studies on toxicity to insects or mammals, the amount between 10 and 1 is more important than the amount between 1 and 0.1, especially where the minimum effective dose required to control insects falls within the higher range.

Loss of residues of fumigants and protectants: opportunity

The rate of loss of chemicals on grain declines as the proportion of chemicals with high binding energies increases. The model of Morton et al (1998), enables a better estimation of residues, especially of low residues, in a framework that has a meaningful chemical interpretation. The model may be relevant to other studies on behaviour of chemicals in commodities, e. g. to sorption and desorption.

Recognition of the movement of molecules to sites of higher binding energy also has implications for bioavailability, and the opportunities arising from this recognition are discussed in Section 2d.

The errors in predicting low residues of Desmarchelier

(1978a), could have been avoided by consideration of different binding energies (Fig. 1), while still retaining the advantages of Eq. 1 as the limiting case of a more general theory.

Constant sorption isotherms

Chemical studies

There are a number of 'isotherms' in the general and stored-product literature which relate concentration in the gas phase (C_v) to that in the commodity or solid phase (C_s). The Freundlich isotherm has been used to model the behaviour of fumigants (Banks, 1986; Hilton and Banks, 1997), though only in a limited form of this equation, Eq. 3a. In this work, C_v is measured and C_s is calculated from the initial mass less that in the vapour phase. From this data, a linear plot is drawn, which passes through the origin. This analysis has been very useful in determining the amount of fumigant that should be applied to obtain a required concentration regime, as the model incorporates the effect of filling ratios (i. e. , on the proportion of empty space in an enclosure). However, the modern form of this equation (Hayward and Trapnell, 1964, with the author's symbols) is given in Eq. 3b, where c_1 and c_2 are constants, and V_{mon} is the volume of sorbed gas corresponding to monolayer coverage.

$$\ln(C_s) = 1/c_2 \ln(C_v) \quad \text{Eq. 3a}$$

$$\ln(C_s) = \ln(c_1 V_{mon}) + \ln(1/c_2) + \ln(C_v) \quad \text{Eq. 3b}$$

Banks (1986) measured C_v and calculated C_s . A more demanding test of Eq. 3 is to plot measured values of C_v and C_s and there are only two cases, to my knowledge, where each has been measured. In the first case, Desmarchelier (1978b) measured dichlorvos residues (C_s) and vapour concentrations (C_v) on wheat in sealed containers. C_v was proportional to applied concentration and to C_s at each of 4 intervals after application, in agreement with Eq. 3a (Fig. 3). However, C_v declined faster than C_s , with the necessary result that Eq. 3a could not apply across all times and concentrations. (That C_v decays faster than C_s was

also shown by Desmarchelier, 1976). In addition, and as a necessary consequence, there is a systematic effect of time after application on the intercept of the plot of C_s versus C_v (Fig. 3). Thus the data shown in Fig. 3 do not satisfy Eq. 3b. This is because the modern interpretation of the Freundlich isotherm assumes one monolayer volume yet, if

one plot data according to this isotherm, more than one monolayer volume is obtained. Thus the analysis contradicts the assumptions (*argumentatio ad absurdum*). Even if one does not accept the modern interpretation, Eq. 3a is only valid if time is specified (which seems to contradict the use of an isotherm).

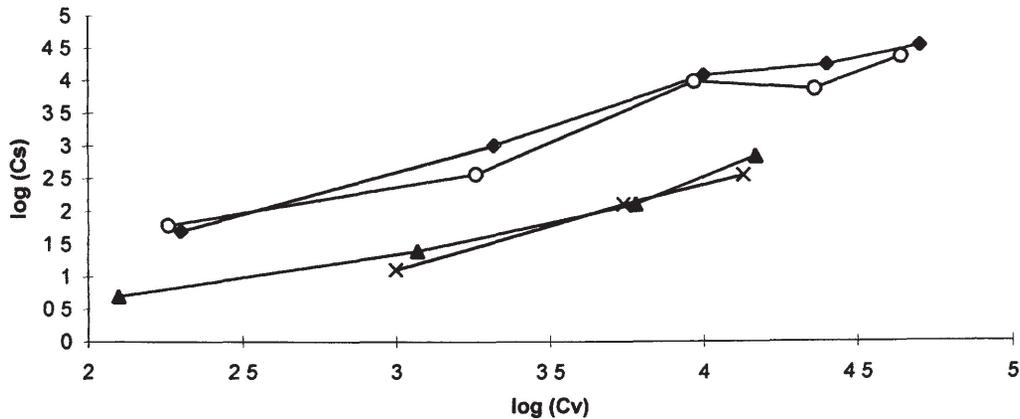


Fig.3. Plots of $\log(C_s)$ versus $\log(C_v)$ for dichlorvos on wheat, at time after application 40 h(◆), 63 h(○), 148h(▲) and 170h(×).

Figure 4 shows a plot of $\ln(C_v)$ versus $\ln(C_s)$ for a hypothetical case based on Fig. 1, where the ratio (C_v/C_s) is 10, but there is an amount of tightly bound sorbed residue equal to 0.01% of the initial value of C_v . This hypothetical

plot shows that the assumption of the Freundlich isotherm gives a good description of the 'data' where C_v is high. However, where C_v is low, the model is a poor one.

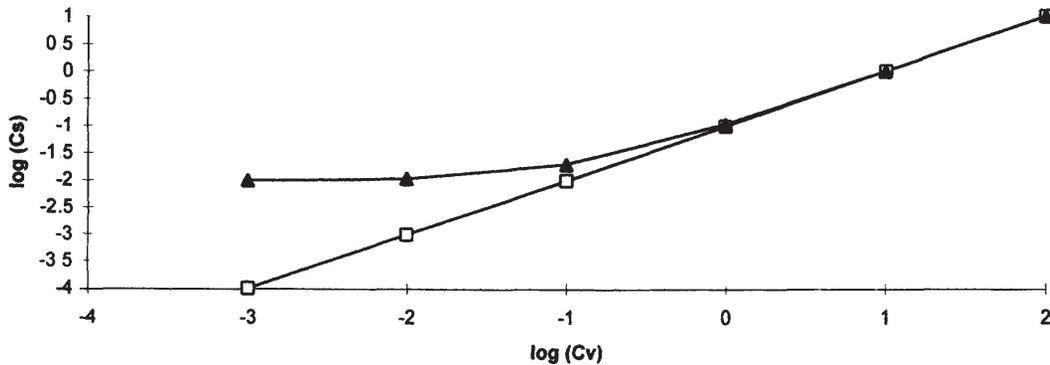


Fig.4. Plots of $\log(C_s)$ versus $\log(C_v)$ for two cases: $C_s = 0.01 C_v$ (□) and $C_s = (0.1 C_v + 0.001(C_v)_0)$, the initial value of C_v (▲).

In the second case, both C_v and C_s were measured by Noack and Wohlgemuth (1985) in a study of phosphine fumigation of wheat, hazelnuts and soybeans under 3 models of fluctuating concentrations. Their data for phosphine on wheat is shown in Figure 5. As with dichlorvos and the hypothetical model, the ratio C_s/C_v increases as C_v declines. This is shown by the systematic curvature in the

graph, i.e., $\log(C_s)$ declines less rapidly than $\log(C_v)$. In addition, Noack et al. (1984) also showed that airing of aged residues had no effect on loss of phosphine. If this data were included in Fig. 5, it would show as a very high value for the ratio C_s/C_v and thus further extend the systematic curvature in Fig. 5. The actual data (Fig. 5) resembles closely the hypothetical data (Fig. 4).

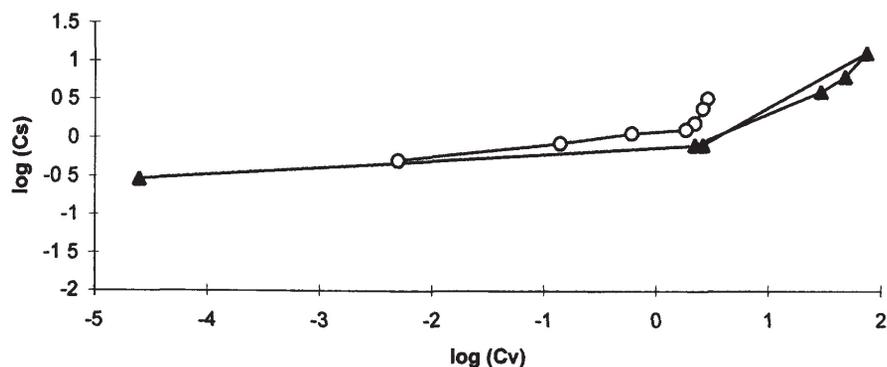


Fig. 5. Plots of $\log(C_s)$ versus $\log(C_v)$ for phosphine (data from Noack and Wohlgemuth, 1985): their Model 2(▲); their Model 3(○).

The hypothetical case shown in Fig. 4 is described by Eqs. 4 and 5, where the subscripts MB and Q refer to the Maxwell-Boltzmann and quantum distributions respectively (cf Fig. 1). The Freundlich isotherm is the limiting case of this situation, where $(C_s)_Q$ is much less than $(C_s)_{MB}$. Thus Eq. 3a is useful for calculation of application rates, where $(C_s)_{MB}$ greatly exceeds $(C_s)_Q$ but not where $(C_s)_Q$ becomes more important. If values of C_s were estimated from measured values of C_v , residues would generally be underestimated, and, sometimes, by considerable amounts.

$$(C_v)/(C_s)_{MB} = \text{constant} \quad \text{Eq. 4}$$

$$C_s = (C_s)_{MB} + (C_s)_Q \quad \text{Eq. 5}$$

Many of the common assumptions about fumigation are, I believe, based on an implicit assumption that the Freundlich, or similar, isotherm applies. It seems to be a common belief, for example, that fumigants can be easily aired from grain, because they are gases. One can consider the continuum gas \rightarrow 'weak' sorption \rightarrow 'strong' sorption, where what applies to a gas, and may largely apply to weak sorption does not apply to strongly sorbed molecules.

It is therefore useful to have the assumptions of the Freundlich isotherm spelt out (Banks, 1986), thus enabling empirical testing, in the traditional scientific manner, leading to improved understanding

Constant sorption isotherms: bioavailability

A number of studies (e. g., Desmarchelier, 1978b) have shown that the biological activity of protectants declines faster than do the residues, measured chemically. The difference between biological efficacy and chemical concentrations is well known in soil chemistry (e. g., available phosphorus) and animal feeding studies (e. g., available lysine). A reasonable explanation for the difference between biological activity and chemical concentration is that surface and vapour phase concentrations decline more rapidly than do total residues. The work on dichlorvos shown in Fig. 3 was conducted to demonstrate a change in a chemical property (the ratio C_v/C_s) compatible with the change in efficacy against insects. In each case (C_s/C_v and insecticidal activity), the chemical behaviour depends not

merely on the total amount but on the time after application (i. e., on 'age of deposit'). Thus the concentration is not a function of state, and continuum chemistry does not necessarily apply.

Constant sorption isotherms: opportunity

As was the case with analysis of residues and with residue breakdown, 'fumigants' and 'protectants' showed similar patterns of behaviour with regard to sorption. Each discipline can learn from each other or, even better, fumigants and protectants should not be regarded as separate disciplines.

One opportunity arising from the work concerns reduction in residues. This can be achieved by both airing and by allowing time to degrade. For low residues, time may become more important than airing (Noack et al., 1984). It is important to realise that this time cannot be predicted by extrapolation of results from models, such as the Freundlich isotherm or first-order kinetics, but must be determined empirically, until better models are developed.

It is common practice to calculate fumigant application in terms of weight of fumigant per volume of air space, whereas protectant application is calculated in terms of weight of chemical per weight of commodity. Thus the weight of fumigant per weight of grain increases with the amount of empty space in an enclosure, whereas the weight of protectant per weight of grain is independent of air space. As general usage of phosphine and non-volatile protectants is based on these assumptions, it is presumed that they are, at least, reasonable approximations. However, it has been shown that this model is not true for dichlorvos, where loss of this chemical, especially from the surface layers, depends to some degree on the ratio of weight to volume (Desmarchelier, 1976). Likewise, for highly sorptive fumigants such as hydrogen cyanide or ethyl formate, the amount of residue will depend, to some degree, on the ratio of weight of chemical to weight of commodity. Thus the calculations appropriate for phosphine (in terms of weight per volume) or for non-volatile chemicals such as deltamethrin (in terms of weight per weight) are limiting

cases. These factors provide opportunities for use of 'fumigants' using models other than those based on weight of chemical per volume. This has led to improvements in potential use patterns for ethyl formate (Annis and Damcevski, unpublished results).

From a number of chemical and biological considerations, it has been shown that residues of chemicals become more tightly bound with time, with the results of increased persistence and reduced efficacy. A possible solution to these problems is to apply chemicals in such a manner that undesirable effects are minimised by reducing the root cause of such effects, namely migration of chemicals to sites of higher binding energies. Reduction of migration of chemicals has long been used in structural sprays, e. g. one method used to increase availability of structural sprays is to apply them in clay carriers, as wettable powders. A recent example of the improved persistence of wettable powders is given in Arthur (1994). Applying insecticides in clay particles to grain can have a similar effect of retaining

efficacy, by preventing migration from the carrier to the wheat. In Fig. 6 the improved efficacy of deltamethrin applied in diatomite relative to its efficacy as an emulsifiable concentrate is shown, from a study of mortality of *Rhyzopertha dominica* (F) on wheat held at 35°C over a period of 18 months (Desmarcelier, Allen, Beckett, Damcevski, Gotzinger and Parsons, unpublished results). The following points are important:

- a) at 20°C, a spray application of 0.08 mg kg⁻¹ deltamethrin killed adult *R. dominica* for 18 months, whereas it killed adults at 30°C for less than 3 months
- b) at 20°C, 0.02 mg kg⁻¹ in either kaolin or diatomite killed adults over a period of 18 months, whereas an application of 0.04 mg kg⁻¹ as a spray gave lower mortality (not shown).
- c) at 30°C, an application of 0.02 mg kg⁻¹ deltamethrin in diatomite, but not in kaolin, killed adults over a period of 18 months.

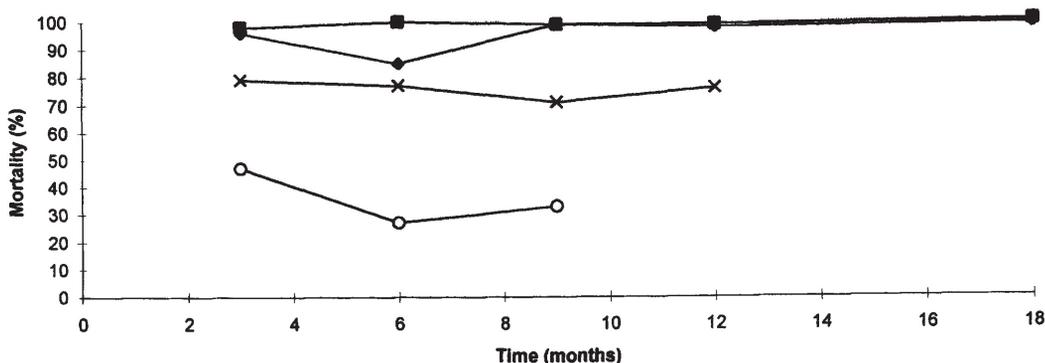


Fig. 6. Toxicity to *R. dominica* of deltamethrin applied: as a spray at 0.08 mg kg⁻¹ at 20°C (◆) and 30°C (○); at 0.02 mg kg⁻¹ in diatomite at 20°C and at 30°C (each ■) and in kaolin at 30°C (×).

There is an extensive literature in general entomology and in stored products on the effect of carrier formulations on insecticidal efficacy. The Symposium in this Conference also summarises recent advances in diatomaceous earths. There is considerable potential to be obtained from combining the two technologies, where it is appropriate to do so. In addition, the effect of cooling on persistence of biological efficacy (Fig. 6) is one of several benefits obtained from cooling, and the effect of cooling in reducing the number of possible generations per year exposed to a chemical is probably at least as important as the effect on adult mortality.

The effect of temperature on rate of loss of chemicals

There are four models in the literature that relate rate of loss to functions of temperature. Literature models use either rate or time to a defined loss (e. g., half-life), but I have altered the models such that times have been replaced by rates, where necessary. These models are:

Model 1 $\log(\text{rate of loss})$ is proportional to $1/(T +$

273);

Model 2 $\log(\text{rate of loss})$ is proportional to T ;

Model 3 $\log(\text{rate of loss})$ is proportional to $aT + bT^2$, where a and b are constants;

Model 4 diffusion control, where rate is proportional to $(T + 273)^{0.5}$.

Model 1 tends to be used by chemists and is the Arrhenius equation. Model 2 is often used by biologists and microbiologists. I have used this model as a simple form of Eq. 1 for small temperature differences (Desmarcelier, 1978a). Model 3 is used by botanists to describe rate of loss of seed viability (Dickie et al., 1990). Model 4 outlines the temperature effect on a process controlled by diffusion (Atkins, 1994).

Botanists often use the expression Q_T . This is the ratio of the rate at T_1 to that at T_2 (and perhaps should be written $Q_{\Delta T}$). The advantage of using ratios, such as Q_T , is that their use reduces the number of degrees of freedom, as shown in Eq. 6 - 7, where $f(T)$ is a function of

temperature, $f(M)$ is a function of moisture, and a , b and c are constants.

$$\log(k) = a + b f(T) + c f(M) \quad \text{Eq. 6}$$

e. g. , $\log(k_1) = a + f(T_1) + c f(M)$ (Eq. 6a) and $\log(k_2) = a + f(T_2) + c f(M)$ (Eq. 6b)

subtracting Eq. 6b from Eq. 6a gives:

$$\log \{ (k_1/k_2) \} = \log(Q_T) = b \{ f(T_1) - f(T_2) \} \quad \text{Eq. 7}$$

If Q_T is plotted against temperature (for constant values of $(T_2 - T_1)$);

Model 1 predicts that Q_T decreases with T ;

Model 2 predicts that Q_T is invariant with T ;

Model 3 predicts that Q_T increases with T ;

Model 4 predicts that Q_T decreases with T , though to a lesser extent than Model 1.

To test which Model best describes the temperature effect on rate of loss of applied chemicals, I examined the data which covers the largest temperature range – this is data for the loss of phosphine over the range minus18 – 35°C (Noack et al. , 1984). Rate constants were obtained from the use of Eq. 1 on the data (Table 1). Measured values of Q_T were compared with those predicted from each of Models 1 – 4 (Table 2). The best Model for predicting the observed Q_T was Model 3, namely the Model used to describe rate of loss of seed viability. The worst Model was the Arrhenius Equation, Model 1. Models 2 and 4 underestimated the effect of temperature on loss of phosphine, but to a lesser extent than Model 1.

Note that, over small temperature ranges, plots of $T(°C)$ against $1/(T + 273)$ are approximately linear, such that it is difficult to decide between these two temperature functions on the basis of R^2 values.

Table 1. Regression coefficients for phosphine on soybeans and wheat, after 14 d fumigation, plotted according to $\ln(R) = a - b t$ (Noack et al. , 1984), where R is residue and t is time (R^2 in the Table is a statistical term, not the residues squared).

Commodity	Temperature (°C)	a	b	R^2
Soybeans	35	3.22	-0.184	0.926
	20	3.31	-0.04858	0.986
	5	3.30	-0.0196	0.971
	-18	3.421	-0.004754	0.971
wheat	35	2.977	-0.3509	0.981
	20	2.776	-0.0594	0.981
	5	2.838	-0.0151	0.841
	-18	2.859	-0.00330	0.788

Table 2. Ratio of $\{k \text{ at } T_1 / (k \text{ at } T_2)\}$, adjusted for 15°C differentials: observed values and those expected if the temperature effect was similar to that causing loss of germination ('seed'), that resulting from diffusion ('diffusion') and that predicted by the Arrhenius equation (Arrhenius).

Commodity	Predicted ratio for model relating it to:	Ratio of rate constants at 2 temperatures		
		35°C to 20°C	20°C to 5°C	5°C to -18°C
soybeans		2.57	1.69	1.78
wheat		3.93	2.62	1.98
mean		1.73	1.14	1*
	T	1	1	1*
	$f(T, T^2)$ (seed model)**	1.20	1.07	1*
	$(T + 273)^{0.5}$ (diffusion model)	0.997	0.998	1*
	$1/(T + 273)$ (continuum model)	0.78	0.85	1*

** the values for $f(T, T^2)$ taken from Dickie et al. , 1990, Eq. 2, Fig. 1.

In addition to the data of Noack et al. , 1984, which covered a range of 53°C, much literature data that covers more limited ranges, such as 20 – 40°C (e. g. Brayn, 1989, Sharp, 1989). These authors calculated rate constants (Eq. 1) for breakdown of 3 organophosphorus insecticides on paddy rice. I used their rate constants to calculate Q_T values. These increased with temperature. The ratio at 40°C to that at 30°C averaged 1.25, standard deviation 0.31 times the ratio at 35°C to that at 25°C, from measurements of 13 rates constants at each temperature. Similarly the value for loss of methyl bromide on sultanas (from the data of Hilton and Banks, 1997) increased over the range 15 – 35°C, with the Q_{10} for 35°C to 25°C averaging 1.12 times the Q_{10} for 25°C to that at 15°C. In each of these examples, the Q_{10} value at the higher temperature range would have been 0.94 that at the lower temperature range, had the Arrhenius equation applied.

These studies on the temperature effect on rates of loss of chemicals show the similarity in behaviour of 'fumigants' and 'protectants' and how studies in one area can help those in another area. They also show that the model from 'continuum chemistry' does not apply.

Temperature effect on loss of chemicals: opportunity

That Q_T increases with temperature is very relevant to loss of chemicals during processing, for the same reason that it is relevant to the loss of germination during heating. Extrapolations to higher temperatures than those studied from 'theoretical' studies using diffusion models or the

Arrhenius equation would underestimate the effect of heat on loss of chemicals during processing. Conversely, they would exaggerate the benefit of cooling in reducing residue breakdown. This factor may be important not only for storage but for the practice of freezing of samples prior to residue determination.

The data in Table 2 do not show a good correlation with data on loss of seed viability. However, that data is least reliable at low temperatures (Dickie et al., 1990). It would be interesting to correlate loss of insecticides with loss of germination over the temperature range used in viability studies, which is often in the range 5–70°C.

The increase in Q_T with temperature for loss of chemicals and for loss of germination are probably related, and qualitatively described in terms of quantum chemistry. As the temperature rises, e.g., proteins may separate from their binding sites, or DNA double helices may uncouple, with a quantum increase in rotational and vibrational energies. This explanation is compatible with the quantum effect of heating on cooking food: after all, one does not obtain a boiled egg by leaving it in water for a long period. Such a quantum theory is relevant to microwave cooking, which imparts energy in quanta, where the quantum of energy is in the range of rotational energies (Atkins, 1993). Microwave irradiation has been used to release fumigants from grain, prior to residue determination (Ren and Desmarchelier, 1998). Microwave energies are also relevant to the fate of residues during cooking with microwave ovens, and to the potential use of microwaves to reduce residues. For example, residues of carbon disulphide in wheat germ, which had persisted during milling of wheat and transport to our laboratory, were released by microwave irradiation for 10 sec from a domestic microwave oven at the lowest setting (Desmarchelier et al., 1998). It may well be the case that microwave cooking has more effect on residues than convective cooking and the effect of microwaves on residues of fumigants and protectants is relevant to the fate of chemicals during processing.

Study of the release of fumigants from whole grain by microwave irradiation (Ren and Desmarchelier, 1998) showed that some chemicals were released more easily than others, in accordance with a theory of quantum binding energies. Study of binding energies by thermal desorption is well-studied in chemistry (Atkins, 1994), and there appears to be no reason why microwave irradiation cannot be used to study differential binding energies.

Assumptions, Refutations, Proposals and Opportunities in ‘Toxicology’

The toxicity of chemicals to insects is usually modelled by probit analysis (Finney, 1971), which is shown in Eq. 8, where Y is mortality, in probits, and C , t , and C_0 refer to

concentration, time of exposure and ‘no-effect’ concentration, and a , b_1 and b_2 are constants found by curve fitting (interactive effects and a possible ‘no effect’ time have been omitted for simplicity).

$$Y = a + b_1 \log(C - C_0) + b_2 \log(t) \quad \text{Eq. 8}$$

Eq. 8 is derived from the response of insects to a single point dose. However, insects exposed for long periods to chemicals are not exposed to a single point dose. Factors of rate(s) of uptake with time and rate(s) of elimination are not used in the derivation of Eq. 8.

In Fig. 7, mortality in probits of *R. dominica* to bioresmethrin at 20°C is plotted against both $\log(C)$, for fixed t , and against $\log(t)$, for fixed C . Many examples of mortality of insects exposed to a single dose of protectant (e.g. Champ et al., 1969; Fig. 7, symbols \times and \blacktriangle) show a rise in mortality with t , which plateaus after a defined period, and then remains constant. There are also many examples in the chemical literature where the amount of chemical absorbed by a solid or bound to an enzyme is described by such curves (with the substitution of concentration, C , for probit mortality, Y). The data in Fig. 7 were obtained to determine whether a theoretical chemical model could help to describe toxicity data.

For insects exposed over considerable periods of time to a stable grain protectant, or to a fumigation at a fixed concentration (e.g., in SIROFLO®), C is constant. If one assumes that rate of uptake is proportional to C (i.e., $dC/dt = kt$) and that rate of elimination is proportional to the amount taken up (i.e., to (dC/dt)), one obtains Eqs. 9 (see Appendix for derivation). The limits of k with respect to t are because the time function has a maximum at maximum mortality, but dead insects do not recover.

$$Y = A + B \log(C - C_0) t(1 - kt), \text{ for } t < 1/2k \quad \text{Eq. 9a}$$

$$Y = A + B \log(C - C_0) k/4 \text{ for } t > 1/2k \quad \text{Eq. 9b}$$

The data recorded in Fig. 7, which were obtained over exposure periods of up to 97 days, are also recorded in Fig. 7(b), after plotting according to Eq. 9. Four different curves were transformed into a single plot that is approximately linear. That is, disparate toxicological data were unified by consideration of physiological factors of uptake and elimination, as modelled by Eq. 9.

Eq. 9 is based on the ‘real-life’ situation where insects are exposed to chemicals over considerable periods of time although the assumption of constant concentration would apply only in some situations. Its derivation is based on a coherent theory of uptake and elimination of chemical by insects, where elimination could be detoxification or elimination or any process that removes a toxicant from the active site(s).

Eq. 9 has the following advantages over Eq. 8:

- a) as it reduces to Eq. 8 when k approaches zero, it retains the utility of Eq. 8, but does not require the assumption of a point source dose (though that assumption can still be

- made).
- b) gives an alternative explanation for data, which is compatible with known biochemistry of insecticides.
 - c) it enables a study of the effect of conditions, such as temperature, on the desorption rate, k .
 - d) where mortality plateaus with increasing time of exposure, the time coefficient obtained from use of Eq 8

- e) it will hopefully help lead to the development of other equations that might be more appropriate to other situations.

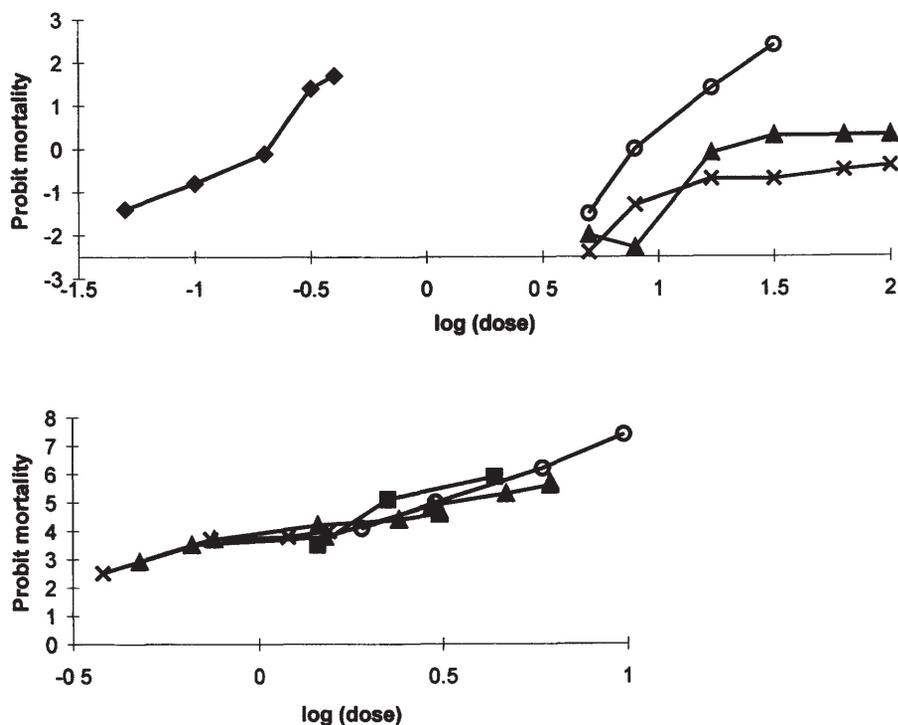


Fig. 7. Mortality in probits to *R. dominica* from bioresmethrin plotted, in top graph, against $\log(\text{dose})$, where dose is: $\log C$, 17 d exposure (▲), $\log t$, for exposure to 0.4 mg kg^{-1} (○), 0.2 mg kg^{-1} (■) and 0.1 mg kg^{-1} (×). The same data is plotted in the bottom graph according to Eq 9.

In unpublished studies from our laboratory, it has shown that k is very temperature dependent, and is greater at 30°C or 35°C for *R. dominica* and for *Tribolium castaneum* (Herbst) than at 20°C , in studies with fenitrothion, bioresmethrin and pyrethrins. Such studies on rate of 'limination' of insecticides are important both for setting doses and for introduction of IPM procedures aimed at reducing the chance of resistance.

Eq. 9 is based on the assumption that k is positive. This results in a new time function, $f(t)$, whose values must necessarily be less than those of t (because t is greater than $t(1-kt)$). In such cases, and if Eq. 9 applies, analysis of the data by Eq. 8 with result in a coefficient for C that is greater than that for t (i.e., in the Ct product, C is more important than t). The case of time being more important than concentration, when determined from Eq. 8, would imply that $f(t)$ is greater than t , e.g., that the rate of uptake (k) increase with time of exposure. This is possible, e.g., it would apply when the initial effect of a chemical

was to destroy some barrier, either physical or biochemical.

Some Examples of IPM

A number of recent studies have advanced integration of chemicals with other processes including heat, cold and hygiene. The use of heat plus diatomaceous earths to control insects in mills is discussed in the session in this Conference on diatomaceous earths, and is a good example of the use of complementary techniques. Table 3 shows some recent Chinese work on the integration of phosphine, protectants and aeration (Lei, 1987; Li et al. 1987; Zhang et al. 1990; Gua et al., 1993). In these studies, phosphine alone did not control psocids (unnamed species) or mites. However, control was achieved by, e.g., upward aeration with a surface application of a protectant, or by aeration plus fumigation. Such use of IPM, of course, requires good integration between the chemical, entomological and engineering components of the problem.

Summary

Chemical and toxicological models used in stored product protection have been very useful. However, they are simplistic and should be regarded as limiting cases of more general models. Their use, or assumptions of continuum chemistry, has led to errors in analytical chemistry, sorption studies and kinetics, each of which result in underestimating the residues of fumigants and protectants. The chance of continuation of such errors will be reduced if we think in terms of the energy distribution shown in Fig. 1, and not merely in terms of that given by the Maxwell-Boltzmann distribution. Recognition of the problem is an important step to solving it, as shown by the examples of the improved efficacy of certain carriers, compared with sprays, and the use of quantum microwave energy to reduce residues.

Eq 9 introduces the possibility of using data on insect mortality to study the uptake and elimination of chemicals, in a way that does not require the assumption of a point

source dose. It has considerable potential as a tool to develop strategies, such as cooling, which have the potential to delay resistance

Chemicals are very versatile, and can be used in many ways, as illustrated by the examples in Table 3 and Fig. 6. Insecticides also have two major problems, namely elicitation of resistance and formation of residues and/or alteration products. There are ways of improving the benefits and reducing the disadvantages. In trying to achieve these aims, I believe that we have more to gain by studying fumigants and protectants as 'Chemicals', rather than emphasising their differences by, e.g., distinctions at conferences

Good Agricultural Practice requires that chemicals be used as part of an IPM program, which must be based on a good integration of chemistry, biology and engineering. The versatility of chemicals enables them to fit into many roles in such programs. I hope that some of the assumptions, refutations and opportunities I have outlined will help in this goal.

Table 3. Comparison of 'smart aeration' with fumigation in recent work from China.

Commodity	Insects present	Did the procedure work?		
		PH ₃	Aeration + PH ₃	Aeration + surface treatment
canola ¹	mites	No		Yes
wheat ²	mites + psocids	No	Yes	
wheat ³	psocids	No		Yes
wheat ⁴	psocids	No	Yes ^a	Yes ^b

a downward aeration. b upward aeration

1 Zhang et al (1990)

2 Gua et al. (1993)

3 Lei (1987)

4 Li et al (1987)

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