Grain protectants and pesticide residues

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Abstract

In the period from 1970 to 1990, the application of grain protectants was one of the methods used by the grain industry to ensure that its product was free from live insects. This use has declined due to an increased requirement for residue-free or low-residue products and to increasing insect resistance to available insecticides. Many of the residue data on grain protectants supplied to the Codex Committee on Pesticide Residues [CCPR] for the setting of Maximum Residue Limits [MRLs] came from the Australian grain industry. These data came from a series of large scale trials in which commercially treated wheat was put through commercial mills and residue testing was conducted on a range of milled and cooked products. Maximum residue limits are set on raw cereals rather than downstream products but it is essential to know what residues occur on these products to assess the dietary intake due to the grain treatment. The estimate of Theoretical Maximum Daily Intake [TMDI], which is widely used internationally, gives a grossly exaggerated estimate of intake which can be corrected only by processing or monitoring data. The limits set by the CCPR on the basis of good agricultural practice tend to reflect the highest possible outcome. Residues found in practice are much lower than the theoretical figure given in trials.

Introduction

Cereal grains form a large proportion of the global diet and as raw or processed cereal products make up a significant part of world trade. Under conditions of low water activity, these grains can be stored for long periods without perceptible chemical or biological decay. However, the grains are susceptible to insect, rodent and bird pests. Control of insects in grain is a much bigger problem for tropical or semitropical countries than it is for those countries where winter temperatures reduces storage insect activity. In bulk grain, insects cause heat and moisture migration which may lead to mould growth and the production of mycotoxins, a potentially much greater hazard than the presence of approved levels of insecticide residues. Grain may be harvested and stored in bulk at over 30°C and unless this grain can be cooled by aeration some early pest control measures are a necessity. One method of control of grain insect pests is by the use of insecticides used as residual protectants. This was a method in much use up to the early 1980s, less so today.

The extent of use of insecticides is influenced by the two factors of resistance and residues. Of these two factors, the lack of effectiveness due to reduced susceptibility of insects to insecticides is probably the major reason for reduced use in the Australian grain industry. The increased requirement for products free of pesticide residues is also important, but experience has shown that insecticides can be used as part of a mix of pest control measures with very low residue outcomes, ranging from zero to low residues well within international standards.

In many countries the use of grain protectants is still an essential pest control measure. In areas such as Africa the use of grain protectants in the form of dilute dusts may be the main method of protection particularly on-farm. Grain protectants have been substituted for traditional preventative measures such as the use of vegetable oils, inert dusts, plant powders or ashes. These materials are not readily available or affordable beyond the regions of traditional use and may be questioned on hygienic grounds. Lacking safe fumigants and the means of applying physical control methods, grain protectants may be the only inexpensive and manageable material for a wide range of storages. In general the advantage of the use of grain protectants is the adaptability of the method to all types and sizes of storage, with freedom from logistic constraints and minimal capital or infrastructure requirements. The presence of residues in cereals and cereal products as a result of the use of grain protectants is discussed in this paper.

Basic Requirements

The decision to use a grain protectant rests on consistency between the following parameters.

Good Agricultural Practice (GAP). The pattern of use determined by efficacy trials.

Maximum Residue Limit (MRL). An MRL for the insecticide on the cereal, set on the basis of the GAP. MRLs may also be set for processed cereal products if the MRL is greater than the cereal MRL but not generally for residues lower than the cereal MRL.

Acceptable Daily Intake (ADI). The maximum amount of the insecticide permitted in the diet from all approved crop and food applications.

Theoretical Maximum Daily Intake (TMDI). A gross overestimate of the total intake which assumes that all foodstuffs in the diet have residues at the MRL.

Estimated Maximum Daily Intake (EMDI). This is also an overestimate as it assumes that all commodities with MRLs are treated with the insecticide and are at the MRL, but it takes into account reduction factors calculated from residue processing data.

An insecticide can be used as a grain protectant only if these parameters fit together. The residues entering the diet as a result of use of the insecticide at the GAP rate must not exceed the ADI. In the absence of real data about actual use and actual residue levels, the TMDI is applied. If the TMDI which is obtained by multiplying all the MRLs by the dietary intake is below the ADI, there will generally be no need for any further data. However, in many cases the TMDI exceeds the ADI by several hundred percent. It is then necessary to obtain a more realistic estimate by measuring actual residues from commer-

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cial use and determining the fate of the residues in the processing from raw cereal to foodstuffs. This will enable an estimated maximum daily intake to be calculated. Finally, an estimate of the actual intake can be obtained by monitoring residues on foodstuffs in retail sales outlets. The TMDI is favoured by theoreticians as it requires no analytical work other than an estimate of the national diet. However, if analytical work is done as described in this paper, or there is extensive monitoring, then a more realistic assessment of residue intake is possible. Countries with a strong preference for using the TMDI in determining their acceptance of a treatment may at the same time fail to detect any residues of the compounds in their monitoring programs.

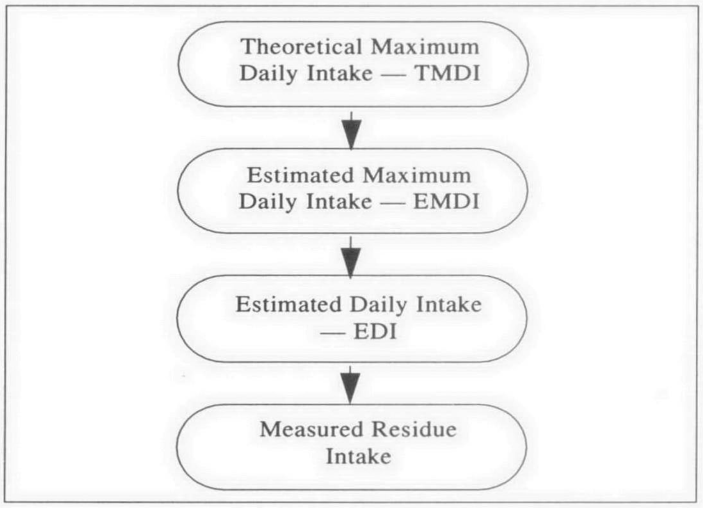

Fig.1. Increasingly realistic predictions.

Commercial Trials

In 1985, a protocol was drawn up by the Australian Wheat Board and the Flour Millers Council to undertake joint commercial-scale trials on insecticide in use and on future compounds when they reached the stage of being ready for introduction into full-scale use. The primary objective was to determine the residues resulting in wheat and in downstream products when a compound was used at the rate which previously entomological trials had shown to be the most effective. This would enable appropriate maximum residue limits to be set and provide an estimate of the actual dietary intake.

The basis form of the trial was to treat up to 500 tonnes of wheat in bulk silos at two rates: the rate required by the GAP and a rate double the GAP rate. The second rate is of no interest to regulatory authorities but enables the millers to anticipate what the residue would be if the commodity were treated twice or accidentally overdosed. It is also useful if the actual residue achieved by the normal application rate falls short of the level expected to be achieved in general practice since it may be difficult to achieve a settled rate in 500 tonnes with a sprayer designed to treat several hundred tonnes per hour.

The steps in the process are as follows:

- Treat up to 500 tonnes at normal rate and twice normal rate
- Sample the grain on day 1
- Analyse the day 1 samples and determine whether to proceed with the trial
- Deliver 50 tonne samples to each of two commercial mills and pilot mill for milling within 4 weeks of treatment. A second delivery is made to the pilot mill after a further 3 months.
- Running samples of wheat, straight run flour, bran, wheatgerm are taken during the milling process, for analysis of residues by two independent laboratories.

After milling a sample of wholemeal is prepared from the following formula:

- Flour 4.1 kg, bran 0.18 kg, pollard 0,27 kg.
- Six bread and noodle products are prepared for residue analysis.

Conditions for preparation of cooked products are:

- White noodles—3% salt—6 minute cooking
- Yellow noodles—1% sodium carbonate—7.5 minute cooking
- Flat bread—1% yeast—1.5% salt—500°C for 30 seconds
- Steamed bread—2% yeast—steam for 20 minutes
- Pan breads—2.5% yeast—2% salt—2% fat—1% improver — 25 minutes

The residues are analysed by standard GLC methods for the organophosphates and deltamethrin and permethrin, and by HPLC methods for the pyrethroids and methoprene.

Table 1. Codex Maximum Residue Limits for insecticide applied to cereals after harvest.

Insecticide	Cereal	Wheat	Barley	Maize	Oats	Sorghum	Wheat bran	Wheat flour
Chlorpyrifos methyl		10	10	10	10	10	20	2
Pirimiphos methyl	10						20	2
Fenitrothion	10						20	2
Methacrifos	10						20	2
Etrimfos		5	5	5			10	1
Malathion	8						20	2
Dichlorvos	5						10	1
Deltamethrin	1						5	0.2
Permethrin	2						5	0.5
Fenvalerate	2						5	0.2
Bioresmethrin		1					5	1
d-Phenothrin		2	2	2			5	1
Pyrethrins	3							
Piperonyl butoxide		10						
Methoprene	5						10	2
Carbaryl		5	5		5	10	20	0.2

Table 2. Ratio of residues between wheat and milled products.

Insecticide	Wheat	Wheatbran	Wheatgerm
Chlorpyrifos methyl	1	3.8	4.2
Pirimiphos methyl	1	3.6	4.5
Fenitrothion	1	3.9	3.7
Methacrifos	1	3.3	4.1
Bioresmethrin	1	3.8	2.3
d-Phenothrin	1	3.6	2.3
Deltamethrin	1	3.2	1.1
Permethrin	1	3.4	1.1
Methoprene	1	2.8	6.8
Dichlorvos	1	1.7	

Results

The Codex list of maximum residue limits in Table 1 gives 16 compounds with limits consistent with their postharvest use. These compounds are the organophosphates — malathion, chloropyrifos methyl, pirimiphos methyl, fenitrothion, methacrifos, etrimfos, dichlorvos; the pyrethroids — deltamethrin, bioresmethrin, d-phenothrin, permethrin, fenvalerate, pyrethrins; and carbaryl, methoprene and piperonyl butoxide (synergist). The Australian grain industry has produced and made available data on the effect of processing on residues on wheat and downstream products for 11 of these compounds.

The results of the determination of residues of eight insects in a range of products from the commercial trials is given in the Tables 3–10. There is a multiplication factor from wheat to bran and from wheat to wheatgerm. MRLs are set for products which have higher residues than the original cereal and, in the case of wheat, this generally means only bran and wheatgerm. The summary given in Table 2 shows that the ration of bran residue to wheat residue is similar for all the insecticides tested and relates to the relative weights of bran and flour. The mean ration of 3.5 means that the bran MRL should be 3.5 times greater than the wheat MRL. Codex has generally set the bran level at twice the wheat MRL. The Australian grain industry imposed a rule of not trading at more than 50% of the MRL to overcome this problem. Other countries, for example the USA, have set milled product tolerances higher than the grain MRL. In practice, actual residues in cereal being traded are usually well below the MRL and the disparity is not usually a problem. In the case of wheatgerm (Table 2), the residue varies with the type of insecticide and increases from the halogen-substituted pyrethroids to bioresmethrin and phenothrin to the organophosphates to methoprene. Wheatgerm collects an unusually high level of methoprene and a large MRL is needed for wheatgerm from methoprene-treated wheat.

The levels given in Tables 3–10 are those on the products. In considering the residue to be expected from these results it must be noted that only the lower application rate reflects the registered GAP use. The higher result is for comparison only. The longer interval is also the only storage period to be considered. Grain protectants are not used when the storage period is expected to be less than about 3 months. The only exception is dichlorvos which is not a grain protectant but a disinfestant used in storage for emergency treatments where it is not possible to use a fumigant. The tables show that, with the exception of dichlorvos and bioresmethrin, there is a measurable residue in all the processed products about 20 weeks after the grain has been treated. (The actual interval in the trials varied from 16 to 26 weeks). The residue found in the product as a percentage of the residue in the flour averages out as follows: white pan bread 45%, steamed and wholemeal pan bread 50%, flat bread 53%, and noodles 60%. Residues of organophosphates are lower in yellow alkaline noodles. Residues of methacrifos, a more volatile, less persistent insecticide, are generally below the average for the organophosphates.

To calculate the loss of the insecticide as a result of cooking, an adjustment must be made for the change in moisture content. The moisture contents used were: steamed bread 40%, wholemeal bread 37%, white bread 35%, flat bread 21%, flour 13%, yellow noodles 12.9%, and white noodles 11.7%. This results in a correction factor of × 1.5 for steamed, wholemeal and white bread, × 1.14 for flat bread and no correction for noodles. The reductions in residues from cooking, allowing for the moisture content differences, are 40% for noodles and flat bread, and 25–32% for steamed and pan breads. Gluten is a commodity much traded internationally but for which no MRLs have been set, the residue being assumed to be less than the cereal MRL. Results of studies shown in Table 12 indicated that for organophosphates the residue level is at about 75% of the value for the wheat at the time of processing. The value for methoprene is lower, and may be higher for pyrethroids. Unless specific tolerances have been set, approval of a residue in gluten is dependent o approval of the use of insecticide on the cereal.

Discussion

Based on these and similar trials, MRLs for all the commonly used grain protectants have either been approved by the Codex Committee on Pesticide Residues (CCPR) or are at an intermediate stage of the Codex approvals procedure. The status of pyrethrins and carbaryl may be in some doubt pending reviews in 1994 and 1996. In many cases the MRL is the same as the maximum recommended application rate. This is necessary for stable compounds such as deltamethrin or permethrin which have very long persistence on stored products. In the case of organophosphates or other compounds for which there is a definite rate of breakdown in storage the MRL can be set below the application rate with an appropriate withholding period. In warm climate areas control measures may require higher application rates than in cooler areas but this need not result in higher residues as the higher application requirement is usually linked to a faster rate of breakdown.

It may be seen in Table 1 that in most cases the MRL is set for cereal grains in general which is taken to include wheat, barley, maize, sorghum, oats and rye. The two exceptions in Table 1 are bioresmethrin and piperonyl butoxide. In both these cases the currently proposed MRLs are applicable to wheat only due to the lack of data on other grains. This is an unacceptable situation for piperonyl butoxide due to its widespread use with pyrethroids on many commodities. Notwithstanding the reluctance of most countries to formally adopt the Codex limits, the Codex system is widely supported, and national MRLs are often based on the Codex MRLs either in full or as a proportion of the limit. In contrast to the grains there are few Codex MRLs for the postharvest use of insecticides on legumes. Table 12 shows that there are recently confirmed MRLs for deltamethrin alone. There are several reasons why the use of grain protectants should not be extended to grain legumes. These include lower effectiveness and a need for much higher application rates, the very high accumulation of residues in extracted oils, and difficulties in controlling usage in small-scale trading. Conformity with the ADI is not the only criterion in approving a grain protectant. As an example, residues in barley may affect the malting process or cause taint in the final product. The treatment of barley is therefore subject to the approval of the maltsters and

Table 3. Residues of dichlorvos in processed products (mg/kg).

Application rate (g/tonne)	6	6	12	12
Interval after application (weeks)	1.7	13	1.7	13
Wheat	2.5	5.2	0.9	
Bran	4.1	0.6	7.3	1.1
Germ	2.6	0.2	5	0.7
Flour	0.3	n	0.4	0.1
Wholemeal	1.3	0.1	1.8	0.2
White pan bread	n	n	0.2	n
Wholemeal pan bread	0.2	n	0.3	n
Flat arabic bread	0.3	n	0.5	n
Steamed bread	0.2	n	0.3	n
Yellow alkaline noodles	n	n	n	n
White noodles	0.2	n	n	n

n = less than 0. 1 mg/kg

Table 4. Residues of methacrifos in processed products (mg/kg)

Application rate (g/tonne)	10	1.0	20	20
Interval after application (weeks)	6	20	6	20
Wheat	4.9	3.7	14.8	13.5
Bran	17.6	15.4	46.7	46.8
Germ	19.4	14.8	57.9	50
Flour(for baking)	0.8	1.3	4.2	3.3
Wholemeal	2.9	3.5	13.3	10
White pan bread	0.3	0.6	1.5	0.7
Wholemeal pan bread	1.1	1.3	4.1	4.1
Flat Arabic bread	2.1	1.9	6.6	5.4
Steamed bread	0.5	0.4	1.4	0.8
Yellow alkaline noodles	0.3	0.3	1.1	1.1
White noodles	0.8	1	2.6	2.7

Table 5. Residues of chlorpyrifos methyl in processed products (mg/kg)

Application rate (g/tonne)	5	5	10	10
Interval after application (weeks)	8	20	8	20
Wheat	2.1	1.9	6.2	4.6
Bran	10.3	8.9	29.1	19.6
Germ	8.7	8.3	28.4	17.5
Flour	0.5	0.5	1.3	1.8
Wholemeal	2.1	1.6	6.1	5.3
White pan bread	0.3	0.2	0.6	0.5
Wholemeal pan bread	1	0.8	3.3	2.4
Flat Arabic bread	0.9	1.2	3.5	2.9
Steamed bread	0.3	0.2	0.5	0.5
Yellow alkaline noodles	0.2	0.3	0.6	1
White noodles	0.4	0.4	0.9	1.5

Table 6. Residues of methoprene in processed products (mg/kg)

Application rate (g/tonne)	1	2
Interval after application (weeks)	16	16
Wheat	0.7	1.1
Bran	2.8	3.7
Germ	4.1	6.1
Flour	0.2	0.4
Wholemeal	0.8	1.2
White pan bread	0.1	0.2
Wholemeal pan bread	0.4	0.5
Flat Arabic bread	0.5	0.6
Steamed bread	0.2	0.2
Yellow alkaline noodles	0.2	0.2
White noodles	0.1	0.2

Table 7. Residues of bioresmethrin in processed products (mg/kg).

Application rate (g/tonne)	1.2	1.2
Interval after application (weeks)	7	26
Wheat	0.65	0.7
Bran	2.5	1.5
Germ	1.4	1.1
Flour	0.2	0.2
Wholemeal	0.6	0.5
White pan bread	0.2	n
Wholemeal pan bread	0.6	0.3
Flat Arabic bread	0.3	n
Steamed bread	0.2	n
Yellow alkaline noodles	0.3	0.2
White noodles	0.3	n

Table 8. Residues of permethrin in processed products (mg/kg).

Application rate (g/tonne)	1.1	1.1	1.5	1.5
Interval after application (weeks)	8	23	8	23
Wheat	0.71	0.59	0.95	0.99
Bran	2.40	2.1	3.6	3.8
Germ	0.75	0.89	1.01	1.55
Flour	0.26	0.25	0.37	0.35
Wholemeal	0.61	0.55	0.94	0.84
White pan bread	0.11	0.11	0.19	0.16
Wholemeal pan bread	0.37	0.21	0.59	0.41
Flat Arabic bread	0.31	0.29	0.44	0.54
Steamed bread	0.05	0.04	0.09	0.05
Yellow alkaline noodles	0.21	0.14	0.28	0.28
White noodles	0.14	0.08	0.23	0.21

Table 9. Residues of deltamethrin in processed products (mg/kg)

Application rate (g/tonne)	0.25	0.25	0.5	0.5
Interval after application (weeks)	8	18	8	18
Wheat	0.17	0.16	0.41	0.35
Bran	0.62	0.65	1.65	1.47
Germ	0.26	0.22	0.61	0.58
Flour	0.04	0.02	0.11	0.11
Wholemeal	0.1	0.15	0.42	0.41
White pan bread	0.03	0.02	0.06	0.04
Wholemeal pan bread	0.07	0.04	0.24	0.15
Flat Arabic bread	0.08	0.07	0.2	0.2
Steamed bread	0.02	0.02	0.06	0.06
Yellow alkaline noodles	0.02	0.02	0.09	0.07
White noodles	0.02	0.02	0.06	0.04

Table 10. Residues of piperonyl butoxide in processed products (mg/kg)

Application rate (g/tonne)	9	9	16	16
Interval after application (weeks)	7	26	7	26
Wheat	5.1	4.5	6.6	6.1
Bran	17.1	16.1	31.2	21.8
Germ	6.8	12.8	14.2	14.6
Flour	2.1	2.3	2.9	1.5
Wholemeal	4.7	5.0	8.5	3.7
White pan bread	1.1	1.6	1.2	–
Wholemeal pan bread	2.7	2.9	5.5	3.5
Flat Arabic bread	1.4	2.2	4.5	2.4
Steamed bread	1.1	3.2	1.8	1.4
Yellow alkaline noodles	0.5	0.9	2.6	1.6
White noodles	1.1	1.7	2.3	1

Table 11. Grain Protectant residues in gluten (mg/kg)

Insecticide	Wheat	Flour	Gluten
Fenitrothion	6.2	1.3	4.2
Chlorpyrifos methyl (mean of 4)	3.7	1.0	3.2
Methoprene(mean of 8)	0.8	0.3	0.45
d-Phenothrin	0.6	0.2	0.8
Piperonyl butoxide	5.3	1.4	7.3

Table 12. Codex postharvest MRLs for legumes (mg/kg)

Commodity	Deltamethrin	Dichlorvos	Malathion
Beans (dry)	1		8
Field peas (dry)	1		
Lentils (dry)	1	2[a]	
Soya beans		2[a]	

[a]Recommended for withdrawal by 1993 JMPR

brewers, and not all grain protectants are acceptable. In commercial trading there are increasing requirements for residue-free product. The use of any of these grain protectants rules out the possibility of the product being traded as residue free. The only exception might be dichlorvos for which the residues may be below the limit of determination a few weeks after treatment. These studies have shown the residues which might be expected from the GAP use of grain protectants. In practice, monitoring studies show that residues are very much below the 'maximum' levels given here. In Australia the increasing problem of insect resistance and the lack of alternative compounds has caused the virtual cessation of the use of grain protectants, although there may be other countries where this technique will continue to be used for some time to come.