The fate of residues of deltamethrin in treated wheat during its transformation into food products

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Abstract

Deltamethrin is an exceptionally potent insecticide which is used at very low application rates against a spectrum of stored-product pests. Recently, studies have been made in many countries on the distribution and fate of deltamethrin residues found at the various processing steps from the day on which the grain is treated until the food made from this grain reaches the consumer's plate.

The data from these studies are presented for wheat, milling fractions, bread, pastries and noodles. Pigs and poultry fed on deltamethrin-treated wheat have shown no or negligible residues in their tissues.

The results show that, at the normal application rates required to give at least six months control of most stored-grain insects, the level of residues in processed and baked products will remain well below the limits accepted by national and international regulatory authorities.

Introduction

Human consumption of foodstuffs prepared from cereals treated by deliberate admixture of insecticides for the control of stored-grain pests must be shown to pose minimal risk for consumers. Many studies are required by governmental authorities and international bodies to demonstrate the innocuity of insecticides used for stored-grain treatments. Deltamethrin is a pyrethroid insecticide exclusive to Roussel Uclaf. It is widely used for post-harvest protection of grains under the trade name of K-Obiol. It is exceptionally potent against the whole spectrum of stored-product pests (Snelson 1987); whilst effective at very low dose levels, it is stable on grains and shows no tendency to penetrate into grain.

A lot of data has been generated in recent years by Roussel Uclaf concerning the fate of residues of deltamethrin in milling, processing and cooking foodstuffs prepared from treated wheat, as well as residues in meat and eggs produced by animals fed on a diet based on treated wheat.

The present paper is a review of the 6 most important of these studies, which have led to the following toxicological evaluation of deltamethrin with the Codex system after the 1993 Codex Committee on Pesticide Residues meeting (See Snelson 1987 for details and on two steps in procedure for elaboration of Codex MRLs) (FAO 1993):

Acceptable Daily Intake (ADI), 0.01 mg/kg of body weight
Maximum Residue Limit (MRL)
Cereal grains, 1 mg/kg, Step CXL
Wheat bran unprocessed, 5 mg/kg, Step 6
Wheat flour, 0.2 mg/kg, Step 6
Wheat wholemeal, 1 mg/kg, Step 6
Meat, 0.5 mg/kg, Step 6
Eggs, 0.01 mg/kg, Step CXL

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Description of the Six Studies

The main features of these studies include:

- Practical applications in industrial units or pilot-plants of commercially available formulations of deltamethrin to wheat grain in bulk quantities (up to 3900t).
- Determination of deltamethrin residues in grain immediately after treatment, after a period of storage (if any) and before milling; in impurities (dust and debris) after grain cleaning; in grain fractions after commercial milling; in baked products such as bread, rolls, croissant, pastries with pork and poultry meat and eggs produced by animals fed on treated grain

Trial done in the U.K.

Halls and Periam, Wellcome Research Laboratories, Internal Report

250-kg batches of an English hard wheat were treated at nominal levels of 1 and 2 mg/kg deltamethrin and then sampled and analysed on the day of treatment and every month during storage up to 9 months. The wheat was then submitted to the Flour Milling and Baking Research Association, Chorleywood, Buckinghamshire to be milled and baked. The wheat was first cleaned of extraneous material, then divided into 2 samples and each submitted to a different milling procedure. The first produced wholemeal flour, the second produced white flour, bran and fine offal. Two different samples of white flour were taken from this procedure, the first reduction flour (the cleanest flour mainly from the centre of grain) and total flour including flour from the bran and fine offal fractions. All these samples were analysed for total deltamethrin content in both batches of treated wheat.

In addition, bread was baked from both wholemeal and total white flours to produce wholemeal and white bread, which were analysed for deltamethrin content.

Trial done in Italy

PR Molinari, Agricultural Chemical Institute, University of Pianceza

This trial was as follows:

- Application was by spraying, nebulisation and dusting of about 6000 t of wheat (soft and durum). Three different formulations of deltamethrin were used (EC, ULV and dust) at 3 different use rates (0.25, 0.5 and 1 mg/kg).
- It was stored in 7 silos of different types (horizontal and vertical) for periods up to 1 year after treatment.
- The wheat was cleaned according to the usual Italian procedures.
- From industrial milling, decortication residues, semolina and offal in the case of durum wheat, and decortication residues, bran and flour in the case of soft wheat, were produced.
- Bread was made from soft wheat flour.

- Pasta was made and cooked with the semolina produced from durum wheat.

Samples of wheat were taken just after treatment and during the storage period, of impurities collected during the cleaning process, of all milling fractions, of bread and pasta (fresh, dried, cooked) and of cooking water. 775 samples were collected and analysed for their deltamethrin content (3 to 5 replicates per sample) by both GLC and HPLC methods.

Trial done in Australia

Anonymous, The Australian Wheat Board and The Flour Millers Council

A report to the JMPR on residue studies of wheat treated with deltamethrin. Two batches of 200 t each of wheat were treated using a conventional high volume spray unit positioned close to the boot of an elevator (grain flow rate = 90 t/hour) during the grain transfer from the road hopper to the trial bin. The formulation used was an emulsifiable concentrate containing 10 g/L deltamethrin. Treatments were applied at two rates = 0.25 mg/kg and 0.50 mg/kg deltamethrin. The commercial milling and pilot milling were performed by the Bread Research Institute of Australia (B.R.I.). The following cooked products were prepared by BRI: white bread, wholemeal bread, flat bread, steamed bread, yellow alkaline noodles and white salted noodles.

Samples were taken from treated wheat, milling fractions and cooked products and analysed for their deltamethrin content by Gas Liquid Chromatography equipped with an Electron Capture Detector.

Milling and baking trial done in France

Roussel Uclaf, Internal Report

216 t of soft wheat were treated in the silos of Grands Moulins de Pantin using a Vobamatic cold nebuliser mounted on the boot of an elevator (100t/hour grain flour) to apply an ULV formulation containing 6g/L of deltamethrin. The target dose was 0.5 mg/kg of deltamethrin but the calculated dose (measurement of the actually consumed product) was only 0.36 mg/kg.

6 days later the treated wheat was processed in the industrial milling facilities of the same company in Paris, following the standard milling process for commercial wheat. 15 different fractions were sampled. Some of these fractions were then utilised for preparing 3 kinds of bread, croissant and genoese cakes. All samples of wheat, fractions, fresh dough and baked foods were analysed for their deltamethrin content, using gas liquid chromatography with Electron Capture Detectors.

Trial done in France on animal feeds

G N Marti-Mestres et al. (1993), Montpellier University, France

3 t of soft wheat were treated in an automatic seed treatment line (capacity 30t/hour) with an EC formulation containing 25 g/L deltamethrin at a target dose of 1.2 mg/kg deltamethrin. The treated wheat was then milled into wholemeal flour and this flour was used as the basic feed source for piglets, laying hens and broilers throughout the current breeding period of these animals. An untreated 3 t batch of the same wheat was milled to produce an equivalent wholemeal flour used to feed control animals of the same age and body weight. The following observations were made on the animals during the trial: daily feed intake, daily weight gain and egg production, animal behaviour and side effects and slaughtering performance.

Deltamethrin residues on wheat were analysed after treatment and on wholemeal flour at intervals up to 360 days after treatment. Animal tissues were analysed: muscle, liver, kidney, fat for pigs, skin, muscle, liver and fat for broilers and whites and yolks for eggs.

Trial done in USA

J T Pitts, Gustafson Inc., Mckinney, Texas

Residue studies were conducted on grain and processed fractions to determine the residues of deltamethrin in or on the fractions as a result of application of deltamethrin to the grain as a postharvest protectant. The untreated grain was prepared, treated and samples processed into fractions. The treatment was performed using an EC formulation containing 25 g/L at a target rate of 0.5 mg/kg. The milling fractions sampled and analysed were flour, bran, middlings and shorts.

An additional study was done specifically on residues of deltamethrin on wheat dust. A known quantity of wheat grain dust was added to clean wheat grain, and the mixture treated with 0.5 mg/kg deltamethrin. Residues of deltamethrin were analysed in both grain and dust.

Results and Discussion

The fate of deltamethrin residues will be discussed for every step of the transformation of the wheat grains.

Step 1. Insecticide application

The yield rate of the application was extremely variable, especially for the 2 treatments performed in commercial installations: the French trial and the Italian trial.

In Italy, 20 samples collected from 7 different silos were analysed in 3 or 5 replicates. The results are shown in Table 1. The actual quantity of deltamethrin found on grain was between 10% and 68% of the calculated application rate, with an average of 37%. In the French trial deposits were found to be 17% to 24% of the calculated rate.

All these applications are done by sprayers or nebulisers intended to produce quite small droplets. We can suppose losses of the product are probably due to impaction on other surfaces and drift of droplets away from the grain.

Halls and Periam in the U.K. trial found around 40% of the applied dose in a semi-industrial application. Carefully managed and designed pilot plants generally achieve 70 to 80% yield rates, but we can assume that commercial spray applications are unlikely to deliver an actual deposit on grain of more than 50% of the targeted application rate of insecticide. This leaves the field open to devices for more accurate dosing, eg. by direct contact or rubbing on the grain layer.

Step 2. Grain storage

Although not being the purpose of this paper, it is well known that deltamethrin is fairly stable on dry wheat (Noble et al. 1982). Table 2 gives Australian data showing that losses at 6 months after application are about 20% of the actual initial deposit. Noble et al. (1982) found that deltamethrin on wheat stored at 25°C and 12% m.c. has a half-life of 114 weeks. Thus, the degradation of deltamethrin during the normal storage period of wheat is extremely limited.

Step 3. Cleaning

Prior to the milling process, the wheat has to be cleaned by means of sifters and dust collectors in order to remove dusts, seeds, straws, stones and soil particles and other foreign elements. In the Italian, French and American trials, specific studies have been performed on cleaning impurities, mainly dust, in terms of deltamethrin residues removed from the grain by this operation. In the Italian trial, 12 samples of treated grain were taken just before cleaning from inside the mill, as well as 12 samples of the dust impurities removed from this wheat after cleaning. All samples were analysed for their deltamethrin content. Results are shown in Table 3.

It is clear that the deltamethrin deposit is much higher on dust impurities than on the proper grain kernel, with a concentration factor varying from 5 to 72. It has not been possible in this industrial large scale trial to determine the exact % of impurities (in w/w) but it is likely to be lower than 1%, probably around 0.8%. Thus, about 20% of the total deltamethrin residue on grain at this stage of processing is removed by the cleaning operation.

In the French trial where the impurities were about 1.5% w/w, we found, for a targeted dose of 0.36 mg/kg 0.064 mg/kg on wheat before cleaning 0.337 mg/kg on impurities which means a concentration factor of 5.25 and 8% of the deltamethrin residue on grain removed by cleaning.

In the American trial, a batch of wheat was carefully cleaned and a known quantity of wheat dust was then added to the clean wheat (0.2% dust w/w). The dusted wheat was treated with deltamethrin and residues on re-cleaned wheat and separated dust gave the following results: targeted rate of application 0.5 mg/kg; first treatment, residue on cleaned wheat 0.31 mg/kg, residue on dust 41 mg/kg. concentration factor: 132; % of deltamethrin removed by the dust, 21%. second treatment; residue on cleaned wheat 0.38 mg/kg, residue on dust 37.5 mg/kg; concentration factor, 99. % of deltamethrin removed by the dust 16.6%.

The very consistent results of these trials confirm that the concentration of deltamethrin is clearly higher on the impurities than on the grain; the lower the % of impurities in grain, the higher the concentration of deltamethrin in these impurities; and the removal of the impurities by the cleaning process of cleaning wheat grain prior to milling it, removes about 20% of the total residues of deltamethrin.

Step 4. Milling

Table 4 gives the different procedures followed in the 5 trials. These processes reflect the different practices of each country in terms of transformation of wheat grain into products for the bakery. The process is basically a separation

Table 1. Italian trial application yield rate

Treatment site	Silo type	Formulation	Targeted rate mg/kg	Achieved rate mg/kg	Analysed rate mg/kg	Yield anal/ achieved %
Lendinara	Vertical	ULV	0.25	0.15	0.02	13
			0.50	0.31	0.02	10
			1.00	0.96	0.17	18
Lendinara	Horizontal	EC	0.25	0.25	0.12	48
			0.50	0.50	0.11	22
			1.00	1.00	0.21	21
Ponte a Rigo	Horizontal	EC	0.25	0.25	0.11	44
			0.50	0.50	0.32	64
			1.00	1.00	0.44	44
La Spezia	Vertical	ULV	0.25	0.19	0.09	47
			0.50	0.44	0.30	68
			1.00	1.03	0.30	31
Sangiorgio di Piano	Vertical	EC	0.25	0.23	0.07	30
			0.50	0.50	0.12	24
			1.00	1.10	0.17	15
Monte Pescali	Vertical	EC	0.25	0.25	0.13	52
			0.50	0.50	0.24	48
			1.00	1.00	0.28	28
Torrume	Horizontal	DP	1.00	1.03	0.47	47
			2.00	2.00	1.25	62

Table 2. Residues of deltamethrin (mg/kg) on grain stored for periods of up to 9 months at various temperature and moisture content combinations.

Mean temperature °C	Moisture content %	Months					
		0	1.5	3	4.5	6	9
27	12.3	0.20	0.20	0.14	0.14	0.15	0.17
28	11.0	0.27	0.21	0.23	—	0.19	—
22-15	10.8	0.14	0.12	0.15	0.11	0.16	—
27	9.7	0.14	0.09	0.12	0.13	0.11	0.10

between pericarp and endosperm of the grain kernel, i.e. between bran and flour. There are two interesting points to be noted: the Italian process includes a grain decortication by abrasion prior to grinding, which removes the pericarp roughness and impurities attached to the caryopsis; the French trial which gives a clear discrimination between the different origins of the flour in the wheat grain kernel (gradient from the pericarp to the centre of the endosperm).

In Table 5 the amounts of deltamethrin residues found in the different milling fractions are mentioned. To eliminate the variability of the initial treatment rates, they are expressed in ratios to the deltamethrin residues in wheat just before grinding. It clearly shows that the bulk of the deltamethrin deposit is on the pericarp (and its exterior part), the residues on flour being extremely low and even below the detection limit in the USA trial. In addition, the Italian process of abrasion of the grain kernels before grinding removes a lot of the deltamethrin deposit, giving further evidence that the penetration of the product through the pericarp is very limited. We can suspect that the deltamethrin content of the flour is caused by a contamination of this flour during the grinding process by contact with the bran. This is shown also to be the difference in residues between first break flour and bran finisher flour. Figure 1 illustrates the distribution of residues, showing that the amount of deltamethrin found in the standard flour does not exceed 30% of the total residue left in grain before milling. In these 5 trials, 101 analysis of standard flour have been performed, and the mean value of deltamethrin residues is 8.9% of the nominal application rate to wheat.

Step 5. Baking

The British, Italian, Australian and French trial included a pilot baking and/or cooking study. The results are summarised in Table 6. In the U.K. trial, the residual levels in baked bread are not lower than in the flour used for bread making, there is no apparent degradation during the baking. In Australia, the degradation during baking or cooking (noodles) varies between 10 and 50%, whereas the French trial shows up to 70% degradation. In Italy, deltamethrin residues were not detectable in the flour used for bread making and in the baked breads. The residues were also below detection limits in fresh, dried and cooked pasta.

Thus, it is quite difficult to draw conclusions about the degradation of deltamethrin during the baking and the cooking process.

Table 3. Deltamethrin (DTM) residue in dust impurities (Italian trial).

Treatment site	Targeted dose rate mg/kg	Actual DTM content in uncleaned grain mg/kg A	DTM content in dust impurities mg/kg B	Concentration factor B/A	Estimated DTM % removed by impurities[a]
San Giorgio	1	0.22	6.25	28	23
	1	0.45	2.47	5	4.5
	0.5	0.03	0.46	15	12
Lendinara	1	0.30	6.70	22	18
	1	0.30	6.76	22	18
	0.5	0.04	1.01	25	20
La Spezia	1	0.22	3.95	18	14
	1	0.05	0.88	18	14
Ponte a Rigo	1	0.36	8.41	23	19
	1	0.37	5.74	16	12
	0.25	0.06	4.33	72	58
	0.25	0.08	4.86	61	49

[a]Assuming a % w/w of impurities of 0.8%

Table 4. Chart of the wheat milling process by country

Milling fraction	U.K.	Italy	Australia	France	USA
Wholemeal flour	Wholemeal flour	—	—	—	—
Residue of decortication (abrasion)	—	Residuo decorticazione	—	—	—
Bran	Bran	Crusca	Bran	Son	Bran
Wheat meal (seed coats and some germ and some bran)	Offal	Farinaccio	Pollard	Remoulage	Shorts
Germ	—	—	Germ	Germe	—
First break flour (from centre of endosperm)	First reduction flour	—	Straight run flour	Farine ler claquage	—
Low grade flour	—	—	Last reduction flour	Farine basse	—
Bran finisher flour (closer to pericarp)	—	—	—	Farine de brosse	—
White flour (standard)	White flour	Farina	White flour	Farine 055	Flour

Step 6. Residues in tissues of animals fed with treated wheat

The targeted dose rate was 1.2 mg/kg of deltamethrin on wheat, i.e. 2.4 times the highest commercial rate. The achieved rate was 1.11 mg/kg on wheat and after grinding into wholemeal flour, the content in the flour was 0.95 mg/kg.

The levels of deltamethrin residues in the animal tissues are summarised in Table 7. In pork tissues, residues were below detection limit for kidney and liver (0.002 mg/kg), very close to detection limits for muscle, and a maximum of 0.03 mg/kg in fat, which can be expected from the high liposolubility of deltamethrin.

In broiler tissues, residues were below detection limits for muscle, fat and liver, but residues were found in the skin up to 0.01 mg/kg. This result was explained by the external pollution by the animal feeds on the feathers of broilers.

In eggs no detectable residue of deltamethrin was found. None of the observations on the animals during the experiment showed any significant difference between treated and control animals in terms of feeding behaviour or growth or production performances.

It was concluded that feeds based on deltamethrin-treated wheat at twice the recommended application rate have no influence on the animals. Deltamethrin residues remain at very low levels, below or close to detection limits, indicating that deltamethrin does not accumulate in animal products.

Table 5. Deltamethrin residues in the milling fractions: ratios to wheat (whole wheat = 100)

Milling fraction	U.K.	Italy	Australia	France	USA
Wholemeal flour	84 (8)	—	—	—	—
Residue of decortication (abrasion)	—	2500 (36)	—	—	—
Bran	450 (8)	330 (36)	(a) 290 (16) (b) 380 (16)	530 (1)	260 (2)
Wheat meal (endosperm and some germ and some bran)	90 (6)	—	(b) 200 (14)	320 (1)	67 (2)
Germ	—	—	(a) 88 (10) (b) 150 (14)	148 (1)	—
First break flour	8 (4)	—	(a) 38 (11) (b) 29 (13)	39 (1)	—
Low grade flour (last reduction)	—	—	(a) 45 (9) (b) 74 (14)	60 (1)	—
Bran finisher flour	—	—	—	270 (1)	—
White flour (standard)	16 (8)	36 (15)	(a) 45 (11) (b) 26 (14)	67 (1)	<4 (2)

Figures in brackets = number of analyses performed, (a) commercial milling (b) pilot milling

Table 6. Deltamethrin residues on flour, fresh dough and baked and cooked products (mg/kg)

France	Fresh dough	Baked products
Wholemeal bread	0.006	< 0.005
White bread traditional	0.006	< 0.005
White bread industrial	0.059	0.018
Croissants	0.028	< 0.005
Genoese cake	0.027	< 0.005

Australia initial application rate	0.25 mg/kg		0.50 mg/kg	
Sampling no.	1	2	1	2
Wholemeal	0.10	0.15	0.42	0.41
Wholemeal bread	0.07	0.04	0.24	0.15
Flat bread (90% wholemeal)	0.08	0.07	0.20	0.20
Flour	0.04	0.02	0.10	0.11
White bread	0.03	0.02	0.06	0.04
Steamed bread	0.02	0.02	0.06	0.06
Yellow noodles	0.02	0.02	0.09	0.07
White noodles	0.02	0.02	0.06	0.04

U.K. initial application rate	1 mg/kg				2 mg/kg			
Sampling no.	1	2	3	4	1	2	3	4
Flour	0.09	0.05	0.09	0.41	0.20	0.20	0.16	0.17
White bread	0.10	n.d.	0.10	0.05	0.29	0.15	0.20	0.11

Table 7. Deltamethrin residues (mg/kg) on tissues of animals fed on a diet based on treated wheat.

Pork	Muscle	Fat	Kidney	Liver
Control	< 0.002	< 0.002	< 0.002	< 0.002
Male	0.003	0.015	< 0.002	< 0.002
Female	0.002	0.03	< 0.002	< 0.002

Broilers	Muscle	Fat	Liver	Skin
Control	< 0.002	< 0.002	< 0.002	< 0.002
Treated	< 0.002	0.002	< 0.002	0.01

Eggs	Whole	Yolk	White
Control	< 0.002	< 0.002	< 0.002
Treated	< 0.002	< 0.002	< 0.002

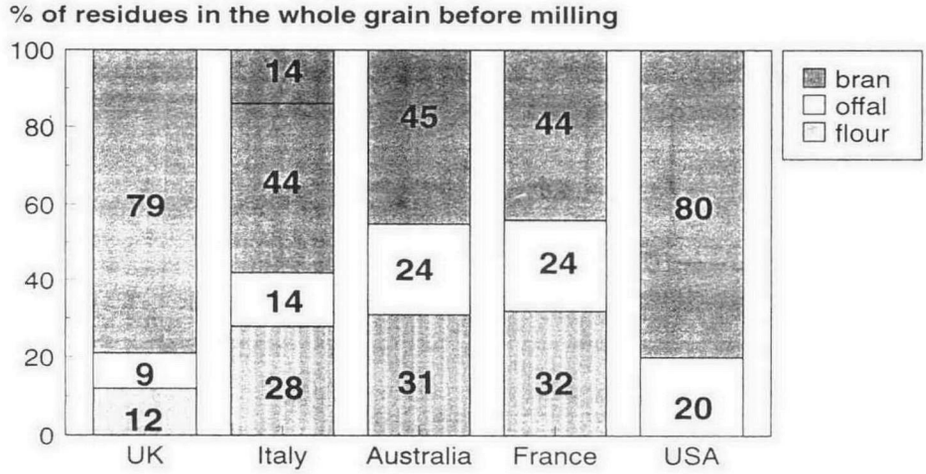

Fig. 1. Distribution of deltamethrin residues in the milling fraction (% of the residues in the whole grain before milling).

Conclusion

Out of the total quantity of deltamethrin applied to wheat for postharvest treatment the losses of insecticide during the various stages of processing are as follows:

- A large proportion is lost during the application, likely around 50% in commercial treatments units.
- A part is degraded (slowly) during the grain storage. But this is disregarded as the storage period may be short.
- A significant amount is removed with the impurities during the cleaning process. It can be estimated at around 10%.
- Another separation is done during the milling process, the less valuable fractions taking most of the residues. Amounts of 25% in bran and 5% in offal are most likely.
- The amount in the flour (10% of the initial applied product to wheat) is partly degraded during the cooking or baking process of the ultimate consumed foods.
- Meat and eggs produced by animals fed on a diet based on treated wheat have shown, extremely low, and more usually undetectable residues of deltamethrin.

The various studies described in this paper show that up to 90% of the nominal applied dose of deltamethrin has actually been lost or eliminated through the various steps of grain processing leading to the flour production. This has led to the setting of very low MRLs by CODEX and other national authorities.

Furthermore, it is to be noted that most large-scale storage facilities now use EC or ULV deltamethrin formulations (K-Obiol) containing piperonyl butoxide, an effective synergist of pyrethroids. This has allowed reduction of application rates from 1 mg/kg to 0.5 mg/kg. This additional factor contributes to maintain deltamethrin residues at levels well below MRLs in wheat grain and its fractions without the need of any with-holding period. It makes deltamethrin one of the most effective and residual grain insecticides in terms of international trading and one of the safest for the consumer.

References

F.A.O. 1993 Codex Alimentarius Commission — Codex Maximum limits for pesticide residues April 1993.

Marti- Mestres, G. N., Cooper, J.M.F., Mestres, J.P.M., De Wilde, G. and Wynn, N.R. 1993. Effects of a supplemented deltamethrin and piperonyl butoxide diet on residues in products of animal origin. Journal of Agricultural and Food Chemistry, 41, 2416–2420.

Noble, R.M., Hamilton, D.J. and Osborne, W.J. 1982. Stability of pyrethroids on wheat in storage. Pesticide Science 13, 246–252.

Snelson, J.T. 1987. Grain Protectants, ACIAR Monograph No. 3, 448 p.