HGCA

PROJECT REPORT No. 45

RESIDUES OF ETRIMFOS AND PIRIMIPHOS-METHYL IN WHEAT AND MALTING BARLEY STORED IN VENTILATED BINS

JANUARY 1992

PRICE £4.00

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RESIDUES OF ETRIMFOS AND PIRIMIPHOS-METHYL IN WHEAT AND MALTING BARLEY STORED IN VENTILATED BINS

by

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Final report of a project by CEM Analytical Services Ltd., The Williams Laboratory, Egham Hill, Egham, Surrey TW0 0EX. The Home-Grown Cereals Authority contributed a grant of £5,000 to enable completion of work at Hampshire Grain Ltd. in 1990 and 1991, initially funded by a consortium of commercial organisations contributing a total of £15,000 (HGCA Project No. 0053/1/91).

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Introduction

The Pesticides (Maximum Residue Levels in Food) Regulations 1988[1] require that certain foods should not contain residues of specified pesticides above a scheduled maximum residue level (MRL). Two schedules of MRLs have been published, the first of which came into force on August 2, 1988, and the second, specifying MRLs for UK approved post-harvest insecticides on cereals, on 31st December, 1988. It is intended to extend and revise the Regulations at regular intervals to take account of new pesticide introductions and to ensure that MRLs are as low as possible consistent with approved use of the pesticides.

These regulations, which give the Minister power to seize and dispose of a food should it have a residue level exceeding the MRL, have caused concern within the cereal trade. Although the decline of residues of pirimiphos-methyl and etrimfos has been investigated on an experimental (20 tonne) scale under ambient storage conditions in the UK[2], there is currently little or no information on the variation in residue levels in batches of grain treated at manufacturers' recommended rates under commercial conditions and using standard application equipment. Information on expected rates of disappearance of residues in grain stored at low temperatures following ambient or refrigerated aeration is also lacking. The possibility of migration of the residue within the grain bulk as a result of the aeration process has been investigated only for one insecticide[3]. The need for more information on these issues has been made urgent by the proposal in the third consultative document "Pesticides: Implementing Part III of the Food and Environment Protection Act, 1985"[4] issued by MAFF in June, 1991 that the maximum residue level for all insecticides currently approved in the UK for admixture in stored grain be reduced from 10 mg/kg to 5 mg/kg, a level only slightly above the manufacturers' recommended application rates.

Materials and Methods

Storage Site

The trial was carried out at Hampshire Grain Ltd, a cooperative grain storage unit at Micheldever Station, Hampshire. All grain-handling, treatment and storage operations connected with the trial were carried out according to the normal commercial practice of the store.

Grain treatment and storage

Grain loads delivered to the storage site by member farmers were routinely sampled on intake using a vacuum spear sampler. The resulting composite sample was analysed for quality and a sub-sample retained for reference purposes. Control samples for residue analysis were prepared using equal proportions of these reference sub-samples from the loads used to fill the monitored bins.

Pirimiphos-methyl was supplied as the Actellic D 25% EC formulation and etrimfos as the Satisfar 50% EC formulation. Dilution, mixing and application of the insecticides followed the normal practice of the store. The formulation concentrates were diluted to 1000 l according to manufacturer's recommendations and the diluted spray liquid pumped from the mixing tank to an enclosed spray nozzle positioned above the chain conveyer. Batches of grain were sprayed as they were conveyed from a 100 tonne holding bin into the storage bins. The mixing tank was emptied and rinsed between treatments using different insecticides. Required pump rates were calculated from the mean time to empty the holding bin through the spray, and measured spray flow rates recorded by store personnel for each batch treated. Because of the hot dry conditions in late summer 1990 wheat and barley crops were harvested below the required moisture contents and were not dried prior to insecticide treatment. Application was at ambient temperature (20° - 26°) according to the treatment schedule shown in Table 1.

Storage bins were of galvanised steel construction with nominal 700 or 800 tonne capacities (Figure 1). Filling of the monitored bins with treated grain took from 4 to 9 days.

Aeration

Each bin was fitted with an external aeration port leading to symmetrically-placed aeration ducts in the base. Top ventilation was provided by an inspection hatch which was opened during aeration cycles. The aeration fan (6.9 KW, axial, Figure 2) was switched on when the evening temperature was considered sufficiently cool and when dry weather was forecast.

Sampling of bins

Four fixed sampling pipes (1 - 1.25" dia.) were fitted to the top inspection hatch of each monitored bin prior to filling so that their bottom ends were positioned at the side and centre of the grain bulk (a) 2 m from the base, and (b) half way up the bin. Grain samples of 1-2 kg were taken using a vacuum sampler (Sample Seeker, Grain Care Ltd) fitted with plastic sampling pipes (i) from these fixed positions, and (ii) from 1.5 - 2.0 m below the surface of the grain bulk at the side closest to the inspection hatch and at the centre of the bin. The six samples were taken immediately after filling each bin and periodically thereafter. Sub-samples (approx. 100 g) were taken for moisture determination and the remainder labelled, sealed in polythene bags and immediately transported to CEM Analytical Services where they were stored at $< -18^{\circ}$ C prior to analysis. Sampling was continued until the grain bins were emptied.

Blockage of one of the sampling tubes prevented more than a single sample (day of treatment) being drawn from the centre/base sampling point in the bin containing wheat treated with pirimiphos-methyl.

Residue Analysis

Grain samples were divided twice using a Riffle divider and prepared by grinding to a fine powder. Analysis for pirimiphos methyl residues followed the manufacturer's recommended procedure[5]; analysis for etrimfos was by a modification of the manufacturer's procedure[6], as residue levels solely of the parent compound were required. Full details of analytical method modifications are given in CEMAS Analytical Report CEMR-048.

Statistical Analysis of Residue Data

Residue data from each bin were statistically analysed (2-way ANOVA) to determine if there was a significant change in mean residue level (all sampling points) over the storage period, and whether the mean residues for the storage period measured at the various sampling points within a bin differed significantly from each other.

The single datum from the centre/base sampling point of the bin containing wheat treated with pirimiphos-methyl was not included in the statistical analysis of residues from this bin. The residue concentration in a missing sample from the top/centre of the bin containing barley treated with etrimfos was substituted by an interpolated value[7].

Grain moisture content

Moisture contents were determined by the oven method (BS 4317/ISO 712) and calculated as a percentage of the wet weight of the grain.

Grain temperature and ambient shade temperature

Monitored bins were fitted with two sets of three fixed thermocouples placed symmetrically within the grain bulk at approximately one third and two thirds of the bin height. These provided continuous temperature measurements which were recorded at the beginning and end of each aeration cycle and at weekly intervals. Maximum and minimum ambient shade temperatures were recorded at the base of one of the monitored bins at weekly intervals.

Results

Grain Treatment

Monitored application rates for insecticide applied to batches of wheat and barley are shown in Table 2. Intended application rates were not achieved for some of the wheat batches due to a malfunctioning spray pump.

Residues

Table 6 gives a summary of residue concentrations from the various sampling positions in the four monitored bins at various times after treatment. Details of the analytical procedures and results have been reported elsewhere[8]. Samples of wheat and barley treated with etrimfos taken 5 and 10 days after treatment were not analysed.

There was no significant difference between the means of the residues (taken over all sampling points) at different sampling times, implying no evidence for any decline in residue levels with time for any of the insecticides in any of the bins.

The residue data provide no evidence for significant upward movement of insecticide in the bins as a result of re-distribution in the vapour phase during aeration of the grain. Such an effect would cause a higher mean residue in samples from the top and middle sampling points than in those from the base, and its magnitude would be related to the total time for which the bin was aerated and the temperature of the air used. The bins containing wheat were aerated for a total of 362 h (etrimfos) and 391.5 h (pirimiphos-methyl) and much of this aeration took place when ambient minimum temperatures were above 10° C; those containing barley were aerated for 128 h (etrimfos) and 57 h (pirimiphos-methyl) when minimum ambient temperatures were considerably cooler. Residue data for bins containing barley were therefore not considered in relation to any potential redistribution effects. The mean residues in the three sections of both wheat bins (taken over all sampling times) vary as top > middle > base, but the differences are of the same order of magnitude as the standard deviations of these means and smaller than some of the differences between mean residues at the centre and side of a bin in a given section.

In each of the bins there was a significant difference between the means of the residues (taken over all sampling times) at the various sampling points ($p < 0.01$). This was expected in the case of the bins containing treated wheat in view of the variation in application rates applied to some of the batches loaded into these bins (Table 2). However, in the case of bins containing barley for which the monitored application rates should have resulted in even treatment at the intended residue levels, not only was the difference between the means of the residues at different sampling points significant, but the coefficients of variation in mean residue levels for samples taken at a single sampling point had a greater range (0.08 - 0.42) than for the wheat samples (0.09 - 0.29) (Table 6). These results imply either considerable heterogeneity in the distribution of residues in the grain in the immediate vicinity of each sampling point, or greater than expected variation due to analytical procedures.

This large variance in residue levels in samples taken from a single sampling point over the sampling period could result from: variation and fluctuations in insecticide concentration applied to the grain in the conveyer; local segregation of dust, chaff and lighter grains during bin loading; variability in extraction of the residue from the sample matrix; and variability in procedures associated with sample clean-up and analytical determination. The contribution from the last of these sources is relatively small, as can be seen from the procedural recovery determinations associated with each sample batch analysis (Table 8). No data is available on the performance of the pump and spraying equipment used in the grain store; storage stability/extractability studies for etrimfos and pirimiphos-methyl residues in wheat and barley have not been published. The proportion of fines in samples taken with a vacuum sampler may increase with the depth of the sample in the bin. A survey of the effect of sampling methods from static grain bulks on sample composition has recently been published[9].

Grain Moisture Content

Grain moisture contents did not vary significantly over the storage period in any of the monitored bins (Table 5).

Grain Temperature

Grain temperatures in bins filled with barley in October were rapidly reduced by aeration. A total of 57 h aeration during a period when minimum temperatures ranged from 2-5° C was sufficient to reduce the temperature in the pirimiphos-methyl-treated barley from 21° to 12°; a total of 128 h aeration was required to effect a similar reduction in temperature in the etrimfos-treated barley when minimum temperatures ranged from 3-10° C. Temperatures in bins filled with wheat in middle to late August took longer to bring down to safe levels, partly because the initial grain temperatures were higher and partly because of higher minimum ambient temperatures (343 h to reduce the temperature of etrimfos-treated wheat from 23.5° to 12.1° C; 373 h to reduce the temperature of pirimiphos-methyl-treated wheat from 26° to 11.8° C). Aeration cycles, grain temperatures and weekly ambient maximum and minimum temperatures are shown in Tables 3, 4 and 7 respectively.

Conclusions

1. This trial was carried out in a well-managed co-operative grain store with grain-handling and treatment operations carried out by trained and experienced personnel. The results therefore provide a fair indication of the extent to which the requirements of the Pesticides (Maximum Residue Levels in Food) Regulations 1988 for insecticide residues in grain can be met by the industry using current commercial practice.

2. No evidence was obtained for any residue decay of either pirimiphos-methyl or etrimfos on wheat over a storage period of 35 weeks or on barley over a storage period of 30 weeks under the storage conditions described in this report.

3. Mean insecticide residues on the barley samples were close to the values calculated from the monitored application rates. Although individual samples contained residue levels above 5 mg/kg, the mean residue from the six sampling points in both bins remained in the range 3.7 - 4.8 mg/kg throughout the trial.

4. Insecticide residues in wheat samples were lower than those calculated from the reported application rates, and no sample gave a residue greater than 2.7 mg/kg. Some apparent loss of residue is not uncommon in insecticide trials on wheat, and reasons for the effect have been discussed by Snelson[5]. However, as malfunctioning application equipment may result in overdosing as well as underdosing, it is important that a continuous record of grain treatment is available and installation of suitable equipment to provide such a record is recommended.

In view of the narrow margin between the proposed MRL for etrimfos and pirimiphos-methyl on cereals and the mean residues found in this trial it is recommended that calibration of application equipment is carried out on a regular basis during grain treatment and that records of this calibration and of pesticide use are maintained on the site.

5. No evidence for redistribution of insecticide was found in the bins containing wheat despite prolonged aeration at temperatures above 10° C.

6. Considerable variation in residue levels of samples drawn from different positions in the bin on a single sampling date was found. This variation was, on average, greater than the variation between residues in samples drawn from the same sampling position over the period

of the trial. Similar results were obtained by Minnett et al. (1984)[6] when sampling from a bin containing wheat treated with fenitrothion, and the effect is discussed by Snelson[5] on the basis of particle segregation by density when grain is loaded into bins. The overall variability in residue levels in samples is presumably due to a combination of fluctuations in application rate, segregation of grains of different density during conveying and loading, separation and local concentration of chaff and dust, extractability of residues from the grain and variation in analytical procedures. Because of the probable variation in residue levels in samples taken from bins or lorries, grain sampling procedures for enforcement of MRLs need to be specified and independently validated by the industry.

Acknowledgements

The author gratefully acknowledges the cooperation and assistance of Mike Clay and Bob Goldsmith of Hampshire Grain Ltd. who set up the sampling stations at short notice and provided records of grain treatment and temperature measurements. Margaret Groves (Southern Counties Agricultural Trading Society Ltd) carried out moisture content determinations throughout the trial. Residue determinations were carried out at CEM Analytical Services by Steve Kennedy and Mike Farrell.

The following organisations contributed to the funding of this work:

CEM Analytical Services
Continental U.K. Ltd
Hampshire Grain Ltd
Home Grown Cereals Authority
ICI Agrochemicals
Pauls Malt Ltd
Sandoz Products Ltd
Southern Counties Agricultural Trading Society Ltd
Segrain Ltd
J Soufflet (UK) Ltd
Weald Granary Ltd
Wiltshire Grain Ltd

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TABLE 1: NOMINAL STORAGE CAPACITIES OF MONITORED BINS AND MANUFACTURERS' RECOMMENDED APPLICATION RATES FOR INSECTICIDES

cereal	varieties	treatment	application rate (g AI/tonne)	storage bin capacity (tonne)
barley	Halcyon	Actellic EC	4.0	700
barley	Pipkin	Satisfar EC	4.2	800
wheat	Avalon/Mercia/ Apollo	Actellic EC	4.0	700
wheat	Pastiche	Satisfar EC	4.2	700

TABLE 2: RECORD OF GRAIN TREATMENT*

grain and treatment	weight** (tonnes)	load ref.**	grain flow rate (tonne/h)	pump rate (l/h)	formulation concn. (ml/l)	calculated application (g AI/tonne)
barley	24.97	1782	30	22	10.66	4.1
(Pipkin)	25.23	1783	"	"	"	"
+	25.61	1786	"	"	"	"
Satisfar	26.68	1788	"	"	"	"
50% EC***	25.45	1789	"	"	"	"
(etrimfos)	24.35	1790	"	"	"	"
	23.52	1801	"	"	"	"
	24.99	1806	"	"	"	"
	24.51	1808	"	"	"	"
	24.33	1811	"	"	"	"
	25.32	1816	"	"	"	"
	18.25	1819	"	"	"	"
	18.69	1822	"	"	"	"
	18.99	1828	"	"	"	"
	24.22	1832	"	"	"	"
	19.84	1831	"	"	"	"
	30.08	1836	"	"	"	"
	25.63	1838	"	"	"	"
	16.03	1840	"	"	"	"
	19.46	1842	"	"	"	"
	25.67	1843	"	"	"	"
	24.56	1844	"	"	"	"
	19.56	1847	"	"	"	"
	14.21	1850	"	"	"	"
	28.00	1857	"	"	"	"
	20.09	1779	"	"	"	"
	24.91	1780	"	"	"	"
	3.85	1781	"	"	"	"

* data supplied by Hampshire Grain Ltd.

** order of load references and weights refers to deliveries into the store; this order is changed during conveying to/from holding bins prior to treatment.

*** calculated at 525 g AI/l[12]

TABLE 2 (Contd.): RECORD OF GRAIN TREATMENT[1]

grain and treatment	weight** (tonnes)	load ref.**	grain flow rate (tonne/h)	pump rate (l/h)	formulation concn. (ml/l)	calculated application (g AI/tonne)
barley	22.44	1797	30	22	21.3	3.9
(Halcyon)	17.88	1799	"	"	"	"
+	20.11	1802	"	"	"	"
Actellic D	17.93	1805	"	"	"	"
25% EC***	19.23	1807	"	"	"	"
(pirimiphos	24.76	1809	"	"	"	"
methyl)	18.96	1812	"	"	"	"
	25.67	1813	"	"	"	"
	22.76	1817	"	"	"	"
	19.35	1818	"	"	"	"
	19.64	1820	"	"	"	"
	19.40	1826	"	"	"	"
	21.86	1827	"	"	"	"
	23.40	1833	"	"	"	"
	25.91	1839	"	"	"	"
	16.88	1845	"	"	"	"
	25.90	1841	"	"	"	"
	24.60	1851	"	"	"	"
	19.27	1855	"	"	"	"
	9.79	1859	"	"	"	"
	25.26	1861	"	"	"	"
	27.46	1863	"	"	"	"
	24.26	1865	"	"	"	"
	20.24	1866	"	"	"	"
	24.34	1867	"	"	"	"
	26.52	1868	"	"	"	"
	22.95	1870	"	"	"	"
	24.15	1872	"	"	"	"
	16.49	1875	"	"	"	"
	22.16	1882	"	"	"	"
	10.61	1885	"	"	"	"

* data supplied by Hampshire Grain Ltd.

** order of load references and weights refers to deliveries into the store; this order is changed during conveying to/from holding bins.

*** calculated at 250 g AI/l[12]

TABLE 2 (Contd.): RECORD OF GRAIN TREATMENT*

grain and treatment	weight** (tonnes)	load ref.**	grain flow rate (tonne/h)	pump rate (l/h)	formulation concn. (ml/l)	calculated application (g AI/tonne)
wheat	24.62	0265	30	22	10.66	4.10
(Pastiche)	28.43	5635	"	"	"	"
+	27.52	5633	"	"	"	"
Satisfar	28.60	5636	"	"	"	"
50% EC***	23.80	0266	"	"	"	"
(etrimfos)	27.64	2112	"	"	"	"
	26.50	0267	"	12	"	2.24
	26.96	5640	"	"	"	"
	26.57	5639	"	"	"	"
	27.52	5633	"	"	"	"
	27.58	5641	"	22	"	4.10
	27.00	5642	"	"	"	"
	29.65	5643	"	"	"	"
	28.41	2172	"	"	"	"
	8.22	2173	"	12	"	2.24
	29.65	5643	"	"	"	"
	28.41	2172	"	22	"	4.10
	8.20	2173	"	"	"	"
	25.14	5253	"	"	"	"
	27.52	5778	"	"	"	"
	26.48	5779	"	"	"	"
	27.62	5780	"	"	"	"
	26.78	5781	"	12	"	2.24
	25.53	5782	"	"	"	"
	26.94	5783	"	"	"	"
	26.43	5132	"	22	"	4.10
	28.11	5133	"	"	"	"
	27.00	5134	"	"	"	"
	27.55	5135	"	"	"	"
	26.14	5136	"	"	"	"
	18.84	5137	"	"	"	"
	25.34	4807	"	"	"	"

* data supplied by Hampshire Grain Ltd.

** order of load references and weights refers to deliveries into the store; this order is changed during conveying to/from holding bins.

*** calculated as 525 g AI/l[12]

TABLE 2 (Contd.): RECORD OF GRAIN TREATMENT*

grain and treatment	weight** (tonnes)	load ref.**	grain flow rate (tonne/h)	pump rate (l/h)	formulation concn. (ml/l)	calculated application (g AI/tonne)
wheat	24.79	5918	30	22	21.3	3.9
(Avalon/	25.87	5919	"	"	"	"
Mercia/	24.16	5504	"	"	"	"
Apollo)	24.17	0357	"	"	"	"
+	6.25	2195	"	"	"	"
Actellic	16.21	0358	"	"	"	"
25% EC***	29.68	0360	"	17	"	3.0
(pirimiphos	39.54	0362	"	"	"	"
methyl)	15.61	0255	"	"	"	"
	28.01	0172	"	"	"	"
	25.90	5005	"	"	"	"
	24.32	0355	"	22	"	3.9
	24.26	0356	"	"	"	"
	25.09	5878	"	"	"	"
	26.77	5986	"	"	"	"
	24.28	0170	"	"	"	"
	27.31	0359	"	"	"	"
	23.96	5506	"	"	"	"
	24.54	5987	"	"	"	"
	23.68	0171	"	"	"	"
	26.49	0361	"	"	"	"
	16.72	2198	"	"	"	"
	28.83	5023	"	"	"	"
	21.32	2199	"	"	"	"
	26.58	5007	"	"	"	"
	24.96	4962	"	"	"	"
	24.33	5006	"	"	"	"
	24.32	0430	"	"	"	"
	29.67	3583	"	"	"	"

* data supplied by Hampshire Grain Ltd.

** order of load reference and weight refers to deliveries into the store; this order is changed during conveying to/from holding bins.

*** calculated as 525 g AI/l[12]

TABLE 3: RECORD OF GRAIN AERATION*

grain	treatment	date	aeration time (h)
barley (Pipkin)	etrimfos	03.10.90	16.0
		09.10.90	15.0
		22.10.90	18.0
		23.10.90	19.0
		31.10.90	20.0
		01.11.90	21.0
		08.11.90	19.0
barley (Halcyon)	pirimiphos methyl	02.11.90	18.0
		05.11.90	20.0
		08.11.90	19.0
wheat (Pastiche)	etrimfos	20.08.90	20.0
		22.08.90	15.5
		23.08.90	12.0
		24.08.90	16.0
		30.08.90	17.0
		04.09.90	19.0
		05.09.90	14.0
		06.09.90	18.0
		07.09.90	18.0
		10.09.90	18.0
		11.09.90	15.0
		13.09.90	16.0
		17.09.90	15.0
		24.09.90	20.0
		01.10.90	16.5
		09.10.90	15.0
		23.10.90	19.0
		31.10.90	20.0
		01.11.90	21.0
		02.11.90	18.0
		05.11.90	20.0
		08.11.90	19.0

data supplied by Hampshire Grain Ltd

TABLE 3 (contd.): RECORD OF GRAIN AERATION*

grain	treatment	date	aeration time (h)
wheat (Avalon/ Mercia/ Apollo)	pirimiphos methyl	20.08.90	7.0
		21.08.90	24.0
		22.08.90	15.5
		23.08.90	12.0
		24.08.90	16.0
		30.08.90	15.0
		04.09.90	19.0
		05.09.90	14.0
		06.09.90	18.0
		10.09.90	18.0
		11.09.90	19.0
		13.09.90	16.0
		17.09.90	15.0
		08.10.90	16.0
		09.10.90	15.0
		23.10.90	19.0
		31.10.90	20.0
		01.11.90	21.0
		02.11.90	18.0
		05.11.90	17.0
		06.11.90	20.0
		08.11.90	19.0
		20.11.90	18.0

* data supplied by Hampshire Grain Ltd

TABLE 4: GRAIN TEMPERATURES IN MONITORED BINS*

grain	treatment	date	days after treatment**	temperature (°C)	s.d.	n
barley (Halcyon)	pirimiphos methyl	22.10.90	-1	20.0	1.9	6
		29.10.90	6	21.0	3.6	5
		05.11.90	13	12.0	2.3	5
		12.11.90	20	10.9	1.1	5
		19.11.90	27	10.9	0.9	5
		26.11.90	34	10.6	0.9	5
		03.12.90	41	11.0	0.8	5
		10.12.90	48	10.3	0.7	6
		17.12.90	55	10.1	0.8	5
		07.01.91	76	9.2	0.6	4
		14.01.91	83	8.9	0.6	4
		21.01.91	90	8.7	0.6	4
		28.01.91	97	8.6	0.5	4
		04.02.91	104	8.1	0.6	5
		11.02.91	111	8.1	0.5	4
		18.02.91	118	7.8	0.6	5
		25.02.91	125	7.9	0.4	4
		04.03.91	132	7.5	0.5	4
		11.03.91	137	7.2	0.5	4
		25.03.91	151	7.2	0.4	4
		02.04.91	159	7.4	0.4	4
		08.04.91	165	7.3	0.4	4
		15.04.91	172	7.3	0.4	4
		22.04.91	179	7.3	0.3	4
		29.04.91	186	7.5	0.3	4
		07.05.91	194	7.5	0.2	4

* data supplied by Hampshire Grain Ltd

** date of treatment of last batch loaded into the bin

TABLE 4 (contd.): GRAIN TEMPERATURES IN MONITORED BINS*

grain	treatment	date	days after treatment**	temperature (°C)	s.d.	n
barley (Pipkin)	etrimfos	02.10.90	4	20.5	2.0	6
		08.10.90	10	19.7	2.5	6
		15.10.90	17	16.9	2.7	6
		22.10.90	24	15.6	1.1	6
		29.10.90	31	14.8	1.5	6
		05.11.90	38	13.0	2.3	6
		12.11.90	45	11.9	2.0	6
		19.11.90	52	11.7	1.7	6
		26.11.90	59	9.2	1.8	6
		03.12.90	66	9.1	2.0	6
		10.12.90	73	8.1	2.3	6
		17.12.90	80	7.8	2.4	6
		07.01.91	101	7.0	1.7	6
		14.01.91	108	6.6	1.7	6
		21.01.91	115	6.5	1.6	6
		28.01.91	122	6.2	1.8	6
		04.02.91	129	5.5	2.4	6
		11.02.91	136	5.9	1.5	5
		18.02.91	143	5.8	1.6	5
		25.02.91	150	5.4	1.2	6
		04.03.91	157	5.3	1.1	6
		11.03.91	164	5.6	0.7	6
		25.03.91	178	6.2	0.4	6
		02.04.91	185	6.8	0.4	6
		08.04.91	191	6.6	0.5	6

* data supplied by Hampshire Grain Ltd
** date of treatment of last batch loaded into the bin

TABLE 4 (contd.): GRAIN TEMPERATURES IN MONITORED BINS*

grain	treatment	date	days after treatment**	temperature (°C)	s.d.	n
wheat (Avalon/ Mercia/ Apollo)	pirimiphos methyl	20.08.90	0	26.0	4.6	6
		28.08.90	8	23.5	2.2	6
		03.09.90	15	20.8	2.6	6
		10.09.90	22	15.7	0.7	6
		17.09.90	29	16.8	0.8	6
		24.09.90	36	16.7	1.0	6
		02.10.90	43	16.8	0.8	6
		08.10.90	49	17.0	0.7	6
		15.10.90	56	16.9	1.0	6
		22.10.90	63	16.2	1.1	6
		29.10.90	70	16.3	1.0	6
		05.11.90	77	13.3	2.2	6
		12.11.90	84	11.8	1.0	6
		19.11.90	91	11.7	0.9	6
		26.11.90	98	11.3	0.6	6
		03.12.90	105	11.5	0.6	6
		10.12.90	112	11.1	0.5	6
		17.12.90	119	11.1	0.4	6
		07.01.91	140	10.2	0.4	6
		14.01.91	147	9.8	0.4	6
		21.01.91	154	9.7	0.4	6
		28.01.91	161	9.6	0.4	6
		04.02.91	168	9.3	0.5	6
		11.02.91	175	9.0	0.5	6
		18.02.91	182	9.0	0.5	6
		25.02.91	189	8.9	0.6	6
		04.03.91	196	8.7	0.6	6
		11.03.91	203	8.3	0.6	6
		25.03.91	217	8.1	0.5	6
		02.04.91	224	8.3	0.5	6
		08.04.91	230	8.1	0.5	6
		15.04.91	237	8.1	0.5	6
		22.04.91	244	7.9	0.5	6
		29.04.91	251	8.0	0.5	6
		07.05.91	259	8.0	0.5	5

* data supplied by Hampshire Grain Ltd
** date of treatment of last batch loaded into the bin

TABLE 4 (contd.): GRAIN TEMPERATURES IN MONITORED BINS*

grain	treatment	date	days after treatment**	temperature (°C)	s.d.	n
wheat (Pastiche)	etrimfos	20.08.90	5	23.5	1.9	6
		23.08.90	8	24.6	2.3	6
		03.09.90	19	22.3	3.0	6
		10.09.90	26	17.2	0.9	6
		17.09.90	33	18.8	1.0	6
		24.09.90	40	17.6	0.8	6
		02.10.90	48	16.6	1.5	6
		08.10.90	54	17.0	1.7	6
		15.10.90	61	18.0	2.2	6
		22.10.90	68	17.5	1.3	6
		29.10.90	75	17.6	1.1	6
		05.11.90	82	12.1	1.6	6
		12.11.90	89	11.2	0.8	6
		19.11.90	96	11.4	0.7	6
		26.11.90	103	11.0	1.0	6
		03.12.90	110	11.4	0.7	6
		10.12.90	117	10.7	0.9	5
		17.12.90	124	10.5	1.2	6
		07.01.91	145	10.6	0.8	6
		14.01.91	152	10.2	0.7	6
		21.01.91	159	10.1	0.6	6
		28.01.91	166	10.4	0.6	6
		04.02.91	173	10.5	0.3	6
		11.02.91	180	10.5	0.2	6
		18.02.91	187	10.3	0.7	6
		25.02.91	194	10.6	0.4	6
		04.03.91	201	10.5	0.4	5
		11.03.91	208	10.1	0.6	6
		25.03.91	222	9.8	0.6	5
		02.04.91	229	10.0	0.6	6
		08.04.91	235	9.9	0.6	6
		15.04.91	242	9.6	0.7	6
		22.04.91	249	9.5	0.6	6
		29.04.91	256	9.5	0.6	6
		07.05.91	264	9.1	0.6	6

* data supplied by Hampshire Grain Ltd
** date of treatment of last batch loaded into the bin

TABLE 5: GRAIN MOISTURE CONTENTS* (Oven Method to BS 4317/ISO 712)

grain	treatment	date	days after treatment**	moisture content (%)	s.d.	n
barley (Halcyon)	pirimiphos methyl	23.10.90	0	12.3	0.2	6
		29.10.90	6	12.5	0.1	6
		05.11.90	13	12.4	0.2	6
		27.11.90	35	12.7	0.2	6
		02.01.90	71	12.5	0.5	6
		21.01.91	90	12.3	0.1	6
		23.05.91	212	12.4	0.4	6
barley (Pipkin)	etrimfos	01.10.90	3	12.0	0.3	6
		05.10.90	7	12.1	0.3	6
		10.10.90	12	12.3	0.2	6
		29.10.90	31	12.2	0.1	6
		27.11.90	60	12.2	0.2	6
		02.01.90	96	12.0	0.4	6
		30.01.91	124	12.2	0.2	5
		02.04.91	186	12.5	0.2	6
wheat (Avalon/ Mercia/ Apollo)	pirimiphos methyl	20.08.90	0	13.2	0.7	6
		25.08.90	5	12.9	1.5	4
		30.08.90	10	13.5	0.6	5
		20.09.90	31	13.2	0.7	5
		19.10.90	60	13.2	0.3	5
		27.11.90	99	13.4	0.5	5
		17.12.90	119	13.2	0.6	5
		21.01.91	155	13.2	0.6	5
		22.02.91	185	13.4	0.6	5
		18.04.91	240	13.1	0.4	5
wheat (Pastiche)	etrimfos	15.08.90	0	11.4	0.9	6
		20.08.90	5	11.8	1.1	6
		25.08.90	10	11.7	0.8	6
		14.09.90	30	11.3	0.8	6
		15.10.90	61	11.6	0.5	6
		16.11.90	93	11.6	0.6	5
		17.12.90	124	11.7	0.4	6
		15.02.91	184	11.7	0.5	6
		18.04.91	245	11.1	1.5	6

* data supplied by Southern Counties Agricultural Trading Society Ltd.
** date of treatment of last batch loaded into the bin

TABLE 6: RESIDUE CONCENTRATIONS OF ETRIMFOS AND PIRIMIPHOS-METHYL IN TREATED GRAIN*

grain	treatment	D.A.T.**	residue concentration (mg/kg)					
			Sampling Position in Bin					
			top		middle		base	
			centre	side	centre	side	centre	side
barley (Halcyon)	pirimiphos methyl	0	4.9	4.5	4.3	3.9	2.2	4.4
		6	5.5	4.6	4.9	3.9	3.9	5.4
		13	5.4	4.5	4.5	4.1	2.0	4.4
		35	5.6	5.0	5.8	4.6	2.5	2.9
		70	4.4	4.5	5.8	3.9	4.6	2.9
		90	6.8	4.3	2.4	5.2	4.7	5.1
		122	4.7	4.4	5.2	3.9	3.3	3.8
		181	5.7	6.7	5.8	4.0	1.3	4.5
		210	4.4	4.3	6.3	3.5	2.0	4.2
		mean	5.3	4.8	5.0	4.1	2.9	4.2
		c.v.	0.14	0.16	0.24	0.31	0.42	0.21
barley (Pipkin)	etrimfos	0	2.3	3.3	5.7	2.5	5.9	5.0
		31	3.6	4.2	6.3	2.9	6.7	6.1
		60	2.9	2.2	4.3	2.5	5.5	5.5
		96	2.3	3.2	4.1	2.3	6.0	5.3
		124	2.7	2.6	5.2	2.8	5.3	5.7
		185	2.8	2.2	3.3	5.5	5.4	6.5
		193	3.0***	2.5	6.0	3.5	5.7	5.6
		mean	2.8	2.9	5.0	3.1	5.8	5.7
		c.v.	0.31	0.25	0.22	0.35	0.08	0.09

* data supplied by CEM Analytical Services Ltd.
** days after treatment of last batch loaded into bin
*** estimated value[7]

TABLE 6 (contd.) RESIDUE CONCENTRATIONS OF ETRIMFOS AND PIRIMIPHOS-METHYL IN TREATED GRAIN*

grain	treatment	D.A.T.**	residue concentration (mg/kg)					
			Sampling Position in Bin					
			top		middle		base	
			centre	side	centre	side	centre	side
wheat (Avalon/ Mercia/ Apollo)	pirimiphos methyl	0	1.9	1.9	0.65	1.5	1.5	1.2
		5	2.6	1.4	1.0	1.2	-	1.1
		10	1.7	2.5	1.0	1.3	-	1.3
		32	1.7	1.5	0.63	1.2	-	1.2
		60	2.5	1.5	0.53	0.76	-	1.4
		99	2.3	2.0	0.83	1.2	-	1.0
		119	1.8	1.7	0.56	1.3	-	1.2
		154	2.1	1.4	0.50	1.3	-	0.67
		186	1.6	1.7	0.72	1.9	-	0.74
		211	1.4	2.0	0.72	1.8	-	0.68
		240	1.3	2.1	0.90	1.4	-	0.96
		mean	1.9	1.8	0.73	1.4		1.0
		c.v.	0.23	0.19	0.26	0.23		0.24
wheat (Pastiche)	etrimfos	0	2.7	1.1	0.89	1.4	0.63	1.0
		30	2.7	1.3	1.9	1.7	1.0	0.88
		61	2.1	1.3	1.5	1.2	0.93	0.75
		93	2.2	1.4	1.8	1.6	1.2	1.0
		124	2.1	1.6	1.9	1.5	1.6	0.99
		184	1.9	1.8	1.6	1.4	1.6	1.5
		216	1.8	1.6	1.5	1.2	1.1	0.79
		245	2.2	1.7	1.9	1.4	1.1	1.0
		mean	2.2	1.4	1.6	1.4	1.2	1.0
		c.v.	0.15	0.20	0.21	0.09	0.29	0.23

* data supplied by CEM Analytical Services Ltd.
** days after treatment of last batch loaded into the bin

TABLE 7: MAXIMUM AND MINIMUM AMBIENT SHADE TEMPERATURES AT STORAGE SITE*

date	temperature (°C) maximum	minimum
20.08.90	18	13
23.08.90	25	14
03.09.90	22	12
10.09.90	20	9
17.09.90	20	10
24.09.90	20	7
02.10.90	18	7
08.10.90	16	3
15.10.90	20	10
22.10.90	16	10
29.10.90	15	5
05.11.90	12	2
12.11.90	12	3
19.11.90	13	6
26.11.90	5	1
03.12.90	6	3
10.12.90	6	0
17.12.90	7	-2
07.01.91	10	-1
14.01.91	9	-1
21.01.91	8	-1
28.01.91	7	1
04.02.91	4	-3
11.02.91	0	-8
18.02.91	7	-8
25.02.91	9	-1
04.03.91	9	1
11.03.91	11	7
25.03.91	15	0
02.04.91	15	0
08.04.91	12	2
15.04.91	14	4
22.04.91	14	1
29.04.91	14	4
07.05.91	10	4

* data supplied by Hampshire Grain Ltd

TABLE 8: PERCENTAGE RECOVERY OF INSECTICIDES FROM PREPARED GRAIN SAMPLES FORTIFIED WITH ANALYTICAL STANDARDS AND TAKEN THROUGH SAMPLE CLEAN-UP AND ANALYSIS PROCEDURES*

CEM batch No.	insecticide	cereal	fortification level (mg/kg)	recovery (%)
128/91	etrimfos	wheat	2.0	97
128/91			2.0	102
132/91			2.0	95
132/91			2.0	97
133/91			2.0	100
133/91			2.0	102
134/91			2.0	98
134/91			2.0	93
124/91			4.0	98
124/91			4.0	96
125/91			4.0	102
125/91			4.0	101
126/91			4.0	108
126/91			4.0	113
127/91			4.0	101
127/91			4.0	106
212/91	etrimfos	barley	2.0	88
211/91			2.0	92
210/91			2.0	95
209/91			2.0	89
208/91			2.0	90
207/91			2.0	92
206/91			2.0	88
207/91			4.0	93
206/91			4.0	95
212/91			6.0	93
211/91			6.0	106
210/91			6.0	95
209/91			6.0	92
208/91			6.0	95

* data supplied by CEM Analytical Services Ltd.

TABLE 8 (Contd.): PERCENTAGE RECOVERY OF INSECTICIDES FROM PREPARED GRAIN SAMPLES FORTIFIED WITH ANALYTICAL STANDARDS AND TAKEN THROUGH SAMPLE CLEAN-UP AND ANALYSIS PROCEDURES*

CEM Batch No.	insecticide	cereal	fortification level (mg/kg)	recovery (%)
154/90	pirimiphos-methyl	wheat	1.0	91
155/90			1.0	103
156/90			1.0	92
157/90			1.0	92
198/90			1.0	91
019/91			1.0	81
020/91			1.0	93
063/91			1.0	88
064/91			1.0	97
065/91			1.0	97
153/90			2.0	90
154/90			2.0	94
155/90			2.0	97
156/90			2.0	95
157/90			2.0	84
198/90			2.0	92
019/91			2.0	82
020/91			2.0	94
063/91			2.0	96
064/91			2.0	95
065/91			2.0	105
153/90			4.0	98
199/90	pirimiphos-methyl	barley	1.0	103
199/90			2.0	98
200/90			2.0	93
201/90			2.0	97
202/90			2.0	101
002/91			2.0	84
018/91			2.0	99
062/91			2.0	97
129/91			2.0	81
130/91			2.0	103
200/90			4.0	91
201/90			4.0	97
202/90			4.0	96
002/90			4.0	94
018/90			4.0	98
062/91			4.0	92
129/91			4.0	89
130/91			4.0	95

* data supplied by CEM Analytical Services Ltd.

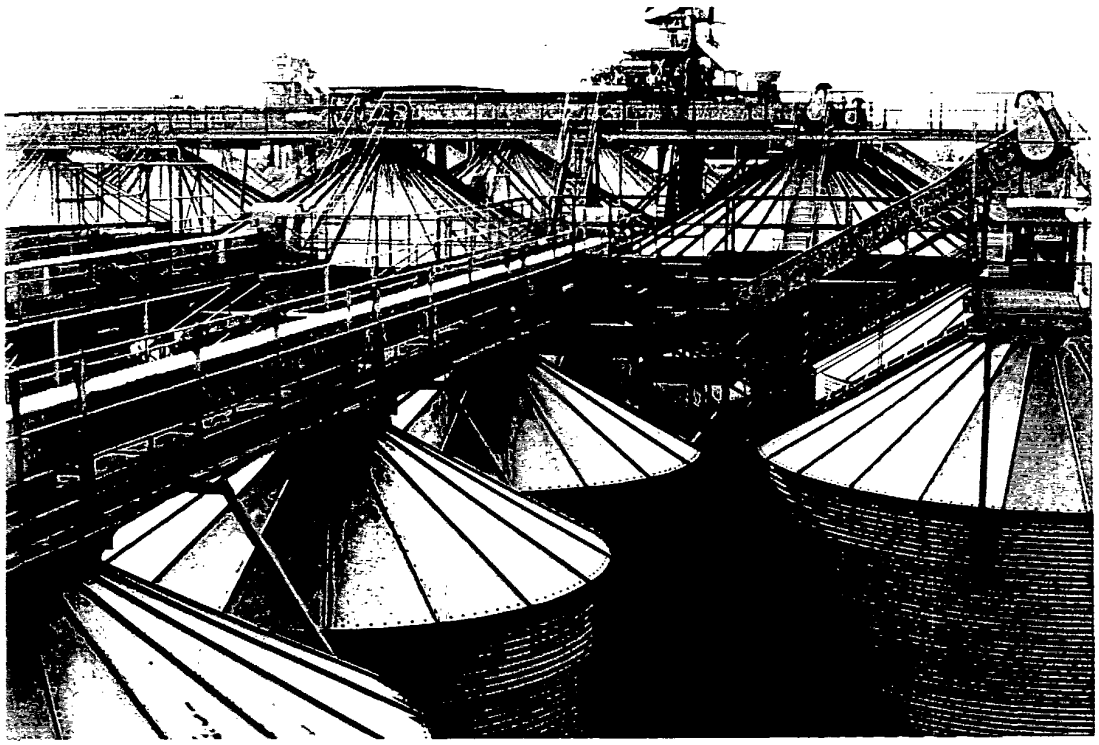

Figure 1: Storage bins (Hampshire Grain Ltd.)

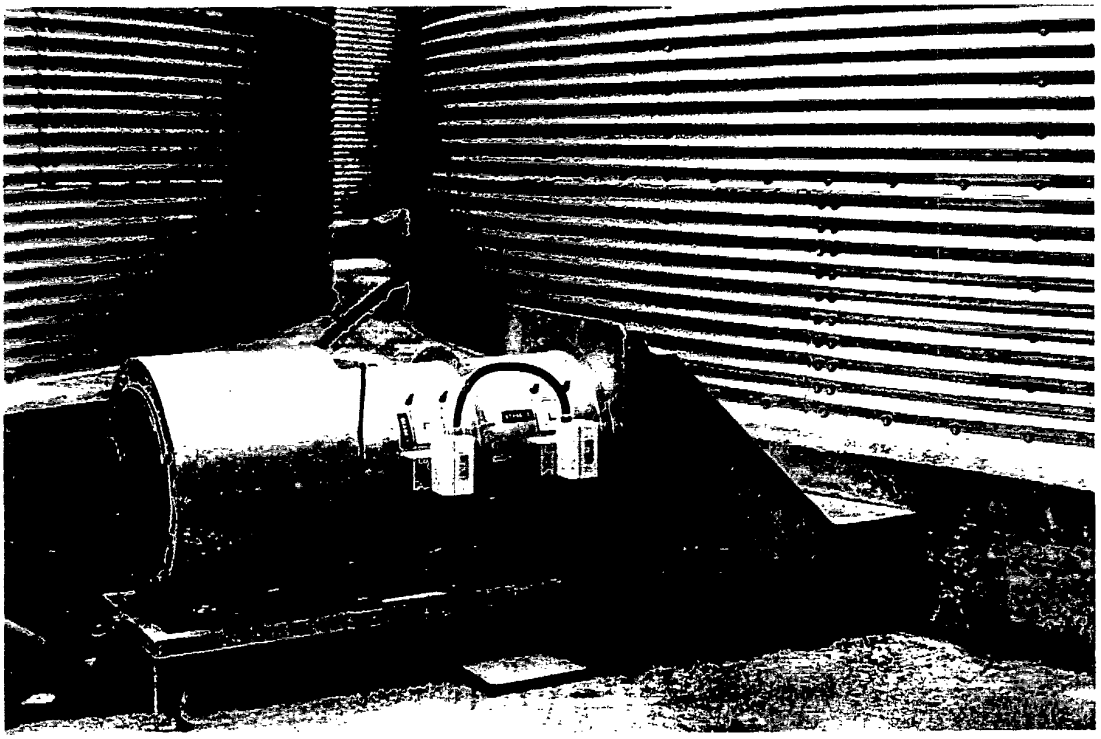

Figure 2: Aeration Fan