5.16 MALATHION (049)

Malathion was considered as a periodic review chemical by the 1999 JMPR and re-evaluated in 2004 and 2005. The manufacturer has supplied a new study on the post-harvest treatment of wheat and processing into flour and bread.

Methods of analysis

The analytical method involved extraction with acetonitrile and analysis by HPLC/MS-MS with external standard calibration. The method determined malathion, malaoxon, and desmethyl malathion in wheat grain and various processed commodities.

A limit of quantitation of 0.01 mg/kg for each analyte was demonstrated for wheat and the processed commodities, and the concurrent recoveries were acceptable.

The Meeting concluded that the method is acceptable for data collection.

Wheat field trials

Three post-harvest experiments were conducted in the USA. The trials were conducted at the maximum GAP: 0.6 kg/L EC applied as a 2.4 kg ai/hL spray (1 application) to empty storage bin surfaces, 60 g/kg DP applied at 0.010 kg ai/metric ton (1 application) to grain in transport wagons prior to entry into storage bins, and 60 g/kg DP applied to the surface of grain in the storage bin at a rate of 0.15 kg ai/100 m^2 (multiple). The subject trials used two applications for the last treatment.

The three experiments were independent, in that three transfer wagons with corresponding bins were utilized. Equipment calibrations and application preparations were conducted independently for each experiment. The experiments were conducted simultaneously at the same geographic location and under identical environmental conditions.

The bins were smaller than those typically used for commercial storage. Each bin was 1.2×1.1×1.2 m (ht), or 1.6 m^3 and was filled with 910 kg wheat. Commercial cylindrical bins may be as large as 32 m diameter × 25 m height and hold 18000 metric tons.

The surface area to volume ratio in the trial bins is 0.82. The surface area to volume ratio in the commercial bin is 0.040. As the malathion DP is applied only to the grain surface (at a fixed m^2 rate), the experimental bin with the lower surface to volume ratio would be anticipated to yield higher grain residues. For commercial size storage units, the major contribution to the wheat residue arises from treatment of the grain on the transport vehicle, i.e., 10 mg/kg. In the trials, the total wheat surface treatment was 4 mg/kg (2×151 g ai/100 m^2 × 1.3 m^2 × 1 / 910 kg). In a typical commercial storage tower, the equivalent total surface treatment would be about 0.014 mg/kg (2×151 g ai/100 m^2 ×3.1416×162 m^2 × 1/18,000,000 kg).

Thus, extrapolation from the small size of the storage containers in the current trials to a typical commercial scale unit would make the treatment of grain in transport the only significant contributor to the overall residue. The theoretical maximum level from malathion application to wheat in the transport vehicle at the maximum rate per GAP would be 10 mg/kg.

The Meeting also noted that the grain moisture was relatively low at 12% and the ambient temperature was cold, at –2.6 to 6.5 °C. Both factors would tend to increase the stability of the malathion, i.e., yield higher residue concentrations on the grain. Literature indicates that increasing temperature and increasing humidity contribute to the decay of malathion on grains.

Residues from the three independently treated bins of wheat are in ranked order: 13, 15, 15 mg/kg, at 29 days after the last of four treatments. The maximum theoretical concentration of malathion on wheat is 36 mg/kg, or 14 mg/kg if the malathion sprayed on the container walls is

considered unavailable. The calculated value of 14 mg/kg is in excellent agreement with the measured residue of 13–15 mg/kg. The combination of freezing storage conditions and the high area to volume ratio means that the residue concentrations found are a significant exaggeration of concentrations in typical commercial practice. The findings are in agreement with previous studies, reported in the literature, which have shown that the initial malathion content on wheat is about 80% of the theoretical value from postharvest treatment.

The relatively short storage interval (29 days after the final treatment) and the freezing ambient temperature would contribute to elevated residues of malathion, relative to extended storage (6 months or more) and a range of ambient temperature. The trials were not conducted so as to mimic typical commercial practice, but do represent a probable worst case scenario.

The Meeting estimated an STMR of 10 mg/kg, and an HR of 10 mg/kg. The Meeting decided to withdraw it previous maximum residue level recommendation of 0.5 mg/kg for wheat grain and to estimate a new maximum residue level of 10 mg/kg.

Wheat processing

Wheat was processed into flour, gluten, and the various by-products by a simulation of commercial milling. Whole wheat and white breads were also prepared. The processing factors and resulting HR-P/STMR-P values are summarized as follows:

Commodity	Processing (Transfer) Factor	HR/HR-P / STMR/STMR-P (mg/kg)
Wheat grain	1	10
Wheat aspirated grain fraction	180	1800
Wheat cleaned	0.8	8
Wheat bran	0.54[a] [2.5]	25[a]
Wheat germ	0.93[b]	-
Wheat flour	0.087	0.87
Whole meal flour	0.75	7.5
Gluten	0.0012	0.012
Whole meal bread	0.12	1.2
Wheat white bread	0.020	0.20

a The 0.54 value determined for wheat bran in the processing study was regarded as very unlikely, given numerous studies in the literature and past experiences with post harvest treatments of grains. The value of 2.5 was selected as appropriate.

b The value of 0.93 measured for wheat germ was considered suspect and not used.

The processing factors for wheat flour, whole meal flour, whole meal bread, and wheat white bread are in reasonable agreement with previous results reported in the literature for flour, whole meal flour, wholemeal bread, and wheat white bread. However, literature values do not agree with the current processing findings for bran. Former studies indicate an increase in residue in the bran (2–3×) relative to the grain for grain stored for a comparable interval after treatment at a similar level. This is expected for a surface residue such as malathion. The present study indicates a decrease in malathion concentration in bran (0.5×) relative to grain. The Meeting concluded that the mechanical separation of grain into bran, and middlings and germ had most likely not been conducted properly.

Based on the wheat grain processing study and an HR of 10 mg/kg for the postharvest treated wheat grain, the Meeting estimated the following HR-P/STMR-P values suitable for use in dietary intake calculations: wheat flour, 0.87 mg/kg; whole meal flour, 7.5 mg/kg; wheat gluten, 0.012 mg/kg; whole meal bread, 1.2 mg/kg; wheat white bread, 0.20 mg/kg.

Given the apparent error in the wheat to wheat bran and germ processing's, the Meeting decided to utilize a processing factor of 2.5 for the conversion of wheat to unprocessed wheat bran,

based on literature values and previous recommendations of JMPR for postharvest treatments of grains with various pesticides, and estimated a maximum residue level of 25 mg/kg for wheat bran and an STMR of 25 mg/kg.

The Meeting recommended withdrawing it previous maximum residue level recommendation of 0.2 mg/kg for wheat flour, as the maximum residue level recommendation of 10 mg/kg for wheat grain will suffice for wheat flour, i.e., the residue declines upon processing.

DIETARY RISK ASSESSMENT

Long-term intake

The current ADI for malathion is 0–0.3 mg/kg bw. The International Estimated Daily Intakes (IEDIs) were calculated for commodities for human consumption for which STMRs were previously estimated by the 1999 JMPR and by the 2004 JMPR. The present Meeting found that IEDI of malathion based on the STMRs estimated for 25 commodities for the thirteen GEMS/Food cluster diets were in the range of 0% to 3% of the maximum ADI (0.3 mg /kg bw). The Meeting concluded that the long-term intake of residues of malathion, resulting from its uses that have been considered by JMPR, is unlikely to present a public health concern.

Short-term intake

An ARfD for malathion of 2 mg/kg bw was established by the 2003 JMPR. The IESTIs of malathion by the general population and by children were calculated for commodities for which STMR and highest residue values were estimated by the 2004 JMPR. The IESTI was 0–4% of the ARfD for the general population and 0–10% of the ARfD for children (2004 JMPR). The IESTIs of malathion by the general population and by children were calculated for wheat grain and processed wheat commodities for which STMR and highest residue values were estimated by the current Meeting. The IESTI for wheat was 7% of the ARfD for the general population and 10% of the ARfD for children for wheat grain and a maximum of 2% of the ARfD for the general population and 2% of the ARfD for children for processed wheat commodities.

The Meeting concluded that short-term intake of residues of malathion from its use in wheat grain and processed wheat commodities arising from use on wheat is unlikely to present a public health concern.