5.11 DICHLORVOS (025)

RESIDUE AND ANALYTICAL ASPECTS

Dichlorvos is an organophosphate insecticide. It is effective against a broad spectrum of insect pests in stored products. It is also used in public health vector control and in animal health for the control of ectoparasites. It was evaluated by JMPR 1965 (T,R), 1970 (T,R), 1993 (T,R), and in 2011 (T) as part of the periodic review programme. The ADI and acute reference dose for dichlorvos were established as 0–0.004 mg/kg bw and 0.1 mg/kg bw, respectively. Dichlorvos was scheduled at the Forty-third Session of the CCPR (2011) for the periodic re-evaluation of residues by the 2012 JMPR.

Animal metabolism

Information on the metabolism of dichlorvos has been evaluated in goats following dermal and oral dosing, in swine and laying hens after dermal application of dichlorvos. The latter information was obtained from studies published in scientific literature.

Dermal treatment

Two lactating goats were treated dermally twice daily for three consecutive days with vinyl-^{14}C-dichlorvos at the target dose rate of 10 mg/kg body weight/day. To dose at an exaggerated rate, the application site of one goat was shaved and occluded with a Teflon patch immediately after each treatment ("occluded goat"). The other treated goat was treated normally, that is, the application site was not shaved nor occluded ("non-occluded"). Treated goats were sacrificed 16–18 hours after the final dose.

The following TRR levels (mg/kg) were found in various tissues of occluded and non-occluded goat, respectively: distal and proximal muscle 2.30 mg/kg (3.6%)–2.56 mg/kg (0.1%) and 0.65 (0.8)–0.55 mg/kg (0.0%); liver 36.1 mg/kg (2.8%)– 9.13 mg/kg (0.5%); kidney 13.5 mg/kg (0.1%) and 3.23mg/kg (0.0%); distal and proximal fat 0.69 mg/kg (0.1%)–0.64 mg/kg (0.0%), and 0.13 mg/kg (0.0%)–0.43 mg/kg (0.0%). The cumulate TRR found in the tissues accounted for 6.7% and 1.3% of the administered dose, for the occluded and non-occluded goats, respectively.

TRR levels found in milk from the occluded goat ranged from 6.09 to 10.76 mg/kg and accounted for 3.5% of the administered dose. The TRR levels found in milk from the non-occluded goat ranged from 0.618 to 1.821 mg/kg and accounted for 0.6% of the administered dose.

Comparison of the TRR levels in proximal and distal muscle and fat samples from both treated animals demonstrated that residue levels were not any higher in the proximal samples, suggesting that dermally absorbed residues were quantitatively distributed throughout the animal's body by the circulatory system.

Material balance for this study, including residues in urine and faeces, accounted for 52.1% and 42.2% of the administered dose for the occluded and non-occluded goats, respectively.

The metabolic fate of vinyl-1-^{14}C-dichlorvos in the occluded goat was examined in the edible tissues and milk. Solvent extraction of tissues and milk removed between 30.7 and 70.5 percent of the TRR. Subsequent acid and/or base hydrolyses of the post-extracted solids quantitatively solubilized the "bound" residues.

Chromatographic analysis of the aqueous extracts demonstrated that neither dichlorvos nor desmethyl dichlorvos, 2,2-dichloroacetic acid, 2,2 dichloro acetaldehyde and 2,2-dichloroethanol were present. Mass spectral analyses of the water-soluble residues suggested that the polar residues found in the tissues represented incorporation of the dechlorinated vinyl portion of dichlorvos into relatively high-molecular weight natural products.

Milk aqueous extract was shown to contain a single radioactive residue which was identified as ^{14}C-lactose.

The organo-soluble residues were further characterized by saponification. Analysis of the saponified-aqueous fractions from milk, liver and fat revealed that ^{14}C-glycerol accounted for 100%, 28.6% and 23.1% of the radiocarbon present in the fraction, respectively.

The "non-saponifiable" (lipid) fraction accounted for approximately 30–50% of radioactivity. These "bound" residues were quantitatively solubilised after acid and/or base hydrolysis resulting in compounds similar to amino acids.

Results from this study showed that vinyl-l-^{14}C-dichlorvos was extensively metabolized in the goat so that the vinyl portion of the molecule was incorporated into various natural products. Natural products identified in this study were lactose (in skim milk) and glycerol, resulting from the saponification of triglycerides present in milk, muscle and fat organo-soluble fractions. Although structural assignments were not made for the water-soluble residues extracted from tissues, five relatively high molecular weight polar compounds, which lacked chlorine atoms, were confirmed by mass spectral analysis. Bound residues solubilised by acid hydrolysis were tentatively identified as amino acids.

Laying hens

The metabolism of dichlorvos was studied on laying hens treated dermally twice daily for three consecutive days with vinyl-1-^{14}C-dichlorvos at the dose rate of 18.7 mg/kg body weight/day.

To maximize absorption of the applied dose, the feathers and down on the application site (vent and fluff area) were clipped-off prior to the first treatment. Treated hens were sacrificed approximately 20–21 hours after the final dose and the total radioactive residue (TRR) levels in selected tissues, were determined by combustion analysis.

The TRRs were 1.48 mg/kg in liver, 0.39 mg/kg in breast muscle, 0.49 mg/kg in fat, 0.88 mg/kg in egg white and 0.86 mg/kg egg yolk. Radioactivity found in the internal tissues and on the proximal and distal skin accounted for 0.3%, 20.0% and 0.8% of the administered dose, respectively.

Solvent extraction of tissues and eggs recovered between 8.6% and 93.5% of the TRR. Subsequent acid and base hydrolysis of the post-extracted solids quantitatively solubilised the "bound" residues.

The parent dichlorvos (0.004 mg/kg, 1.1% of TRR) and des-methyl dichlorvos (0.039 mg/kg, 7.8% of TRR) were identified in breast muscle and fat.

Results from this study showed that vinyl-1-^{14}C-dichlorvos was extensively metabolized in poultry. Majority of the radioactivity was incorporated into water-soluble natural products, amino acids and glycerol (fats), resulting from the saponification of triglycerides present in the organic extracts of liver, fat, and egg yolk.

Oral application of dichlorvos

Cows

In an early non GLP study four cows were treated with ^{32}P-labelled dichlorvos on the first day with 1 mg/kg bw dose in capsule and followed after 7 days by a 20 mg/kg bw dose. Following the 1 and 20 mg/kg bw oral doses the total radioactivity in milk reached an approximate plateau (0.6 mg/kg dichlorvos equivalent) between 12 and 24 hours and 10.5–11.1 mg/kg between 8 and 12 hours, respectively. The radioactive residues in milk declined continuously to 1.3 mg/kg dichlorvos equivalent after 6 days. The organosoluble residues in milk were much lower reaching the maximum of 0.077 mg/kg after one hour of administration of 20 mg/kg bw dose.

In another experiment cows were administered ^{32}P-dichlorvos at 1 mg/kg bw and 20 mg/kg bw. Following oral administration, the majority (68–100%) of radioactivity was eliminated in urine and faeces within a week of administration. The majority of radioactivity in urine was present as mono- or di-methyl phosphates (70–98%) and desmethyl dichlorvos (0–30%). Radioactivity

eliminated in milk of cows peaked at 0.61 mg/kg and 11.1 mg/kg dichlorvos equivalent approximately 12 hours after administration of 1 mg/kg and 20 mg/kg dose, respectively. It was concluded that dichlorvos was rapidly metabolized *in vivo* predominantly *via* cleavage of the P-O (vinyl) bond.

Swine

The Metabolic fate of dichlorvos in swine was studied by short and long-term oral and inhalation exposure utilising ^{32}P-, ^{36}Cl- and ^{14}C-labelled dichlorvos. Pregnant sows were administered, in the form of slow release polyvinylchloride pellets, a nominal dose of 4 mg/kg bw per day of ^{14}C-dichlorvos for up to 4 weeks before birth of piglets. Radioactivity was retained in tissues of both sows and piglets (levels not specified), but analysis showed that dichlorvos, demethyl dichlorvos, dichloroacetaldehyde or dichloroacetic acid were absent. Metabolites in liver and muscle tissues were identified as ^{14}C-carbon dioxide, glycine and serine, and a number of intermediates derived from these, including glucose, fatty acids, choline, ribonucleic acid and cholesterol. Similar experiments using ^{36}Cl-dichlorvos demonstrated that radioactivity was present as chloride ion and not as organochlorine compounds directly related to dichlorvos.

In three separate trials pregnant sows were fed non-labelled, and ^{14}C- and ^{36}Cl-labelled dichlorvos separately and in combination during the last third of the sows' gestation period at a rate of 4 mg of dichlorvos per kg of body weight per day. Samples of brain, kidney, liver, quadriceps muscle, and mesenteric fat from the sows, and muscle and liver from the piglets were analysed with GC method. No residues of dichlorvos, demethyl dichlorvos, dichloroacetaldehyde, dichloroacetic acid, or dichloroethanol were found in the tissues of the sows and piglets (LOQ was not given), although the tissues contained ^{l4}C and ^{36}Cl residues ranging from 0.3 to 18.0 mg/kg equivalents. The ^{14}C and ^{36}Cl residues in the tissues were assumed to be due to degradation of the vinyl group in dichlorvos into ^{36}Cl ions and the incorporation of the ^{14}C into normal tissue constituents such as glycine, serine, creatine, glucose, glycogen, fatty acids, cholesterol, choline, lecithin, and ribonucleic acid.

In summary, vinyl-l-^{14}C-dichlorvos was extensively metabolized. Neither dichlorvos nor desmethyl dichlorvos, 2,2-dichloroacetic acid, 2,2 dichloro acetaldehyde and 2,2-dichloroethanol were present in detectable concentrations in tissues, milk and eggs, except dichlorvos (0.004 mg/kg, 1.1% of TRR) and des-methyl dichlorvos (0.039 mg/kg, 7.8% of TRR) in poultry breast muscle and fat following extremely high dose. The phosphorus moiety of the molecule was excreted via urine and faeces as mono- or di-methyl phosphates and desmethyl dichlorvos. The dechlorinated vinyl portion of dichlorvos was incorporated into various natural products such as amino acids and glycerol (fats). Organochlorine compounds deriving from the vinyl moiety were not present.

Plant metabolism

Wheat grains were topically treated with ^{14}C-dichlorvos. Some of the grains were dissected manually into pericarp, endosperm, and germ, and the total radioactivity in each fraction was determined. Other part of grain was crushed and extracted with (a) chloroform, (b) acetone, (c) saline. The saline extract and remaining part of the grains extracts were digested with protease and assayed for ^{14}C. The results show that dichlorvos rapidly diminished after the grains saturated and the protein was phosphorylated. Dichlorvos amounted to 24%, 8% and 3% of radioactivity in chloroform 2, 7 and 14 days after treatment. The protease extract did not contain dichlorvos. The dichlorvos degraded to dimethyl phosphate and fairly stable phosphorylated protein derivatives.

^{32}P-labelled trichlorfon and ^{36}Cl-dichlorvos were applied to cotton leaves by petiole injection. Leaf samples were collected after application then residues extracted by partitioning into chloroform and water. Dichlorvos was present in low concentrations amounting to 0.8%, 0.9% and 0.1% of applied dose 1, 24 and 48 hours after trichlorfon administration.

Following dichlorvos application, more than 80% of the applied radioactivity was lost within 48 hours of treatment, presumably due to volatilisation. Dichlorvos was the predominant residue immediately after application (37% of applied radioactivity), but declined to less than 0.1% of applied radioactivity after 48 hours. Dimethyl phosphate was detected at up to *ca.* 13% of applied radioactivity after 24–48 hours.

The half-lives of dichlorvos degradation were determined in cotton, bean, tomato and potato plants following treatment with ^{32}P-labelled dichlorvos. The plants, with or without roots, were placed in a formulated 0.1–0.2% ^{32}P-dichlorvos solution or given a foliar application by dipping the whole plants into solutions of the labelled material. Between 60–80% of radioactivity was lost from the plants by volatilisation. In cotton, dichlorvos was degraded with a half-life of 4.6 hours, while half-lives of dichlorvos degradation of 6.8, 4.6 and 6.8 hours were determined for beans, tomatoes and potatoes, respectively. It was stated, without giving full details of characterization, that dimethyl phosphate was the predominant radioactive species identified.

Faba and soya beans were treated with ^{14}C-labelled dichlorvos at 12 mg/kg and 24 mg/kg dose rate. The treated grains were stored for 30 weeks under simulated local storage conditions. The residues on the seed coat (external extract) were removed with a mixture of water and acetone (3:1). Washed beans were then crushed in a mortar and Soxhlet extracted with 95% methanol for 24 hours.

The surface residues decreased with storage time and amounted to 15–21% of the actual applied dose for both beans by the end of the experiment. The radioactivity in the internal extract increased from 20% to 57% for faba beans and from 36% to 62% for soya beans in relation to the actual doses of 12 and 24 mg/kg applied, respectively. Non-extractable residues slowly increased with time, and amounted to 8–10% and 9–11% of the actual applied doses in faba beans and soya beans after 30 weeks. The total recovered radioactivity was over 81% of the applied doses.

Dichlorvos alone was present in the external extracts. Desmethyl-dichlorvos, dimethylphosphate and monomethylphosphate were the main degradation products of ^{14}C-dichlorvos in the internal extract. Desmethyl-dichlorvos could only be extracted after acid hydrolysis indicating that it was present in conjugated form. The isolated metabolites suggested that dichlorvos is degraded in both stored faba and soya beans via two main pathways to give a number of metabolites. The major degradation pathway is cleavage of the P-O-CH_3 bond to give desmethyl dichlorvos. Hydrolysis of desmethyl dichlorvos gave monomethyl phosphate. The minor pathway is the hydrolysis of the P-O-vinyl ester linkage to give dimethyl phosphate.

In summary dichlorvos is rapidly metabolized, with a half-life in cotton, beans, potato and tomato of about 4.6–6.8 hours and in cereals of 27–54 hours. Most of the radioactivity was lost by volatilization. The main routes of degradation of dichlorvos in plants were found to be: (i) hydrolysis to form the major metabolite dimethyl phosphate and dichloroacetaldehyde; (ii) demethylation of dimethyl phosphate to monomethyl phosphate and inorganic phosphates; (iii) conversion of dichloroacetaldehyde to 2,2-dichloroethanol, which is then conjugated and/or incorporated into naturally occurring plant components; and (iv) loss by volatilization.

Methods of residue analysis

The methods used in the studies carried out with stored plant commodities were similar and based on extraction with a 4:1 mixture of acetonitrile: water followed by partitioning into dichloromethane, the concentrated extract was purified by gel permeation chromatography and analysed by GC-FPD (flame photometric detection).

Milk samples were extracted with a mixture of ethanol, diethyl ether and petroleum ether in the presence of sodium oxalate. The dried concentrated extract was cleaned up on GPC column. The dichlorvos residues were determined with GC-FPD.

Animal tissue samples were extracted with dichloromethane, cleaned up on GPC and analysed by GC-FPD.

The validated LOQ was 0.01 in all matrices, and the recoveries ranged between 70–120%.

Some of the studies published in scientific papers employed colorimetric method based on enzyme inhibition and spectrophotometric detection. The LOQ of the methods for plant materials was 0.1 mg/kg. The recovery varied but was in the acceptable range of 70–110%

Dichlorvos residues may also be quantitatively determined with several multi residue methods used currently by regulatory laboratories.

Stability of residues in stored analytical samples

Peanut samples were obtained from a facility which was treated for 9 months at the daily rate of 18 g ai/1000 m^3) air space. The samples stored at -20 ºC were analysed on days 0, 39, 74, and 136 days after storage. The remaining residues were ≥ 70% in all samples demonstrating that residues of dichlorvos in peanuts are stable up to 136 days under frozen conditions. The maximum period of storage prior to analysis of all the bulk peanut samples in the facility was 134 days.

Winter wheat of about 12% moisture content was treated at a 15 mg/kg calculated deposit rate. Samples were stored for 8 weeks at -18 °C. The residues remaining in wheat grain varied in the range of 57% and 144% with an average of 90%.

Wheat grains of 9, 11, 13 and 14% moisture content were treated with dichlorvos at 50 mg/kg and stored for 11 months at -15 °C. At the end of the storage period, the samples contained 49, 43, 34 and 34 mg/kg of dichlorvos residues, respectively, corresponding to losses of 2%, 14%, 32 and 32% of initial dichlorvos.

It is apparent from the results that the disappearance of dichlorvos on wheat is dependent on both moisture content and temperature, which are affecting the stability of the residues. The stability of residues in commodities for which residue levels could be estimated was supported by the reported storage stability tests.

Definition of the residue

Biotransformation studies indicated that dichlorvos is rapidly absorbed by all routes of exposure and rapidly metabolized.

In lactating goats treated dermally the following TRR levels (mg/kg) were found in various tissues of occluded and non-occluded goat, respectively: distal and proximal muscle 2.30–2.56, 0.65–0.55; liver 36.1; 9.13; kidney 13.5; 3.23 distal and proximal fat 0.69–0.64, 0.13–0.43. The aggregated TRR found in the tissues accounted for 6.7% and 1.3% of the administered dose, for the occluded and non-occluded goats, respectively. The phosphorous moiety was mainly excreted as phosphates via urine.

Neither dichlorvos nor desmethyl dichlorvos, 2,2-dichloroacetic acid, 2,2 dichloroacetaldehyde and 2,2-dichloroethanol were present in tissues and milk. The dechlorinated vinyl portion of dichlorvos was incorporated into natural products such as glycerol, lactose and amino acids.

In dermally dosed laying hens TRR levels found in egg yolks ranged from < 0.014 to 0.863 mg/kg, and in egg whites ranged from 0.015 to 0.876 mg/kg., The parent dichlorvos (0.004 mg/kg, 1.1% of TRR) and des-methyl dichlorvos (0.039 mg/kg, 7.8% of TRR) were only present in breast muscle and fat following dermal treatment with grossly exaggerated dose (18.7 mg/kg bw) Consequently, these compounds would not be detectable under practical use conditions.

Animal transfer studies with exaggerated oral dose resulted in non-detectable residues in meat, liver, kidney and fat of cows, similarly no residue was detectable in poultry meat, fat, liver, kidney and eggs.

Dichlorvos concentration in/on treated plants declined rapidly partly by evaporation due to its high vapour pressure. The parent compound was the predominant residue immediately after application and degraded rapidly via (i) hydrolysis to form the major metabolite dimethyl phosphate and dichloroacetaldehyde; (ii) demethylation of dimethyl phosphate to monomethyl phosphate and inorganic phosphates; (iii) conversion of dichloroacetaldehyde to 2,2-dichloroethanol. The metabolites are conjugated and/or incorporated into naturally occurring plant components such as phosphorylated protein derivatives. The dimethyl phosphate is a common metabolite of several other pesticides.

Analytical methods are available for determining dichlorvos residues in plant and animal tissues, milk and eggs. In supervised trials on plant commodities the parent dichlorvos was the only residue component measured.

Dichlorvos residues are present in muscle at about 4 times higher concentration than in fat and are about equally distributed between egg yolk and egg white, Further, the parent dichlorvos has high water solubility (245 g/L) and log P_{ow} value of 2.

Based on the metabolism studies on plants and animals and availability of analytical methods, the Meeting recommended the following residue definition for dichlorvos.

Definition of the residue for compliance with the MRL and for estimation of dietary intake for plant and animal commodities*: dichlorvos.*

The residue is not fat-soluble.

Residues deriving from post-harvest use of dichlorvos

Treatment of bagged, packed or covered commodities according to US GAP

The US GAP specifies a minimum of 7 day intervals between applications at 15–70 g ai/1000 m^3 except on cocoa beans and whole peanuts where daily applications should not exceed 18 g ai/1000 m^3 of head space. Bulk unpacked food and feed should be removed or covered before the treatment begins. The US GAP does not specify a withholding period. Therefore, the residues measured in bagged, packed and covered commodities can only be considered for estimating maximum residue levels when the trial conditions are compared to US GAP. The residues deriving from dichlorvos application according to US GAP are summarized below.

Following multiple treatments the residue levels generally increased with the number of dichlorvos applications and they were typically the highest in the samples taken from top boxes followed by those from the side and interior of the piles. Consequently, for estimating maximum residue levels only the highest residue was considered from each trial which included sequential sampling or sampling from different positions of the treated commodities.

Study 1: In a simulated warehouse experiment in USA four applications were made at one week intervals at the nominal maximum GAP rate of 70 g ai/1000 m^3 for each application. Thirteen commodities (breakfast cereal, cocoa beans, coffee beans, cookies, crackers, dried beans, field corn, flour, oats, peanuts, soya beans, sugar and walnuts) were selected for evaluation to provide data on typical residues to be expected following storage in the facility.

The commodities were kept in their commercial packing and were placed on pallets in three to five tiers with four to five bags per tier. Two replicate samples were taken from the top tier, opposite sides of the pallet and from the interior of the pallets about 6 hours after the pesticide application.

The highest average residues detected in bagged commodities after sequential treatments 1–4 were: breakfast cereals: 0.02 mg/kg; cocoa beans: < 0.01 mg/kg; coffee beans: 0.43 mg/kg; cookies: 0.06 mg/kg; crackers: 0.29 mg/kg; dried beans: 0.12 mg/kg; field corn: 0.66 mg/kg; flour: 0.45 mg/kg; oat: 0.65 mg/kg; peanut: 3.49 mg/kg; peanut nutmeat: 0.28 mg/kg; soya beans: 0.13 mg/kg; sugar: 0.04 mg/kg; walnut meat: < 0.01 mg/kg;

No residue was detectable in pre-treatment samples.

Study 2: Dichlorvos was applied weekly in USA for 21 weeks at a rate of about 53 g/1000 m^3 (0.76 × max GAP). Samples were collected before applications 2, 8 and 16 (1 week after last application) and 6 hours after applications 1, 3, 5, 9, 13, 17 and 21. The residues were determined with an enzyme inhibition method (LOQ 0.1 mg/kg). Though the surface of the bags contained relatively high dichlorvos residues, no residue (< 0.1 mg/kg) was determined in any samples of beans, flour, noodles, raisins, rice and sugar.

Detectable residues were present in wheat flour (0.1 mg/kg) and in peanut (1.6 mg/kg).

Study 3: Bulk commodities including cocoa beans, coffee beans, dried beans, field corn, flour, oats, soya beans, sugar, tree nuts (walnuts) and wheat were treated without cover in a simulated warehouse experiment at the maximum US GAP rate of 70 g ai/1000 m^3. Some of the commodities were covered with plastic sheet. Post-application samples were collected within a day of application.

The average residues measured in duplicate samples taken from tote bins covered with plastic sheets were: cocoa beans: < 0.01 mg/kg; coffee beans: 0.02 mg/kg; field corn: < 0.01 mg/kg; flour: 0.02 mg/kg; soya beans: < 0.01 mg/kg and sugar: < 0.01 mg/kg;

The samples taken before dichlorvos treatment did not contain detectable residues.

Studies conducted according to Australian GAP

In Australia, dichlorvos can be used as surface spray or fumigant for protection of stored grains, applying EC formulation at 6 g ai /t grain or 12 g ai/t grain with withholding periods of 7 and 28 days respectively. It can also be applied as fog at 70 g ai/1000 m^3 or 3.5 g ai/50 m^2.

Study 4: In laboratory scale experiments wheat (*ca.* 1 kg samples) was treated with dichlorvos at rates equivalent to 6 and 12 g ai/t and then the stored at 20 °C or 30 °C for up to 8 weeks in closed screw cap jars. The residues in stored wheat were 0.7 mg/kg, 2.8 mg/kg and 4.1 mg/kg 7 days after treatment at 6 g ai/t. The residues were 2.2 and 1.4 mg/kg four weeks after treatment at 12 g ai/t rate.

Study 5: Residues on stored paddy rice was studied at commercial rice storage facilities and laboratory scale experiments in Australia. Dichlorvos was applied to paddy rice at 6 or 12 g ai/t rate then paddy rice was stored for up to 28 days after application. Seven days after treatment at 6 g ai/t rate the residue was 2.9 mg/kg in paddy rice, while following 12 g ai/t treatment the residues were 1.9, 2.8 and 5.2 mg/kg 28 days after application.

Study 6: Dichlorvos was applied as a direct spray application with diluted EC formulation at 5, 10 and 15 g/t paddy rice in a jar and small bin tests. 30 days after the treatment with dichlorvos at 15 mg/kg rate, the paddy rice contained 0.87 mg/kg residue.

In summary, residues in commodities treated according to US GAP were

	Covered	Packed or bagged
Cocoa beans:	< 0.01 mg/kg	< 0.01 mg/kg
Coffee beans:	0.02 mg/kg	0.43 mg/kg
Dried beans:		0.12 mg/kg
Peanut		3.5 mg/kg 1.6 mg/kg
Soya beans:	< 0.01 mg/kg	0.13 mg/kg
Oats:		0.65 mg/kg
Field corn:	< 0.01 mg/kg	0.66 mg/kg
Walnuts:	< 0.01 mg/kg	< 0.01 mg/kg
Flour:	0.02 mg/kg	0.45 mg/kg
Sugar:	< 0.01 mg/kg	0.04 mg/kg

Because only one or two independent residue data are available for each commodity treated according to US GAP, the database is considered insufficient for the estimation of maximum residue levels.

The Meeting considered that the residues in wheat 7 and 28 days after treatments with 6 g ai/t and 12 g ai/t, respectively, were not different and could be combined.

In wheat treated according to Australian GAP the residues were: 0.7, 1.4, 2.2, 2.8 and 4.1 mg/kg.

The residues in paddy rice following treatments according to Australian use pattern were: 0.87, 1.9, 2.8, 2.9 and 5.2 mg/kg.

The residues in other cereal commodities can be expected to be in the same range because the decline of dichlorvos is mainly influenced by the moisture content of the grains and the temperature

of storage. Therefore, the residues in wheat should cover the expected residues in other cereal products except rice.

However, the Meeting noted that including cereal grains excluding rice would result in long-term intake of 220% of maximum ADI of 0.004 mg/kg. Therefore the Meeting recommends maximum residue levels, STMR and HR values wheat only and for rice and resulting processed products.

The Meeting estimated a maximum residue level of 7 mg/kg, HR of 4.1 and STMR of 2.2 mg/kg for wheat.

The Meeting estimated a maximum residue level of 7 mg/kg, HR of 5.2 and STMR of 2.8 mg/kg for rice.

The Meeting withdraws its previous recommendations for maximum residue levels of 5 mg/kg for cereal grains.

Fate of residues during processing

The effect of processing was studied on peanut, corn, wheat, rice, cotton seed and soya bean following treatment with dichlorvos at recommended or exaggerated rates.

Study P1: As part of the study on residues in bulk peanut an exaggerated 40× rate was used (843 g ai/1000 m^3). The whole peanut samples were processed into fractions of meal, crude oil, refined oil, and soapstock.

Study P2: Field corn, wheat, rice, cotton seed, and soya beans were treated with dichlorvos at an exaggerated 12× rate of 842 g ai/1000 m^3 in a simulated warehouse. The treated commodities were processed in a pilot scale facility applying methods representing the industrial practice as close as possible.

Study P3: Residues in various wheat grain and milled products were determined in pilot scale trials (2 tonnes of grain treated at each rate). Wheat was treated with dichlorvos at rates of 6, 12 and 20 g ai/t. From the milled products noodles and breads were prepared.

Study P4: Winter wheat was treated at a 15 g ai/t calculated deposit rate. Samples were collected after 0, 0.5, 1, 2, 3, 4, 5, 6, 8, 12, and 16 weeks of storage. The dichlorvos residues were determined in the milling fractions and in bread made from the patent flour fraction.

Study P5: Rice was treated at 12 g ai/t in 2 commercial scale trials and 6 or 12 g ai/t in laboratory scale trials. Dichlorvos residues were determined in paddy rice, brown rice, white rice, hulls and bran by GC.

*Study P6***:** Soya beans were treated with water emulsion of dichlorvos at an intended rate of 20 g ai/t. After 7 days the treated beans were milled and the meal extracted for oil with large-scale laboratory equipment representing the industrial process.

Study 7: Potatoes were sprayed with a mixed solution containing dichlorvos. Initial residues in unwashed potatoes were 0.92 mg/kg. Washing for 1 minute in water removed > 96% of residues. No dichlorvos residues (< 0.001 mg/kg) were detected in wet or dry starch.

The processing factors (P_f) calculated from the studies are summarized in the following table. Factors are indicated with a "<" (less than) sign when the residue in the processed commodity is below the LOQ of the analytical method. The calculation is then made with the LOQ of the analytical method and the residue concentration of the RAC (raw agricultural commodity).

Treated commodity (RAC)	Processed commodity	P_f Median or best estimate	RAC STMR/HR	STMR-P/HR-P	
Whole wheat (Study P3)	Bran	1.73	2.2, 4.1	3.81	7.09
	Germ	1.02		2.24	4.18
	Flour	0.10		0.22	0.41

	Whole meal flour	0.40		0.88	1.64
Whole wheat (Study P4)	Bran	1.78	2.2, 4.1	3.92	7.30
	Flour low grade	0.10		0.23	0.42
	Patent flour	0.09		0.20	0.38
	Bread	1.00		0.88	1.64
White flour (Study 3)	White bread	0.33	2.2 4.1	0.073	0.14
	White noodles	0.6		0.132	0.25
Whole meal flour	Whole meal bread	0.14		0.123	0.23
	Flat bread	2.25		1.98	3.69
Whole rice (Study 2 and Study 5)	Polished rice	0.005	2.8, 5.2	0.014	0.03
	Brown rice	0.16		0.448	0.83
	Hulls	5.47		15.3	28.4
	Bran	1.05		2.94	5.46

Based on the residues measured in cereal grains and taking into account the best estimates for the processing factors, the Meeting estimated maximum residue levels for: rice polished 0.15 mg/kg, rice husked: 1.5 mg/kg and rice bran: 15 mg/kg,

The Meeting withdraws its previous recommendations for maximum residue levels of 1 mg/kg for wheat flour, 10 mg/kg for wheat germ and 2 mg/kg for wheat wholemeal.

Residues in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of dichlorvos in livestock on the basis of the diets listed in OECD Feed Table 2009 (available from the FAO website: http//www.fao.org/agriculture/crops/core-themes/theme/pests/pm/jmpr/jmpr-docs/en/). Calculation from highest residue, STMR and STMP-P values provides the levels in feed suitable for estimating MRLs, while calculation from STMR and STMR-P values for feed is suitable for estimating STMR values for animal commodities.

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations for beef cattle, dairy cattle, broilers and layer are provided in Annex 6 and summarized below.

	Animal dietary burden, dichlorvos, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	2.40	2.40	2.31	2.31	4.16[a]	4.16[b]	3.04	3.04
Dairy cattle	1.96	1.96	2.31	2.31	3.66[c]	3.66	1.98	2.23
Poultry - broiler	3.58[d]	3.58	2.61	2.61	2.96	2.96	0.22	0.47
Poultry - layer	3.58	3.58[e]	2.61	2.61	2.59	2.59	1.32	1.32

[a] Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat and mammalian milk.

[b] Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat and mammalian milk.

[c] Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian milk.

[d] Highest maximum poultry dietary burden suitable for MRL estimates for poultry meat and eggs.

[e] Highest mean poultry dietary burden suitable for STMR estimates for poultry meat and eggs.

Farm animal feeding studies

Dairy cows

Nine Holstein cows were orally dosed with encapsulated test material for 28 days at 2, 6, and 20 ppm levels based on dry matters.

Milk samples were collected in the morning and in the evening daily for 28 days. Equal portions of morning and evening milk were composited and then analysed.

Within 15 hours after administering the last dose, all cows were sacrificed muscle, perirenal and omental fat, liver, and kidneys samples were collected.

The LOQ of the method was 0.01 mg/kg for all matrices. No detectable dichlorvos residue was present in any of the samples.

Laying hens

Thirty two white leghorn laying hens were orally dosed with encapsulated dichlorvos for 42 days at nominal dose rates of 0, 2.0, 6.0 and 20 ppm for 42 days. Each capsule contained half a dose and each hen received two capsules per day, one in the morning and one in the evening. Nominal dose concentrations were 0.0 ppm (controls), 2.0 ppm, 6.0 ppm and 20.0 ppm.

Eggs were sampled from 1 to 42 days. Whole eggs (yolks and albumin) were collected as one sample and egg shells were discarded. Eggs within each group were pooled to form one composite sample and weighed.

All hens were sacrificed on day 43, and muscle (breast and thigh), liver, peritoneal fat, and kidneys tissues were collected from each hen.

None of the egg or tissue samples contained detectable residues. The LOQ of the methods was 0.01 mg/kg.

Animal commodity maximum residue levels

Animal feeding studies indicated that there was no detectable residue in milk, meat, eggs and edible offal even at exaggerated continuous dose of 20 ppm in feed on dry weight basis, which was about 5 times higher than the calculated maximum animal burden. The Meeting noted that the metabolism study following dermal application at extreme dose rate revealed that dichlorvos residues may occur at trace levels in poultry tissues. However, it was concluded that dichlorvos residues would not be present under practical conditions.

The Meeting estimated maximum residue level of 0.01* mg/kg for meet, fat and edible offal of mammals and poultry, and mammalian milks and eggs. The estimated HR and STMR values for animal commodities are 0 mg/kg.

DIETARY RISK ASSESSMENT

Long-term intake

The evaluation of dichlorvos resulted in recommendations for MRLs and STMR values for raw and processed commodities. The residue data were used to calculate dietary intake. The results are shown in Annex 3.

The International Estimated Daily Intakes (IEDIs) of dichlorvos, based on the STMRs estimated, were 5–30% of the maximum ADI of 0.004 mg/kg bw for the thirteen GEMS/Food cluster diets. The Meeting concluded that the long-term intake of residues of dichlorvos resulting from its uses that have been considered by JMPR unlikely to present a public health concern.

Short-term intake

The IESTI of dichlorvos calculated on the basis of the recommendations made by the JMPR was from 80% of the ARfD (0.1 mg/kg bw) for children and 60% of the general population.

The Meeting concluded that the short-term intake of residues of dichlorvos resulting from its uses that have been considered by JMPR unlikely to present a public health concern.