DICHLORVOS (025)

EXPLANATION

Dichlorvos was previously evaluated at the 1965, 1966, 1967, 1969, 1970 and 1974 Meetings and is included in the CCPR periodic review programme (ALINORM 89/24A Appendix V.; ALINORM 91/24 para 360; ALINORM 91/24A para 316). MRLs have been recommended for dichlorvos in a wide range of food commodities.

The compound was first described as an insecticide by CIBA in 1951. It was later introduced by Ciba ("Nogos"/"Nuvan"), Shell ("Vapona") and Bayer ("Dedevap"). It is now manufactured by at least 14 basic producers.

During the past 19 years (since the 1974 residue submission) the use of the compound has been extended to other crops or the recommendations have been adapted to current needs and in some cases uses were discontinued. Consequently additional residue studies have been carried out either to support existing MRLs or to provide a basis for new ones.

The residue studies conducted between 1974 and 1992, as well as the currently recommended uses, are reviewed in this monograph.

USE PATTERN

Dichlorvos is an organophosphate insecticide. It combines both contact and stomach action and has a marked vapour action. It is effective against a broad spectrum of insect pests in the field and in stored products, and is often used in public health vector control and in animal health for ectoparasite control.

In vegetables, dichlorvos provides control of aphids, white flies, thrips, leafhoppers, diamond back moth, whites, armyworms, snout moths, leaf and flea beetles and root maggots. In deciduous fruits, it has good activity against leafroller moths, apple leaf miner, aphids, psyllids, blossom weevil, saw flies, tiger moth, plum curculio and gelechiid moth. In plantation crops (cotton, coffee, tea, cocoa etc.) it is used for the control of leafrollers, hairy caterpillars, thrips, mealybugs, jassids, bollworms, aphids, psyllids and white flies. Dichlorvos is also effective against planthoppers, grasshoppers, leafminers, roller moths, beetles, rice bugs, caterpillars, rice hispa, armyworms and cutworm in rice. Other uses include pest control in ornamentals, oil crops, citrus, tropical fruits, mushooms and greenhouses.

Dichlorvos is officially registered and/or approved for use all over the world. Details of the local use recommendations in the various crops and commodities are summarized in Table 1. The number of applications is often not specified as this depends on pest incidence.

Table 1. Registered or approved uses of dichlorvos. For animals/cattle see Indoor uses at end of Table.

| Crop | Country | | Applicat | ion | | PHI ² , days |
|----------------------------|--------------|-----------------------------------|----------|------------------------|----------|----------------------------|
| | | Formulation ¹ , type | No. | g ai/hl | kg ai/ha | |
| Apple/pome fruits | Austria | EC; foliar | >1 | 75 | | 14 |
| | Greece | EC; foliar | >1 | 50-75 | | 7 |
| | India | EC; foliar | 1-2 | 20-50 | | |
| | Italy | EC; foliar | >1 | 45.5 | | 7 |
| | Jordan | EC; foliar | weekly | | 0.3-0.5 | 2-3 |
| | Lebanon | Ec; foliar | >1 | 63 | | 2 |
| | Portugal | EC; foliar | >1 | 75-100 | 0.75-1.0 | 7 |
| | Spain | EC; fly trap | | | | |
| | Switzerland | EC; foliar | >1 | 50 | | |
| Avocado | Columbia | EC; foliar | >1 | 16 | | 7 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Beans | Jordan | EC; foliar | >1 | | 0.4-0.6 | 2-3 |
| | Lebanon | EC; foliar | 1 | 63 | | 2 |
| | Malaysia | EC; knapsack | >1 | 111-166 | | 7 |
| | South Africa | EC; full cover | >1 | 100 | | 3 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| | Venezuela | EC; foliar | >1 | | 0.75-1.0 | 20 |
| Berries (small fruits) | Netherlands | EC; foliar EC; space treatment | >1 >1 | 50 60 | 0.3-1.2 | F4 G10-1 |
| | New Zealand | EC; broadcast LV or HV | >1 | 60 | 0.5-0.8 | 2 |
| | South Africa | EC; full cover | >1 | 50 | | 2 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Brassica (excl cabbage) | Jordan | EC; foliar | >1 | | 0.3-0.5 | 2-3 |
| | Malaysia | EC; knapsack | >1 | 111-166 | | 7 |
| | Netherlands | EC; foliar | 2-6 | | 0.6-1.0 | 4 |
| | New Zealand | EC; broadcast | 1-2 | | 0.3-0.75 | 3 |
| | Peru | EC; HV | 2-3 | | 0.25-0.5 | 2-3 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Cabbage | Brazil | EC; spray | >1 | 70 | | 7 |
| | France | EC; foliar | 5-8 | 125 | 1.0 | 5 |
| | Peru | EC; HV | 2-3 | | 0.37-0.5 | 2-3 |
| | Portugal | EC; foliar | >1 | 75-100 | 0.75-1.0 | 7 |
| | South Africa | EC; full cover | | 100 | | 2 |
| | Venezuela | EC; foliar | >1 | | 1.0-1.5 | 20 |
| Cereal grains | Argentina | EC; spray | | 10-20 mg/kg | | |
| | Australia | EC; spray | | 500 g/hl 6-12 mg/kg | | 7-28 |
| | Austria | OL; fogging | | 14-21 mg/kg | | 28 |

| Crop | Country | | Applicat | ion | | PHI ² , days |
|-----------|----------------|----------------------------------|----------------|--|-----------|----------------------------|
| | | Formulation ¹ , type | No. | g ai/hl | kg ai/ha | - |
| | Czechoslovakia | EC; fumigation | | 0.5-1 % | | |
| | France | EC; fumigation KN; fumigation | | 19 q 3.5 mg/kg | | |
| | India | EC; foliar spray | 2 | | 0.5 | F |
| | Italy | SO; spray/aerosol | | 2.2-10.2 mg/kg | | 1 |
| | Netherlands | UL; spray | | 7-14 mg/kg | | 14-28 |
| | New Zealand | EC; broadcast | | | 0.35-0.75 | F 3 |
| | Nigeria | EC; fogging | | 20 mg/kg | | 7 |
| | Poland | AE; fumigation | | 7-21 mg/kg | | 3 mo. |
| | Spain | OL; atomizer | | 2.1-4.9 mg/kg | | 15 |
| | Switzerland | AE; spray | | | | |
| Cocoa | Columbia | EC; foliar | >1 | 10-40 | | 21 |
| | Netherlands | UL; spray | | 7-14 mg/kg | | 14-21 |
| | Switzerland | AE; spray | | | | |
| Coffee | Columbia | EC; foliar EC; spray | | 30 10 g/m³ | | 21 |
| | Indonesia | EC; foliar | | 100-150 | | 21 |
| | Netherlands | UL; spray | | 7-14 mg/kg | | 14-28 |
| Cotton | Columbia | EC; foliar | >1 | | 0.4-0.6 | |
| | Greece | EC; foliar | >1 | 40-60 | | 7 |
| | Pakistan | EC; foliar | 2-3 | | 0.625 | 2 |
| | Sudan | EC; foliar | | | 0.714 | |
| Cucumber | Canada | EC; spray KN; fogging | | 6 g/1000 m ² 35 g/1000 m ³ | | G7 |
| | Czechoslovakia | EC; spray | 1 | 100-300 | | 7 |
| | Greece | EC; foliar | 3-4 | 75-100 | | |
| | India | EC; foliar spray | 2 | | 0.05 | |
| | Jordan | EC; foliar | >1 | | 0.4-0.6 | |
| | Lebanon | EC; foliar | >1 | 63 | | 2 |
| | Malaysia | EC; knapsack | >1 | 111-166 | | |
| | Netherlands | AE; aerosol EC; foliar | >1 up to 15 | 2.7 g/ 100 m ³ 50 | 0.5-1.8 | 3 |
| | Poland | EC; evaporation EC; spray | >1 | 5-6 g/100 m ³ 50 | | 7 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Dates | U.A.E. | EC; foliar/aerial EC; foliar | >1 >1 | 75-100 75-100 | | 3 |
| Egg plant | Italy | EC; foliar | >1 | 48.9-97 | | 7 |
| | Jordan | EC; foliar | >1 | | 0.4-0.6 | 2-3 |
| | Poland | EC; fogging | 2 | 5-6 g/100 m ³ | | 7 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Grapes | Austria | EC; foliar | | 75 | | 14 |
| | Chile | EC; foliar | >1 | 50-75 | | 2 |
| | France | EC; foliar | 2-3 | | 1.25 | 5 |
| | Greece | EC; foliar | >1 | 50-75 | | 7 |
| | Lebanon | EC; foliar | >1 | 63 | | 2 |

| Crop | Country | | Applicat | ion | | PHI ² , days |
|----------------|------------------|--|-------------|---|----------|----------------------------|
| | | Formulation ¹ , type | No. | g ai/hl | kg ai/ha | |
| | South Africa | EC; full cover | 1-3 | 75 | | 7 |
| | Switzerland | EC; foliar | >1 | 50 | | |
| Indoor uses, s | see end of Table | | | | | |
| Lettuce | France | EC; foliar | >1 | | 1.0 | 5 |
| | Greece | EC; foliar | >1 | | 0.5-0.75 | 7 |
| | Netherlands | EC; foliar AE; space treatment | up to 15 | 50-60 2 g /100 m ³ | 0.5-1.8 | 10-14 |
| | Turkey | EC; foliar | 1-2 | | 1.0 | 5 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Melon | Netherlands | EC; foliar space treatment | up to 15 >1 | 50-60 2 g/100 m ³ | 0.5-1.8 | 10 |
| Mushroom | Canada | KN; fogging | | $10 \text{ g}/1000 \text{ m}^3$ | | 1 |
| | Czechoslovakia | EC; spray | | 1.2 % | | 2-3 |
| | Greece | EC; spray | | 5-10 g/100 m ³ | 1 | |
| | Netherlands | EC; space treatment EC; foliar AE; aerosol | | 41.5 83.0 2.75 g/100 m ³ | | 2 4 2 |
| | New Zealand | EC; fogging | | 500 | | 1-3 |
| | Poland | EC; thermal spray | >5 | 8 g/100 m³ | | 1 |
| | Spain | OL; fogging | 1 | $0.7~\mathrm{g/100~m}^3$ | | 4 |
| Onion | Austria | EC; foliar | >1 | 50 | | 14 |
| | Brazil | EC; spray | >1 | 70 | | 7 |
| | Greece | EC: foliar | >1 | 40-60 | | 7 |
| | Jordan | EC; foliar | >1 | | 0.4-0.8 | 2-3 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Pea | France | EC; foliar | >1 | | 1.0 | 5 |
| | Greece | EC; foliar | >1 | 40-60 | | 7 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Peach | Austria | EC; foliar | >1 | 75 | | 14 |
| | France | EC; foliar | >1 | 125 | | 5 |
| | Greece | EC; foliar | >1 | 50-70 | | 7 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Peanuts | Greece | EC; foliar | >1 | 40-60 | | 7 |
| | India | EC; foliar spray | >1 | | 0.37 | |
| | Venezuela | EC; foliar | >1 | | 0.75 | 2 |
| Peppers | Chile | EC; foliar | >1 | | 0.05 | 2 |
| | Czechoslovakia | EC; foliar | 1 | 0.1-0.3% | | 7 |
| | Jordan | EC; foliar | >1 | | 0.4-0.6 | 2-3 |
| | Malaysia | EC; knapsack | >1 | 111-166 | | 7 |
| | Netherlands | space treatment | >1 | $2 \text{ g}/ 100 \text{ m}^3$ | | 3 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Potato | Chile | EC; foliar | >1 | | 0.06-0.1 | 2 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| | Venezuela | EC; foliar | | | 0.1-0.15 | 20 |
| Rice | Bangladesh | EC; foliar | 1-2 | | 0.5 | 14-21 |

| Crop | Country | | Applicat | ion | | PHI ² , days |
|-------------|----------------|--|----------|--|----------|----------------------------|
| | | Formulation ¹ , type | No. | g ai/hl | kg ai/ha | |
| | Colombia | EC; foliar | >1 | | 0.3-0.5 | 7 |
| | Ecuador | EC; foliar | >1 | 250 | 0.5 | 7 |
| | India | EC; foliar spray | 1-3 | | 0.37-0.5 | |
| | Indonesia | EC; layer treatment | | 0.5-1 g/m ² | | |
| | Malaysia | EC; knapsack | >1 | 111-222 | | 7 |
| | Nigeria | EC; thermofog EC; HV | | 20 mg/kg | 0.75 | 7 |
| Sorghum | Nigeria | EC; HV | ; HV >1 | | 0.75 | |
| | Indonesia | EC; layer treatment | >1 | $0.5-1 \text{ g/m}^2$ | | |
| Soya bean | Colombia | EC; foliar | >1 | | 0.5 | 7 |
| | India | EC; foliar spray | 2 | | 0.22-0.3 | |
| | Indonesia | EC; layering | >1 | $0.5-1 \text{ g/m}^2$ | | |
| Tea | Indonesia | EC; foliar | >1 | 100-150 | 0.5-0.75 | 7 |
| | Turkey | EC; foliar | >1 | 75 | | 5 |
| Tomato | Bolivia | EC; foliar | >1 | | 0.3-0.5 | 2-10 |
| | Brazil | EC; spray | >1 | 70 | | 7 |
| | Canada | EC; spray UN; fogging | | 6 g/100 m ² 35 g/1000 m ³ | | g7 |
| | Chile | EC; foliar | >1 | | 0.05 | 2 |
| | Czechoslovakia | EC; foliar | >1 | 0.1-0.3% | | 7 |
| | Ecuador | EC; foliar | >1 | 100 | 0.4 | 1 |
| | Jordan | EC; foliar | >1 | | 0.4-0.6 | 2-3 |
| | Lebanon | EC; foliar | >1 | 63 | | 7 |
| | Malaysia | EC; knapsack | >1 | 111-166 | | 7 |
| | Netherlands | EC; foliar AE; space treatment | up to 15 | 50-60 2 g/100 m ³ | 050-1.8 | 3 |
| | South Africa | EC; full cover | >1 | 100 | | 2 |
| | Switzerland | EC; foliar | >1 | 50 | | 7 |
| Indoor uses | Australia | EC; spray space treatment | | 3 g/m² 7 g/m³ | | |
| | Canada | EC; spray EC; direct spray ³ | | 0.25 g/m ² 0.06-0.11 g/cow | | |
| | France | KN; aerosol | 1 | 0.077 g/m³ | | |
| | Netherlands | AE; space treatment | | 1 g/ m^3 | | |
| | Switzerland | AE; aerosol | | | | |

Code for formulation: AE Aerosol dispenser; EC Emulsifiable concentrate; KN Cold-fogging concentrate; OL Oil-miscible liquid; SO Spreading oil; UL Ultra low-volume (ULV) liquid.
Pre-harvest interval refers to outdoor or field use unless it is specified (F-field, G-greenhouse).
Applied directly on cattle.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised trials have been carried out in a number of countries during the period 1973-1992. Results of these and some earlier trials are given in Tables 2-14. Samples from the trials performed after 1973 were analyzed by gas chromatography and the residues were determined as parent dichlorvos. The residue data in earlier trials were obtained by an automated cholinesterase-inhibition method.

In the Tables the countries (except the UK) are indicated by three-letter codes as follows:

ARG-Argentina, AUL-Australia, AUS-Austria, BGD-Bangladesh, BOL-Bolivia, BRA-Brazil, CAN-Canada, CHI-Chile, COL-Columbia, CZE-Czechoslovakia, ECU-Ecuador, FRA -France, GRE-Greece, IND-India, INS-Indonesia, ITA-Italy, JOR-Jordan, LEB-Lebanon, MAL-Malaysia, NET-Netherlands, NZE-New Zealand, NIR-Nigeria, PAK-Pakistan, PER-Peru, POL-Poland, POR-Portugal, SAF-South Africa, SPA-Spain, SUD-Sudan, SWI-Switzerland, TUR-Turkey, UAE-United Arab Emirates, VEN-Venezuela.

Underlined residues in the Tables are from treatments in accordance, or approximately in accordance, with GAP.

<u>Apples</u>. Five field trials were carried out in Switzerland by applying dichlorvos at a rate of 1.5 kg ai/ha or with a spray ai concentration of 0.05-0.1%. Residue data are summarized in Table 2. Residues decreased from 0.05-0.45 mg/kg at 0-1 day to <0.02 mg/kg within 14 days.

Cherries. Cherries were treated at the recommended and double rates (0.65- $\overline{1.25~kg}$ ai/ha) in South Africa. The residues (Table 3) were 0.05-0.39 mg/kg and <0.02 at days 2 and 8, respectively.

<u>Peaches</u>. Four field trials were carried out in France and Switzerland. Single applications were made on peach trees at a rate of 50 or 125 g ai/hl. The residue data are shown in Table 4. Residues in peaches decreased from 0.69 mg/kg immediately after treatment to <0.02-0.15 mg/kg in five days and <0.02-0.05 mg/kg in seven days.

Table 2. Residues in apples from supervised trials in Switzerland.

| Year | | Арр | olication | | Res | cation | Ref. | | | |
|------|-------|-----|-----------|---------|------|--------|-------|-------|-------|-----|
| | Form | No. | g ai/ha | g ai/hl | 0-1 | 3-4 | 5-7 | 14 | 21 | |
| 1970 | 50EC | 1 | | 50 | 0.05 | 0.03 | <0.03 | | | 6. |
| 1971 | 50EC | 1 | | 100 | 0.45 | 0.14 | 0.1 | | | 7. |
| 1971 | 500EC | 3 | 1500 | | 0.2 | 0.05 | <0.02 | <0.02 | <0.02 | 8. |
| 1992 | 500EC | 3 | 1500 | | | | <0.02 | <0.02 | <0.02 | 9. |
| 1992 | 500EC | 3 | 1500 | | | | <0.02 | <0.02 | <0.02 | 10. |

Table 3. Residues of dichlorvos in cherries and strawberries from supervised trials.

| Crop/country/year | | P | Application | | Residue | es (mg/kg |) at days a | fter last app | olication | Ref. |
|-----------------------|--------|---|-------------|-------|---------|-----------|-------------|---------------|-----------|------|
| | Form | 9 | | | | 2 | 3 | 4-5 | 7-8 | |
| Cherry, SAF, 1979 | 100 EC | 1 | 625 | 50 | 0.24 | 0.05 | <0.02 | <0.02 | <0.02 | 18 |
| Cherry, SAF, 1979 | 100 EC | 1 | 1250 | 100 | 1.39 | 0.39 | 0.16 | 0.04 | <0.02 | 19 |
| Strawberry, SWI, 1967 | 50 EC | 1 | | 0.05% | | 0.35 | 0.07 | | <0.02 | 20 |

Table 4. Residues of dichlorvos in peaches from supervised trials.

| Country, Year | | Applicati | on | | Residues (mg/kg) at days after last application | | | | | | | |
|---------------|------|-----------|---------|------|---|-----------|------------|------------|------------|----|--|--|
| | Form | No. | g ai/hl | 0 | 1 | 2 | 4 | 5 | 6-7 | | | |
| FRA, 1973 | 50EC | 1 | 0.125% | | | 0.32-0.38 | 0.05-0.08* | 0.09-0.15* | 0.01-0.05* | 81 | | |
| FRA, 1973 | 50EC | 1 | 0.125% | | | | <0.02 | <0.02 | <0.02 | 82 | | |
| SWI, 1969 | 50EC | 1 | 0.05% | 0.69 | 0.43 | 0.24 | | | | 55 | | |
| SWI, 1970 | 50EC | 1 | 0.05% | | 0.13 | 0.10 | 0.05 | | 0.04 | 56 | | |

^{*} Replicate samples from a single trial.

 $\underline{\text{Grapes}}$. Three field trials were carried out in France and Switzerland. One or three applications were made at a rate of 1.0 -1.25 kg ai/ha. The residue data are given in Table 5. Residue values were 0.23-1.14 mg/kg, <0.03-0.11 mg/kg and <0.02-<0.03 mg/kg after pre-harvest intervals of zero, three and ten days, respectively.

Table 5. Residues of dichlorvos in grapes from supervised trials.

| Country Year | | Ap | plication | | Residues (mg/kg) at days after last application | | | | | | Ref. |
|-----------------|--------|-----|-----------|---------|---|------|-------|-------|-------|-------|------|
| | Form | No. | g ai/ha | g ai/hl | 0 | 1 | 3 | 5-7 | 10-14 | 17 | |
| FRA, 1971 | 50EC | 1 | 1250 | | | | | | <0.02 | <0.02 | 46 |
| SWI, 1973 | 50EC | 1 | 1000 | | 0.23 | 0.05 | <0.03 | <0.03 | <0.03 | | 47 |
| SWI, 1992 | 500 EC | 3 | 1200 | | 1.14 | | 0.11 | 0.08 | <0.02 | | 48 |

<u>Strawberries</u>. A single trial was reported from Switzerland. The residues are shown in Table 3.

Dates. Two field trials were carried out in Iraq (Ref.43) according to the $\overline{\text{GAP}}$ in UAE. Date trees were sprayed once with dichlorvos at 0.95-2.0 kg ai/ha. No measurable residue (<0.03 mg/kg) was detected in mature fruits 138 days after the treatments.

Avocados. A single field trial was carried out in Australia (Ref.3). Dichlorvos was applied once to avocado trees at a rate of 50 g/hl. Results showed an initial deposit of 0.07 mg/kg and no measurable residues (<0.01/0.02 mg/kg) in whole fruit, pulp or peel of avocados at day 3.

 $\underline{\text{Onions}}$. Two field trials were carried out in Switzerland (Refs. 52-53.) with 40% higher than the recommended rate. There were three foliar applications (1 week interval) at a rate of 0.56 kg ai/ha. No measurable residues (<0.02 mg/kg) were detected in onion bulbs during the first 7 days after the last application.

Brassicas. Ten field trials were carried out with Brussels sprouts, cabbage, cauliflower and kale in India, The Netherlands and Switzerland. One to four applications were made at a rate of 0.5-0.8 kg ai/ha or as

0.05--0.075% ai spray solution. The results are summarized in Table 6. Residues were at or below $0.04~\rm mg/kg$ after a pre-harvest interval of 5 days.

Table 6. Residues of dichlorvos in brassica vegetables and kale from supervised trials.

| Crop, Country, Year | | А | pplication | | F | Residues (ı | mg/kg) at d | ays after la | ıst applica | tion | Ref. |
|-------------------------------|-------|-----|------------|---------|------|-------------|-------------|--------------|-------------|-------|------|
| | Form | No. | g ai/ha | g ai/hl | 0 | 5 | 7-8 | 10-11 | 14 | 18 | |
| Brussels sprouts SWI, 1970 | 50EC | 1 | | 0.05% | 1.25 | <0.03 | <0.03 | <0.03 | | | 15 |
| SWI, 1965 | 50EC | 1 | | 0.05% | 1.35 | <0.04 | | | | | 16 |
| NEL, 1982 | | 1 | 750 | 75 | | <0.01 | | | | | 108 |
| NEL, 1982 | | 1 | 750 | 75 | | <0.01 | | | | | 109 |
| Cabbage SWI, 1992 | 500EC | 4 | 800 | | 0.66 | | <0.02 | | <0.02 | | 17 |
| Cabbage, red NET, 1964 | 50 EC | 1 | | 0.075% | | | | <0.02 | | | 2 |
| Cauliflower SWI, 1965 | 50EC | 1 | | | 0.37 | <0.04 | | | | | 16 |
| Cauliflower IND, 1980 | 100EC | 3 | 500 | | | | | <0.02 | | <0.02 | 13 |
| Cauliflower IND, 1980 | 100EC | 3 | 625 | | | | | <0.02 | | <0.02 | 14 |
| Kale, NEL, 1982 | | 1 | 750 | 75 | | 0.04 | | | | | 108 |
| NEL, 1982 | | 1 | 750 | 75 | | 0.03 | | | | | 108 |

Cucumbers. Two field trials were carried out in Switzerland according to $\overline{\text{GAP}}$ (Refs. 41, 42). Cucumber plants were sprayed three times with dichlorvos at a rate of 0.6 kg ai/ha. No measurable residues (<0.02 mg/kg) were detected on the day after the last treatment.

<u>Egg plants</u>. Two field trials were carried out in India (Ref. 45) with three foliar applications at rates of 0.37 and 0.62 kg ai/ha. Less than 0.02 mg/kg residues were measured in egg plant fruits, twenty one days after the last application.

 $\underline{\text{Mushrooms}}$. Four glasshouse trials were carried out in The Netherlands and the United Kingdom with fogging or thermal spray applications at rates between 11 and 21 g ai/100 m³. Residues were between 0.03 and 0.11 mg/kg two days after the treatment (Table 7).

<u>Peppers</u>. A single residue trial was carried out in India. Three <u>applications</u> were made to chilli plants at a rate of 0.4 kg ai/ha. Residues were <0.04 mg/kg at seven and fourteen days after the last application (Ref. 59).

Table 7. Residues of dichlorvos in mushrooms from supervised trials.

| Country, Year | _ | Application | | | Residues (mg/kg) at days after last application | | | | | |
|---------------|------------------|-------------|--------------------------|-------|---|------|--|----|--|--|
| | Form No. g ai/hl | | 0 | 1 | 2 | 3 | | | | |
| NET, 1964 | | | 100ml/100 m ³ | <0.01 | <0.01 | | | 1 | | |
| UK, 1963 | 50 EC | 1 | 11 g/100 m ³ | 0.3 | | 0.03 | | 88 | | |
| | | | | 0.14 | 0.02 | | | 88 | | |
| | | | | 0.04 | <0.02 | | | 88 | | |

| | | | | 0.06 | 0.12 | | | 88 |
|----------|-------|---|---------------------------|------|------|-----------|------|-----|
| UK, 1964 | 50 EC | 1 | 17 g/100 m ³ | 25.6 | 0.9 | 0.08 | 0.27 | 99 |
| UK, 1964 | 50 EC | 1 | 21.2 g/100 m ³ | | | 0.04-0.06 | | 100 |
| | | | | | | 0.09-0.11 | | 100 |

 $\underline{\text{Tomatoes}}$. Two field trials were conducted in Switzerland according to GAP. Three applications were made at a rate of 70 g ai/hl. Residues were <0.02-0.09 mg/kg, <0.02-0.03 mg/kg and <0.02 mg/kg after zero, one and three days respectively (Refs. 73-74).

<u>Lettuce</u>. Trials were carried out in the field and in glasshouses in Germany, Switzerland and the United Kingdom. One or three applications were made at a rate of 0.5 or 1.25 kg ai/ha, (50 g ai/hl or 0.5 or 1.0 g ai/100 $\rm m^3$. Residue data are given in Table 8. In field trials, no measurable residues (<0.0002-<0.03 mg/kg) were detected within two days after the last application. In greenhouse trials, somewhat higher residue levels were detected; however, these residues decreased from 0.6-3.0 mg/kg at 1 day to 0.13-0.4 mg/kg within 4 days.

Table 8. Residues of dichlorvos in lettuce from supervised trials.

| Country Year | | | Application | | | ation | Ref. | | | |
|-----------------|--------|-----|-------------|-------------------------|------|---------|---------|----------|---------|-----|
| | Form | No. | g ai/ha | g ai/hl | 0 | 1 | 2 | 3-4 | 5-7 | |
| GER, 1972 | 50 EC | 1 | | 0.05% | 0.05 | 0.005 | <0.0002 | <0.0002 | <0.0002 | 107 |
| SWI, 1972 | 50 EC | 1 | 500 | 60 | 0.72 | <0.03 | <0.03 | <0.03 | <0.03 | 49 |
| SWI, 1992 | 500 EC | 3 | 1250 | | 0.71 | | | <0.02 | <0.02 | 50 |
| SWI, 1992 | 500 EC | 3 | 1250 | | 5.94 | | | <0.02 | <0.02 | 51 |
| UK, 1964 | 50 EC | 1 | | 1g/100 m ³ | | 1.6-3.0 | 0.2-0.6 | 0.13-0.3 | | 87 |
| UK, 1964 | 50 EC | 1 | | 0.5g/100 m ³ | | 0.6-2.2 | 0.2-0.5 | 0.2-0.4 | | 87 |

 $\underline{\text{Beans}}$. Trials were carried out in Switzerland and the United Kingdom. After three foliar applications at a rate of 1.2 kg ai/ha, no measurable residues (<0.02 mg/kg) were detected in beans at a PHI of three days. The results are shown in Table 9, which also includes the results of post-harvest treatments (see below).

Table 9. Residues of dichlorvos in beans from supervised trials.

| Crop/Year Country | Application | | | Residue, mg/kg, at PHI, days | | | | | Ref. |
|-----------------------|-------------|-----|-------------------------|------------------------------|---|-------|------|------|------|
| | Form | No. | g ai/ha | 0-1 | 3-4 | 7 | 14 | 21 | |
| Bean pods, SWI, 1992 | 500 EC | 3 | 1250 | 0.07 | <0.02 | <0.02 | | | 12 |
| Beans, dry, SWI, 1970 | 70 AE | | 20 mg/kg [*] | 13.1 | | 6.75 | 1.85 | 1.48 | 11 |
| Beans, dry, UK, 1963 | 50 EC | | 1 g/1000 m ³ | 2.5-0.47 | <lod< td=""><td></td><td></td><td></td><td>86</td></lod<> | | | | 86 |

^{*} Treated in glass bottles

Peas. In a recent Swiss trial (Ref. 54), pea plants were treated with $\overline{\text{dichlorvos}}$ at a rate of 1.25 kg ai/ha. Three applications were made over a period of three weeks. The spray concentration was three times that given in the national recommendation. No measurable residues (<0.02 mg/kg) were detected in pods or peas four days after the last treatment. The pod:pea ratio increased from 0.7:1 at day zero to about 1:1 in seven days.

Soya beans. Two field trials (Refs. 69-72) were carried out in India.

Application rates were 0.3-0.6 kg ai/ha (foliar). No measurable residue (<0.02 mg/kg) was detected in soya beans after application (21 days PHI).

Witloof chicory. A single trial was reported from The Netherlands $\overline{\text{(Netherlands, 1993)}}$ in which dichlorvos was applied at a rate of 4 g/100 m³. No residue (<0.01 mg/kg) was detected 14 days after treatment.

Rice. Six field trials were conducted in Bangladesh (Refs. 60-61), Columbia (Ref. 62) and India (Refs. 63-64). One or two applications were made at rates of 0.37-1.0~kg ai/ha. After foliar application no measurable residues (<0.02-<0.05 mg/kg) were detected in either rice grain or straw.

Sorghum. Two field trials were carried out in India. Two applications were made with a two-week interval at a rate of 30 or 50 g ai/hl. No measurable residues (<0.02 mg/kg) were detectable in either grain or straw thirteen days after the last treatment (Refs. 67-68).

<u>Cotton</u>. Field trials were carried out in India. Three to five foliar <u>applications</u> were made in combination with either phosphamidon or diazinon at rates of 0.20-0.37 kg ai/ha. Residues in cotton seeds were <0.01-<0.05 mg/kg at or after 23 days follwing the last application (Refs. 39-40).

<u>Peanuts</u>. In the field trials in India, peanut plants were treated twice with dichlorvos at a rate of 250 g ai/ha. The residue data are given in Table 10 together with the results of Swiss trials on stored peanuts. No measurable residues (<0.03 mg/kg) were detected in peanuts after foliar treatment.

| Country Year | | | Application | | | Residues (n | ng/kg) at days | after last a | pplication | | Ref. |
|-----------------|--------|-----|-------------|---------|---------|-------------|----------------|--------------|------------|-------|------|
| | Form | No. | g ai/ha | g ai/hl | 1 | 7 | 12-14 | 16 | 21 | 60 | |
| IND, 1974 | 100 EC | 2 | 250 | 50 | | | <0.03 | <0.03 | | <0.03 | 57 |
| | | 2 | | | | | <0.03 | <0.03 | | <0.03 | 57 |
| | | 2 | | | | | <0.03 | <0.03 | | <0.03 | 57 |
| SWI, 1970 | 7 EC | 1 | 10 mg/kg | 1% | 4.7-5.0 | 2.5-2.7 | 2.1 | | 1.5 | | 58 |
| SWI, 1970 | 7 EC | 1 | 20 mg/kg | 1% | 9.1 | 4.5 | 3.1-3.3 | | 2.5-2.6 | | 58 |

Table 10. Residues of dichlorvos in peanuts from supervised trials.

 $\underline{\text{Cacao beans}}$. Foliar treatment was at a rate of 0.5 kg ai/ha in Brazil. Residue data are shown in Table 11, which also gives the results of storage trials in The Netherlands and Switzerland (see below). No measurable residue (<0.02 mg/kg) was detected in dried seeds 32 days after application.

| Table 11. Residues of dichlorvos in cacao beans from supervised trials | Table | 11. | Residues | of | dichlorvos | in | cacao | beans | from | supervised | trials |
|--|-------|-----|----------|----|------------|----|-------|-------|------|------------|--------|
|--|-------|-----|----------|----|------------|----|-------|-------|------|------------|--------|

| Country, year, crop | | Application | | | | ues (mg/kg) at c applicatio | | Ref. |
|-------------------------|--------|-------------|----------|--------------|--------------|--------------------------------|------------|------|
| | Form | No. | g ai/ha | g ai/hl | 0 | 21 | >32 | |
| BRA, 1982, seed | 100 EC | 1 | 500 | 3.33% | | | <0.02* | 35 |
| NET, 1966, seeds | | | | 20% strips** | | | <0.01-0.02 | 112 |
| husk | | | | | | | n.d0.3 | |
| kernels | | | | | | | 0.01 | |
| kernel, roasted | | | | | | | <0.01 | |
| SWI, 1972, seed | 50 EC | 1 | 10 mg/kg | 0.25% | 4.5 | <0.1 | | 37 |
| seed, roasted butter | | | | | <0.1 0.15 | <0.1 <0.1 | | |

| SWI, 1972, seed | 50 EC | 1 | 100 mg/kg | 0.1% | 64 | 13-15 | 37 |
|-------------------------|-------|---|-----------|------|------------|------------|----|
| seed, roasted butter | | | | | 0.2 0.8 | 0.2 0.1 | |
| SWI, 1972, seed | 50 EC | 1 | 500 mg/kg | 5% | 370 | 50 | 37 |
| seed, roasted | | | | | | 0.5 | |

^{*} seeds were collected 32 days after foliar treatment and dried for two weeks at room temperature

Tea. A single field trial was reported from China (Zongmao and Haibin, $\overline{1968}$). The application rate was 1.0 kg/ha. The half-life was 0.2 days. After 6 days residues were below 0.1 mg/kg, the limit of determination.

Post-harvest applications

Beans. Two trials were carried out in Switzerland and the United Kingdom. $\overline{\text{Applications}}$ were at a rate of 20 mg/kg and 1 g/1000 m³. In dry beans, residues decreased from 13 mg/kg immediately after treatment to less than 1.5 mg/kg at 21 days. The results are shown in Table 9.

 $\underline{\text{Soya beans}}$. A post-harvest application (La Hue et al., 1973) was carried out in the USA at a rate of 20 mg/kg. The initial residues, 4.5-3.2 mg/kg immediately after treatment, decreased to <0.02 mg/kg within 21 days.

Cereals. Numerous (18) trials were carried out in Argentina, Austria, $\overline{\text{Brazil}}$, France, Germany and Switzerland on wheat, barley and rye. Applications were made as aerosol, fogging or by hanging "Vapona" strips over the barley, rye and wheat storage areas. Application rates were between 7 and 38 mg/kg or 0.3 and 5.6 g ai/ton grain or 1 strip/40 m³. The residue data are given in Table 12.

Table 12. Residues of dichlorvos in stored cereals from supervised trials.

| Crop Country, Year | , | Application | Resid | ues (mg/kg) at | intervals (days | s/months) after l | ast application | on | Ref |
|--------------------------------|------------------|-------------------------------|-------------------------------------|----------------|-----------------|-------------------|-----------------|------|-----|
| | Form | Rate, ai | 0-1d | 14-17d | 21d | 1-2m | 3m | >6m | |
| Wheat, ARG, 1979 | 600 EC | 3.2 mg/kg | | | | | | <0.2 | 21 |
| Wheat ⁴ , AUS,1975 | 70 AE | 14 mg/kg | 5.6-14 | 5.0 | 3.5 | 1.9 | | | 22 |
| Wheat, BRA, 1975 | 2.5 EC | 1.25 mg/kg | | | | | | 0.05 | 113 |
| Barley, FRA, 1969 Wheat | 70 AE | 7.4 mg/kg | 0.53-0.75 1.5-2.6 | 0.7 | | | | | 23 |
| Wheat, FRA, 1982 | mixture | 3.48 mg/kg | 3.4 ¹ -1.96 ² | 0.75 | | 0.46-0.33 | | | 84 |
| Wheat, FRA, 1986 | mixture | 3.48 mg/kg | 1.563 | <u>1.26</u> | | 0.90 | 0.53 | | 85 |
| Wheat, GER, 1977 | vapona strips | 1 strip/ 40 m ³ | | | | | <0.01- 0.02 | | 114 |
| Rye, GER, 1977 | vapona strips | 1strip/ 40 m ³ | | | | | <0.01- 0.02 | | 115 |
| Barley, SWI, 1969 | 70 AE | 7mg/kg | 1.2 | 0.2 | 0.14 | | | | 24 |
| Barley, SWI, 1972 | 70 AE | 5.6 mg/kg | 3.0 | 1.8 | 0.66-0.74 | 0.31-0.68 | | | 25 |
| Barley, SWI, 1976 | | 38.5 mg/kg | 15.0 | 12.5-21.5 | 4.0-5.4 | 2.2-4.6 | | | 27 |
| Wheat, SWI, 1969 | 70 AE | 7mg/kg | 1.8-2.0 | 0.8-0.9 | | 0.5 | | | 28 |
| Wheat, SWI, 1970 | 70AE | 20 mg/kg | | 3.1-3.6 | | | | | 29 |
| flour | | | | 0.14-0.18 | | | | | |
| bread | | | | <0.02 | | | | | |
| Wheat ⁴ , SWI, 1975 | 70 AE | 15 mg/kg | 7.8 | 4.8-6.0 | 4.4-5.2 | 2.1-5.0 | 1.5-1.9 | 0.2- | 30 |

^{**} Resin strips of $6.25 \times 25 \times 0.5$ cm containing 20% dichlorvos were placed in 3×4.5 m rectangle and held at room temperature.

| Crop Country, Year | А | pplication | Residues (mg/kg) at intervals (days/months) after last application | | | | | | |
|--------------------------------|-------|------------|--|---------|----------|-----------|-----------|-----|----|
| | Form | Rate, ai | 0-1d | 14-17d | 21d | 1-2m | 3m | >6m | |
| | | | | | | | | 0.4 | |
| Wheat ⁴ , SWI, 1975 | 70 AE | 17.5 mg/kg | 10.8-11.1 | 2.2-2.2 | 1.5-1.25 | 0.92-0.41 | | | 31 |
| Wheat ⁴ , SWI, 1976 | 70 AE | 15 mg/kg | 9.7-12.5 | 0.4-0.6 | 0.2-0.3 | | | | 32 |
| Wheat, SWI, 1977 | 70 AE | 14 mg/kg | | 2.6-2.4 | | | <0.12 | | 33 |
| Wheat, SWI, 1977 | 70 AE | 29 mg/kg | | | | 2.4 | 0.82 | | 34 |
| Wheat, SWI, 1977 | 70 AE | 28 mg/kg | | | | 0.7 | 0.39-0.64 | | 34 |

¹at day 0 after application

Stored rice was treated in Switzerland with 75-150 mg ai/m 3 . Residue data are shown in Table 13. Residues were between 0.12 and 0.23 mg/kg after about three weeks. After 2 months only 0.04 mg/kg was found.

Table 13. Residues of dichlorvos in stored rice from supervised trials in Switzerland in 1965.

| Commodity | | | Application | | Residues (| mg/kg) at dag | ys after last | application | Ref. |
|----------------|------|-----|-----------------------|-----------|------------|---------------|---------------|-------------|------|
| | Form | No. | g ai/ha | g ai/hl | 10-12 | 17 | 23-24 | 60 | |
| Rice | 20EC | 1 | 75 mg/m ³ | spray | <0.04 | | | | 65 |
| Rice, ground | | | | | <0.04 | | | | |
| Rice, polished | 20EC | 1 | 75 mg/m ³ | dispenser | | | 0.12 | | 65 |
| Rice, ground | | | | | | | 0.16 | | |
| Rice | 2EC | 1 | 150 mg/m ³ | spray | 0.5 | 0.2 | 0.23 | 0.04 | 66 |

<u>Cereals and other crops</u>. Trials were reported from India in which residues of dichlorvos in various commodities in food storage warehouses were determined at different geographical locations (Rajak, 1973). Nuvan 100 EC was applied at recommended and higher rates to the walls and the floor. The results are summarized in Table 14.

Table 14. Residues of dichlorvos in commodities stored in food storage warehouses treated with Nuvan 100 EC in India (Rajak, 1973).

| Commodity, location | Application rate, g ai/100 m ² | | Residue | es (mg/kg) at | days after tre | atment | |
|----------------------------|--|---------------|---------|---------------|----------------|--------|-------|
| | | 0 (1 hour) | 1 | 2 | 4 | 8-11 | 16-22 |
| Wheat, Rajasthan | 100 | 3.6 | 2.5 | 0.88 | 0.6 | | |
| Wheat, Maharashtra | 10* | 0.13 | 0.06 | 0.04 | 0.04 | 0.03 | 0.08 |
| Wheat, Assam | 10* | | 1.0 | 0.58 | 0.39 | 0.1 | 0.004 |
| Wheat Mixed, Assam | 10* | | | | 0.05 | 0.007 | 0.002 |
| Wheat Mixed, Assam | 35 | | | | 0.99 | 0.23 | 0.006 |
| Wheat, Assam | 10* | | | | 0.48 | 0.16 | 0.002 |
| Wheat ¹ , Assam | 10* | | | | 0.76 | 0.2 | 0.09 |
| Wheat, Assam | 35 | | 2.4 | 1.9 | 1.5 | 0.67 | 0.09 |

²at day 3 after application

³at day 1 after application

⁴sampled at the surface and at 2 m depth

| Commodity, location | Application rate, g ai/100 m ² | | Resid | ues (mg/kg) a | t days after ti | reatment | |
|--|--|---------------|-------|---------------|-----------------|----------|-------|
| | | 0 (1 hour) | 1 | 2 | 4 | 8-11 | 16-22 |
| Wheat ¹ , Uttar Pradesh | 50 | | 0.86 | 0.64 | 0.43 | 0.13 | 0.03 |
| Wheat, Uttar Pradesh | 50 | | 0.66 | 0.47 | 0.23 | 0.1 | 0.03 |
| Wheat ¹ , Uttar Pradesh | 10* | | 0.49 | 0.28 | 0.18 | 0.03 | 0.02 |
| Wheat, Uttar Pradesh | 10* | | 0.36 | 0.16 | 0.07 | 0.03 | 0.02 |
| Maize, Rajasthan | 10* | 0.75 | 0.44 | 0.24 | 0.14 | | |
| Paddy, Rajasthan | 10* | 0.51 | 0.35 | 0.15 | 0.1 | | |
| Rice, Tamil Nadu | 10* | | 0.22 | | 0.11 | 0.03 | 0.01 |
| Coriander, Assam | 10* | | 1.2 | 0.51 | 0.26 | 0.19 | 0.02 |
| Coriander, Assam | 35 | | 2.3 | 2.1 | 1.5 | 0.57 | 0.09 |
| Cumin, Assam | 10* | | | | 0.89 | 0.37 | 0.1 |
| Cumin ¹ , Assam | 10* | | | | 1.1 | 0.45 | 0.12 |
| Gram, Rajasthan | 10* | 0.61 | 0.33 | 0.14 | 0.11 | | |
| Gram ¹ , Uttar Pradesh | 50 | | 1.3 | 0.58 | 0.2 | 0.07 | 0.03 |
| Gram, Uttar Pradesh | 50 | | 0.99 | 0.46 | 0.19 | 0.05 | 0.02 |
| Gram ¹ , Uttar Pradesh | 10* | | 0.59 | 0.29 | 0.17 | 0.05 | 0.02 |
| Gram ¹ , Uttar Pradesh | 10* | | 0.78 | 0.49 | 0.23 | 0.14 | 0.04 |
| Gram, Uttar Pradesh | 10* | | 0.36 | 0.11 | 0.08 | 0.04 | 0.02 |
| Gram and Pulse, Tamil Nadu | 10* | | 0.26 | | 0.06 | 0.04 | 0.02 |
| Black gram, Maharashtra | 10* | 0.34 | 0.03 | 0.02 | 0.02 | 0.01 | 0.004 |
| Red gram, Maharashtra | 10* | 0.22 | 0.05 | 0.03 | 0.01 | 0.009 | 0.006 |
| Groundnut ¹ , Uttar Pradesh | 50 | | 1.7 | 0.95 | 0.32 | 0.18 | 0.09 |
| Groundnut, Uttar Pradesh | 50 | | 1.3 | 0.72 | 0.3 | 015 | 0.06 |
| Groundnut ¹ , Uttar Pradesh | 10* | | 0.78 | 0.49 | 0.23 | 0.14 | 0.04 |
| Groundnut, Uttar Pradesh | 10* | | 0.67 | 0.37 | 0.18 | 0.11 | 0.03 |
| Lentil, Rajasthan | 100 | 2.7 | 1.3 | 0.75 | 0.6 | | |
| Soya bean, Maharasthra | 54,5 | 1.3 | 0.2 | 0.16 | 0.13 | <0.04 | <0.04 |
| Linseed, Rajasthan | 100 | 2.7 | 2.0 | 0.91 | 0.67 | | |
| Linseed, Maharasthra | 54,5 | 1.1 | 0.49 | 0.29 | 0.22 | 0.07 | 0.02 |
| Mustard, Assam | 10* | | 0.81 | 0.62 | 0.43 | 0.25 | 0.09 |
| Mustard, Assam | 35 | | 1.8 | 1.4 | 0.95 | 0.89 | 0.12 |
| Sesame, Tamil Nadu | 10* | | 0.18 | | 0.11 | 0.06 | 0.04 |
| Mahua-raisin, Maharashtra | 54,5 | 1.6 | 0.63 | 0.16 | 0.15 | 0.05 | 0.01 |

^{*} Treated at the recommended rate

<u>Peanuts</u>. In post-harvest trials in Switzerland, stored peanuts were sprayed with dichlorvos at a rate of 10 or 20 mg/kg. The residue data are in Table 10. Residues decreased from 4.7-9.1 mg/kg immediately after treatment to 2.5-4.5 mg/kg in 7 days and 1.5 to 2.6 mg/kg in 21 days.

¹ Sprayed directly on bags

<u>Cacao beans</u>. Trials were carried out in The Netherlands and Switzerland. Treatments were made with dichlorvos at a rate of 0.25-5.0% ai in the spray solution. In one trial 20% strips were also used. Residue data are shown in Table 11.

 $\underline{\text{Coffee}}$ beans. Coffee beans were sprayed with dichlorvos at concentrations of 10 and 20 mg/kg using a 7 EC formulation. No measurable residue (<0.5 mg/kg) was detected in the beans, four months after application (Ref. 38).

ANIMAL TRANSFER STUDIES

Residues of dichlorvos in livestock (cattle, sheep, goats and pigs) and poultry were discussed in the 1970 Evaluations (FAO/WHO, 1971). Since then further trials have been carried out. The new information is discussed below.

Hens. Twelve egg-laying hens confined in batteries in an $8.6~\text{m}^3$ building were sprayed with dichlorvos, applying a mist spray three times at three-day intervals (Hurt, 1964). The dosage rate was $50~\text{mg/m}^3$, double the recommended rate. Six eggs were collected at random on each day. Residues of dichlorvos in the eggs were first detected 2 days after the first treatment. The residue concentration varied from <0.03 to 0.11 mg/kg during the trial. There was no increase in the concentration following consecutive treatments, and the residue declined below the limit of determination 3 days after the last application. Three birds were killed 18 hours after the 3rd treatment and the breast and leg muscles were analyzed. The residues found were between <0.01 and 0.05 mg/kg. Egg production was not affected by the treatments.

Cattle. Each of three cows was sprayed for 31 consecutive days with 59 ml of 1% dichlorvos solution, for the control of horn fly and mosquitoes. Milk samples were collected after 2 hours and 1, 2, 4, 8, 16, 24 and 31 days. Tissue and blood samples were taken one day after the final treatment. No dichlorvos was detected in any milk samples (<0.003 mg/kg) or body tissues (<0.002 mg/kg) from the treated cows (Ivey and Eschle, 1970).

In another experiment, dairy cows were dosed orally with dichlorvos at rates of 1.3, 1.8 and 2.6 mg/kg body weight in the form of polyvinyl chloride pellets. No dichlorvos residues (<0.04 mg/kg) were detected in milk samples collected at 1, 3, 7, 10 or 14 days (Lloyd and Matthysse, 1971).

In a dermal application experiment, six cattle and two dairy cows were sprayed once with 15 litres of an emulsion of "Nuvan" 100 EC at a concentration of 1500 mg/kg. Cattle were slaughtered 1, 3 and 7 days after treatment. Milk samples from the dairy cows were taken 6 h, and 1, 3 and 7 days after treatment (control 1 day before treatment). No measurable residue of dichlorvos was found in milk (<0.005 mg/kg) or in muscle, liver, kidney or fat (<0.02 mg/kg) (Ref.80).

FATE OF RESIDUES

In animals

Animal metabolism studies showed that dichlorvos is readily absorbed, hydrolysed and effectively eliminated. The metabolic pathways were identical in the mammalian species studied, including humans. The main metabolic degradation routes are by hydrolyis, oxidation and demethylation (Figure 1).

<u>Pigs</u>. In studies by Potter *et al*. (1973), nine pigs received a single oral dose of $[1^{-14}\text{C}]\text{vinyl-dichlorvos}$ (ca. 40 mg dichlorvos/kg feed) formulated as slow-release PVC pellets. After treatment, groups of three pigs were slaughtered after 2, 7 and 14 days. Various tissues were analyzed at each interval. The ¹⁴C content of the tissues, as dichlorvos equivalents, varied from 1.6 mg/kg in subcutaneous fat to 33 mg/kg in liver after 2 days, and from 1.9 mg/kg in brain to 9.7 mg/kg in liver after 14 days, but no dichlorvos, demethyl-dichlorvos, dichloroacetaldehyde or dichloroacetic acid could be detected. The mean residues found are given in Table 15.

Figure 1. Metabolic pathways of dichlorvos in mammals

Table 15. 14C residues in tissues from pigs dosed with [14C]dichlorvos.

| Substrate | | chlorvos, | |
|----------------------|--------|-----------|---------|
| | 2 days | 7 days | 14 days |
| Adrenals | 8.7 | 6.5 | 4.6 |
| Bladder | 8.1 | 8.0 | 5.6 |
| Blood | 6.5 | 3.7 | 2.8 |
| Brain | 2.5 | 1.9 | 1.9 |
| Carcase | 5.2 | 5.1 | 4.2 |
| Duodenum | 12.3 | 5.6 | 3.1 |
| Femur | 11.7 | 7.4 | 5.4 |
| Gastrocnemius muscle | 6.3 | 4.6 | 4.8 |
| Kidney | 12.2 | 7.6 | 4.0 |
| Liver | 32.9 | 30.9 | 9.7 |
| Lungs | 8.6 | 5.3 | 3.8 |
| Mesenteric fat | 2.6 | 4.2 | 2.5 |
| Pancreas | 9.6 | 5.7 | 3.5 |
| Quadriceps muscle | 4.7 | 4.8 | 4.3 |
| Salivary gland | 10.0 | 5.6 | 3.7 |
| Spiral colon | 8.1 | 3.8 | 3.5 |
| Spleen | 11.5 | 7.0 | 4.3 |
| Stomach | 7.1 | 4.7 | 3.0 |
| Subcutaneous fat | 1.6 | 4.0 | 2.2 |
| Thyroid | 5.0 | 5.1 | 5.5 |

In the 14-day trial, the radioactivity administered was distributed as follows: 61.8% in the pellets recovered from the faeces, 5.6% in the remainder of the faeces, 3.6% in the urine, 14.1% in the expired air and 9.6% in the carcase. It was concluded that the ^{14}C present in the tissues was the result of incorporation of one- and two-carbon fragments from the vinyl moiety of dichlorvos into normal tissue constituents.

In plants

The metabolism of dichlorvos in plants was described on the basis of published ^{32}P studies in the 1970 monograph (FAO/WHO, 1971). New data including studies with ^{14}C in wheat and ^{32}P in various plants, and of dislodgeable residues in turf and grass are summarized below.

The main routes of degradation of dichlorvos in plants were found to be (Figure 2):

- cleavage of the vinyl ester bond to form the major metabolite dimethyl phosphate;
- 2. demethylation to monomethyl phosphate and phosphoric acid;
- 3. demethylation of dichlorvos to demethyl-dichlorvos (minor pathway);
- 4. loss by volatilization (thermal, solar).

<u>Cotton</u>. Cotton plants of the Deltapine Smooth leaf variety were grown in a $\overline{\text{glasshouse}}$ and treated by injecting aqueous solutions of $^{32}\text{P-labelled}$ dichlorvos (100 ig) into the petioles of individual, fully expanded leaves. Leaf samples were collected 1, 24 and 48 hours after the treatment. Dichlorvos was rapidly lost from leaf surfaces by volatilization and

hydrolysis with a half-life of only a few hours. Samples were partitioned into chloroform and aqueous fractions. Identification of the parent compound and metabolites was based mainly on co-chromatography of radioactive material with authentic compounds after two-dimensional TLC. Enzymic hydrolysis was also employed in identifying conjugates. The studies showed 81.2% loss as volatiles, 12.3% as dimethyl phosphate (major metabolite), 2.2% as phosphoric acid + methyl phosphate and 0.1% as demethyl-dichlorvos (minor metabolites) after 48 hours. No parent residue was detectable at this time (Bull and Ridgway, 1969). Unextractable residues corresponded to less than 5% of the applied radioactivity. The detailed fate of dichlorvos in cotton leaves over the 48-hour test period is shown in Table 16.

In another greenhouse study cotton plants of 15 cm height, with or without roots, were placed in a formulated 0.1-0.2% [32 P]dichlorvos solution. Foliar experiments were also performed by dipping plants into solutions of the labelled ai. Dichlorvos was degraded with a half-life of 4.6 hours. Dimethyl phosphate was a major metabolite detected during the 24-hour test period. Here again about 80% (78.4%) of the radioactivity was lost by volatilization, confirming the 1969 study (Dedek et al., 1979).

Figure 2. Main plant metabolites of dichlorvos

Table 16. Relative concentrations of radioactive compounds obtained from individual cotton leaves after petiole injection with 100 32 P-labelled dichlorvos.

| Compound | Q | of dose | |
|-----------------------------------|------|---------|------|
| | l h | 24 h | 48 h |
| ${ m H_3PO_4}$ + methyl phosphate | 0.9 | 1.1 | 2.2 |
| dimethyl phosphate | 6.0 | 13.3 | 12.3 |
| O-demethyl-dichlorvos | 1.7 | 0.2 | 0.1 |
| dichlorvos | 36.8 | 0.1 | 0.0 |
| unextractable | 1.0 | 4.5 | 4.2 |
| lost (volatile) | 53.6 | 80.8 | 81.2 |

Bean, potato and tomato. The above study by Dedek et al. (1979) also included greenhouse-grown bean, potato, and tomato plants of 15 cm height treated in the same way. Dichlorvos was degraded with a half-life of 6.8, 4.6 and 6.8 hours in beans, tomatoes and potatoes respectively. Dimethyl phosphate was a major metabolite detected during the 24 hour test period. Volatile radioactivity accounted for about 60% of the 32 P in all three plant species. In vitro homogenate experiments with beans showed a longer half-life, 32.6 hours, than that measured when dichlorvos was applied to the leaf surface.

<u>Wheat</u>. The fate of [14 C]dichlorvos applied to stored wheat grain was investigated (Rowlands, 1970). Grains at moisture levels of 18% and 10.6% were topically treated with [14 C]dichlorvos at a rate of 40 ig ai/10 g sample. Treated samples were stored in sealed glass jars in darkness at 20°C and sampled over a period of 10 days.

The uptake of dichlorvos was rapid at the higher moisture level. Within 2 days the water-extractable bound activity reached a maximum and remained stable for 7 days, after which time the phosphorylated protein was converted to a more stable demethyl from. The uptake rate decreased once all the protein had been phosphorylated, so excess dichlorvos would be lost from the grain by volatilization.

Dichlorvos broke down rapidly on grain to give mainly dimethyl phosphate (about 2 mg/kg at day 10) and phosphorylated protein derivatives, which were mainly water-soluble. Lesser amounts of demethyl-dichlorvos (about 0.5 mg/kg at day 10), monomethyl phosphate (about 0.2-0.25 mg/kg at day 10) and traces of phosphoric acid (undetectable-0.05 mg/kg at day 10) were also found. The water content did not affect the rate of degradation.

In an another study wheat and sorghum were treated commercially with 6 mg/kg dichlorvos. The loss of dichlorvos was faster from small grain bulks and from the surface of large bulks than within large bulks. Dichlorvos had a half-life of 54 hours on wheat and 27 hours on sorghum. It was also degraded in sealed containers that were not chemically inert (Desmarchelier, 1977).

Turf and lawn. Six 0.61 x 2.44 m (1.49 m 2) plots in California, USA, were sprayed with "Dichloron" (2.6% dichlorvos + 3.0% chlorpyrifos) at the maximum recommended rate (3.8 litre of product in 605.7 litre of water for 508 m 2 of lawn). Leaf samples were taken 0, 2, 6, 10, 24, 72 and 96 hours after application.

The dislodgeable foliar residue level was calculated from the residue concentration measured on the grass surface with a regression equation established before the experiment. The surface residue was 0.10 $\,$ ig/cm² immediately after application. This level dropped rapidly below 0.06 ig/cm² after 2 hours and the residue was undetectable (<0.12 mg/kg) after 23 hours. In the air 1.9 \pm 0.5 ig/kg dichlorvos was detected immediately after spraying (Goh et al., 1986a)

Similar experiments were performed in lawn plots using all and half the recommended quantity of water, and with and without post-spray irrigation. The results showed the dissipation of the dislodgeable residue to be remarkably similar to that found in the previous experiments, suggesting that the dilution factor of the spray is of minor importance in the field dissipation of dichlorvos (Goh et al., 1986b).

In water

The hydrolysis of dichlorvos at a concentration of 10 mg/kg in aqueous media follows first-order kinetics. The rate of hydrolysis appears to be strongly influenced by the ionic strength of the solution. Half-lives at 30°C and pH 1, 5, 7 and 9 were found to be 74, 50, 18 and 16 hours respectively. At 20°C and pH 13 the half-life was 1.3 x 10^{-2} hours (Suter, 1981).

In micro-ecosystems containing sediments from a recultivated gravel pit and the drainage ditch of a fruit orchard, dichlorvos was very rapidly degraded to CO_2 . After 16 days incubation, 76 and 69% of the applied 1.0 mg [^{14}C]dichlorvos/litre was mineralized to $^{14}\text{CO}_2$ in the two systems, respectively. Unchanged parent compound could be detected until day 7

(0.5%) and day 3 (3.1%) respectively. The following compounds occurred as intermediate products of this mineralization.

- I phosphoric acid, 2,2-dichloroethyl methyl phosphate, sodium phospate, demethyl-dichlorvos.
- II 2,2-dichloroethanol.
- III 2,2-dichloroacetaldehyde.
- IV dichloroacetic acid.

Contamination of surface waters with dichlorvos is unlikely to be more than transient owing to the rapid and extensive metabolism (Fritz, 1987c).

The photolytic degradation of dichlorvos was tested in water and aqueous methanolic solutions at 20°C . Dichlorvos was degraded with a half-life of about 6 hours in water, but was stable in methanolic solution (Ref. 76).

In soil

The leaching characteristics of dichlorvos in aged and non-aged BBA 2.1 soil were studied. [$^{14}\mathrm{C}$]dichlorvos equivalent to 1 kg ai/ha was applied to soil and aged for 0, 2, 8 and 12 days. In a column leaching study 35%, 10%, 2% and <0.1% of the applied radioactivity was detected in the leachate, respectively. Up to 15% of the radioactivity in the leachate was dissolved $^{14}\mathrm{CO}_2$. 2,2-dichloroethanol and demethyl-dichlorvos corresponded to about 10% and 1% respectively. Parent dichlorvos was rapidly mineralized in the soil, and was not detectable in any leachates. Within 2 days of ageing, 60-65% of the parent compound was detected as $^{14}\mathrm{CO}_2$ (Fritz, 1987a).

The loss of dichlorvos in soil perfusion systems of Houston black clay under sterile and non-sterile conditions was reported (Lamoreaux and Newland, 1978). The perfusion technique involved continually perfusing a column of soil with an aqueous solution containing 1000 mg/l dichlorvos. The pesticide was extracted from the perfusing water. After 10 days 70% and 50% losses of dichlorvos were observed under non-sterile and sterile conditions respectively.

Dichlorvos was converted to dichloroethanol, dichloroacetic acid and ethyl dichloroacetate by a microbial enrichment derived from sewage (Lieberman and Alexander, 1983).

The degradation of dichlorvos was investigated in sterile and non-sterile standard 2.1 soil of the BBA and in a natural biologically active soil (Fritz, 1987b). After an incubation period of 2 days 1.2% of the unchanged parent compound could be detected in soil 2.1 and none in the second system. During the same period 60-61% of the applied radioactivity was measured as $^{14}\mathrm{CO}_2$. The decomposition of the active ingredient was slower in sterile standard soil 2.1, where the half-life was 8.7 days and less than 1% $^{14}\mathrm{CO}_2$ was formed.

On the basis of various soil and microbial degradation studies, the pathway shown in Figure 3 has been proposed for dichlorvos breakdown.

Figure 3. Proposed pathway for the breakdown of dichlorvos in soil.

In storage and processing

The persistence of dichlorvos on stored commodities is strongly dependent on the temperature and moisture content or relative humidity. For instance, a moisture content of 12% in wheat is roughly equivalent to 60-65% relative humidity (RH).

 $\underline{\text{Cereals}}$. The reported half-lives on wheat are 10 days at 25°C and 12% moisture content, 25 days at 21°C and 9.3% moisture content, and 1.8 days

at 35°C and 13.7%. The Australian Grain Industry uses an estimated half-life of 7 days at 30°C and 50% RH, and 28 days at 20°C and 50% RH (Webley, 1993).

In Switzerland stored wheat treated with 20 mg/kg dichlorvos was processed. The results are included in Table 12. After 14-16 days, between 3.1 and 3.6 mg/kg residue remained in the whole wheat. The flour prepared from the treated wheat contained 0.14-0.18 mg/kg, and the bread no measurable residues (<0.02 mg/kg).

The rapid disappearance of dichlorvos in comparison with most other grain protectants makes it difficult to obtain accurate measurements of persistence in a commercial trial. Preliminary laboratory-scale trials were therefore undertaken to determine the persistence on cereals and milled products, although in commercial practice the milled products are not directly treated. Dichlorvos was added directly in aqueous solution followed by tumbling. One kg of each commodity was treated at 6 and 12 mg ai/kg and the commodity was stored in closed screw-top glass jars at 0, 20 and 30°C. The initial moisture content of wheat lots ranged from 13.05 to 13.47%. The results are shown in Table 17.

Table 17. Disappearance of dichlorvos from wheat, chickpeas and milled products under laboratory conditions.

| Commodity | Appl. rate, g ai/t | Storage temp. °C | Re | esidues (mg | /kg) after v | veeks of sto | rage |
|-----------|-----------------------|------------------|--------------------|--------------------|--------------|--------------|------------|
| | | | 1 | 2 | 4 | 6 | 8 |
| Flour | 1 | 0 20 30 | 1.0 0.2 1.2 | 0.3 | 0.9 | 0.9 | 1.0 |
| | 2 | 0 20 30 | 1.8 0.5 0.1 | 2.0 0.5 | 2.3 0.2 | 2.3 0.1 | 1.8 |
| Bran | 6 | 0 20 30 | 7.5 4.0 0.3 | 9,5 1.9 | 8.4 1.0 | 7.8 0.4 | 1.6 |
| Germ | 6 | 0 20 30 | 6.3 1.8 1.8 | 4.3 | 5.1 | 4.5 | 1.8 |
| Wheat | 6 | 0 20 30 | 5.5 2.8 0.7 | 5.5 1.2 0.1 | 4.7 0.5 | 4.0 0.3 | 4.8 |
| Wheat | 12 | 0 20 30 | 10.2 4.7 2.0 | 10.4 3.0 0.3 | 10.7 1.4 | 0.5 | 7.3 |
| Chickpea | 6 | 0 20 30 | 3.5 1.0 0.4 | 3.2 0.5 0.1 | 2.6 0.2 | 2.2 0.2 | 2.7 0.1 |
| Chickpeas | 12 | 0 20 30 | 7.3 2.9 1.2 | 7.5 1.5 0.3 | 6.0 0.9 | 5.7 0.5 | 4.2 0.1 |

The distribution and stability of dichlorvos in milling fractions were studied in a laboratory-scale experiment (Webley, 1993). 3 kg samples of wheat were treated with dichlorvos at 6 and 12 g ai/ton and were milled on a Buhler mill after 3 days. Flour, bran and wheat were stored at 20 and 30°C for 8 weeks in closed screw-topped glass jars. The results are shown in Table 18. Residues on flour and bran decreased to about 1/4-1/5 of the initial concentration after 2 weeks at 30°C and had a half-life of about 7 days at 20°C .

Table 18. Residues of dichlorvos in wheat and milling fractions during storage (laboratory-scale).

| Commodity, [treatment rate] | Storage temp. °C | | Residues (| mg/kg) after v | veeks of storag | ie |
|-----------------------------|---------------------|-------------|------------|----------------|-----------------|-----|
| | | 1 | 2 | 4 | 6 | 8 |
| Wheat [12 g/ton] | | 7.2 | 2.2 | 2.2 | 0.4 | |
| Flour | 20 30 | 0.4 0.2 | 0.3 | 0.1 | | |
| Bran | 20 30 | 9.7 11.7 | 7.5 1.2 | 1.1 | | 0.2 |
| Wheat [6 g/ton] | | 4.1 | 5.0 | 1.3 | | |
| Flour | 20 30 | 0.3 0.1 | 0.2 0.1 | 0.1 | | |
| Bran | 20 | 6.4 | 4.8 | 0.9 | | 0.3 |

Pilot-scale milling trials were carried out with commercially treated wheat (Webley, 1993a). Dichlorvos was applied at rates of 6, 12 and 20 mg/kg on wheat lots of 6 tons each. The treated wheat was bagged and that from each treatment was divided into two 3-ton lots. The initial moisture content of the wheat was approximately 11% (Webley 1993b). Two days after treatment, analyses of lots treated at 6, 12 and 20 mg/kg showed residues of 3.4, 8.3 and 14.8 mg/kg respectively. The lots were milled 10 and 90 days after treatment. Arabic flat bread, steamed bread, yellow alkaline noodles and white salted noodles were prepared from the milled products. The results are summarized in Table 19.

Table 19. Dichlorvos residues (mg/kg) in pilot milling trials.

| Appl. Rate (mg/kg) | | 6 | 1: | 2 | 20 |) |
|----------------------------|------|------|------|------|------|------|
| Interval to milling (days) | 10 | 90 | 10 | 90 | 10 | 90 |
| Commodity | | | | | | |
| Wheat | 2.5 | | 5.2 | 0.9 | 6.1 | 1.0 |
| Wheat, conditioned | 0.7 | 0.1 | 1.4 | 0.2 | 2.1 | 0.3 |
| Bran | 4.1 | 0.5 | 7.3 | 1 | 11.5 | 1.4 |
| Germ | 2.6 | 0.3 | 5.0 | 0.8 | 7.0 | 1.0 |
| Flour | 0.3 | <0.1 | 0.4 | <0.1 | 0.6 | 0.1 |
| Wholemeal | 1.3 | 0.1 | 1.8 | 0.2 | 2.1 | 0.3 |
| White-bread | <0.1 | <0.1 | 0.2 | <0.1 | <0.1 | <0.1 |
| Wholemeal bread | 0.2 | <0.1 | 0.3 | <0.1 | 0.3 | <0.1 |
| Flat bread | 0.3 | <0.1 | 0.5 | <0.1 | 0.6 | <0.1 |
| Steamed bread | 0.2 | <0.1 | 0.3 | <0.1 | 0.2 | <0.1 |
| Yellow alkaline noodles | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| White salted noodles | 0.2 | <0.1 | <0.1 | <0.1 | 0.3 | <0.1 |

The results show a loss of dichlorvos in the milling process of about 60%. The loss in processing may be largely attributable to the scouring and conditioning process with probably some additional loss in the milling itself. In calculating the reduction in residue in the cooked products the differences in moisture content were taken into account by the following factors: 1.5 for white, wholemeal and steamed bread, 1.14 for flat bread,

and 1.0 for noodles. This gives a loss of 75% of the dichlorvos residue in the production of pan breads, about 65% in the case of Arabic flat bread (this tends to retain a higher residue owing to the short, 30-second, heat treatment), and 55% in white noodles. There is a 100% loss in yellow noodles owing to the alkali (1% sodium carbonate by flour weight). There were no detectable residues in any cooked products produced from wheat stored for 3 months after treatment, even after an application of 20 g/ton.

The cold-storage stability of dichlorvos and other pesticides was reviewed by Kawar et al. (1973). Wheat samples with moisture contents ranging between 13% and 17% were treated with dichlorvos at a rate of 24 mg/kg and stored at -15°C. After 2 months, 15 mg/kg (62.5% of the initial concentration of dichlorvos), was lost. When stored at 5°C, 50% and 80% was lost after seven and thirty days respectively.

In an another study, 50 mg/kg dichlorvos was added to wheat samples of 9.3-13.7% moisture content and stored at $-15^{\circ}\mathrm{C}$ for 11 months. The losses were only between 2% and 22% at different moisture levels. Even though these two experiments showed two different levels of loss, they indicate that the breakdown of dichlorvos cannot be completely prevented even under cold storage conditions.

 $\underline{\text{Cacao}}$. Cacao beans were treated with dichlorvos at a rate of 10, 100 and $\underline{500}$ mg/kg and stored at room temperature. After 21 days, as shown in Table 13, no residues (<0.1 mg/kg) were detected in whole or roasted cacao beans treated at 10 mg/kg. Samples treated at 100 and 500 mg/kg contained 15 and 50 mg/kg after 21 days. About 99% of these residues was lost on roasting.

 $\underline{\text{Endive}}$. Cutting, washing and cooking endive containing 0.31 mg/kg $\underline{\text{dichlor}}$ vos resulted in 6% and 84% losses of residues after washing and cooking respectively (Netherlands, 1993)

<u>Lettuce</u>. Washing head lettuce containing 0.75 mg/kg dichlorvos removed 24% of the residue (Netherlands, 1993).

Chickpeas. Laboratory-scale trials were undertaken to determine the persistence of dichlorvos on chickpeas. Dichlorvos was added directly in aqueous solution followed by tumbling. One-kg portions of chickpeas were treated at 6 and 12 mg/kg and stored in closed screw-top glass jars at 0, 20 and 30°C. The initial moisture content of the commodities was not reported. The results are shown in Table 17.

<u>Potatoes</u>. In a Japanese trial (Tsumura *et al.*, 1992) potatoes were sprayed with a formulated mixture of dichlorvos at a concentration of 0.2% ai in the spray solution. After storing at room temperature for 86 days 0.92 mg/kg was still measured in whole potatoes, but about 97% of this surface residue could be removed by washing. When the washed potatoes (containing 0.03 mg/kg dichlorvos) were processed into dry and wet starch, no residues (<0.001 mg/kg) were detected.

 $\underline{\text{Soya beans}}$. In a USA trial (La Hue et al., 1973), whole soya beans containing 0.92-1.5 mg/kg residue were processed into hulls, toasted hulls, flakes, crude oil and refined oil. Residues were 5.4-6.0 mg/kg, <0.02 mg/kg, 0.2 mg/kg, 0.55 mg/kg and <0.02 mg/kg in hulls, toasted hulls, flakes, crude oil and refined oil respectively.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Analyses by the Food Inspection Services of The Netherlands in 1976 showed the following residues (mg/kg) in fruit and vegetables (number of samples are in parentheses): endive <0.05 (2); lettuce <0.05 (9), >0.2 (1); celery <0.05 (1); spinach <0.05 (1); cauliflower <0.05 (1); leek <0.05 (1), <0.1 (1); cucumber <0.05 (7); paprika <0.05 (4); tomato <0.05 (2); radish <0.05 (2); blackberry <0.05 (1) (Netherlands, 1993).

METHODS OF RESIDUE ANALYSIS

Dichlorvos can be determined by many published multi-residue procedures.

The samples from supervised trials before 1972 were analyzed by the

automated cholinesterase inhibition method described in the 1970 Evaluations. Since then all samples have been analyzed by gas chromatography.

Plant material is Soxhlet-extracted with methylene chloride or acetone. After evaporating the solvent hexane is added. Clean-up involves extracting the organic phase with water and the aqueous phase with ethyl acetate, followed by drying of the organic phase with sodium sulphate. The final determination is by GLC using a phosphorus-specific flame-photometric detector. The recovery ranges from 70 to 100% and the limit of determination is 0.02-0.03 mg/kg. The method is valid for commodities such as peaches, tomatoes, rice and wheat grain (Ref. 79).

With further clean-up, based on partitioning between the water phase (saturated with sodium chloride) and hexane/ether 1:1, the same procedure was adopted for meat, cheese, milk and stored cereals. The limit of determination was 0.01-0.02~mg/kg with recoveries of 68%-110% (Ref. 77).

For food and beverages, the sample homogenized with water or a portion of the beverage is shaken vigorously in an Erlenmeyer flask after adding sodium sulphate, phosphotungstic acid and ethyl acetate. The final determination of dichlorvos is by GLC as before. The same method can be used with slight modification for blood and animal tissues with a detection limit of $0.01~\mathrm{mg/kg}$ (Zweig, 1972).

For the determination of dichlorvos in air, the dichlorvos is trapped in glass tubes containing potassium nitrate connected to a vacuum pump. Sampling tubes should be stored below room temperature before analysis. After eluting the trapped dichlorvos with distilled hexane, determination is by GLC with flame-photometric detection. A limit of determination of 0.2 $\,\mathrm{mg/m^3}$ was reported. The recovery was above 80% (Bryant and Minett, 1978).

Another method involves condensing dichlorvos in a U-tube immersed in salt-ice mixture (-20°C). Air is sucked into the tube with a vacuum pump for a period of 30-60 min. After washing the tube with acetone (5 ml), dichlorvos is determined by GLC using either an FPD or AFID. The limit of determination was 0.056 mg ai/m 3) with 80-100% recovery (Ref. 78).

NATIONAL MAXIMUM RESIDUE LIMITS

The reported national MRLs are summarized below. They all refer to dichlorvos.

The three-letter country codes are as follows: ARG-Argentina, AUL-Australia, AUS-Austria, BGD-Bangladesh, BOL-Bolivia, BRA-Brazil, CAN-Canada, CHI-Chile, COL-Columbia, CZE-Czechoslovakia, ECU-Ecuador, FRA -France, GRE-Greece, IND-India, INS-Indonesia, ITA-Italy, JOR-Jordan, LEB-Lebanon, MAL-Malaysia, NET-The Netherlands, NZE-New Zealand, NIR-Nigeria, PAK-Pakistan, PER-Peru, POL-Poland, POR-Portugal, SAF-South Africa, SPA-Spain, SUD-Sudan, SWI-Switzerland, TUR-Turkey, UAE-United Arab Emirates, VEN-Venezuela.

| Country → Commodity ↓ | ARG | AUL | AUS | BRA | CAN | CHI | CZE | FRA | GRE | IND |
|-----------------------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Apple | | | 0.1 | | | | | | 0.1 | - |
| Cabbage | | | | 0.5 | | | | 0.1 | | |
| Cacao beans | | 5 | | | | | | | | |
| Cereal grains | 2 | 2 | 2 | | | 2 | 2 | 2 | | 1 |
| Coffee beans, green | | 2 | | | | | | | | |
| Cotton | | | | | | | | | 0.1 | |
| Cucumber | | | | | | | 0.1 | | | |
| Eggs | | 0.05 | | | | | | | | |
| Fruits | | 0.1 | | | | | | | | |

| $\begin{array}{c} \text{Country} \rightarrow \\ \text{Commodity} \downarrow \end{array}$ | ARG | AUL | AUS | BRA | CAN | CHI | CZE | FRA | GRE | IND |
|--|-----|------|-----|-----|--------------------------------------|-----|-----|-----|-----|-----|
| Grapes | | | 0.1 | | | 0.1 | | 0.1 | 0.1 | |
| Lentils | | 2 | | | | | | | | |
| Lettuce | | 1 | | | | | | 0.1 | 0.1 | |
| Meat | | 0.05 | | | | | | | | |
| Milk, whole | | 0.02 | | | | | | | | |
| Mushroom | | 0.5 | | | | | 0.1 | | | |
| Non-perishable packaged food | | | | | 0.5 ¹ 2.0 ² | | | | | |
| Nuts | | 2 | | | | | | | | |
| Onion | | | 0.1 | 0.5 | | | | | 0.1 | |
| Other foods ³ | | 0.1 | | | | | | | | |
| Pea | | | | | | | | 0.1 | 0.1 | |
| Peach | | | 0.1 | | | | | 0.1 | 0.1 | |
| Peanuts | | 2 | | | | | | | 0.1 | |
| Peppers | | | | | | 0.5 | 0.1 | | | |
| Potato | | | | | | 0.5 | | | | |
| Poultry | | 0.05 | | | | | | | | |
| Rice | | | | | | | | | | 1 |
| Soya beans | | 2 | | | | | | | | |
| Tomato | | 0.5 | | 0.5 | 0.25 | 0.5 | 0.1 | | | |
| Vegetables (except lettuce) | | 0.5 | | | | | | | | |

National MRLs (continued)

| Country/Commodity | ITA | JOR | MAL | NET | NZE | PER | POL | POR | SAF | SPA |
|---------------------------|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|
| Apple | 0.1 | 0.1 | | | | | | 0.1 | | |
| Bean | | 0.5 | 0.1 | | | | | | 0.3 | |
| Berries + small fruits | | | | 0.1 | 2.0 | | | | 0.1 | |
| Brassica (excl.cabbage) | | 0.1 | | | 2.0 | 0.5 | | | | |
| Cabbage | | | | | | 0.5 | | 0.1 | 0.1 | |
| Cacao beans | | | | 5 | | | | | | |
| Cereal grains | 2 | | | 2 | 2 | | 2 | | | 2 |
| Chicken meat | | | | 0.05 | | | | | | |
| Coffee beans (green) | | | | 2 | | | | | | |
| Cucumber | | 0.5 | | 0.1 | | | 0.3 | | | |
| Eggs | | | | 0.05 | | | | | | |
| Egg plant | 0.1 | 0.5 | | | | | 0.1 | | | |
| Fruits | | | | 0.1 | | | | | | |
| Grapes | | | | | | | | | 0.1 | |
| Legume vegetables (fresh) | | | | 2 | | | | | | |

| Country/Commodity | ITA | JOR | MAL | NET | NZE | PER | POL | POR | SAF | SPA |
|------------------------|-----|-----|-----|--------|-----|-----|-----|-----|-----|-----|
| Meat | | | | 0.05 | | | | | | |
| Milk | | | | 0.02 | | | | | | |
| Mushroom | | | | 0.1 | | | 0.1 | | | 0.1 |
| Onion | | 0.5 | | | | | | | | |
| Other food commodities | | | | <0.024 | | | | | | |
| Other vegetables | | | | 0.1 | | | | | | |
| Peanuts | | | | 2 | | | | | | |
| Peppers | | 0.5 | | | | | | | | |
| Pulses | | | | 2 | | | | | | |
| Tomato | | 0.5 | | | | | | | 0.1 | |
| Wheat, wholemeal | | | | 0.5 | | | | | | |

| Country/Commodity | SWI | TUR | UAE | VEN |
|--------------------------|------|-----|-----|-----|
| Apple | 0.1 | | | |
| Avocado | 0.3 | | | |
| Bean | | | | 0.3 |
| Berries + small fruits | 0.3 | | | |
| Brassica (excl. cabbage) | 0.3 | | | |
| Cabbage | | | | 0.2 |
| Cereals | 2 | | | |
| Cocoa beans | 2 | | | |
| Cucumber | 0.3 | | | |
| Dates | | | 3 | |
| Egg plant | 0.3 | | | |
| Grapes | 0.1 | | | |
| Lettuce | 0.3 | 0.2 | | |
| Milk | 0.01 | | | |
| Onion | 0.3 | | | |
| Pea | 0.3 | | | |
| Peach | 0.1 | | | |
| Peanuts | 0.3 | | | 0.2 |
| Peppers | 0.3 | | | |
| Potato | 0.3 | | | 0.3 |
| Rice | 2 | | | |
| Sorghum | 2 | | | |
| Soya bean | 2.0 | | | |
| Tomato | 0.3 | | | |

^{1 &}lt;6% fat

APPRAISAL

Dichlorvos was previously evaluated at the 1965, 1966, 1967, 1969, 1970 and 1974 Joint Meetings and it is included in the CCPR periodic review programme.

Dichlorvos, an organophosphorus insecticide, combines both contact and stomach action and has a marked vapour action. It is effective against a broad spectrum of insect pests in the field and in stored products. In addition to plant and stored product protection, it is often used in public health vector control and in animal health for ectoparasite control. The compound is registered for use on over 30 commodities in many countries.

Residues from supervised field trials or specific studies were evaluated for $45\ \text{commodities}.$

Following foliar application at recommended or double rates, the

² >6% fat

³ Other foods for which no MRL is specified

⁴ Below the limit of determination

residues in most of the plant commodities tested (apples, avocados, beans, Brussels sprouts, cacao beans, cabbages, cauliflower, chilli peppers, cotton seed, cucumbers, dates, egg plants, lettuce, onions, peanuts, peas, rice, sorghum, soya beans, strawberries, tea, tomatoes, witloof chicory) were below the limit of determination (0.01--0.04~mg/kg), except tea 0.1 mg/kg). Detectable residue were reported in four commodities with maximum values of 0.05 mg/kg in cherries, 0.15 mg/kg in peaches, 0.08 mg/kg in grapes and 0.04 mg/kg in kale.

Residues in samples of endive, celery, spinach, cauliflower, leeks, cucumbers, paprika, tomatoes, radishes and blackberries moving in commerce in The Netherlands were below the limit of determination (<0.05 mg/kg). A residue of 0.1 mg/kg was found in one of 10 lettuce samples.

Following the post-harvest or indoor application of dichlorvos, residues were present in detectable amounts in beans (1.85 and 1.48 mg/kg after 14 and 21 days), wheat (0.41-5.0 mg/kg after 1-2 months), barley (0.14-0.74 mg/kg after 21 days), rice (0.12-0.23 mg/kg after 23-24 days), lettuce (0.2-0.4 mg/kg after 3-4 days) and mushroom (0.02-0.12 mg/kg after 1 day). The results of supervised trials on barley, wheat and rice were supported by the extensive studies in India on a wide variety of stored commodities including cereals.

The very limited data base for most of the crops and/or the discrepancy between the trial conditions and current GAP for beans, cacao beans, coffee beans, cotton seed, egg plant, indoor lettuce, peanuts, peppers and soya beans did not allow the estimation of maximum residue levels, although the Meeting took into account that the results are mutually supportive for many commodities.

The Meeting was also concerned about the lack of frozen storage stability tests of residues in fruit and vegetable samples in view of the period of several months which often elapsed between sampling and analysis, and the substantial decrease of dichlorvos residues in wheat samples stored at $-15^{\circ}\mathrm{C}$.

In the absence of this information and as a result of the limited residue data, the previous recommendations for fruits and vegetables were withdrawn.

The animal metabolism studies showed that dichlorvos is readily absorbed, hydrolysed and effectively eliminated. The metabolic pathway was identical in the mammalian species studied. The studies on laboratory animals are discussed as part of the toxicological evaluation.

Residues of dichlorvos in the eggs of hens receiving a mist spray three times at a rate of $50~\text{mg/m}^3$ were first detected 2 days after the first treatment. The residue concentration varied from <0.03 to 0.11 mg/kg during the trial. There was no increase in the concentration following consecutive treatments, and the residue declined below the limit of determination 3 days after the last application. Three birds were killed 18 hours after the 3rd treatment and the breast and leg muscle analysed. The residues found were between <0.01 and 0.05 mg/kg. Egg production was not affected by the treatments.

Various tissues of pigs which had received a single oral dose of vinyl-1- 14 C-dichlorvos (ca. 40 mg dichlorvos/kg feed) were analysed at 2, 7 and 14 days after the treatment. The 14 C content of the tissues expressed as dichlorvos varied from 2.5 mg/kg (in brain) to 33 mg/kg (in liver) after 2 days, and from 1.9 mg/kg to 9.7 mg/kg after 14 days, but no dichlorvos, demethyl-dichlorvos, dichloroacetaldehyde or dichloroacetic acid could be detected.

Three cows were sprayed for 31 consecutive days with 59 ml of 1% dichlorvos solution for the control of horn fly and mosquitoes. Milk samples were collected at 2 hours and 1, 2, 4, 8, 16, 24 and 31 days. Tissue and blood samples were taken one day after the final treatment. No dichlorvos was detected in any milk samples (<0.003~mg/kg) or body tissues (<0.002~mg/kg) from the treated cows.

Dairy cows were dosed orally at rates of 1.3, 1.8 and 2.6 mg/kg body weight with dichlorvos in the form of polyvinyl chloride pellets. The PVC formulation prevents substantial absorption by the animal, but may release the compound only much later in the manure. As the absorbed amount is

unknown the non-detectable dichlorvos residues (<0.04 mg/kg) in milk samples, collected between 1 and 14 days, cannot be related to the dose.

In a dermal application experiment, six cattle and two dairy cows were sprayed once with 15 litres of an emulsion of NUVAN 100 EC at a concentration of 1500 mg/kg. Cattle were slaughtered 1, 3 and 7 days after treatment. Milk samples from two dairy cows were taken 6 h and 1, 3 and 7 days after treatment (control 1 day before treatment). No measurable residues of dichlorvos were found in milk (<0.005 mg/kg) or in muscle, liver, kidney or fat (<0.02 mg/kg).

In plants, the main routes of degradation of dichlorvos were found to be cleavage of the P-C bond to form the major metabolite dimethyl phosphate, demethylation to monomethyl phosphate and phosphoric acid, demethylation to demethyl-dichlorvos (a minor pathway), and loss by volatilization.

Cotton plants of the Deltapine Smooth leaf variety were grown in a glasshouse and treated by injecting aqueous solutions of $^{32}\text{P-labelled}$ dichlorvos (100 µg) into the petioles of individual, fully expanded leaves. Leaf samples were collected 1, 24 and 48 hours after the treatment. The analyses showed 81.2% loss as volatiles, 12.3% as dimethyl phosphate (the major metabolite), 2.2% as phosphoric acid + methyl phosphate and 0.1% as demethyl-dichlorvos (minor metabolites) within 48 hours of application. No parent residue was detectable at this time. Non-extractable residues corresponded to less than 5% of the applied radioactivity.

Greenhouse-grown bean, potato, and tomato plants of $15\,\mathrm{cm}$ height, with or without roots, were placed in formulated 0.1--0.2% $^{32}\mathrm{P}\text{--}dichlorvos$. Dichlorvos was degraded with a half-life of 6.8, 4.6 and 6.8 hours on beans, tomatoes and potatoes, respectively. Dimethyl phosphate was a major metabolite detected during the 24--hour test period. Volatile radioactivity amounted to about 60% in all three plant species.

Wheat grain at moisture levels of 18% and 10.6% was topically treated with $^{14}\mathrm{C}\text{-}\mathrm{dichlorvos}$ at a rate of 40 ig ai/10 g sample. Treated samples were stored in sealed glass jars in darkness at 20°C and sampled over a period of 10 days. the uptake of dichlorvos was rapid at the higher moisture level. Within 2 days the aqueous-extractable bound activity reached a maximum and remained stable for 7 days, after which the phosphorylated protein was converted to a more stable demethyl form. The uptake rate decreased once all the protein had been phosphorylated, so excess dichlorvos would be lost from the grain by volatilization.

Dichlorvos broke down rapidly on grain to give mainly dimethyl phosphate (about 2 mg/kg at day 10) and phosphorylated protein derivatives, which are mainly water-soluble. Lesser amounts of demethyl-dichlorvos (about 0.5 mg/kg at day 10), monomethyl phosphate (about 0.2-0.25 mg/kg at day 10) and traces of phosphoric acid (undetectable-0.05 mg/kg at day 10) were also found.

The hydrolysis of dichlorvos at a concentration of 10 mg/l in aqueous media follows first order kinetics. The rate of hydrolysis appears to be strongly influenced by the ionic strength of the solution. Half-lives at 30°C determined at pH 1, 5, 7 and 9 were 74, 50, 18 and 16 hours respectively. At 20°C and pH 13, the half-life value is 1.3 x 10^{-2} hours.

In micro-ecosystems containing sediments from a recultivated gravel pit and the drainage ditch of a fruit orchard, dichlorvos was very rapidly degraded to $\rm CO_2$. After 16 days incubation, 76 and 69% of the applied 1.0 mg $^{14}\text{C-dichlorvos/l}$ was mineralized to $^{14}\text{CO}_2$ in the two systems, respectively. Unchanged parent compound could be detected until day 7 (0.5%) and day 3 (3.1%), respectively. The following dichlorvos metabolites occurred as intermediary products: phosphoric acid, mono(2,2-dichloroethyl) monomethyl ester, sodium salt, demethyl-dichlorvos, 2,2-dichloroethanol, 2,2-dichloroacetaldehyde and dichloroacetic acid. Contamination of surface waters by dichlorvos is unlikely owing to rapid and thorough metabolism.

The photolytic degradation of dichlorvos was studied in water and aqueous methanolic solutions at 20 $^{\circ}\text{C}$. It was degraded with a half-life of about 6 hours in water but was stable in methanolic solution.

Dichlorvos was applied to soil at a rate corresponding to 1 kg ai/ha and aged for 0, 2, 8 and 12 days. In a column leaching study 35%, 10%, 2%

and <0.1% of the applied radioactivity was detected in the leachate respectively. Up to 15% of the radioactivity in the leachate was dissolved $^{14}\mathrm{CO}_2$. 2,2-dichloroethanol and demethyl-dichlorvos corresponded to about 10% and 1% respectively. Parent dichlorvos was rapidly mineralized in the soil, and it was not detectable in any leachates. Within 2 days of ageing, 60-65% of the parent compound was detected as $^{14}\mathrm{CO}_2$.

Dichlorvos was very rapidly degraded to the final mineralization product CO_2 in non-sterile standard soil 2.1 of the BBA and in a natural biologically active soil. After an incubation period of 2 days, 1.2% of the unchanged parent compound could be detected in soil 2.1 and none in the second system. During the same period 60-61% of the radioactivity applied as the parent compound was measured as $^{14}CO_2$. The decomposition of the active ingredient was slower in sterile standard soil 2.1. The half-life was 8.7 days. Less than 1% $^{14}CO_2$ was formed.

Dichlorvos was converted to dichloroethanol, dichloroacetic acid and ethyl dichloroacetate by a microbial enrichment derived from sewage.

The persistence of dichlorvos in stored commodities is strongly dependent on the temperature and moisture content or relative humidity (RH). A moisture content of 12% in wheat is roughly equivalent to 60-65% relative humidity. Reported half-lives are 10 days at 25°C and 12% moisture content, 25 days at 21°C and 9.3% moisture content, and 1.8 days at 35°C and 13.7%. The Australian Grain Industry uses an estimated half-life of 7 days at 30°C and 50% RH, and 28 days at 20°C and 50% RH.

Stored wheat lots treated with 6, 12 and 20 mg/kg dichlorvos were processed and the residues were analysed in milling fractions and baked products. The results indicate that the loss in processing may be largely attributable to the scouring and conditioning process. The ratios of dichlorvos residues in bran, germ and flour to wheat were on average 1.5, 1.0 and 0.1, respectively. The residues (mg/kg) detected were as follows: in white bread <0.02-0.2, in wholemeal bread and steamed bread 0.2-0.3, and in Arabic flat bread 0.3-0.6. In calculating the reduction in residue in the cooked products the differences in moisture content were taken into account by the following factors: 1.5 for white, wholemeal and steamed bread, 1.14 for flat bread, and 1.0 for noodles. This gives a loss of 75% of the dichlorvos residue in the production of pan breads, about 65% in the case of Arabic flat bread, which tends to retain a higher residue owing to the short (30 second) heat treatment, and 55% in white noodles. There is a 100% loss in yellow noodles owing to the alkali treatment (1% sodium carbonate by flour weight). There were no detectable residues in any cooked products produced from wheat stored for 3 months after treatment even at an application rate of 20 g/tonne.

In cacao beans about 99% of the residue was lost after roasting. Cacao butter contained 1.3-3.3% of the residues detected in the un-roasted cacao beans.

Washing removed 97%, 24% and 6% of the initial dichlorvos residues from potatoes, lettuce and endive. Cooking endive resulted in an 84% loss of residues.

Whole soya beans containing 0.92-1.5 mg/kg residues were processed into hulls, toasted hulls, flakes, crude oil and refined oil. Residues were 5.4 - 6.0 mg/kg, <0.02 mg/kg, 0.2 mg/kg, 0.55 mg/kg and <0.02 mg/kg respectively.

Storage stability tests of dichlorvos in wheat samples with moisture contents ranging between 13% and 17% indicated that 2 months after treatment 62.5% of the initial concentration (20 mg/kg) was lost at -15°C. When stored at 5°C, 50% and 80% was lost after seven and thirty days respectively. In another study, 50 mg/kg dichlorvos was added to wheat samples of 9.3-13.7% moisture content and stored at -15°C for 11 months. The losses were between only 2% and 22% at different moisture levels.

Although these two experiments showed two different levels of loss, they indicated that the breakdown of dichlorvos cannot be completely prevented even under cold storage conditions.

Dichlorvos can be determined by many published multi-residue procedures.

The samples from supervised trials before 1972 were analysed by an automated cholinesterase-inhibition method described in the 1970 Evaluations. Since then all samples have been analysed by gas chromatography using phosphorus-specific flame-photometric detectors.

RECOMMENDATIONS

On the basis of the data on residues from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits.

Definition of the residue: dichlorvos.

| Commodity | Reco | Recommended MRL (mg/kg) | | | | | |
|--------------------------------------|--------|-------------------------|--------------|--|--|--|--|
| CCN Name | New | Previous | PHI, days | | | | |
| VP 0061 Beans | W | 0.5 for vegetables | | | | | |
| SB 0715 Cacao beans | W | 5 | | | | | |
| GC 0080 Cereal grains | 5 (Po) | 2 | 30 | | | | |
| SB 0716 Coffee beans | W | 2 | | | | | |
| PE 0112 Eggs | W | 0.05 | | | | | |
| AO2 0001 Fruits | W | 0.1 | | | | | |
| MM 0814 Goat meat | W | 0.05 | | | | | |
| VD 0533 Lentil (dry) | W | 2 | | | | | |
| VL 0482 Lettuce, Head | W | 1 | | | | | |
| MM 0097 Meat of cattle, pigs & sheep | W | 0.05 | | | | | |
| MM 0095 Meat | 0.05* | - | | | | | |
| ML 0106 Milks | 0.02* | 0.02 | | | | | |
| VD 0541 Soya bean (dry) | W | 2 Po | | | | | |
| AO1 0002 Vegetables (except) | W | 0.5 ¹ | | | | | |
| CF 0654 Wheat bran | 10 | | | | | | |
| CF 1211 Wheat flour | 1 | | | | | | |
| CF 1210 Wheat germ | 10 | | | | | | |
| CF 1212 Wheat wholemeal | 2 | | | | | | |

Note: W: the previous recommendation is withdrawn.

FURTHER WORK OR INFORMATION

Desirable

- 1. Storage stability tests carried out on major commodities at or below $18^{\circ}\text{C}\,.$
- 2. Residue data on milled products of cereals other than wheat.
- 3. An animal transfer study on poultry.

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