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Food and Agriculture Organization of the United Nations

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**Interim Chemical Review Committee** Fifth session Geneva, 2 – 6 February 2004 Item 5(a) of the provisional agenda<sup>\*</sup>

# INCLUSION OF CHEMICALS IN THE INTERIM PRIOR INFORMED CONSENT **PROCEDURE - SUPPORTING DOCUMENTATION**

# **Mevinphos**

# Note from the Secretariat

Annexed to this note is the documentation provided by Jordan in support of their notification 1. of final regulatory action on Mevinphos.

UNEP/FAO/PIC/ICRC.5/1

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# List of Documentation Annexed to UNEP/FAO/PIC/ICRC5/11/Add.1

Supporting documentation on mevinphos from Jordan:

English translation of Regulatory action against mevinphos Excerpt of WHO pesticide classification, 2003 Excerpt of the Pesticide Manual, 10<sup>th</sup> edition - mevinphos Focused summary – Mevinphos Report of JMPR 1972 - mevinphos

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# Translations of document No. 2 Re: Regulatory action against mevinphos Session 331 of the Agricultural Pesticide committee Date 9/8/1994 Excerpts of the minutes related to the control actions against mevinphos

The committee of pesticides met on Tuesday the 9th / 8/1994 under the chair ship of Eng. Mr. Mazin Alhafawna and the membership of:

- 1\Dr. Eisa Abanba
- 2\ Eng. Said Magad
- 3\Dr. Mazin Akkawi

4\ Eng. Ahmed Alhafawna

5\ Eng. Mahmoud Altibish

6\ Eng. Khalaf Alogla

Absentee: Eng. Khalid Musfat

The following issues were discussed:

1\ Study of the insecticide Mevanate 24 % SC presented by the Arab Company for Manufacture of pesticide (intended to be produced locally), the active ingredient is mevinphos.

The committee decided to refuse registration because of its high toxicity.

Other issues were discussed in this meeting but were not translated as they were not relevant.

Signature of attendants:

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Representative of faculty of Agriculture, Jordanian University, Dr. Mazin Akkawi Committee chair, Eng. Mazin Alhafawna Representative of Ministry of Health, Dr. Eisa Abanba

Head of Pesticide analytical center, Eng. Ahmed Alhafawna

|                              | active ingredients of pesticides | LD <sub>50</sub> Remarks |                | 0.93 DS 53; EHC 121; HSG 64: IARC 53: ICSC 04: IA MR 1000 | DS 57; EHC         | 1.12 DS 88; EHC 175; HSG 94 |                     | 39 Adjusted classification: see note 1. 1000 102 | 5000 Adjusted classification: see note 2. ITSC 407 | JMPR 1986a: see note 3 | 1.8 Extremely hazardous by skin contact (TD in 11.1 in in 1 |                       |                  | 1                  |                   |                  | 2.6 DS 68; JMPR 1997a |                   | D26 DS 70; JMPR 2000 |               |                         | D10000 Adjusted classification: see notice 2 1 5 | 1 See note 3: ICSC 979 | D4 DS 14; ICSC 924: IMPR 1008h | 13 See note 3; DS 6; HSG 74: YARC 30: YCSC 5: 70 mm 1000 | 14 See note 3; DS 7; EHC 145; HSG 75; IARC 30: ICSC 676- TAPP |                             |          |            | 0.2 Tre 16    |           |                     | 1.3 Extremely hazardous by skin contact (LD <sub>30</sub> 9.4 mg/kg in rate) |                | - |   |        |
|------------------------------|----------------------------------|--------------------------|----------------|---|--------------------|-----------------------------|---------------------|--|--|------------------------|---|-----------------------|------------------|--------------------|-------------------|------------------|-----------------------|-------------------|----------------------|---------------|-------------------------|--|------------------------|--------------------------------|--|---|-----------------------------|----------|------------|---------------|-----------|---------------------|--|----------------|---|---|--------|
|                              | ive ingredient                   | F1                       | 。              | S-I-S   | 2                  |                             |                     | FM   |  |                        | H<br>,  |                       | 2                |                    |                   |                  |                       |                   |                      |               | I-S                     | FST  | F-S                    | Ι                              | I  | Ţ   | FST                         |          |            | r N           |           | -                   | I-S-I  |                |   |   |        |
| ) 1                          | graue acti                       | g                        |                | و ر   |                    |                             |                     |  |  |                        |   |                       |                  |                    | 20                |                  |                       |                   |                      | S I           |                         |  |                        |                                | OP<br>L  | -1<br>-1  |                             |          |            | S             |           |                     |  |                |   |   |        |
| tachnical . ~                |                                  |                          | 7757           |   |                    |                             | 8907                | c/cl   |  |                        | 3010  |                       |                  |                    | 7500              | 3018             |                       |                   |                      | - [           | - [                     | - ľ  | <u> </u>               | -                              | 3018 0   |   | 1674 HG                     | 3018 OP  | 3018 OP    | 2629          | 1704 0    | 3018 OP             | 3018 OP  |                |   |   |        |
| (Class Ta)                   |                                  | CA3 110                  | 116-06-3       | 56073-10-0  | 28772-56-7         | 63333 35 7                  | 1-00-00000          | 0-10-766   | 1-00-6747  | 54503 82 0             | 24934-91-6  | 3691-35-8             | 56073-07-5       | 104653-34-1        | 87-66-6           | 298-04-4         | 2104-64-5             | 13194-48-4        | 00035 00 0           | 0-00-0000     | 118 74 1                | 1-4/-011   | 76710 65 0             | 0-00-01/07                     | 7-96-00  | 0-00-0/7  | 62-38-4                     | 298-02-2 | 13171-21-6 | 62-74-8       | 3689-24-5 |                     | 13071-79-9   | 2 <sup>7</sup> |   | ; | 1<br>2 |
| Table 1. Extremely hazardous | Common name                      |                          | Aldicarb [ISO] | Brodifacoum [ISO]   | Bromadiolone [ISO] | Bromethalin [ISO]           | Calcium cyanide [C] | Captafol [ISO]                                   | -<br>-<br>-  | Chlorethoxyfos [ISO]   | Chlormephos [ISO]   | Chlorophacinone [ISO] | Difenacoum [ISO] | Difethialone [ISO] | Diphacinone [ISO] | Disulfoton [ISO] | EPN                   | Ethoprophos [ISO] | Flocoumafen          | Fonofos [ISO] | Hexachlorobenzene [ISO] | Mercuric chloride [ISO]                          |                        | Parathion [ISO]                | Parathion-methyl [ISO]                                   |   | Phenylmercury acetate [ISO] | PL       |            | Sultent right |           | Leoupirimios [ISO*] | I erbutos [ISO]  |                |   |   |        |

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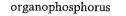
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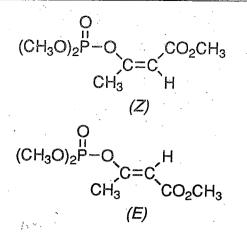
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# U EDITION

mevinphos

# Insecticide Acaricide





# NOMENCLATURE

Common name mevinphos (BSI, E-ISO, (m) F-ISO, ESA). The isomer should be stated, as (E)- or (Z)- [or cis or trans (with respect to the carbon chain)]. IUPAC name 2-methoxycarbonyl-1-methylvinyl dimethyl phosphate; methyl 3-(dimethoxyphosphinoyloxy)but-2-enoate. C.A. name methyl 3-[(dimethoxyphosphinyl)oxy]-2-butenoate. CAS RN [26718-65-0], formerly [298-01-1] (E)-isomer; [338-45-4] (Z)-isomer; [7786-34-7] (Z)- + (E)-isomers. Development code OS-2046 (Cyanamid) Official code ENT 22 374.

# **PHYSICO-CHEMICAL PROPERTIES**

**Composition** Tech. contains > 60% m/m of the (E)-isomer and c. 20% m/m of the (Z)-isomer.

Mol. wt. 224.1 Mol. formula C7H13O6P

Form Colourless liquid; (tech., pale yellow liquid). M.p. (*E*)-isomer 21 °C; (*Z*)-isomer 6.9 °C B.p. 99-103 °C/0.3 mmHg V.p. 17 mPa (20 °C) SG/density 1.24 (20 °C); (*E*)-isomer 1.235; (*Z*)-isomer 1.245 K<sub>ow</sub> P = 1.34 Solubility Completely miscible with water and most organic solvents, e.g. alcohols, ketones, aromatic hydrocarbons, and chlorinated hydrocarbons. Slightly soluble in aliphatic hydrocarbons, petroleum ether, ligroin, and carbon disulfide. Stability Stable at ambient temperatures but hydrolysed in aqueous alkaline solution,  $DT_{50}$  120 d (pH 6), 35 d (pH 7), 3 d (pH 9), 1.4 h (pH 11).

# COMMERCIALISATION

History Insecticide reported by R. A. Corey *et al.* (*J. Econ. Entomol.*, 1953, 45, 386). Introduced by Shell Chemical Co., USA (now American Cyanamid Co.), and later by Amvac Corp. Patents US 2685552 Manufacturer Amvac; Comlets; Cyanamid; Hui Kwang.

## APPLICATIONS

Mode of action Systemic insecticide and acaricide with contact, stomach, and respiratory action. Short residual activity. Cholinesterase inhibitor. Uses Control of chewing and

mevinphos 703

sucking insects, and spider mites on a wide range of crops, including pome fruit, stone fruit, berry fruit, citrus fruit, strawberries, melons, vines, hops, water melons, vegetables, cucurbits, aubergines, ornamentals, beet, potatoes, cotton, oilseed rape, cereals, clover, lupins, trefoil, okra, sorghum, etc. Phytotoxicity Non-phytotoxic. Formulation type EC; SL. Compatibility Compatible with most insecticides, acaricides, and fungicides, but incompatible with those which are alkaline in reaction. Principal tradename 'Phosdrin' (Cyanamid, Amvac), 'Duraphos' (Amvac).

#### ANALYSIS

Product analysis by glc with FID (CIPAC Proc., 1981, 3, 283). Residues determined by glc with FPD (Pestic. Anal. Man., 1979, I, 201-H, 201-I; Man. Pestic. Residue Anal., 1987, I, 3, 6, S8, S13, S17, S19; Anal. Methods Residues Pestic., 1988, Part I, M2, M5, M12; A. Ambrus et al., J. Assoc. Off. Anal. Chem., 1981, 64, 733). Details available from Amvac Chemical Corp.

# MAMMALIAN TOXICOLOGY

Reviews Pesticide residues in food. FAO Agricultural Studies, No. 90; WHO Technical Report Series, No. 525, 1973. 1972 Evaluations of some pesticide residues in food.
AGP:1972/M/9/1; WHO Pesticide Residues Series No. 2, 1973. Acute oral LD<sub>50</sub> for rats 3-12, mice 7-18 mg/kg. Skin and eye Acute percutaneous LD<sub>50</sub> for rats 4-90, rabbits 16-33 mg/kg. Mild irritant to skin and eyes (rabbits). Inhalation LC<sub>50</sub> (1 h) for rats 0.125 mg/l air. NOEL In 2 y feeding trials, rats receiving 4 mg/kg diet and dogs receiving 5 mg/kg diet showed no ill-effects. ADI (JMPR) 0.0015 mg/kg b.w. [1972]. Toxicity class WHO Ia; EPA I.

#### ECOTOXICOLOGY

**Birds** Acute oral  $LD_{50}$  for mallard ducks 4.63, chickens 7.52, pheasants 1.37 mg/kg. **Fish**  $LC_{50}$  (48 h) for rainbow trout 0.017, bluegill 0.037 mg/l. Bees Toxic to bees;  $LD_{50}$  0.027 µg/bee.

#### ENVIRONMENTAL FATE

Animals In mammals, following oral administration, elimination occurs in 3-4 days in the form of metabolites in the urine and faeces. Plants In plants, hydrolysed rapidly to less toxic products, including phosphoric acid dimethyl ester and phosphoric acid. The (E)-isomer is more rapidly degraded than the (Z)- isomer. Metabolism and degradation have been reviewed (K. I. Beynon *et al.*, *Residue Rev.* 1973, 47, 55).

704 mevinphos

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(i) Comments on the typical use of the chemical within the notifying country, with comments on possible misuse (if appropriate). The product was registered to be used as fungicide.

# Focused Summery-Mevinphos

# **1\INTRODUCTION:**

This section should provide a brief statement / summary of the final regulatory actions and the reasons for the action taken (e.g. occupational health concerns, environmental concerns). Could include:

(g) The events that led to the final regulatory action

The insecticide Mevanate 24 % SC was presented for registration by the Arab Company for Manufacture of pesticide (intended to be produced locally), the active ingredient is mevinphos. The control action was taken in the session No. 331, dated 9/8/1994.

(h) Significance of the regulatory action, e.g. one use or many uses, level or degree of exposure;

The banning of mevinphos would reduce the hazards to human health, low residues on crops and more healthy food for consumers and workers (source; notification form).

© An overview of the regulatory system of the notifying country if relevant;

Pesticides were used to be regulated by the law of Agriculture No. 20 for the year 1973, through a multi-stake holder committee called the Agricultural Pesticides Committee. Recently the law was amended to the Interim Law of Agriculture No. 44 for the year 2002. According to this law a national multi-stake holder committee called Pesticides Registration Committee is formed and responsible for registration, re-registration and cancellation of registration of pesticides within the Hashemite Kingdom of Jordan. The pesticide division within the ministry of agriculture is responsible for approval of label while the provinces had the authority of granting license for retailers as well as inspection of any miss-use or off law activities.

# (g) Scope of the regulatory action-precise description of the chemicals subject to the regulatory action;

It is prohibited to place on the market or use plant products containing mevinphos. The decision at that time was the refusal of registration for local production of the formulation Mevanate 24% SC. This decision was interpreted to include all formulations containing mevinphos.

# 11\ RISK EVALUATION;

This section should provide evidence that a risk evaluation was carried out under the prevailing conditions of the notifying country. It should confirm that criteria Annex 11 (b) are met. May include:

(1) Key finding of a national risk evaluation;

High toxicity of the product.

(Minutes of the meeting did not clearly indicate a mational exposure data was generated or considered in making a national risk evaluation).

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(m)Key data reviews consulted and a brief description;

pesticide manual

(n) Reference to national studies, e.g. toxicological and ecotoxicological studies;

No national study was carried out.

(o) Summary of actual (or potential) human exposure and or environmental fate.

No data

111\ RISK REDUCTION AND RELEVANCE TO OTHER STATES This section should provide evidence that the control action is of relevance to other states. Could include information on the followings:

(j) Estimation of quantities of chemicals used or imported/exported at the time of the regulatory action and if possible information on ongoing trade;

The Hashemite Kingdom of Jordan has imported and used 5940 Kg of mevinphos in 1992. Jordan has no information on ongoing trade.

(k) Relevance to other states, i.e. those with similar conditions of use; The Hashemite Kingdom of Jordan has no information.

 (l) Comments on the typical use of the chemical within the notifying country, with comments on possible misuse (if appropriate).
 The product was registered to be used as insecticide.

Regards,,,,

مدير وهاية النبات

الهندين محمود الغتروم DIRECTOR OF PLANT PROTECTION MAHMOUD AL-KTOOM

HEAD OF PESTICIDE DIVISION LINA AL-HMOUD



# MEVINPHOS

JMPR1972

# <u>Explanation</u>

This pesticide was evaluated toxicologically by the 1965 JointMeeting (FAO/WHO, 1965). Since this evaluation the results of someadditional experimental work have been reported.

IDENTITY

Chemical name

dimethyl 2-methoxycarbonyl-1-methylvinyl phosphate

# Synonyms

2-carbomethoxy-1-methylvinyl dimethyl phosphate, alpha isomer;

1-methoxycarbonyl-1-propen-2-yl dimethyl phosphate

Phosdrin insecticide (R), Phosdrin(R), OS-2046

In the reports provided to the Meeting several other chemical names are used for this compound, slightly different from those mentioned above.

Structural formula

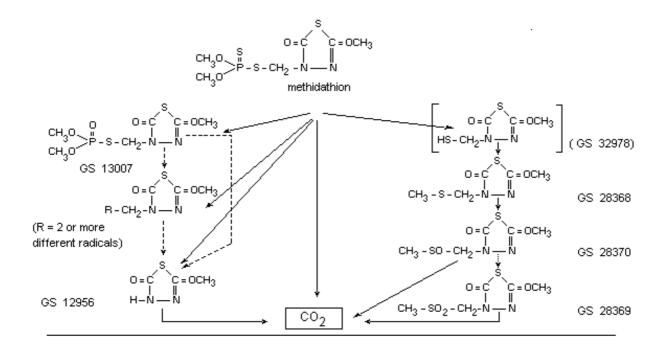


Figure 6. Metabolites of methidathion identified in beans, alfalfa, migratory locust and rat.

Mevinphos is comprised of two geometric isomeric forms. The<u>cis</u> isomer possesses higher insecticidal activity than the<u>trans</u> isomer. At least 60% of <u>cis</u>-isomer is in the technical material.

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# Other information on identity and properties

Analysis of a typical sample of technical mevinphos(Phosdrin(R)) gave the following results:

|                               | <u>%</u> W        |
|-------------------------------|-------------------|
| <u>cis</u> -mevinphos         | 62                |
| <u>trans</u> -mevinphos       | 28                |
| methyl aceto acetate          | 2                 |
| methyl-2-chloro aceto acetate | 2                 |
| dimethyl methyl phosphonate   | 2                 |
| others (less than 1% w each)  | _ <u>4</u><br>100 |

Physical and chemical properties of technical mevinphos(Phosdrin(R))

| Physical state: | liquid                 |
|-----------------|------------------------|
| colour:         | pale yellow            |
| Boiling range   | 99-103° C at 0.3 mm Hg |

|         | Vapour pressure: | 1.24 x $10^{-4}$ mm Hg at 20° C   |
|---------|------------------|---|
|         | Solubility:      | miscible with water, acetone, carbon<br>tetrachloride, chloroform, ethyl-,<br>isopropyl- and methyl alcohols, benzene,<br>toluene, xylene and other highly aromatic<br>petroleum fractions. Slightly soluble in<br>carbon disulfide and kerosene. |
|         | Stability:       | stable under normal storage conditions.<br>Decomposed at high temperatures.   |
| aqueous | Hydrolysis:      | <pre>mevinphos is hydrolysed in</pre>   |
|         | Compatibility:   | mevinphos is compatible with mostpesticides.  |

EVALUATION FOR ACCEPTABLE DAILY INTAKE

# BIOCHEMICAL ASPECTS

## Absorption and distribution

Mevinphos is rapidly excreted by cattle. Milk from a cow dosed with 2 mg/kg (<sup>32</sup>P) mevinphos (80% cis, 20% trans isomer)contained 0.06 ppm after 6 hours and only 0.007 ppm after 96 hours. Milk from a cow receiving 1 mg/kg/day for 7 days produced milk containing approximately 0.05 ppm up to 14 days after dosage; this probably consisted mainly of the trans isomer. Milk and tissues from cattle receiving up to 20 ppm mevinphos in the diet for 12 weeks contained less than 0.03 ppm (Casida et al., 1958).

# Biotransformation

The main metabolite of both isomers in plants is dimethylphosphate, although this is formed less rapidly from the trans- than from the cis- isomer (Casida et al., 1956; Spencer and Robinson, 1960). Trans- mevinphos is degraded faster than the cis- isomer by mouse liver homogenates; this was shown to be due to involvement of two enzyme systems (Morello et al., 1968). The cis- isomer is 0-demethylated by a glutathione-dependent soluble enzyme, whereasthe trans- isomer is hydrolysed at the P-O bond by a

non-glutathione- dependent enzyme (Morello et al., 1967; Hutson et al., 1972). Cis- desmethyl-mevinphos and dimethyl phosphate were identified in mouse liver as the main metabolites of the cis- and trans- isomers, respectively (Morello et al., 1967; 1968).

# Effects on enzymes and other biochemical parameters

The cis form is about 100 times more active than the transform in inhibiting bovine RBC and mouse brain cholinesterases (Morello <u>et al.</u>, 1967).

#### TOXICOLOGICAL STUDIES

## Special studies on reproduction

In a three-generation study, groups of 10 male and 20 female rats received diets providing 0, 0.06 and 1.2 mg/kg body-weight/day approximately of mevinphos (60% <u>iso</u>-isomer, 40%<u>trans</u>-isomer). Each generation was bred twice. No effects were noted on fertility, gestation, lactation and viability of young at the 0.06 level. In the 1.2 mg/kg group the lactation index was reduced. No gross abnormalities were observed in the pups of these litters examined (Estep <u>et al.</u>, 1967).

# Special studies on neurotoxicity

Technical mevinphos was administered by gavage to groups of six hens pre-medicated with atropine sulphate and protopam sulphate. The test group received 7.5 mg/kg on two occasions, each dose separated by an interval of three weeks. A positive control group received triorthophenyl phosphate (0.5 mg/kg). No signs of neurotoxicactivity were evident in test and negative control groups. Positive controls developed ataxia and the histological examination of the sciatic nerve showed swollen oxons, myelin degeneration and fragmentation of the axis cylinders (Natoff <u>et al.</u>, 1972).

## Acute toxicity

Acute toxicity of mevinphos has been studied in the rat, (Simpson <u>et al.</u>, 1972). Results of these studies are summarized in Table 1.

#### TABLE 1

Acute toxicity of mevinphos in the rat

| Material                | Species | LD <sub>50</sub><br>mg/kg | References                       |
|-------------------------|---------|---------------------------|----------------------------------|
| Technical<br>mevinphos  | Rat     | 1.4                       | Simpson <u>et al.</u> ,<br>1972. |
| <u>Cis</u> -mevinphos   | Rat     | 1.4                       | Ibid.                            |
| <u>Trans</u> -mevinphos | Rat     | 81.8                      | Ibid.                            |

# Short-term studies

Rat (technical mevinphos)

Groups of 12 male and 12 female rats received technical mevinphos in the diet at 0, 0.1 and 12.5 ppm for 13 weeks. Reduction of plasma, RBC and brain cholinesterase activities occurred in the 12.5 ppm female group and of plasma and RBC cholinesterase activities in the male group of the same dietary level. The male rats of this group also exhibited slightly reduced body-weights. At the 0.1 ppm level the exposed and control animals did not differ in relation to body-weight, food intake, organ weights, pathology, haematology and clinical chemistry tests (Simpson <u>et al.</u>, 1972).

Rat (<u>cis</u>-mevinphos)

Groups of 12 males and 12 females received <u>cis</u>-mevinphos in the diet at 0, 0.1 and 12.5 ppm for 13 weeks. Significant reductions of the cholinesterase activity were found in the plasma, RBC and brain of male and female rats receiving 12.5 ppm. The plasma cholinesterase level was also reduced at 0.1 ppm, in the females only. Other parameters were similar in the exposed and control animals (Simpson <u>et al.</u>, 1972).

Rat (trans-mevinphos)

Groups of 12 males and 12 females received <u>trans</u>-mevinphos in the diet at 0, 10, 50, 250 and 1 250 ppm for 13 weeks. Cholinesterase activity was significantly reduced in the plasma, RBC and brain of females at all treatment levels, and in the males of the 250 and 1 250 ppm groups. Erythrocyte cholinesterase was also inhibited at 50 ppm in the males. In the 10 ppm males no reductions in cholinesterase activity were found. Body-weights and haemoglobin levels of males and females exposed to 250 and 1 250 ppm were significantly reduced. At 1 250 ppm, food intake, organ weights and serum protein levels were

reduced, and the blood urea level and serum alkaline phosphatase activity were increased in both sexes. Eight males and six females fed 1 250 ppm died during the test. SGPT activity was elevated at 1 250 ppm in the females only. Females at 250 ppm were found to have increased blood urea levels and increased SGPT (Simpson <u>et al.</u>, 1972).

In another experiment, groups of ten males and ten females received  $\underline{trans}$ -mevinphos in the diet at 1, 5, 10, 25 and 50 ppm. Erythrocyte cholinesterase activity was reduced in the 5, 10, 25 and 50 ppm males and the 10, 25 and 50 ppm females. Brain cholinesterase activity was reduced only in the 50 ppm female group. No significant changes in plasma cholinesterase activity was found in either males or females (Simpson <u>et al.</u>, 1972).

#### Dog

Groups of four male and four female dogs received daily oral doses of 0, 0.025, 0.075, 0.25 and 0.75 mg of mevinphos/kg/body-weight for two years. Vomiting occurred in several of the animals receiving 0.25 and 0.75 mg/kg dosages; two males in the 0.75 mg/kg group were killed after 27 and 83 weeks dosing because of continuing vomiting and anorexia. The general health and growth rates of the other dogs remained unaffected throughout the study. No morphological changes attributable to mevinphos were found in the tissue of the dogs. Plasma and RBC cholinesterase depression were observed at 0.075 mg/kg and higher dosages, but not at 0.025 mg/kg. After two years dosing, inhibition of brain cholinesterase activity occurred in the 0.25 and 0.75 mg/kg females and the 0.75 mg/kg males, but not at lower dosages (Wilson et al., 1971).

Long-term studies

Rat

Groups of 24 male and 24 female rats were given diets containing 0.37, 1.11, 3.71 and 11.14 ppm of mevinphos (60% <u>cis</u>-isomer) for two years. A group of 48 male and 48 female rats acted as controls. No differences were noted in general health, behaviour or mortality between exposed and control animals. Transient reductions in body-weight occurred at two higher dosage levels during the first six months of the test. No differences in organ weight or morphological changes occurred which could be attributed to treatment; the haematological picture was unaltered. Experimental groups showed no differences from controls in the number or types of tumours developing during the two-year period. Erythrocyte and brain cholinesterase activities were reduced at the 3.71 and 11.14 ppm levels, respectively; lower levels did not affect the enzymes. No effects were found on the plasma cholinesterase in the 0.37 ppm group (Simpson et al., 1971).

#### OBSERVATIONS IN MAN

The effect of mevinphos on plasma and red blood cell cholinesterase was observed in groups of volunteers (five test and two control). Mevinphos was diluted in corn oil and administered in capsules at dosage levels of 1.0, 1.5, 2.0 or 2.5 mg/man/day. Baseline plasma and RBC cholinesterase levels were measured twice weekly during a pretreatment period followed by a 30-day test period during which the test dose was administered daily. Borderline depression (20%) in RBC cholinesterase occurred with dose levels of 1.5 and 2.0 mg/man/day and the highest dose produced a 24% decrease. Plasma cholinesterase was not significantly affected at any dose level (Rider <u>et al.</u>, 1972).

#### COMMENT

The data requested by the 1965 Joint Meeting has now been supplied. Mevinphos, a mixture of <u>cis</u> and <u>trans</u> isomers is rapidly metabolized in plants and animals. In plants, the <u>cis</u> isomer disappears more rapidly than the <u>trans</u> isomer. The <u>cis</u> isomer is more slowly degraded in animals.

In a reproduction study in rats, a reduced lactation index was observed at 1.2 mg/kg/day, with no indications of teratogenic effects.

Studies in rats with technical, <u>cis</u> and <u>trans</u> mevinphos indicated that the no effects for cholinesterase activity at 0.37 ppm is less than 0.1 ppm and 1 ppm, respectively. Results showed no evidence of carcinogenicity.

A two-year study in dogs indicated a no-effect level based upon cholinesterase depression to be 0.025 mg/kg.

Studies in humans indicated a reduction of cholinesterase activity at levels exceeding 1 mg/man/day.

#### TOXICOLOGICAL EVALUATION

# Level causing no toxicological effect

Rat: 0.37 ppm in the diet, equivalent to 0.02 mg/kg body-weight/day

Dog: 0.025 mg/kg body-weight/day

Man: 1 mg/man/day, equivalent to 0.014 mg/kg body-weight/day

ESTIMATE OF ACCEPTABLE DAILY INTAKE FOR MAN

0 - 0.0015 mg/kg body-weight

RESIDUES IN FOOD AND THEIR EVALUATION

# USE PATTERN

Mevinphos is a systemic organo-phosphorous insecticide with a relatively short action; the material has both contact and systemic activity. It is recommended particularly for the control of a wide range of vegetable pests, especially when applications shortly before harvest are necessary, and for the control of aphids, leafrollers and mites in fruit.

According to the information available, mevinphos is officially registered and/or approved for use in

| Argentina      | Dem. Rep. of Germany | Norway         |
|----------------|----------------------|----------------|
| Australia      | Fed. Rep. of Germany | Peru           |
| Austria        | Greece               | Philippines    |
| Belgium        | Hungary              | Portugal       |
| Brazil         | Italy                | South Africa   |
| Bulgaria       | Jugoslavia           | Sweden         |
| Canada         | Mexico               | Switzerland    |
| Colombia       | Morocco              | Tunisia        |
| Czechoslovakia | Netherlands          | United Kingdom |
| Denmark        | New Zealand          | United States  |
| Finland        | Nicaragua            | Uruguay        |
| France         | Nigeria              |                |

# Use recommendations

Typical application rates for mevinphos are in the range 0.125 - 0.50 kg a.i./ha. In the United States, up to 1.0 kg a.i./ha is registered. The recommended period between treatment and harvest varies from country to country, but is typically between 1 and 7 days for outdoor crops, and 7 to 14 days for glasshouse crops.

Multiple applications of mevinphos can be made, depending on pest incidence, and use recommendations allow for these treatments.

The detailed use recommendations are given in Table 2.

TABLE 2 Recommended applications of mevinphos to crop foliage

|     |                            |  | Dosage |
|-----|----------------------------|--|--------|
| rat | e<br>Crop                  | Pest(s)                                    | (kg a. |
| i/h | a)                         |  |        |
|     |                            |  |        |
|     | FRUIT                      |  |        |
|     | Pome fruit (apples, pears) | aphids, mites <sup>1</sup> , scale insects | 0.125  |

- 0.25

caterpillars, fruit flies,

| rate   |   | Dosage |
|--|---|--------|
| Crop   | Pest(s)   | (kg a. |
| i/ha)  |   | . 2    |
|  |   |        |
| Stone fruit (peaches,<br>0.50                      | lygus bugs, grasshoppers, mealybugs,  | 0.25 - |
| apricots, cherries)                                | leafrollers and psyllids  |        |
| Citrus (oranges, grapefruit,<br>- 0.25             | aphids  | 0.125  |
| lemons)  | leafrollers, mites, mealybugs,<br>woolly whitefly <sup>2</sup> , orange tortrix <sup>3</sup> ,<br>caterpillars, scale insects, cutworms | 0.25 - |
|  |   |        |
| Grapes<br>0.50                                     | aphids  | 0.25 - |
| 1.0  | mites, caterpillars, leafrollers,<br>leafhoppers, lygus bugs  | 0.25 - |
| 1.0  |   |        |
| Strawberries<br>- 0.25                             | aphids, spider mites  | 0.125  |
|  | grasshoppers, strawberry leafrollers,<br>salt marsh caterpillares <sup>4</sup>  | 0.25 - |
| 1.0  |   |        |
| VEGETABLES   |   |        |
| Brassicas (broccoli, cabbage,<br>- 0.25            | aphids  | 0.125  |
| cauliflower, collards,<br>Brussels sprouts)<br>1.0 | caterpillars, bugs, mites, leafhoppers,<br>leafminers, beetles, thrips  | 0.25 - |
| Spinach, lettuce                                   | aphids  | 0.125  |
| - 0.25<br>1.0                                      | caterpillars, mites, bugs, leafhoppers,<br>leafminers   | 0.25 - |
| Peas, beans  | aphids  | 1.125  |
| - 0.25   |   |        |
| 0.50   | beetles, weevils, mites, pea moth,  | 0.25 - |
|  | caterpillars  |        |
| Cucurbits (melons,<br>- 0.25                       | aphids  | 0.125  |
| cucumbers)   | mites, caterpillars, bugs, thrips,<br>beetles, leafminers, leafhoppers  | 0.25 - |

cutworm

| Root, tuber and bulbous                           | aphids   | 0.125  |
|---|--|--------|
| vegetables<br>(carrots, potatoes, turnips<br>0.50 | thrips, cutworms, caterpillars,<br>mites, bugs, leafhoppers, leafminers, | 0.25 - |
| and onions  | mealybugs  |        |
| Tomatoes<br>- 0.25                                | aphids, whitefly <sup>5</sup>  | 0.125  |
|   | mites, fruit flies, mealybugs,   | 0.25 - |
| 0.50  | thrips   |        |

<sup>1</sup> Mites are principally Tetranychidae, Tarsonemidae and Eriophyidae.

<sup>2</sup> Aleurothrixus floccosus

<sup>3</sup> Argyrotaenia citrana

<sup>4</sup> Estigmene acrea

<sup>5</sup> Trialeurodes vaporariorum and Bemisia spp.

Officially approved pre-harvest intervals

Officially approved pre-harvest intervals have been established in a number of countries. The situation in each country is described in Table 3. The information has been obtained principally from the Regulatory Authorities. Every attempt has been made to have these data current, but since legislation and regulations do change, some of these changes may not yet be known.

With regard to pre-harvest intervals, these normally refer to an upper application rate of 0.5 kg/ha, but since official recommendations in some countries, especially in the case of tree fruits, are on the basis of spray concentrations rather than rate per hectare, this upper rate may not always be precise. At a typical spray volume in tree fruits of 1 000 l/ha, 0.05% a.i. w/w would be equivalent to 0.5 kg a.i./ha. In the United States, an upper rate of 1 kg/ha is now sometimes recommended for certain row crops attacked by resistant pests. In this case, approved pre-harvest intervals are lengthened accordingly, as shown in Table 3. Only crops likely to be of importance in international trade are included.

| CROP                   | COUNTRY                       | PHI<br>(days) |
|------------------------|-------------------------------|---------------|
| <u>General classes</u> |                               |               |
| All                    | Hungary<br>Portugal<br>Sweden | 5<br>4<br>4   |
| Outdoor                | Denmark                       | 4             |

TABLE 3 OFFICIALLY APPROVED PRE-HARVEST INTERVALS

| Glasshouse | Denmark              | 7       |
|------------|----------------------|---------|
| Fruit      | Argentina<br>Austria | 1<br>14 |
|            | Belgium              | 7       |
|            | Canada               | 1       |
|            | Canada (high rate)   | 3       |
|            | Italy                | 5       |
|            | Netherlands          | 7       |
|            | Norway               | 7       |
|            | United Kingdom       | 3       |

TABLE 3 (Cont'd.)

| CROP                                  | COUNTRY  | PHI<br>(days)  |
|---------------------------------------|--|--|
| Pome fruit                            | Australia<br>Switzerland   | 2<br>21  |
| Stone fruit                           | Australia<br>Switzerland   | 2<br>2<br>21   |
| Vegetables                            | Argentina<br>Australia<br>Austria<br>Belgium<br>Brazil<br>Canada<br>Canada (high rate)<br>Colombia<br>Mexico<br>Netherlands<br>Norway<br>S. Africa<br>Switzerland<br>United Kingdom<br>Uruguay | 3<br>2<br>4<br>7<br>4<br>1<br>3<br>10<br>4<br>7<br>7<br>7<br>4<br>10<br>3<br>1-4 |
| Leafy vegetables                      | Netherlands  | 7-14   |
| <u>Specific crops</u><br><u>Fruit</u> |  |  |
| Apples<br>Cherries                    | U.S.A 0.25-05 kg/ha<br>" " " " "   | 1<br>2   |

|                     | 2  |
|---------------------|--|
| Colombia            | 15   |
| U.S.A 0.25-05 kg/ha | 1  |
| Switzerland         | 21   |
| U.S.A 0.25-05 kg/ha | 2  |
| U.S.A 0.25-05 kg/ha | 1  |
| U.S.A 0.25-05 kg/ha | 1  |
| U.S.A 0.25-05 kg/ha | 1  |
| U.S.A 1 kg/ha       | 2  |
|                     | Colombia<br>U.S.A 0.25-05 kg/ha<br>Switzerland<br>U.S.A 0.25-05 kg/ha<br>U.S.A 0.25-05 kg/ha<br>U.S.A 0.25-05 kg/ha<br>U.S.A 0.25-05 kg/ha |

<u>Vegetables</u>

Beans

Mexico 1 U.S.A. - 0.25-05 kg/ha 1

# TABLE 3 (Cont'd.)

| ROP COUNTRY           |                               | PHI<br>(days) |
|-----------------------|-------------------------------|---------------|
| Beet-roots            | West Germany                  | 14            |
| Broccoli, cabbage     | West Germany                  | 7             |
|                       | U.S.A 0.25-05 kg/ha           | 1             |
|                       | U.S.A. – 1 kg/ha              | 3             |
| Brussels sprouts      | West Germany                  | 14            |
|                       | U.S.A 0.25-05 kg/ha           | 3             |
|                       | U.S.A. – 1 kg/ha              | 3             |
| Carrots               | U.S.A 0.25-05 kg/ha           | 2             |
| Cauliflower           | U.S.A. – 1 kg/ha              | 3             |
| Celery                | Weet Germany                  | 14            |
|                       | U.S.A 1 kg/ha                 | 5             |
| Collards              | U.S.A 0.25-05 kg/ha           | 3             |
|                       | U.S.A 1 kg/ha                 | 7             |
| Cucumbers(outdoors)   | West Germany                  | 3             |
|                       | U.S.A 0.25-05 kg/ha           | 1             |
| Cucumbers(glasshouse) | Belgium                       | 3             |
|                       | West Germany                  | 4             |
|                       | Mexico                        | 3             |
| Gherkins              | U.S.A 0.25-05 kg/ha           | 1<br>3        |
| GHErkins              | Belgium<br>Mexico             | 3             |
| Lettuce (outdoors)    | Mexico<br>U.S.A 0.25-05 kg/ha | 2             |
| Lettuce (outdoors)    | U.S.A 1 kg/ha                 | 4             |
|                       | 0.5.A 1 kg/lla                | 7             |
| Lettuce (glasshouse)  | Belgium                       | 7             |
|                       | Netherlands                   | 7             |
|                       | U.S.A 0.25-05 kg/ha           | 10            |
| (winter)              | Belgium                       | 14            |
|                       | Netherlands                   | 14            |
| Melons (outdoors)     | Brazil                        | 4             |
|                       | U.S.A 0.25-05 kg/ha           | 1             |
| Melons (glasshouse)   | Belgium                       | 3             |
|                       | Mexico                        | 3             |
| Onions                | West Germany                  | 14            |
|                       | U.S.A 0.25-05 kg/ha           | 1             |
| Peas                  | West Germany                  | 7             |
|                       | Switzerland                   | 21            |
|                       | U.S.A 0.25-05 kg/ha           | 1             |
| Peas for processing   | Belgium                       | 4             |
|                       | Netherlands                   | 4             |
| Potatoes              | West Germany                  | 7             |
|                       | U.S.A. 0.25-05 kg/ha          | 1             |
| Spinach*              | U.S.A. 0.25-05 kg/ha          | 4             |
| -                     |                               |               |

# TABLE 3 (Cont'd.)

| CROP                  | COUNTRY             | PHI<br>(days) |
|-----------------------|---------------------|---------------|
| Tomatoes (outdoors)   | Brazil              | 4             |
|                       | Colombia            | 8             |
|                       | West Germany        | 3             |
|                       | S. Africa           | 2             |
|                       | U.S.A 0.25-05 kg/ha | 1             |
| Tomatoes (glasshouse) | Belgium             | 3             |
|                       | West Germany        | 4             |
|                       | Mexico              | 3             |
| Turnips               | U.S.A 0.25-05 kg/ha | 3             |

\* Netherlands - Leafy vegetables (lettuce endive), spinach, glasshouse summer (1 March - 1 Nov.) 7 days; winter 14 days.

# RESIDUE DATA RESULTING FROM SUPERVISED TRIALS

A substantial amount of data on the residues resulting from supervised trials was available. These trials were carried out in different countries on food crops, especially vegetables and fruit, grown under various conditions, using various pre-harvest intervals (PHI).

Table 4 summarizes the range of residue levels which have been found when the product is used according to the conditions of "good agricultural practice".

TABLE 4 Residues of mevinphos in crops following recommended foliage treatments

| of<br>Crop | Maximum<br>recommended        | Minimum<br>pre-harvest |                    |                     | Range                |       |
|------------|-------------------------------|------------------------|--------------------|---------------------|----------------------|-------|
| resu       | _                             | rate<br>(kg a.i./ha)   | interval<br>(days) | Number of<br>trials | Number of<br>results | (ppm) |
| - 0.       | Brassicas <sup>1</sup><br>.90 | 0.5 - 1.0              | 1 - 7              | 18                  | 45                   | <0.01 |
| - 0.       | Spinach<br>.80                | 1.0                    | 4                  | 15                  | 21                   | 0.01  |
| - 0.       | Lettuce<br>.50                | 0.5 - 1.0              | 2 - 14             | 21                  | 22                   | <0.02 |
| - 0.       | Tomatoes<br>20                | 0.5                    | 1                  | 13                  | 48                   | <0.02 |

TABLE 4 (cont'd)

| of  | Crop                | Maximum<br>recommended | Minimum<br>pre-harvest |                     |                      | Range |
|-----|---------------------|------------------------|------------------------|---------------------|----------------------|-------|
| res | ults                | rate<br>(kg a.i./ha)   | interval<br>(days)     | Number of<br>trials | Number of<br>results | (ppm) |
| - 0 | Cucumbers<br>.20    | 0.5                    | 1 - 3                  | 10                  | 26                   | <0.01 |
|     | Peas                | 0.5                    | 2                      | 5                   | 10                   | <0.05 |
| - 0 | Beans<br>.20        | 0.5                    | 2                      | 7                   | 13                   | <0.05 |
|     | Root vegetables     | 0.5                    | 2                      | 4                   | 7                    | <0.05 |
| - 0 | Onions<br>.10       | 0.5                    | 2                      | 1                   | 2                    | <0.05 |
| - 0 | Apples<br>.45       | 0.5                    | 3                      | 8                   | 23                   | <0.05 |
| - 0 | Pears<br>.12        | 0.5                    | 3                      | 2                   | 4                    | <0.02 |
| - 0 | Peaches<br>.29      | 0.5                    | 3                      | 4                   | 9                    | 0.03  |
| - 0 | Apricots<br>.10     | 0.5                    | 3                      | 2                   | 5                    | <0.01 |
| - 0 | Grapes<br>.27       | 1.0                    | 3                      | 7                   | 20                   | <0.02 |
|     | Citrus<br>.11       | 1.0                    | 1                      | 6                   | 13                   | <0.01 |
|     | Cherries<br>.90     | 0.5                    | 3                      | 5                   | 14                   | 0.09  |
|     | Strawberries<br>.58 | 1.0                    | 1                      | 8                   | 22                   | <0.05 |
|     | Melons<br>.03       | 0.5                    | 1                      | 5                   | 6                    | <0.02 |

<sup>1</sup> Includes broccoli, cabbage, cauliflower, Brussels sprouts and collards.

In most cases normal dosage rates were applied in accordance with label recommendations. However, in some experiments higher dosages are also included. Since local recommendations, particularly regarding the minimum pre-harvest interval, vary widely, the standard taken for stating the ranges in Table 4 is the minimum pre-harvest interval commonly used in practice. In U.S.A., where both recommendations and cropping conditions are sometimes rather different from those in other countries, ranges deriving from commonly employed practice have been estimated on the basis of data only from U.S.A. For guidance, the minimum pre-harvest intervals used for deriving the ranges from the data are stated briefly in the third column of the table. The variation in pre-harvest interval for some of the crops is due to variation in upper dosage rate, or whether the crops are grown under glass or not.

Detailed mevinphos residue data, obtained from supervised trials with mevinphos on fruit and vegetables are given below. It should be noted that:

- (a) All application rates refer to active ingredient; the sum of <u>cis</u> and <u>trans</u> mevinphos.
- (b) Lbs/acre has been regarded as being essentially equivalent to kg/ha.

#### <u>Brassicas</u>

Brassicas treated with Phosdrin according to the most extreme current practice (i.e., for 0.5 kg/ha, PHI one day for broccoli and cabbage and three days for cauliflower, collards and sprouts; for 1.0 kg/ha, PHI three days for broccoli, cabbage, sprouts and cauliflower and seven days for collards) contained residues of mevinphos in the range of less than 0.01 ppm to 0.9 ppm, the upper figure being estimated from the data for sprouts.

#### <u>Spinach</u>

Recommended applications of mevinphos (i.e., 0.5 kg a.i./ha, minimal PHI four days, up to 1 kg a.i./ha, minimal PHI seven days) resulted in residues not exceeding 0.5 ppm, four and seven days, respectively, after the final application.

#### <u>Lettuce</u>

The basis for deriving the range of residues from non-U.S.A. data was that of current recommendations in the Netherlands, and U.S.A. data is that of current recommendations. On this basis the range of residue levels reported was from <0.02 - 0.50 ppm.

Under all these conditions, it has been shown that the residues of mevinphos did not exceed 0.50 ppm, when label recommendations were followed, i.e. PHI for lettuce grown outdoors was 4-7 days and for glasshouse lettuce 7-14 days, depending on application rate and growing period. In winter, the longer PHI's are recommended.

#### <u>Beans</u>

Residues of mevinphos did not exceed 0.05 ppm (maximum dosage rate of 0.5 kg a.i./ha) when beans were treated with 0.5 kg/ha mevinphos and sampled two days later.

#### <u>Peas</u>

Residues of mevinphos did not exceed 0.05 ppm in peas which had

received recommended treatments of mevinphos (maximum of 0.5 kg a.i./ha), sampled two days after application.

#### Root vegetables, bulbs and tubers

With a final treatment to harvest interval of two days, mevinphos residues in carrots, turnips, onions and potatoes did not exceed 0.10 ppm, following recommended applications of mevinphos (maximum dosage rate of 0.5 kg a.i./ha).

#### Tomatoes

At a dosage rate of up to 0.50 kg a.i./ha, and an interval between the final application and harvest of one day, residues of mevinphos ranged from less than 0.02 ppm to 0.08 ppm; at the double dosage rate, i.e. up to 1 kg a.i./ha, residues ranged from 0.05 - 0.2 ppm.

#### <u>Cucumbers</u>

In cucumbers grown under glass, three days after application of mevinphos at a maximum dose of 0.5 kg a.i./ha, residues did not exceed 0.13 ppm. Similarly, in cucumbers grown outdoors, residues were less than 0.10 ppm one day after recommended applications.

# Melons

Residues of mevinphos in whole melons did not exceed 0.05 ppm one day after the final treatment at a maximum of 0.5 kg a.i./ha.

# <u>Gherkin</u>

After recommended applications at a maximum of 0.5 kg a.i./ha, residues did not exceed 0.1 ppm after a PHI of three days in gherkins grown under glass.

## Top fruit

Studies with mevinphos on top fruit are summarized in Table 5.

TABLE 5 Mevinphos residues on fruit

| Fruit    | Maximum<br>treatment<br>(kg a.i/ha) | Pre-harvest<br>interval<br>(days) | Residues<br>(ppm) |
|----------|-------------------------------------|-----------------------------------|-------------------|
| Apples   | 0.5                                 | 3                                 | 0.45              |
| Pears    | 0.5                                 | 3                                 | 0.14              |
| Peaches  | 0.5                                 | 3                                 | 0.29              |
| Apricots | 0.5                                 | 3                                 | 0.10              |
| Cherries | 0.5                                 | 3                                 | 0.90              |

Citrus 1.0 1 0.11

# <u>Grapes</u>

At an application rate of 1.0 kg a.i./ha and a PHI of three days, the maximum residue of mevinphos in grapes was 0.27 ppm.

# <u>Strawberries</u>

Following applications of mevinphos to strawberries grown outdoors at a maximum rate of 1.0 kg a.i./ha, with a minimum PHI of one day, the maximum residue was 0.14 ppm; at a slightly higher treatment level, i.e. 1.25 kg a.i./ha, the maximum residue was 0.45 ppm.

FATE OF RESIDUES

## General comments

Mevinphos residues in crops decrease rapidly, partly due to volatilization and partly through degradation. The principal degradation products are dimethyl phosphate and acetoacetic acid.

Provided mevinphos is used according to the conditions of good agricultural practice, detectable residues will not occur in meat, milk and milk products. Livestock is unlikely to be exposed to mevinphos residues in feed since crops used for animal feeds are rarely treated. Nevertheless, data are available to show that cattle eating feed containing high levels of mevinphos do not produce meat or milk containing appreciable residues.

#### In animals

Casida <u>et al.</u> (1958) conducted studies with mevinphos fed to cattle at levels of up to 20 ppm, expressed on the dry matter content (far in excess of levels which could occur in practice). From the results of these studies, the authors stated that mevinphos had no tendency to accumulate in any tissue, but was rapidly detoxified in the animal.

Feeding of <sup>32</sup>P-labelled mevinphos for seven consecutive days to a cow at a level of 40 ppm, in dry matter, did not lead to levels of mevinphos in whole milk above 0.06 ppm at any time during the study. Mevinphos residues in the tissues from this cow at autopsy at the end of the seven-day period were essentially found only in the liver (0.3 ppm) and kidneys (0.04 ppm).

In a more extensive experiment, 12 lactating cows were fed for a 12-week period at levels of 1, 5 and 20 ppm on the total diet. Samples of milk were taken periodically and samples of fat, liver, kidney, muscle, heart and brain at the end of the feeding period from all treatments. All contained less than 0.03 ppm mevinphos (limit of determination of the analytical method).

However, their experiments showed that in the case of the <u>cis</u>-isomer of mevinphos, dimethyl phosphate was the main degradation product together with very small amounts of mevinphos acid (the free carboxylic acid). In the case of the <u>trans</u>-isomer, the same products were found, although there was even less of the carboxylic acid. Desmethyl derivatives (where the methoxyl groups joined to the P atoms would have been hydrolysed to hydroxyl groups) were not detected.

# <u>In plants</u>

Casida <u>et al.</u> (1956) reported that after applying mevinphos to vegetable crops as a foliar spray, 90% of the amount applied was lost within two days and 99% in four days. From experiments in which pea and bryophyllum plants absorbed <sup>32</sup>P-labelled mevinphos through their roots, it may be concluded that within 12 hours after application losses occurred primarily through volatilization, whereas thereafter decomposition made the greater contribution. Using similar methods with labelled mevinphos applied to cucumber, maize, bean and pea seedlings, they reported that the <u>cis</u>-isomer declined more rapidly than the <u>trans</u>-isomer.

Spencer and Robinson (1960) grew pea seedlings in gravel and applied  $^{32}P$ -labelled mevinphos via the roots. Like Casida <u>et al.</u> (1956) they found that the <u>trans</u>-isomer degraded somewhat more slowly than the <u>cis</u>-one. This conclusion is further supported by those field residue studies by Shell where <u>cis</u>- and <u>trans</u>-isomers were analysed separately.

When pea plants were exposed to labelled <u>cis</u>-mevinphos acid instead of mevinphos, degradation of the acid was somewhat slower than that of <u>cis</u>-mevinphos. Moreover, although dimethyl phosphate was still the main degradation product, desmethyl mevinphos acid was also formed. For these reasons, the main degradation pathway of mevinphos acid was also formed.

For these reasons, the main degradation pathway of mevinphos must have been direct to the dimethyl phosphate and could not have been primarily via the carboxylic acid.

# <u>In soil</u>

In soil, mevinphos appears to be decomposed primarily by chemical hydrolysis (Hindin, 1963). Getzin and Chapman (1959) studied the fate of <sup>32</sup>P-labelled mevinphos in soil and the subsequent uptake in pea plants by an enzyme inhibition method. There is a positive correlation with organic matter content and base-exchange capacity.

Most mevinphos was held by peat (127 mg/100 g soil) and least by sand (3-8 mg/100 g soil).

In sand, the residues in peas reached 170 ppm after two days, decreasing to 8.5 ppm after 14 days; in muck soils, the residues in the pea plant were 0.82 ppm and 0.05 ppm, respectively, after the same periods.

# Residues after harvest

The comparatively rapid decline in mevinphos residues seen in the growing crop usually continues after harvest whilst the commodity is being stored or transported to the market. Thereafter, the various commercial and domestic processes reduce levels still further, often to below the limits of analytical determination. Consequently, residues at harvest bear little relation to residue levels in food when it is ready to eat. At the latter point, mevinphos residues often may not be detectable, even though residues near the proposed tolerance levels were present at harvest time.

## Residues in crops stored under ambient conditions

Studies have been undertaken in which samples of fruit and vegetables have been stored at ambient temperatures for 2 - 9 days. Table 6 summarizes typical figures for the decline in residues in cabbage, broccoli, cauliflower, lettuce and spinach stored in ambient conditions (Shell Research Ltd., 1957, 1971, 1972; Shell Chimie, 1972).

TABLE 6 Decline of residues in leafy vegetables after harvest

| Time<br>(days) | Red cabbage |       | of mevinphos (g<br>Cauliflower | -    | Spina | ach |
|----------------|-------------|-------|--------------------------------|------|-------|-----|
| Harvest        | 0.2         | 0.27  | 0.06                           | 0.15 | 0.35  | 8.7 |
| 2              | 0.11        | 0.09  | <0.02                          | 0.10 | 0.30  | 5.2 |
| 4              | 0.06        | 0.02  | -                              | 0.05 | 0.20  | 2.7 |
| 6              | 0.02        | -     | -                              | -    | -     | 1.1 |
| 8              | -           | <0.02 | -                              | -    | -     | -   |
| 9              | 0.01        | -     | -                              | -    | -     | -   |

Comparable data for fruits were also obtained and are summarized in Table 7.

TABLE 7 Decline of residues in fruits after harvest

| Time (days) | Apple |      | mevinphos (ppm<br>Peaches | )<br>Strawber | ries |
|-------------|-------|------|---------------------------|---------------|------|
| Harvest     | 0.72  | 1.29 | 2.9                       | 0.34          | 0.11 |
| 2           | -     | -    | -                         | 0.25          | 0.04 |
| 3           | -     | -    | 2.7                       | _             | -    |
| 6           | 0.07  | -    | -                         | _             | -    |
| 9           | -     | 0.21 | -                         | -             | -    |

# Effect of deep-freeze storage

Laws (1959) studied the effect of deep-freeze storage on residues of

mevinphos in cabbage; samples were taken after six weeks and six months of deep-freeze storage. Practically no decrease of mevinphos residues occurred during these storage periods.

# Effects of domestic processing

The data shown in Table 8 are representative of those available for the effect of washing in cold water (Shell Research Ltd., 1972; Shell Development Co., 1962).

TABLE 8 Mevinphos residues in leafy vegetables after washing

| Crop        | Initial residues<br>(ppm) | Residues after washing<br>(ppm) |
|-------------|---------------------------|---------------------------------|
| Spinach     | 1.10<br>0.96<br>0.50      | 0.54<br>0.66<br>0.35            |
| Cabbage     | 0.11<br>0.02              | 0.03<br><0.01                   |
| Broccoli    | 1.60<br>0.14              | 0.72<br>0.10                    |
| Cauliflower | 1.00<br>0.74<br>0.09      | 0.09<br>0.52<br>0.05            |

In general, the lower initial residues were derived from produce which had been stored under ambient conditions. In some cases the proportionate loss after washing was less from crops containing lower than from those containing higher residue levels.

A study by Wit (1972) demonstrated that household washing and subsequent cooking of endive resulted in a loss of 50% of the residue occurring in the crop at the retailer. In lettuce, household washing removed about 48% of the initial residue. Data are given in Table 9.

TABLE 9 Mevinphos residues in vegetables after washing and cooking

| Vegetable | Average residue, 4 replicates (ppm) |                 |                 |  |
|-----------|-------------------------------------|-----------------|-----------------|--|
|           | initial residue                     | after washing   | after cooking   |  |
| Endive    | 0.12(0.08-0.15)                     | 0.10(0.02-0.16) | 0.06(0.03-0.09) |  |
| Lettuce   | 0.54(0.36-0.80)                     | 0.28(0.24-0.30) |                 |  |

Whilst the residue data used as the basis for proposing tolerances were based on the crops as picked, many crops, especially lettuce and brassicas, are trimmed before cooking. Table 10 gives data which show the difference between residues in the outer leaves and the trimmed produce and which are typical of all available data. In general outer leaves represent 10-20% of the weight of the untrimmed crop (Shell Research Ltd., 1957, 1960, 1971; Shell Chimie, 1971).

In melons, 75-90% of mevinphos residues were found to be present in

the rind. Peeling reduced levels in cucumbers and peaches by up to 50%, in apples by up to 60% and in pears by between 50 and 75%. In citrus, residues were confined primarily to the peel, and where residues were reported in peel, they were usually below 0.01 ppm in the pulp (Shell Development Co. 1957, 1958; Shell Chimie, 1970; Shell Research Ltd., 1957, 1972; Shell Chemical Co., 1961).

Cooking vegetables and fruits reduces residues as illustrated by the data given in Table 11 (Shell Research Ltd., 1960, 1972).

TABLE 10 Residues of mevinphos in outer leaves and trimmed crop

| Crop             | External leaves<br>(ppm)             | Trimmed crop<br>(ppm)                  |
|------------------|--------------------------------------|--|
| Lettuce          | 0.50<br>0.24<br>0.17                 | 0.40<br>0.20<br>0.12                   |
| Cabbage          | 0.59<br>0.50<br>0.08<br>0.64<br>0.22 | <0.05<br>0.08<br><0.02<br>0.02<br>0.02 |
| Brussels sprouts | 0.63<br>0.25<br>0.02                 | 0.08<br>0.16<br><0.02                  |

# TABLE 11 Mevinphos residues in crops after cooking

|          | Residues (ppm) |               |  |
|----------|----------------|---------------|--|
| Crop     | Before cooking | After cooking |  |
| Broccoli | 0.09           | 0.02          |  |
| Cabbage  | 0.03           | 0.01          |  |
| Spinach  | 2.70           | 0.81          |  |
|          | 1.10           | 0.36          |  |
| Beans    | 15.01          | 7.40          |  |

# TABLE 11 (cont'd)

| Residues (ppm) |                                |  |
|----------------|--------------------------------|--|
| Before cooking | After cooking                  |  |
| 1.10           | 0.59                           |  |
| 0.65           | 0.26                           |  |
| 0.60           | 0.43                           |  |
|                | Before cooking<br>1.10<br>0.65 |  |

<sup>1</sup> Spiked sample.

#### Blanching and canning

In the canning of fruit and vegetables, which involves considerable heat treatments, virtually all mevinphos residues are eliminated.

A study by Dormal <u>et al.</u> (1959) demonstrated that blanching and canning spinach, peas and beans effectively removed all residues of mevinphos. Similar studies also showed the complete elimination by commercial canning of residues of mevinphos present at harvest on spinach and peaches; 40% of the residues of mevinphos present were removed from beans purely by the process of blanching, while this reduction was increased to 99% on subsequent bottling (Shell Research Ltd., 1960, 1971; Shell Chemical Co., 1957).

# Processing of wine

Painter <u>et al.</u> (1959) added mevinphos to grape must, and residues of mevinphos were found in wine prepared from the must. Measurable amounts of mevinphos were also retained in the sediment.

# Mevinphos residues in certain crops after harvest

Whilst canning effectively removes residues from treated crops, the effects of the milder domestic processes are variable and the available data are summarized under individual crop headings.

Where possible an estimate is made of the level which could be expected in the food when ready to eat if the crop were at the proposed tolerance level at harvest. In the great majority of cases, harvest time levels will be well below the proposed tolerances, so that the estimate made here for residues at the point of consumption will in general be well above those occurring in practice.

## <u>Brassicas</u>

The combined effects of delay between harvest and marketing, washing, removal of outer leaves and cooking are likely to reduce harvest residues of about 1.0 ppm to a maximum of 0.05 ppm.

#### Spinach

The combined effects of washing, transport and cooking would be expected to reduce harvest residues of about 1.0 ppm to around 0.15 ppm.

## Peas, beans, carrots, turnips and potatoes

Residue levels observed at harvest where crops had been treated according to good agricultural practice were invariably less than 0.05 ppm, and no processing work was undertaken in these crops.

# Apples, pears, peaches, apricots, cherries and strawberries

The principal losses of residue in fruits occur during transport to the market. Such factors as peeling, washing and cooking are not always relevant and are not considered here. In estimating losses there are great variations in the times and conditions of transport. Thus, apples and pears from distant countries may experience shipment periods of several weeks whereas fruits such as cherries and strawberries may be eaten within a matter of days after harvest. Thus, in the case of apples it is probable that residues at the proposed-tolerance level could decline to below the limits of determination where long shipment periods are involved. In the case of strawberries which reach the market in two days, residues could decline to between 50% and 70% of their harvest values.

#### Melons and citrus fruit

These fruits are peeled before being eaten. Residues in melons of 0.05 ppm at harvest would not be likely to contain detectable levels in the edible portion. The same is true of citrus fruit.

## <u>Lettuce</u>

Some reductions in residues will occur between harvest and consumption due to transport and removal of outer leaves. Washing will also have some effect (residues decline by washing about 50%). Precise figures of residue losses between harvest and the moment of consumption are difficult to estimate, especially in view of the widely varying conditions and times of transport from one country to another.

#### METHODS OF RESIDUE ANALYSIS

Residues of mevinphos are best determined by gas-liquid chromatography. Alternatively, an enzyme inhibition cholinesterase method may be employed.

# Gas chromatographic methods

Because of their accuracy, specificity, sensitivity and speed, gas chromatographic methods of analysis are the methods of choice.

Mevinphos can be determined by using a flame photometric detector (Beroza and Bowman, 1968; Brody <u>et al.</u>, 1966). A specific method for the analyses for residues of both the <u>cis</u> and <u>trans</u> isomers of mevinphos has been developed (Shell Research Ltd., 1957-72) and satisfactorily used on crops down to a general level of 0.01 ppm for each isomer. The crops are extracted by maceration with chloroform. Low water content crops are dampened with water before extraction. Co-extracted natural products can be removed by cleanup using a liquid - liquid chromatographic technique, followed by analysis of the mevinphos-containing extract Using this procedure, mean recoveries of 80-115% from crops at the 0.02 - 0.20 ppm level may be achieved for each isomer.

A thermionic detector has also been employed in the analyses of crops for residues of mevinphos (Winterlin, 1970; Shell Chemical Co., 1969). The crops are extracted with either ethyl acetate or chloroform, followed by a column adsorption chromatographic cleanup, if required, and determination by GLC equipped with a thermionic flame detector. This provides a quick and sensitive means for the detection, as well as the separation of the two isomers of mevinphos. These thermionic detector methods are capable of detecting levels of mevinphos as low as 0.01 ppm, with recoveries in the range of 90% to 110%.

## Enzyme inhibition

A specific enzymatic method for the detection and determination of

mevinphos in crops and animal products has been developed (Shell Development Co., 1964). The samples for analysis are extracted with chloroform, transferred to water, and determination is effected by a standard enzyme inhibition spectrophotometric method. Using this procedure, the limit of determination of mevinphos is 0.02 ppm for crops, 0.01 ppm for milk and up to 0.10 ppm for animal tissue. Recoveries are in the range of 80% to 110%.

#### Bioassay Methods

Bioassay methods have been described but such techniques have now been largely superseded.

## NATIONAL TOLERANCES

Officially approved tolerances for mevinphos have been established in some countries. The information presented in the following table has been obtained principally from the regulatory authorities. Every attempt has been made to present the most recent data, but the following list is not a fully authentic one. The figures in table 12 refer to the sum of <u>cis</u> and <u>trans</u> mevinphos.

#### APPRAISAL

Mevinphos is a systemic, rather volatile organo-phosphorous insecticide, which is used on a considerable scale in many countries, especially on vegetables and fruit, for the control of a wide range of pests, such as aphids, leafrollers and spider mites. This pesticide is recommended, particularly when control of pests is necessary, a relatively short time prior to harvest.

Technical mevinphos contains no less than 60% of the <u>cis</u>-isomer of mevinphos, and about 28% of <u>trans</u>-isomer. The former possesses considerable higher insecticidal activity than the latter.

The principal impurities in the technical material are methyl acetoacetate, methyl-2-chloro acetoacetate and dimethyl methyl phosphonate (each of the components mentioned comprise about 2% by weight of the total technical mevinphos).

Mevinphos is mainly used as an emulsifiable liquid. The concentration rates of use range from 0.125-0.5 kg a.i./ha., applied as a foliage spray; in U.S.A. up to 1 kg a.i./ha. is registered to accommodate extreme pest conditions.

The residue data available were obtained from many countries with different climatic and growing conditions and those presented are, with a few exceptions, representative of levels likely to occur at harvest under conditions of good agricultural practice.

Information is available on the fate of mevinphos residues in animals, in plants and in soil; residue data on animal tissues and products of animal origin, such as milk, show that residues occur only from feeding levels far in excess of those which are likely to occur in practice. Provided mevinphos is used according to conditions of good agricultural practice, no measurable amounts of residue will occur in meat, milk and milk products. TABLE 12 Examples of national tolerances reported to the meeting  $^1$ 

| Country                 | Crop(s)  | Tolerance<br>(ppm)    |
|-------------------------|--|-----------------------|
| Argentina               | peas, beans, cucumbers, citrus<br>lettuce, melons, apples, pears, grapes<br>brassicas, spinach, cherries, peaches<br>and plums | 0.25<br>0.5<br>1.0    |
| Australia               | fruits and vegetables  | 0.25<br>(recommended) |
| Belgium                 | spinach<br>other vegetables, fruit   | 0.3<br>0.1            |
| Brazil                  | peas<br>lettuce<br>broccoli, spinach, turnips  | 0.25<br>0.5<br>1.0    |
| Canada                  | all treated crops  | 0.25                  |
| Czechoslovakia          | leafy vegetables, cabbage  | 0.1                   |
| Fed. Rep. of<br>Germany | spinach<br>vegetables and top fruit<br>other crops   | 0.3<br>0.1<br>0.05    |
| Hungary                 | all crops  | 0.1                   |
| Yugoslavia              | apples<br>crops other than apples  | 0.5<br>0.1            |
| Netherlands             | spinach<br>other vegetables, fruit   | 0.3<br>0.1            |
| Switzerland             | vegetables )<br>top fruit )<br>grapes )  | 0.25                  |
| South Africa            | tolerances vary according to crop  | 0.25 - 1.0            |
| U.S.A.                  | citrus, peas, beans, cucumbers, root veg.<br>apples, pears, grapes, lettuce, melons<br>stone fruit, brassicas, strawberries    | 0.25<br>0.5<br>1.0    |

<sup>1</sup> Additional tolerances may exist in some countries for crops grown for local consumption. These tolerances do not appear.

When mevinphos was applied to plants, it was shown that it decreased rapidly within 12 hours after application, primarily through volatilization; thereafter degradation was mainly responsible for decrease in residue levels, the principle degradation products being dimethyl phosphate and acetoacetic acid.

Little information is available on mevinphos residues in foods in commerce.

A number of methods for residue analysis based on gas chromatographic procedures are available for specific determination of mevinphos <u>cis</u>-and <u>trans</u>-isomers. The GLC methods of analysis are the methods of choice, based on accuracy, specificity, sensitivity and speed. Recommendations are given for the most appropriate extraction procedures for residues in crops. These procedures can be used and adapted for regulatory purposes as required.

The limit of determination of the GLC methods mentioned is as low as 0.01 ppm for both <u>cis</u>- and <u>trans</u>-mevinphos in crops, with recoveries in the range of 90 - 110%.

Alternatively, an enzymatic method for the detection and determination of mevinphos residues may be used. The limit of determination of the latter method is 0.02 ppm of mevinphos (both isomers) for crops, 0.01 ppm for milk and 0.1 ppm for animal tissue. Recoveries are in the range of 100 - 110%.

Various rates of application and pre-harvest intervals occur in different countries. It has been demonstrated that considerable losses of residues available at harvest occur whilst the commodity is being stored or transported to market. Thereafter, various commercial and domestic processes reduce levels still further, often below the limits of determination. Consequently, residues at harvest bear little relation to residue levels in food at the time of consumption.

## RECOMMENDATIONS

| TOLERANCES  | ppm  |
|---|------|
| Brassicas (broccoli, Brussels sprouts, cabbage,<br>cauliflower, collards) cherries, strawberries. | 1    |
| Lettuce, spinach, apples, grapes, peaches.  | 0.5  |
| Cucumbers, tomatoes, apricots, citrus fruits, pears.  | 0.2  |
| Carrots, beans, onions, peas, potatoes, turnips   | 0.1  |
| Melons  | 0.05 |

FURTHER WORK OR INFORMATION

NONE

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See Also:

Toxicological AbbreviationsMevinphos (PDS)Mevinphos (FAO Meeting Report PL/1965/10/1)Mevinphos (Pesticide residues in food: 1996 evaluations Part II Toxicological)Mevinphos (Pesticide residues in food: 1997 evaluations Part II Toxicological & Environmental)