APPENDIX A

The major chemical categories of pesticides are chlorohydrocarbons, organophosphates, carbamates, nitrophenols, azo and hydrazines, diphenylcarbinols, fluorinated, formamidines, organometallic, mercaptans, sulfoxides, sulfones and sulfonates, thiocarbonates, dithiocarbamates, heterocyclicsulfur, hydrocarbons, alcohols and phenols, carboxamides, carboximides, amine derivatives, pyridine heterocyclics, imidazoles, triazoles, benzimidazoles and thiophanates, pyrimidines, quinozaline, S-alkyl dialkylcarbamothioates, ureas, carboxylic acids and derivatives, dinitroanilines, and triazines. An example of the structures of each chemical type is shown in Table A1 (3). MAI

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Table A1 Chemical categories of pesticides

Structures Name CH_3 Chlorohydrocarbons CH_2 $(H_3CO)_2 P$ Organophosphates Q-CO-NH-CH₃ Carbamates NO_2 O о-С-О-СН(СН₃)₂ Nitrophenols O_2N CH-C₂H₅ CH_3 Azo and Hydrazines N = N - SOH Diphenylcarbinols CC1CH₂-C-CH₂-CH₂-F Formamidines ____ CH_3

Name

Structures

Organometallic

Mercaptans and thioethers

Cl

OH

C₆H₅-S-CH₂-SO₂-NH₂

Sn-OH

OH

Sulfoxides, sulfones, and sulfonates

Cl₂CH-CH-SO-CH-CHCl₂ Cl Cl H₃C-SO₂-S-CH₂-CH-CH₃ OH

Thiocarbonates

Cl₃C-SO₂-CCl₃

O || (H₃C)₂N-C S-CH₂-COOH

Dithiocarbamates

 $\begin{bmatrix} \mathbf{C} & \mathbf{S} & \mathbf{S} \\ \mathbf{H}_3\mathbf{C})_2\mathbf{N}\mathbf{-C} & \mathbf{S} \\ \mathbf{S} & \mathbf{S} \end{bmatrix}_2$

Name Structures

Hydrocarbon

Alcohols and phenols

Carboxamides

$$NC - C - O - CO - NH - CI$$

$$CH_3$$

$$CI$$

$$CH_3$$

$$CI$$

 H_3C $N-C_{13}H_{27}$ H_3C

 C_6H_5

Pyridine heterocyclics

Amine derivatives

Imidazole and triazole

$$CI \longrightarrow O-CH-N$$
 $(H_3 C)_3 C$
 $C \searrow O$

Name

Structures

Pyrimidines

$$CH_3$$
 OH N N N N N N

Quinoxalines

$$N$$
 S
 S
 S

S-Alkyl dialkylcarbamothioates

$$C_2H_5$$
 $N-C$ $S-C_2H_5$

Ureas

Carboxylic acids and derivatives

$$CI \longrightarrow CH_2 \longrightarrow COOH$$

Benzimidazoles and thiophanates

APPENDIX B

The organic phosphorus compounds constitute the second important group of pesticides. These compounds are either derivatives of phosphoric acid, pyrophosphoric acid, fluorophosphoric acid, the two isomers, thiophosphoric acid and thionophosric acid, and dithionopyrophosphoric acid. Phosphonates are also to be found among the organic phosphorus pesticides (19).

A list of some organophosphorus pesticides including of their strusture properties, toxicology, nomenclature and uses are in page 89-94 (58).

B.1 profenofos

Common name profenofos.

Chemical name (*IUPAC*) 0-=4-bromo-2-chlorophenyl*O*-ethyl S-propyl phosphorothioate.

Structural formular

Empirical formular C₁₁H₁₅BrClO₃PS (373.6)

Development Insecticide

Properties

Pure profenofos is a pale yellow liquid; **b.p.** 110 °C/0.001 mmHg; **v.p.** 1.3 mPa (20°C) ; ρ 1.455 g/cm³ at 20 °C; $n_{_D}^{_{25}}$ 1.5493 – 1.5495. **Solubility** (20°C) : 20 mg/1 water; miscible with most organic solvents. **Stability**: on hydrolysis (20°C) DT₅₀ (calculated) 93 d (pH5), 14.6 d (pH7), 5.7 h (pH9).

Uses

Non-systemic broad spectrum insecticide for use against insect pests and mites on cotton. Effective by contact and ingestion and, due to its translaminar effect, it kills lepidopterous larvae on the untreated side of the leaves. Rates of application for sucking insects and mites are 250-500 g AI/ha; for chewing insects 400-1200 g/ha.

The separate optical isomers, due to the chiral phosphorus atom, show different types of insecticidal activity and ability to inhibit acetylcholinesterase

Toxicology

Mammalian toxicity. Acute oral LD₅₀ for rats 358 mg TC/kg. Acute percutaneous LD₅₀ for rats c. 3300 mg/kg; slight irritant to skin and eyes of rabbits. Acute inhalation LC₅₀ (4-h) for rats c. 3 mg/l air. In feeding trials NOEL (EC formulation 380 g AI/l) for rats (2-y) 0.3 mg AI/kg diet, for lifetime study 1.0 mg AI/kg diet.

B.2 prothiofos.

Common name prothiofos

Chemical name (*IUPAC*) O-2,4-dichlorophenyl O-ethyl S-propyl phosphorodithioate.

Structural formular

Empirical formular C₁₁H₁₅Cl₂O₂PS₂ (345.2)

Development Insecticide

Properties

Prothiofos is a colourless liquid; **b.p.** 125-128 $^{\circ}$ C/0.1 mm Hg; **v.p.** <1.0 mPa (20 $^{\circ}$ C); $d_{_4}^{_{20}}$ 1.3; $n_{_D}^{_{20}}$ 1.5694. **Solubility** (20 $^{\circ}$ C) : 0.05 mg/1 water: > 200 g/1 dichloromethane, propan-2-ol, toluene.

Uses

Insecticide used against leaf-eating lepidopteran larvae, generally in fruits and vegetables at 50-75 g AI/hl. Also for public health use against Homoptera.

Toxicology

Mammalian toxicity. Acute oral LD_{50} : for rats c. 1500 mg/kg; for mice c. 200 mg/kg. Acute percutaneous LD_{50} for rats > 5000 mg/kg. Acute inhalation LC_{50} (4-h) for rats > 2.7 mg/l air (aerosol). In 2-y feeding trials NOEL for rats 5 mg/kg diet.

B.3 Chlorpyrifos

Common name Chlorpyrifos

Chemical name (IUPAC) O,O-diethyl O-3,5,6 = trichloro-2-pyridyl phosphorothioate.

Structural formular

$$\begin{array}{c|c}
S \\
I \\
CI \\
CI
\end{array}$$

$$\begin{array}{c}
OP(OCH_2CH_3)_2 \\
CI
\end{array}$$

Empirical formular C₉H₁₁Cl₃NO₃PS (350.6)

Development Insecticide

Properties

Chlorpyrifos forms colourless crystals with a mild mercaptan odour; **m.p.** 42-43.5 °C; **v.p.** 2.5 mPa (25°C). **Solubility** (25°C) : 2 mg/l water; 6.5 kg/kg acetone; 7.9 kg/kg benzene; 6.3 kg/kg chloroform; 450 g/kg methanol. **K**_{ow} 50 000. **Stability**

: rate of hydlorysis increases with pH, the presence of copper and possibly of other metals that can form chelates, hydrolysis DT_{50} 1.5 d (water at pH8 and 25° C) to 100 d (phosphate buffer at pH7 and 15° C). Persists in soil for 60-120 d, being degraded initially to 3,5,6-trichloropyridin-2-ol. **Corrosive** to copper and brass.

Use

A broad range of insecticide effective by contact, ingestion and vapour action, but not systemic. Controls Coleoptera, Diptera, Homoptera and Lepidoptera in soil or on foliage of citrus, coffee, cotton, maize and sugar beet. Also used against household pests (Blattellidae, Muscidae, Isoptera) mosquitoes (larvae and adults) and the control of ectoparasites on cattle and sheep. Volatile enough to form insecticidal deposits on nearby, untreated surfaces. Typical rates: 240-1200 g AI/ha for EC and 500-2500 g/ha for GR.

Toxicology

Mammalian toxicity. Acute oral LD₅₀: for rats 135-163 mg/kg; for guinea-pigs 500 mg/kg; for rabbits 1000-2000 mg/kg. Acute percutaneous LD₅₀ (in solutions) for rabbits c. 2000 mg/kg. Acute inhalation LC₅₀ (4-h) for rats > 0.2 mg/l (max. achievable level). In 2-y feeding trials NOEL, based on blood plasma cholinesterase activity: for rats 0.03 mg/kg daily; for dogs 0.01 mg/kg daily. Rapidly detoxified in rats, dogs and other animal species. ADI for man 0.01 mg/kg body weight.

B.4 Dichlorvos

Common name Dichlorvos.

Chemical name (IUPAC) 2,2-dichlorovinyl dimethyl phosphate (I).

Structural formular

$$\begin{array}{c}
O \\
\parallel \\
Cl_2C = CHOP(OCH_3)_2
\end{array}$$

Empirical formular C₄H₇Cl₂O₄P (221.0)

Development Insecticide

Properties

Dichlorvos is a colourless to amber liquid, with an aromatic odour; **b.p.** 74°C/l mmHg; **v.p.** 290 mPa (20°C); d₄²⁵ 1.42; n_D²⁵ 1.45. **Solubility** (20°C): c. 10 g/l water; 2-3 g/kg kerosene; miscible with most organic solvents and aerosol propellants. **Stable** to heat but is hydrolyzed by water, a saturated aqueous solution at room temperature is converted to dimethyl hydrogen phosphate and dichloroacetaldehyde at rate of c. 3%/d, more rapidly in alkali. **Corrosive** to iron and mild steel.

Uses

A contact and ingested insecticide with fumigant and penetrant action. It is used: as a household and public health fumigant, especially against Diptera and Culicidae, to protect s tored products at 0.5-1.0 g AI/100 m³; for crop protection against sucking and chewing Coleoptera, Homoptera and Lepidoptera

in cotton, fruit, ornamentals and vegetables at 300-1000 g/ha. It is non-persistent. Also used as an anthelmintic by incorporation in animal feeds.

Toxicology

Mammalian toxicity. Acute oral LD₅₀: for rats c. 50 mg/kg; for mice 140-275 mg/kg. Acute percutaneous LD₅₀ for rats c. 300 mg/kg. Acute inhalation LC₅₀ (4-h): for rats > 0.1 mg/l air (vapour), c. 0.5 mg/l air (aerosol). In 2-y feeding trials NOEL for rats 10 mg/kg diet. ADI for man 0.004 mg/kg body weight.

B.5 Methamidophos

Common name Methamidophos.

Chemical name (IUPAC) O,S-dimethyl phosphoramidothioate (I).

Structural formular

Empirical formular C₂H₈NO₂PS (141.1)

Development Insecticide

Pure methamidophos forms colourless crystals; **m.p.** 46.1 °C; **v.p.** 2.3 mPa (20°C); $n_{_{D}}^{_{40}}$ 1.5092; $d_{_{4}}^{^{20}}$ 1.31. **Solubility** (20°C) : > 200 g/l water, dichloromethane, propan-2-ol. **Stable** at ambient temperature but decomposes on heating without boiling;

hydrolysis DT₅₀ 40 h (pH2, 40°C), 120 h (pH9, 37°C).TC grade and TK are **corrosive** to mild steel and copper-containing alloys. **Incompatible** with alkaline pesticides.

Uses

Acaricide and insecticide effective against a broad range of Acarina, Diptera, Homoptera and Lepidoptera on cotton, fruits, potatoes, tobacco and vegetables. It is systemic in action when applied to the base or trunk of deciduous trees; defoliation has occurred when applied as a foliage spray to deciduous fruit. At 0.5-1.0 kg/ha its contact activity persists for 7-21 d.

Toxicology

Mammalian toxicity. Acute oral LD₅₀: for rats, mice and dogs c. 20 mg/kg. Acute percutaneous LD₅₀: for rats c.130 mg/kg; for rabbits c.100 mg/kg. Acute inhalation LC₅₀ (4-h) for rats 0.2 mg/l (aerosol). In 2-y feeding trials NOEL for dogs and rats 2 mg/kg diet. ADI for man 0.0006 mg/kg.

B.6 Mevinphos

Common name Mevinphos.

Chemical name (*IUPAC*) methyl 3-(dimethoxyphosphinoyloxy) but -2 -enoate; methyl 3-dimethyloxyphosphinyloxy)but-2-enoate:2-methoxycarbony l-1-methylvinyldimethyl phosphate).

Structural formular

$$(CH_{3}O)_{2}P - O C = C COOCH_{3}$$

Empirical formular C7H13O6P (224.1)

Development Insecticide

Properties

TC contain > 60% m/m of the (E)-isomer and c. 20% m/m of the (Z)-isomer. It is a pale yellow liquid; **b.p.** 99-103 °C/0.3 mmHg; **v.p.** 17 mPa (20 °C); d_{20}^{20} 1.24. The (E)-isomer has **m.p.** 21 °C, n_{D}^{20} 1.4452, d_{D}^{20} 1.2345; the (Z)-isomer, **m.p.** 6.9 °C, n_{D}^{20} 1.4524, d_{D}^{20} 1.245. *Solubility*: TC mevinphos miscible with water, alcohols, ketones, chlorinated hydrocarbons, aromatic hydrocarbons: slightly soluble in aliphatic hydrocarbons. **Stable** when stored at ambient temperatures but hydrolysed in aqueous solution, DT₅₀ 120 d (pH6), 35 d (pH7), 3 d (pH9), 1.4 h (pH11). Not compatible with Bordeaux mixture, lime sulfur or other alkaline products. Corrosive to cast iron, mild and some stainless steels and brass; non-corrosive to glass and many plastics by passes slowly through thin films of polythene.

B.7 Parathion-methyl

Common name .Parathion-methyl;

Chemical name (*IUPAC*) o,o- dimethyl o-4-nitrophenyl phosphorothioate.

Structural formular

$$NO_2$$
 OP(OCH₃)₂

Empirical formular C₈H₁₀NO₅PS (263.2)

Development Insecticide

Properties

Pure parathion-methyl forms colourless crystals; **m.p.** 35-36°C; **v.p.** 0.2 mPa (20°C); d_4^{25} 1.358; n_D^{25} 1.5515. **Solubility** (20°C): 55 mg/l water;> 200 g/l dichloromethane, propan-2-ol; TC(c.80% pure) a light to dark tan-coloured liquid; f.p.c 29 °C; d_1^{20} 1.20-1.22. **Stablility**: isomerised to the O,S-dimethyl analogue on heating; hydrolysed by alkali

Uses

A non-system contact and ingested insecticide with some fumigant action. It is generally recommended at 15-25 g AI/hl to control Coleoptera, Homoptera and Lepidoptera on cereals, cotton, fruits, grapes and vegetables.

Toxicology

Mammalian toxicity. Acute oral LD₅₀: for rats c. 6 mg/kg; for male mice c.25 mg/kg. Acute percutaneous LD₅₀ (24-h) for rats c. 50 mg/kg. Acute percutaneous LC₅₀ (4-h): for rats 0.17 mg/l (aerosol). In 2-y feeding trials NOEL for rats 2 mg/kg diet. ADI for man 0. 02 mg/kg body weight.

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