Section 2
CHEMISTRY ASSESSMENT

1. OVERVIEW

Chlorpyrifos is an organophosphorus insecticide used for the control of *Coleoptera*, *Diptera*, *Homoptera* and *Lepidoptera* in soil or on foliage in a wide range of crops. Crops include fruit (pome, stone and citrus fruit, strawberries, figs, bananas), nuts, vines, vegetables (potatoes, asparagus), grains (rice, cereals, maize, sorghum), cotton, mushrooms and ornamentals. The mode of chlorpyrifos action is non-systemic, and exposure of insects to the active (via contact, ingestion and/or inhalation) affects the nervous system by inhibiting the activity of acetyl cholinesterase.

Chlorpyrifos is included in Schedule 6 of the SUSDP, although formulations containing chlorpyrifos concentrations of 5 % or less are included in Schedule 5.

The physico-chemical properties of chlorpyrifos are given in Appendix 1, along with the relevant chemistry details.

There are 13 chlorpyrifos TGAC manufacturers currently approved in Australia. The chemistry aspects (synthetic process, quality control procedures, batch analysis results and analytical methods) were evaluated previously and found acceptable.

2. DECLARATION OF COMPOSITION (DOC) FOR CHLORPYRIFOS TGAC

Details of the 13 chlorpyrifos TGAC manufacturers are tabulated below. Also included in the table are details of: (i) the purity of chlorpyrifos; (ii) the specification limit for the toxic micro-contaminant sulfotep (*O*,*O*,*O*,*O*-tetraethyldithiopyrophosphate); and (iii) an indication of whether all impurities which could be present at a concentration of 1 g/kg or more are listed in the DoC.

Licensed Chlorpyrifos Manufacturer	TGAC Approval No.	Chlorpyrifos purity	Sulfotep levels	Other Impurities listed in DoC
Dow Chemical Company, Michigan, USA	P44112	NLT 990 g/kg	NMT 0.3 g/kg	3
	P44113	NLT 990 g/kg	NMT0.3 g/kg	3
	P44160	NLT 970 g/kg	NMT 2 g/kg	3
Dow AgroSciences Ltd, Norfolk UK	P44111	NLT 970 g/kg	NMT 2 g/kg	3
	P49340	NLT 180 g/kg	*	N/A
Luxembourg Industries (Pamol) Ltd, Tel-Aviv, Israel	P46670	NLT 940 g/kg	NMT 2 g/kg	3
	P48643	NLT 990 g/kg	NMT 0.3 g/kg	3
Lupin Agrochemicals Inc, India	P46796	NLT 940 g/kg	NMT 2 g/kg	3
Makhteshim Chemical Works Ltd, Israel	P44005	NLT 970 g/kg	**	3
Ficom Organics Ltd, India	P46642	NLT 940 g/kg	NMT 2 g/kg	3
Gharda Chemicals Ltd, India	P46888	NLT 980 g/kg	NMT 2 g/kg	3
Hubei Sanonda Company Ltd, China	P47254	NLT 940 g/kg	Not detectable	3
Aimco Pesticides Ltd, India	P48459	NLT 940 g/kg	NMT 2 g/kg	3
3M Canada Inc, Ontario	P49124	NLT 190 g/kg	*	N/A
Excel Industries Ltd, Bombay, India	P47155	NLT 960 g/kg (965 g/kg)	NMT 2 g/kg	3
Mitsu Industries Ltd, India	P48077	NLT 940 g/kg	NMT 2 g/kg	3
Cheminova Agro A/S, Denmark	P48521	NLT 960 g/kg	NMT 2 g/kg	3

NLT: Not Less Than; NMT: Not More Than; N/A: Not Applicable

*The manufacturing concentrate is prepared using chlorpyrifos TGAC that has a maximum sulfotep concentration of 2 g/kg. Hence, the levels of impurities in the manufacturing concentrate will not exceed those present in the technical material.

**Sulfotep was not listed on the DoC. However, the manufacturer tested for the presence of the impurity, and determined that it was not detected.

Chlorpyrifos purity: The FAO Specification Limit for chlorpyrifos technical is 940 g/kg minimum. The NRA approved sources of chlorpyrifos TGAC have minimum chlorpyrifos limits of between 940 g/kg and 990 g/kg.

Impurities: All impurities that could be present in the chlorpyrifos TGAC (at concentrations of 1 g/kg or more) were listed in the DoCs. The specification limit for *O*,*O*,*O*,*O*-tetraethyldithiopyrophosphate (sulfotep) was 2 g/kg maximum, with the highest purity (99%) chlorpyrifos TGACs specifying a sulfotep limit of 0.3 g/kg maximum.

Toxic Impurities: It is considered that other compounds of toxicological significance (N-nitrosamines, halogenated dibenzo-pi-dioxins, or halogenated dibenzofurans and PCBs) are not expected in chlorpyrifos TGAC due to the raw materials and synthetic route used.

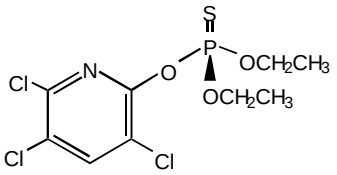
Manufacturing concentrates: There are two approved sources of chlorpyrifos manufacturing concentrates, containing a minimum of 180 to 190 g/kg chlorpyrifos. In manufacturing concentrates, the chlorpyrifos is present in a micro-encapsulated form (0.5 µm polyurea coating) that is suspended in an aqueous mixture. The capsule wall protects the chlorpyrifos from any physical damage, enabling the concentrate formula to withstand the effects of strong acids and bases. Since the manufacturing concentrate is prepared using the chlorpyrifos TGAC, any impurities present will not exceed those present in the technical material.

3. ACTIVE CONSTITUENT

3.1. Chemical Identity

Chlorpyrifos is a broad-spectrum organophosphorus pesticide, displaying insecticidal activity against a wide range of insect and arthropod pests. Technical chlorpyrifos has a minimum purity of between 940 and 990 g/kg. Manufacturing concentrates contain a minimum of 180 to 190 g/kg chlorpyrifos.

Common name:	Chlorpyrifos
IUPAC Name:	*O*,*O*-diethyl*O*-3,5,6-trichloro-2-pyridyl phosphorothioate
CA Name:	*O*,*O*-diethyl*O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate
CAS Registry No.:	2921-88-2
Empirical formula:	$C_9H_{11}Cl_3NO_3PS$
Molecular weight:	350.6
Structural formula:	



3.2. Physical and Chemical Properties

Physical and chemical properties of the pure active constituent

Colour	white/colourless crystalline solid
Odour	odourless
Physical state	crystalline solid
Melting point	41 to 43.5 ^{o}C
Octanol/water partition coefficient (Log P)	4.70 (McDonald *et al*., 1985)
Vapour pressure	1.87 x 10^{-5} mm Hg (2.5 mPa) at 25 ^{o}C (Brust, 1964)
Density/specific gravity	1.38 g/cm^3 at 46 ^{o}C
Dissociation constant	Chlorpyrifos does not contain any readily dissociable groups
Solubility in water	2 mg/L at 23 ^{o}C (Hummel and Crummet, 1964); 1.39 mg/L at 25 ^{o}C (Drummond, 1986)
Solvent solubility	Benzene - 7900 g/kg; acetone – 6500 g/kg; chloroform – 6300 g/kg; carbon disulfide – 5900 g/kg; carbon tetrachloride – 3100 g/kg; chloroform – 6300 g/kg; diethyl ether – 5100 g/kg; ethanol – 630 g/kg; ethyl acetate - >2000 g/kg; isooctane – 790 g/kg; methanol – 450 g/kg; methylene chloride – 4000 g/kg; propylene glycol – 40 g/kg; toluene – 1500 g/kg; trichloroethane – 4000 g/kg; triethylene glycol – 50 g/kg; xylene – 4000 g/kg (Drummond, 1986; Hummel and Crummet, 1964);
Stability	Chlorpyrifos is stable in air (non-volatile) and is not sensitive to UV radiation. It is stable to neutral and weakly acidic solutions, but is hydrolysed by strong bases. Chlorpyrifos is thermally sensitive to temperatures over 50 ^{o}C, and undergoes violent exothermic decomposition above 130 ^{o}C. The half-life of the aqueous methanolic solution at pH 6.0 is 1930 days.
Hydrolysis	The rate of chlorpyrifos hydrolysis increases with both pH and temperature. At 25 ^{o}C, pH 8 $t_{½}$ = 23 days pH 7 $t_{½}$ = 35 days pH 5 $t_{½}$ = 63 days At pH 7.0, 35 ^{o}C $t_{½}$ = 12 days 25 ^{o}C $t_{½}$ = 35 days 15 ^{o}C $t_{½}$ = 100 days
Corrosiveness	corrosive to copper and brass
Hazchem code	2WE
Fire and explosion hazard	Unknown
Extinguishing media	Dry chemical, water spray or regular foam

Hazardous combustion products	Thermal decomposition may release toxic and/or hazardous gases

Physical and chemical properties of the TGAC

Colour	White to light yellowish-brown crystalline solid
Odour	mild mercaptan odour

Other characteristics are as listed above for the pure active constituent.

3.3. Chemistry Aspects

The chemistry aspects (manufacturing process, quality control procedures, batch analysis results, and analytical methods) of chlorpyrifos TGACs were evaluated and found acceptable.

4. FORMULATION OF END-USE PRODUCT

Chlorpyrifos is used in a formulated form as a broad spectrum insecticide for the control of *Coleoptera*, *Diptera*, *Homoptera* and *Lepidoptera* in soil or on foliage in a wide range of crops. Crops include fruit (pome, stone and citrus fruit, strawberries, figs, bananas), nuts, vines, vegetables (potatoes, asparagus), grains (rice, cereals, maize, sorghum), cotton, mushrooms and ornamentals. The chlorpyrifos formulations are available as emulsifiable concentrates (EC), baits, granules, ultra-low volumes (ULV), liquid concentrates (LC), wettable powders (WP) and dusts. The mode of chlorpyrifos action is non-systemic, and exposure of insects to the active (via contact, ingestion and/or inhalation) affects the nervous system by inhibiting the activity of acetyl cholinesterase.

5. DECLARATION OF COMPOSITION

The FAO monograph specifications for the Technical chlorpyrifos are listed below:

Chlorpyrifos content:	not less than 940 g/kg
Impurities:	Water: 1 g/kg maximum
	Acetone insolubles: 5 g/kg maximum

Chlorpyrifos TGACs from 13 approved sources comply with the FAO specifications for the content of the active constituent (the minimum chlorpyrifos limits are between 940 g/kg and 990 g/kg).

Toxic Impurities

The specification limit for the toxic impurity sulfotep (*O*,*O*,*O*,*O*-tetraethyldithiopyrophoshate) is 2 g/kg maximum. All of the approved chlorpyrifos TGAC sources comply with this sulfotep specification, and the highest purity chlorpyrifos TGACs (99%) specify a sulfotep limit of 0.3 g/kg maximum. The levels of sulfotep in the Manufacturing Concentrates do not exceed those present in the technical material, since the Manufacturing Concentrates are prepared using the chlorpyrifos TGAC.

Other compounds of toxicological significance (N-nitrosamines, halogenated dibenzo-pi-dioxins, or halogenated dibenzofurans and PCBs) are not expected in chlorpyrifos TGAC due to the raw materials and synthetic route used.

6. CONCLUSION

The NRA will introduce a compositional standard for all chlorpyrifos TGACs which is based on the latest FAO specifications for this chemical. In addition, the level of sulfotep should be $\leq$2 g/kg.

7. BIBLIOGRAPHY

Brust H.F. (1964) A summary of chemical and physical properties of *O*,*O*-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl)phosphorothioate. DowElanco, Indianapolis, IN (unpublished report).

Drummond J.N. (1986) Solubility of chlorpyrifos in various solvents. DowElanco, Indianapolis, IN (unpublished report).

Hummel R.A. and Crummet W.B. (1964) Solubility of ethel *O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate in various solvents. DowElanco, Indianapolis, IN (unpublished report).

McDonald I.A., Howes, D.A. and Gillis, N.A (1985) The determination of the physicochemical parameters of chlorpyrifos. DowElanco, Indianapolis, IN (unpublished report).