Australian Pesticides &
Veterinary Medicines Authority

The reconsideration of approvals of the active constituent azinphos-methyl, registrations of products containing azinphos-methyl and their approved labels

Preliminary Review Findings

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FOREWORD

The Australian Pesticides & Veterinary Medicines Authority (APVMA) is an independent statutory authority with responsibility for the regulation of agricultural and veterinary chemicals in Australia. Its statutory powers are provided in the Agvet Codes scheduled to the *Agricultural and Veterinary Chemicals Code Act 1994*.

The APVMA can reconsider the approval of an active constituent, the registration of a chemical product or the approval of a label for a container for a chemical product at any time. This is outlined in Part 2, Division 4 of the Agvet Codes.

The basis for the current reconsideration is whether the APVMA is satisfied that continued use of the active constituent azinphos-methyl and products containing azinphos-methyl in accordance with the instructions for their use:

- would not be an undue hazard to the safety of people exposed to it during its handling or people using anything containing its residues; and
- would not be likely to have an effect that is harmful to human beings; and
- would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment; and
- would not unduly prejudice trade or commerce between Australia and places outside Australia.

The APVMA also considered whether product labels carry adequate instructions and warning statements.

A reconsideration may be initiated when new research or evidence has raised concerns about the use or safety of a particular chemical, a product or its label.

The reconsideration process includes a call for information from a variety of sources, a review of that information and, following public consultation, a decision about the future use of the chemical or product.

In undertaking reconsiderations (hereafter referred to as reviews), the APVMA works in close cooperation with advisory agencies including the Office of Chemical Safety, the Department of the Environment and Heritage, and state departments of agriculture as well as other expert advisers as appropriate.

The APVMA has a policy of encouraging openness and transparency in its activities and community involvement in decision-making. The publication of review reports is a part of that process.

The APVMA also makes these reports available to the regulatory agencies of other countries as part of bilateral agreements. The APVMA recommends that countries receiving these reports will not utilise them for registration purposes unless they are also provided with the raw data from the relevant applicant.

This document sets out the preliminary review findings relating to the active constituent azinphos-methyl and products containing azinphos-methyl that have been nominated for review by the APVMA. The preliminary review findings and proposed recommendations are based on information collected from a variety of sources. The information and technical data

required by the APVMA to review the safety of both new and existing chemical products must be derived according to accepted scientific principles, as must the methods of assessment undertaken.

The review summary (Volume 1) and the technical reports (Volume 2 & 3) for all registrations and approvals for azinphos-methyl are available from the APVMA web site: http://www.apvma.gov.au/chemrev/chemrev.html.

TABLE OF CONTENTS

1 OCCUPATIONAL HEALTH AND SAFETY ASSESSMENT

1.1 TOXICITY AND HEALTH EFFECTS RELEVANT TO OCCUPATIONAL EXPOSURE

1.1.1 Toxicology

Azinphos-methyl is of high acute toxicity in mammals via all routes of administration.

Consistent with the cholinergic effects of organophosphates, signs of acute azinphos-methyl intoxication include diarrhoea, salivation, lacrimation, vomiting, muscle tremors, paralysis, ataxia and convulsions.

Azinphos-methyl (technical grade) is a slight eye irritant but not an irritant to rabbit skin. Some formulations of azinphos-methyl, namely E 1582 19.5% EC 00126/0667, Guthion 2F 20% and Guthion fruit tree & garden spray 13%, were classified as severely irritating to rabbit eyes. Guthion 2F 20% and Guthion fruit tree & garden spray (13%) were classified as slight and severe irritants to rabbit skin, respectively.

Azinphos-methyl, including 35% WP and 35% FL formulations, are skin sensitisers in guinea pigs. However, no irritant or allergic skin reactions were reported for azinphos-methyl when patch tested in human subjects.

With the exception of benzazimide, a toxicologically significant metabolite, no other metabolites of azinphos-methyl have been investigated.

Oral studies conducted in rats indicate that azinphos-methyl is rapidly and completely absorbed from the gastrointestinal tract, distributed mainly in blood plasma, adrenals, kidney and liver with little evidence of accumulation in tissues. Excretion, primarily in urine followed by bile, is also rapid occurring within 48 hours of dosing irrespective of the route of administration. It is metabolised to a number of metabolites. The toxicokinetic characteristics of the metabolite benzazimide are generally similar to azinphos-methyl. No data were available on the comparative toxicity of other metabolites.

A number of repeat dose animal studies were considered suitable for regulatory purposes by DHAC. Inhibition of cholinesterase in plasma, RBC and brain is the most critical effect in acute and repeat dose studies. The lowest NOEL reported for plasma/RBC ChE inhibition was 0.125 mg/kg bw/day, reported in a 2 year dog study. NOHSC considered the NOELs of 1 and 0.25 mg/kg bw/day for plasma/RBC ChE inhibition, established in humans following single and 4-week repeated oral dose studies, respectively, to be the most appropriate values for the purpose of the OHS risk assessment.

1.1.2 Dermal absorption

The OHS risk assessment considered a dermal absorption of 30% (i.e dermal absorption factor of 0.3), derived from well-conducted human and rat studies, to provide a sufficiently conservative estimate for both SC and WP formulations.

1.1.3 Health effects resulting from occupational exposure

In general, health effects reported as resulting from occupational exposure to azinphos-methyl related to depletion in plasma and RBC ChE activity. No sensitisation reactions or other adverse effects have been reported as a result of occupational exposure to azinphos-methyl during manufacturing and formulation activities.

The little available information reveals increased sister chromatid exchanges in people occupationally exposed to organophosphorous based pesticides. However, the DHAC's assessment of health effects concluded that based on weight-of-evidence azinphos-methyl was considered non-genotoxic. The biological significance of the occupationally reported effects and their possible link to increased susceptibility to cancer remain to be elucidated.

No definitive evidence exists to support the role of organophosphorous based pesticides in chronic subclinical neurological damage.

Azinphos-methyl ranked fifth among the registered pesticides selected on the basis of high incidence of pesticide poisonings, relatively high toxicity and high usage as was concluded from the examination of the Poison Control Centre and California data. Azinphos-methyl available poisoning incident data indicates that it is a significant problem particularly for field worker poisoning, many of which cases involved violation of re-entry interval or exposure to spray drift.

1.2 USE PROFILE

Most applications of azinphos-methyl products are made by ground spray application. Ground applications are conducted using mechanised sprayers (airblast, air shear) or by handheld sprayers. Aerial application is a minor method throughout Australia, and is severely restricted in Tasmania.

The main application methods include orchard airblast, used mainly for pome and stone fruit as well as for blueberries, macadamias, lychees and kiwi fruit. Other significant application methods include air shear (using misters/mist blowers) and CDA (controlled droplet application) equipment. Electrostatic sprayers, butt spraying (using hand held equipment or orchard airblast equipment with nozzles turned off or redirected) and spot spraying (using hand held equipment) are used to a lesser degree.

Information provided indicates that application methods, application rates and work rates are similar for all orchard crops. Typical work rates for pome fruit, stone fruit and blueberries ranged from 2 to 60 ha/day (average 9.3 ha/day) and maximum work rates ranged from 2 to 60 ha/day (average 17.9 ha/day). Application rates ranged from 0.25 to 2 kg ai/ha (average 0.89 kg ai/ha). Total ai handled per day ranged from 0.7 to 58 kg (average 8.8 kg).

1.3 HAZARD OVERVIEW

1.3.1 Acute toxicity

The acute toxicity of azinphos-methyl technical in mammals was high via all routes of administration. Consistent with the cholinergic effects observed with other organophosphates, signs of acute azinphos-methyl intoxication included diarrhoea, salivation, lacrimation and vomiting (muscarinic effects), muscular tremors and paralysis (nicotinic effects), and restlessness, ataxia and convulsions (CNS effects). The oral LD_{50} values in rats ranged from 4.4 to 26 mg/kg bw using a variety of vehicles, and was 15 mg/kg bw in mice. The oral LD_{50} in guinea pigs was 80 mg/kg bw, and >10 mg/kg bw in dogs.

Azinphos-methyl was highly toxic in rats via inhalation, with a LC_{50} value of 132 mg/m^3 in a head-only, 4-h exposure study. The acute dermal toxicity of azinphos-methyl was high in rats and moderate in rabbits, with LD_{50} values of 72.5 and 1380 mg/kg bw, respectively. Azinphos-methyl technical was a slight eye irritant, but not a skin irritant in rabbits, and was a skin sensitiser in guinea pigs.

1.3.2 Repeat dose toxicity

In order to perform a occupational risk assessment careful consideration needs to be given to the selection of the appropriate toxicological endpoint and duration of dosing. An inspection of all repeat dosing studies in the database indicated that the most sensitive endpoint by all routes of administration, durations and species was cholinesterase inhibition. This endpoint is also considered relevant for an occupational risk assessment. As humans are the species, which are being protected, it is appropriate that human data, of suitable quality and availability, is used for risk assessment purposes. The dietary risk assessment for azinphos-methyl is based on the inhibition of plasma cholinesterase in a 4-week oral dosing study in humans (NOEL = 0.25 mg/kg bw/day for plasma/RBC ChE inhibition). Although a 4-week repeat dosing study may be considered to be too short to ensure life-long dietary protection it is the consistency of the endpoint in relation to the dosing duration and its occurence in all species, which is important. Consequently the same study in humans can be used as the basis of the occupational risk assessment. However, since the volunteers in the human study ingested azinphos-methyl a dermal absorption factor needs to apply to make the risk assessment relevant for the major occupational route of exposure, ie. dermal. A study conducted in human volunteers is the most relevant dermal absorption study and considering the variability of dermal absorption rates in the study, the highest mean value of 29.3% (rounded to 30%) will be used in the OHS risk assessment (Selim, 1999).

1.4 HEALTH EFFECTS ARISING FROM OCCUPATIONAL EXPOSURE

Two company communications reported that regular medical examinations revealed no clinically relevant sensitisation reactions or other relevant adverse effects in male or female workers involved in azinphos-methyl production and formulation under prevailing industrial hygiene conditions (Miksche, 1981; Kehrig, 1999).

A published report on working conditions at a plant formulating azinphos-methyl in Australia in 1965 indicated that atmospheric levels of azinphos-methyl were between 0.5 and 1.0 mg/m^3 (ie. above the NOHSC exposure standard). During one year, 2 workers showed symptoms of

OP poisoning, with one requiring hospitalisation. An additional 13 workers exhibited depletions in plasma ChE activity of up to 75% (average 40%) of pre-exposure levels. The latter showed near full recovery of ChE activity 15 days after removal from the workplace. As azinphos-ethyl was also used at this plant, it was not possible to attribute these effects solely to azinphos-methyl (Simpson, 1965).

In a study of orange grove workers, greater than 20% inhibition of plasma and RBC ChE levels was reported in some workers 8 and 11 days after spraying with azinphos-methyl SC (4.2 kg ai/ha). In contrast, no inhibition of plasma or RBC ChE levels were found in workers re-entering sprayed areas between 7 and 11 days after spraying reported in a similar study. However, the validity of this latter study is questionable due to data limitations (Waggoner et al 1970a & 1970b). US citrus pickers exposed to azinphos-methyl WP and SC formulations showed more than 20% inhibition of plasma ChE activity and RBC ChE activity, at re-entry days 2, 4, 5 and 6 (Lamb, 1980).

Statistically significant inhibition of RBC ChE activity (median 19%) was also found on re-entry day 44 in peach orchard workers exposed to azinphos-methyl during a re-entry study conducted in California (McCurdy *et al.,* 1994). Apparently no significant perturbations in ChE activity were found in US peach and apple harvesters exposed to azinphos-methyl (Hernandez *et al*., 1992; Appendix 2).

Comment: In general, no adverse health effects have been observed in male or female workers involved in azinphos-methyl production and formulation under normal safety precautions. A single report indicated that azinphos-methyl caused generalised dermatosis in an individual with apparently hypersensitive and dry skin, however, no effects on any internal organs such as the liver could be attributed to azinphos-methyl with adequate certainty. Additionally, no further details on the chemical, affected individual, or the severity of the skin reaction were discussed.

A number of occupational studies conducted in agricultural workers demonstrated greater than 20% inhibition of plasma and/or RBC ChE activity, which was probably attributable to azinphos-methyl exposure.

1.5 PRODUCT FORMULATIONS

Formulations of azinphos-methyl currently registered in Australia for agricultural uses are suspension concentrates (SC) containing either 200 or 350 gram (g) active ingredient (ai) per litre (L). A summary of formulation types and packaging sizes is provided in Table 1.

Table 1: Formulation types and packaging sizes for azinphos-methyl products registered for agricultural use

Formulation type	Code*	Packaging size and type
SC 200 g/L	**200 SC**	10 L
SC 350 g/L	**350 SC**	1L, 5 L, 20 L or 25 L containers

SC – suspension concentrate;
* these codes are used henceforth in the report
Source: APVMA and product labels

Technical grade azinphos-methyl is not manufactured in Australia. The active is imported by two of the registrants for the formulation of end use products. This assessment does not address worker exposure and risk during manufacture/formulation. Individual premises, manufacturing/formulation processes and exposure control measures may vary within workplaces. However, in manufacturing/formulation plants workers are expected to follow good manufacturing practices, and have adequate quality control and monitoring facilities.

1.6 OCCUPATIONAL EXPOSURE

Azinphos-methyl products are used in a number of agricultural situations. To facilitate the exposure assessment and risk assessment, rather than consider each individual use situation separately, exposure scenarios were developed, coded and grouped where possible. This allows maximisation of available data and simplifies the assessment.

1.6.1 End use exposure

Azinphos-methyl is used outdoors as a foliar spray. The extent of exposure is dependent on the mode of application. Exposure is expected to be limited to inhalation and dermal routes during mixing/loading and application. There is a potential for accidental ocular exposure to azinphos-methyl. Apart from providing suitable safety directions on the label to prevent eye irritation ocular exposure is not considered to be a primary route of exposure for OHS risk assessment.

Mixing/loading of **SC** formulations is often carried out by open pour in open air and application is by orchard sprayer, boom (limited), or hand spraying (limited). The most commonly available pack size for the **SC** formulations is 10 L, but the packaging type or design (eg neck opening size) is not known.

The agricultural exposure scenarios identified of azinphos-methyl are:

Scenario (1)	Mixing/loading SC for spray application in pome and stone fruit-overall spray, soil drench and butt spray
Scenario (2)	Mixing/loading and SC for spray application in citrus-overall spray
Scenario (3)	Mixing/loading and SC for spray application in macadamias, lychees, grapes and kiwi fruit-overall spray
Scenario (4)	Mixing/loading and SC for spray application in blueberries-overall spray
Scenario (5)	Mixing/loading and SC for vertical Boom application in citrus-overall spray
Scenario (6)	Mixing/loading and SC for concentrate or semi-concentrate sprayers (airblast, airshear, CDA, electrostatic) in all crop situations (3-8 times 49 gai/100mL)
Scenario (7)	Application of spray by mechanised ground equipment (air-blast sprayer, airshear spray, vertical boom, controlled droplet applicators and electrostatic) in pome fruit, stone fruit, citrus, macadamias, lychees and blueberries -overall spray
Scenario (8)	Mixing/loading/application by hand-held equipment in grapes, pome and stone fruit-soil drench, butt treatment or spot treatment

The following table details the use pattern parameters identified and considered in the agricultural exposure assessment.

Table 2: Use pattern parameters used in the risk assessment

Scenario number	Scenario description	Situation/crop	Application (use) rate* & spray volume**	Work rate (ha/6 hr work day)***	Total ai handled/day
1 & 7	**Mechanised ground spray application** ***Orchard air-blast equipment***[1]	Overall spray and butt and soil spray/drench[2] in pome fruit and stone fruit (49 g ai/100L)	dilute: **0.98 kg ai**/2000 L/ha concentrate: **0.29 kg ai**/600 L/ha	15 - 20 ha/day	19.6 kg/day 5.9 kg/day
2 & 7	**Mechanised ground spray application** *Orchard air-blast equipment*	Overall spray in citrus[3] (49 g ai/100 L)	dilute: **1.47-2.45 kg ai**/3000 - 5000 L/ha	15 – 20 ha/day	49 kg/day
3 & 7	**Mechanised ground spray application** *Orchard air-blast equipment*	Overall spray in grapes, kiwi fruit, lychees, macadamia *(49 g ai/100 L)*	dilute: **0.49 kg ai**/1000 L/ha concentrate: **0.2-0.29 kg ai**/400 - 600 L/ha	10 - 15 ha/day	7.35 kg/day 4.41 kg/day
4 & 7	**Mechanised ground spray application** *Orchard air-blast equipment*	Overall spray in blueberries *(49 g ai/100 L)*	concentrate: **0.18 kg ai**/300 L/ha	15 - 20 ha/day	2.94 kg/day
6 & 7	**Mechanised ground spray application** ***Boom spray (vertical)***[4]	Citrus *(49 g ai/100 L)*	dilute: **4.9 kg ai**/10000 L/ha	15 – 20 ha/day [5]	98 kg/day
7	**Mechanised ground spray application** ***Air shear spray (misters)***[6]	Pome fruit, stone fruit, grapes, kiwi fruit, macadamias[7] and lychees *(98 g ai/100 L)*	concentrate: **0.2-0.5 kg ai**/200 – 500 L/ha	15 - 20 ha/day	9.8 kg/day

[1] Orchard air blast equipment can be configured to spray dilute or concentrated sprays.
[2] Butt spray and soil spray/drench are only recommended as dilute sprays.
[3] Filling the tank is a significant time factor in citrus application.
[4] Vertical boom sprays are dilute sprayers only.
[5] See Footnote 3.
[6] Air shear (misters) are designed for concentrate spraying only.
[7] Air shear use is between 15-20% of all uses for macadamias.

7	**Mechanised ground spray application** ***Controlled Droplet Applicators (CDA)***[8]	Pome fruit, stone fruit, macadamias and lychees *(49 g ai/100 L)*		15-20 ha/day	4.9 kg/day
7	**Mechanised ground spray application** *Electrostatic sprayers*[9]				
8	**Hand held outdoor application** (***knapsack & vehicle mounted equipment)******* ***Spot-treatment***[10]	Grapes *(49 g ai/100 L)*	dilute: **0.74 kgai**/1500 L/ha	1 ha/d (vehicle mounted spray tank) 0.27 ha/day (knapsack)	0.735 kg/day (vehicle mounted) 0.198 kg/day (knapsack)
8	**Hand held outdoor application** (***knapsack & vehicle mounted equipment)******* ***Soil drench***[11]	Pome fruit, stone fruit *(49-98 g ai/100 L)*	Dilute: **0.74kgai-1.47kgai**/1500 L/ha		1.47 kg/day (vehicle mounted) 0.397 kg/day (knapsack)

ai-active ingredient

* Label recommended application rate/dilution considered to be representative for most crops

** Spray volume as advised by APVMA and considered to be representative for most crops

*** Work rate as advised by APVMA and considered to be representative for most crops

**** 1 ha/day is POEM default value; for knapsack (15 L tank capacity), work rate is expected to be less (based on POEM default maximum of 400 L spray/day, equivalent to 0.27 ha/day)

The following points are assumed in the exposure assessment:

- a normal work day of 8 hours, consisting of a 6 hour application period – an internationally accepted default value;

- exposure estimates represent the exposure of a worker after all protection provided by clothing, protective clothing or engineering controls specified on registered product labels are taken into consideration;

[8] CDA sprayer are similar to misters in terms of volumes applied. Refers to production of droplets using a spinning disc. This type of equipment is used by a minority of growers. Most use air assisted equipment.

[9] There appears to be only one commercial electrostatic orchard sprayer on the market and it is actually an air shear machine with the facility to charge the droplets as they leave the machine.

[10] The only spot treatment actually recommended on labels is for control of scale on grapevines. However, it is possible that if separate high volume butt sprays and soil drenches are required in pome and stone fruit that these would be carried out using this type of application. Nevertheless, advice from the pome and stone fruit industries is that spot spraying is rarely if ever used.

[11] See Footnote 10. However, growers may use small under-tree herbicide booms with either very coarse nozzles or no nozzles at all to carry out soil drenches.

- 5% penetration of liquid products (SC) through PVC (or other chemically resistant) gloves, consistent with POEM default;
- dermal penetration of 30 % in humans, as determined in Section 2;
- 100% absorption of inhaled dose, default value (Thongsinthusak *et al*., 1993); and,
- average body weight 70 kg, consistent with the World Health Organisation.

1.6.1.1 Predicted exposure

German model

Information on the German Model, Uniform Principles for Operator Peotection was submitted by Bayer Australia Ltd in November 1999 (Lundehn, 1992). The German Model was reviewed by Van Hemmen (1993). The data set used is based on the above unpublished studies carried out by the German industry. Dermal exposure was assessed with pads and hand washing. For respiratory exposure assessment, both particulates and vapours were collected by personal sampling. The exposure data were grouped according to the specific techniques used and the geometric means of the 90th percentiles were calculated for each group. The relative exposure of different body parts is pre-determined. In this case, the distribution over the body for upwards application (high crop) with vehicle mounted is 6% for hands, 11% for head and 83% for the rest of the body. The applicant provided exposure estimates derived from the German model during application of Gusathion M EC (emulsifiable concentrate) 19.5 and Gusathion WP 25 on high crops[12] and field crops[13] using tractor mounted and hand held equipment. It should be noted that exposure estimates in field crops were not assessed in this review as this situation is not relevant to Australian uses of azinphos-methyl.

The following parameters and assumptions were used in the German modelling:

Inhalation absorption	100%
Dermal absorption	30%
Average body weight	70 kg
Formulation type	19.5 EC and 25 WP
Application rate	3000 g azinphos-methyl/ha for high crops/tractor mounted and hand-held equipment
Work rate	8 ha/day for high crops / tractor mounted 1 ha/day for high crops / hand spray
Spray volume	Not provided
Packaging type	WP packed in water-soluble bags Packaging not known for EC
PPE scenarios:	Three scenarios were considered:

I No PPE when handling the concentrate and during application.

[12] High crops stand for crop systems such as orchards in which application is directed sideways and/or upwards
[13] Field crops stand for crop systems such as vegetables in which application is directed downward from a low level.

II With PPE: gloves during mixing/loading and application; standard protective garment (equivalent to one layer of clothing) and sturdy footwear during mixing/loading and application.

III With PPE: as above and additional PPE (half mask with combination filter during mixing/loading and application) in field crops; hood and visor during application.

Table 3: Mixer/loader/applicator exposure during Gusathion M EC 19.5 and WP 25 application to high crops based on German model estimates

Situation/ Application rate, work rate (amount ai handled)	PPE*	Actual exposure							
		mg/person/day)						mg/person/ kg ai handled)	
		M/L**		I		M/L/A		M/L/A	
		Dermal	*Inhalatic*	*Derma*	*Inhalatic*	*Derma*	*Inhalatic*	*Derma*	*Inhalation*
High crops, tractor mounted EC 3 kg ai/ha, 8 ha/day (24 kg ai /day)	I. no protective clothing and no gloves	57.6	0.0144	276	0.432	333.6	0.4464	13.9	0.0186
	II. protective clothing and gloves during M/L/A	0.576		40.488		41.06		1.71	
	III. as above plus half mask with filter during M/L/A		0.00029	13.12	0.00864	13.696	0.0089	0.57	0.00037
High crops, hand-held EC 3 kg ai/ha 1 ha/day (3 kg ai/day)	I. no protective clothing and no gloves	615.0	0.15	121.2	0.9	736.2	1.05	245.4	0.35
	II. protective clothing and gloves during M/L/A	6.15		18.468		24.618		8.206	
	III. as above plus half mask with filter during M/L/A		0.003	4.788	0.018	10.938	0.021	3.646	0.007
High crops, tractor mounted WP 3 kg ai/ha, 8 ha/day (24 kg ai /day)	I. no protective clothing and no gloves	0.0	0.0	276	0.432	276	0.432	11.5	0.018
	II. protective clothing and gloves during M/L/A			40.488		40.488		1.687	
	III. as above plus half mask with filter during M/L/A			13.128	0.00864	13.128	0.00864	0.55	0.00036

High crops, hand-held WP 3 kg ai/ha, 1 ha/day (3 kg ai /day)	I. no protective clothing and no gloves			121.2	0.9	121.2	0.9	40.4	0.3
	II. protective clothing and gloves during M/L/A			18.468		18.468		6.16	
	III. as above plus half mask with filter during M/L/A			4.788	0.18	4.788	0.18	1.60	0.06

ai- active ingredient; M/L - mixing/loading; A – application; M/L/A - mixing/loading/application

* All estimates assume 1% transmittance through gloves, 5% transmittance through protective clothing (worn during both M/L and application, however model does not consider dermal body exposure during M/L) and 2 % transmittance through half mask with filter.

** Model assumes zero exposure during mixing/loading WP (WP is packed in water soluble bags which are passed unopened into spray tank).

In the German model, the product formulations used in exposure assessment (19.5 EC and 25 WP) differ from those used in Australian agricultural applications (20/35 SC). The cab type, spray volume and packaging type (EC formulation) used in the modelling are not known. Therefore this data will not be considered for azinphos-methyl exposure estimation.

US-Canada model: Pesticide Handlers Exposure Database (US EPA, 1999)

The Pesticide Handler's Exposure Database (PHED) is based on the principle that most dermal and respiratory exposure relates more to the formulation type, conditions of use, environmental conditions and personal protective measures than the physical and chemical properties of the active ingredient. PHED contains measured exposure data collected from field workers and allocates these into four separate worker groups (mixer/loaders, applicators, mixer/loader/applicators and flaggers). Exposure scenarios were identified for aerial/chemigation application in cotton, ground boom application in cotton and tomatoes, and airblast application in pecans, citrus, grapes, apples and stone fruit. For each scenario, exposures were determined for one or more crops, which were chosen as representative of the typical amount of active ingredient handled daily. Some of the scenarios identified in PHED were not relevant as some of the crops and application methods differ significantly from Australian practices. The following scenarios were considered:

Mixing/loading liquids for airblast spray application in citrus (1.40-2.24 kg ai/ha), grapes (0.84-1.12 kg ai/ha), apples (0.56-1.12 kg ai/ha) and stone fruits (0.981-2.24 kg/ai ha) with 8.09 ha treated for all scenarios.

Applying sprays using an airblast sprayer (same treatment scenarios as above). Mixing/loading/applying sprays using a low pressure hand wand, spot treatment (ornamentals treated with 1.20-4.79 g/L at 151.4 L/day). The worker is assumed to be wearing long pants, long sleeve shirt, but no gloves. Additional PPE includes a double layer of clothing and gloves. Mixing is assumed to be carried out under open conditions and spraying by an open cab tractor. The following parameters and assumptions were made in the PHED modelling:

Inhalation absorption	100%
Dermal absorption	30%
Average body weight	70 kg

Formulation type	liquid (10 to 34.9% ai)
Work rate	8.09 ha /day
Spray volume	not provided
Packaging type	not provided

Table 4: Mixer/loader and applicator exposure during application to citrus, grapes, apples and stone fruit by airblast spray based on PHED estimates

Model study	PPE*	Maximum Application rate, work rate (maximum amount ai handled)	Dose range			
			mg/kg bw/day)			mg/person/kg i andled/day**)
			Dermal	*Inhalation*	*Total*	*Total*
M/L Liquids for airblast spray application (Citrus, grapes, apples and stone fruit)	no gloves	8.09 ha/day 2.24 kg ai/ha (18.12 kg ai/day)	0.8-1.7	0.0003-0.0007	0.80-1.70	3.09-6.57
	double layer of clothing and gloves		0.007-0.014	0.00024-0.00096	0.0072-0.015	0.028-0.058
Applying spray using an airblast sprayer	no gloves		0.1-0.21	0.0013-0.0025	0.10-0.21	0.39-0.811
	double layer of clothing and gloves		0.035-0.07	0.00025-0.0005	0.035-0.070	0.135-0.27
M/L/applying liquid using a low pressure hand wand(spot treatment)	no gloves	4.79 ai g/L 151.4 L/day (0.725 kg ai/day)	2.4	0.0007	2.4	231.7
	double layer of clothing and gloves		0.073	NA	0.073	7.05

M/L - mixing/loading; NA-not applicable; ai-active ingredient

* Open mixing.

** dermal and/or inhalation dose (mg/kg bw/day) x 70 kg bw (OCS assumption) / amount ai handled /day.

The amount of azinphos-methyl handled/day is similar to that used in Australia for pome and stone fruit treated by an airblast sprayer (Scenario 1 and 7); however, for mixing/loading and application of liquids by hand held equipment, the amount of azinphos-methyl handled/day is lower than that used in the Australian situation for hand held equipment (Scenario 8). This review recognises the following limitations with PHED data:

The assumed area treated per day by airblast spray is less than that anticipated in the Australian end use situation (Australian work rate ranges from 15 to 20 ha/day).
The formulation type for liquids was not specified.
Exposure values were presented as dose ranges.
Packaging information was not provided

In the absence of suitable worker exposure studies, the results from PHED are used in the risk assessment to estimate exposure of Australian workers to SC formulations. However, the

results will be used only as an approximate guide to supplement other modelled or surrogate data. The results from the scenarios discussed above have been standardised to the Australian situation. Standardised exposure estimates are presented in Table 5.

Table 5: PHED estimates standardised for Australian end users applying SC products

Exposure Scenario		PPE	Application rate, work rate (maximum amount ai handled)	Dose range		
				mg/kg bw/day)*		
				Dermal	Inhalation	Total
1 Open mixing loading for airblast spray application in pome and stone fruit	SC	protective clothing no gloves	49 g ai/100L 2000 L/ha 20 ha/day (19.6 kg ai/day)	0.86-1.83	0.0003-0.0007	0.86-1.84
		double layer of clothing and gloves		0.007-0.015	0.00026-0.001	0.0078-0.016
7 Open mixing/loading & application using mechanised equipment (air blast sprayer)		protective clothing no gloves		0.11-0.23	0.0014-0.0027	0.11-0.23
		double layer of clothing and gloves		0.038-0.076	0.00027-0.0005	0.038-0.076
8 Open mixing/ loading & application using hand held equipment		protective clothing no gloves	98 g ai/100L 1500 L/ha 1 ha/day (1.47 kg ai/day	4.87	0.0014	4.87
		double layer of clothing and gloves		0.148	-	0.148

* standardised to Australian use pattern (amount ai handled per day); PPE as per study assumptions.
* assuming 100% inhalation absorption. Dermal absorption 30%

UK model Predictive Operative Exposure Model

POEM, a descriptive model, provides surrogate exposure values, which are derived from the levels determined in several exposure field studies for each of several different scenarios. Exposure calculations are divided into two parts: contamination from handling the concentrated product and contamination during actual application of the dilute spray. The model assumes that the level and distribution of potential dermal contamination are mainly dependent on the handling techniques used during preparing the pesticide product for use, the type of application equipment employed and the work practices of the individual operator. In this model, exposure during mixing/loading is confined to the hands only; no respiratory exposure is estimated. Dermal (hands, trunk and legs) and inhalation exposure is estimated during spray application. In using POEM, it is necessary to make assumptions in order to estimate the actual exposure. These assumptions may be based on laboratory or field data, but in the absence of such data conservative estimates are to be made.

The use of exposure values derived from predictive models (such as POEM), involves the use of conservative assumptions for unknowns and a range of values for a particular method of spraying. Such modelling is internationally accepted as the first step in a tiered risk

assessment (Tier 1). The end use parameters, resultant exposure estimates and risk assessment for each end use scenario are presented and discussed under the designated scenario numbers below and in the risk assessment (Section 8.1). The following parameters are common for all POEM estimates.

Inhalation absorption	100% (default value)
Dermal absorption	30%
Average body weight	70 kg
Hand contamination design)	0.5 (POEM default for 10 and 25 L container of unspecified design) 0.10 (POEM default for 10 and 25 L container with wide neck (45 mm)) 0.20 (POEM default for 5 L container of unspecified design) 0.01 (POEM default for 5 L container with wide neck (45 or 63 mm))

The POEM model **Vehicle mounted (without cab) air assisted: application volume 500L/ha (V-500)** was used to estimate applicator exposure in the following scenarios:

Scenario (1)	Mixing/loading aSC for spray application in pome and stone fruit-overall spray, soil drench and butt spray
Scenario (2)	Mixing/loading SC for spray application in citrus-overall spray
Scenario (3)	Mixing/loading SC for spray application in macadamias, lychees, grapes and kiwi fruit-overall spray
Scenario (4)	Mixing/loading SC for spray application in blueberries-overall spray
Scenario (7)	Application of spray by mechanised ground equipment in pome fruit, stone fruit, citrus, macadamias, lychees and blueberries

The POEM model **Hand held outdoor hydraulic nozzle (H-Nozzle)** was used to estimate applicator exposure in the following scenario:

Scenario (8)	Mixing/loading/application by hand-held equipment in grapes, pome and stone fruit- soil drench, butt treatment or spot treatment.

A qualitative exposure risk assessment was conducted for application methods that cannot be modelled such as orchard airshear ground spray, vertical (oscillating) boom spray, CDA and hand held electrostatic applications. A summary of the caveats and parameters specific for each scenario, and dermal and inhalation doses are presented in Table 6.

Table 6: Agricultural uses of azinphos-methyl, exposure scenarios, caveats, parameters and absorbed doses (POEM)

Exposure Scenario*/Equipment	Estimate No	Container size	Spray volume (L/ha) Application dose (kg or L product/ha) Max. work rate (ha/day)	Daily absorbed dermal dose (mg/kg bw/day)			Daily inhaled dose (mg/kg bw/day)	Total absorbed dose (mg/kg bw/day)
				*M/L***	*A*	*M/L/A****	*A*****	*M/L/A*
1 & 7 **M/L/A in pome and stone fruit** ***Vehicle mounted (without cab) air assisted***	Estimate 1-1	25 L container-non specific design container	Spray volume 2000 L/ha (high volume) 1.96 kg 500 g/kg WP/ha 2.8 L 350 g/L SC/ha 20 ha/day	0.113	0.179	0.292	0.002	0.294
	Estimate 1-2	25 L wide neck container		0.023		0.202		0.204
	Estimate 1-3	5 L container non specific design		0.180		0.359		0.361
	Estimate 1-4	5 L wide neck container		0.009		0.188		0.190
	Estimate 1-5	25 L container-non specific design container	Spray volume 600 L/ha (low volume) 0.588 kg 500 g/kg WP/ha 0.84 L 350 g/L SC/ha 20 ha/day	0.038		0.217		0.219
	Estimate 1-6	25 L wide neck container		0.008		0.187		0.189
	Estimate 1-7	5 L container non specific design		0.06		0.239		0.241
	Estimate 1-8	5 L wide neck container		0.003		0.182		0.184
2 & 7 **Mixing/loading/ application as an overall spray in citrus** ***Vehicle mounted (without cab)***	Estimate 2-1	25 L container-non specific design container	Spray volume 5000 L/ha (high volume) 4.9 kg 500 g/kg WP/ha 7 L 350 g/L SC/ha 20 ha/day	0.225	0.179	0.404	0.002	0.406
	Estimate 2-2	25 L wide neck container		0.045		0.224		0.226
	Estimate 2-3	5 L container non specific design		0.420		0.599		0.601

air assisted	Estimate 2-4	5 L wide neck container		0.021		0.200		0.202
3 &7 **M/L/A in macadamias, grapes, lychees and kiwi fruit** ***Vehicle mounted (without cab) air assisted***	Estimate 3-1	25 L container-non specific design container	Spray volume 1000 L/ha (high volume) 0.98 kg 500 g/kg WP/ha 1.4 350 g/L SC/ha 15 ha/day	0.038	0.179	0.217	0.002	0.219
	Estimate 3-2	25 L wide neck container		0.008		0.187		0.189
	Estimate 3-3	5 L container non specific design		0.075		0.254		0.256
	Estimate 3-4	5 L wide neck container		0.004		0.183		0.185
	Estimate 3-5	25 L container-non specific design container	Spray volume 600 L/ha (low volume) 0.59 kg 500 g/kg WP/ha 0.84 L 350SC g/L/ha 15 ha/day	0.038		0.217		0.219
	Estimate 3-6	25 L wide neck container		0.008		0.187		0.189
	Estimate 3-7	5 L container non specific design		0.045		0.224		0.226
	Estimate 3-8	5 L wide neck container		0.002		0.181		0.183
4 & 7 **M/L/A in blueberries** ***Vehicle mounted (without cab) air assisted***	Estimate 4-1	20 L container-non specific design container	Spray volume 300 L/ha (low volume) 0.42 kg 350 g/kg WP/ha 0.735 L 200 g/L SC/ha 20 ha/day	0.021	0.179	0.200	0.002	0.202
	Estimate 4-2	20 L wide neck container		0.004		0.183		0.185
	Estimate 4-3	5 L container non specific design		0.026		0.205		0.207
	Estimate 4-4	5 L wide neck container		0.001		0.180		0.182

5 & 6 **M/L for vertical boom application in citrus** **M/L for concentrate or semi-concentrate sprayers**	Estimate 5-1	25 L container non specific design	Spray volume 10 000 L/ha (high volume) 9.8 kg 500 g/kg WP/ha 14 L 350 g/L SC /ha 20 ha/day	0.45	NA	NA	NA	NA
	Estimate 5-2	25 L wide neck container		0.090				
	Estimate 5-3	5 L container non specific design		0.840				
	Estimate 5-4	5L wide container		0.042				
8 **M/L/A in stone and pome fruit and grapes** ***Hand-held outdoors hydraulic nozzles⊗*** ***Vehicle mounted****) (not in Australia, knapsack)l***	Estimate 8-1a	25 L container-non specific design container	Spray volume 1500 L/ha (high volume) 2.94 kg 500 g/kg WP/ha 4.2 L 350 g/L SC/ha 1 ha/day (vehicle mounted) 0.27 ha/day (knapsack)	1.013	0.208	1.221	0.002	1.222
	Estimate 8-1b			0.038		0.246		0.247
	Estimate 8-2b			0.008		0.216		0.217
	Estimate 8-3b			0.015		0.223		0.225
	Estimate 8-4b			0.001		0.209		0.210

M/L-Mixing/loading; A-Application; M/L/A-Mixing/loading/Application; ai- active ingredient; NA-not applicable

* PPE for all study models is assumed to be one layer of clothing during application plus gloves during mixing/loading.

** Open mixing and loading.

*** POEM estimates inhalation exposure during application only.

**** number of transfer operations during mixing/loading into vehicle mounted spray tanks (including orchard sprayer) = total product applied per day ÷ container size

1.6.1.2 Measured exposure studies

A worker exposure study was submitted in June 2004 (Maasfeld W, 1999) and is summarised below.

Maasfeld W (1999): Determination of Exposure during Mixing/loading and Application of Gusathion WP 25 in High Crops. Study No: not stated. Lab: Bayer AG, Crop Protection Development, Institute for Metabolism Research and Residue Analysis, D-51368 Leverkusen, In Germany. Sponsor: Bayer Corporation. Study Duration: September 1998 to February, 1999. Report No. MR-121/99, Report Date, April 15, 1999.

Study and observations: The purpose of the study was to determine the extent of exposure in workers applying the product Gusathion WP 25 to high crops (ie. pome and stone fruits). The product contains the active ingredient (a.i.), azinphos-methyl at 250 g/kg. In Italy the product used was Gushathion M and in France, Gushathion XL (both WP formulations containing 250 g/kg azinphos-methyl).

The application was performed in high crops (apples, peach and pears) for a normal working day with tractors with enclosed cabins. Details of the type of cabins are not provided as to whether they were fitted with appropriate filtering devices to protect against chemicals. A total of eight farmers were monitored. Both the formulation used in Italy and France contains 250 g/kg azinphos-methyl. In Italy azinphos-methyl was applied to pome fruits at a rate of 1200 g a.i. per ha whereas in France the application rate is 759 g/ha. The field part of the study was performed at two farms in the region of Ravenna (Italy), at one farm in the region of Nimes (France) and two farms in the region of Tours (France) from September 28 to October 15, 1998. A total of eight workers (five farmers in Italy and three farmers in France) were involved in the study. All workers were farmers by profession and familiar with the equipment they were using and the operations being monitored.

Personal protective equipment: The farmers used the following protective equipment during mixing/loading: Protective gloves (rubber or nitrile), safety goggles and a half-mask with particle filter and/or gas filter. During the study the workers wore their usual work clothing. In Italy the workers wore overalls, jeans and shirt. In France the workers wore similar garments, however, two workers did not wear jeans beneath the overalls.

Biological monitoring: Biological monitoring was performed in the collected urine of the workers for six consecutive days. The urine collection started in the morning of the day before the application started (= day 0), thus a control sample was generated. Then urine was collected for the next five days. At the end of all collection periods the containers were forwarded to the Institute for analysis. Monitoring was throughout all the working days. For Italy, due to national regulations concerning organophosphates, about 4 hours of application was allowed whereas in France the monitoring was up to 9.5 hours. During this time an area of 3.5 to 9.3 ha was treated and between 2.75 and 6.25 kg of the active azinphos-methyl was applied corresponding to 11 to 25 kg product.

Dermal exposure: After the water soluble bags were put into the spray tank most workers rinsed their gloves by holding them into the stream of water still running into the spray tank. When the loading cycle was finished they took off the protective gloves and put them apart for the next loading cycle. When the worker had finished his last tasks (cleaning) and had taken off the protective gloves, they were rinsed with about 200 mL isopropanol for each

glove. Both gloves rinsings were collected in one bottle, which was then placed in a cool box for storage. Whenever a worker wished to wash his hands he received soap and water (total volume of 1000 mL) to do so. An aliquot from the hand wash water was taken as a sample and stored in the same way as other samples. On completion of the total monitoring period the worker removed his clothes and overalls (both sleeves, torso and both legs), Jeans, shirt (1st layer beneath) and undergarments (short sleeved T shirt and pants) were wrapped in aluminium foil, put into separate bags and stored in a cool box.

Inhalation exposure monitoring: Inhalation exposure sampling was performed by use of personal air sampling pumps throughout the day and sampling device collected at the end of working day. No differentiation was made between mixing/loading and application as every worker carried out these activities. Sampling was during the whole day and the same worker did mixing/loading and application.

Field recovery: Assessment of the stability of residues in the biological samples as well as in the dosimeters for dermal and inhalation exposure under field, storage and transit conditions was carried out at three sites (two in Italy and one in France). The stability of the metabolite in an acidic medium was assessed by fortifying urine from unexposed persons with methylsulfonylmethylbenzazimide (MSMB: a metabolite of azinphos-methyl). Field recovery and blank samples were prepared and treated in the same manner as the test samples. Concerning dermal dosimeters a defined volume of a standard solution of azinphos-methyl was applied to:

- pieces of cotton/polyester garment (representing the outer clothing layer),
- pieces of cotton (representing the undergarments), and
- hand wash water.

The same process of application of azinphos-methyl was carried out for the sampling tubes for inhalation. Hand wash water samples were fortified at levels of 10 µg and 100 µg/L and stored in the same way as the test samples.

Analytical methods: Azinphos-methyl and MSMB were quantified using liquid chromatography. The limit of quantitation of MSMB in urine was 0.2 µg/L, whereas azinphos-methyl was quantifiable at 10 µg/L (for both, garments residues dissolved in a methanol/water mixture after extraction by isopropanol and hand wash water) and 0.3 µg for the inhalational tubes. For biomonitoring calculation of the excreted amount as azinphos-methyl equivalent was performed as follows:

- Determination of the concentration of MSMB in the daily urine
- Conversion of the concentration to the absolute amount per day by multiplying with the volume of the daily urine
- Conversion to azinphos-methyl equivalents F = 1.326 = 317.3 g $mole^{-1}$/239.3 g $mole^{-1}$
- Urine was collected and MSMB measured for 5 days after exposure.

From the results of a dermal pharmacokinetic study with human volunteers, it was known that 90% of the total radioactivity excreted in urine occurred within 5 days (Selim, 1999). The percentage of a dermal applied dose (5 µg ai/cm^2 - 25 WP formulation) excreted via urine and faeces was 19.22% and 2.59% respectively. Thus 88.1% of the excreted azinphos-methyl is found in the urine (ie. 19.22/19.22+2.59). Analysis (radioactivity measurement) of the urine from the pharmacokinetic study with human volunteers has shown that MSMB accounts for

9.2% of the total metabolites in urine. As this compound was used as a specific marker for exposure to azinphos-methyl the conversion factor for the total residue in urine was 10.87 (100%/9.2%). The 'internal' (= absorbed) dose of µg azinphos-methyl was calculated as follows:

Internal dose = (Sum of azinphos-methyl equivalents in urine from day 1 to 5) x (100/90) (correction for collection efficiency) x (100/88.1) (correction for excretion via urine, as percentage of total excretion) x (100/9.2) (correction for percentage of MSMB)

Sum of azinphos-methyl equivalents day 1 to 5 x 13.71

The calculation of the corresponding external (= dermal) dose, assuming that by far the most of the internal dose results from dermal exposure was performed:

External dose = Sum of azinphos-methyl equivalents day 1 to 5 x 100/90 (correction for collection efficiency) x 100/19.22 (correction for excretion via urine) x 100/9.2 (correction for percentage of MSMB)

Sum of azinphos-methyl equivalents day 1 to 5 x 62.84

Findings: The conditions of the study with respect to worker ID, country, treated acreage, amount of the product used, kg active substance and the total monitoring time is provided in Table 7. The chemical was applied on pears, nectarines and peaches in Italy and in France it was applied on pears and apples.

Table 7: Actual study conditions

Worker ID (country)	Monitoring period	Area treated (ha)	Amount of product (kg)	Amount of a.i. (kg)
A (Italy)	10.08-15.11 (no break)	5	20	5
B (Italy)	10.05-14.50 (no break)	8.3	25	6.25
C (Italy)	8.35-14.01 (no break)	5	20	5
D (Italy)	8.32-13.30 (no break)	8.3	25	6.25
E (Italy)	14.10-18.31 (no break)	4	16	4
G (France)	8.59-18.20 (incl break for lunch)	7.9	16	4
H (France)	9.05-17.21 (incl break for lunch)	9.3	15	3.75
I (France)	9.10-15.30 (incl break for lunch)	3.5	11	2.75

The exposure results on garments are given in Table 8. The measured amounts are summed up to give total exposure on garments.

Table 8: Dermal exposure (only garments) during the study

Worker	Overalls			1st layer beneath		Undergarments		Total (µg)
	Sleeves (µg)	Torso (µg)	Legs (µg)	Jeans (µg)	Shirt/sweat (µg)	T-shirt (µg)	Pants (µg)	
A	3330	1900	3650	95	699	17	<10	9700
B	2010	1180	3710	79	166	18	<10	7170
C	1070	472	1950	29	36	<10	<10	3570
D	516	118	1810	68	57	<10	<10	2580

E	1110	492	1600	42	106	<10	<10	3360
G	4320	1300	16600	-	80	<125	72	22500
H	1380	1220	3420	-	44	<10	<10	6070
I	212	356	940	46	10	<10	<10	1570

Three workers provided additional garments:
Socks: A (10 µg), G (<10 µg), H (186 µg)
Cap: G (33 µg), H (55 µg)

The results of hand washings and gloves rinsings are given in Table 9.

Table 9: Results of hand washings and gloves rinsings

Worker ID	Hand washings (µg)	Gloves rinsings (µg)
A	60	262
B	183	2450
C	56	261
D	47	1610
E	<10	220
G	921	660
H	59	1690
I	66	235

The exposure by inhalation was not measured separately for loading and application. Therefore, the results of the inhalation exposure were referred to as 'potential inhalation exposure' as the workers used filtering masks during mixing/loading. As the pumps were operated with a nominal flow rate of 2 L/min, the potential inhalation exposure is corrected for an average breathing rate of 29 L/min.. The results are presented in Table 10.

Table 10: Potential inhalation exposure

Worker ID	Concentration in inhalation tubes (µg)	Potential inhalation exposure (µg)
A	3.1	45
B	9.4	136
C	<0.3	2.2
D	1.05	15
E	<0.3	2.2
G	7.4	107
H	<0.3	2.2
I	<0.3	2.2

The results of the biomonitoring giving the excreted amount of MSMB per day, azinphos-methyl equivalents (Azm-e), internal dose and corresponding external dose are given in Table 11.

Table 11: Results of the biomonitoring (urine)

Worker ID	Amount of MSMB excreted at					Sum excreted		Int. dose (µg)	Ext. dose (µg)
	Day 1 (µg)	Day 2 (µg)	Day 3 (µg)	Day 4 (µg)	Day 5 (µg)	MSMB (µg)	Aam-e (µg)		
A	0.24	0.69	0.35	0.17*	0.16*	1.6	2.1	29	134

B	1.33	2.31	1.56	1.00	0.78	7.0	9.3	127	582
C	0.59	0.65	0.60	0.29*	0.27*	2.4	3.2	44	200
D	0.35	0.57	0.68	0.23	0.13*	2.0	2.6	35	163
E	0.14*	0.37	0.21*	0.22*	0.29*	1.2	1.6	22	102
G	0.91	2.71	1.59	1.37	0.86	7.4	9.9	135	620
H	0.38	0.44	0.65	0.61	0.36	2.4	3.2	44	203
I	0.11*	0.39	0.86	0.52	0.44	2.3	3.1	42	193

- Cconcentration of MSMB in urine was <LOQ (limit of quantitation) and further calculations were performed with half amount of LOQ (which means 0.1 x volume of urine for that day)

Field and laboratory recoveries were comparable suggesting stability of the analyte was acceptable. A slight difference was observed with respect to the recoveries on garments. Covered undergarments had better recoveries than uncovered outer garments (mean 78% vs. 60%). The results presented show the exposure (kg a.i., acres treated, time duration etc.). For a better comparison between workers and exposure to azinphos-methyl, the exposure data on the passive dosimetry was standardised to the amount of a.i. handled and is presented in Table 12.

Table 12: Standardised dermal and inhalation exposure in mg/kg a.i. handled

Worker ID	Outer clothing mg/kg a.i.	1st layer beneath mg/kg a.i.	Undergarments mg/kg a.i.	Gloves rinsings mg/kg a.i.	Hand washings mg/kg a.i.	Potential inhalation mg/kg a.i.
A	1.77	0.159	0.004*	0.052	0.012	0.0090
B	1.10	0.039	0.004*	0.392	0.029	0.0218
C	0.70	0.013	0.002*	0.052	0.011	0.0004*
D	0.39	0.020	0.002*	0.258	0.008	0.0026
E	0.80	0.037	0.003*	0.055	0.001*	0.0006*
G	5.55	0.020	0.049	0.165	0.230	0.0268
H	1.60	0.012	0.003*	0.453	0.016*	0.0006*
I	0.55	0.020	0.004*	0.085	0.024*	0.0008*

- value was < LOQ (at least one, if the exposure comprises more than one value)

The results show that the exposure is relatively low. The low concentration of azinphos-methyl found on clothing, gloves and hand washings may be due to the presentation of the product and the mode of application. Therefore dermal exposure seems to be low. The WP formulation was packed in water-soluble bags and the application was performed with enclosed cabs (enclosed cabs used were air condition cabs fitted with a pesticide filtering system). Potential inhalation exposure was also quite low.

DISCUSSION

The results of the biomonitoring showed that the internal dose of six out of eight workers are in a very narrow range of a factor of 2 (ie. 22 µg – 44 µg), and only two workers (B and G) were at around 130 µg. Worker G also had the highest exposure with the passive dosimetry samples. A comparison of the dermal exposure on garments with the estimated external dermal dose on skin shows that less than 3% of the potential exposure reached the skin (620 µg vs. 22,500 µg). The percentage of penetration may be even less as only the garments are taken into account for this comparison omitting further possible dermal exposure (e.g. hands, face) which are difficult to estimate.

With worker B the situation was different. Although MSMB was detected in his urine over the whole period, this metabolite was already detected (and confirmed) in his urine the day before he started the application. As the worker had no other contact to azinphos-methyl this effect may possibly be due to dietary exposure. The time course shows that excretion is similar to the excretion of the other workers but with an offset (background) due to the already available amount at day 0. Therefore, the calculated internal dose possibly overestimates the actual dose received by spraying azinphos-methyl.

The results showed that the individual internal doses were roughly about 0.5 µg/kg bw. Even the values of workers B and G were only a factor of three higher and the internal dose of B is only partly related to spraying of azinphos-methyl.

CONCLUSION

The data indicated that even when spraying operations were conducted in two different locations the exposure of operators to azinphos-methyl was low when the product was packed in water-soluble bags and the application performed using tractors with enclosed cabins. All workers wore gloves and respiratory gear during mixing/loading.

1.6.2 Post-application exposure

Post-application exposure can be anticipated when workers re-enter areas of treated crops to check pest kills, irrigate, weed, prune, thin or harvest crops. The type of activity, timing and frequency of re-entry activities is dependent on the crop. Potential for exposure will be determined by factors such as the physico-chemical properties of the active, the amount of active applied, the interval between spraying and re-entry, the nature and duration of the particular re-entry activity, the density of foliage and spacing of crops and environmental conditions that affect the breakdown of residues. Harvesting of agricultural crops may be either a mechanical or manual activity. Mechanical harvesting is not expected to be of OHS concern as no worker exposure is anticipated, however, if it does occur, worker exposure is expected to be minimal. Manual harvesting would result in exposure, and would depend on the quantity of residues present at the time of harvest. Chemical-specific and surrogate studies with measured post-application exposure and dislodgeable foliar residue data were provided. Only studies, which are relevant to the assessment of re-entry exposures, are described below. Other post-application data are included as an appendix.

1.6.2.1 Measured post-application exposure studies

McCurdy AS, Hansen ME, Weisskopf CP, Lopez, Schneider F, Spencer J, Sanborn JR, Kreiger RI, Wilson BW, Goldsmith DF, Schenker MB, (1994) Assessment of azinphosmethyl exposure in California peach harvest workers, Archives of Environmental Health, July/August, vol 94, 4, 289-296.

The above study was conducted on 20 peach orchard workers who entered the orchards 30 days after the crops were sprayed with azinphos-methyl at a rate of 1.5 lb/acre (1.7 kg/ha). Workers spent a total of 6 weeks in the peach orchards. The most intense work exposures and monitoring activities (propping, thinning and harvesting) occurred on days 1, 2 and 3 of the initial 21 day period. The remaining days were spent in the orchard carrying out similar activities. Of the 20 workers, 10 worked as thinners, 6 worked as proppers, 3 worked as irrigators and 1 as a supervisor on the 1st day. On the 2nd and 3rd day, all worked as harvesters.

Workers spent 8 hours in the orchards each day. Twelve study personnel who did not perform agricultural work served as controls.

The 10 workers selected to work in a shift wore long-sleeved 100% cotton-knit undershirts under buttoned-up long-sleeved shirts and knee-length cotton-acrylic blend athletic socks. The PPE, wipe samples taken from face, neck and hands, and hand wash samples were all sent to the laboratory for analysis of residues. Foliage samples were taken for measurement of DFR levels of azinphos-methyl in three to four locations within each field on all 3 exposure days. Plasma and erythrocyte ChE levels were estimated for all workers six days prior to exposure and on Day 3 of exposure. Urine samples were collected for estimation of dimethylphosphate, dimethylthiophosphate and dimethyldithiophosphate 6 days pre-exposure, on days 1, 2, 3 and on day 44.

Daily monitoring for 3 days was carried out for azinphos-methyl and the metabolite (oxon) residues on the shirts, on the hands, and in the hand washes for all groups. Harvesters exhibited the highest levels. Erythrocyte ChE levels decreased by 7% over the initial 3-day period and by 19% over the 6 week season while plasma ChE levels decreased by 9% over the initial 3 day period of exposure when compared with the baseline median value for all agricultural workers. All agricultural workers showed steadily increasing levels of urinary azinphos-methyl metabolites throughout the period of exposure. DFRs ranged from 0.32 – 0.96 $\mu g/cm^2$ during the 3-day exposure period.

Spencer JR, Hernandez BZ, Schneider FA, Sanborn JR, Margetich SS, Begum S, Wilson BW (1993) Dermal and urinary monitoring of peach and apple harvesters exposed to organophosphate residues in Sutter, Stanislaus and Madera Counties, HS-1577.

Study and observations: Peach and apple harvesters who were exposed to azinphos-methyl (Guthion 50 WP) treated crops at 5 different sites were monitored in 1989 and 1990 in Madera, Sutter and Stranislaus counties in California. The workers were all male and consisted primarily of pickers, but some members performed other tasks as well such as sorting, fruit hauling, supervising or irrigating. In Sutter county, on the first day of the study, workers performed thinning and propping tasks (peaches only). The Granny Smith apple trees were supported by cross-wires to form a hedge row in order to permit easy access to the apples. Peaches were treated once each season while apples were treated five times each season.

The typical work attire consisted of 100% cotton, long-sleeved buttoned white shirt worn under a regular cotton work shirt, long pants, tennis shoes, socks and a baseball cap. The shirts covered the hip region and were tucked into the workers' trousers. All apple harvesters were required to wear nylon knit gloves while picking to maintain the fruits "bloom"; ie, their natural waxy, powdery coating.

All hand harvesters used ladders to reach the fruit. Work days at all sites consisted of 8 hours with the exception of one site where apple harvesters worked 10 hours each day. Peach harvesters reached into the tree to pick the fruit, which sometimes caused the worker to be immersed in the foliage from head to knee. Apple harvesters came into contact with the treated foliage primarily via the hands and arms. They did not have extensive full-body contact with the foliage because the apples were easily accessible in the hedge rowed trees. Additionally, the foliage was sparser than that in the peach orchards. Harvesters did not thin fruit during the harvest season.

The leaves were sampled on each study day for dislodgeable foliar residues (DFR). Samples were taken from 10 trees in each of 3-5 locations within each orchard, depending on the size of the orchard, at a height of 5-6 feet. In addition to the DFR samples taken on study days from the above described five locations, six orchards (in addition to the five locations already described) in Sutter County were also sampled several times in the first week post-application, then weekly for 7-11 weeks to allow characterisation of azinphos-methyl decay and estimation of half-life. Dermal exposure was measured by clothing dosimeters that were worn by each worker for the entire workday. At the end of the monitoring period, clothing dosimeters were stored separately.

Hand residue samples were obtained from the peach harvesters by wipes followed by a wash. The apple harvesters had their nylon-knit harvester gloves collected and stored separately. Their hand residue sample consisted of two sequential skin wipes of ungloved hands. Face and neck residues were obtained by wiping these regions with pre-moistened disposable wipes. All dermal exposure samples were frozen until chemical extraction was performed. Urine samples were analysed for dimethylphosphate metabolites and creatinine.

Findings: The results following Guthion 50WP applications are presented in Table 13.

Table 13: Dislodgeable foliar residues and dermal exposure values following azinphos-methyl application in apple and peach orchards

Crop (County,year)	Days post-application (task)	Application rate	Mean dermal exposure (mg/8 h day)	Mean UPE (metabolite in urine) (µg)[e]	Dislodgeable foliar residues (µg/cm^2)	Transfer Coefficient (cm^2/hr)[a]
Peaches (Sutter, 1989)	31(Propping) 31(Thinning) 32((Picking) 33 (Picking)	1.68 kg ai/ha	0.70 13.00 15.62 15.47	0.56 1.92 3.00 3.74	0.50 0.49 0.66 0.62	175 3316 3038[b]
Peaches (Sutter, 1990)	52 (Picking) 53 (Picking)	1.68 kg ai/ha	12.02 14.04	1.06 1.86	0.36 0.61	3526[b]
Peaches (Stanislaus, 1989)	34 (Picking) 35 (Picking) 36 (Picking)	0.91 kg ai/ha	0.44 1.25 4.30	14.17 9.27 16.03	0.009 0.011 0.07	9332[b] -
Apples (Madera, 1989)	42 (Picking) 43 (Picking) 44 (Picking)	1.96 [1.68 – 2.24] kg ai/ha	1.84[c] 2.02 1.66	0.89 0.71 1.32	0.59 0.70 0.58	359[b]
Apples (Madera 1990)	23 (Picking) 24 (Picking) 36 (Picking)	2.24 ai/ha	1.51[d] 6.52[d] 6.46[d]	10.15 5.86 8.80	0.32 0.55 0.79	872[b]

**half-life was reported to be 18.5-43 days.
a calculated using study parameters (ie. TC=Dermal exposure/DFR).
b averaged value for harvesting
c not measured, mean of days 2 & 3 exposure)
d exposure for 10 hours
e dimethyl phosphate metabolite in urine

The above table outlines exposure data for harvesters (peaches and apples) and thinners and proppers (peaches). Exposure to the torso and arms (shirt region) appeared to be the largest

component of dermal exposure and accounted for 77±12% of the total. Hand exposure accounted for 30 ± 8.8%, whereas face/neck residues consisted of no more than 4%. The transfer coefficient (TC) was calculated using the dermal exposure and DFR values from the study and were in the range from 175-9332 cm^2/hr. The TCs for picking peaches were three times greater in Stanislaus county relative to Sutter county. Although the prevailing weather conditions were not described for either county the author stated that the values were skewed by the extremely low DFR values (0.009-0.07 $\mu g/cm^2$). The calculated half-life of 18.5-43 days for azinphos-methyl foliar residues was similar to the half-life estimates in other studies. There was no relationship between dermal absorption and excreted urinary metabolite, as apple harvesters wearing gloves had more urinary metabolites than the ungloved peach harvesters. The author states that occlusion of the hand may have increased the availability of the residues. Therefore estimating hand exposures using only those residues reaching the hand beneath the glove may not account for all the residues available for dermal absorption.

Comment

The results from this study were considered suitable for the assessment of post-application exposure for workers entering orchards to harvest peaches and apples. In the study, the application rates varied between 0.91 to 1.68 kg ai/ha for peaches, and 1.96 to 2.24 kg ai/ha for apples. For Australian crops (apples and peaches), the maximum application rate is 0.98 kg ai/ha. However, it should be noted that the head and thigh regions were not monitored in the study. Caps/hoods and long underwear have been included in previous DFR monitoring studies, but they were excluded from this study because of the risk of heat stress for the harvesters.

Tinsley IJ, Jenkins JJ, Evaluation of Airborne and Dislodgeable Residue Levels of Azinphos-methyl and Azinmethyl-oxon following application of Guthion 35 WP to apples in Hood River, Oregon, Test Facility Study Number, PIAP 1001-92, Bayer Corp. Report Number, 108566, 12 May, 1994.

Study and observations: The purpose of the study was to determine airborne and dislodgeable residues of azinphos-methyl and azinphos-methyl-oxon following application of Guthion 35 WP to apples. The study was conducted according to the US EPA's Good Laboratory Practice Standards, 40 CFR 160. Guthion 35 WP was applied as per the label rate of 1 lb/acre in 200 gals of water (1.121 kg ai/ha in 909 L/ha) using an airblast sprayer. The treated plot was subdivided into three subplots. For codling moth control, 4 applications were made over 3 months. The second application was 21 days after the first application. Sampling started with the second application (on 21 day). Leaf samples were collected from apple foliage and herbacious ground cover in between applications to determine the DFR. Three apple DFR samples were collected before the second application of Guthion. For the second and subsequent applications, post-application samples were collected as soon as the spray had dried, at 4 and 12 hours post application and at 1, 2, 3, 5, 7, 10, 14 and 21 days post-application. In addition to these intervals, 28 and 35 days post-application samples after the final Guthion application were also collected. Three separate DFR samples (one from each subplot) were collected at each sampling interval. Each DFR sample consisted of a total 50 leaf discs collected from five different trees (10 leaf discs from each tree). For herbacious ground cover DFR, 2 samples were collected in each of the subplots. Six control ground cover DFR samples were collected before the second application of Guthion. For the second and subsequent applications, post-application samples were be collected as soon as the spray had dried, and at 1, 2, 3, 5, 7, 10, 14 and 21 days post-application. In addition to these intervals, 28

and 35 days post-application samples after the final Guthion application were also collected**.** Calculated leaf DFR recoveries were 96.69% $\pm$ 16.8% for azinphos-methyl. The estimated half-life for azinphos-methyl was 21 days. Air sampling was carried out on the days (0, 1, 2, 3, 5, 7, 10, 14 and 21) for about 2 hours during post-application. In addition to these intervals, 28 and 35 days post-application samples after the final Guthion application were also collected. These results are not discussed in this report as they are not relevant for DFR studies. Climate parameters such as relative humidity, solar radiation, wind direction, wind speed and temperature were monitored.

Findings: The results following Guthion 35 WP applications are presented in Table 14.

Table 14: Dislodgeable foliar residues following azinphos-methyl application

Days post application	Dislodgeable foliar residues ($\mu g/cm^2$)*
1	1.40
2	1.35
3	1.42
5	1.32
7	1.42
10	1.09
14	1.03
21	0.69
28	0.62
35	0.49

Maximum DFR value for that day sample after 4th application

The results from this study were considered suitable for the estimation of post-application exposure of workers required to re-enter orchards for various tasks, eg harvesting apples which were treated with azinphos-methyl using airblast spray. The formulation type used in the study was the WP at a rate of 1.46 kg ai/ha, which is higher than the Australian rate of 0.98 kg ai/ha WP.

Marien K, Dislodgeable Foliar Residue Levels of Azinphos-methyl and Azinphos-methyl-oxon on an apple orchard in the lower Yakima Valley of Washington State, Bayer Corp. Study Number, 93E003, Bayer Corp. Report Number, 106719, 14 June, 1996.

Study and observations: In this study, Guthion 50 WP was applied at a rate of 1 lb/acre in 100 gals of water (1.21 kg/ha in 455 L/ha) using an airblast sprayer with four applications carried out from June to September. Azinphos-methyl was applied on June 1, 21, July 12, August 4 and September14. [Please confirm dates.] Prior to the initial application, control samples were collected. Samples were collected and analysed for residue levels once the spray was dry and at 4 and 12 hours after application. Further samples were collected at 1, 2, 3, 5, 7, 10, 14 and 21 days after application and, in addition, 28 days after application and at harvest (37 days). Local weather conditions were considered when determining the residue levels. The month of June had a rainfall of 0.72 inches, July had 0.58 inches and the month of August had a rainfall of only 0.17 inches. The summer was cool and moist, with the month of August being the warmest. The half-life for azinphos-methyl when applied to apple orchards was approximately 14 days.

The treated orchard was divided into three distinct sub-plots, with each sub-plot providing a separate dislodgeable residue composite sample at each time point. Each sub-plot was buffered by at least two rows from the perimeter, and the sub-plots were separated from each other by a two-tree buffer. A sub-plot consisted of seven rows with each row containing five trees. For each application, the sub-plot provided composite samples for seven time intervals before a sample was taken from a previously sampled tree. As a result, a tree was not sampled more than twice for each application. Each composite sample consisted of 5 trees sampled diagonally within the sub-plot, with each tree providing 10 leaf-punch sub-samples collected underneath and outside of the canopy at ground height (total 50 leaf-punch samples for each DFR values).

Findings: The results following Guthion 35 WP applications are presented in Table 15

Table 15: Dislodgeable foliar residues following azinphos-methyl application

Days post application	Dislodgeable foliar residues ($\mu g/cm^2$)
1	3.64
2	3.84
3	3.41
5	2.74
7	2.52
10	2.41
15	1.73
21	1.09
28	1.12
37	0.71

Equal amounts azinphos-methyl were applied for each application and similar amounts of residue were found on the leaves after each application (ranging from 3.1 $\pm$ 0.23 to 4.5 $\pm$ 0.39) with the exception of the third application, which had the two initial high readings (4.9 $\pm$ 0.62 & 4.8 $\pm$ 0.26 respectively). The decay constants ranged from 0.08 to 0.05 resulting in a DFR half-life that appeared to increase with each application, ie. from 9 to 14 days. In the study the month of August had the two longest half-life values (13 and 14 days) which may be due to the minimal rainfall in the August.

The above table outlines DFR data for workers who may be required to re-enter orchards after spraying, in between applications and at regular intervals post-spraying. The results from this study were considered suitable for the estimation of post-application exposure of workers required to re-enter orchards for various tasks. The formulation type used in the study was the WP at a rate of 1.4 kg ai/ha, which is higher than the rate used in Australia; ie. 0.98 kg ai/ha.

Ellisor GK (1998) Evaluation of foliar residues of Guthion on apples, Bayer Corp. Study Number 94P002, Bayer Corp. Report Number 107249, Bayer Corp., Agriculture Division, Research and Development Department, Kansas City, Missouri.

Study and observations: The purpose of this study was to assess the potential risk to workers who are in contact with Guthion-treated foliage during post-application activities. Four applications of Guthion 50 WP at the rate of 0.56-1.12 kg ai/ha were carried out in apple orchards at two trial locations (New York and California) with 14 days between treatments. Treatment plots in both trial locations consisted of sufficient apple trees to provide the

necessary samples, which totalled 420 apple trees in the first location and 1400 apple trees in the second location. The apples in New York were of Ida-Red and Delicious variety and in California of Granny Smith and Fuji variety. DFR samples were collected at the following intervals: pre-treatment, immediately after the spray had dried (IASD –approximately 2 hrs), 24 hours, 2, 3, 4, 5, 6, 7, 9, 11 and 14 days post-application.

Samples were also collected 21, 28 and 35 days after the fourth (final) application in each trial. The pre-treatment samples collected prior to the first application in each trial served as controls. Each DFR sample consisted of 48 leaf punch samples (from 6 trees), 3 DFR samples were collected at each interval, one from each subplot. Summary of azinphos-methyl dislodgeable residue data for all 4 applications from both trials were provided in the study results. Results are provided in Table 16.

Table 16: Dislodgeable foliar residues following azinphos-methyl application

Sampling interval	California Trial	New York Trial
Appl 1		
Pre-appl	<0.002	<0.003
2 hrs	2.08	1.75
Day 1	2.04	1.56
Day 2	1.70	0.457
Day 3	1.75	0.430
Day 4	1.37	0.443
Day 5	1.05	0.406
Day 6	0.74	0.325
Day 7	0.63	0.289
Day 9	0.76	0.267
Day 11	0.81	0.205
Day 14	0.67	0.180
Appl 2		
2 hrs	1.47	1.80
Day 1	1.48	1.57
Day 2	1.48	1.60
Day 3	1.72	1.43
Day 4	2.03	1.36
Day 5	1.66	1.28
Day 6	1.30	1.23
Day 7	1.18	1.15
Day 9	1.44	0.97
Day 11	1.50	0.91
Day 14	1.35	0.57
Appl 3		
2 hrs	1.35	1.96
Day 1	1.24	2.02
Day 2	1.38	1.26
Day 3	1.45	1.02
Day 4	1.41	1.05
Day 5	1.62	0.91
Day 6	1.02	0.45

Day 7	1.12	0.40
Day 9	1.26	0.22
Day 11	1.63	0.25
Day 14	1.58	0.28
Appl 4		
2 hrs	1.58	1.68
Day 1	1.15	1.34
Day 2	1.62	0.76
Day 3	1.79	0.74
Day 4	1.64	0.49
Day 5	1.27	0.51
Day 6	1.50	0.41
Day 7	1.46	0.48
Day 9	1.94	0.36
Day 11	1.82	0.38
Day 14	1.55	0.27
Day 21	1.50	0.16
Day 28	1.15	0.09
Day 35	1.09	0.04

The above table summarises the DFR data. Four applications were made in total and most applications were made on consecutive days. The California part of the study was conducted from mid-May to late-July of 1994 and the weather was extremely dry, warm to hot, humid with no significant rainfall. There were only 3 slight rainfall events, first of 0.3 inch (7.6 mm) on day five after the first azinphos-methyl application, followed by 0.1 inch (2.5 mm) on day 6 and another 0.1 inch on day 7. In the New York trail, conducted from early June to mid-August of 1995, the weather was wet, mild to warm, humid with several major rainfall events. Significant rainfall occurred after each of the four, test product application, with the largest rainfall occurring after Application 3 and 4. After the 24-hour (Day 1) sampling interval following the first application, 1.33 inches (33.8 mm) of rain fell in this trial. It is apparent that rainfall in the New York trial contributed to an appreciable reduction in foliar residues relative to that in the Californian trial. The DFR data from California estimated a half-life ranging from 62 to 83 days (ie. 8.8 to 11.8 weeks) whereas in New York the estimate ranged from 4.0-9.4 days.

The results from this study were considered suitable for the estimation of post-application exposure of workers required to re-enter orchards for various tasks, the formulation type used in the study was the WP at a rate of 0.56 –1.12 kg ai/ha, which is comparable to the rate used in Australia; ie. 0.98 kg ai/ha.

Lamb DW (1980) Early studies with azinphos-methyl to determine re-entry times for citrus pickers. Mobay Chemical Corporation, Stanley Research Centre, Stilwell, Kansas, USA. In "Field worker Exposure During Pesticide Application: Studies in Environmental Science No. 7". (eds: Tordoir WF and Van Heemstra-Liquen. Elsevier Publishing Co. NY, 121-127.

Study and observations: This study monitored plasma and red blood cell (RBC) ChE activities in a group of citrus pickers in California, USA, together with foliar and patch residue analyses to determine a re-entry interval for azinphos-methyl. The main study consisted of 3 separate monitoring trials. The workers involved in the study were 21 year of age or older and had no

recent exposure to and ChE inhibiting pesticides. Trial blocks were sprayed at rates of 370 mg/m^2 (azinphos-methyl WP), 250 mg/m^2 (azinphos-methyl SC), and 417 mg/m^2 (azinphos-methyl SC). Fifteen workers re-entered the blocks sprayed at 370 mg/m^2 (WP formulation), whilst 19 workers re-entered the blocks, which had azinphos-methyl SC applied at 250 and 417 mg/m^2 (sex, age and body weight range of the workers unspecified).

The workers involved in the 3 trials entered the treated fields at 7 days post spray. The area to be monitored was divided into 5 blocks for the 3 trials (2nd and the third block for trial 2 and block no 4 and 5 for the trial 3). Although, it was stated that the workers in blocks sprayed at 417 mg/m^2 worked only half-days due to limited availability of citrus for harvesting and cooler weather conditions. Individual plasma and RBC ChE values were determined prior to re-entry, and on various occasions. The method used for plasma and RBC ChE assay was the "pH stat assay for human blood Cholinesterase" recommended by the US Public Health Service (time and method of blood collection were not specified). Only the workers whose ChE levels were within the normal range participated in the study.

Dermal exposure was determined from patches placed on the arms and heads of workers. Residues on gloves were estimated, and personal air monitoring carried out. Residues on gloves, arm and head patches, and the concentrate in the air appeared to be higher in the first study than that determined in the second and third studies. The exposure samples were taken only for 60 minutes. As whole body exposure was not measured in the trials, these values for dermal exposures are not considered in this assessment. Dislodgeable residues were calculated for leaves and fruit.

Findings: There was considerable variability in the results but with little or no indication of a decline in residue concentration up to approximately 30 days after application in leaves and up to 60 days in fruit. Therefore a half-life for the DFR could not be reliably determined. The median DFR in trial 1 was 0.73 μg/cm^2 for the leaves (between 16-32 days) and 0.15 μg/cm^2 for the fruit (between 16 and 32 days). In trial 2, the foliar DFR was 0.35 μg/cm^2 between day 16 and 24 and for the fruit it was 0.07 μg/cm^2 between day 8 and 16. In the 3rd trial the median DFR for leaves and fruit was 0.84 and 0.24 μg/cm^2 respectively (duration not indicated). Sixty minute samples of the gloves had an exposure value (median) of 52.6 μg/cm^2 in trial 1, 20.4 μg/cm^2 in trial 2 and 46.1 μg/cm^2 in trial 3.

The azinphos-methyl concentrations in the air surrounding the workers (60 minute sample) on day 7 post-spray at application rate of 370, 250 and 417 mg/m^2 were 0.14, 0.08 and 0.05 μg/L, respectively (time and the methods of sample collection and analysis unspecified). Plasma and RBC ChE data established for the workers in different trials are presented in Table 17. Greater than 20% depressions in plasma ChE activity were seen in workers exposed to 370 mg of azinphos-methyl WP/m^3 at the 8 and 10th days. Because of this finding, further testing of workers involved in this trial was not continued. No inhibition of plasma ChE was noted in any of the workers exposed to azinphos-methyl SC at the rate of 250 mg/m^2 (measured at the 11, 14, 18 and 21 days). However, the depressions in RBC ChE activity in workers exposed to azinphos-methyl SC at the rate of 250 mg/m^3 on the 14, 18 and 21 days exceeded 20%. The depressions in plasma and RBC ChE activities seem to be related to azinphos-methyl exposure and were considered to be toxicologically significant. RBC ChE activity inhibition seen in trials 2 appeared to be slightly more pronounced (22-40%) than the RBC ChE inhibition noted in trial 1 (12-14%). According to the data, it seems that the RBC ChE inhibition occurred more slowly and later relative to plasma ChE inhibition. The lack of ChE

activity inhibition in blocks 4 and 5 workers may perhaps be due to low concentration of azinphos-methyl in the spray mix (and the shorter exposure period in block 4 and 5).

Table 17: Mean plasma and RBC ChE values (percent of pre-exposure) in workers exposed to azinphos-methyl

Sampling day	Trial 1		Trial 2		Trial 3	
	Plasma	RBC	Plasma	RBC	Plasma	RBC
8	72 (28%)	86			104	
10	60 (40%)	88				
11			119	100	101	104
14			98	78 (22%)	110	96
16					110	104
18			105	72 (28%)		
21			87	60 (40%)		

Values in parentheses represent percent ChE activity depression; Trial 1 = Block sprayed with azinphos-methyl WP at 370 mg/m^2; Trials 2 & 3 = Blocks sprayed with azinphos-methyl SC at 250 mg/m^2; Trials 4 & 5 = Blocks sprayed with azinphos-methyl SC at 417 mg/m^2.

Conclusions: Under the conditions of the study, greater than 20% inhibition in plasma ChE activity was seen in workers exposed to azinphos-methyl WP at the 8 and 10th days after application. Greater than 20% inhibition in RBC ChE activity was seen in workers exposed to azinphos-methyl SC at 14, 18 and 21 days after application. The depressions in plasma and RBC ChE activities appeared to be related to the amount of azinphos-methyl applied and were considered to be toxicologically significant. RBC ChE inhibition appeared to have occurred later relative to plasma ChE inhibition. Since workers wore overalls and gloves it was not expected that there would be a relationship between RBC ChE inhibition and DFR values. This was observed. The amount of azinphos-methyl found on gloves appeared to correlate with the rate of application. The RBC ChE and DFR exposure was more for WP formulation (trial 3) than SC formulation.

Davis JE, Stevens ER & Staiff DC (1983) Potential exposure of apple thinners to azinphos-methyl and comparison of two methods for assessment of hand exposure. Bull. Environ. Contam. 31, 631-638.

This study was conducted to determine potential dermal and respiratory exposures that occur while thinning apples at various times after application of azinphos-methyl and to compare hand exposures assessed using hand rinses and two types of absorbent gloves.

Workers were monitored 1, 2, 6 and 9 days after airblast application of a 50% WP formulation of azinphos-methyl, with the spray containing 3 g/L which was applied at 750 L/ha. Exposure was monitored using multi-layered gauze pads, ethanol hand rinses, absorbent gloves (cotton and nylon) and personal air monitoring pumps. Apart from the use of gloves, the workers did not use any other PPE. Gauze pads were attached to the forearms. As only forearms exposures were measured by gauze pads, these exposure values are not considered in this assessment. Hand exposures obtained by rinsing with ethanol were significantly lower than those obtained by using either type of gloves (2 and 9 days exposure). When mean exposures were compared, those obtained by using cotton and nylon gloves were approximately 5 and 4 times larger, respectively, than those obtained by using hand rinses. Exposure periods for the workers were approximately 2 hours. DFRs were estimated from the leaf punch samples. Each of the sample consisted of 30 punches, 5 from each of 6 trees. Details of DFR estimation are not provided. The DFR results are presented in Table 18.

Table 18: Dislodgeable foliar residuesand hand exposure with ethanol rinses or glovesfollowing azinphos-methyl application

Re-entry interval (days post application)	Dislodgeable foliar residues (μg/cm^2)**	Ethanol rinses μg/hour (no of replicates)	Cotton gloves μg/hour (no of replicates)	Nylon gloves μg/hour (no of replicates)
1	1.7	-	-	-
2	1.9	1800 ± 300 (6)	8500 ± 700 (5)	7000 ± 2000 (5)
6	1.4	-	-	-
9	1.4	960 ± 340 (6)	5200 ± 2200 (11)	3900 ± 900 (11)

As the total body exposure was not measured in this study, only DFR values will be considered in this assessment.

Waggoner TB, Olson TJ & Lamb DW (1970a) Determination of the hazards to workers picking citrus treated with guthion spray concentrate formulation (3.75 lbs. AI/acre). Study no: not stated, Research Department, Chemagro Corporation. Sponsor: Bayer AG. Study duration: not stated, Report no. 28428. Report date: November 3, 1970.

Pre GLP, non-quality assured study. No test guidelines were cited.

Study and observations: In this study, plasma and erythrocyte (RBC) ChE levels in citrus pickers working in a grove of oranges sprayed with guthion SC (azinphos-methyl) in California were investigated. Nineteen workers (age: 21 years or older, 12 males and 7 females, bw: unspecified) who had no recent exposure to any ChE inhibiting agents were chosen for the study. Baseline plasma and RBC ChE activities of each of them were established using data from 3 determinations carried out at 7, 5 and 3 days before commencement of the study. It was stated that during this time they were not allowed to work in orchards, which had been sprayed with any ChE inhibiting pesticides. The orange grove used in the present study had not been sprayed with ChE inhibiting pesticides for at least 30 days prior to the test. This grove was subdivided into two blocks (sizes unspecified) and subsequently sprayed with azinphos-methyl (purity, source and batch not specified) at 4.2 kg ai/ha, one week apart. For exposure monitoring two workers were selected to wear new cotton gloves, two absorbent pads (one on the forearm and one on the head) and an air-sampling device to monitor inhalation exposure. The remaining 17 workers wore their own gloves while harvesting the fruit. For DFR, four average size of leaves were collected from 6 trees for each sample comprising of a representative number from the interior and exterior portion of the tree. Five pounds of the fruit were also collected at the same time in the same manner as the leaves.

Findings: Individual pre-exposure ChE activities appeared variable with about 10-50% variability in plasma ChE and about 10-20% variability in RBC ChE data. At the shortest re-entry day (day 7 after spraying), 2 males/19 showed ≥20% plasma ChE inhibition compared to their respective pre-exposure averages after 3-4 h exposure. At the first re-entry on day 11

after spraying, 4/19 workers had an indication of a depression of plasma ChE levels (3 male workers, and 1 female worker) in comparison to their pre-exposure data. However, due to wide individual variability in pre-exposure plasma ChE data observed, the changes noted above could not be attributed to azinphos-methyl exposure with any certainty.

Post-exposure RBC ChE inhibition was variable (about 3-10%) and the inhibition was not significant in 17/19 individuals at any of the re-entry days. RBC ChE was depressed by about 27% in one male worker at re-entry day 7, and by about 26% in a female worker at reentry day 8 after spraying, compared to their pre-exposure averages. No concurrent changes in plasma ChE was noted in either of these workers. Although it was stated that urine samples from all workers were collected, no urinary excretion data for the parent compound or its metabolites were provided.

The residue concentrations in gloves, patches (arm and head) and from the inhalation exposure monitoring showed that the highest levels were in gloves; an average of 46 μg/cm^2. Post-treatment samples of leaves and fruit were collected from Blocks 1 and 2 for residue analysis (at 1, 7/8 and 14 days after spraying). The DFR values are presented in Table 19.

Conclusions: Plasma and RBC ChE levels in 19 individuals who worked in a grove of orange sprayed with azinphos-methyl at 4.2 kg ai/ha were determined. Some inhibition of plasma and RBC ChE was seen in several individuals. However, the validity of the findings of this study is reduced due to wide variability in individual pre-exposure plasma ChE data, lack of statistical analysis, data limitations and sensitivity of the ChE assay used. As azinphos-methyl residues persist for quite a long time exposure to these residues continues for a long time and this may be the reason for worker exposure and the effect on RBC ChE.

Table 19: Dislodgeable residues following azinphos-methyl application

Days post application	Dislodgeable foliar residues (μg/cm^2)	Dislodgeable fruit residues (μg/cm^2)
Block 1		
1	1.52	6.01
7	1.62	4.52
14	0.92	6.84
Block 2		
1	3.03	10.56
8	0.83	2.32

Waggoner TB, Olson TJ & Lamb DW (1970b) Determination of the hazards to workers picking citrus treated with Guthion wettable powder formulation. Study no: not stated, Research Department, Chemagro Corporation. Sponsor: Bayer AG. Study duration: not stated, Report no. 28250. Report date: November 25, 1970.

Pre GLP, non-quality assured study. No test guidelines were cited.

Study and observations: In this study, plasma and erythrocyte (RBC) ChE levels in citrus pickers working in a grove of oranges sprayed with guthion WP formulation (azinphos-methyl) were investigated. Fifteen workers (age: 21 years or older, 12 males and 3 females, body weight range not stated) who had no recent exposure to any ChE inhibiting agents were chosen for the study. Baseline plasma and RBC ChE levels of the workers were established

using data from 3 determinations carried out at 7, 5 and 3 days prior to the commencement of the study. It was stated that during this time the workers were not allowed to work in orchards, which had been sprayed with any ChE inhibiting pesticides, and also the grove used had not been sprayed with such chemicals for at least 30 days prior to commencement of the study. The orange grove was subdivided into 3 blocks (unspecified sizes) and each was sprayed with azinphos-methyl WP formulation (purity, source, batch and formulation details not provided) at 4.2 kg ai/ha, on days 1, 4 and 10 days. Workers entered block 1 on the 8th day after spraying and picked fruit for 4 days. The workers spent about 6-7 h in the orchard each day, and there was no rainfall during the study. RBC and plasma ChE levels in workers were assayed using blood samples collected at 8 and 11 days after spraying. Blood samples were collected by venipuncture upon completion of a full working day. The ChE assay used was the "pH Stat assay for human blood cholinesterase" recommended by the US Public Health Service. The enzyme activity was expressed as μmoles acetylcholine/min/mL. Post-exposure ChE activity data were compared with respective pre-exposure values to assess exposure effects.

Dermal exposure was monitored by measuring residue concentrations in gloves and skin patches (one on the forearm and one on the head) after each day's work. Inhalational exposure was measured using a personal air-sampling device. Post-treatment samples of leaves for DFR monitoring and fruit for dislogeable residues were collected daily up to day 58 in Block 1, day 51 in Block 2 and day 41 in Block 3. For DFR, four average size of leaves were collected from 8 trees for each sample comprising of a representative number from the interior and exterior portion of the tree. Five pounds (2.25 kg) of the fruit were also collected at the same time in the same manner as the leaves.

Findings: Individual pre-exposure ChE data in this study did not show high variability as observed in the previous study by the same authors (Waggoner et al 1970a). The variability in 11 workers was about 10% and 15% for plasma and RBC ChE, respectively. However, in 4 workers, the variability was higher, being about 25-66% for plasma ChE. The variability in RBC ChE data in these persons was about 10-30%. At the earliest re-entry day, ie at 7 days after spraying, 7/15 (4 males and all 3 females) and 5/15 workers (3 males and 2 females) exhibited depressions in plasma (about 22-65%) and RBC ChE (about 20-31%) levels, respectively compared to their pre-exposure values. On this sampling day, 4/15 (2/sex) workers showed inhibitions in both plasma and RBC ChE levels. At day 11 after spraying, 10/15 (7 males and all 3 females) and 5/15 (2 males and all 3 females) workers exhibited depressions in plasma (about 20-80%) and RBC ChE (about 24-32%) levels, respectively. Five out of 15 workers (3 males and 2 females) showed reductions in both plasma and RBC ChE activities on this sampling day. The reductions in plasma and RBC ChE activities that observed on both sampling days appear to be related to azinphos-methyl exposure.

Table 20: Dislodgeable residues following azinphos-methyl application

Days post application	Dislodgeable foliar residues (μg/cm^2)	Dislodgeable fruit residues (μg/cm^2)
Block 1		
0	1.3	0.21
1	0.45	1.01
3	1.2	0.64
7	0.74	0.53
9	2.2	0.52
11	0.82	0.95
15	0.62	1.05

23	0.63	-
30	0.40	0.61
47	0.55	2.23
58	0.28	0.29
Block 2		
0	0.78	0.56
2	0.90	0.64
4	0.64	0.82
6	0.52	0.36
8	0.57	0.21
13	0.49	0.80
15	1.06	2.06
20	1.15	-
27	1.08	0.71
51	0.42	1.64
Block 3		
0	0.81	0.77
3	0.66	0.83
6	0.82	1.00
13	1.05	0.82
19	0.77	1.12
23	0.64	0.38
41	-	0.55

Although urine samples from all workers were collected, no details on analyses were provided. Plasma ChE data of 2 workers at 7 days after spraying, and RBC ChE data of one worker at day 11 after spraying were not provided. The DFR values are presented in Table 19. The DFR half-life was in the range of 47 to more than 51 days. In fruit the residue dissipation half life was not achieved by day 58. The residues in gloves from one hour of picking ranged from 12.6 to 88.0 μg/cm^2 and exposure to workers was more from dermal route than inhalation.

Conclusions: Plasma and RBC ChE levels in 15 workers who worked in a grove of orange sprayed with azinphos-methyl at 4.2 kg ai/ha were evaluated. Greater than 20% inhibition in plasma and/or RBC ChE activities, probably attributable to azinphos-methyl exposure, was noticed in some workers as assayed at 8 and 11 days after spraying. In comparison to the study author's previous investigation with azinphos-methyl SC, the exposure duration in the present study is longer (6-7 vs 3-4 h). The validity of the findings of this study, however, is reduced due to lack of statistical analysis, data limitations (clinical observations, urinary data) and sensitivity of the ChE assay used. Long-term exposure to azinphos-methyl (most of it in gloves/hands) is related to persistence of azinphos-methyl residues. As most of the exposure in the study subjects was on the hands, it can be concluded that hand exposure is the most likely cause of ChE depression.

Waggoner TB, Olson TJ & Lamb DW (1970c) Determination of the hazards to workers picking citrus treated with Guthion Spray Concentrate Formulation (2.25 lbs. AI/acre). Study no: not stated, Research Department, Chemagro Corporation. Sponsor: Bayer AG. Study duration: not stated, Report no. 28251. Report date: November16, 1970.

Pre GLP, non-quality assured study. No test guidelines were cited.

Study and observations: In this study, plasma and erythrocyte (RBC) ChE levels in citrus pickers working in a grove of oranges sprayed with Guthion SC formulation (azinphos-methyl) were investigated. Fifteen workers (age: 21 years or older, 11 males and 4 females, body weight range not stated) who had no recent exposure to any ChE inhibiting agents were chosen for the study. Baseline plasma and RBC ChE levels of the workers were established prior to the commencement of the study. It was stated that during this time the workers were not allowed to work in orchards, which had been sprayed with any ChE inhibiting pesticides, and also the grove used had not been sprayed with such chemicals for at least 30 days prior to commencement of the study. The orange grove was subdivided into 3 blocks (unspecified sizes) and each was sprayed with azinphos-methyl SC formulation (purity, source, batch and formulation details not provided) at 2.8 kg ai/ha. Workers entered block 1 on the 7th day after spraying and picked fruit on days 7 and 10 through 14 and they entered Block 3 on 7th day after treatment and picked on 7th day through 11. The workers spent about 6-7 h in the orchard each day, and there was no rainfall during the study. RBC and plasma ChE levels in workers were assayed using blood samples collected at 3rd and 6th day (day 11 and 14 after spraying) on Block 2 and 2nd and 5th day (day 8 and 11 after spraying) after picking (not collected on Block 1). Blood samples were collected by venipuncture upon completion of a full working day. The ChE assay used was the "pH Stat assay for human blood cholinesterase" recommended by the US Public Health Service. The enzyme activity was expressed as μmoles acetylcholine/min/mL. Post-exposure ChE activity data were compared with respective pre-exposure values to assess exposure effects.

Dermal exposure was monitored by measuring residue concentrations in gloves and skin patches (one on the forearm and one on the head) after each day's work. Inhalational exposure was measured using a personal air-sampling device. Post-treatment samples of leaves for DFR monitoring and fruit for dislodgeable residues were collected daily up to day 29 in Block 1, day 27 in Block 2 and day 24 in Block 3, after spraying. For DFR, four average size of leaves were collected from 6 trees for each sample comprising of a representative number from the interior and exterior portion of the tree. Five pounds of the fruit were also collected at the same time in the same manner as the leaves.

Findings: The highest concentration of residues was found on the gloves. The concentration on the gloves ranged from 23.1 to 97.1 μg/cm^2. The concentration in the gloves was from 14 to 60 times more than the concentration on the fruit (0.59 to 4.48 μg/cm^2). The DFR values are presented in Table 20. Individual pre-exposure ChE data in this study did not show the high variability observed in the previous study by the same authors (Waggoner et al 1970a). The variability in workers was about 10% and 60% for RBC ChE. Plasma ChE levels were unchanged throughout the test. RBC ChE levels were about 24-124% compared to their pre-exposure values. The reductions in RBC ChE activities observed on sampling days appear to be related to azinphos-methyl exposure. Although urine samples from all workers were collected, no details of the analyses were provided.

Table 21: Dislodgeable residues following azinphos-methyl application

Days post application	Dislodgeable foliar residues (μg/cm^2)	Dislodgeable fruit residues (μg/cm^2)
Block 1		
0	0.71	2.65
6	0.69	2.83

15	0.51	1.17
22	0.58	2.87
29	0.47	1.77
Block 2		
0	0.55	1.87
3	0.47	3.38
7	0.26	1.61
16	0.50	0.59
21	0.34	0.88
27	0.26	-
Block 3		
1	0.72	4.48
6	0.42	1.77
15	0.44	1.69
22	0.51	-
24	0.15	-

In Block 1, half-life on the leaves and fruit was more than 29 day, on Block 2 it was more than 27 days and on Block 3 it was 24 days for the leaves but for the fruits it was 15 days.

Conclusions: Plasma and RBC ChE levels in 15 workers who worked in a grove of oranges sprayed with azinphos-methyl at 2.8 kg ai/ha were evaluated. Greater than 20% inhibition in RBC ChE activities, probably attributable to azinphos-methyl exposure, was noticed in some workers as measured 8, 11 and 14 days after spraying. In comparison to the study author's previous investigation with azinphos-methyl SC, the exposure duration in the present study is longer (6-7 vs 3-4 h). The validity of the findings of this study, however, is reduced due to lack of statistical analysis, data limitations (clinical observations, urinary data) and questionable sensitivity of the ChE assay used. As azinphos-methyl residues persist for a long time on the leaves, it is the cause of exposure in the workers which is mostly on gloves/hands and, this may be the cause for effect on RBC ChE.

1.7 OCCUPATIONAL RISK ASSESSMENT

The occupational risk assessment takes into consideration the hazard of the chemical as determined by toxicology data (Section 2), its use pattern in Australia, including formulation and packaging types (Section 3) and worker exposure for each exposure scenario (Section 4). Given that a human NOEL was used to estimate risk a MOE of 10 or more is considered to be acceptable.

1.7.1 Risk from end use exposure

Rather than assessing each end use situation separately, the risk to workers is categorised by scenarios. This simplifies the assessment process and allows the identification of issues relating to product formulation type and application method. The risk for each end use scenario is summarised in Table 21. The results of the risk assessment are discussed by application type and scenario following the table.

Table 22: Margin of Exposure (MOE) for workers handling azinphos-methyl

EXPOSURE SCENARIO	Data source/model (Estimate No)		Australian application rate, spray concentration, total ai applied per day	MOE**								
				Dermal MOE			Inhalation MOE			Total MOE****		
				M/L	*A*	*M/L/A*	*M/L*	*A*	*M/L/A*	*M/L*	*A*	*M/L/A*
1 & 7	POEM Estimate*	1-1*	0.98 kg ai/ha, 0.049 %, 19.6 kg ai/day	2.2	1.39	0.85	NM	125		2.2	1.37	0.84
		1-2		11		1.23				11		1.22
		1-3		1.39		0.69				1.39		0.69
		1-4		28		1.32				28		1.31
		1-5		6.58		1.15				6.58		1.13
		1-6		31		1.33				31		1.31
		1-7		4.17		1.04				4.17		1.03
		1-8		83		1.37				83		1.35
	PHED	Liquids		56	11	9.2	833	1667	555	52	11	9.05
2 & 7	POEM Estimate*	2-1*	49 kg ai/day, 0.049 %	1.11	1.39	0.62	NM	125		1.11	1.37	0.61
		2-2		5.56		1.11				5.56		1.10
		2-3		0.59		0.42				0.59		0.41
		2-4		12		1.26				12		1.23
3 &7	POEM Estimate*	3-1*	7.35 kg ai/day, 0.049 %	6.58	1.39	1.15	NM	125		6.58	1.37	1.13
		3-2		31		1.33				31		1.31
		3-3		3.33		0.98				3.33		0.97
		3-4		63		1.36				63		1.34

		3-5		6.58		1.15			6.58		1.13
		3-6		31		1.33			31		1.31
		3-7		5.56		1.11			5.56		1.10
		3-8		125		1.37			125		1.36
4 & 7	POEM Estimate*	4-1*	2.94 kg ai/day, 0.049 %	12	1.39	1.25	NM	125	12	1.37	1.23
		4-2		62.5		1.37			63		1.35
		4-3		9.6		1.22			9.6		1.21
		4-4		250		1.39			250		1.38
5 & 6	POEM Estimate*	5-1*	98 kg ai/day, 0.049%	0.55	NA						
		5-2		2.79							
		5-3	Protective clothing during	0.29							
		5-4	M/L/A, gloves during M/L	5.9							
	POEM Estimate* Vehicle mounted	8-1b*	98 g ai/100 L; 1500 L/ha; 1 ha/day	6.58	1.202	1.106	NM	125	- 6.58	1.19	1.10
		8-2b	(1.47 kg ai/day)	31		1.157			31		1.15
		8-3b		17		1.12			17		1.11
		8-4b		250		1.196			250		1.18
	PHED (liquid) Vehicle mounted	SC		NA		6	NA		NA		6

M/L – mixing/loading; A– application; NM-Not measured: POEM does not estimate inhalation exposure during M/L; NA- not applicable.
Highlighted values refer to SC formulation contained in wide neck containers-
* Numbers shown for the POEM estimates identify each exposure scenario.
** MOE = NOEL ÷ absorbed dose; human oral NOEL = 0.25 mg/kg bw/day. These MOEs are calculated based on absorbed dermal dose available where dermal absorption factor of 30% has been considered in calculating dermal absorbed value.
**** total MOE = 1 ÷ (1 ÷ dermal MOE + 1 ÷ inhalation MOE).

DISCUSSION

Mechanical application:

The mixing/loading operations are anticipated to be carried out in the open air using open-pour systems. Exposure estimates for mixer/loaders and applicators are based on applications by airblast orchard sprayer.

Applications by airblast equipment

The majority of growers treat their crops with azinphos-methyl using orchard airblast equipment. PHED was considered suitable to assess scenarios 1, 7 and 8 only. The UK POEM was used in the exposure assessment for all other scenarios. Most exposures occurred during application of SC formulations, with the dermal route contributing the most to risk. The products are in SC formulation and exposure by inhalation will be minimal or negligible.

Scenario (1)	Mixing/loading SC for spray application in pome and stone fruit-overall spray, soil drench and butt spray

For dilute spraying, POEM estimates revealed that MOE for mixer/loaders using SC in standard containers were low, but were relatively higher (less than 10) for workers mixing/loading concentrate spraying (Table 22). MOE were high (> 10) when workers use SC formulation in wide neck containers. The MOE for mixer/loaders using liquids were high according to PHED data. No information was provided on container sizes and packaging type for the PHED data. PHED database did not specify the formulation type of the liquid formulation.

Scenario (2)	Mixing/loading SC for spray application in citrus-overall spray

For citrus, mixer/loader MOE were very low ($\leq$ 1). However, the MOE were higher when workers used SC in wide neck containers (Table 23). POEM indicated that exposure estimates are reduced when smaller containers with wide necks are used.

Scenario (3)	Mixing/loading SC for spray application in macadamias, lychees, grapes and kiwi fruit-overall spray

As in Scenario (1) above, MOE for mixer/loaders increase significantly (> 10) when workers use containers with wide necks. In conclusion, for scenarios 1, 2 and 3, the risk of exposure to mixer/loaders is considered acceptable provided that workers use SC formulation packaged in wide neck containers in accordance with label instructions.

Scenario (4) and (7)	Mixing/loading SC for spray application in blueberries-overall spray and Application of spray by mechanised ground equipment (air-blast sprayer, airshear spray, vertical boom, controlled droplet applicators and electroastatic)-overall spray

Spray volumes used in the treatment of blueberries are low (300 mL/ha), which is responsible

for the lower exposure estimates for mixer/loaders. The MOE were high when workers used SC in standard containers. MOE increased significantly when mixer/loaders used SC in wide neck containers (Table 23). MOEs were low for applicators. The risk to applicators of 350 g/L SC is similar to those handling lower concentrations of azinphos-methyl 200 g/L SC as the amounts of ai in the spray is similar.

The overall conclusion is that mixer/loaders/applicators using SC formulations will not be adequately protected according to current label instructions (including safety directions to use respirator, gloves and overalls). It is noteworthy that when considering the exposure estimates for risk assessment, conservative assumptions are deduced for the following:

1. Australian workers are expected to treat orchards, vines and fruits 2-6 times (most often 2-3 times) a season;
2. the NOEL is determined from a well conducted human study; and,
3. the skin absorption value used in the POEM estimates (30%) is based on a well conducted human study (See Section 2).

Therefore, worker risk could be reduced to an acceptable level if mixer/loader exposure were totally eliminated through the use of SC contained in wide neck containers and workers wearing protective waterproof clothing and impervious footwear. Applicator exposure can be minimised by using enclosed cabs, and impervious footwear in addition to the existing personal protective equipment for all existing products, however full face-piece respirator is not required as MOEs for inhalation exposure are acceptable for all the scenarios (SC 350 and 200 g/L).

Scenario (5) Mixing/loading WP and SC for vertical Boom application in citrus-overall spray

Scenario (6) Mixing/loading WP and SC for concentrate or semi-concentrate sprayers (airblast, airshear, CDA, electrostatic) in all crop situations

Mixing/loading SC for boom application in citrus and mixing/loading concentrated or semi concentrated spray is performed at a higher spray volume, but with the same concentration of azinphos-methyl in the spray as that used in other scenarios (ie. 0.049%). Therefore, applicator exposure should be the same as that discussed in scenario 7. MOE for mixer/loaders are shown in Table 22 to be very low when using SC in standard containers (< 1); MOE are higher when using wide neck containers containing SC formulation but are nonetheless below the acceptable value of 10. Smaller containers with wide neck showed higher MOE than larger containers.

To reduce the risk of exposure during mixing/loading of concentrated or semi-concentrated spray:

1. Workers should use small size containers with wide necks and,

2. Water-proof clothing and footwear are recommended for mixing/loading all products of azinphos-methyl.

Applications by air shear, vertical boom, electrostatic and CDA equipment

Applications by air shear sprayer, vertical boom, electrostatic and CDA were indicated on the labels but are uncommon and unlikely to result in additional exposure when compared with airblast applications. The APVMA has advised the OCS that applications by electrostatic equipment are extremely rare, and air shear use in Australia constitutes between 15-20% of total uses in macadamias. Vertical boom sprayers are used to deliver very dilute spray (spray volume at 10,000 L/ha); air shear (misters) and CDA are concentrated sprayers (low volume spray 500 L/ha). However, the amount of azinphos-methyl in the spray is the same for all mechanical equipment used (vertical boom, CDA, airshear, electrostatic, and airblast). It is expected that applicator exposure is higher with vertical boom than airblast. However, vertical boom vehicles are usually equipped with enclosed cabs with appropriate filtering devices to protect against chemicals, which minimises exposure. The overall risk to workers during application by vertical boom, CDA, electrostatic and air shear is expected to be similar to airblast application (without cab). The precautions and restrictions, which are associated with airblast application, should also be observed for application by the other methods.

Hand-Held Application

Scenario (8) Mixing/loading/application by hand-held equipment in grapes, pome and stone fruit

The risk assessment for this scenario relied on PHED and POEM. PHED data were available for mixer/loaders/applicators using liquid formulations. PHED data assumed hand held equipment attached to vehicle mounted equipment. POEM modelled for hand held equipment attached to vehicle-mounted equipment as knapsack application is not carried out in Australia.
Daily doses via inhalation were comparatively low, although it is not possible to fully estimate exposure, as POEM does not consider inhalation exposure during mixing/loading. The formulation is in SC form and inhalation exposure will be minimal during mixing/loading.

Vehicle-mounted equipment

According to POEM estimates, MOE for mixer/loaders/applicators are low when workers use SC formulation in standard containers. MOEs are higher when workers use wide neck containers, but are nonetheless below the acceptable value of 10 (Table 22). PHED data showed that mixer/loader/applicators handling liquids also had relatively low MOE (Table 22). The overall conclusion is that mixer/loader/applicators applying SC formulation outdoors by hand application for soil drench or spot treatment will not be adequately protected when using the product according to label instructions. Therefore hand-held applications of azinphos-methyl are not supported.

Mechanical and hand-held application

In general, the risk assessment conducted for all scenarios indicates the need for protective waterproof clothing and impervious footwear in order to minimise workers' exposure during mixing/loading and use of closed cabs during mechanical application and subsequently, the risk of adverse health effects. Given that workers may be involved in a number of activities, and to facilitate worker mobility, it is proposed that one layer of clothing should be worn under waterproof clothing. However, it is imperative that this outer protective layer is properly rinsed (ie. under shower or hosed down) prior to its removal in order to eliminate chemical residues and prevent possible contamination of under clothes and skin.

Safety directions

The current safety directions for SC products containing 350 g/kg azinphos-methyl or less include (as listed in the FAISD Handbook), cotton overalls buttoned to the neck and wrist, a washable hat, elbow length PVC gloves and full face-piece respirator (with combined dust and gas cartridge/canister) during preparation and application of spray.

Exposure estimates were calculated using POEM and PHED with the underlying assumption that workers wear only gloves and one layer of clothing during mixing/loading and application (Section 4.1.2). POEM assumes hand contamination as the only source of exposure during mixing and loading. Full body exposure is assumed only during application. Therefore it is recommended that wide neck containers should be used for packing the SC products and during mixing/loading workers should wear waterproof clothing over one layer of their own clothing, impervious footwear and elbow length PVC gloves. During application it is recommended that workers use closed cab fully equipped with appropriate filters, impervious footwear, elbow length PVC gloves and one layer of clothing.

1.7.2 Risk from post-application exposure

The exposure studies presented in Section 7.2 were used to determine risk for workers who are required to perform tasks at specified intervals post-application. The calculated MOE using these study data are presented in Table 23.

Table 23: Re-entry MOE for specified activities in treated crops.

Crop/Post-application interval (days)	Transfer coefficient cm^2/h (High/Low*)	Measured DFR ($\mu g/cm^2$)(High/Low)	Calculated dermal exposure** (mg/kg bw/day)	MOE*** (High/Low)
Fruit trees (e.g. pome, stone, citrus)				
7	(L) 1,000 (H) 3,000	(L) 0.4 (H) 2.52	(LTC&DFR) 0.014 (LTC-HDFR) 0.09 (HTC-LDFR) 0.04 (HTC&DFR) 0.26	(LTC&DFR) 18 (LTC-HDFR) 3 (HTC-LDFR) 6 (HTC&DFR) 1
14		(L) 0.18 (H) 1.58	(LTC&DFR) 0.006 (LTC-HDFR) 0.054 (HTC-LDFR) 0.019 (HTC&DFR) 0.16	(LTC&DFR) 42 (LTC-HDFR) 5 (HTC-LDFR) 13 (HTC&DFR) 2
21		(L) 0.16 (H) 1.5	(LTC&DFR) 0.005 (LTC-HDFR) 0.05 (HTC-LDFR) 0.016 (HTC&DFR) 0.15	(LTC&DFR) 50 (LTC-HDFR) 5 (HTC-LDFR) 16 (HTC&DFR) 2

35		(L) 0.011 (H) 1.09	(LTC&DFR) 0.0004 (LTC-HDFR) 0.04 (HTC-LDFR) 0.001 (HTC&DFR) 0.11	(LTC&DFR) 625 (LTC-HDFR) 6 (HTC-LDFR) 250 (HTC&DFR) 2
52-53	3526****	(L) 0.36 (H) 0.61	(TC&LDFR) 0.044 (TC&HDFR) 0.074	(TC&LDFR) 6 (TC&HDFR) 3
Vines (e.g. grapes, kiwi)				
7	(L) 5,000 (H) 10,000	(L) 0.4 (H) 2.52	(LTC&DFR) 0.07 (LTC-HDFR) 0.45 (HTC-LDFR) 0.13 (HTC&DFR) 0.86	(LTC&DFR) 4 (LTC-HDFR) 1 (HTC-LDFR) 2 (HTC&DFR) <1
14		(L) 0.18 (H) 1.58	(LTC&DFR) 0.03 (LTC-HDFR) 0.27 (HTC-LDFR) 0.06 (HTC&DFR) 0.53	(LTC&DFR) 8 (LTC-HDFR) 1 (HTC-LDFR) 4 (HTC&DFR) <1
21		(L) 0.16 (H) 1.5	(LTC&DFR) 0.03 (LTC-HDFR) 0.25 (HTC-LDFR) 0.05 (HTC&DFR) 0.5	(LTC&DFR) 8 (LTC-HDFR) 1 (HTC-LDFR) 5 (HTC&DFR) <1
Nut trees (e.g. macadamia) and lychees				
7	(L) 500 (H) 2,500	(L) 0.4 (H) 2.52	(LTC&DFR) 0.007 (LTC-HDFR) 0.045 (HTC-LDFR) 0.03 (HTC&DFR) 0.22	(LTC&DFR) 36 (LTC-HDFR) 6 (HTC-LDFR) 8 (HTC&DFR) 1
14		(L) 0.18 (H) 1.58	(LTC&DFR) 0.003 (LTC-HDFR) 0.027 (HTC-LDFR) 0.015 (HTC&DFR) 0.13	(LTC&DFR) 83 (LTC-HDFR) 9 (HTC-LDFR) 17 (HTC&DFR) 2
21		(L) 0.16 (H) 1.5	(LTC&DFR) 0.003 (LTC-HDFR) 0.025 (HTC-LDFR) 0.013 (HTC&DFR) 0.13	(LTC&DFR) 83 (LTC-HDFR) 10 (HTC-LDFR) 19 (HTC&DFR)

				2
Berries (e.g. blueberries)				
1	(L) 400 (H) 1,500	(L) 0.45 (H) 3.64	(LTC&DFR) 0.006 (LTC-HDFR) 0.05 (HTC-LDFR) 0.023 (HTC&DFR) 0.19	(LTC&DFR) 42 (LTC-HDFR) 5 (HTC-LDFR) 11 (HTC&DFR) 1
2		(L) 0.46 (H) 3.84	(LTC&DFR) 0.006 (LTC-HDFR) 0.05 (HTC-LDFR) 0.024 (HTC&DFR) 0.19	(LTC&DFR) 42 (LTC-HDFR) 5 (HTC-LDFR) 10 (HTC&DFR) 1
3		(L) 0.43 (H) 3.41	(LTC&DFR) 0.006 (LTC-HDFR) 0.047 (HTC-LDFR) 0.022 (HTC&DFR) 0.18	(LTC&DFR) 42 (LTC-HDFR) 5 (HTC-LDFR) 11 (HTC&DFR) 1

* In pome/stone/citrus fruit cultivation high exposure to foliar residues is likely following tasks such as hand thinning, hand harvesting, pruning, training, staking, topping, and tying. Other tasks such as irrigation and weeding are considered to be low exposure activities. In vines, activities such as grape girdling are considered likely to result in much higher exposure than tasks such as hand harvesting, leaf pulling, thinning, pruning, and training/tying. In nut trees such as the macadamia activities such as harvesting, pruning, thinning (mature) are anticipated to result in high transfer whereas irrigation, thinning (immature), and weeding are considered to be low exposure. In berries, activities such as hand pruning (late season, full foliage) and hand harvesting are considered to result in a higher exposure than hand weeding (all growth stages), irrigation (early season, low foliage), hand pruning (early season, low foliage), and thinning (early season, low foliage).
** Dermal exposure calculated by using the formula: Exposure (mg/kg bw) = DFR x TC/1000 (µg/mg) x 8 hrs/day x dermal abs./bw; bw = 70 kg, dermal abs. = 30%); *** MOE = NOEL/exposure; **** TC value taken from Spencer JR et al. (1993).

The post-application exposure for workers in various crops treated with azinphos-methyl was calculated from data derived from chemical-specific re-entry studies. Where necessary the resulting post-application exposure was adjusted to match Australian application rates.Where estimates of actual transfer coefficients (TC) were not calculated, surrogate values were used. Surrogate crop dislodgeable residue transfer coefficients, which are a reflection of the type and duration of work activity undertaken are independent of the pesticide or rate of application, were used as required. Since all exposure studies were conducted in apple, peach or orange orchards, no pesticide specific data was available for grape and kiwi vines, macadamia and lychee trees, or blueberries. However, the dislodgeable foliar residue (DFR) data derived from apples, peaches and oranges were used as a surrogate on the basis that the dissipation rate was likely to be the same.

The dermal exposure resulting from post-application activities in all crops was estimated using the TC and DFR values and a 30% dermal absorption factor. In estimating the dermal exposure both high and low TC and measured DFR values were considered to give a range of exposure scenarios for post-application days 7, 14, 21, 35 and 52-53. These results are shown in Table 23. It is apparent from the results that the measured azinphos-methyl DFR values declined slowly (ie. a slow dissipation rate) which resulted in a MOE for activities such as hand harvesting of fruit (pome, stone and citrus), nuts and blueberries being generally less than 10. Since it would not be appropriate to consider the lowest DFR as being sufficiently conservative for regulatory purposes calculating an average MOE (ie. for high and low DFRs)

for high foliar exposure activities, such as hand harvesting and pruning, shows that this would result in an unacceptable risk for these crops. Although wearing other types of PPE such as chemical-resistant gloves may give adequate protection for hand harvesting this is not considered to be practical. Mechanical harvesting may be a viable option although hand harvesting is the normal practice in Australia.

1.8 FINDINGS

1.8.1 Overview

Azinphos-methyl is registered for use in a number of agricultural applications. It has no registered home or veterinary uses. This review considers only the end uses and products, which have potential for occupational exposure and which are included on current Australian labels. Currently there are 4 azinphos-methyl products registered in Australia, all SC formulations.

1.8.2 Worker exposure during mixing/loading and application

Products containing azinphos-methyl are applied in pome and stone fruit, citrus, grapes, blueberries, macadamias, lychees and kiwi fruit. The products are applied by ground spray equipment (vehicle driven or hand held). In ground spraying, products are applied by mechanised sprayers (airblast, air shear - misters/mist blowers, vertical boom, CDA, electrostatic sprayers) or by handheld sprayers (for spot spraying and soil drenching). The main application method used is orchard airblast application. The worker exposure during application by vertical boom, CDA, electrostatic and air shear is expected to be similar to airblast application (without cab). To assist in the worker exposure assessment, end use situations were grouped into exposure scenarios, based on application method. In the absence of acceptable worker exposure data, PHED model data provided by the applicant were used (where possible) in the exposure assessment by standardising to Australian use patterns. OCS used UK POEM for all other scenarios in the exposure assessment.

Worker exposure estimates were calculated with the underlying assumption that workers wear gloves and one layer of clothing during mixing/loading and application. POEM assumes hand contamination as the only source of exposure during mixing and loading. Full body exposure is assumed only during application. A dermal absorption factor of 30% (Selim 1999) and default inhalation absorption factor of 100% were used in the exposure estimation.

The dermal exposure for applicators was high when using an SC formulation. Daily doses via inhalation were comparatively low for all scenarios. The risk assessment of azinphos-methyl indicated a need to reduce exposure during mixing/loading and application in a number of end use situations. Therefore, wide-neck containers and appropriate chemical-resistant gloves and boots are recommedned for mixing/loading. No PPE is considered adequate to afford adequate protection during application. However, engineering controls, such as the use of an enclosed tractor cab fitted with charcoal filter (to filter incoming air), could provide adequate protection during application. If maintenance during application is required (eg. to clear a blocked nozzel) then the applicator should have access to water-proof clothing (similar to that for mixing/loading) which should be located outside the cab but protected from contamination (ie. in a waterproof container) and then suitable wash equipment needs to be available to wash the hands to minimise any subsequent contamination of the tractor cab.

1.8.3 Post-application exposure

Post-application exposure for workers entering treated areas was assessed from data provided in chemical-specific re-entry studies and surrogate studies. Most of the chemical specific studies studies provided DFR data but in two studies the blood ChE activity among hand harvesters was measured. A risk assessment of possible post-application activities indicated that the MOE was not acceptable for many post-application activitites, including hand pruning and hand harvesting of pome and stone fruit, blueberries, kiwi fruit, macadamias and lychees. The risk assessment was supported by the observation that several hand harvesters had significant reductions in RBC and plasma ChE activity despite wearing gloves. This was mainly the result of the persistence of azinphos-methyl in crops, including the harvested fruit. Mechanical harvesting of the fruit would seem to be the only option to minimise the post-application risk to workers but this may not overcome the problem of residues on the harvested fruit for the purpose of overcoming the dietary risk.

1.9 REFERENCES

Davis JE, Stevens ER, Staiff DC (1983) Potential exposure of apple thinners to azinphosmethyl and comparison of two methods for assessment of hand exposure, Bull. Environ. Contam., 31, 631-638.

Department of Health and Aged Care (2000) Review of the Mammalian Toxicology and Metabolism/Toxicokinetics ofAzinphos-methyl, Chemicals Review and International Harmonisation Section, Chemicals and Non-Prescription Drugs Branch, Therapeutics Goods Administration, Canberra, Australia.

Eiden Catherine (1999) Human Health Risk Assessment, Azinphos-Methyl, USEPA Office of Pesticide Programs, Health Effects Division (7509C).

Ellisor GK (1998) Evaluation of foliar dislodgeable residues of Guthion on cotton, Bayer Corp. Study No., 94P003, Report No.,107248, Bayer Corp. Agriculture Division, Research and Development Department, Missouri.

Ellisor GK (1998) Evaluation of foliar residues of Guthion on apples, Bayer Corp. Study Number 94P002, Bayer Corp. Report Number 107249, Bayer Corp., Agriculture Division, Research and Development Department, Kansas City, Missouri.

Kehrig B (1999) Occupational medical experience with azinphos-methyl. In company communication to Dr KG Heiman dated July 21, 1999. WD-DO medical Services, Bayer AG. Unpublished. [Bayer; sub: 11943, Vol 1].

Lamb DW (1980) Early studies with azinphos-methyl to determine times for citrus pickers, Field worker exposure during pesticide application studies in Environmental Science, No., 7, Tordoir, WF and Van Heemstra-Lequin, Ed. Elsevier Scientific Publishing Co., New York, 121-127.

Lander F & R□nne M (1995) Frequency of sister chromatid exchange and hematological effects in pesticide-exposed greenhouse sprayers, Scand. J. Work Environ. Health, 21, 283-288.

Laurent C, Jadot P & Chabut C (1996) Unexpected decrease in cytogenetic biomarkers frequencies observed after increased exposure to organophosphorous pesticides in a production plant, Int. Arch. Occup. Environ. Health, 68, 399-404.

Lundehn JR and Westphal D (1992) Uniform Principles for Safeguarding the Health of Applicators of Plant Protection Products, Berlin 1992

Maasfeld W (1999): Determination of Exposure during Mixing/loading and Application of Gusathion WP 25 in High Crops, Bayer AG, Crop Protection Development, Institute for Metabolism Research and Residue Analysis, D-51368 Leverkusen, In Germany, Report No. MR-121/99, Report Date, April 15, 1999.

Marien K (1996) Dislodgeable Foliar Residue Levels of Azinphos-methyl and Azinphos-methyl-oxon on an apple orchard in the lower Yakima Valley of Washington State, Bayer Corp. Study Number, 93E003, Bayer Corp. Report Number, 106719.

Miksche L (1981) Information on effects on man/occupational experience. Study number and duration: not stated. Medical Department, Bayer AG, Leverkusen, Germany. And in-company fax message. Unpublished. [Bayer; sub: 9691, Vol 8].

National Occupational Health and Safety Commission (1994a) Control of Workplace Hazardous Substances [NOHSC:1005(1994), 2007(1994)], Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1994b) National Code of Practice for the Labelling of Workplace Substances [NOHSC:2012 (1994)], Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1994c) National Code of Practice for the Preparation of Material Safety Data Sheets [NOHSC:2011(1994)], Australian Government Publishing Service, Canberra.

National Registration Authority for Agricultural and Veterinary Chemicals (1997), Guidelines for Registering Veterinary Chemicals, Canberra, Australia

National Occupational Health and Safety Commission (1998) Approved Criteria For Classifying Hazardous Substances Revised Edition [NOHSC:1008(1999) Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (2001 draft update) List of Designated Hazardous Substances, Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1995a) Exposure Standards for Atmospheric Contaminants in the Occupational Environment, Guidance Note [NOHSC:3008(1995)] and National Exposure Standards [NOHSC: 1003(1995)], Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1998) Guidelines for Health Surveillance[NOHSC: 7039(1998)], Organophosphate Pesticides Revised Edition Australian Government Publishing Service, Canberra.

Selim S (1999) Absorption, excretion, balance and pharmacokinetics of ^{14}C radioactivity after single dose dermal application of three dose levels of ^{14}C labelled Guthion to healthy volunteers, XBL study no: 98052, Pharma Bio-Research Code PBR-963691, Bayer Corporation, 17745 South Metcalf, Stilwell, KS 66085.

Simpson GR (1965) Exposure to guthion during formulation. Arch Environ Health, 10: 53-54. Report No. 1582. [Bayer; sub: 9691, Vol 8].

Spencer JR, Hernandez BZ, Schneider FA, Sanborn JR, Margetich SS, Begum S, Wilson BW (1993) Dermal and urinary monitoring of peach and apple harvesters exposed to organophosphate residues in Sutter, Stanislaus and Madera Counties, HS-1577.

Steenland K (1996) Chronic neurological effects of organophosphate pesticides, British Medical Journal, 312, 7042, 1312-1313.

Stokes L, Stark A, Marshall E & Narang A (1995) Neurotoxicity among pesticide applicators exposed to organophosphates. Occup Environ Med, 52 (10): 648-653.

Thongsinthusak T, Ross JH, Meinders D (1993) Guidance for the Preparation of Human Pesticide Assessment Documents, Department of Pesticide Regulation, California Environmental Protection Agency, HS-1612, May 1993.

Tinsley IJ, Jenkins JJ (1994) Evaluation of Airborne and Dislodgeable Residue Levels of Azinphosmethyl and Azinmethyl-oxon following application of Guthion 35 WP to apples in Hood River, Oregon, Test Facility Study Number, PIAP 1001-92, Bayer Corp. Report Number, 108566.

Van Hemmen JJ (1993) Predictive Exposure Modelling for Pesticicde Registration Purposes. Ann. Occup. Hyg., vol 37, p 541-564.

Waggoner TB, Olson TJ, Lamb DW (1970) Determination of the hazards to workers picking citrus, treated with Guthion spray concentrate formulation, Reports number, 28428 (3/11/70), 28251 (7/10/70), 28250 (25/11/70), Chemagro Corporation, Research Department (OHS 1,2,3).

Zweig G, Leffingwell JT, Popendorf W (1985) The relationship between dermal pesticide exposure by fruit harvesters and dislodgeable foliar residues, Journal of Environmental Science and Health, Part B20 (1), 27-60.

Studies noted but not included in the review

Frankin CA, Fenske RA, Greenhalgh R, Mathieu L, Denley HV, Leffingwell JT, & Spear RC (1981). Correlation of urinary pesticide metabolite excretion with estimated dermal contact in the course of occupational exposure to Guthion.

The study evaluated exposure to and absorption of Guthion 50 WP in orchardists in British Columbia. Seventeen orchardists sprayed Guthion 50 WP by orchard airblast equipment in British Columbia. Ultra low volume procedures were followed with an application rate of 1.25 lb/acre (1.4 kg/ha) in 50-70 gal/acre (467-654 L/ha). The maximum concentration of azinphos-methyl in the spray (1.07% ai) in the study is higher than the Australian situation

(0.049 % ai). No information was provided on the work rate and mixing/loading procedure. Fourteen workers sprayed for 1 day, two for 2 days, and two for 3 days. Application time was for 2.5-9 days. Workers wore cotton shirts, trousers, long sleeved coveralls, half face respirator, gloves, boots and hats. Residents from the same area acted as controls. Urinary metabolites were measured in 24 hr samples collected at each spraying day and post application. Cholinesterase activity was measured in blood samples at pre-exposure, post exposure and as soon as possible after spraying. Air samples were collected using personal air-sampling pumps attached to the worker's collar. Patches were pinned to the underside of the clothing against the skin at the following locations: chest, back, upper arm, lower arm, upper leg and lower leg.

The mean air concentration based on seven samples was 0.05 mg/m^3. Of the 16 patches analysed, 9 had detectable levels of Guthion (>0.1 μg). Penetration through clothing was detectable for two or more regions in five cases and was observed on upper patches of 4 workers who wore rubber coats over cotton clothing. The levels of Guthion on the patches ranged from 1.8 to 18.8 ng/cm^2 per kg of active ingredient. The lower arm was found to have higher exposure. There was neither a linear nor a log-linear correlation found between the patch data and the total 48 hr urinary output. The main exposure was found to be at the unpatched portions of the body, the face, hands and neck. Urinary metabolites analysed showed that the majority of workers excreted 40% or less of their total metabolites in the morning void. A weak correlation was found between the amount of active ingredient and the 24 hr urinary output. The study concluded that a 48-h urine collection is a minimum when estimating total dermal absorption of azinphos-methyl. The study indicated that the most exposure was found in the unpatched areas which warranted a revision of the location of patches. No depressions of either red blood cell or serum cholinesterase activity were seen on exposure days greater than 15% of the pre-exposure value. Depressions seen on post exposure days did not exceed the variation observed in the control group.

Franklin CA, Miur NI & Moody RP (1986) The use of Biological monitoring in the estimation of exposure during the application of pesticides.

The study provided a discussion on data analysed for urinary alkyl phosphate metabolites in orchardists exposed to azinphos-methyl. Twenty three orchadists in British Columbia, Onatrio and Nova Scotia, sprayed their properties with azinphos-methyl 50 WP at the rate of 0.8 to 2.6 kg ai/ha by orchard airblast equipment, except for one property. All workers wore cotton pants, long sleeved shirts and heavy cotton coveralls with 6 patches pinned under the clothing and 4 patches outside. Body, face, head and hand exposure were investigated. All workers used organic respirators and, with the exception of one, all wore gloves. Some wore plastic face shields and the majority wore hats. Exposure estimates derived from metabolite data were compared with estimates derived from patch data by integrating the data from field studies and the laboratory studies.

The study concluded that the exposure estimate of 5200 μg from patches in the Ontario study was in relatively close agreement with the metabolite estimate of 6880 μg. However, the Nova Scotia estimate of 5620 μg (including hands) or 4260 μg (without hand estimate) was much higher than the metabolite estimate of 1920 μg. The study suggested that urinary metabolite data provide a more reliable and accurate estimate of exposure than patch data.

Franklin CA (1984) Estimation of dermal exposure to pesticides and its use in the risk assessment

The study discusses traditional methods used for estimating dermal exposure on the applicator's body. The study suggested that the urinary concentration of dimethyl thiophosphate (DMTP) is a good indicator of dermal exposure to azinphos-methyl. A strong correlation was found between the amount of azinphos-methyl sprayed and the 48 hr DMTP output. Measured levels of DMTP in urine were seen in all workers, whereas only some showed quantifiable exposure as estimated by patches. Also, there was no significant depression of cholinesterase levels in any of these applicators.

Krieger RI & Dinoff TM (year not stated) Estimation of pesticide handler exposures using biomonitoring.

Abstract only. No results or data discussed.

Wilson BW, Sanborn JR, O'Malley MA, Henderson JD & Billitti JR (1997) Monitoring the pesticide-exposed worker.

The paper provides a general discussion on illnesses caused by organophosphates in California Agriculture. In addition, the study reviews protocols for monitoring urine for organophosphates and determining cholinesterase activity.

Hernandez BZ, Sanborn JR, Schneider FA, Spencer JR & Kreiger RI (1992) Dermal and biological monitoring of tree fruit harvesters exposed to foliar azinphos-methyl residues, California Department of Pesticide Regulation (CDPR), Worker Health and Safety Branch, Sacramento, California

The following is an abstract of the above study conducted by CDPR as part of its exposure methods validation process. Peach and apple harvesters were monitored over two years for their exposure to azinphos-methyl residues. The levels of exposure were measured by dermal monitoring (normal clothing and hand washes), dislodgeable foliar residue data, cholinesterase monitoring, and quantitation of urinary dialkyl phosphates. Mean dermal exposure was 1.8 mg/day in apples and 15.7 mg/day in peaches. Urinary results indicated an apparent mean percent dermal absorption of 19% in peaches and 55% in apples. According to the authors, there was no correlation between dermal dosimetry and urinary monitoring values. No significant change in cholinesterase levels was observed. No conclusions could be drawn from the above abstract as the data provided were inadequate.

Inkmann-Koch, May 1986, Assessment of the inhalatory and dermal exposure during follow-on work being common practice after applications of Gusathion MS in grape growing

The above refers to a 2 page letter containing dermal and inhalatory exposure values for grapegrowers. Gusathion contains azinphos-methyl and demeton-S-methylsulfone. No DFR data were provided, and therefore a post-exposure was not possible.

Gusathion MS containing azinphos-methyl (25%) and demeton-S-methylsulfone (7.5%) was applied to grapes at a maximum rate of 3 kg/ha in volumes of 1000-1500 L of spray fluid/ha. The amounts of active ingredient applied were 750 g azinphos-methyl and 225 g demeton-S-methylsulfone/ha. Hand and inhalation exposures were estimated during the performance of leaf work in vineyards at different time-intervals ranging from 2-96 hours after spraying. No

DFRs were provided. According to the author, because of the minimal amount of data available and because environmental factors were not taken into consideration, the values obtained were viewed as an approximate estimate only. A post-exposure assessment was therefore not possible.

Pauluhn J, Assessment of the potential health hazard to persons caused by re-entry exposure, June 1986

An analysis of the re-entry hazard potential was conducted based on the assessment of Inkmann-Koch of inhalation and dermal exposure for workers after application of Gusathion MS in vineyards. A 100% dermal penetration rate was assumed. No DFR data were provided. For the reasons described in the previous study (see above), the exposure data from this study is considered an approximate estimate only, and a post-exposure assessment was not possible.

Knarr RD, Re-entry intervals for azinphos-methyl, oxydemeton-methyl, disulfoton, and anilazine, Mobay Corporation, Corporate Occupational and Product Safety, Kansas City, MO 6412 (OHS 6)

Re-entry intervals were determined for azinphos-methyl, oxydemeton-methyl, disulfoton and anilazine based on dislodgeable foliar residue data and transfer coefficients. The crops were grouped according to crop height and re-entry tasks. The crops that were likely to produce similar exposures were grouped together. For each group, a transfer coefficient, relating to the amount of expected exposure to the DFR present, was either determined experimentally through a worker-exposure study, or adopted from published literature. Within each group, dislodgeable residue decay data were developed for representative crops. Since dislodgeable residue values were not available for every compound on every crop, appropriate surrogate crops were chosen within each group for each compound to calculate re-entry intervals. In each case, the surrogate crop had an application rate equal to or greater than the crops it represented. In the study several crops were examined, however, only crops for which foliar residues were available, ie. cotton, grapes, corn, cantaloupe, apple, and peaches were considered.

No exposure or dermal data were provided. Application rates varied from 0. 56 kg ai/ha to 2.24 kg ai/ha, the number of applications varied from 1-7 overall, and re-entry intervals varied from 2-92 days for cotton, 0-90 days for corn and grapes, 0 days for cantaloupe, 0-35 days for apples, and 4-16 days for peaches. The study lacked sufficient data required for regulatory evaluation.

MacDougall D & Waggoner TB, Synopsis of investigations to determine re-entry times for pickers in citrus treated with GUTHION, Report No. 28746, Chemagro Corporation, Research Department, December 1970.

The results of previous studies described in the Chemagro Reports (Waggoner et al., 1970) are summarized in this report, and will therefore not be discussed further.

Zweig G, Leffingwell JT & Popendorf W (1985) The relationship between dermal pesticide exposure by fruit harvesters and dislodgeable foliar residues, Journal of Environmental Science and Health, Part B20 (1), 27-60.

Twenty five blueberry harvesters were monitored on days 2, 4,and 6 following application of various chemicals. This was not considered in the risk assessment as this study is not relevant for azinphos-methyl use.

Special Data Call-In Notice for Incident Data on Acute Poisonings to Agricultural Workers Associated with the Use of Azinphos-methyl (1994).

The above refers to a letter from the Miles Inc. Agriculture Division to the USEPA discussing a report from the American Association of Poison Control Center's (AAPCC) Toxic Exposure Surveillance System on 'Azinphos-methyl Exposure Experience Data'. This data will not be used in the risk assessment, as it is not possible for regulatory evaluation.

Information on effects on man/occupational exposure (1981)

Translation of a German letter from Bayer to the Health Department regarding health of workers exposed to Gusathion MS. This information will not be used in the risk assessment, as it is not possible for regulatory evaluation.

1.10 APPENDIX 1: OVERSEAS REGULATORY ASSESSMENTS/ACTIONS

US EPA

The Health Effects Division (HED) of the Office of Pesticide Programs, US EPA conducted a Human Health Risk Assessment in 2001 to determine the re-registration status of azinphos-methyl based on data from various agencies. US EPA published an Interim Re-registration Eligibility Decision (IRED) Fact sheet along with detailed RED document in October 2001. Azinphos-methyl is widely used in agriculture and provides important pest control benefits to growers of orchard fruit, nuts and other crops. However, azinphos-methyl posed a high degree of risk to agricultural workers, as well as significant ecological risks. To improve worker safety and lessen ecological risks the US EPA has decided to cancel, phase out or continue under time-limited registration for products. The important issues covered in the IRED are given below:

1. Worker Risk Reduction

    - 28 crop uses will be cancelled without phase out since safer pest control alternatives are available (includes citrus and berries)
    - 7 crop uses will be phased out over 4 years, allowing time to shift to safer pest control alternatives (includes nectarines and plums); and
    - 8 crop uses will be issued time-limited registration for 4 years, allowing time to develop safer pest control alternatives (includes grapes, strawaberries and pecans)

2. Risk mitigation (in the phase out period)

    - increase restricted entry intervals (REIs)
    - increase pre-harvest intervals (PHI)
    - require close transfer system
    - require enclosed cabs or maximum PPE for applicators
    - registrants must conduct studies and provide data comparing exposure to airblast applicators with enclosed cabs, chemical resistant suits, monitoring ChE levels of harvesters and glove feasibility study
    - limit application and frequency and amount of azinphos-methyl spraying

It should be noted that

- apples have a re-entry period (Restricted entry interval - REI) of 102 days for hand harvesting,
- blueberries low bush, REI, 38 days for hand harvesting
- blueberries highbush, REI, 161 days for hand harvesting
- cherries are mechanically harvested but the REI proposed is 65 days for irrigating and scouting
- grapes, 100 days for hand weeding and 169 days for bunch thinning and hand harvesting
- peaches, 96 days for hand thinning and harvesting
- pears and plums, 102 days for harvesting

EPA was not able to identify mitigation measures that would bring the risks of essential azinphos-methyl uses to levels that the Agency considered reasonable.

2 RESIDUES AND TRADE ASSESSSMENT

2.1 RESIDUES EVALUATION

Residues and metabolism data have been provided in support of the review of azinphos-methyl. Studies submitted are listed in Appendix 2. This has included plant and animal metabolism studies, animal transfer data and Australian and overseas crop residue data. Additional information that had been submitted to the PACC in support of the establishment of MRLs, is also included. Recent data reviewed by JMPR, which have not been submitted by the Registrant, have also been incorporated into the discussion where relevant.

2.1.1 Metabolism

Metabolism data for plants, laboratory and food animals were considered. Studies in plants demonstrated that the main residue present in plant material was the parent compound azinphos-methyl. Small quantities of mercaptomethylbenzazimide and desmethyl azinphos-methyl were also found in apples, while small quantities of benzazimide and anthranilic acid were found in oranges.

When azinphos-methyl was fed to cows and goats, no parent compound was found in tissues or milk other than in fat, where 5% of the total residue was found as parent. The major metabolite found in liver, kidney, muscle and fat was methylsulfonylmethylbenzazimide. A major portion of the residue (up to 83% of the radioactivity in the liver) was found conjugated with the protein fraction. Essentially the same metabolites as in the tissues are found in milk, but these are different to those found in plant commodities.

From a residues definition perspective, consideration could be given to separate definitions for plant and animal commodities, as the parent azinphos-methyl is not a suitable measure of GAP when feeding treated plant commodities to animals. However, Codex and overseas regulatory authorities all use the parent only as the residue definition and harmonisation with these bodies is appropriate.

2.1.2 Analytical methods

2.1.2.1 Submitted methods

There were 12 analytical methods submitted for plant materials, including colorimetric and gas chromatographic methods. There were also photofluorometric, gas chromatographic or liquid chromatographic methods submitted in support of animal tissues and milk. The methods currently listed by the US EPA for determination of azinphos-methyl in crops and animal tissues and milk are acceptable for analysing azinphos-methyl shown in Table 24.

Table 24: Acceptable methods for analysing azinphos-methyl

Method reference.	Sample matrix	Technique		LOQ, mg/kg
		Extraction	Instrument	
Gas Chromatographic Method For Determination Of Guthion Residues In Plant Material. (Westburg & Becker 1981	Moist crops containing chlorophyll and oilseed crops	Crops: acetone Oilseed: Pet ether	Gas chromatography	Not given
A Method For The Determination Of Guthion And Guthion Oxygen Analog In Bovine Tissues And Milk Utilizing Gas Chromatography And	Tissues and milk	Soxhlet extraction with pet ether	Gas chromatography and also HPLC.	0.001-0.01

High Pressure Liquid Chromatography. (Wargo *et al* 1978)				

The method for animal tissues and milk was validated satisfactorily.

2.1.2.2 Stability of pesticide residues in stored analytical samples

Data were presented for stability of azinphos-methyl residues in apples, pears, blueberries, milk and liver that demonstrated that azinphos-methyl was reasonably stable when stored frozen at –18°C to –24°C. Data were also presented that demonstrated that azinphos-methyl was stable in orange and peach juices when stored at 0-20°C, but was unstable at 40°C, with a half-life of 7 days.

2.1.3 Residue definition

The data presented support the present residue definition of the parent azinphos-methyl *per se.* However, when azinphos-methyl is fed to animals, the residues found in tissues and milk were not the parent, except in fat, where it formed about 5% of the total residue. After three days, the major metabolite found in liver, kidney, muscle and fat was methylsulfonylmethylbenzazimide. A great portion of the residue (up to 83% of the radioactivity in the liver) was found conjugated with the protein fraction.

However, to maintain harmony with other regulatory agencies throughout the world, and because there are no registered uses in major animal feed commodities, the current residue definition of azinphos-methyl should be maintained for both the plant and animal material.

2.1.4 Residues in foods and animal feeds

2.1.4.1 Plant commodities

Residues data for pome fruit, stone fruit, citrus fruit, grapes, litchis, blueberries and macadamias were considered. The data is summarised in Table 25.

Table 25: Residues of azinphos-methyl in fruit commodities at the withholding period.

	Application rate	**WHP**	**Retreatment**	**Azinphos-methyl residues (mg/kg)**	
Commodity	**(kg ai/100L)**	**(Days)**	**Interval (Days)**	**HR**	**STMR**
Pome fruit	0.044-0.100	14	14-21	1.1	0.225
Citrus fruit	0.029-0.034	14	21-29	0.85	0.45
Stone fruit	0.025-0.050	14	7-25	2.6	0.33
Grape	0.042-0.050	14	7	0.767	?
Macadamia	0.049, 0.098	7	14-16	<0.01	?
Litchis	0.049-0.098	1	6-13	1.0	?
Blueberry	840g ai/ha	14	?	1.0	?

Not all data presented addressed the GAP for Australia. Most of the data were generated overseas. No data were presented to support the use in kiwifruit. All residues data indicated compliance with the Australian MRLs, except for peach, where a maximum residue of 2.6 mg/kg occurred in fruit in one trial, and where an increase of the MRL to 5 mg/kg will be required. An increase in the MRL for blueberry from 1 mg/kg to 2 mg/kg will also be required, due to the uncertainty of the available data.

2.1.5 Animal transfer studies and required animal commodity MRLs

Three levels of azinphos-methyl (11, 33 and 77 ppm) were fed to cattle in alfalfa pellets for 28.5 days. Tissue samples were analysed for the presence of azinphos-methyl and its oxygen analogue. Residues were <0.01 mg/kg in all tissues, including muscle, fat, liver and kidney. Residues in all milk samples were <0.001 mg/kg.

2.1.6 Effect of processing on residues

The data demonstrate that residues of azinphos-methyl can be reduced during processing. Overall, the data indicate that for citrus and apple, most of the residues are on the skin and are removed with the skin. Residues in peaches are reduced to LOQ during the canning process. Highest residues to occur on minor animal feed commodities were 6.4 mg/kg in apple pomace, 2.3 mg/kg in grape pomace, and 2.4 mg/kg in citrus peel/rind. However, these feeds form no more than 20% of the diet of cattle or sheep. Should continued registration of azinphos-methyl products be supported, the following MRLs will need to be established in Table 4 of the *MRL Standard*:

Apple pomace, dry	8 mg/kg;
Grape pomace, dry	3 mg/kg,
Citrus peel/rind	3 mg/kg.

2.1.7 Crop rotation

Three separate studies on crop rotation were presented. However, the crops for which registration is current are not broadacre crops that are replanted or are at risk from carryover of residues. Therefore the above three studies were not evaluated.

2.2 DIETARY RISK ASSESSMENT

The following health standards (Table 26) have been recommended by the Office of Chemical Safety, Department of Health and Ageing (ADI and ARfD lists, as of 29 March 2005).

Table 26: ADI and ARfD recommended for azinphos-methyl

Compound	Dietary Standard, mg/kg bw		No Observable Effect Level (NOEL), mg/kg bw	Safety Factor	Reference (OCS/ JMPR, date)
Azinphos-methyl	ADI[14]	0.025	0.25	10	28/02/05
	ARfD[15]	0.075	0.75	10	28/02/05

The end-points for the ADI and the ARfD were based on the level at which there was no inhibition of cholinesterase activity.

[14] http://www.tga.gov.au/docs/pdf/adi.pdf
[15] http://www.tga.gov.au/docs/pdf/arfd.pdf

2.2.1 Chronic dietary exposure assessment

The chronic dietary exposure to azinphos-methyl is estimated by the National Estimated Daily Intake (NEDI) calculation encompassing all uses of the chemical and the mean daily dietary consumption data derived from the 1995 National Nutrition Survey of Australia. The NEDI calculation is made in accordance with international guidelines[16] and is a conservative estimate of the dietary exposure to chemical residues in food. The NEDI for azinphos-methyl is 14.7% of the ADI. Details of the calculation can be found in Appendix 3.

It is concluded that the chronic dietary exposure of azinphos is acceptable.

2.2.2 Acute dietary exposure assessment

The acute dietary exposure is estimated by the National Estimated Short Term Intake (NESTI) calculation. The NESTI calculations are made in accordance with the deterministic method used by the JMPR[16] with 97.5th percentile food consumption data derived from the 1995 National Nutrition Survey of Australia. NESTI calculations are conservative estimates of acute exposure (24 hour period) to chemical residues in food.

The NESTIs for all relevant commodities for azinphos-methyl are summarised in Table 27.

Table 27: NESTIs for all relevant commodities for azinphos-methyl.

Code	Food	NESTI (%ARfD)		Code	Food	NESTI (%ARfD)	
		2 years +	2-6 years			2 years +	2-6 years
FB 0020	Blueberries	21.7	63.2	MM 0095	Meat [mammalian]	0.5	0.9
FC004	Oranges, raw (including peeling)	9.8	31.6	ML 0106	Milks	2.0	5.1
FC 0203	Grapefruit (raw)	9.5	0.0	FP 0226	Apple, raw, unpeeled	14.8	45.2
FC 0204	Lemon, raw (including peel)	2.5	0.0	FP 0230	Pear, raw, unpeeled	16.1	60.7
FC 0206	Mandarin, raw	10.1	36.0	FS 0240	Apricot, raw	25.2	103.7
MO 0105	Edible offal (mammalian)	0.2	0.1	FS 0245	Nectarine, raw, unpeeled	34.0	77.5
FB 0269	Grapes	7.9	18.5	FS 0247	Peach, raw, unpeeled	36.7	90.2
FI 0341	Kiwifruit	14.9	10.7	FS 0248	Plum, raw	21.3	36.5
FI 0343	Litchi	3.9	12.6	FS 0244	Cherry, raw	7.0	24.6
TN 0669	Macadamia nut	0.0	0.0				

The highest acute dietary intake was estimated at 104% of the ARfD for apricots, in 2-6 year old children. It is concluded that the acute dietary exposure of azinphos-methyl is not acceptable for apricots Consequently, the MRL for stone fruit will need to be modified to support this change. All other acute exposures were considered acceptable.

2.3 RESIDUE RELATED ASPECTS OF TRADE

Blueberries, kiwifruit, litchis and macadamia nuts are not considered major export

16. Food and Agriculture Organisation of the United Nations, Submission and evaluation of pesticide residues data for the estimation of maximum residue levels in food and feed, 2002, Rome.

commodities[17] and the overall risk to Australia's export trade is considered to be small. However, use of azinphos-methyl may result in detectable residues in these commodities other than macadamias, and the growers/ producers/ stakeholders should become aware of any potential trade risks to their industry.

2.3.1 Commodities exported

Citrus, stone and pome fruits, and grapes are all exported and are listed in Part 5B[12], and require consideration of trade issues.

2.3.2 Destination and Value of Exports

The three largest export markets for individual commodities by value for the season 2002/2003 are shown in Table 28 (*The Australian Horticultural Statistics Handbook 2004*).

Table 28: The three largest export markets for individual commodities by value for the season 2002/2003.

Commodity	Destinations	Value, $ million
Apples	UK, Malaysia, India	41.4
Pears	Singapore, Malaysia, Indonesia	22.0
Apricots	Singapore, Bahrain, France	0.8
Cherries	Hong Kong, Taiwan, Singapore	13.7
Nectarines	Taiwan, Hong Kong, Singapore	22.7
Peaches	Taiwan, Singapore, UAE	5.5
Plums	Hong Kong, Taiwan, Singapore	26.2
Oranges	USA, Hong Kong, Malaysia	146.4
Lemons/limes	Japan, Hong Kong, Singapore	6.1
Grapes	Hong Kong, Malaysia, Indonesia	95.4

2.3.3 Comparison of Australian MRLs with Codex Alimentarius Commission (Codex) and overseas MRLs.

The Codex Alimentarius Commission is responsible for establishing Codex Maximum Residue Limits (MRLs) for pesticides. Codex MRLs are primarily intended to facilitate international trade, and accommodate differences in Good Agricultural Practices (GAP) employed by various member countries. Some countries may accept Codex MRLs when importing foods. Azinphos-methyl has been considered by Codex. The following relevant Codex and international MRLs (Table 29) have been established for azinphos-methyl:

Table 29: Comparison of overseas MRLs and tolerances that have been established.

Commodity	Tolerance, mg/kg			
	Australia	Taiwan	Codex	EU
Apple	2	2	2	0.5
Pear	2	2	2	0.5
Apricot	2	2	1	0.5
Cherry	2	2	2	0.5
Nectarine	2	2	2	0.5
Peach	2	2	2	0.5
Plum	2	2	2	0.5

[17] Part 5B of the Vet Requirements Series and Ag Requirements Series, Overseas Trade Aspects of Residues in Food Commodities, August 2004.

Commodity	Tolerance, mg/kg			
	Australia	Taiwan	Codex	EU
Orange	2	2	1	1
Lemon	2	2	1	1
Grape	2	0.5	1	1

Furthermore, Hong Kong and Singapore adopt the standards of Codex for azinphos-methyl.

2.3.3.1 Animal commodities

Animal commodities have MRLs set at or about the limit of analytical quantification, so that any animal eating treated produce should not produce any quantifiable residues in its tissues, so that there is no trade risk associated with animals consuming azinphos-methyl treated feeds. The data indicate that residues of 77 ppm azinphos-methyl in feed will not produce residues in animal tissues and milk. The maximum residues to occur in animal feeds (6.4 ppm) are well below this, so that compliance with the MRLs for animal tissues should occur.

2.3.4 Potential risk to trade

Export of treated produce containing measurable residues of azinphos-methyl may pose a risk to Australian trade in situations where: (i) no residue tolerance (import tolerance) is established in the importing country; or (ii) where residues in Australian produce are likely to exceed a residue tolerance (import tolerance) established in the importing country.

Australian MRLs tend to be the same as Codex for pome and stone fruit, except for apricots, where the Australian MRL is double that of Codex. Australia's MRLs for grapes and citrus are also double that of Codex. However, when comparison is made with the monitoring data found in Section 1.7, there have been no reported violations of the MRL, nor have there been residues that have exceed half MRL. Furthermore, to the evaluator's knowledge, there have been no trade incidents involving this chemical in pome, stone or citrus fruits, or in grapes.

Therefore, it is concluded that the potential for prejudice to Australia's trade is acceptable and not undue.

2.4 CONCLUSION

The residues aspects of the use of azinphos-methyl on crops were reviewed as part of the third cycle of the Existing Chemicals Review Program of the APVMA. The Chemistry and Residues Program has examined the metabolism, analytical methods and residues data and concludes that there is no undue hazard to the health of consumers, except from apricots, for which the acute dietary exposure calculations indicated an unacceptable level of risk in children. Consequently, the CRP recommends the withdrawal of the uses of azinphos-methyl on apricots, maintaining all other uses except kiwifruit. No data were available to support the ongoing use in kiwifruit and data should be requested from the registrants to support this use, if it is still required. Changes and additions to the *MRL Standard* will need to be made.

When treated commodities are fed to animals, there are no residues found in the animal tissues or in milk. Additions to Table 4 the *MRL Standard* will need to be made for fruit processing wastes identified in the review for the minor animal feeds of apple pomace, grape pomace and citrus peel/rind.

The current residue definition of azinphos-methyl *per se* was considered adequate. Analytical methods are available which address this residue definition.

The potential for prejudice to trade was found to be acceptable and not undue.

2.5 REPORT SUMMARIES

2.6 METABOLISM

Metabolism studies were submitted for consideration, including studies in apples, oranges, beans, sorghum, lettuce and cotton, as well as animal metabolism studies in rats, poultry, cattle and goats. The plant studies in beans, sorghum, lettuce and cotton were not considered in detail as there are no registrations in these commodities and the studies did not enhance the elucidation of the metabolism of azinphos-methyl any further. The studies in poultry were not considered, as poultry diet does not include possible treated commodities.

2.6.1 Apple metabolism

RMK 1-4: **Investigations of the Metabolism of Azinphos-methyl on Apples I. Determination of the ^{14}C-accountability and the Metabolite Pattern**. Dräger, G. (1987). Bayer AG, Institute for Metabolism Research, Monheim, 1987. Report Number PF 2916.

RMK 1-5: **The Metabolism of Azinphos-methyl In Apples**. Krolski, M.E. (1988). Mobay Corporation, Agricultural Chemicals Division, Kansas, USA. Report No. 95647.

BMK 1-1 **The Metabolism of Azinphos-methyl in Apples and Apple Cell Suspension Cultures.** Koerster, J.; Draeger, G.; Bornatsch, W; Brauner, A.; Kraussmann, E.U (1988). Bayer AG, Institute for Metabolism Research, Monheim. Report No MR 98534.

Apples growing outdoors were treated with [phenyl-UL-^{14}C] azinphos-methyl (WP 25) at a rate of 0.235 mg/apple (with a small brush). The tree was covered to protect it from rainfall. At days 7, 21 and 35 apples were harvested and separated into peel and pulp (Drager, 1987).

The concentration of residue (expressed as azinphos-methyl equivalents) decreased from 2.4 mg/kg on day 7 to 1.3 mg/kg on day 35, mainly due to weight gain of the fruit. The relative amount of radioactivity that was able to be rinsed from the surface decreased with time (from 91.8% on day 7 to 68.0% on day 35) while the levels of radioactive residues recovered in the peel and pulp increased (Table 30). This was mainly due to an increase of the level of the water soluble radioactivity in peel and pulp (from 3.7% on day 7 to 22.4% on day 35). Insoluble radioactivity accounted only for 5.2% on day 35.

Table 30: Distribution of radioactivity in different fractions of apple treated with [phenyl-UL-^{14}C]-azinphos-methyl (values in percent of recovered radioactivity)

Report	Rate	Crop	Crop Part/Fraction	Distribution of Radioactivity (%)		
				7 days[a]	21 days[b]	35 days [c]
Drager, G. 1987	0.235 mg a.i./apple	Apple	**Surface rinse**	91.8	79.8	68.0
			Peel			
			Organosoluble	1.7	1.7	1.9
			Water soluble	2.7	6.7	13.8

			Insoluble	0.9	3.4	3.5
			Total	5.3	11.8	19.2
			Pulp			
			Organosoluble	1.6	2.1	2.5
			Water soluble	1.0	4.8	8.6
			Insoluble	0.3	1.5	1.7
			Total	2.9	8.4	12.8

[a] 100% corresponds to 2.4 mg/kg azinphos-methyl equivalents.
[b] 100% corresponds to 1.9 mg/kg azinphos-methyl equivalents.
[c] 100% corresponds to 1.3 mg/kg azinphos-methyl equivalents.

The radioactivity rinsed from the apple surface corresponded exclusively to unmetabolised azinphos-methyl. In the organosoluble extracts from both peel and pulp, azinphos-methyl was the major compound. Unidentified metabolites accounted for a total of 0.3% on day 7 and 1.1% on days 21 and 35 (Table 31). In the water-soluble portion of the extracts of peel and pulp the concentrations of the same two compounds increased with time. On day 35 a conjugate of mercaptomethylbenzazimide with 2-(1-glucopyranosyl)-propionic acid (M19) amounted to 9.2%. The second major metabolite was desmethyl azinphos-methyl (MO2) and accounted for 6.0% of the recovered radioactivity. The structures of these two metabolites were identified in a later study (Koester *et al.,* 1988). In the water soluble fraction 7.3% was not identified.

Table 31: Distribution of metabolites (% of recovered radioactivity) in apples after application of [phenyl-UL-^{14}C] azinphos-methyl

Report	**Crop**	**Applic. Rate**	**Crop Part**	**Days After applicat**	**100%**	**Metabolites (% of recovered radioactivity) [1])**							
					mg/kg	**P**	**M01**	**MO2**	**M08**	**M12**	**M19**	**Unknown [2])**	**Remainder [3])**
Drager, G. 1987	Apple	0.235 mg a.i./ apple	Whole Apple	7	2.4	95.1	-	1.2	-	-	1.1	0.3	2.3
				21	1.9	82.5	-	2.4	-	-	4.1	1.1	9.4
				35	1.3	71.2	-	6.0	-	-	9.2	1.1	12.5
Krolski, M.E. 1988 a	Apple	0.25 mg a.i./ apple = 5.6 kg a.i./ha	Surface	0		98	-	-	<1	-	-	-	-
			Peel	0	1.15	1	-	-	<1	-	-	-	<1
			Pulp	0		-	-	-	-	-	-	-	<1
			Surface	7		87	-	-	-	-	-	-	-
			Peel	7	1.04	4	-	-	<1	-	-	<1	4
			Pulp	7		2	<1	-	-	-	-	<1	<1
			Surface	14		70	-	-	1	-	-	-	-
			Peel	14	0.86	10	<1	-	2	-	-	-	9
			Pulp	14		3	-	-	<1	-	-	<1	3
			Surface	21		66	-	-	2	-	-	-	-
			Peel	21	0.83-	11	-	-	(<1)	(2)	-	4	9
			Pulp	21		4		-	-	-	-	3	2

- not found ( ) found as conjugate (released by hydrolysis)

1) Identification of metabolites

P azinphos-methyl	M08 benzazimide
MOI azinphos-methyl oxygen analogue	MI2 anthranilic acid
MO2 desmethyl azinphos-methyl	M19 3-(3-thiomethyl benzazimido)-2-(1-glucopyranosil)-propionic acid

2) Organosoluble compounds not identified
3) Remaining radioactivity in water soluble and unextracted fractions (not identified)

In a separate study mature apples were treated with [phenyl-UL-^{14}C]azinphos-methyl (WP 35) at a rate corresponding to 5.6 kg a.i./ha (with a small brush). Apples were harvested 0, 7 ,14, 21 days post-treatment and separated into peel and pulp (Krolski, 1988).

The concentration of residue (expressed as azinphos-methyl equivalents) decreased from 1.15 mg/kg on day 0 to 0.83 mg/kg at the end of the study. The relative amount of radioactivity that was rinsed from the surface decreased from 98% on day 0 to 67.0% on day 21 while that in the peel and pulp increased (from < 1 to 33%, respectively) (Table 32).

Table 32: Distribution of radioactivity in different fractions of apple treated with [phenyl-UL-^{14}C]-azinphos-methyl (values in percent of recovered radioactivity)

Report	Rate	Crop	Crop Part/ Fraction	Distribution of Radioactivity (%)			
				0 days [1]	7 days	14 days	21 days
Krolski, M.E. -1988 a	0.25 mg a.i./apple = 5.6 kg a.i./ha	Apple	**Surface rinse**	98	88	72	67
			Peel				
			Extracted	1	5	12	15
			Insoluble	<1	4	9	9
			Total	1	9	21	24
			Pulp				
			Extracted	<1	2	4	7
			Insoluble	<1	<1	3	2
			Total	<1	2	7	9

1 100% corresponds to 1.15, 1.04, 0.86 and 0.83 mg/kg azinphos-methyl equivalents on days 0, 7, 14 and 21.

The radioactivity rinsed from the apple surface contained as the major compound unchanged azinphos-methyl (> 97%). With time, low amounts of benzazimide (M08) (2% on day 21) were also detected. The major compound extracted from peel and pulp was azinphos-methyl. Its concentration increased from 1 to 11% in the peel and from 0 to 4% in the pulp within the 21 day period. Trace amounts of azinphos-methyl oxygen analogue (MO 1) (<1%) were detected in the peel and pulp on days 14 and 7, respectively. In the peel additionally benzazimide (M08) was found (maximum concentration 2% on day 14). Unidentified radioactivity amounted to 4 and 3% in peel and pulp after 21 days, respectively. Hydrolysis of the 21 day peel solids resulted in release of benzazimide (M08) (< 1%) and anthranilic acid (M12) (2%).

From both studies it can be concluded that the major part of azinphos-methyl remains on the apple surface. Azinphos-methyl is slowly absorbed into the apple peel and pulp. In apples variety "James Grieve" azinphos-methyl only was found at a low concentration and was metabolised mainly to two water-soluble compounds (Dräger, 1987). These metabolites were also formed in apple cell suspension cultures and were identified as desmethyl azinphos-methyl (MO2) and a conjugate of mercaptomethylbenzazimide, ie. (3-(3-thiomethyl benzazimido)-2-(1-gluco-pyranosyl)-propionic acid (M19)) (Koester *et al.,* 1988)

The study confirmed that there was little metabolism of azinphos-methyl when applied as a topical treatment to apples.

A possible degradation pathway would involve cleavage at the thio phosphate ester group, leaving mercaptomethylbenzazimide, cleavage of the thiomethyl group leaving benzazimide and ring opening to form anthranilic acid.

2.6.2 Orange metabolism

RMK 2-8: **The Metabolism of Guthion in Oranges.** Gronberg, R.R.; Pither, K.M.; and Flint, D.R. (1975). Mobay Chemical Corporation. Report No 44756.

Oranges growing outdoors were treated with an emulsion of [carbonyl-^{14}C] azinphos-methyl (2L, 1.38 pints/ 100 gallons, corresponding to 0.173 L/100 L). The tree was protected from rainfall. Seven and 28 days post-treatment, oranges were harvested and separated into peel and pulp. The total radioactive residue 7 and 28 days post-treatment amounted to 0.51 and 0.62 mg/kg azinphos-methyl equivalents, respectively. Only 3.8 and 3.5% of these residues were recovered in the pulp. Due to the low quantity it was not characterised. The majority of the radioactivity (> 90%) was found in the peel. On day 7 the major part of radioactivity was organosoluble (46.6%); the second major part was insoluble (35.4%). Till day 28 the organosoluble radioactivity decreased to 29.5% whereas that of the insoluble fraction increased to 49.7%. Most of this fraction was released by repeated hydrolysis leaving 13.7 and 9.9% of the total recovered radioactivity as insoluble on days 7 and 28, respectively (Table 33).

Table 33: Distribution of radioactivity in various fractions of oranges treated with [carbonyl-^{14}C]-tzinphos-methyl (values in percent of recovered radioactivity)

Report	Rate	Crop	Crop Part	Distribution of Radioactivity (%)			
				after 7 days		after 28 days	
				A[1])	B[2])	A[1])	B[2])
Gronberg, R.R., Pither, K.M., Flint, D.R. 1975	not reported	Orange	Pulp	3.8	3.8	3.5	3.5
			Peel				
			Surface Rinse	5.6	-	1.1	-
			Organosoluble	46.6	67.5	29.5	49.1
			Water soluble	8.6	15.0	16.2	37.5
			Insoluble	35.4	13.7	49.7	9.9

1) Distribution after direct extraction
2) Distribution after repeated extraction and hydrolysis of the water soluble and insoluble fraction

In the organosoluble fraction the major part was unchanged azinphos-methyl, ie. 45.0 and 25.0% of the total radioactivity recovered on days 7 and 28, respectively. Metabolites were mostly conjugated and released by repeated hydrolysis of the water soluble and the insoluble residues. They comprised methylbenzazimide (M07), benzazimide (MO8) or hydroxymethylbenzazimide (M06) (amounting to a maximum of 10.0% on' day 28), anthranilamide (M13), anthranilic acid (M12) and benzamide (M14) (Table 34). Among the water-soluble radioactivity amounting to 15.0 and 37.5% (days 7 and 28, respectively) after the hydrolysis steps at least six compounds were detected but could not be identified.

It can be concluded that the presence of azinphos-methyl residues is limited to the orange peel (> 95%). Azinphos-methyl is hydrolysed in the peel and the benzazimide moiety is further metabolised to benzazimide (M08) or hydroymethylbenzazimide (M06), anthranilamide (M13), anthranilic acid (M12) and benzamide (M14). Mainly conjugated metabolites are found within the peel.

Table 34: Distribution of metabolites (% of recovered radioactivity) in oranges after application of [carbonyl-^{14}C[azinphos-methyl

Report	Crop	Applic. Rate	Crop Part	Days after Applic	100% = mg/kg	Metabolites (% of recovered radioactivity) [1])													
						P	MO1	M03	M04	M05	M07	M08	M12	M13	M14	M17	M18	Unknown[2]	Remainder[3]
Gronberg,R.R., Pither, K.M., Flint, D.R. 1975	Orange	0.173 I/ 1001	Peel	7	0.51	45.0	-	-	-	-	0.4	7.2 [4])	2.0	1.4	-	-	-	11.5	32.5 [5])
				28	0.62	25.0	-	-	-	-	-	10.0[4])	1.6	-	2.8	-	-	9.7	50.9 [6])

\- not found ( ) found as conjugate (released by hydrolysis)

1) Identification of metabolites (for structures see scheme given at the end of section 6.1)

M05	mercaptomethylbenzazimide	M13	anthranilamide
M07	methylbenzazimide	M14	benzamide
M08	benzazimide	M17	cysteinylmethylbenzazimide
MI2	anthranilic acid	Ml8	desmethyl azinphos-methyl oxygen analogue glucoside

2) Organosoluble compounds not identified

3) Remaining radioactivity in water soluble and insoluble fractions/unextractable solids (not identified)

4) Benzazimide or hydroxymethylbenzazimide

5) The water soluble residues amounted to 15% and consisted of at least 6 metabolites; radioactive residue in the pulp (3.8%) was not identified

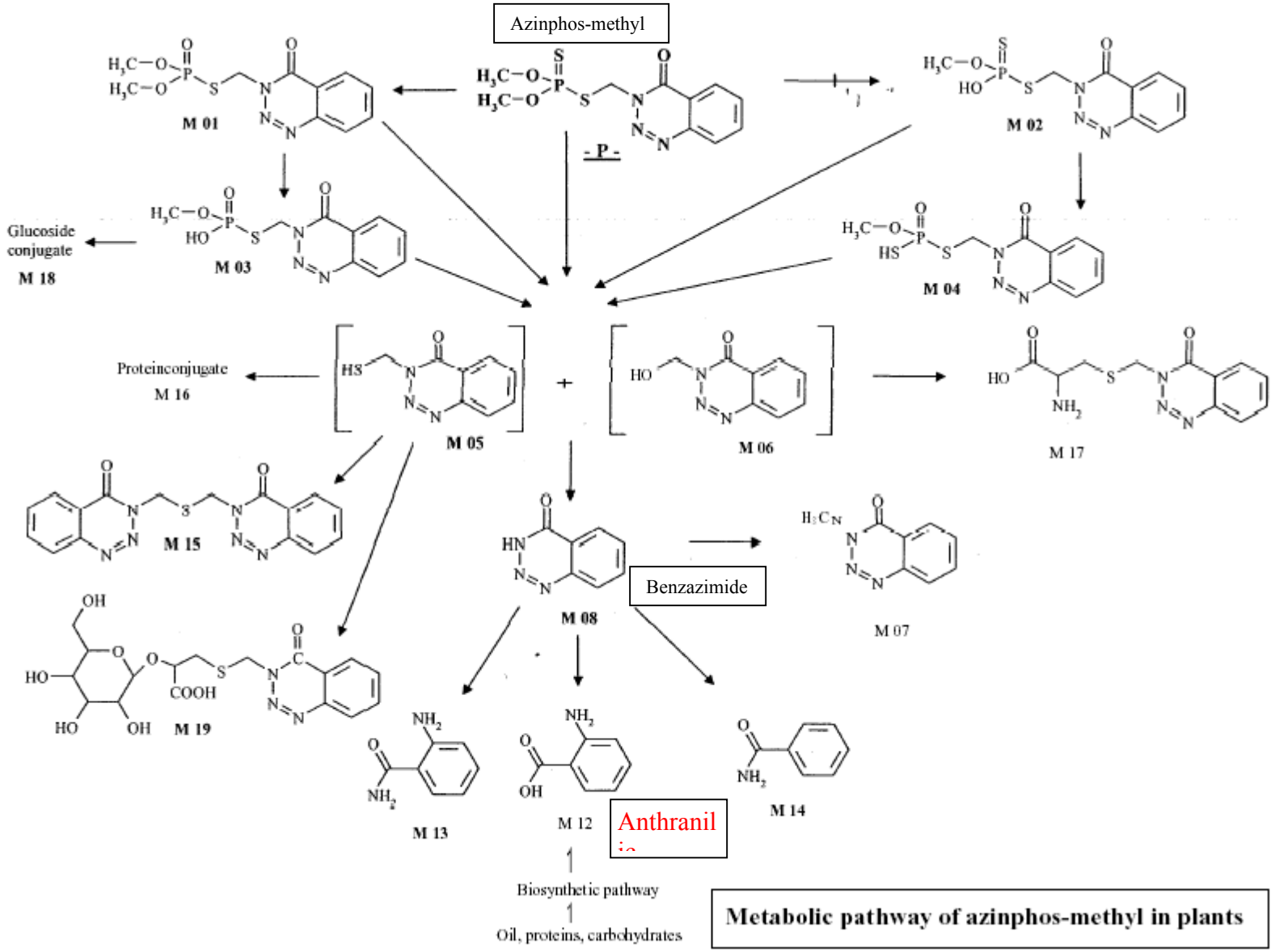
6) The water soluble residues amounted to 37.5% and consisted of at least 6 metabolites; radioactive residue in the pulp (3.5%) was not identified

2.6.3 Summary of Plant Metabolism

When azinphos-methyl is applied to plants, it predominantly remains on the plant surface (fruit skin or leaves) or in the peel (oranges). A large portion can easily be washed off by rain or irrigation. Under outdoor conditions and at high relative humidity, the rate of degradation on the surface of plants is higher than in the greenhouse.

When taken up into plant tissue, organosoluble compounds do not accumulate but azinphos-methyl is degraded to water-soluble metabolites initiated by hydrolysis of the ester linkage with the benzazimide moiety. Studies in plant cell cultures (apple) and intact plants reveal a similar metabolic pattern.

A number of chemicals were identified as possible metabolites that could occur when azinphos-methyl is applied to plants. The parent compound only has to be regarded as the residue of concern. A schematic representation of the metabolism of azinphos-methyl in plants follows.


Azinphos-methyl
M 01
M 02
- P -
Glucoside conjugate
M 18
M 03
M 04
Proteinconjugate
M 16
M 05
M 06
M 17
M 15
M 08
Benzazimide
M 07
M 19
M 13
M 12
Anthranil
M 14
Biosynthetic pathway
Oil, proteins, carbohydrates
Metabolic pathway of azinphos-methyl in plants

2.6.4 Animal metabolism

2.6.4.1 Summary of metabolism and kinetics in laboratory animals

Studies on rats showed a high degree of absorption of the radioactivity (three hours after oral dosing the concentration of radioactivity in the blood had reached its highest value) followed by fast elimination from the body. Thus, > 94% of the orally administered dose had been eliminated after two days. The bile-fistulated animals eliminated 27% of the applied amount with the bile within one day, of which more than 60% was eliminated within eight hours. Part of the radioactivity eliminated with the bile was subject to an enterohepatic circulation. The highest levels of radioactivity are found in highly perfused organs such as liver and kidney. Sixteen days post-application extremely low levels were found in all organs.

In metabolism studies, about 75% of the total dose was identified. The unidentified metabolites accounted for about 20% but none of the individual compounds constituted more than 5% of the total dose. The major compounds found in urine and faeces 48 hours post-application are methylsulfinylmethylbenzazimide (M10), methylsulfonylmethylbenzazimide (Ml1), cysteinylmethylbenzazimide sulfoxide (M20) and cysteinylmethylbenzazimide sulfone (M21). The first step in the process of degradation is cleavage of the organophosphorus ester with the benzazimide moiety followed by a methylation and oxidation reactions. Reactions catalysed by transferases produce the cysteine conjugates.

Benzazimide, a metabolite of azinphos-methyl, had a very similar biokinetic behaviour as the active substance itself. The radioactivity of benzazimide was fast and completely absorbed in the GIT; this was followed by fast elimination from the body. Within two days, > 99% of the orally administered dose was eliminated in urine and faeces. The highest' levels of radioactivity were found in the highly perfused elimination organs liver and kidneys. Ten days post-application extremely low levels of radioactivity were found in all organs.

2.6.4.2 Metabolism and kinetics in lactating farm animals

BR 1-2: **Nature and Extent of Guthion Residues in Milk and Tissues Resulting from Treated Forage.** Everett, L.J.; Anderson, C.A., and MacDougall, D. (1966). J. Agr. Food Chem. 14: 47-53.

RMK 4-15 **Metabolism of Azinphos-methyl in Lactating Goats.** Gromberg, R.R.; Lemke, V.J. and Lasley, M.B. (1988). Mobray Corporation, Kansas, USA. Report No 95649

The metabolism of azinphos-methyl was studied with [^{32}P]-labelled and [methylene-^{14}C]-labelled azinphosmethyl in lactating cows and with [phenyl-UL-^{14}C]azinphos-methyl in lactating goats.

Two lactating cows each of 364 kg weight were orally administered with a single dose of [^{32}P]azinphos-methyl at a rate of 5.0 mg/kg body weight or with a single dose of [methylene-^{14}C]azinphos-methyl (2.66 mg/kg). These doses corresponded to about 70 and 37 mg azinphos-methyl per kg green forage, respectively. In the [^{32}P]-study blood and milk were sampled regularly; urine and faeces were sampled at time of elimination. The cow was sacrificed after five days. Samples of tissues and organs were removed and analysed for total radioactive residues. In the [^{14}C]-study only milk was sampled and analysed for residues.

In the blood no organosoluble residues were present in samples containing the highest level of radioactivity indicating that azinphos-methyl was rapidly hydrolysed; in urine at least six different water soluble metabolites were detected. The radioactivity in the milk rose rapidly within the first 24 hours and remained at this level through 48 hours and then declined. The maximum radioactivity was found in the 24 hour sample amounting to 2.16 mg azinphos-methyl equivalents per litre; only 0.003 mg/1 of the radioactivity corresponded to organosoluble compounds. Five days after dosing [^{32}P]azinphos-methyl, kidneys and liver contained the highest concentrations of radioactive residues amounting to 0.57 and 1.46 mg azinphos-methyl equivalents per kg; thereof 0.06 and 0.10 mg/kg were organosoluble, respectively.

In the [^{14}C]-study the organosoluble radioactivity in the milk decreased within 20 hours to a level of about 40%, while the water-soluble portion increased to about 60%; this ratio remained constant till the end of the study on day 3. About 68% of the water soluble radioactivity was identified as lactose indicating that the methylene group of azinphos-methyl was metabolised and incorporated into sugars. The remaining unidentified radioactivity is supposed also to be incorporated into naturally occurring substances.

Two lactating goats (41 and 62 kg) received daily oral treatments of [phenyl-UL-^{14}C]azinphos-methyl in form of gelatine capsules on three consecutive days after milking in the afternoon. The dose of 0.5 mg/kg body weight corresponds to approximately three times the tolerance level in registered crops. Milk was collected in the morning and afternoon. About 17 hours after the last treatment the animals were sacrificed; the excreta were not analysed (Gronberg *et al.,* 1988). The results of the study are given in Table 35.

Table 35: Distribution of total radioactive residue (azinphos-methyl equivalents) and metabolites in different organs, tissues and milk after oral application of [phenyl-UL-^{14}C]azinphosmethyl to lactating goats (values are given in percent)

Report	Dose mg/kg bw	Time (days)	Compound [3]	Distribution of Compound (%) [1]				
				Milk [2]	Liver	Kidney	Muscle	Fat
Gronberg,R.R.	3 x 0.5	3	Parent	0	0	0	0	5
			Cl	5	0	2	0	0
			C2	4	0	1	0	0
			C3	0	<1	0	0	1
			C4	7	1	2	2	0
			C5	42	8	19	33	40
			C6	4	<1	1	0	3
			C7	1	0	1	0	0
			C8	9	2	2	7	8
			C9	5	1	1	5	3
			C10	9	<1	11	<1	0
			C11	0	4	0	3	0
			C12	11	83	58	50	40
			Loss	3	0	2	0	0
			Total	100	100	100	100	100
			mg/kg 4	**0.08**	**0.75**	**0.30**	**0.07**	**0.04**

1 Average from both goats
2 Milk sample of day 3, morning
3 Parent azinphos-methyl (P): structures are given in the scheme at the end of section 5.1
CI desmethyl isoazinphos-methyl (M04)

C2 desmethyl azinphos-methyl oxygen analogue (M03)
C3 methylthiomethylbenzazimide (M09)
C4 methylsulfinylmethylbenzazimide (M10)
C5 methylsulfonylmethylbenzazimide (Ml1)
C6 benzazimide (M08)
C7 benzamide (M14)
C8 benzamide type conjugate, benzamide was released on base hydrolysis
C9 methylbenzazimide type conjugate, anthranilic acid was released on base hydrolysis
C 10 unknown compounds each representing ### 4% of the residue
C11 water soluble activity that was not characterised
C12 methylbenzazimide type structures conjugated with protein which were released by protease enzyme

4 Values corresponding to azinphos-methyl equivalents

The amounts of milk produced by the goats did not differ significantly before and after administration of azinphos-methyl. The levels of radioactive residues recovered in the milk from both goats were very comparable. About 16 hours after oral administration the milk sampled in the morning contained 0.07 to 0.08 mg/l azinphos-methyl equivalents. In the milk sampled 24 hours after administration the levels ranged from 0.03 to 0.04 mg/l. Unchanged azinphos-methyl was not found in the milk; desmethyl isoazinphos-methyl (M04) and desmethyl azinphos-methyl oxygen analogue (M03) amounted to 5 and 4% of the residue. The major compound was methylsulfonylmethylbenzazimide (Ml 1) and accounted for 42%. Other compounds identified were metabolites of the benzazimide moiety released by hydrolysis of the organophosphorus ester; these metabolites partly were conjugated.

The levels of radioactivity recovered in the different tissues from both goats were nearly equivalent as were the amounts and patterns of metabolites. Unchanged azinphos-methyl was detected only in fat (5% of total residue in fat); desmethyl isoazinphos-methyl (M04) and desmethyl azinphos-methyl oxygen analogue (M03) were detected only in kidney (2 and 1%) and milk (5 and 4%). The major compound identified in each tissue and organ was methylsulfonylmethylbenzazimide (Ml1) (8 to 40%). Up to 83% of the residue of each sample was a methylbenzazimide type structure conjugated with protein (C12).

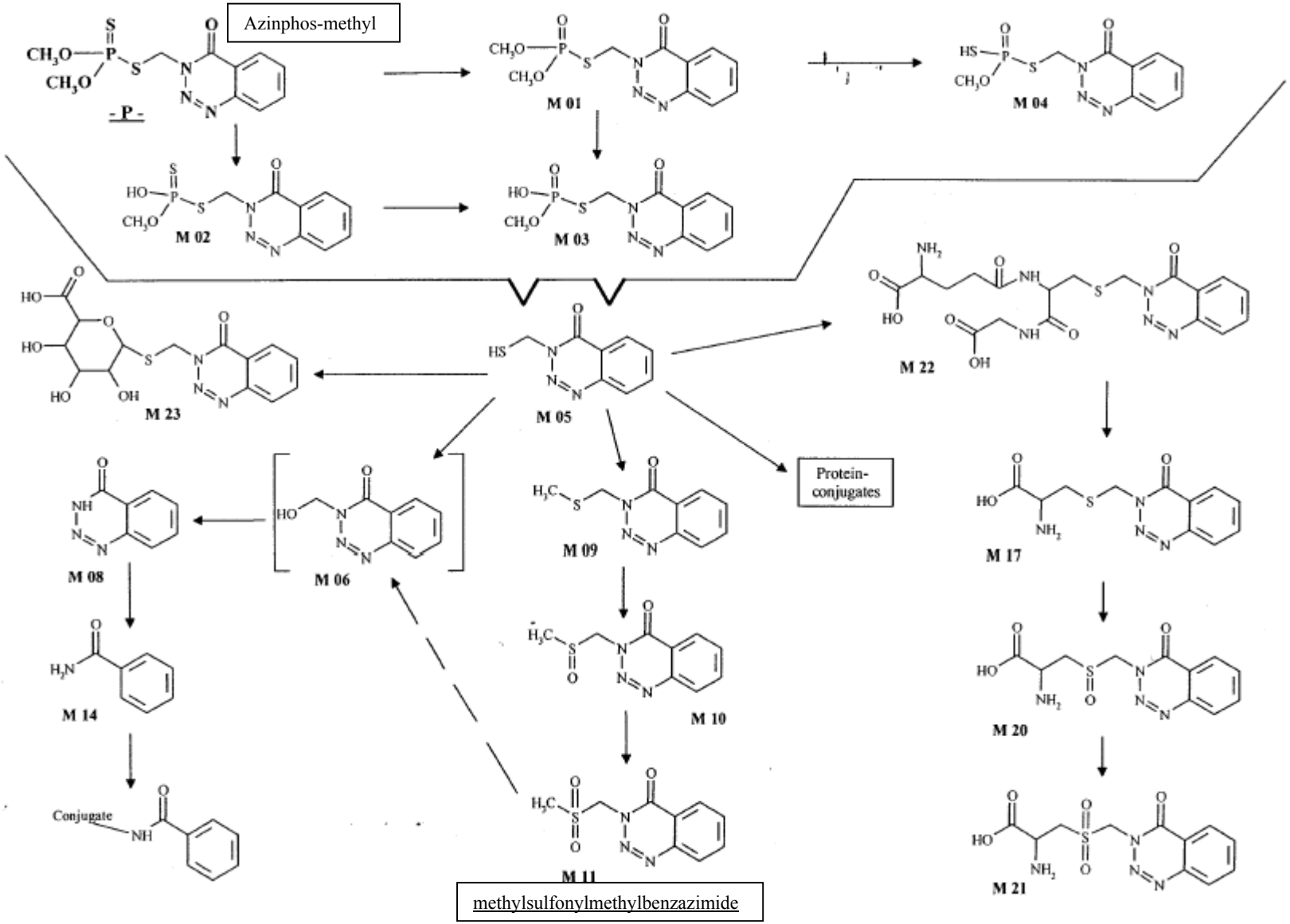
A proposed metabolic pathway in lactating goats is given at the end of the summary. The first step in the process of degradation of azinphos-methyl (P) is the cleavage of the organophosphorus ester bond probably yielding mercaptomethylbenzazimide (M05) and/or hydroxymethylbenzazimide (M06). A major part of these hydrolysis products is conjugated with the protein fraction of tissues and organs and to a limited extent with milk protein. Mercaptomethylbenzazimide (M05) undergoes methylation to methylthiomethylbenzazimide (M09). Oxidation of the sulfur atom yields methylsulfinylmethylbenzazimide (M10) and methylsulfonylmethylbenzazimide (Ml1). Further metabolism of the benzazimide structure yields benzamide (M14). By a minor pathway azinphos-methyl is transformed to desmethyl isoazinphos-methyl (M04) and desmethyl azinphosmethyl oxygen analogue (M03).

2.6.5 Summary on the metabolism in lactating ruminants

In the [^{32}P]-study in blood samples no organosoluble residues were present indicating that azinphos-methyl is rapidly hydrolysed. In the [^{14}C]-study < 1% of the total dose was recovered in the milk within three days. The [^{14}C]-methylene group of azinphos-methyl was metabolised and incorporated into sugars and probably other naturally occurring substances. In the metabolism study with lactating goats unchanged azinphos-methyl only was found in the fat tissue. After three days the major metabolite found in liver, kidney, muscle and fat was methylsulfonylmethylbenzazimide (M11). A great portion of the residue (up to 83% of the

radioactivity in the liver) was found conjugated with the protein fraction. It was identified as methylbenzazimide type structures. Essentially the same metabolites as in the tissues are found in milk (with the exception of unchanged azinphosmethyl that was found only in fat tissue). The first step in degradation is cleavage of the organophosphorus ester yielding mercaptomethylbenzazimide (M05) that is methylated and oxidised as well as conjugated to protein.

Figure: Proposed metabolism of azinphos-methyl in animals



2.7 ANALYTICAL METHODS

There were 12 Studies submitted relating to analytical methods for plant materials, including colorimetric and gas chromatographic methods. There were also 3 photofluorometric, gas chromatographic or liquid chromatographic methods submitted in support of animal tissues and milk. These methods are shown in Table 36.

Table 36: Summary of analytical methods used for the determination of azinphos-methyl in plant and animal material.

Method (reference)	Sample material	Extraction solvent	Clean-up	% recovery and fortifications	LOQ (mg/kg)
Plant material					
Colorimetric Determination Of Guthion Residues In Crops. (Meagher, W.R.*et al*., 1960)	Cottonseed, cole crops and fruit	Acetone	Acidification and chloroform partitioning	80-100+ for range 0.05 to 1.0 mg/kg	0.15
Improved Multiresidue Gas Chromatographic Determination Of Organophosphorus, Organonitrogen, And Organohalogen Pesticides In Produce, Using Flame Photometric And Electrolytic Conductivity Detectors. (Luke *et al.* 1981)	Fruit and vegetables	Acetone	Solvent partitioning	None given	Not given
Colorimetric Determination Of Guthion Residues In Plant Material. (Adams 1959)	Green fruit and vegetables	Chloroform after acidification	Alumina column	65-100+ for range 0.2 to 0.5 mg/kg	0.1
Method For Gas Chromatographic Determination Of Residues Of Azinphos-Methyl And Demeton-S-Methyl-Sulfone In Plant Material. (Seym 1992)	Apples, pears and peaches	Acetone	Silica-gel	80-102 for range 0.04 – 1.0 mg/kg	0.04
Determination Of Residues Of Guthion M-E In Soybeans By Thermionic Emission Gas Chromatography. (Olson 1969)	Soybeans	Chloroform	Solvent partitioning	72-100+ for range 0.025-0.05 mg/kg	0.005
Gas Chromatographic Method For Determination Of Guthion Residues In Plant Material. (Westburg & Becker 1981)	Moist crops containing chlorophyll and oilseed crops	Crops: acetone Oilseed: Pet ether	Solvent partition and column chromatography	82-111 for 1.0 mg/kg	?
Interference Study For Azinphos-Methyl In Plant Material. (O'Neil and Howard 1990)	Pure standards	NA	NA	NA	NA
Animal tissues and milk					
Spectrophotofluorometric Method For Guthion Residues In Milk And Animal Tissues. (Adams and Anderson 1966)	Milk and tissues	Acetone	Alumina column	79-116 for 0.1-0.4 mg/kg	0.005-0.03

Method (reference)	Sample material	Extraction solvent	Clean-up	% recovery and fortifications	LOQ (mg/kg)
Organochlorine And Organophosphorus Pesticides. DFG-Method S10 Of The DFG-Method Compellation. "Manual Of Pesticide Residue Analysis". (Specht *et al.* 1976)	Tissues, eggs and milk	Soxhlet extraction with pet ether	Solvent partition + florisil column	Not given	?
A Method For The Determination Of Guthion And Guthion Oxygen Analog In Bovine Tissues And Milk Utilising Gas Chromatography And High Pressure Liquid Chromatography. (Wargo *et al* 1978)	Tissues and milk	Acetone and dichloromethane	Solvent partition	53-111 for 0.005-0.1 mg/kg	0.001-0.01
Confirmatory Procedure For The Analytical Residue Method For Guthion And Guthion Oxygen Analog In Bovine Tissues And Milk. (Wargo *et al* 1978)	Tissues and milk	Acetone and dichloromethane	Solvent partition	NA	NA
Photofluorometric Method For The Determination Of Guthion Residues In Milk And Animal Tissue. (Adams 1961)	Tissues and milk	Acetone	Solvent partition	79-106 for 0.1-0.4 mg/kg	0.01-0.02

Most methods determine the parent compound only, while some include the oxygen analogue. The USEPA currently has listed the methods of Wargo *et al* (1978) and Westburg and Becker (1981) as their reference methods. These methods both utilize gas chromatography as the quantifying instrumentation, with extraction occurring with solvent. Both methods would be acceptable for monitoring for azinphos-methyl in plant or animal material. The reference to the methods can be found at http://www.epa.gov/oppbead1/methods/ram12b.htm.

2.8 MAGNITUDE OF RESIDUES IN CROPS, LIVESTOCK AND PROCESSED COMMODITIES

Residues data were submitted for many commodities, including almond, apple, apricot, cotton, grapefruit, grape, lemon, nectarine, orange, peach, pear, pecan, plum, potato and walnut. Data were also retrieved from archives for macadamia and litchi. As azinphos-methyl is not registered for almonds, cotton, pecan, potato and walnut, no consideration was given to these. All others will be considered in this review under the groupings of the *MRL Standard*.

2.8.1 Pome Fruit (apples, pears)

RR 1-2: Residue Trials With Gusathion MS In Apples In Germany. Anonymous (1975). (In German). Bayer Leverkusen Trial Nos 4206-08/75.

RR 1-3: Residue Trials With Gusathion MS WP In Apples In Germany. Anonymous (1978). (In German). Trial No 4201/78.

RR 1-4: Residue Trials With Gusathion MS In Apples In Germany. Anonymous (1982). (In German). Trial Nos 4200-82, 4201-82, 4208-82, 4210-82.

RR 1-5: Residue Trials With Gusathion 200 EC In Apples In France. Anonymous (1984). (In German). Trial Nos 4300-84, 4301-84.

RR 1-6: Residue Trials With Gusathion MS In Apples In France. Anonymous (1991). (In German). Trial Nos 0525-91, 0526-91.

RR 1-7: Residue Trials With Gusathion MS In Apples In Portugal. Anonymous (1982). (In German). Trial Nos 4206-82, 4207-82.

RR 2-22: Residue Trials With Gusathion MS In Pears In Germany. Anonymous (1982). (In German). Trial Nos 4203-82, 4204-82, 4209-82, 4211-82.

RR 2-23: Residue Trials With Gusathion MS In Pears In France. Anonymous (1982). (In German). Trial No 0527-91

RR 2-24: Residue Trials With Gusathion 35 WP In Pears In South Africa. Anonymous (1986). South African Bureau of Standards Report No 311/88966/C123.

Schedule 1: Determination of residues of azinphos-methyl in apples. Clark, DV and Shields, R (1989). Analchem Consultants. Confidential report.

Trial details and results for all apple and pear trials are shown in Table 37.

Table 37: Residues of azinphos-methyl in whole fruit following treatment and sampling of <u>pome fruit</u> in both Europe, South Africa and Australia.

Crop	Location	Dates	Formulation	No of applic^{n}s (interval)	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Residues of azinphos-methyl (mg/kg)	Refs
Apple	Germany	1975, 1978	MS (25%)	5-6 (12-14 days)	0.05-0.1	1000-2000	0	0.87, 1.07, 0.82, 2.5	4206/75 4207/75 4208/75 4201/78
							7	0.55, 0.55, 0.71	
							14	**0.29, 0.15, 0.18, 1.1**	
							21	0.24, 0.24, 0.14, 0.74	
							28	0.19, <0.01, 0.09, 0.64	
							35	0.47	
		1979, 1982	WP (25%)	4-5 (14-15 days)	0.05	1500	0	3.2, 0.85, 0.40, 1.3	4200/82 4201/82 4208/82 4210/82
							10	1.4, 0.15, 0.23, 0.39	
							21	0.42, <0.01, 0.15, 0.52	
							28	0.22, 0.05, 0.21	
							35	0.22, 0.08, 0.20	
	France	1984	EC 200	5 (14 days)	0.04	800	12	0.18, 0.20	4301-84 4300-84
		1991	MS (25%)	3 (21 days)	0.044	1000	0	0.30, 1.2	0526-91 0525-91
							14	**0.11, 0.27**	
							28	<0.04, 0.31	
	Portugal	1982	MS (25%)	5 (21 days)	0.087-0.1	700	0	0.32, 0.32	4206-82 4207-82
							14	**0.17, 0.29**	
							28	0.04, 0.08	
							35	0.04, 0.07	
							42	0.05, 0.06	
	Australia	1988	FL 350	13 (14 days)	0.05	600	**14**	**0.8**	Schedule 1
Pear	Germany	1982	MS (25%)	5 (14-21 days)	0.05	1500	0	0.49, 0.18, 0.98, 1.7	4203-82 4204-82 4209-82 4211-82
							10	0.25, 0.08, 0.09, 0.91	
							21	0.09, 0.07, 0.03, 0.61	
							28	0.07, 0.01, 0.02, 0.40	
							35	0.04, 0.02, 0.28	
	France	1991	MS (25%)	3 (21 days)	0.044	1000	0	0.31	0527-91
							14	**0.11**	
							28	<0.04	
	South Africa	1985	WP 35	3 (18 days)	0.015	1200	0	0.84	311/88966 /C123
							7	0.21	
							12	0.29	
							22	0.21	
							28	0.14	
							35	0.06	
							42	<0.05	

Note: Values in bold indicate figures used for determining STMR in pome fruit.

At the withholding period of 14 days, the residues found in pome fruit in all trials were 0.11, 0.11, 0.15, 0.17, 0.18, 0.27, 0.29, 0.29, 0.8 and 1.1 mg/kg, following treatment at intervals between 14 and 21 days. The STMR value for pome fruit is 0.225 mg/kg and the maximum value is 1.1 mg/kg azinphos-methyl. All residues complied with the current MRL of 2 mg/kg and the MRL is considered to be appropriate.

The stage of development of the fruit at the time of final treatment was not able to be determined from the German language trial data sheets and not all trials incorporated the Australian GAP of treatment rate or interval between treatments.

2.8.2 Citrus Fruits (grapefruit, lemon and orange)

RR 1-10: Azinphos-Methyl (2S, 2L, 35WP) - Magnitude Of The Residue On Grapefruits. Leslie WL (1990). Mobay Corporation. Report No 100074.

RR 1-12: Azinphos-Methyl (2S & 35WP) - Magnitude Of The Residue On Lemons. Leslie WL (1990). Mobay Corporation. Report No 100076.

RR 2-14: Azinphos-Methyl (2S, 2L, 35WP) - Magnitude Of The Residue On Oranges. Leslie WL (1990). Mobay Corporation. Report No 100075.

Trial details for all orange, lemon and grapefruit trials are shown in Table 38. No Australian trial data were available.

Table 38: Details of trials to measure residues of azinphos-methyl on citrus fruit following treatment.

Crop	Location	Date	Formulation	No of applic^{n}s (interval)	Rate (kg ai/100L)	Volume (L/ha)	Refs
Grapefruit	California	1988	2S	2 (29 days)	0.277	1270	M100074
	Florida	1987-88	2L	2 (29 days)	0.072	4676	
	California	1988	35 WP	2 (29 days)	0.180	1270	
	Florida	1987-88	35 WP	2 (29 days)	0.072	4676	
Lemon	California	1988	2S	2 (21 days)	0.359	935	M100076
	California	1988	35 WP	2 (26 days)	0.280	1215	
Orange	California	1988	2S	2 (26 days)	0.277	1215, 1870	M100075
	Florida	1987-88	2L	2 (29 days)	0.072	4676	
	California	1988	35 WP	2 (26 days)	0.180	1215, 1870	
	Florida	1987-88	35 WP	2 (29 days)	0.072	4676	

Fruit were sampled and the pulp and skin separated and analysed separately. Fruit at the time of sampling were described as "mature". The above information concerning rate was worked out using the unclear data and trial sheets included in the submitted report. The JMPR[18] recording of the same data confirmed that the rate of application was 3.36 kg ai/ha, with varying volumes of water, and would give equivalent rates of 71-359 g ai/100L. The results of the analyses are shown in Table 39, and include whole fruit results scaled down to the Australian rate of 49 g ai/100L.

[18] Pesticide Residues in Food – 1991. Volume 113/1. Evaluations 1991 Part I - residues

At the withholding period of 14 days, the unscaled residues found in citrus fruit in all trials were 0.15, 0.22, 0.25, 0.28, 0.32, 0.37, 0.48, 0.53, 0.55, 0.64, 0.83 and 0.85 mg/kg, following treatment at intervals of 21 –29 days. The STMR value for citrus fruit is 0.42 mg/kg and the maximum value at 14 days is 0.85 mg/kg azinphos-methyl. Residues complied with the current MRL of 2 mg/kg and this value is considered appropriate.

Table 39: Compilation of residues data following use of azinphos-methyl on citrus fruit

Fruit	Application No	PHI (days)	Residue (mg/kg)			
			Rind	Pulp	Whole fruit	Scaled fruit result
Grapefruit	1	3	<0.01, 9.2, 0.11, 3.09	<0.01, <0.01, <0.01, 0.06	<0.01, 1.7, 0.03, 0.69	
		7	0.79, 3.1, 0.20, 2.2	0.01, 0.02, <0.01, 0.08	0.17, 0.78, 0.05, 0.53	
		14	1.3, 1.5	0.03, 0.07	**0.25, 0.37**	**0.18, 0.26**
	2	**14**	1.08, 2.5, 1.04, 3.0	0.06, 0.02, 0.05, 0.03	**0.32, 0.55, 0.28, 0.64**	**0.06, 0.39, 0.05, 0.44**
		21	3.8	0.02	0.85	
Lemon	1	3	0.90, 0.71	0.02, 0.06	0.46, 0.32	
		7	0.69, 0.89	0.04, <0.01	0.36, 0.33	
	2	**14**	1.7, 1.5	0.03, 0.02	**0.83, 0.53**	**0.12, 0.09**
Orange	1	3	0.75, 3.54, 0.24, 3.39	0.02, 0.12, 0.01, 0.27	0.22, 0.90, 0.07, 0.98	
		7	0.30, 5.0, 0.24, 4.01	0.02, 0.09, 0.01, 0.27	0.09, 1.2, 0.07, 1.05	
	2	**14**	0.52, 3.4, 0.74, 1.66	0.01, 0.08, <0.01, 0.05	**0.15, 0.85, 0.22, 0.48**	**0.03, 0.58, 0.06, 0.33**

Note: Values in bold indicate figures used for determining STMR in citrus fruit.

2.8.3 Stone Fruit (apricot, nectarine peach, plum)

RR 1-8: Residue Trials With Gusathion 35 WP In Apricots In South Africa. Anonymous (1986). South African Bureau of Standards. Report No 311/88029/C340.

RR 2-13: Determination Of Residues Of Gusathion 25 WP In/On Nectarine Under Actual Use Conditions In Italy. Seym M (1993). Bayer AG Report No RA-2082/92.

RR 2-15: Residue Trials With Gusathion 200 EC In Peaches In France. Anonymous (1984). (In German). Trial Nos 4302-84, 4303-84.

RR 2-16: Determination Of Residues Of Gusathion 25 WP In/On Peach Under Actual Use Conditions In Italy. Seym M (1993). Bayer AG Report No RA-2083/92.

RR 2-17: Determination Of Residues Of Gusathion MS In/On Peach Under Actual Use Conditions In Spain. Seym M (1993). Bayer AG Report No RA-2086/91

RR 2-18: Residue Trials With Gusathion 35 WP In Peaches In South Africa. Anonymous (1986). South African Bureau of Standards Report No 311/88974/C195.

RR 2-19: Residue Trials With Gusathion 35 WP In Peaches In South Africa. Anonymous (1991). South African Bureau of Standards Report No 311/88103/H266.

RR 2-20: Residue Trials With Gusathion 35 WP In Peaches In South Africa. Anonymous (1991). South African Bureau of Standards Report No 311/88102/H265.

RR 2-21: Residue Trials With Gusathion 35 WP In Peaches In South Africa. Anonymous (1992). South African Bureau of Standards Report No 311/88297/J86.

RR 3-26: Residue Trials With Gusathion MS In Plums In Germany. Anonymous (1975). Trial Nos 4200/75, 4201/75, 4202/75.

RR 3-27: Azinphos-Methyl (2S & 35 WP) - Magnitude Of The Residue In Plums/Prunes. Leslie WL (1990). Mobay Corporation Report No 100079.

No data was submitted for cherries, but data was available in the 1991 JMPR review that were referenced.

Table 40: Residues of azinphos-methyl in whole fruit following treatment and sampling of stone fruit in both Europe and South Africa.

Crop	Location	Dates	Form	No of applic^{n}s (interval)	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Residues of azinphos-methyl (mg/kg)	Refs
Apricots	South Africa	1985-86	WP	1	0.05, 0.10	2500	0	4.2, 5.6	311/88029/ C340
							7	0.29, 0.56	
							14	**0.14, 0.15**	
							28	<0.05, 0.05	
							35	<0.05	
Nectarine	Italy	1992	25 WP	2 (20 days)	0.075	1500	0 (pre spray)	0.14, <0.04	RA-2082/92
							0 (post spray)	0.60, 0.51, 0.72	
							7	0.42, 0.30	
							15	**0.24, 0.12**	
							20	0.18, 0.08, 0.14	
Peach	France	1984	EC 200	3 (14-20 days)	0.040	1400	**15**	**2.6**	4302-84 4303-84
							28	0.06	
	Italy	1992	25 WP	2 (21 days)	0.075	1500	0 (pre spray)	0.23, 0.16	RA-2083/92
							0 (post spray)	0.86, 0.96	
							7	0.66, 0.45	
							15	**0.25, 0.29**	
							20	0.14, 0.28	
	Spain	1991	27.5 WP (MS)	2 (21 days)	0.040	1500	0	1.4, 1.1	RA-2086/91
							14	**0.76, 0.20**	
							28	0.24, 0.06	
	South Africa	1986	35 WP	2 (7 days)	0.0175	3000	0	2.7	311/88947/ C195
							7	0.78	
							14	**0.26**	
							21	0.16	
							29	0.10	
							35	0.10	
							42	0.05	
		1990, 1991	35 WP	3 (14 days)	0.025, 0.050	2000, 3000	0	2.4, 4.9, 1.6, 2.4, 1.3, 2.0	311/88103/ H266
							7	1.3, 2.3, 0.73, 1.9, 0.57, 0.76	311/88102/ H265
							10	1.4, 3.2, 0.64, 1.7, 0.56, 1.2	311/88104/ H267
							14, 15	**0.78, 1.7, 0.56, 1.0, 0.42, 0.60**	
							21, 22	0.26, 1.8, 0.21, 0.38, 0.45, 0.36	
							21 canned	<0.01, <0.01, <0.01, <0.01	
		1992	35 WP	2-3 (25 days)	0.025	3500	0	1.4, 2.8	311/88297/J 86
							0 canned	0.02	
							3	0.87, 2.0	
							7	0.30	
							14	**0.33**	
							21	0.30	
							21 canned	<0.02	
							28	0.12	

Crop	Location	Dates	Form	No of applic^{n}s (interval)	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Residues of azinphos-methyl (mg/kg)	Refs
	Germany	1982	25 WP	5 (14 days)	0.050	1500	0	2.0, 0.18	4203-82
							10	0.81, 0.08	4204-82
							21	0.30, 0.07	
							28	0.19, 0.01	
							35	0.20, <0.01	
		1982	25 WP (MS)	4 (14 days)	0.050	1500	0	0.98, 1.7	4209-82
							10	0.09, 0.91	4211-82
							21	0.03, 0.61	
							28	0.02, 0.40	
							35	0.02, 0.28	
Plum	Germany	1975	MS	3 (14 or 28 days)	0.050	1500	0	0.22, 0.24, 0.09	4200/75
							7	0.11, 0.17, 0.08	4201/75
							14	**0.04, 0.03, 0.04**	4202/75
							21	0.08, 0.10, 0.02	
							28	0.06, 0.09, 0.02	
	USA	1988	2 SC	3 (10 days)	0.036-0.485	5028	7	0.73, 2.8, 0.46	M100079
							14	**0.89, 0.02, 0.47**	
					4.766	Aerial – 50-100	7	0.11, 0.99	
							14	**<0.01, 0.45**	
			WP	3 (10 days)	0.045-0.485	5028	7	0.28, 0.45, 2.2, 0.47	
							14	**0.37, 0.44, 1.8, 0.48**	
						Aerial 50-100	7	0.16, 0.03	
							14	**0.14, 0.02**	
Prune	USA	1988	WP	3 (10 days)	0.045-0.485	5028	7	0.57	
							14	**0.43**	
						Aerial 50-100	7	0.02	
							14	**<0.01**	
Cherry	Canada	?	50 WP	3-5 (?)	0.88 kg ai/ha	?	0	2.9, 2.4, 2.4, 2.1	JMPR 1991
							7	1.3, 1.6, 0.7, 1.3	
							14	**0.59, 0.60, 0.06, 0.10**	
	USA	?	50 WP	2-5	0.56-0.84 kg/ha	?	7	1.7, 0.05, 0.46, 0.18, 0.57, 0.31, 0.16, 0.21, 1.6, 0.42, 0.75, 0.51	
			360 FL				**14**	**0.40, <0.02, 0.42, 0.11, 0.20, 0.75, 0.30, 0.11, 1.4, 0.52, 0.93, 0.29**	
							21	0.24, 0.08, 0.39, 0.34, 0.38,	

Note: Values in bold indicate figures used for determining STMR in stone fruit.

At the withholding period of 14 days, the residues found in stone fruit in all trials were <0.01, <0.01, <0.02, 0.02, 0.02, 0.03, 0.04, 0.04, 0.06, 0.10, 0.11, 0.11, 0.12, 0.14, 0.14, 0.15, 0.20, 0.20, 0.24, 0.25, 0.26, 0.29, 0.29, 0.30, 0.33, 0.37, 0.40, 0.42, 0.42, 0.43, 0.44, 0.45, 0.47, 0.48, 0.52, 0.56, 0.59, 0.60, 0.60, 0.7, 0.75, 0.78, 0.89, 0.93, 1.0, 1.4, 1.7, 1.8 and 2.6 mg/kg, following treatment at intervals between 10 and 28 days. The STMR value for stone fruit is

0.33 mg/kg and the maximum value is 2.6 mg/kg azinphos-methyl. The value of 2.6 mg/kg in peaches did not demonstrate compliance with the present Australian MRL of 2 mg/kg. Therefore, reconsideration needs to be given to setting a separate MRL for peaches at 5 mg/kg azinphos-methyl.

2.8.4 Grapes

RR 1-11: Determination Of Residues Of Gusathion 25 WP In/On Grape Under Actual Use Conditions In Italy. Seym M (1994). Bayer AG Report No RE-2084/92.

Reference: Relationship between Azinphos-methyl Usage and Residues in Grapes and in Wine in Australia. Goodwin S and Ahmad N (1998). Pestic Sci 53: 96-100.

Trial detail and results are shown in Table 41 and 42.

Table 41: Residues of azinphos-methyl in grapes following treatment at 0.050 kg ai/100L.

Crop	Location	Dates	Form	No of applic^{n}s (interval)	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Residues of azinphos-methyl (mg/kg)	Refs
Grape	Italy	1992	WP 25	2 (?)	0.050	1000	0	0.41-1.6	RA-2084-92
							7	0.24-0.35	
							15	**0.10-0.21**	
							20	<0.04-0.61	
	Australia	1993-95	WP 35, SC 20	2 (7 days)	0.042	Air blaster, hand spray	0-28	See below	Goodwin and Ahmad

Table 42: Residues of azinphos-methyl in grapes (n=3) following treatment by either air-blast or hand-held sprayer at various application rates.

Treatment (kg ai/100L)	Azinphos-methyl residue (mg/kg) (±SE)					
	Week 1	Week 2	Week 3	Week 4	Week 5	Wine*
Air-blast sprayer - WP						
0.0245	0.376±0.06	0.830±0.50	*0.259±0.02	0.117±0.10	0.081±0.06	0.032
0.042	0.712±0.21	0.633±0.37	***0.721±0.45**	0.226±0.07	0.201±0.07	0.041
0.084	1.154±0.05	0.802±0.32	*0.909±0.62	0.437±0.25	0.202±0.07	0.107
Air-blast sprayer – SC						
0.024	0.502±0.25	0.507±0.23	*0.234±0.06	0.115±0.04	0.113±0.06	0.019
0.048	0.713±0.11	0.868±0.32	***0.767±0.38**	0.226±0.06	0.277±0.02	0.017
0.096	1.931±0.18	1.079±0.36	*1.910±0.63	0.985±0.11	0.955±0.12	0.160
Hand sprayer – WP						
0.0245	3.81±1.20	2.21±0.90	1.96±0.20	*1.61±0.50	1.64±0.05	0.188
0.042	9.67±2.50	7.09±1.80	4.15±3.90	*4.34±2.60	2.05±0.70	0.519
0.084	15.54±4.40	10.52±0.70	8.73±0.30	*3.31±1.60	2.79±0.50	1.754
Hand sprayer – SC						
0.024	4.26±0.70	3.83±0.70	3.04±0.4	*1.95±0.5	2.04±0.3	0.199
0.048	11.66±1.8	8.14±1.7	5.81±1.8	*2.41±0.3	2.27±0.3	0.504
0.096	15.94±6.5	13.32±0.7	10.26±0.8	*2.36±3.4	2.98±0.3	1.588

* - Wine was made from these batches of grapes.

Following storage of the wine at 4° for 12 months, there were no detectable residues present.

The hand spray results are not normal industry practice and will not be considered in affirming the MRL. The maximum residue, at 14 days and later, for the label rate of 0.050 g ai/kg is 0.767 mg/kg whilst the STMR is unable to be estimated as details of individual data were not available. The MRL of 2 mg/kg for grapes is considered adequate.

2.8.5 Macadamias

Summary data were submitted for macadamias from trials conducted in Australia. Detailed submissions were retrieved from archives dated 1992, when use was first registered. Details of the trials and results are shown in Table 43.

Table 43: Residues in macadamia kernals following treatment with azinphos-methyl.

Crop	Location	Dates	Form	No of applic^{n}s (interval)	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Residues of azinphos-methyl (mg/kg)	Refs
Macadamia	QLD	1988-89	WP 350	9 (14-16 days)	0.049	High	**7**	**<0.01**	14/89a
							14	<0.01	
							21	<0.01	
	QLD	1988-88	WP 350	9 (14-16 days)	0.098	High	**7**	**<0.01**	14/89b
							14	<0.01	
							21	<0.01	

These data support the present MRL of *0.01 mg/kg with a WHP of 7 days.

2.8.6 Litchis

Summary data were submitted for litchis from 6 trials conducted in Australia. Detailed submissions were retrieved from archives dated 1992, when use was first registered. Details of the trials and results are shown in Table 44.

Table 44: Residues in litchis following treatment at 49-98 g/100L.

Crop	Location	Dates	Form	No of applic^{n}s (interval)	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Residues of azinphos-methyl (mg/kg)	Refs
Litchi	NSW	1987-89	WP 350	1-3 (6-13 days)	0.049	High	0	0.3	90/87a; 9/88a; 24/89a
							1	**1.0**	
							3	0.1	
							5	0.2	
							7	0.1, 0.4	
							10	0.1	
							14	0.2, 0.6, <0.05	
							21	<0.05	
	NSW	1987-89	WP 350	1-3 (6-13 days)	0.098	High	0	0.9	90/87b; 9/88a; 24/89b
							1	**0.8**	
							3	0.2	
							5	0.3	
							7	<0.1, 1.1	
							10	0.1	
							14	0.7, 0.3	
							21	0.5	

No further data were available to determine an STMR at the WHP of 1 day, nor to estimate with reasonable confidence the maximum residue at the WHP. There was also no significant difference between the residues from the 2 application rates. From the data it appears that

residues do not decline over the period examined (viz 21 days) at either application rate and that residues could exceed the maximum of 1 mg/kg. Residues could be expected to comply with the MRL of 2 mg/kg.

2.8.7 Blueberries

As no data were submitted for blueberries, a minor crop, the data used in the 1991 JMPR review were referenced to enable the use to continue. Limited data were also available from the PACSC report of November 1986, held by the APVMA Chemistry and Residues Program. Details of the trials are shown in Table 45.

Table 45: Residues in blueberries following treatment with azinphos-methyl.

Crop	Location	Dates	Form	No of applic^{n}s (interval)	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Residues of azinphos-methyl (mg/kg)	Refs
Blueberry	Tasmania	1985-86	50% ?	2 (?)	0.55 kg ia/ha	?	32	<0.05	PACSC
	USA	?	35 WP 24 SC	3 (?)	0.84 kg ai/ha	?	0	10.5, 8.9, 0.22, 7.4, 0.80, 9.1, 0.30	JMPR
							3	8.6, 6.6, 0.14, 3.5, 0.63, 1.3, 0.60	
							7	3.6, 2.2, 0.11, 4.6, 0.59, 4.3, 0.64	
							14	1.03	

None of these data support the Australian GAP of 49g ai/100L with a WHP of 14 days. Indications from available labels which describe the Australian GAP are that the Australian rate is 1500L/ha, and this is equivalent to 15x49=735g ai/ha, which is only slightly lower than that used by the USA. The residues data above do not demonstrate compliance with the current Australian MRL of 1 mg/kg and by extrapolation would require an MRL of 2 mg/kg with a 14 day WHP. However, there is only the one data point at 14 days, and the confidence about this figure would be unacceptable. The JMPR recommended, on the basis of the data, an MRL of 5 mg/kg with a PHI of 7 days. The CRP is of the opinion that this MRL and WHP should be adopted, in harmonisation with that of Codex, where a CXL of 5 mg/kg was adopted in 1995.

2.8.8 Residues in processed commodities

RR 6-49: Azinphos-Methyl (Guthion 2S Formulation) - Magnitude Of The Residue In Unprocessed Apples And Apple Processed Commodities. Grace TJ (1990). Mobay Corporation, North Carolina. Report No M100081.

RR 7-50: Azinphos-Methyl (Guthion 2L Formulation) - Magnitude Of The Residue In Unprocessed Cottonseed And Cottonseed Processed Commodities. Grace TJ (1990). Mobay Corporation, North Carolina. Report No 100080.

RR 7-51: Azinphos-Methyl (Guthion 2S Formulation) - Magnitude Of The Residue In Unprocessed Grapes And Grape Processed Commodities. Grace TJ (1990). Mobay Corporation, North Carolina. Report No 100084.

RR 7-52: Azinphos-Methyl (Guthion 2L Formulation) - Magnitude Of The Residue In Unprocessed Oranges And Orange Processed Commodities. Grace TJ (1990). Mobay Corporation, North Carolina. Report No M100085.

RR 8-53: Azinphos-Methyl Residue Determinations In Olive Samples, As Well As In The Respective Oils And Aqueous Phases, Coming From Field Trials, Carried Out In

Italy With Gusathion 25 PB. Fabbrini R (1992). Bayer Italia, Milan. Report No BAY-07/92.

RR 2-20: Residue Trials With Gusathion 35 WP In Peaches In South Africa. Anonymous (1991). South African Bureau of Standards Report No 311/88102/H265.

RR 2-21: Residue Trials With Gusathion 35 WP In Peaches In South Africa. Anonymous (1992). South African Bureau of Standards Report No 311/88297/J86.

RR 5-30: Summary Of Residue Data On Raw Agricultural Commodities/Processed Commodities Used As Animal Feeds- Potential For Secondary Residues In Animal Tissues And Products. Leslie WL (1990). Mobay Corporation, North Carolina. Report No M100100.

Reference 1: Reduction of azinphos-methyl, chlorpyrifos, esfenvalerate and methomyl residues in processed apples. Zabik MJ *et al* (2000). J Agric Food Chem 48: 4199-4203.

Data for apples, oranges, peaches and grapes were evaluated for this review, as these commodities are all registered uses for the active. Data for cottonseed and olives were not evaluated. Details and data are shown in Table 46.

Table 46: Effect of processing on residues of azinphos-methyl in apples, peaches, citrus and grapes.

Fruit	Location	Form	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Commodity	Residues of azinphos-methyl (mg/kg)	Residues* scaled for application rate (mg/kg)	Refs
Apple	USA	2S	2.677	313	0	Whole fruit	3.74		100081
						Wet pomace	7.64		
						Dry pomace	21.84	0.41	
						Juice	1.26		
	USA	WP	1.176 kg/ha	?	6	Whole fruit	0.34, 0.32		Ref 1
						Slices	0.025, 0.058		
						Juice	0.023, 0.016		
					24	Whole fruit	0.24, 0.16		
						Slices	0.012, 0.016		
						Juice	0.005, 0.008		
					34, 37	Whole fruit	0.068, 0.109, 0.174		
						Slices	0.007, <0.004, 0.058		
						Juice	<0.004, <0.004, 0.030		
Grape	USA	2S	0.056-.179	468-1505	0	Whole fruit	1.88		100084
						Wet pomace	5.75	5.75	
						Dry pomace	1.66		
						Juice	1.90		
					7	Whole fruit	0.19		
						Raisins (sun dried)	0.29		
						Raisins (oven dried)	0.72		
						Raisin waste (Sun dried)	4.00		
						Raisin waste	2.43		

Fruit	Location	Form	Rate (kg ai/100L)	Volume (L/ha)	PHI (days)	Commodity	Residues of azinphos-methyl (mg/kg)	Residues* scaled for application rate (mg/kg)	Refs
						(Oven dried)			
Peach	South Africa	WP	0.025, 0.05	2000-3500	21	Whole fruit	0.21, 0.38, 0.30		311/88103/H266
						Canned fruit	<0.01, <0.01, <0.02		311/88102/H265
			0.025	3500	0	Whole fruit	2.8		311/88104/H267
						Canned fruit	0.02		311/88297/J86
Orange	USA	2L	0.92	366	7	Whole fruit	4.66		100085
						Wet pulp	0.02		
						Dry pulp	0.02		
						Peel	5.57	0.30	
						Juice	<0.02		
						Oil	34.71		
						Molasses	0.61		
Orange	USA	2S, 2L, WP	0.071-0.274	1215-4676	14	Rind	0.52, 3.4, 0.74, 1.66	0.09, 2.4, 0.21, 1.15	M100075
						Pulp	0.01, 0.08, <0.01, 0.05		
						Whole fruit	0.15, 0.85, 0.22, 0.48		
Lemon	USA	2S, WP	0.28-0.36	1160-1215	14	Rind	1.7, 1.5	0.24, 0.26	M100076
						Pulp	0.03, 0.02		
						Whole fruit	0.83, 0.53		
Grape-fruit	USA	2S, 2L, WP	0.071-0.287	935-4676	14	Rind	1.3, 1.5, 1.08, 2.5, 1.04, 3.0	0.91, 1.03, 0.19, 1.75, 0.19, 2.10	M100074
						Pulp	0.03, 0.07, 0.06, 0.02, 0.05, 0.03		
						Whole fruit	0.25, 0.37, 0.32, 0.55, 0.28, 0.64		

The data demonstrate that most of the residues were contained in the rind/peel for all citrus fruits. Processing of apples and grapes resulted in the concentration of residues in the pomace, while in peaches canning left very little residue in the canned fruit.

The data generated at times other than the equivalent to the WHP of 14 days could misrepresent the true effect of processing at 14 days. This is especially true for the apple data, where exaggerated applications rates were used to produce some of the data above. The ratio of azinphos-methyl in pomace to whole apple for this exaggerated trial is 5.8. Applying this factor to the Ref 1 data (highest residue 1.1 mg/kg), the highest residue expected in apple pomace would be 6.4 mg/kg. The scaled data for citrus, which was generated at various rates compared with the Australian rate of 49 g ai/100L, indicated the highest residue likely to occur in citrus peel/rind at 14 days PHI is 2.4 mg/kg. From the above data, the highest residue likely to occur in grape pomace is 5.8 mg/kg azinphos-methyl at the time of treatment, but no data were available at the WHP of 14 days. The ratio of pomace to whole grape is 3.05

and applying this to the data in Section 3.4 gives an average residue in grape pomace at 14 days PHI of 2.3 mg/kg.

The data demonstrate that residues of azinphos-methyl can be reduced by processing. Overall, the data indicate that for orange, apple and peach, most of the residues are on the skin and are removed with the skin. Highest residues to occur on minor animal feed commodities were 6.4 mg/kg in apple pomace, 2.3 mg/kg in grape pomace, and 2.4 mg/kg in citrus peel/rind.

2.8.9 Residues in animal tissues and milk following consumption of treated commodities

RR 5-31: The Effect Of Feeding Guthion To Dairy Cattle. Wargo JP (1978). Mobay Corporation Colorado. Report No 66448

RR 5-32: Residue Experiment: Guthion, Cattle Tissues And Milk. Anonymous (1978). Mobay Corporation, Colorado. Report No 66449.

RR 5-33: Residue Experiment: Guthion, Cattle Liver And Milk. Anonymous (1978). Mobay Corporation, Colorado. Report No 66450.

RR 5-34: Residue Experiment: Guthion, Cattle Liver And Milk. Anonymous (1978). Mobay Corporation, Colorado. Report No 66451.

RR 5-35: The Effect Of Daily Oral Administration Of Guthion To Cattle At Doses Of 5 And 15 ppm For 30 Days. Crawford CR and Anderson RH (1973). Baychem Corporation. Report No 35408.

Data were also presented for poultry and eggs, but as the commodities represented by present registrations were not considered as poultry foods, these data were not evaluated. Three levels of azinphos-methyl (11, 33 and 77 ppm) were fed to cattle in alfalfa pellets for 28.5 days. Samples were analysed for the presence of azinphos-methyl and its oxygen analogue. Residues were <0.01 mg/kg in all tissues, including muscle, fat, liver and kidney. Residues in all milk samples were <0.001 mg/kg. Residues in animal feeds demonstrate that residues of azinphos-methyl for citrus, apple and peach, are on the skin and are removed with the skin. Highest residues to occur on these minor animal feed commodities were 6.4 mg/kg in apple pomace, 2.3 mg/kg in grape pomace, and 2.4 mg/kg in citrus peel/rind. The STMR-P values for these commodities are 0.41, 2.3 and 0.54 mg/kg for apple pomace, grape pomace and citrus peel/rind, respectively. These commodities form no more than 20% of the diet of cattle, sheep or pigs. The following Table 47 shows the calculations regarding the maximum feeding levels for cattle, based on the above residues for in these minor commodity groups.

Table 47: Calculations of the theoretical maximum anticipated dietary exposure and maximum feeding level (MFL) for cattle.

Feed group	Feed commodity	% in the diet	Feed intake, kg/animal/day[a]	STMR-P mg/kg	% DM[b]	Intake of chemical X, mg/animal/day[c]	Proposed MRL (mg/kg)
Fruit by-products	Apple pomace, dry	20	4	0.41	100	1.64	8
	Grape pomace, dry	20	4	2.3[d]	100	9.2	4
	Citrus pulp	20	4	0.54	100	2.16	3

[a]Based on assumed feed consumption of 20 kg dry matter/day
[b]Estimate of percentage dry matter. Applied to MRLs expressed on a fresh weight basis
[c]Based on assumed bodyweight of 500 kg
[d]Not an STMR-P as only a mean and standard deviation were available for 6 results in Section 3.4

Maximum anticipated dietary exposure:	9.2 mg/animal/day
equivalent to:	0.0184 mg/kg bw
equivalent to:	0.46 ppm in the diet
MFL (Based on the available animal feeding data (Attachment 2)):	77 ppm in the diet
equivalent DDIL:	3.08 mg/kg bw

As feeding levels up to 77 ppm in feed produce no residues in cattle tissues or milk, the levels found in these processing commodities should not produce residues in animal tissues and milk, as they are well below the 77 ppm fed experimentally. However, the MRLs proposed above, which are much lower than the maximum experimental level, reflect the GAP about these processed commodities.

2.8.10 Storage Stability

RR 8-54: Stability Of Guthion Residues During Frozen Storage. Adams JM (1961). Chemagro Corporation. Report No 6973.

RR 8-55: Raw Data And Chromatograms For The Storage Stability Study For Guthion And Guthion Oxygen Analog From Bovine Tissues And Milk. Unknown author and date. Mobay Corporation. Report No 66447.

RR 8-56: Storage Stability Study For Guthion And Guthion Oxygen Analog In Bovine Liver And Milk. Pollock RJ (1978). Mobay Chemical Corporation. Report No 66446.

RR 8-57: The Effect Of Frozen Storage At 0 To -10°F On Guthion Residues In Apples. Author unknown (1977). Mobay Chemical Corporation. Report No 52589.

RR 8-58: The Effect Of Frozen Storage At 0 To -10°F On Guthion Residues In Pears. Author unknown (1977). Mobay Chemical Corporation. Report No 52938.

RR 8-58: Effect Of Frozen Storage On Guthion Residues In Various Crops. Author unknown (1962). Mobay Chemical Corporation. Report No 8682.

Reference: Degradation of the insecticide azinphos-methyl in orange and peach juices during storage at different temperatures. Kyriakidis NB *et al* (2001. Food Addit. Contamin. 18: 309-313

The results from the above studies are summarised in Table 48.

Table 48: Effect of storage at –18°C to –24°C on stability of azinphos-methyl residues in food commodities.

Commodity	Initial analysis		Final analysis		% change
	Residue (mg/kg)	Date	Residue (mg/kg)	Date	
Green beans	1.46	14/3/60	2.5	21/6/61	+71
	1.07	31/7/61	1.10	28/2/62	+3
Currants	4.78	10/2/60	2.73	21/6/61	-43
	2.15	10/2/60	2.89	21/6/61	+34
Spinach	26.5	11/3/59	26.8	21/6/61	+1
Blueberries	10.89	1/2/60	11.3	21/6/61	+4
	4.24	1/2/60	4.55	21/6/61	+7
	2.27	1/2/60	1.64	21/6/61	-28
Milk	0.912, 0.902	23/3/78	0.914, 0.75, 0.787	20/4/78	-10
Liver	0.898, 1.187	23/3/78	0.853, 0.910, 0.930, 0.904	21/4/78	-14
Liver	1.05	?	0.88	+ 4 weeks	-16
Milk	0.92	?	0.83	+ 2 weeks	-10
Apples	1.0	30/4/73	0.69	24/2/77	-31

Commodity	Initial analysis		Final analysis		% change
	Residue (mg/kg)	Date	Residue (mg/kg)	Date	
Pears	1.0	24/4/73	1.02	22/3/77	+2

The data indicate that azinphos-methyl residues are reasonably stable in the commodities when frozen at –18 to –24°C.

A separate study into the effect of temperature on the stability of azinphos-methyl in orange and peach juices (Kyriakidis NB *et al*) indicated that residues were relatively stable at 0°C and 20°C, with half-lives of 450 and 90 days respectively, but unstable at 40°C, with a short half-life of 7 days.

2.8.11 Carry-over of residues in rotational crop studies

RMK 1-1: Guthion-^{14}C Residues In Field Rotational Crops From Aged Soil (Interim Report). Gronberg RR (1976). Mobay Chemical Corporation. Report No 48668.

RMK 1-2: Guthion Residues In Field Rotational Crops. Groberg RR and Morris RA (1979). Mobay Chemical Corporation. Report No 67271.

RR 1-3: (Phenyl-Ul-^{14}C) Azinphos-Methyl Rotational Crop Study. Chopade HM and Bosnak LL (1990). Mobay Corporation, Kansas. Report No 99849.

Three separate studies into the carry-over were presented. However, the crops for which registration is current are not crops that are replanted or are at risk from carryover of residues. Therefore the above three studies were not evaluated.

APPENDIX 1: MRL HISTORY TABLE

Date	Commodity	MRL (mg/kg)	Comments
1962	Fruit	2	
	All other products	1	
1963	Fruit	2	
	All other uses	1	
1968	Fruits	2	
1971	Pastures	–	Should not result in residues in or on human food
1974	Pastures	–	Should not result in residues in or on human food
1976	Grapes	2	Minor use consideration
1978	Oilseeds	*0.05	Established for azinphos ethyl not methyl; use pattern on Gusathion A product label
1978	Kiwifruit	2	Whole fruit (*0.05 mg/kg for edible portion)
1986	Raspberry	1	Tasmanian request for blueberries and raspberries
	Blueberry	1	
	Milk products	*0.05	Delete NDR in pasture uses

The history table shows that the existing MRLs for oilseeds and animal commodities seem to be related to registered uses for azinphos ethyl; records show that the Gusathion A label included uses for oilseeds and pastures. The MRL for raspberries is not related to a registered or permit approval of azinphos-methyl.

APPENDIX 2: CHRONIC DIETARY INTAKE CALCULATION

Azinphos methyl

Calculation of NEDI

ADI for azinphos-methyl = 0.025 mg/kg of body weight)

Commodity	Food Consumption g/kg bw/day		MRL/STMR mg/kg	NEDI mg/kg bw/day	% of ADI	comments
FB 0204 Blueberries	0.029		5	0.00014500	0.6%	All berries consumption
FC 0001 Citrus fruits	2.1336		0.45	0.00096012	3.8%	STMR used
MO 0105 Edible offal (mammalian)	0.0136	*	0.05	0.00000068	0.0%	assume nil residues
FB 0269 Grapes	0.7939		2	0.00158780	6.4%	includes wine
FI 0341 Kiwifruit	0.0225		2	0.00004500	0.2%	
FI 0343 Litchi	0.0256		2	0.00005120	0.2%	Strawberry consumption
TN 0669 Macadamia nuts	0.0082	*	0.01	0.00000008	0.0%	Pecan consumption used.
MM 0095 Meat [mammalian]	1.7294	*	0.05	0.00008647	0.3%	assume nil residues
ML 0106 Milks	8.9933	*	0.05	0.00044967	1.8%	assume nil residues
FP 0009 Pome fruits	1.1687		0.225	0.00026296	1.1%	STMR used
FS 0012 Stone fruits	0.2788		0.33	0.00009200	0.4%	STMR used
Total				0.003680979	mg/kg bw/day	

* At or about the limit of determination

** Equivalent to 14.7 % of the ADI

These calculations have been made in accordance with 'Guidelines for Predicting Dietary Intake of Pesticide Residues' (World Health Organization)

NEDI - National Estimate of Dietary Intake
Mean body weight 67 kg
ADI - Acceptable Daily Intake
(Chemicals Safety Unit, Commonwealth Department of Human Services and Health)

MRL - Maximum Residue Limit
STMR - Supervised Trial Median Residue

APPENDIX 3: ACUTE DIETARY EXPOSURE – 2 YEARS AND OVER

Azinphos-methyl Acute Dietary Intake _ 2 years + Date 20/06/2005

Acute RfD	0.075 mg/kg bw

Commodity

Code	Name	MRL mg/kg	STMR or STMR-P, mg/kg	Process factor	HR or HR-P, mg/kg	Large portion, g/kg bw	Body weight, kg	Large portion, kg	Unit weight, g	% edible portion	Unit weight, edible portion, kg	Variability factor	Case	NESTI, mg/kg bw/day	% acute RfD
FB 0204	Blueberries	2			5	3.249	67	0.218	1.8	100	0.002	3	Case 1	0.0162	21.7
FC004	Oranges, raw (including peeling)	2			0.85	5.761	67	0.386	131	73	0.096	3	Case 2a	0.0073	9.8
FC 0203	Grapefruit (raw)	2			0.85	4.6269	67	0.310	256	49	0.125	3	Case 2a	0.0071	9.5
FC 0204	Lemon, raw (including peel)	2			0.85	0.734	67	0.049	108	67	0.072	3	Case 2b	0.0019	2.5
FC 0206	Mandarin, raw	2			0.85	5.1881	67	0.348	168	74	0.124	3	Case 2a	0.0076	10.1
MO 0105	Edible offal (mammalian)	0.05			0.05	2.927	67	0.196			0.000	3	Case 1	0.0001	0.2
FB 0269	Grapes	2			0.77	7.657	67	0.513	8	100	0.008	3	Case 1	0.0059	7.9
FI 0341	Kiwifruit	2			2	3.403	67	0.228	76	97	0.074	3	Case 2a	0.0112	14.9
FI 0343	Litchi	2			1	2.937	67	0.197	16	100	0.016	3	Case 1	0.0029	3.9
TN 0669	Macadamia nut	0.01			0.01	0.35	67	0.023	2.4	100	0.002	3	Case 1	0.0000	0.0
MM 0095	Meat [mammalian]	0.05			0.05	7.791	67	0.522			0.000	3	Case 1	0.0004	0.5
ML 0106	Milks	0.05	0.05			29.654	67	1.987			0.000		Case 3	0.0015	2.0
FP 0226	Apple, raw, unpeeled	2			1.1	6.328	67	0.424	138	92	0.127	3	Case 2a	0.0111	14.8
FP 0230	Pear, raw, unpeeled	2			1.1	6.149	67	0.412	166	98	0.163	3	Case 2a	0.0121	16.1
FS 0240	Apricot, raw	2			2	8.442	67	0.566	35	96	0.034	3	Case 2a	0.0189	25.2
FS 0245	Nectarine, raw, unpeeled	2			2	9.015	67	0.604	136	92	0.125	3	Case 2a	0.0255	34.0
FS 0247	Peach, raw, unpeeled	5			2.6	8.029	67	0.538	98	87	0.085	3	Case 2a	0.0275	36.7
FS 0248	Plum, raw	2			1.8	7.029	67	0.471	66	94	0.062	3	Case 2a	0.0160	21.3
FS 0244	Cherry, raw	2			1.4	3.731	67	0.250	4.5	85	0.004	3	Case 1	0.0052	7.0

Case 1. Composite sampling data reflect the residue level in the food, based upon HR or HR-P
Case 2. Composite residue data do not reflect the residue level in individual food commodity units.
Case 2a. Unit weight edible portion is less than large portion weight.
Case 2b. Unit weight edible portion exceeds large portion weight.
Case 3. Processed commodity, where bulking or blending means that the STMR-P represents the likely highest residue

APPENDIX 4: ACUTE DIETARY EXPOSURE CALCULATIONS – 2-6 YEARS

_Azinphos-methyl Acute Dietary Intake _ 2-6 years Date 20/06/2005

Acute RfD	0.075 mg/kg bw

Commodity

Code	Name	MRL mg/kg	STMR or STMR-P, mg/kg	Process factor	HR or HR-P, mg/kg	Large portion, g/kg bw	Body weight, kg	Large portion, kg	Unit weight, g	% edible portion	Unit weight, edible portion, kg	Variability factor	Case	NESTI, mg/kg bw/day	% acute RfD
FB 0020	Blueberries	2			5	9.474	19	0.180	1.8	100	0.002		Case 1	0.0474	63.2
FC004	Oranges, raw (including peeling)	2			0.85	17.776	19	0.338	131	73	0.096	3	Case 2a	0.0237	31.6
FC 0203	Grapefruit (raw)	2			0.85	0	19	0.000	256	49	0.125	3	Case 2b	0.0000	0.0
FC 0204	Lemon, raw (including peel)	2			0.85	0	20	0.000	108	67	0.072	3	Case 2b	0.0000	0.0
FC 0206	Mandarin, raw	2			0.85	18.7158	19	0.356	168	74	0.124	3	Case 2a	0.0270	36.0
MO 0105	Edible offal (mammalian)	0.05			0.05	0.847	19	0.016			0.000	3	Case 1	0.0000	0.1
FB 0269	Grapes	2			0.77	18	19	0.342	8	100	0.008	3	Case 1	0.0139	18.5
FI 0341	Kiwifruit	2			2	1.333	19	0.025	76	97	0.074	3	Case 2b	0.0080	10.7
FI 0343	Litchi	2			1	9.474	19	0.180	16	100	0.016	3	Case 1	0.0095	12.6
TN 0669	Macadamia nut	0.01			0.01	1.168	19	0.022	2.4	100	0.002	3	Case 1	0.0000	0.0
MM 0095	Meat [mammalian]	0.05			0.05	13.715	19	0.261			0.000	3	Case 1	0.0007	0.9
ML 0106	Milks	0.05	0.05			76.325	19	1.450			0.000		Case 3	0.0038	5.1
FP 0226	Apple, raw, unpeeled	2			1.1	17.474	19	0.332	138	92	0.127	3	Case 2a	0.0339	45.2
FP 0230	Pear, raw, unpeeled	2			1.1	24.268	19	0.461	166	98	0.163	3	Case 2a	0.0455	60.7
FS 0240	Apricot, raw	2			2	35.368	19	0.672	35	96	0.034	3	Case 2a	0.0778	103.7
FS 0245	Nectarine, raw, unpeeled	2			2	15.895	19	0.302	136	92	0.125	3	Case 2a	0.0581	77.5
FS 0247	Peach, raw, unpeeled	5			2.6	17.053	19	0.324	98	87	0.085	3	Case 2a	0.0677	90.2
FS 0248	Plum, raw	2			1.8	8.684	19	0.165	66	94	0.062	3	Case 2a	0.0274	36.5
FS 0244	Cherry, raw	2			1.4	13.158	19	0.250	4.5	85	0.004	3	Case 1	0.0184	24.6

Case 1. Composite sampling data reflect the residue level in the food, based upon HR or HR-P
Case 2. Composite residue data do not reflect the residue level in individual food commodity units.
Case 2a. Unit weight edible portion is less than large portion weight.
Case 2b. Unit weight edible portion exceeds large portion weight.
Case 3. Processed commodity, where bulking or blending means that the STMR-P represents the likely highest residue

3 ENVIRONMENTAL ASSESSMENT SUMMARY

3.1 ENVIRONMENTAL EXPOSURE

3.1.1 Environmental Release

3.1.1.1 Application and Use Pattern.

Azinphos-methyl is registered for use on orchard crops (pome and stone fruits, citrus) for the control of codling moth, lightbrown apple moth, oriental fruit moth, bryobia mite, pear and cherry slug, aphids, scale, root borer, curculio beetle and Fullers rose weevil. Other crops on labels are grapes, blueberries, kiwifruit, litchis and macadamias. These use patterns are to control similar insects as for orchard crops as well as fig longicorn and elephant weevil on grapes and macadamia nut-borer and fruit-spotting bug on litchis and macadamias. The maximum use rates stated on the labels (tree butt and soil drench) correspond to 98 g ac/100 L, but most rates correspond to 36-49 g ai/100 L. Greater than 90% is used in various orchard crops.

Normal practice in orchards situations is to spray to runoff, normally requiring 1500-3000 L/ha of spray solution for mature pome and stone trees, but this could be as high as 4000 L/ha for larger trees and in citrus 6000-10,000 L/ha. These figures correspond to application rates of between 735 g ac/ha and 1470 g ac/ha for most pests, but could be as high as 2940 g ac/ha for 98 g ac/100 L at 3000 L/ha. For citrus the maximum application rates correspond to 2.9-4.9 kg ac/ha again based on 49 g ac/100 L spray.

The use pattern in pome fruit, as stated on the label, is with the emergence of first codling moth in October or as dictated by pest monitoring. Directions for scale in stone fruit is at early bud swell. For citrus, at least two scheduled summer applications (say December & February) are recommended, and on macadamias and litchis the label notes pest numbers as the trigger to regular spray schedules. For blueberries directions are to apply at 14 day intervals after flowering. The label directions generally have 2-3 week intervals between spray applications.

Azinphos-methyl is also currently used for macadamias and a range of other minor crops. The Agricultural Assessment Report indicates that use in citrus and grapes is very low. The primary registrant indicates that use in grapes is limited only to the Hunter Valley (NSW) for longicorn beetle and elephant weevil control.

3.1.1.2 Pome Fruit

Apples are a major orchard crop throughout Australia. The main growing areas are adjacent to Melbourne and in the Goulburn Valley in Victoria; the Orange, Bathurst, Batlow and MIA regions in NSW; the Donnybrook and Manjimup regions in WA; the Derwent, Huon and Tamar Valleys in Tasmania; the Adelaide Hills in SA and around Stanthorpe in Qld (Morenos, Australian Horticultural Corporation 1995). These regions tend to have mild summer temperatures, a cool autumn and cool to cold winter. Apples grow in a range of soils, but generally require good drainage, and do best in deep, well-drained loam and clay loam soils (Taylor *et al*., 1990). Both apples and pears may require irrigation to maintain water supplies during dry seasons, but generally grow in relatively high rainfall areas. As good

drainage is important for apples, orchards may be on sloping sites to ensure good runoff. Spacing of 6.1 m X 6.1 m (250 trees/ha) was an old standard but high densities of up to 1000 trees/ha (3.2 m between trees) are becoming common (Taylor *et al*. 1990).

Pears are produced in several of the same areas as apples, although in somewhat heavier loamy soils and will tolerate some waterlogging (Taylor *et al*. 1990), with 87% of Australian production (4 000 ha) from the Goulburn Valley (Mitchelmore and Morenos 1995). Soils in pear and apple orchards in the Goulburn Valley, and possibly other areas of Australia, may have significantly higher organic carbon contents than typical Australian soils due to the management practices of green manure crops and inter-row mulching. In addition, most orchard topsoils (2-15 cm depth) in these areas have acidic pHs (pH 5.3-6.3 is considered optimal) with 63% of topsoils <5.2 (Jobling et al. 1994) mainly due to nitrogen fertiliser and irrigation. Cropping practices here range from traditional orchards of about 280 trees/ha on deep soils using flood irrigation to high density (1,500-2,500 trees/ha) planting on shallow soils with tree line microjet or trickle irrigation (Jerie and McNab 1994).

Nashis are produced largely in the same areas as apples/pears with the Goulburn Valley and Batlow areas as major production regions. Production is increasing rapidly with around 100 t in 1987 rising to a predicted level of more than 7000 t in 1997 (Coombs, 1995).

Apple & Pear Australia Limited (APAL, 2006) indicate that in 2004 the industry produced 254,925 t apples (down on the 2003 season from 326,072 t due to unfavourable seasonal conditions). This volume in 2004 was produced from over 10 million trees. The industry produced 138,548 t pears (up on the 2003 season from 135,919 t). This volume in 2004 was produced from over 1.6 million trees (excluding Nashi). About 80% of Australia's Nashi production comes from Victoria's Goulburn Valley, and some 40 commercial growers operate throughout the country. The industry now produces around 5,500 tonnes annually. ABS (2006) indicates that there were 912 apple and pear growers in 2005.

3.1.1.3 Stone fruits

Stone fruits are grown in many of the same regions as irrigated fruits and vines, noting the chill requirement for most stone fruit to produce, and most of the crop is irrigated, at least during spring-summer. Peaches and nectarines, which are by far the largest volume stone fruits, production is dominated by the MIA, Murray and Goulburn Valley irrigation areas with around 89% of production in NSW/Vic/SA. Apricot areas are predominantly (~93 %) in the Murray irrigation regions of Victoria and SA, due to their preference for free draining, non-acid soils and hot dry summers. The minor stone fruit crops are cherries and plums, with the former mainly produced (~70 % of Australian total) through central and southern NSW and plums in similar regions as these other stone fruits.

ABS (2006) indicates that production of apricots, cherries, nectarines, peaches, and plums + prunes was respectively, approximately 20,000 t. 8,000 t, 40,000 t, 90,000 t and 33,000 t. Corresponding tree numbers ranged from approximately 600,000 for apricots to 90 million for peaches. There were 1224 stone fruit growers in 2005.

3.1.1.4 Macadamias

The Australian Macadamia Society (AMS, 2006) indicates that the number of macadamia growers is estimated at 800 within Australia. The majority of the plantings are in northern

New South Wales and south-eastern Queensland. There are a few plantings on the New South Wales mid-north coast, central and northern Queensland. Most of the plantings are on the coastal plains east of the Great Dividing Range with some pockets on tablelands in north Queensland. There are also minor plantings in Western Australia. Current estimates are that the Australian industry has about 4,100,000 trees covering an area of 15,000 hectares, varying in age from newly planted to over 20 years old. 98% of these trees are the commercially preferred *Macadamia integrifolia* species. Of this total, about 80% are Hawaiian selections. The remainder are Australian, including some relatively new releases. Of the total trees planted, it is estimated that 45% are mature (15 years plus), 30% in the early bearing stage and 25% not yet bearing.

Information presented by the primary registrant in response to DEH's initial assessment indicates that current use is limited, with limited sales in Queensland and in NSW use appears to be once per season on some orchards but averages less than one spray per season across NSW. Also, the registrant states that between rows of macadamias there is a swath of mown grass and broadleaf plants to prevent erosion and maintain soil stability. Underneath the trees the ground is kept clean of weeds and mulch etc to allow equipment to pick up nuts as they fall.

3.1.1.5 Citrus

According to Australian Citrus Growers (ACG, 2006), 32,000 hectares of citrus are currently planted, with about 2800 growers, The major production regions are in the Riverland, South Australia; Murray Valley, Victoria and New South Wales; Riverina, New South Wales and the Central Burnett region in Queensland. There are also additional plantings throughout Western Australia, inland and coastal New South Wales, regions in Queensland, as well as smaller plantings in the Northern Territory. The larger plantings in the inland irrigated zones of the MIA and Murray River together comprise around 90% of the total citrus grown (Cope and Forsyth, 1995) .

The use of azinphos-methyl in citrus is very minor.

3.1.1.6 Grapes

Wine grapes are grown widely in southern Australia, including south western WA, south eastern SA, south eastern Queensland, and various areas in Victoria, Tasmania and NSW. Vineyards occur near the coast, in river valleys and in the tablelands, slopes and plains, under a wide range of temperature conditions, aridity, rainfall, relative humidity and sunshine hours, and on slopes ranging from relatively steep to very flat. Water management includes dryland and various methods of drip, spray and flood irrigation (Dry and Smart, 1988; Davidson, 1992).

The total area of grapevines has increased greatly since 1990 to 166,700 ha in 2004, the majority used for wine production. The largest producing state is South Australia (59,800 ha), followed by Victoria (36,300 ha) and New South Wales (32,300 ha). The majority of the area (at least 114,000 ha) is now drip or trickle irrigated (ABS, 2005).

Use of azinphos-methyl in grapes has declined, with only one region, the Hunter Valley, NSW, currently using it. This use is for fig longicorn beetle and elephant weevil, grape pests unique to the region.

3.1.1.7 Minor Uses:

Lychees (more properly know as litchis) are grown in much the same tropical and sub-tropical areas as macadamias (~1500 ha in 1994, Coombs, 1995). Australia is a relatively small producer of lychees with 4,000-6,000 tonnes produced by 250 commercial growers. Production is spread 2,500 km along the east coast that with variation in cultivars allows the season to be spread from November/December until February/March. The bulk of production is consumed on the domestic market (Sydney and Melbourne) (QDPI, 2006).

Kiwifruit (~1 200 ha in 1994) are mostly grown in N-E Victoria, southern QLD and northern NSW, with around 4 000 t of production (Coombs, 1995). This is mainly an irrigated crop. ABS (2006) indicates that there were about 50 kiwifruit growers in 2005.

Blueberries (~350 ha in 1993) produced around 1000 t of fruit valued at $12M, with >70% of plantings in NSW (largely on the mid-north coast) and lesser areas (~8%) in Victoria and other cooler regions (Coombs, 1995). This crop requires well drained, acid soils (pH 4.8-5.5), good quality/quantities of irrigation water and has a cold chill factor. Blueberries belong to the Azalea family and require similar growing conditions. The spineless shrubs can be either evergreen or deciduous, vary from 1-3 metres in height and are long lived (30+ years). Soil must be acid (pH4.5-5.5), well drained and have high organic matter. Planting distances for the larger varieties should be 1.2 m between plants and 3-4 m between rows (ABGA, 2006).

3.2 ENVIRONMENTAL FATE

3.2.1 Chemical Degradation

Most of the following reports for chemical fate and degradation were submitted in response to the data call-in, unless otherwise stated. The studies presented here were largely performed according to Good Laboratory Practices and according to internationally acceptable guidelines, although some studies are now quite old and obviously were not conducted according to current protocols. The degradation products detected appear to arise from proposed pathways suggested in the literature (Engelhardt, G., *et al*., 1984).

In general the most definitive studies, ie the best described and using modern guidelines, are summarised first, followed by older or poorly described tests that are considered to be supportive only. Many studies used ^{14}C-labelled azinphos-methyl, and mainly this was a uniformly ring-labelled form, but when this was not the case the report will note the different label positions.

3.2.1.1 Hydrolysis as a function of pH

Study 1

The hydrolysis of radio-labelled azinphos-methyl was determined at pH 4, 7 and 9 at a concentrations of approximately 1 and 10 mg/L in sterile aqueous solutions (Wilkes, *et al*., 1979a). Although the study was not conducted according to the current Guidelines, it is considered acceptable.

The sterile buffered solutions were kept at 30 or 40 ˚C in the dark and sampled at days 0, 1, 2, 4, 7, 14, 21 and 30. The solutions were analysed by liquid scintillation counting (LSC) and

TLC, with azinphos-methyl and metabolites identified using reference standards. For quantification, the TLC spots were scraped and analysed by LSC. Sterile handling techniques were used during sample preparations.

Based on the linear plots using semi-log graph paper, use of first order kinetics was considered suitable. From the first-order rate constant the half-lives were calculated using a curve fitting program and are given in Table 49.

Table 49: The half-lives of azinphos-methyl in a range of sterile buffered solutions.

Temperature	Initial	Half-lives in days		
	Concentration	pH 4	pH 7	pH 9
30 °C	1 mg/L	38.9	23.1	2.2
	10 mg/L	42.2	25.2	2.5
40 °C	1 mg/L	17.8	11.0	1.1
	10 mg/L	21.3	12.1	1.3

Several hydrolysis products were identified, with the major metabolites being hydroxy-methyl benzazimide and benzazimide, which were measured as a single analyte by TLC. These major metabolites were found after 30 days in the 10 ppm hydrolysis studies at 12.2%, 14.2% and 38.9% for pH 4, 7, and 9 respectively, plus anthranilic acid, which reached levels around 18-22% at pH 9 after 30 days. These tests were conducted at elevated temperatures and were not extrapolated to 25 °C, and so their relevance to environmental conditions is unclear, but shallow ponds of water may approach these higher temperatures in Australian conditions during the main use period (spring and summer).

Study 2
The hydrolysis of azinphos-methyl (Guthion, purity not given) was determined at pH 5, 7 and 9 at a concentration of 10 mg/L in distilled water (Flint, *et al*., 1970). The buffered solutions were kept at 30˚C and 50˚C with sampling at various time intervals. The solutions were extracted and analysed by gas chromatography (GC). There was no indication given in the report that conditions were sterile.

The half-lives were calculated at 30 °C as 17.3 days (pH 5), 10.0 days (pH 7) and 0.5 days (pH 9) and for 50 °C the half lives were given as 1.8 days (pH 5), 1.3 days (pH 7) and 0.08 days (pH 9). It is assumed that these were calculated using first order kinetics. This study was conducted in conjunction with a trial on leaching/runoff, not in accordance with current guidelines, and the hydrolysis result is considered to be supportive only.

Study 3
A summary of a test of hydrolysis of azinphos-methyl (Guthion, formulation) was provided (Wilmes, 1982a). It was determined at pH 4, 7 and 9 at a concentration of 1 mg/L in buffered solutions kept at 30 ˚C and 40 ˚C with sampling at various times up to 30 days. Obviously further test details are available, but these were not provided and detract from the utility of this report, which appears to be a re-write of data in Wilkes *et al*. above. Half-lives (30 ˚C) were calculated to be 38.9 days (pH 4), 23.1 days (pH 7) and 2.2 days (pH 9). Due to the lack of detail provided this is regarded as a supportive study only.

Study 4
^{14}C-azinphos-methyl was applied (Heuer *et al*., 1974) to glass beads (dry and wet) and in aqueous solutions (pH 8.6, 9.6 and 10.7) then exposed to three temperature regimes (6, 25

and 40 °C) over 25 days. The study did not follow any standard protocol, as the usual range for hydrolysis studies is pH 4, 7 and 9, but the authors state this was due to lack of hydrolysis at lower pHs noted in earlier studies. No details are provided of general test conditions or concentrations used to allow assessment of the integrity of this study.

Azinphos-methyl degraded relatively slowly on dry glass beads with little effect apparent due to temperature, while on wet beads (pH 9.6) the degradation rate was more like that in solution, while somewhat slower and increasing at higher temperatures. In solution degradation was significantly faster at highest temperature and higher pH, with half-lives apparently around 0.5 day at these two higher pHs. Half-lives were of the order of 2-7 days at 6 or 25 °C at the higher pHs (also at pH 8.6 and 40 °C), but increased to 28-36 days at the two lower temperatures at pH 8.6. The test indicates hydrolysis will occur, but largely under more extreme conditions that would be rare in natural aquatic systems. (Supportive study only)

3.2.1.2 Conclusions

From these four reports, it may be concluded hydrolysis of azinphos-methyl is relatively slow at pH 4, moderate at pH 7 and rapid at pH 9 using the Netherlands classification scheme (Mensink, et al., 1995). A number of hydrolysis products are formed, largely a series of benzazimides that eventually lead to anthranilic acid. Hydrolysis could be a significant contributor to the overall degradation of azinphos-methyl in the environment, particularly under alkaline conditions.

3.2.2 Photodegradation

3.2.2.1 Aqueous Photolysis

Study 1
The photolysis of ^{14}C-azinphos-methyl in pH 4 acetate buffered water solution was studied (Morgan, 1987a) using sunlight as the light source, basically in accordance with the US protocol 162-1 (US EPA, 1982). Presumably the pH 4 solution was used to avoid hydrolysis effects, which have been shown to be negligible in acid conditions.

An aqueous solution of radio-labelled azinphos-methyl (concentration 10.3 mg/L, in deionised water/acetonitrile/acetate solution, 17-29 °C) was irradiated for around 87 hours using natural sunlight (February, Kansas City, Missouri) in quartz cells. The irradiated solution and covered control were sampled (0, 4, 5, 8, 32, 56 and 87 hours) then directly subjected to LSC to determine recoveries of ^{14}C-label, and to HPLC to determine proportions of photolyte species. The final (87 h) solution was subjected to HPLC/LSC, then GC and MS to identify the photolytes.

After 87 h of exposure, significant degradation of azinphos-methyl (approximately 60%) had occurred with around 42% of the applied azinphos-methyl remaining. By contrast the dark controls had 100% of the original azinphos-methyl at the conclusion of the experiment. The photolytic half-life for exposure under these conditions was determined as 76.7 hours, which should be treated with some caution as it is almost the same time as the entire exposure experiment.

The main photo-degradation products identified were benzazimide, which reached 39.1% of original ^{14}C-activity after 87 hours, and anthranilic acid, which reached 7.2%, also after 87

hours. In addition another 12.1% was unidentified products. The limited analysis of photo-degradation products is a deficiency in the study and it was not clear whether the solutions were sterile. However, the study does show that photo-degradation in water is possible and that benzazimide is likely the main product, which then undergoes further degradation.

Study 2
The photolysis of azinphos-methyl was studied using an artificial light source in buffered water solution (Hellpointner, 1994) according to German guidelines (UBA, 1990).

An aqueous solution of unlabelled azinphos-methyl (concentration ~5 mg/L) in HPLC grade water/acetonitrile (9:1, pH not given) was irradiated for 60 minutes using a mercury vapour lamp in a standard merry-go-round apparatus. A UV filter (Duran 50) was used to cut out wavelengths below 295 nm. The irradiated solutions were sampled (0-60 min, at 6 min intervals), and azinphos-methyl determined by HPLC, with the test half-life estimated as around 41 min. Photo-degradation products were not identified.

Due to the high intensity of light used, the results were used in two computer models (GC-SOLAR, Zepp and Cline, 1977; and an arithmetic model, Frank and Klopffer, 1985) to estimate the field half-lives for azinphos-methyl. These produced a range of half-lives for azinphos-methyl dependent on the location/weather conditions. For GC-SOLAR these half-life estimates were 0.7-0.9 days (spring and summer, 30° latitude) or 0.9-1.4 days (spring and summer, 50° latitude), while for the other model these half-lives ranged from 0.9-5.5 days (German summer June, 50° latitude).

Again, the lack of analysis of degradation products is a deficiency in the study. However, the study does show that relatively rapid photo-degradation in water is likely, although the pH of the irradiation solution was not given.

Study 3
A study was undertaken to determine the photo-transformation of ^{14}C-azinphos-methyl in water (Wilkes *et al*., 1979b). While this study was conducted before current EPA Test Guidelines were in place, the procedures were basically in accordance with the guidelines.

The method used artificial light (mercury lamp) to irradiate a 10 ppm solution of azinphos-methyl in buffered solution (pH 4.35, 30 °C) in a photochemical reaction assembly connected to gas traps. Samples were collected hourly up to ten hours and then at various intervals up to 48 hours. Degradation products were extracted with methanol or ethyl acetate from various traps and solutions and were subjected to two-dimensional TLC and LSC against a range of standards. Practically all of the ^{14}C-label was recovered from the original water phase (101.6% of initial dose) with only 0.8% recovered from the traps and tubing, indicating the absence of volatile products. Overall recoveries were good, ranging from 99.7-103.5% of the applied radio-label over some twenty sampling times. The second order plot was linear and gave a half-life of 9.4 hours for azinphos-methyl under these conditions.

The main degradation products were a group of benzazimides, which reached 15-20% of applied ^{14}C-label after 4-5 h irradiation, and these peaked around 33-40% after 14-48 h. These further degraded to the other major product, anthranilic acid, which reached 4.9% of applied ^{14}C-label after 5 h irradiation, and peaked around 9% after 14-48 h. Despite esterification of the anthranilic acid product with some of the added internal standards, resulting in an unknown ”X” on TLC plates, the quantitative recovery was good.

Study 4
The photolysis of azinphos-methyl (Guthion, purity not given) was determined at concentrations of 5 and 16 mg/L in distilled water (Wilmes, 1982b). The solutions were irradiated with mercury lamps. There was no indication given in the report that conditions were sterile or of analytical methods, except that identification used mass spectrometry.

The photolytic half-lives for azinphos-methyl were calculated as approximately 30 hours and for the major degradation product (benzazimide) as approximately 80 hours. (Supportive study only).

Study 5
^{14}C-azinphos-methyl was applied to glass plates and in aqueous solution (Liang and Lichtenstein, 1972) then exposed to different light wavelengths (sunlight, red - 656 nm, yellow – 589 nm or UV - 254 nm) temperatures and pHs, along with covered controls. Azinphos-methyl degraded very slowly on glass plates. Degradation in water was rapid only under UV exposure with only 2-5% of the original ^{14}C-azinphos-methyl persisting after 1-2 days exposure. In the other treatments, azinphos-methyl degraded more slowly, increasing at higher temperature (>37 °C) and pH (10-11) levels, and azinphos-methyl was reported as relatively stable at pH 6-9.

DEH notes that these studies were not performed to current international requirements and the description of the methodology used is brief and is missing critical information on exposure conditions and degradation products. Therefore the results are regarded as having limited value. (Supportive study only)

3.2.2.2 Photolysis Rate on Soil and Plants

Study 1
The photolysis study (Morgan, 1987b) of ^{14}C-azinphos-methyl (phenyl-ring label) on soil was conducted according to US EPA Guideline 161-3.

The 1 mm layer of an air dried sandy loam soil (2.4% organic matter, 66% sand, 32% silt and 2% clay, pH 5.1, bulk density 1.40) in petri dishes was dosed with 14C-labelled azinphos-methyl (33.8 µg/cm^2, equivalent to 3.4 kg/ha). The dosed soil was exposed to summer sunlight (Missouri) in a cooled soil photolysis module (15 °C) for 30 days of continuous exposure through a quartz cover plate. The temperature and radiation were monitored and replicate dark controls used.

Soils were sampled at 0, 4, 8, 16 and 31 days and the soil samples were extracted and then analysed by HPLC and LSC. Residual ^{14}C-label in the soil was determined by combustion of the soil followed by LSC. Recoveries for total radioactivity averaged 102% (94.9-104.6%) and temperatures reached maxima of 34.2 °C (exposed) and 27.4 °C (dark controls), averaging 17.7 °C and 17.0 °C, respectively, for the entire period. Degradation was relatively slow with around 80% of the parent recovered after 31 days exposure, only small amounts of degradation products were detected (maximum 3.3%) and the half-life was reported as 99 days. However, this figure appears to be the total degradation through all mechanisms (that is not allowing for the dark control rate, as the following study quotes this net photolytic half-life as 232 days). The results show that photo-degradation is unlikely to be a significant degradation pathway in soils.

Study 2
A repeat study (Gronberg, 1989) was conducted, using similar conditions and equipment, as above, but a different soil (Fresno sandy loam, pH 7.1) and location (Kansas), with sunlight exposure for 30 days. Samples were taken only at 0, 15 and 30 days and gave an extrapolated half-life of 66 days, but a net photolytic half-life of 241 days, considering degradation occurring in the dark controls, and support the conclusion above.

Study 3
In a general study (Stegh and Wilmes, 1982) investigated the procedure for a standardised test regime for photolytic degradation of pesticides on silica gel as part of a proposal to develop an OECD screening test for photo-degradation. Gusathion (ai azinphos-methyl) was among the 20 or so pesticides they used to test their system, comparing the results on silica gel to the more standard soil TLC plate method (Korte). In the proposed test system the calculated half-life for Gusathion M was 11 days. (Supportive study only)

Study 4
The photolysis of azinphos-methyl (Chukwudebbe *et al*., 1989) on glass surfaces was determined under artificial light and natural sunlight, along with other OP insecticides. The studies were not conducted according to standard protocols (US EPA, etc) but aimed to follow degradation of OPs and the formation of metabolites, which might display toxicity themselves. This study noted that UV light and natural sunlight degraded azinphos-methyl effectively with around 31% (72 h) and 37% (25 h) disappearing during the exposure periods, respectively. (Supportive study only)

Study 5
In an early trial (Liang and Lichtenstein, 1976), ^{14}C-azinphos-methyl (labelled at carbonyl) was applied to glass plates, bean and corn leaves, plus three soil types and then exposed, with covered controls, to 8 h sunlight or UV light (254 nm). Dark controls showed little degradation (96.8-99.6% unchanged azinphos-methyl) while on glass plates only 28.2% and 46.7% azinphos-methyl remained for UV and sunlight exposures, respectively. In soils the photo-degradation was somewhat slower with 75.3% (sand), 83.5% (loam) and 91.1% (muck) of the azinphos-methyl remaining after 8 h exposure to sunlight, but this may largely be due to surface area, moisture or other effects since azinphos-methyl was mixed with the soil rather than applied to the surface. Degradation of azinphos-methyl, when applied to leaf surfaces, was around 20% (corn) and 40% (beans) of applied after 8 h sunlight exposure. (Supportive study only)

Study 6
^{14}C-azinphos-methyl (carbonyl label) was applied to glass plates and bean leaves (Wieneke and Steffens, 1975) then exposed (1-28 days) to artificial light (14000 lux) in growth chambers and to natural sunlight. Dark controls were included but the report notes the growth chambers received little radiation <430 nm. As well, they reported photo-degradation of azinphos-methyl in water exposed to daylight and the artificial light for either 3 or 7 days. The details in this published paper are insufficient to derive degradation half-lives, but it is obvious that sunlight (most likely the UV portion) degraded significantly more azinphos-methyl than the artificial light (no UV).

Azinphos-methyl degraded very slowly on glass plates and they reported 95.9-97.4% unchanged azinphos-methyl after 28 days, in contrast with the preceding study. Degradation

and absorption on leaf surfaces was significantly greater with ~80% and 40% of applied ^{14}C-label stripped off leaves with water after 1 and 14 days exposure, respectively. Benzene extraction of leaves further recovered around 20 and 60% of the label, at these times, largely as azinphos-methyl (>90%). Due to the different extraction procedures the results may not be comparable with the previous study. Aqueous solutions exposed to sunlight (including UV) showed 16.1% water soluble degradates after 7 days compared to 5.9% for artificial light and 3.3% for the dark control after 7 days. (Supportive study only)

Study 7
In conjunction with an aquatic photolysis trial (above), ^{14}C-azinphos-methyl was applied to glass surfaces (Liang and Lichtenstein, 1976) and exposed to sunlight, red light, yellow light or UV light (254 nm) with covered controls. Dark controls showed little degradation with >97% unchanged azinphos-methyl for treatments in water or on glass plates. Only UV light degraded azinphos-methyl to any extent on glass surfaces with 55.6% of the original label remaining after 2 h, compared with 97.4-100.4% remaining after 5 h of the other two wavelengths used. (Supportive study only)

3.2.2.3 Summary and conclusions from photodegradation studies

Aqueous
Based on five studies using artificial light and sunlight, photo-degradation of azinphos-methyl in water is possible, with benzazimide and anthranilic acid the major metabolites. The half-lives were determined for two of these studies and ranged from <0.5-3 days. The half-life under environmental conditions was determined by modelling as 0.9-5.5 days for German spring and summer conditions.

DEH concludes that photodegradation in water could be a significant route of degradation under Australian environmental conditions but the turbidity in Australian natural waters could decrease the rate of degradation.

Soil/Plants
Based on 2 soil photolysis studies using natural sunlight, the net half-life of photo-degradation of azinphos-methyl in air dried soils was calculated to be 232-241 days in sunlight. The main metabolites occurred at low concentrations and were not identified. On glass plates azinphos-methyl degradation was relatively slow, but on plant surfaces dissipation of azinphos-methyl appeared more rapid than from soils with 20-40% degradation after 8 h exposure to sunlight.

There were several additional studies that used artificial light. These showed that exposure to UV light was effective in degrading azinphos-methyl, but the visible wavelengths were not effective. Half-lives for UV exposures were determined in the order of hours (2-8) depending on conditions used, but as these studies used different lamps and conditions they cannot be readily related to natural conditions.

Photodegradation on plant surfaces may be a major route for environmental degradation in Australia, given the high light levels during summer, when most azinphos-methyl use occurs.

3.2.3 Degradation

3.2.3.1 Soil and Aquatic Metabolism

Aerobic Soil Metabolism

Study 1

The degradation of ^{14}C-azinphos-methyl was studied in two German soils (Laacherhof and Standard Soil No.1) under aerobic conditions (Wagner *et al*., 1982).

A sandy loam field soil (clay 19.8%; OC 0.8%; pH 6.0) was dosed with labelled azinphos-methyl (carbonyl-^{14}C) at 119 mg/kg. The standard silt loam soil (sand 43.3%, silt 50.9%, clay 5.8%; OC 2.66%; pH 6.1) was similarly dosed with azinphos-methyl (carbonyl-^{14}C) at 4.5 mg/kg and in a separate test with azinphos-methyl (phenyl-UL-^{14}C) at 0.6 mg/kg. The soils at 75% of field capacity were incubated in a stream of moist air for a total of 222, 552 and 365 days, respectively. Volatile products were trapped in gas traps (H_2SO_4 and NaOH). The soil and traps were sampled as indicated in Table 49.

Samples were taken after 37, 67, 100, 136, 164 and 197 days and in standard soil continued up to 350-500 days. Samples were successively extracted with chloroform, acetone and water, then extracts were filtered, concentrated and subjected to TLC, radio-counting, NMR and mass spectrometry, along with combustion of the soil residue, to define the pattern of metabolites. Around 93% of the azinphos-methyl was decomposed in the field soil after 197 days, while degradation was slower in the standard soil, as evidenced by the lower CO_2 production, and this is most likely due to lower microbial activity in this stored soil (see Table 50).

Table 50: ^{14}CO2 trapped during aerobic soil metabolism of azinphos-methyl.

All results as % of initial applied dose	Days After Treatment (DAT)						
	37	67	100	164	197	222 *	365/552*
Laagerhof	1.39	5.06	9.26	15.13	16.98	18.58	
Std Soil 1 (C-label)			1.55	3.45	4.26	4.91	8.99
Std Soil 1 (U-label)	2.15	2.89	4.35	5.91	6.74	7.08	9.98

* exact DAT varies

The principal metabolites were a range of benzazimide products, further degrading to salicylic acid and CO_2. The authors suggest a basic degradation framework (see Attachment 2), simplified into three main streams (demethylation, cleavage or re-arrangement of the thio-phosphate moiety, and oxidation/cleavage at thio-phosphate) that produce a range of products, many of which were transient and difficult to resolve. The half-life of azinphos-methyl was determined to be 48.6 days under aerobic soil metabolism conditions in the Laacherhof field soil, assuming first order kinetics. This was reported in a revision of the data from the original paper, but half-lives in the standard soil are not quoted and not able to be derived from the data provided. The appearance of $^{14}CO_2$ from both label positions indicates the aromatic moiety is mineralised as well as the thioester side chain. The study was performed to current BBA standards (German) and the study is acceptable to DEH. These soil degradation data are combined with microbial degradation data and appear in a technical publication (see below Engelhardt *et al*., 1984) elucidating the proposed degradation pathways for azinphos-methyl in soils.

Study 2
The degradation of azinphos-methyl in one soil under both aerobic and anaerobic conditions was studied to meet US requirements (Gronberg, *et al*., 1979).

Radio-labelled azinphos-methyl (^{14}C- uniformly ring labelled) was used to dose a sandy loam soil (pH 7.9, OC 1.4%, sand 73%, silt 17% and clay 10%) at 2 ppm in soil. The soils were then moistened to the required field capacity (63%) and incubated in a standard apparatus for up to 365 days. After 30 days four flasks were flooded with water to 1 cm depth, evacuated and recharged with a nitrogen atmosphere (3X), sealed and sampled in duplicate at 30 and 60 days after flooding. While this process is expected to establish anaerobic conditions, there was no evidence that these conditions were maintained. Volatile products were trapped in NaOH and acetone/dry ice gas traps and a sterilised soil was followed through the same process, with sampling up to 120 DAT. All soils were incubated at 22˚C.

Duplicate soil samples were taken at 0, 1, 3, 7, 14, 30, 60 and 120 DAT and single samples at 186, 242, 304 and 365 DAT. These samples were analysed by extraction of the soil and the extracts were analysed by TLC to identify metabolites and scintillation counting to quantify the residues. Relatively small amounts of $^{14}CO_2$ were found in NaOH traps and little ^{14}C-label was detected in the acetone/dry ice gas traps (maximum 4.1%). Non-extractable (soil bound) ^{14}C-label rose from 3.7% at day 0 to 72.7% after 365 days. The parent compound degraded in parallel with this declining from 92.9% at day 0 to 1.6% after a year, and a range of metabolites (largely benzazimides) were detected, with mercapto-methyl-benzazimide peaking at 3.5% after 120 days. As well, the azinphos-methyl oxygen analog was detected reaching a maximum of 5.3% (of applied label) at 186 DAT, somewhat in contrast to other degradation studies where it is rarely reported. Material accountability averaged 103% over the 12 sampling times. From this data the half-life of azinphos-methyl was determined to be 21 days in aerobic soil, somewhat longer (68 days) in the additional anaerobic phase, and considerably longer (355 days) in sterile soil. This is an older study but it was performed well, and is still considered acceptable.

Soil/Microbial Degradation

Study 1
A short paper (Engelhardt *et al*., 1981) describes degradation products detected when ^{14}C-azinphos-methyl treated soils fortified with *Pseudomonas fluorescens* were incubated at 28 °C for 15 days. The two major products were benzazimide and anthranilic acid, and while other metabolites were detected these were in low amounts. (Supportive study only)

Study 2
A published paper (Engelhardt *et al*., 1984) defines likely degradation pathways in two soils treated with ^{14}C-azinphos-methyl [carbonyl and phenyl-ring labels] and fortified with *P. fluorescens* and describes the range of metabolites that were detected and identified. Methods followed German soil degradation test protocols (BBA, 1980). The soils used were a natural field soil (clay loam, pH 6.0, OM 0.8%) dosed with carbonyl-label and Standard soil No.1 (sandy loam, pH 6.1, OM 2.66%) treated with carbonyl- and phenyl-ring labelled material. This appears to be a published version of the two trials reported above (see Wagner *et al*., 1982).

Study 3
An early paper (Schultz *et al*., 1970) examined ^{14}C-azinphos-methyl degradation in two soil

types and defined a set of products, largely a group of benzazimides, that were non-toxic towards mosquito larvae in bio-assays. Both laboratory and field tests resulted in a similar range of products, but it would appear the ^{14}C-label was on the thioester side chain since no anthranilic acid was reported as being detected. When azinphos-methyl granules were incorporated in soil, 50% disappeared in 28 days and residues were detectable for up to 5 months, whereas an emulsion applied to the soil surface resulted in 50% loss in the first 12 days. (Supportive study only)

Study 4
A published report (Leoni, et al., 1992) evaluated the degradation of 10 pesticides, including azinphos-methyl, in activated sewage sludge as a measure of their persistence in soil. The % degradation of the pesticides was correlated to the soil half-lives reported in the literature and appears to give adequate correlation to be useful as a screening test. azinphos-methyl was 30% degraded during the 9 hour test in sewage sludge. (Supportive study only).

Other Literature Reports

A paper (Staiff, *et al*., 1975) describes a trial devised to evaluate azinphos-methyl residues in soil (sandy loam, pH 6.6-7.8) after spillage of the concentrate or disposal of spray mixtures on soil. Undiluted concentrate (18.1% azinphos-methyl), dilute spray (0.045% azinphos-methyl) and concentrated spray (0.36% azinphos-methyl) were directly applied to small soil plots and sampled for azinphos-methyl residues for up to 8 years. Leaching did not appear to be significant below 30 cm depth, and results indicate residues persisted from concentrate "spills" for at least 8 years, but the method used may not readily distinguish between the parent compound and several degradation products. In the most realistic dosing with normal spray solution, little azinphos-methyl (~1-2 ppm) persisted beyond one year, but with concentrated spray the results are more variable showing levels of azinphos-methyl residues around 35-55 ppm persisting up to two years. (Supportive study only)

Another paper (Iwata, *et al.,* 1975), largely concerned with post-application occupational transfer of OP pesticides, followed the degradation of azinphos-methyl (and other OPs) applied at relatively high concentrations (500 ppm) to dust material from ten soil types. Soils were sieved (150 μm), which obviously changed the soil characteristics, and the fine material was used for azinphos-methyl (and other OP) treatment, after adding water to 40% saturation. Dusts were sampled periodically over 200 days to determine persistence/degradation of azinphos-methyl.

The report notes that azinphos-methyl showed high variability of persistence with different soil types reaching low levels (<10 ppm) in two dusts at 74 days, but persisted (>100 ppm) in three others at 150 days. By comparison, parathion dissipated (<10 ppm) from practically all dusts in ~50 days and ethion persisted (~300 ppm) in all dusts for >200 days. The reasons for this variability with azinphos-methyl are not provided nor obvious from the paper, which recommended further field investigations. (Supportive study only)

Another publication (Read, 1976) compared the efficacy and persistence of 24 chemicals (including azinphos-methyl) against root maggots in rutabagas when applied to the soil surface, mixed into the top 3 cm of soil or as a band 3 cm deep in the soil. Details of methods are limited, but azinphos-methyl (at 7 treatment concentrations: 2-100 ppm) was relatively persistent in soil (assessed as % of larvae killed over time) when banded, but somewhat less so in the other treatments. At 20 ppm banded azinphos-methyl provided >90% control for >90

days, while surface applied and soil mixed azinphos-methyl persisted >30 days. As well, at the highest dose rate (100 ppm) azinphos-methyl persisted >60 days (surface), >90 days (mixed) and >150 days (banded) which is comparable with the results in the two trials above. (Supportive study only)

Conclusions

A range of soil metabolism studies were performed using several soil types (two acceptable and seven supportive studies). It is concluded that microbial degradation of azinphos-methyl in soil systems is moderate under aerobic conditions (half-lives 21-49 days), and somewhat slower under anaerobic conditions (half-life 68 days). The considerably longer half-life (355 days) under sterile conditions indicates these rates are highly dependent on microbial activity. The main metabolites were similar throughout the degradation studies, largely a group of benzazimides and anthranilic acid, and eventually more complete mineralisation yielding CO_2. In Australia it is likely that hydrolysis and microbial degradation will occur in soils, especially under alkaline conditions, and it is expected this will occur at similar rates to those quoted above, depending on soil types/pH.

There were no studies provided on aquatic aerobic metabolism. However, the azinphos-methyl half-lives in the aquatic phase of the mesocosms were typically ~1-2 days (see Section 3.3.2.7).

3.2.4 Mobility

3.2.4.1 Soil Adsorption/Desorption

Study 1

A soil adsorption/desorption study was performed using the standard batch method (Lenz, 1979). This was performed according to older (non-current) guidelines with equilibration in water as opposed to 0.01M $CaCl_2$. Samples were allowed 24 hours for equilibration, then the liquid phase was separated by centrifugation and the liquid analysed by LSC. Desorption was evaluated using four successive desorption steps, allowing 24 hour for each desporption. From the LSC data the concentration of azinphos-methyl in the aqueous phase was determined and used to determine the adsorption and desorption coefficients for all the soils used.

Three soils were used in the study and the characteristics of these are presented Table 51. Azinphos-methyl adsorbed rapidly to all three soil types and log plots against concentration showed good linear fits and therefore use of the Freundlich equation was appropriate. Azinphos-methyl desorbed equally in the four steps with around 11% (silt loam), 21% (sandy loam) and 24% (silty clay) of the absorbed azinphos-methyl being released equally in each step. The results are summarised in Table 52.

Table 51: Characteristics of test soils used by Lenz.

Origin	Soil Type	Organic Matter	pH	% Sand	% Silt	% Clay
Merril	Sandy loam	2.8	6.6	74	14	14
Concord	Silt loam	5.0	7.9	18	57	25
Stanley	Silty clay	0.5	6.0	0	41	59

Table 52: The adsorption/desorption coefficients.

		Adsorption		
Origin	**Soil Type**	**K_d µg/g soil**	**K_{oc}**	**K_{ddes} µg/g soil**
Merril	sandy loam	7.60	472	12.28
Concord	silt loam	16.75	583	27.50
Stanley	silty clay	9.85	3396	12.30

The results of the adsorption/desorption experiment for azinphos-methyl show that it is moderately absorbed to the three soils tested. While there is general dependence on the organic matter content of the soil for two of the soils, the high Koc for the silty clay soil indicates that interaction with other soil components is significant. However, desorption was consistent for all soils and indicates that azinphos-methyl does not interact irreversibly with clay minerals. Azinphos-methyl can be rated as having medium mobility in soil.

Study 2

A soil adsorption/desorption study was performed using the standard batch method (Ziegler and Hallenbeck, 1987). This was performed according to US EPA guidelines (163-1) with 24 h equilibration of ^{14}C-labelled azinphos-methyl in 0.01M $CaCl_2$. Four soils were used in the study and the characteristics of these are presented in Table 53.

Azinphos-methyl adsorbed rapidly to all three soil types and log plots against concentration show good linear fit, therefore use of the Freundlich equation is appropriate. Recoveries averaged close to 100%. These results are summarised in Table 54.

Table 53: Characteristics of test soils.

Soil Type	CEC Meq/100 g	Organic Matter %	pH	% Sand	% Silt	% Clay
Silt loam	26	2.9	5.9	17	66	17
Sandy loam	10	1.1	6.6	56	30	14
Sand	6	1.0	4.3	88	7	5
Clay loam	21	2.2	6.4	21	50	29

Table 54: The soil adsorption/desorption coefficients.

Soil Type	Adsorption/desorption		
	K_d µg/g soil	**K_{oc}**	**K_{ddes} µg/g soil**
Silt loam	12.7	829	16.9
Sandy loam	4.0	693	6.8
Sand	6.8	1282	9.1
Clay loam	8.4	723	11.7

The results of the adsorption/desorption experiment for azinphos-methyl show that it is moderately absorbed to the four soils tested and this appears dependent on the organic matter content of the soil, and interaction with clay minerals is not indicated in these soils. Azinphos-methyl desorbed readily from the soils and can be rated as having medium mobility in these soil tests.

Study 3

Soil adsorption of azinphos-methyl (Guthion, SC formulation) was determined in three amended soils and at three concentrations (2.67, 3.55 and 4.44 µg/mL) using standard batch

methods (Flint, *et al* 1970). The fractions were extracted and analysed by GC. The adsorption isotherms were plotted and slopes Kd, determined. There was no desorption phase in the study. This study (Flint, *et al.*, 1970) was not performed or reported to current Guidelines, but in general used similar methodology and is considered to provide adequate results.

Additionally, a column leaching study using the same three soils was conducted that determined the amount of rainfall required to leach the surface applied azinphos-methyl "one foot into the soil". As well, an experimental runoff trial was undertaken in constructed plots (15, 20 and 30 feet long) using these same three soils. Azinphos-methyl was applied at a very high rate (20 lbs ai/ ac = 22.4 kg/ha) to the upper slope (10') of plot surfaces, which were artificially watered periodically (2, 9, 16, 23, and 37 DAT) with all runoff collected and tested for azinphos-methyl. The plots were shielded from natural rainfall and results are shown in Table 55.

Table 55: Details of the soil used and results reported by Flint *et al*. (1970).

Soil	pH	% OC	% sand	% silt	% clay	K_d (mL/gm)	K_{oc} (mL/gm)	Leaching *
Silt loam (+sand)	6.4	0.81	56.4	33.1	10.5	3.33	407	62" (157 cm)
Silt loam	5.5	1.05	16.7	62.8	20.5	11.04	1051	195" (495 cm)
Silt loam (+OM)	5.4	2.67	24.2	56.8	19.0	28.50	1067	186" (472 cm)

* Amount of rain equivalent required for residues in a soil column to move 1 foot (30 cm).

The results of this adsorption/desorption experiment for azinphos-methyl show that it is moderately to strongly absorbed to the "three" soils tested and shows that sorption is dependent on the organic matter content of the soil. The column leaching show that even with extreme rainfall events, significant leaching is unlikely.

In the small field plots artificial rain (1.3 inches [3.3 cm] of irrigation) soon after application (2 days) caused significant amounts of azinphos-methyl to appear in runoff, maximum of 1.4% of applied, but the amount of azinphos-methyl in runoff decreased rapidly with time. Rain later caused only minor amounts (0.05% of applied at 9 DAT, 0.5 inches [1.3 cm] irrigation) of azinphos-methyl to appear in runoff. The high application rate and small size of the test system make it difficult to assess this trial's applicability to field use, but it indicates azinphos-methyl is likely to appear in surface runoff when heavy rain occurs soon after application (see field studies, Section 3.2.5).

Overall, azinphos-methyl can be rated as having medium mobility in soil and appears to bind to the organic fraction of the soil. While there is limited potential for leaching, rain soon after application could cause contamination through runoff to occur.

Study 4

A paper (Martin and Camazano, 1984) traced the adsorption of azinphos-methyl by a specific group of clay minerals (smectites) and noted the effects this adsorption had on hydrolysis rates for azinphos-methyl. They calculated the Freundlich constants for the adsorption process at 30 °C and 45 °C, noting that hydrolysis of azinphos-methyl occurred in this system at pH 6 when azinphos-methyl is generally fairly stable below pH 9. (Supportive study only)

Study 5
A short paper (Reduker *et al*., 1988) studied the adsorption and soil column mobility of azinphos-methyl (and chlorothalonil) on a sandy bog soil to assess the likely leaching ability of the chemical if used in cranberry culture. A pronounced delay was evident between adsorption and desorption and <22% of the applied chemical was recovered, suggesting irreversible binding and/or degradation occurred. (Supportive study only)

3.2.4.2 Mobility Using Soil Columns

Study 1
In an aged soil leaching study, radio-labelled (phenyl-^{14}C)-azinphos-methyl (196 µg), equivalent to 1 kg ai/ha, was added to two soils then aged for 0, 30, 62, and 92 days (Fritz, 1988). The characteristic of the soils used are given in Table 56. These aged soils (containing ~6-9% of unchanged azinphos-methyl after 30 days) were layered on the top of packed fresh soil columns (height of 28 cm), then water (393 mL) was washed through the columns over a 48 hour period in accordance with BBA guidelines. The columns were sectioned into 3 segments of equal size and analysed for ^{14}C-label (azinphos-methyl and degradation products), plus the percolates (collected as two equal fractions) were tested similarly. Table 57 gives the results.

Table 56: Soil characteristics for soils used in column leach study.

Soil	Classification	pH	Organic Matter	Sand	Silt	Clay
Standard 2.1	sand	5.6	0.75	87.8	8.7	3.5
Höfchen	silt	5.3	1.8	2.3	88.6	9.1

Table 57: Distribution 14C-label in soil columns and leachates as percentage of applied.

Soil	Aging Time (days)	CO_2	Column Segment			Leachate Fraction	
			Top	Middle	Bottom	I	II
Standard 2.1	0	Nil	66.1	12.6	9.6	0.1	10.4
Höfchen	0	Nil	70.1	13.9	9.7	<0.1	4.4
Standard 2.1	30	3.3	89.0	5.8	2.5	0.4	6.8
Höfchen	30	1.8	90.1	5.6	2.1	<0.1	1.5
Standard 2.1	62	6.2	85.6	5.8	2.2	0.3	6.8
Höfchen	62	3.5	88.6	1.5	2.0	<0.1	0.9
Standard 2.1	92	9.9	81.6	5.6	1.2	2.5	4.3
Höfchen	92	3.6	88.3	2.0	1.3	<0.1	.09

Some movement occurred with no aging (0 days), with 5-10% of the radio-label appearing in leachate. However, there was only a small amount of unchanged azinphos-methyl detected in the leachate, 0.3% and 0.2% of applied radioactivity for soil 2.1 and Höfchen respectively, and generally low levels (1.8-9.9%) of other components produced with aging. There was no azinphos-methyl detected in the other leachates. For all aged soils, 80-90% of the applied label remained in the upper third of the soil columns for both soil types, with around 1% (silt) and 4-7% (sand) appearing in the leachate. Non-extractable label increased progressively from ~5% in non-aged soil to ~70% after 92 days aging. Overall recoveries were in the range of 96-108% and a range of degradation products were identified, largely a group of "benzazimides". This study, which DEH regards as acceptable, indicates that azinphos-methyl is unlikely to leach significantly in field use, especially after aging, but some of its

more polar degradation products may be more mobile.

Study 2
In an older study (Atwell and Close, 1976) soil column leaching was studied using ^{14}C- ring labelled azinphos-methyl added to a silt loam soil, then aerobically aged for 28 days. The soil was then layered on top of a 30 cm packed soil column (1.5 cm ID) and leached with the equivalent of 12.5 mm rainfall daily for 45 days (total volume ~100 mL/column). The soil (3.0% sand, 75% silt, 22% clay, 2.3% OM, pH 6.4) was dosed with labelled azinphos-methyl at a rate of 1 ppm. The leachate, "aged" soil and the soil column (6 equal segments) were extracted and subjected to TLC and scintillation counting to determine the degree of leaching and the degradation products.

After the 28 days aging, only 19% unchanged azinphos-methyl remained, suggesting a half-life ~10 d, while 5.3% of the label was present as benzazimide and 13.7% as unidentified soluble degradation products. A further 62% of the ^{14}C-label could only be extracted bound to the OM fractions (50.1% - humic acid, 10.5% - fulvic acid, 1.4% - humin). After leaching 90% of the label remained in the top 10 cm of the column and only 4.4% appeared in the leachate, most likely soluble degradation products, but these were insufficient to identify. (Supportive study only)

Study 3
A series of column leaching studies are very briefly reported (Wagner, 1974-79) with few details on methods and results, except that GC was used as the detection method and limits of determination ranged from 0.01-0.1 µg/mL leachate. Ten standard columns, some in duplicate (6 sand and 4 sandy loam), had various rates (~0.5-1.25 kg ai/ha) of azinphos-methyl loaded and columns were leached with the equivalent of 180-250 mm of rainfall over two days.

Table 58: Soil characteristics for soils used in column leaching study.

Soil	Classification	pH	Organic Carbon	Sand	Silt & Clay
ID No. 2.1	Sand	6.6	0.51%	93.8%	6.2%
ID No. 2.2	Sand	6.0	2.44%	89.5%	10.1%
ID No. 2.3	Sandy loam	5.2	0.57%	81.5%	19.5%

No azinphos-methyl was detected in the leachate from any column, but due to the lack of detail these studies are regarded as supportive only.

3.2.4.3 Soil TLC – Rf values

In an old study (Thornton, *et al*., 1976) twenty four pesticides, including Guthion (ai azinphos-methyl) were subjected to TLC on soil plates coated with six different soil types (see Table 59). Radio-labelled pesticides were spotted in triplicate onto the prepared soil plates (20 cm X 20 cm) and developed with distilled water, then air dried and exposed to X-ray film to detect relative movement of each compound from the origin.

Five mobility classes were defined: immobile, low, intermediate, mobile and highly mobile. Azinphos-methyl produced a range of R_f values from 0.11-0.24 (av 0.18) in this test and has a low mobility ranking, which indicates it is unlikely to leach significantly under field conditions.

Table 59: Soil characteristics for soils used in TLC study.

Soil	Classification	pH	OM %	Sand %	Silt %	Clay %
Vero Beach	Sand	5.9.	0.8	92	1	7
Merrill	Sandy loam	6.6	2.8	74	14	13
Howe	Sandy clay loam	5.5	0.6	56	21	23
Concord	Silt loam	7.9	5.1	18	57	25
Hagerstown	Silty clay	6.7	2.1	4	53	43
Stanley	Silty clay	6.0	0.5	0	41	59

3.2.4.4 Modelling

The leaching characteristics of azinphos-methyl and its likely concentration in groundwater were estimated (Schäfer and Borchers, 1995) using PELMO (a modification of PRZM). The model simulated "worst case" European conditions with two application rates and a standing water table at 110 cm. In both scenarios tested and simulated for ten seasons there was no indication of azinphos-methyl (<<0.1 µg/L) reaching this relatively shallow groundwater. (Supportive study only)

3.2.4.5 Conclusions from Mobility Studies

Soil adsorption/desorption
The soil adsorption/desorption of azinphos-methyl was determined in two acceptable studies using 7 different soils. The K_{oc}s averaged 757 (range 407 to 1172, discarding one abnormal value of 3396) and show that azinphos-methyl is moderately absorbed to the six soils tested. The sorption appears strongly dependent on the organic matter content of the soil. The desorption studies indicated azinphos-methyl desorbs fairly readily and constantly from adsorption sites. These tests rank azinphos-methyl as having medium mobility in soils, which is supported by several other reports.

Leaching
Several soil column leaching studies using a range of different soils, both fresh and aged, showed there was little leaching of azinphos-methyl (<0.3%). Some metabolites were detected in the leachate, generally in low amounts (<5% of applied). In the one instance where there was no aging around 10% of applied radioactivity appeared in leachate, mainly as degradation products. Soil R_f values were determined on TLC plates and indicated low mobility. Azinphos-methyl is unlikely to leach under field conditions.

Volatility
No studies on volatilisation of azinphos-methyl from soils presented, but this is not expected to be a significant route for the dissipation from soil, particularly where binding to soil organic matter occurs.

3.2.5 Field Studies

There were several field and modelling studies presented that assess field dissipation and these are summarised below.

3.2.5.1 Terrestrial Field Dissipation - field crops

Study 1

This study (Coody, 1992) followed the dissipation of azinphos-methyl from a 2.1 ha (5.2 ac) cotton crop cultivated as a typical commercial operation, including eight applications of azinphos-methyl (total 4 kg ai) for the season. The soil was a fine sandy loam (pH 6.2, OM 0.8%) and the trial area was bunded so all runoff was collected through a flume that automatically measured and sampled runoff. Spray application discs and distribution cards were also deployed, however, due to weather delays and rapid crop growth (canopy closure) these did not provide useful data.

"Typical agronomic practices" for Mississippi were used, with cultivation, application of herbicides (treflan and fluometuron), a plant growth regulator (mepiquat) and 10 applications of a pyrethroid insecticide (cyfluthrin) in addition to the 8 azinphos-methyl treatments later in the crop cycle. The crop was planted mid May but due to poor establishment it was replanted two weeks later. June and July were very wet with >3 times the average seasonal rainfall received, and this delayed the start of the azinphos-methyl applications. Azinphos-methyl was applied with a ground rig using hollow cone nozzles set ~0.5 m above the canopy to apply a nominal 0.28 kg ai/ha (0.25 lb/ac), but calculated rates averaged 0.235 kg ai/ha (0.21 lb/ac). Soil, runoff water and leaf samples were collected for azinphos-methyl residue analysis from the trial plot and from a nearby persistence plot where bare soil and cotton plants were sprayed only once and sampled at –1, 0, 1, 3, 7, 14 and 28 DAT.

In the persistence trial little rain fell, and azinphos-methyl had a calculated half-life of 5.66 days in soil, and 1.17 days on/in cotton leaves. The report references a parallel study in Georgia (Coody, 1991 – see below) where the comparable half-lives were 6.4 and 0.53 days. In the main trial area, one extreme rainfall event (77 mm) occurred 3 days after the third azinphos-methyl application and this caused the only measured runoff event. Runoff was calculated as 0.518 ML, containing 482 kg sediment and 28.77 ug/L azinphos-methyl (total 15 g of ai or 2.7% of the 553 g ai applied 3 days before). Samples were analysed using extraction and partitioning followed by GC or HPLC.

The persistence results indicate that in field use azinphos-methyl can be rated as readily degradable (Mensink, *et al*., 1995), but it also demonstrates the propensity for potentially toxic runoff to occur, especially when rainfall soon after application causes OPs to enter water from wash-off /runoff. The likelihood of this occurring clearly increases when the OPs are frequently applied, such as in this trial where repeat applications occurred every 3-7 days, and especially in summer rainfall zones. These results concur with the earlier experimental plot trials reported above (see Section 3.2.4.1 Study 3) and with the incidence reports from the US (see Section 3.3.7). The US EPA rated this study as "marginal" in its review because the absolute application rate could not be confirmed, but it is regarded as likely to be near the figures quoted above. Apart from this, and the obvious vagaries of the weather associated with this field trial, the results appear to give a useful report on possible field dissipation of azinphos-methyl.

Study 2

This study (Coody, 1991) followed the dissipation of azinphos-methyl from a 20 ha (50 ac) cotton crop surrounding a farm pond (1.42 ha, 3.5 ac) and was cultivated as a typical commercial operation. All runoff from a bunded area (3.6 ha) was collected through a flume

that automatically measured and sampled runoff. The soil was a sandy clay loam outside the bunded fumes area and within the bunded area a sandy loam . It was noted in the report that the soil is surface sealing which causes the soil to be relatively erosive and therefore the runoff and erosion was considered to be higher than would be expected for these soil types. Spray application discs and distribution cards were also deployed, however, due to rapid crop growth (canopy closure) these did not provide useful data on the actual application rates.

"Typical agronomic practices" for Georgia were used, with cultivation, application of herbicides and 10 applications of a pyrethroid insecticide (cyfluthrin) in addition to the 8 azinphos-methyl treatments every 3 days later in the crop cycle (applications from 1st August, day 0). The crop was planted mid May but due to poor establishment it was replanted two weeks later. Above average rain occurred in June and July. Azinphos-methyl was applied with a ground rig using hollow cone nozzles set ~0.5 m above the canopy to apply a nominal 0.28 kg ai/ha (0.25 lb/ac), with calculated rates averaged 0.27 kg ai/ha (0.24 lb/ac), based on volume of azinphos and water added to spray tank and the daily sprayer calibration results. However, based on the analysis of the spray solution (collect during each application) the average application was 0.22 kg ai/ha (0.20 lb/ac), which was used for measurements of run off. Soil, runoff water and leaf samples were collected for azinphos-methyl residue analysis from the trial plot and from a nearby persistence plot where bare soil and cotton plants were sprayed only once and sampled at –1, 0, 1, 3, 7, 14 and 28 DAT.

Areas of the paddock (0.1 ac) were set aside for the persistence trial. One area of the paddock was bare but tilled soil where only one application was made (on day 7, one day before first rainfall event in Table 59) for the soil persistence trial and for the leaf persistence trial an area of the planted paddock was only sprayed once (day 15 of trial). Sampling in the soil persistence trial was to a depth of 2.54 cm (1 inch) in triplicate on day –1, 0 (immediately following application), 1, 3, 7, 14 and 29. Leaf punch samples (1 cm dia., 200 leave punches per sample, 3 samples per sample time) were taken from leaves that received direct application on day –1, 0 (immediately following application), 0.5, 1, 2, 5 and 10. No new leaves were sampled.

Significant rainfall events that caused runoff during and following the azinphos-methyl applications occurred on days 8, 26, 31 and 61 with rainfall of 32, 61, 37 and 33 mm respectively during and following the azinphos-methyl applications. Samples were analysed using extraction and partitioning followed by GC or HPLC. Table 60 gives the volume of these runoff events and the analysis from the bunded area.

Table 60: Details of the 4 runoff event monitored during the field trial

DAT	Rainfall	Total runoff, $L \times 10^3$	Conc. of ai µg/L	Total ai transported, g	% of total applied
8	32	31	116	3.6	0.17
26	61	283	29.4	8.3	0.13
31	37	246	5.35	1.3	0.02
61	33	13.6	0.88	.012	<0.01

In the persistence trial the half life of azinphos-methyl was calculated as 6.44 days in the top 2.5 cm of soil ($r^2 = 0.911$). The half-life in leaf persistence trial was 0.53 days on/in cotton leaves (analysis of total leaf residues). These results indicate that in field use azinphos-methyl can be rated as readily degradable (Mensink, *et al*., 1995).

The main trial demonstrated the propensity for potentially toxic runoff to occur, especially when rainfall soon after application causes OPs to enter water from wash-off /runoff. The likelihood of this occurring clearly increases when the OPs are frequently applied, such as in this trial where repeat applications occurred every 3-7 days, and especially in summer rainfall zones. The US EPA has announced the cancellation of uses of azinphos-methyl in such areas, principally east of the Mississippi and in Louisiana.

Analysis of the water in a tile drain (3 tile drains on the field drained to the farm pond) did not show any azinphos-methyl (detection limit 0.07 μg/L). These samples were taken after the large rainfall event (day 26) on day 28 and continued daily for 5 days, with a follow up sample 5 days later. The farm pond water was sampled at 11 or 5 sampling sites starting on day 26 and then daily for 5 days, with sediment samples taken on day 27. Results are given in Table 61.

Table 61: Results of analysis from farm dam after major runoff event.

Date	Average Con. μg/L	Range	No of samples
26/8	1.29	0.21-5.97	11
27/8	2.25	0.99-6.75	11
29/8	2.38	2.18-2.83	5
30/8	2.72	2.55-2.93	5
31/8	1.99	1.47-2.46	5

Table 61 shows that there was significant azinphos-methyl in the dam waters. In the first two sampling days the range of concentrations across the pond (the 11 sampling sites were distributed around the pond) was large, with the authors noting that the higher concentrations were associated with samples taken away from the shore. The authors indicate that this may be due to the inflow of water not mixing with the existing water in the dam, and flowing over the dam wall (the pond was essentially full before the runoff event from previous rains, the runoff volume was calculated as 37% of the total capacity of the dam). There was a significant fish kill on 28 August with 500-1000 fish killed. It is noted that while environmental stressors from the runoff event could have caused the fish kill, the maximum concentration of azinphos-methyl is close to the lowest fish LC50s.

These results concur with the earlier experimental plot trials reported above (see Section 3.2.4.1 Study 3) and with the incidence reports from the US (see Section 3.3.7). The results appear to give a useful report on possible field dissipation of azinphos-methyl in cotton but the relevance to orchard applications is unclear. Nevertheless, the study does clearly show that following application there is rapid dissipation from leaves, with half life of 0.54 days, and degradation in soil, half life of 6.5 days. What is clear, however, is that despite the rapid degradation, runoff could be a potential route of environment contamination and at levels likely to cause adverse effects.

Study 3

At two sites in California, Chualar and Fresno azinphos-methyl was applied to plots of alfalfa at 3.36 kg ai/ha. There was two plots per site, one receiving a single application and the other 2 applications 7 days apart. The plots were sprayed at green-up after previously being cut (green–up is when the plants begin to re-grown after harvest). The plots were then use for kinetic study (single application) and leachability study (2 applications). All plots were irrigated as required for normal commercial plant growth which amounted to between 410-436 mm (16.25-17.15 inches) over 90 days from the last application.

The soil analysis was conduct by taking 5 samples per site and analysing these separately. For one site, Fresno, the soil was a sandy loam with little variation but at the other site, Chualar, there was considerable variation over the samples. These results are detail in Table 62.

Table 62: Characteristics of the soils at Chualar and Fresno for first horizon only.

Site	Boring No.	Classification	pH	Organic matter, %
Chualar	1	Sandy loam	7.8	1.44
	2	Sand	6.9	0.50
	3	Loam sand	7.3	1.24
	4	Sandy loam	7.0	1.77
	5	Sandy loam	8.0	0.24
Fresno	1	Sandy loam	7.6	0.75
	2	Loamy sand	7.8	0.57
	3	Sandy loam	7.7	0.38
	4	Sandy loam	8.6	0.20
	5	Sandy loam	8.7	0.45

The plots were samples on 0, 3, 7, 14, 28, 60 and 90 DAT. Each plot was Sectioned in to 3 Sections for sampling with 5 samples per Section, with corresponding core Section from each Section pooled together, thus 3 samples per plot was analysed. The sampling was done by coring to 1.22 metres (4 ft) and each core Sectioned into 15 cm lengths (6") for pooling and analysis. The exception was the 0 DAT for the single application were the 15 cores were taken to 15 cm deep and these were analysed separately to establish the uniformity of the application.

The samples were analysed by GC following extraction of the soils and partitioning (hexane/acetonitrile then aqueous methanol/dichloromethane). Recoveries studies were conducted over the range 0.01 to 1.0 ppm and for Fresno ranged from 70 to 120%, a mean of 92% and for Chualar recoveries were better with a range of 90-104% and a mean of 97%. The limit of detection was determined to be 0.01 mg/kg soil.

When the cores were weighed, it was noted that there was considerable variation in the weight per 15 cm soil horizon, a range of 2 two fold, therefore all results were converted from the normal mg/kg (ppm) to total active per core. As two different core diameters were employed, this was further normalised to μg/100 cm^2 area of soil sampled. (DEH calculates that if all three Section in a plot had concentrations at the detection limit of 0.01 μg/g soil, then the 'normalised' result is 19.9 μg/100 cm^2.)

Table 63 gives a summary of the results as average of samples for the 0-15 cm Sections and the dissipation half lives.

Table 63: Concentration of azinphos-methyl residues in soil following application to alfalfa in California expressed as μg/100 cm^2. Multi = 2 application 7 days apart, DAT 0 = 0 days after second application.

Sample	DAT							
	0	3	7	14	28	60	Half-life, days	R^2
Chualar, single	652	467	466	316	155	13.4	10.9	0.985
Chualar, multi	723	984	565	567	152	67.2	15.5 *	0.926
Fresno, single	884	563	510	172	22.5	-	5.3	0.986
Fresno multi	519	589	173	154	44.3	-	7.7*	0.914

*Calculated by DEH.

The results in Table 63 for the single application show half lives of 5.3 and 10.9 days with good correlations, indicating a good fit to first order kinetics. The multiple applications, while not intended as a kinetic study, nevertheless gave half-lives reasonably consistent with those of the kinetic studies. As the average air temperatures for Chualar were 5-10°C cooler than those at Fresno, this temperature would explain the differences in the rates of dissipation at the two sites.

There was no detectable residues below the 15 cm soil cores from the multiple applications sites and only one detection in one section in Chualar site on day 28 (0.09 mg/kg in 15-30 cm depth core). There was no evidence of leaching from any plot. The sampling of the 15 cores taken on day 0 for all plots clearly showed that the application was not uniform, with the relative standard deviation ranging from 64% to 150% of the mean. The mean application rate per square centimetre was 6.5 and 8.8 μg/cm^2 for Chualar and Fresno single application plots respectively and 16.3 and 11.7 μg/cm^2 for the multiple sites respectively. Given the presence of the alfalfa crop and the 'normal' variation in field application, the results are not that surprising. (Note a single application at 3.36 kg ai/ha corresponds to 33.6 μg/cm^2).

The study clearly shows that rapid dissipation of azinphos-methyl residues from soil, with half lives similar to that in other studies, and that leaching is unlikely, mainly due to the rapid dissipation in soil.

Study 4

An extensive agricultural runoff and water monitoring study was performed as a special study (Toll, 1993) to assess/reduce the potential risk of fish kills. The study was undertaken in 17 different waterways adjacent to sugarcane crops in Louisiana that had been reported as having azinphos-methyl related fish kills in the previous two years. The overall site included extensive waterways adjacent to cane fields. Water sampling stations were established in waterways at >60 locations in an area where ~24 000 ha of sugarcane were sprayed with azinphos-methyl (some with two applications) at 200 g ai/L using a total of ~100 000 L of product. The trial was in conjunction with the Louisiana Department of Agriculture and Forestry, who authorised each application, and only fields sprayed within 5 miles of a sampling station were included (~2 800 ha) as the trial attempted to relate azinphos-methyl levels in water to runoff events and recent azinphos-methyl applications.

The rainfall data presented notes that only one rainfall event (44 mm) in the entire trial was intense enough to trigger runoff from recently sprayed sugarcane fields. Notably this was from a group of 5 smaller sites (3.2-16 ha) sprayed within a larger (~400 ha) approved area,

which was stopped due to "the weather". Sampling could not be conducted during this storm runoff event and only 3 water samples were collected downstream of the application site. Needless to say, azinphos-methyl levels in the water tested were below detection limits. This was a well planned and executed cooperative large-scale field trial where everything went as expected except for the weather conditions needed to consistently produce runoff.

The conclusions of the trial are worth reporting, in that use of azinphos-methyl was lower due to lower pest (cane borer) pressure and a prescriptive use condition that led to alternate chemical use of Baythroid (cyfluthrin). The lower seasonal rainfall (with less runoff) and label changes, highlighting the risk reduction measures, appear to have reduced fish kill incidents associated with this azinphos-methyl use in sugarcane in the trial season 1993 (note: 1991 – 15 incidents, 1992 – 7, 1993 – 0[19]).

Other Published Studies

A published study (Granovsky, *et al*., 1996) followed the dissipation of azinphos-methyl from leaves and soil in sugarcane field plots (9 rows X 150 m) and in particular monitored azinphos-methyl in runoff. They correlated levels in runoff to the plant/soil levels and wash-off/runoff caused by rainfall events then modelled the dissipation of azinphos-methyl from both leaves and soil. Azinphos-methyl was applied to maturing sugar cane, in conjunction with a fertiliser rate trial, with up to three azinphos-methyl applications (0.82 kg/ha each) later in the season over three consecutive years (1993-95). The azinphos-methyl was applied using a ground-based sprayer (high rig), except in one instance where a helicopter was used due to wet ground, and the soil type is described as Commerce silt loam, but no other details are provided (eg pH, OM).

Leaf and surface soil (2.5 cm) samples were collected daily after each application and then less frequently (2-7 days apart), and in each plot runoff was channelled to sumps with flow meters and automatic water samplers installed. Samples were extracted by three separate methods (one for each type) with the final azinphos-methyl determination by GC. Leaf residues were converted to g/ha by using a standard leaf area index computation. The authors note that "individual applications differed in the amounts of azinphos-methyl that reached the canopy leaves", and "total azinphos-methyl detected in both leaves and surface soil did not exceed 50% (350-400 g/ha) of the amount applied (820 g/ha)". No explanation for this is proposed, such as application losses, delays in sampling, extraction/recovery losses, etc. However, the maximum leaf residues are comparable with levels reported in other field trials.

The conclusions of the trial are that the amounts of azinphos-methyl appearing in runoff are highly correlated to the residual azinphos-methyl levels on plants and the surface soil, and the propensity for azinphos-methyl to wash-off plants with rainfall events soon after application. Even relatively small rain events dislodged a high percentage of the residual azinphos-methyl. As an example the initial spray (on the 19 August 1993) produced residual leaf azinphos-methyl levels of 340 g/ha and following, 8 mm rain 1 day later, these levels were reduced to 20 g/ha, with higher soil surface levels reflecting these losses. The modelling of these data derived half-lives for azinphos-methyl of 2-8 days as leaf deposits and 6-66 days for soil.

An earlier published study (Smith, *et al*., 1983) reported the edge of field losses of azinphos-methyl (and fenvalerate) from sugarcane treatments for cane borer in an IPM system.

[19] Possibly 2 azinphos-methyl related fish kills were reported, one appears to be a drift/overspray onto a pond – viz not runoff; the other was runoff related, but arose from treatment outside the trial area in neighbouring Arkansas.

Azinphos-methyl was applied (0.84 kg/ha) four times per year in 1980 and 1981 with runoff samples (water and sediment) collected within 8 hr of storm events and analysed by extraction and GC.

Rainfall was around average in 1980 and abnormally low in 1981, but the amount of runoff was higher in 1981, and azinphos-methyl losses appear to correlate with the proximity between runoff and spray events, rather than overall rainfall. Seasonal losses of azinphos-methyl in runoff were 0.08% (1980) and 0.55% (1981) of the total applied, with three rain events within 5 days of spraying in 1981 accounting for ~70 % of total losses, while one event in 1980 accounted for ~55% of 1980 losses. (Supportive study only)

3.2.5.2 Terrestrial Field Dissipation - Horticulture

Study 1

The following study (Anonymous, 1983) on the dissipation of azinphos-methyl applied to apple orchards was performed by Michigan State University according to a US EPA guidelines (to construct and validate a model: Pesticide Orchard Ecosystem Model or POEM).

The apple trees (av height 3 m) were treated over two seasons with azinphos-methyl as a wettable powder (50W, 50% ai) applied with a purpose built low pressure, low volume sprayer. The average rate was stated to be 1.62 ± 0.38 (1976) and 1.64 ± 0.33 kg/ha 50% w.p. /100 L/ha (1977) (the units used are unfamiliar but is assumed to be around 0.8 kg ai/100 L/ha). It is not clear in the paper what actual volume was applied, that is around 1000 L/ha per application as is typical of low volume orchard applications. In Australia high volume sprayers in the larger orchard trees may use up to 6000 L/ha, thereby applying a maximum of ~3 kg ai/ha per application. Label instructions state that semi-concentrate (low volume) sprayers should increase the mixing rate in proportion to the decrease in spray volume, viz constant rate of ai applied. If we assume these rates for each application were 0.8 kg ai/ha, then this is somewhat lower than Australian use, but if we presume 1000 L spray/ha then the resulting 8 kg ai/ha is significantly higher.

There were four plots treated together with an untreated control, each set up such that all runoff from the plots was collected separately. Plots were mown prior to the first spray treatment and as required after that (nil in 1976 and twice more in 1977). Filter paper traps were placed at ground level throughout the plots to determine the horizontal distribution of spray, and samples were taken from each ground level segment (soil, litter/moss, and grass/broadleaf plants), both in-row and between row, along with the canopy (2 cm discs from apple leaves).

The soils were sampled prior to and then periodically after each application. A final trial year (1978) was monitored to test the model's predictions against measured field data for residues of azinphos-methyl in the different orchard segments. All results are provided as $\mu g/cm^2$, which makes sense from an application perspective, but is more difficult to interpret than the usual basis of residue per mass of plant or soil material.

For azinphos-methyl there was significant movement from the trees (target) to other segments (soil, grass, litter) during three seasons studied. However, there were few detections in runoff, largely due to the rare occurrence of runoff events (nil - 1976 and 6 – 1977) at this site because of one dry season plus the heavy ground cover. Azinphos-methyl residues on the tree canopy apparently dissipate at a rate of 4.9% per day on average, and the residue levels found

in 1978 largely matched the model's predictions. Rainfall increased the loss of dislodgeable azinphos-methyl residues, especially "heavy" rain soon after application, plus the model suggests that around 25% of the daily losses are redistributed within the orchard under dry conditions. Losses from the orchard's soil segment were estimated at 7.9% per day.

Model simulations were run changing various factors such as temperature, rainfall, soil pH and volatility. Heavy rainfall and increased volatility produce more rapid attenuation of azinphos-methyl residues whereas increased temperature hardly affects the rate.

Study 2
An older study (Kuhr, *et al*., 1973) followed dissipation of azinphos-methyl in soils under a commercial apple orchard. Several insecticides were used in a seasonal program (13 applications) from April to August. Four applications of azinphos-methyl were made (June 7, 18, 30 and July 19) at 0.82 kg/ha each and soil cores (0-5 cm) taken from under trees (mid-canopy). Parallel sampling was conducted at a nearby Experiment Station treated with 7 applications of azinphos-methyl at 0.82 kg/ha over three months (June-August) at ~2 week intervals. While methods are clearly not as sensitive as in current tests, there was a relatively stable level of azinphos-methyl in the commercial orchard with a peak soil concentration of 1.6 ppm rapidly falling below detection limits two weeks after azinphos-methyl spraying ceased. In the more controlled system soil azinphos-methyl levels peaked at 4.2 ppm after the final application and had dissipated to LOD levels around 6 weeks later. The trial was not conducted according to current protocols and noted that parent azinphos-methyl only was followed, that is no metabolites, and the information is regarded as supportive only.

Study 3
Yet another study (Yaron, *et al*., 1974) followed the persistence of azinphos-methyl in an irrigated soil in Israel using a high rate (1 g/m^2or ~10 kg/ha) in test plots growing potatoes with two rates of water application. Only traces of azinphos-methyl were detected in soil below 12 cm, even under heavy irrigation, and azinphos-methyl did not persist in soil with only trace amounts detectable after 30-40 days. The half-life under these conditions was estimated at 5 days. (Supportive study only)

3.2.5.3 Water monitoring studies

Study 1
A literature report (Bushway, et al., 1982) provides brief data on a field survey for azinphos-methyl residues in water and blueberries, conducted in a coastal area of Maine, where this crop is concentrated (~20 000 ac) and azinphos-methyl use is extensive. Concern is expressed for water quality and any possible effects on adjacent marine clam culture, a major local industry. Azinphos-methyl residues were detected in water at two of the seven selected sites, notably 3 times in a well (1.9, 11.2 and 24 ppb) in a sprayed blueberry field and not unexpectedly in wash effluent at the processing factory (12.7 ppb). The authors report that ~12 inches of rainfall occurred during the two month survey period and residues detected on fruit samples were low (<LOD-0.112 ppm, cf MRL of 5 ppm), while no adverse effects were observed in Maine clams.

Literature
A series of studies have investigated various aspects of azinphos-methyl contamination in a South African river, arising from use in stone and pome fruit orchards in the catchment area. The following studies investigated the relative importance of runoff and spray drift to

azinphos-methyl contamination in the river, and the effectiveness of a constructed vegetated wetland in reducing insecticide concentrations and toxicity due to runoff or spray drift. Studies of the toxicity to aquatic/benthic invertebrates of azinphos-methyl in simulated runoff or spray drift contamination events are discussed in Section 3.3.2.8

Study 1

Dabrowski and Schulz (2003) reported a study where a runoff formula developed by Reus et al (1999) and basic drift values (95th percentiles from tables by Ganzelmeier et al, 1995) were integrated into a geographical information system (GIS) to predict runoff and spray drift–related loading of azinphos-methyl in the Lourens River, South Africa. They first validated GIS-integrated calculations in tributaries of the river, finding that measured loads were well predicted for both runoff ($r^2 = 0.95$; $p < 0.0001$; $n = 9$) and spray drift ($r^2 = 0.96$; $p = 0.0006$; $n = 8$). They then extrapolated the results to the catchment scale containing 400 ha of orchards. The GIS-integrated calculations predicted similar loads of azinphos-methyl to those measured in the Lourens River mainstream for six runoff events (predicted values between a factor of 1.03 and 1.86 lower) and six spray drift events (predicted values between a factor of 1.1 and 2.4 higher). Mean measured loads per event were significantly ($p = 0.004$) higher for runoff (27.8 ± 19.1 g) than for spray drift (0.69 ± 0.32 g).

Based on long-term meteorological data and average application regimes, the investigators concluded that runoff leads to a higher annual load (47.6 g) than spray drift (5.5 g) in the Lourens River. The investigators discussed possible reasons for the greater importance of runoff. Runoff-induced pesticide loading can occur long after the previous application, so that runoff integrates chemical input over a large time span, whereas with spray drift contamination only occurs during application, in combination with specific meteorological requirements which further restrict the potential for contamination. Hence the spatial and temporal scale of runoff contamination is far greater than spray drift. In the area investigated windbreaks also reduced the potential for spray drift to carry. Hence the investigators stressed the need for measures to reduce runoff losses, focussing first on a catchment scale and second on addressing problem areas on a subcatchment scale. They noted that available options included the use of agricultural best management practices, implementation of buffer strips, and the use of constructed wetlands to reduce aqueous and suspended particle–associated pesticide input from tributaries into the Lourens River mainstream.

Study 2

Schulz et al (2003) reported a study to ascertain the retention, fate, and effects of spray drift-borne azinphos-methyl in a 0.44 ha vegetated wetland built along a tributary of the Lourens River, South Africa. Composite water samples taken at the inlet and outlet during five spray drift trials in summer 2000 and 2001 revealed an overall reduction of azinphos-methyl levels by ~90% and a retention of azinphos-methyl mass by ~61%. Samples were collected at the inlet, outlet, and four platforms within the wetland to determine the fate and effect of azinphos-methyl in the wetland after direct spray drift deposition in the tributary 200 m upstream of the inlet. Peak concentrations decreased, and the duration of exposure increased from inlet (0.73 g/L; 9 h) via platforms 1 and 4 to outlet (0.08 g/L; 16 h). Azinphos-methyl sorbed to plants or plant surfaces, leading to a peak concentration of 6.8 g/kg dw. The living plant biomass accounted for 10.5% of the azinphos-methyl mass initially retained in the wetland, indicating processes such as volatilization, photolysis, hydrolysis, or metabolic degradation as being very important. Azinphos-methyl was not detected in sediments. Water samples taken along two 10 m transects situated perpendicular to the shore indicated a homogeneous horizontal distribution of the pesticide: 0.23 ± 0.02 and 0.14 ± 0.04 g/L ($n = 5$),

respectively.

Both Copepoda ($p = 0.019$) and Cladocera ($p = 0.027$) decreased significantly 6 h postdeposition and remained at reduced densities for at least 7 d. In parallel, the chlorophyll a concentration showed an increase, although not significant, within 6 h of spray deposition. The study highlights the potential of constructed wetlands as a risk-mitigation strategy for spray drift-related pesticide pollution.

Study 3

Schulz and Peall (2001) reported a study to ascertain the retention of runoff-related agricultural pollution, including azinphos-methyl and other insecticides, in a 0.44 ha vegetated wetland built along a tributary of the Lourens River, South Africa, Retention of water-diluted azinphos-methyl introduced via runoff at a level of 0.85 µg/L was between 77 and 93%. During a period of 5 months, an increased concentration of azinphos-methyl (43 µg/L) was detected in the suspended particles at the wetland inlet. No organophosphorus pesticides were found in the outlet suspended-particle samples, highlighting the retention capability of the wetland.

A toxicological evaluation employing a *Chironomus* bioassay in situ at the wetland inlet and outlet revealed an 89% reduction in toxicity below the wetland during runoff.

US EPA

In their review of azinphos-methyl, the USEPA report on several water monitoring studies over a considerable time period (US EPA 1999). Of note is the work by the United States Geological Survey (USGS) conducted from 1993 to 1997 in 40 water basins across the US. Of the 5133 water samples analysed, there were 164 positive detections for azinphos-methyl, some 3.2% of the total, with the highest at 1.0 µg/L. Four of these detections were in ground water with a maximum of 0.064 µg/L. However, as the recovery for azinphos-methyl in the multi-residues analysis was very poor at 13%, this is expected to be a significant under-reporting of the true situation. Potentially there could be approximately ten times increase in the number of reported positives and in the maximum concentration detected. Due to the poor recoveries, DEH considers the report indicative only but notes with some concern the potentially high level of positive results possible if a more suitable analysis method had been used.

Two other monitoring studies were briefly mentioned in the US EPA review. One was conducted by the USGS but used the same analytical method as above and the same low recovery. The other was conducted in South Florida in an area with minimal use of azinphos-methyl and used a method with poor limits of detection, which ranged from 0.25 to 9 µg/L over the study period (1988 to 1993). Again the usefulness of the study is limited due to poor detection limit.

The US EPA review indicates that in 1598 wells sampled from 1971 to 1991, there were no detections of azinphos-methyl. However, they also report that there were 16 detections in 60 samples taken during July/August in two counties (Clarke and Frederick County, Virginia) with intensive agriculture. The US EPA considers the aquifers in these counties highly vulnerable to contamination and notes that there are significant uncertainties with the data.

Australian water monitoring

Azinphos-methyl was not tested for in recent Australian pesticide surveys in the

Murrumbidgee Irrigation Area (Bowmer, et al., 1998), but it was not considered a major use chemical for this region. Another major water monitoring survey is for the cotton growing region of northern NSW (Muschal, 1997 & 1998), but again azinphos-methyl is not used for cotton and was not tested for.

3.2.5.4 Modelling of aquatic exposure

Study 1
A modelling study (Lin, 1995) examines azinphos-methyl use in irrigated almond orchards in California and estimates aquatic exposures from this use pattern. A GIS based model (US EPA – PIRANHA: Burns, *et al*., 1992) was used to simulate the potential aquatic exposure from applications of azinphos-methyl and recommend modified use patterns that may mitigate potentially hazardous environmental effects. The results of the orchard airblast study of the Spray Drift Task Force were used in this to model the efficacy of adding a buffer zone around orchards in reducing aquatic exposure. PIRANHA combines other exposure models (PRZM, EXAMS and FGETS) within a GIS shell with mapping, climatic, bio-geographic and physiographic information to evaluate the aquatic ecosystem hazard.

Rainfall data showed this study area to be quite dry (av 288 mm) and variable (120 –700 mm) with predominantly winter rainfall. Needless to say, these almonds (3.4% of overall study area) require widespread irrigation during the growing season and unfortunately there is little standing water (0.17%) within the study zone. Most of the natural streams (0.87%) only flow intermittently, while irrigation distribution canals form the majority of flowing watercourses in the study area. The model simulated a worst case situation for use in almonds with one dormant (winter) spray plus two summer sprays at 2.2 kg/ha.

The model comes up with "the obvious" for air blast orchard spraying in that where almonds and water are adjacent a buffer zone is required to avoid azinphos-methyl residues reaching water. There was some interface between the only permanent watercourse (Kern River) and orchards, but this was somewhat difficult to define given the scale of maps supplied.

This model appears more useful in defining differences between treatment scenarios. However, the scenario tested is not useful for most of Australia's pome fruit areas, but may provide insight to the situation in our inland irrigation areas (some pome and stone fruit).

Study 2
An older modelling study (Red et al., 1984) examined the likely occurrence of azinphos-methyl (and four other pesticides) in runoff from three "seed orchards" using the field scale model CREAMS. Topographic, soil, rainfall and other data from the three sites were used to estimate the frequency of exceeding the LC_{50} value for bluegill sunfish in runoff from these orchards in Arkansas, Louisiana and Mississippi. Azinphos-methyl was assumed to be applied on the first day of five consecutive months at a rate of 3.4 kg/ha, and the simulation was run over 50 years. The model indicated that in 30 of the 50 years at least one runoff event would occur with azinphos-methyl concentration > LC_{50} and as many as 10-12 of these events might occur in rare seasons (a similar pattern was displayed by fenvalerate in this model, as well).

The application rate used in the model is similar to many situations in Australian orchards (1-2 kg/ha), but the monthly re-spray interval may be shorter here with label recommendations stating 2-3 weeks. As well, the US model was applied to a sub-tropical area likely to experience extreme rainfall events more frequently than most Australian orchard areas.

However, crops such as macadamias and litchis would be grown in comparable conditions. These results support other studies indicating azinphos-methyl is subject to wash-off and is likely to enter aquatic systems in storm runoff, particularly if heavy rain occurs soon after application. DEH regards this study as supportive only.

US EPA Modelling

In the US EPA review for azinphos-methyl (US EPA 1999), the results for a number of modelling scenarios was presented using PRZM and EXAMS. In these models the maximum label rates for a range of crops was used together with available weather and environmental fate data for each scenario. These models include aerial spray drift (assumed as 5% of application rate) as well as runoff as source of contamination to estimate the maximum estimated environmental concentration (EEC). The results indicate the cotton has the highest EEC at 87 μg/L, the highest for orchards was peaches at 40.6 μg/L and the lowest 4.4 μg/L for pears. Estimates for contamination in vulnerable groundwater (using SCI-GROW) indicate that maximum contamination is from cotton use at 0.85 μg/L and for orchard (pome and nut) 0.40 μg/L.

3.2.5.5 Field studies – Conclusions

Crop Trials

US field trials on cotton, sugar and alfalfa, while not particularly relevant to the Australian use patterns, give a strong indication of azinphos-methyl's ability to enter waterways, particularly with runoff from heavy rainfall events. In two trials in cotton, the field half-life of azinphos-methyl in soil was 5.7 and 6.4 days and on foliage 1.2 and 0.5 days respectively. There were rainfall events in the cotton trials that caused runoff to occur, with a maximum of 2.7% of the active applied detected in the runoff waters from one rainfall event.

Two trials were conducted in California in fields of alfalfa, with the half lives in soil of 5.3 and 10.9 days for single applications. In plots receiving 2 applications there was no evidence of leaching despite high total application rates used (6.72 kg ai/ha).

The results indicate that in field use azinphos-methyl can be rated as readily degradable and leaching is unlikely but these field trials also demonstrated the propensity for potentially toxic runoff to occur, especially with rainfall soon after application. The likelihood of this occurring clearly increases when the OPs are frequently applied, such as in the cotton trials where repeat applications occurred every 3-7 days, and especially with heavy rainfall. These results concur with the incidence reports from the US (Section 3.3.7).

An extensive agricultural runoff and water monitoring study was performed as a special study to assess/reduce the potential risk of fish kills. The overall site included extensive waterways adjacent to cane fields. The study was undertaken in 17 different waterways that had been reported as having azinphos-methyl related fish kills in the previous two years. However, only one rainfall event (44 mm) in the entire trial triggered runoff from recently sprayed sugarcane fields. Sampling could not be conducted during this storm runoff event and in samples collected later azinphos-methyl levels were below detection limits. The lower seasonal rainfall (with less runoff) and label changes appear to have reduced fish kill incidents associated with this azinphos-methyl use in sugarcane in the one year trial (note: 1991 – 15 incidents, 1992 – 7, 1993 – 0).

A published study followed the dissipation of azinphos-methyl from leaves and soil in

sugarcane field plots and in particular monitored azinphos-methyl in runoff. Azinphos-methyl was applied to maturing sugar cane three times (0.82 kg/ha each) later in the season over three consecutive years (1993-95). The conclusions of the trial were that the amounts of azinphos-methyl appearing in runoff are highly correlated to the residual azinphos-methyl levels on plants and the surface soil. There was a propensity for azinphos-methyl to wash-off plants with rainfall events soon after application. Even relatively small rain events dislodged a high percentage of the residual azinphos-methyl. The modelling of these data derived half-lives for azinphos-methyl of 2-8 days as leaf deposits and 6-66 days for soil.

Apple orchards trials designed to provide information on off-site movement of azinphos-methyl, largely for modelling purposes, showed little runoff due to seasonal and site conditions (low rainfall and heavy ground cover). There were four plots treated together with an untreated control, each set up such that all runoff from the plots was collected separately. Plots were mown prior to the first spray treatment and as required after that (nil in 1976 and twice more in 1977). The soils were sampled prior to and then periodically after each application.

For azinphos-methyl there was significant movement from the trees (target) to other segments (soil, grass, litter) during three seasons studied. However, there were few detections in runoff, largely due to the rare occurrence of runoff events at this site because of one dry season plus the heavy ground cover. Azinphos-methyl residues on the tree canopy apparently dissipate at a rate of 4.9% per day on average, and the modelling suggested that around 25% of the daily losses are redistributed within the orchard under dry conditions. Losses from the orchard's soil segment were estimated at 7.9% per day. Rainfall increased the loss of dislodgeable azinphos-methyl residues, especially "heavy" rain soon after application. These presumably might enter runoff where bare soil situations occur in orchards, for example in Australian macadamias.

Monitoring studies

Studies investigating aspects of azinphos-methyl contamination in a South African river as a result of spray application to stone and pome fruit orchards in the catchment area showed that the contribution from runoff was substantially greater than that due to spray drift. This was though to be due to the differing spatial and temporal scales of runoff contamination and spray drift in this catchment. A vegetated wetland constructed along a tributary of the river was shown to be a useful technique for minimising the movement of azinphos-methyl contamination into the river, either from spray drift or runoff (dissolved in the water or adsorbed to suspended particles) sources.

Water monitoring studies conduct across the USA by the USGS show that in the 5133 surface samples taken some 164 (3.2%) contained detectable levels of azinphos-methyl, 4 of which were groundwater. In the US EPA review of this report, it was considered that there was considerable under-reporting of the true level due to poor recoveries of azinphos-methyl in the analytical method used (13%). There were 16 detections in 60 groundwater samples in two counties in Virginia, USA, both with intensive agriculture and vulnerable aquifers.

As azinphos-methyl does not have significant use in the MIA and is not a cotton insecticide, it has not been tested for in major Australian water monitoring surveys in the MIA and northern NSW rivers programs.

3.2.6 Bioaccumulation

3.2.6.1 Bioaccumulation and Elimination

The bio-accumulation of azinphos-methyl was studied (Lamb and Roney, 1976) in channel catfish (*Ictalurus punctatus*), basically according to US EPA Guidelines.

The fish were exposed to water containing ^{14}C-azinphos-methyl at a target concentration of 15 µg/L (nominal) under-flow through conditions. The water was sampled before the study and during the bio-accumulation phase. The concentration of azinphos-methyl was relatively constant throughout the study with a mean of 15.3 µg/L (range 7.3 to 17.3 µg/L), as determined by radiometric analysis. The stability of the stock solution was not determined.

The accumulation phase lasted for 28 days and the depuration for a further 28 days. The fish were to be sampled at 0, 1, 4, 7, 10, 14, 21 and 28 days during the uptake and the depuration phases. Whole fish, edible and non-edible tissues were analysed by radiometric analysis. Unfortunately, the 0 time samples for uptake were taken after 1, 2 and 6 h and for depuration at 5 h. Azinphos-methyl accumulated to a steady state plateau in ~1 day with a steady state concentration in tissues around 0.6 mg/kg (total radioactivity) for whole fish. The depuration rate was somewhat slower, with 90% reduction in the residues of azinphos-methyl in whole fish after 7-10 days. The nature of the 14C-residues in the tissues was not determined.

The steady state bio-accumulation factor was determined to be 63X. Elimination of azinphos-methyl from these fish was somewhat slower, and both rates are partly confounded by the lack of actual zero time samples, but still indicative of rapid depuration. Bio-accumulation in the aquatic environment is not expected.

3.2.7 Summary of Environmental Fate and Degradation

3.2.7.1 Hydrolysis

Azinphos-methyl is reported from four experiments to be relatively stable in low pH aqueous buffers but more rapid hydrolysis occurs at higher pH (half-lives: ~39-42 days @ pH 4; ~23-25 days @ pH 7; ~2-2.5 days @ pH 9). A number of hydrolysis products are formed, largely a series of benzazimides that eventually lead to anthranilic acid. Hydrolysis could be a significant contributor to the overall degradation of azinphos-methyl in the environment, particularly under alkaline conditions.

3.2.7.2 Photolysis

Aquatic

Based on five studies using artificial light and sunlight, photo-degradation of azinphos-methyl in water is possible, with benzazimide and anthranilic acid the major metabolites. The half-lives were determined for two of these studies and ranged from <0.5-3 days. The half-life under environmental conditions was determined by modelling as 0.9-5.5 days for German spring and summer conditions.

It is concluded that photodegradation in water could be a significant route of degradation under Australian environmental conditions but the turbidity in Australian natural waters could

decrease the rate of degradation.

Soil/Plants
Based on 2 soil photolysis studies using natural sunlight, the net half-life of photo-degradation of azinphos-methyl in air dried soils was calculated to be 232-241 days in sunlight. The main metabolites occurred at low concentrations and were not identified. On glass plates azinphos-methyl degradation was relatively slow, but on plant surfaces dissipation of azinphos-methyl appeared more rapid than from soils with 20-40% degradation after 8 h exposure to sunlight.

There were several additional studies that used artificial light. These showed that exposure to ultra violet (UV) light was effective in degrading azinphos-methyl, but the visible wavelengths were not effective. Half-lives for UV exposures were determined in the order of hours (2-8) depending on conditions used, but as these studies used different lamps and conditions they cannot be readily related to natural conditions.

Photodegradation on plant surfaces may be a major route for environmental degradation in Australia, given the high light levels during summer, when most azinphos-methyl use occurs.

3.2.7.3 Metabolism in Soils

A range of soil metabolism studies were performed using several soil types (two acceptable and seven supportive studies). It is concluded that microbial degradation of azinphos-methyl in soil systems is moderate under aerobic conditions (half-lives 21-49 days), and somewhat slower under anaerobic conditions (half-life 68 days). The considerably longer half-life (355 days) under sterile conditions indicates these rates are highly dependent on microbial activity. The main metabolites were similar throughout the degradation studies, largely a group of benzazimides and anthranilic acid, and eventually more complete mineralisation yielding CO_2. In Australia it is likely that hydrolysis and microbial degradation will occur in soils, especially under alkaline conditions, and it is expected this will occur at similar rates to those quoted above, depending on soil types/pH.

3.2.7.4 Aquatic Metabolism

There were no studies provided on aquatic aerobic metabolism. However, the azinphos-methyl half-lives in the aquatic phase of the mesocosms were typically ~1-2 days.

3.2.7.5 Mobility in Soil

Soil adsorption/desorption
The soil adsorption/desorption of azinphos-methyl was determined in two acceptable studies using 7 different soils. The K_{oc}s averaged 757 (range 407 to 1172, discarding one abnormal value of 3396) and show that azinphos-methyl is moderately absorbed to the six soils tested. The adsorption appears strongly dependent on the organic matter content of the soil. The desorption studies indicated azinphos-methyl desorbs fairly readily and constantly from adsorption sites. These tests rank azinphos-methyl as having medium mobility in soils, which is supported by several other reports.

Leaching
Several soil column leaching studies using a range of different soils, both fresh and aged, showed there was little leaching of azinphos-methyl (<0.3%). Some metabolites were

detected in the leachate, generally in low amounts (<5% of applied). In the one instance where there was no aging around 10% of applied radioactivity appeared in leachate, mainly degradation products. Soil R_f values were determined on TLC plates and indicated low mobility. Azinphos-methyl is unlikely to leach under field conditions.

Volatility
No studies on volatilisation of azinphos-methyl from soils presented, but this is not expected to be a significant route for the dissipation from soil, particularly where binding to soil organic matter occurs.

3.2.7.6 Field Dissipation

Crop Trials
US field trials on cotton, sugar and alfalfa, while not particularly relevant to the Australian use patterns, give a strong indication of azinphos-methyl's ability to enter waterways, particularly with runoff from heavy rainfall events. In two trials in cotton, one in Mississippi and the other Georgia, the field half-life of azinphos-methyl in soil was 5.7 and 6.4 days and on foliage 1.2 and 0.5 days respectively. There were rainfall events in the cotton trials that caused runoff to occur, with a maximum of 2.7% of the active applied detected in the runoff waters from one rainfall event.

Two trials were conducted in California in fields of alfalfa, with the half-lives in soil of 5.3 and 10.9 days for single applications. In the plots receiving 2 applications there was no evidence of leaching despite high total application rates used (6.72 kg ai/ha).

The results indicate that in field use azinphos-methyl can be rated as readily degradable but it also demonstrates the propensity for potentially toxic runoff to occur, especially with rainfall soon after application. The likelihood of this occurring clearly increases when the OP are frequently applied, such as in these trials in cotton where repeat applications occurred every 3-7 days, and especially in summer rainfall zones. These results concur with the incidence reports from the US (see Section 3.3.7).

An extensive agricultural runoff and water monitoring study was performed as a special study to assess/reduce the potential risk of fish kills. The overall site included extensive waterways adjacent to cane fields. The study was undertaken in 17 different waterways that had been reported as having azinphos-methyl related fish kills in the previous two years. Only one rainfall event (44 mm) in the entire trial triggered runoff from recently sprayed sugarcane fields. Sampling could not be conducted during this storm runoff event and in samples collected later azinphos-methyl levels were below detection limits. The lower seasonal rainfall (with less runoff) and label changes appear to have reduced fish kill incidents associated with this azinphos-methyl use in sugarcane in the one year trial (note: 1991 – 15 incidents, 1992 – 7, 1993 – 0).

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For azinphos-methyl there was significant movement from the trees (target) to other segments (soil, grass, litter) during three seasons studied. However, there were few detections in runoff, largely due to the rare occurrence of runoff events at this site because of one dry season plus the heavy ground cover. Azinphos-methyl residues on the tree canopy apparently dissipate at a rate of 4.9% per day on average, and the modelling suggested that around 25% of the daily losses are redistributed within the orchard under dry conditions. Losses from the orchard's soil segment were estimated at 7.9% per day. Rainfall increased the loss of dislodgeable azinphos-methyl residues, especially "heavy" rain soon after application. These presumably might enter runoff where bare soil situations occur in orchards, for example in Australian macadamias.

3.2.7.7 Monitoring studies

In one of a series of studies investigating aspects of azinphos-methyl contamination in a South African river as a result of spray application to stone and pome fruit orchards in the catchment area, it was shown that the contribution from runoff was substantially greater than that due to spray drift. An evaluation of the use of a vegetated wetland constructed along a tributary of the river to intercept water containing azinphos-methyl residues from spray drift indicated it sorbed to plants or plant surfaces, leading to a peak concentration of 6.8 µg/kg dry weight (accounting for ~10% of the initial mass), but was not detected in sediment. Volatilization, photolysis, hydrolysis, or metabolic degradation were therefore assumed to have been important in its dissipation. There was an overall reduction of azinphos-methyl levels by ~90% and a retention of azinphos-methyl mass by ~60%. Peak concentrations decreased, and the duration of exposure increased from the inlet (0.73 g/L; 9 h) to the outlet (0.08 g/L; 16 h). A separate study showed that the wetland retained 77-93% of azinphos-methyl entering in runoff (ie largely adsorbed to suspended particles).

Water monitoring studies conducted across the USA by the United States Geological Survey (USGS) show that in the 5133 surface samples taken some 164 (3.2%) contained detectable levels of azinphos-methyl, 4 of which were in groundwater. In the US EPA review of this report, it was considered that there was considerable under-reporting of the true level due to poor recoveries of azinphos-methyl in the analytical method used (13%). There were 16 detections in 60 groundwater samples in two counties in Virginia, USA, both with intensive agriculture and vulnerable aquifers.

As azinphos-methyl does not have significant use in the Murrumbidgee Irrigation Area (MIA) and is not a cotton insecticide, it has not been tested for in major Australian water monitoring surveys in the MIA and northern NSW rivers programs.

3.2.7.8 Bio-accumulation

A bioaccumulation study with azinphos-methyl and channel catfish (*Ictalurus punctatus*) based on US EPA Guidelines indicated rapid uptake and depuration, with the steady state bioaccumulation factor determined to be 63. Based on this study, azinphos-methyl is not expected to bioaccumulate.

3.2.8 Conclusions

Azinphos-methyl appears readily degradable by microbiota in soil and is ranked as moderately degradable in soils. Bio-accumulation is not expected. Due to the moderate binding in soil and fairly rapid degradation, leaching is not expected. Field reports, largely from the US, indicate azinphos-methyl may appear in waterways due to wash-off/runoff from recently treated areas. South African studies also show the importance of runoff in azinphos-methyl contamination.

Azinphos-methyl is not expected volatilise from soil, but appears to wash-off leaves and other surfaces, especially soon after application. No information was presented on the photolysis in the vapour phase, but as azinphos-methyl degraded in the photolysis studies and other organophosphates are known to degrade in the atmosphere, it is not expected to persist in the air.

3.3 ENVIRONMENTAL EFFECTS

The main proponent (Bayer) submitted reports of studies on the toxicity of azinphos-methyl in a range of organisms, in accordance with US EPA Guidelines, plus several studies from Maketshim-Agan were submitted, and these are summarised below. These studies are rated by Environment Australia as being reliable, acceptable or for information only. The ratings can be described as:

Reliable: There is a high level of confidence in the results. The study has been performed satisfactorily and while there are only minor problems, they do not affect the results.

Acceptable: The results of the study are scientifically sound but there is a lower level of confidence in the results due to a significant problem or lack of critical information. Often the results are nominal only.

For information: There are sufficient problems in the test that the results are not suitable for regulatory use.

A large number of reports of toxicity tests on birds, mammals and aquatic animals are included in the US review of azinphos-methyl (see US EPA, 1999; pp 30-47) that quotes a larger range of tests/species. Not all of these were provided for review in Australia and they have not been sought since the results and review comments can be seen in the US report. Where insufficient species have been provided, selected US EPA review results have been included in the Tables, as they may add useful supporting data for assessing the risk from azinphos-methyl use.

3.3.1 Avian Toxicity

A number of studies were submitted in regard to the avian toxicity of azinphos-methyl. All adequate results are compiled in Table 64 below.

3.3.1.1 Acute Tests

Study 1
A standard acute oral toxicity test was conducted (Stubblefield, 1987) using adult bobwhite quail (*Colinus virginianus*), given a single dose of technical grade azinphos-methyl (88.8% ai) by gavage. Doses, in corn oil, were 0 (control), 5.6, 11.2, 23, 45 and 90 mg/kg and birds were observed for 14 d. Birds were weighed and feed consumption was recorded for days 0-3, 4-7 and 8-14, and all birds in the 3 highest doses underwent post mortem examination, along with controls. Only one bird survived from the two highest dose rates and only one bird died within the other dosage groups, demonstrating a distinct threshold typical of many OPs. The test was performed well and a valid LD_{50} of 32 mg/kg BW was derived. (Reliable study)

Study 2
In a similar study (Grimes and Jaber, 1988) dosed adult bobwhite quail with azinphos-methyl (as technical) using gavage. Doses were 0 (control), 15, 30, 60, 120, and 240 mg ai/kg (nominal) and birds were observed frequently and weighed, with feed consumption recorded for days 0-3, 4-7 and 8-14. No birds died in the control or lowest treatment groups. Deaths occurred (40%) at the 30 mg/kg rate and all birds died in the three highest dosage groups. Toxicity was noted within minutes at the two highest rates with 100% mortality in <1 day. A valid LD_{50} of 33 mg/kg BW was deduced. (Reliable study)

Study 3
In a further study (Schmuck, 1997) dosed adult bobwhite quail with azinphos-methyl (as 200 g/L SC formulation) using gelatine capsules. Doses, in water, were 0 (control), 20, 40, 80, 150, 220 and 300 mg/kg and birds were observed as above. Deaths only occurred at the two highest dose rates and only one bird exhibited adverse symptoms within the other dosage groups. A valid LD_{50} of 271 mg/kg BW was deduced. (Reliable study)

Table 64: Summary of oral toxicity of azinphos-methyl in birds. Results expressed as test material used. US EPA = from US EPA Review, reports not sighted by DEH. R = reliable study, A = acceptable

Species	Test	Test Material	LD_{50} (mg/kg BW)	NOEL	Reference
Bobwhite	acute oral	Tech.(88.8% ai)	32 (25-41), R	5.6	Stubblefield, 1987
Bobwhite	acute oral	Tech.(88.8% ai)	33 (25-41), R	15	Grimes & Jaber, 1988
Bobwhite	acute oral	SC (20% ai)	271 (229-397), R	80	Schmuck, 1997
Mallard	acute oral	Tech.(90% ai)	136		US EPA supplemental
Bobwhite	Acute 5 d dietary	Tech. (92% ai)	LC_{50} 488 ppm	-	US EPA core
Mallard	Acute 5 d dietary	Tech. (92% ai)	LC_{50} 1940 ppm	-	US EPA core
Ring-neck pheasant	Acute 5 d dietary	Tech. (92% ai)	LC_{50} 1821 ppm	-	US EPA core

Japanese quail	Acute 5 d dietary	Tech. (92% ai)	LC_{50} 639 ppm	-	US EPA supplemental
Mallard	1 gen dietary	Tech.(88.8% ai)		10.5 ppm, R	Toll, 1988
Bobwhite	1 gen dietary	Tech.(88.4% ai)		15.6 ppm, R	Beavers *et al*., 1989

Additional study

Two trials (Grau, 1985a, & 1985b) tested the toxicity of azinphos-methyl to Japanese quail (*Coturnix coturnix*) and canaries (*Serinus canarius*). These synoptic reports appear to be range tests and were conducted with formulated product (Gusathion MS WP 32.5 blue – 250 g/kg azinphos-methyl and 75 g/kg demeton-S-methyl) at doses from 25 to 200 mg/kg of body weight as a single oral dose by gavage or gelatine capsule. Birds were observed for a further 7 days after dosing. LD_{50}s are estimated as 100-150 mg/kg and 100-200 mg/kg, respectively, noting the possible additive effect of demeton-S-methyl. (For information only)

Conclusion

In the acute studies above, deaths occurred in high dose treatments and the results are fairly similar on an ai basis, given the slight differences in procedures, such as carrier/diluent, dosing and formulation. In these regimes a typical OP threshold was noted below which few effects or deaths occurred, but severe effects/death were apparent above this level. The acute oral LD_{50}s for bobwhite quail ranks azinphos-methyl as highly toxic to birds (US EPA, 1982).

There were no acute dietary studies presented to DEH but the US EPA review (US EPA, 1999) contains results of 4 such studies. The results are presented in Table 64, together with the US EPA rating of the quality of the study (core = reliable; supplemental = acceptable). These results rate azinphos-methyl as slightly toxic to highly toxic.

3.3.1.2 Chronic Tests

A chronic study (Toll, 1988) investigated the effects of azinphos-methyl (88.8% ai tech.) incorporated in the diet of mallard ducks (*Anas platyrhynchos*) in a single generation reproduction trial (US EPA Guideline, 1983). Adult ducks kept as pairs in an animal house were fed one of four dose rates (0, 12, 35 and 101 ppm, nominal or 0, 10.5, 32.5 and 96.3 ppm, analytical averages) mixed into commercial pelleted game bird ration. Birds were observed daily, feed intake was determined weekly and BW was measured at 0, 2, 4, 8 and 20 weeks. Eggs were collected daily and weekly batches were incubated then hatched and hatchlings were marked, weighed and grown on untreated food for 14 d, then reweighed and sacrificed.

There were few effects obvious on reproduction at all levels tested, except a small decrease in hatching rate (~11%) at the highest dose, giving a reproduction NOEC of 35 (32.5) ppm. However, females at the 35 ppm rate showed a significant decrease in weight gain and so the NOEC is 12 (10.5) ppm. (Reliable study)

Another similar study (Beavers, *et al*., 1989) investigated the effects of azinphos-methyl (88.4% ai) incorporated in the diet of bobwhite quail (*Colinus virginianus*) on single generation reproduction. Adult quail were fed one of four dose rates (0, 15.6, 36.5 and 87.4 ppm, mean measured level) mixed into commercial rations. The trial was conducted as above according to the US EPA Guideline.

There were no obvious effects on reproduction or on body weight of off-spring at the 15.6 and

36.5 ppm levels in these tests. However, 6 females died in the 36.5 ppm group, although the report attributes these to physical injury or egg-yolk peritonitis. Females at the 87 ppm rate showed a significant decrease in weight gain and there were treatment related mortalities and overt signs of toxicity in both sexes, and the report gives a reproduction NOEC of 36.5 ppm. Given the number of deaths at this level that resulted in a large decrease in hens and the total eggs laid, a NOEC of 15.6 ppm would appear more appropriate. (Reliable study)

3.3.1.3 Literature reports

A recent literature report compares laboratory results to a controlled field study (Matz, *et al*., 1998). This was undertaken to explore the relationship between the quotient risk indices (Q) to field results. In the field test northern Bobwhite chicks in enclosed alfalfa plots (0.2 ha) were exposed to spray at 0.0, 0.77 and 3.11 kg ai/ha. During spraying the chicks were confined to the coop to avoid direct overspray. Chick survival was significantly lower at 3.11 kg ai/ha 0-5 days post spray and in the later period 6-10 days post spray for both treatments. The brain acetylcholinesterase, growth, and weight of crop contents were reduced in both treatments. Raptors were seen in the area and chicks disappeared between dawn and dusk - chicks were in the coops during the night to limit predation.

In the laboratory study, bobwhite chicks were exposed to azinphos-methyl at 0, 150, 240, 380, and 600 ppm in food for 5 days. Chick survival was significantly reduced at 600 ppm and acetylcholinesterase and growth were reduced in all treatments. Based on exposure of food items in the Kenaga nomogram (Fletcher et al 1994), the 150 ppm exposure was considered approximately equivalent to 3.11 kg ai/ha but the effects on survival were only significant at 600 ppm. It was concluded that the observed effects in the field differ from the laboratory results and predicted risks because alternate routes of exposure, behavioural responses, influence of environmental variability or indirect effects (predation) were not included in the quotient method.

Other published reports show that azinphos-methyl was toxic towards birds in field studies conducted in an apple orchard (Burgess, *et al*., 1999). Following commercial orchard operations using azinphos-methyl, there were some toxic effects to nesting tree swallows and eastern bluebirds in Canada. This is reviewed in more detail below (Section 3.3.6.3).

3.3.2 Aquatic toxicity

3.3.2.1 Acute Tests - Fish

The submission contains data from a number of acute toxicity tests for azinphos-methyl in fish, which are summarised in Table 65. In the main, tests presented were conducted according to appropriate standard protocols (US EPA, OECD, ASTM) and largely complied with GLP. Some minor deviations do not appear to have affected the results, and obviously some older tests pre-date current protocols, but these are all regarded as reliable. As well, some synoptic reports that appear to come from screening tests were provided, (see Table 66), and are regarded as for information only.

Table 65: Aquatic toxicity tests of azinphos-methyl in fish. Results expressed as μg/L of test substance. All regarded as reliable or reviewed by US EPA and rated as core study.

Organism	US EPA Test unless otherwise	Test substance	LC_{50} (μg/L)	NOEC	Reference
Rainbow trout	Static 96 h	Tech. 87.3% ai	3.0	1.0	Carlisle, 1984a
Rainbow trout	Static 96 h OECD	WP, 25% ai	21.5	<6.15	Dorgerloh, 1995
Rainbow trout	Static 96 h OECD	SC 200 18.7% ai	40.1		Dorgerloh, 1997
Rainbow trout	Static 96 h	2S 22% ai	28		Nelson, 1978
Bluegill sunfish	Static 96 h	2S, 22% ai	40		Nelson, 1978
Bluegill sunfish, 7 studies	Static 96 h	All tech. 93% ai	range of 4.1-34		US EPA review, all rated core
Sheepshead minnow	Flow-through. 96 h	Tech. 88.8% ai	1.86	0.70	Boeri, 1989a
Sheepshead minnow	Static 96 h	Tech. 92% ai	3.2	0.52	Surprenant, 1989 *

* Makhteshim-Agan study

Table 66: Toxicity tests of azinphos-methyl in fish. Results expressed as μg/L of test substance. R = reliable study, A = acceptable, I = information only.

Organism	Test	Test Substance	LC_{50} (μg/L)	Reference
Rainbow trout	Static 96 h	Tech. 92.6% ai	20 A	Hermann, 1978
Golden orfe	Static 96 h	Tech. 92.6% ai	120 A	Hermann, 1979
Red feather	Static 96 h	WP, 25% ai	10-100 I	Hermann, 1973a
Guppy	Static 96 h	WP, 25% ai	10-100 I	Hermann, 1973b
Goldfish	Static 96 h	WP, 25% ai	10-100 I	Hermann, 1973c
Mirror carp	Static 96 h	WP, 25% ai	10-100 I	Hermann, 1973d

The static tests in Table 65 were all conducted in a similar manner, mostly using groups of 10 fish per treatment, with the test concentrations measured at the start and end of trials (mean values used), and a light:dark cycle of 16:8 hours. Oxygen levels, water temperature and pH were measured daily and fish were assessed for toxicity symptoms, with removal of any dead fish from treated aquaria. Mortalities in control groups were low and conditions largely kept within guideline values for the different species tested.

Onset of measured symptoms was relatively rapid and the probit plots were fairly steep, with the results that the difference between NOECs and LC_{50}s were relatively small. These results indicate that azinphos-methyl can be ranked as very highly toxic to fish, and all tests show relatively consistent values when adjusted on the basis of the active ingredient content.

The results in Table 66 are from synoptic reports, with only nominal concentrations used. However, the tests using the technical active were more detailed, used at least 5 concentrations and are rated as acceptable. The other 4 tests using the EUP were regarded as for information only due to the lack of details, limited number of test concentrations used (3 only) and broad concentration ranges quoted.

3.3.2.2 Chronic Tests - Fish

Further fish tests were reported for exposures of longer duration such as chronic one

generation and early life-stages tests based on US EPA and OECD guidelines. These studies are examined in more detail below and the results are included Table 67.

Table 67: Chronic aquatic toxicity tests of azinphos-methyl in fish. # Indicates synoptic report only. ELS = early life stage. R = reliable study, A = acceptable, I = information only

Organism	Test	LC_{50} (µg/L)	MATC µg/L	Test substance	Reference
Rainbow trout	Flow-through 21 d	2.33 A	0.39 A	Tech. 91% ai	Grau, 1989
Rainbow trout	ELS		0.66 R	Tech. 88.8% ai	Surprenant, 1988a
Sheepshead minnow	1 generation		0.29 R	Tech. 92.5 %	Dionne, 1991
Rainbow trout #	ELS	0.91 A	0.29-0.47 A	Tech. (purity not given)	Carlisle, 1985

Study 1

A prolonged exposure (21-day) fish study was conducted under flow-through conditions according to OECD Guideline No. 204 (Grau, 1989). The test substance used was the TGAC (91% ai) and acetone was used as solvent. There was ten fish per test concentration with no replicates. Nominal concentrations were 0.39, 0.84, 1.8, 3.9, 8.4 and 18 µg/L, with mean measured concentration of 0.61, 0.81, 2.2, 4.8, 9.6 and 22 µg/L. While the analytical results show the targeted concentrations were satisfactory, there was only 3 measurements for nominal concentration of 0.61 to 3.9 (0, 12 and 21 DAT) and 2 for the highest (0 and 7 DAT). This is a weakness in the study. The LOEC was 0.84 µg/L, based on reduced food intake of the fish. The study is rated as acceptable due to lack of replicates and the minimal number of analyses performed.

Study 2

An early life stage study was conducted according to an in-house protocol of Springborn Life Sciences (Surprenant, 1988a). Rainbow trout embryos and larvae were exposed to TGAC azinphos-methyl ranging from 0.062 to 1.0 µg/L nominal. Exposure was for 25 days in the embryonic and 60 days as larvae for a total of 85 days. Weekly analysis established mean exposures of 0.051, 0.14, 0.23, 0.44 and 0.98 µg/L. The viability and survival of larvae was comparable to control for all test concentrations. On termination of the test, there was reduced survival at 0.98 µg/L only compared to control, no effect on growth or length of larvae at 0.44 µg/L or less (the 0.98 µg/L was not included in the statistical analysis but there were apparent effects on growth and length of larvae). Fish exposed to 0.44 µg/L were lethargic and exhibited a loss of equilibrium. Based on larvae survival, the MATC was between 0.44 and 0.98 µg/L (geometric mean 0.66 µg/L) and based on subjective behavioural responses, the NOEC was 0.23 µg/L. While this test was not conducted according to a regulatory Guideline, the results are considered to be reliable.

Study 3

A full life cycle fish study was conducted according to US EPA Guideline 72-5 using sheepshead minnow (Dionne, 1991). Sheepshead minnow were continuously exposed to 5 flow-through concentrations of radiolabelled azinphos-methyl from eggs to maturity and their progeny for 28 days post-hatch. The mean measured concentrations (radiometric analysis) were 0.031, 0.046, 0.092, 0.20, 0.41 µg ai/L, with samples taken 0, 1, 5 DAT, then weekly till 113 DAT. The highest test concentration was also analysed by HPLC and the mean

concentration over the total exposure was 0.47 µg/L.

Survival in the first generation was affected compared to controls at 0.41 µg/L but not in lower test concentrations. There was no effect on hatching success, growth (length and weight) or reproductive success at any concentration. Hatching success of the second generation was empirically estimated to be affected at 0.41 µg/L but not at other test concentrations. However, survival and growth were not affected at 0.41 µg/L. Based on the adverse effects on survival in the first generation and the second generation hatching success, the MATC was determined to be between 0.20 and 0.41 µg/L and the geometric mean 0.29 µg/L. The study is considered to be reliable.

Study 4
A second early life stage study was conducted according to an in-house protocol using rainbow trout embryos and larvae, similar to the previous study (Carlisle, 1985) Exposure was for a total of 49 days in the embryonic and larva stages. Weekly analysis established mean exposures of 0.29, 0.47, 1.14, 3.08 and 4.75 µg/L. On termination of the test, there were no survivors at the two highest test concentrations and reduced survival at 1.14 µg/L (54%) compared to control. There were significant effects on biomass and length of larvae at 0.29 µg/L or greater and one replicate from this test concentration was significantly affected but the difference (13%) was considered a threshold effect. Four fish in the 0.58 µg/L test group were showing clinical signs on termination of the test. Based on biomass and length of larvae, the MATC was 0.29-0.47 µg/L and an LC_{50} of 0.91 (0.48 – 2.48) µg ai/L was calculated.

3.3.2.3 Acute Tests - Invertebrates

Table 67 summarises the reports provided from toxicity tests with aquatic invertebrates that were conducted in line with current guidelines (OECD or US EPA).

Table 68: Aquatic toxicity tests of azinphos-methyl in invertebrates. R = reliable study, A = acceptable, I = information only

Organism	Test	Test material	LC_{50} (µg/L)	NOEC	Reference
Daphnia	flow-thru. 48 h	WP 50, 50% ai	4.4 R	2.4	Surprenant, 1987a
Daphnia [#]	static 48 h	Tech.	1.1 A		Lamb, 1980
Daphnia	static 48 h	SC 200, 20% ai	14.7 R	3.0	Heimbach, 1997
Xanthocnemis zealandica	static 48 h	WP 50, 50% ai	32.2 I		Hardensen and Wratten, 1996
Austrolestes colensonis	static 48 h	WP 50, 50% ai	88.5 I		As above
Mysid shrimp	flow-thru. 96 h	Tech.	0.234 R	0.071	Boeri, 1989b
Mysid shrimp	static 96 h	Tech.	0.12 R	<0.089	Surprenant, 1989b
Mysid shrimp	flow-thru. 96 h	Tech.	0.22 R	<0.13	Surprenant, 1988b
Eastern oyster	flow-thru. 96 h	Tech.	>3100 A	2000	Surprenant, 1987b
Quahog clam	static 48 h	Tech.	7500 A	5200	Surprenant, 1989c

Daphnia

The flow-through and static tests of Surprenant (1987a) and Heimbach (1997) respectively were conducted in accordance with testing guidelines for daphnia (OECD or US EPA) with few deviations from standard protocols. These tests used different formulations and this should be borne in mind when comparing results. For the daphnid tests groups of 10 or 20 daphnia per treatment were used, with the test concentrations measured at the start and end of trials (mean values used), and a light:dark cycle of 16:8 hours. Oxygen levels, water temperature and pH were measured daily, and largely kept within guideline values, when the organisms were assessed for toxicity symptoms, along with removal of any dead animals from treated aquaria. Mortalities in control groups were low. Both these studies are considered reliable.

The study of Lamb (1980) was conducted according to older US EPA Guidelines and the information presented is somewhat brief. It appears that nominal concentrations were used but apart from this the study would meet minimal current requirements and is therefore rated as acceptable.

Mysid

The two flow-through studies using the mysid shrimp were conducted according to US EPA Guidelines. There were 20 shrimp per treatment (2 replicates X 10), but a re-circulating flow-through system was used in natural seawater aquaria for the flow-through test. All concentrations were measured, with samples taken at 0, 48 and 96 hours for Surprenant's study and at 0 and 96 hours for Boeri's study. The static test was conducted to US EPA FIFRA Guidelines with the test solutions sampled at 0 and 96 hours. The EC_{50} was determined using moving average angle analysis rather than the preferred probit. Using probit analysis the EC_{50} is 116 (106-130) ng/L and there is minimal difference between the two results. All these studies are considered to be reliable.

All the results indicate that azinphos-methyl is very highly toxic towards marine crustaceans.

Molluscs

Oysters (2 replicates X 15) were assessed for shell growth under flow-through conditions, with the mean measured azinphos-methyl concentrations slightly less than target levels. This study was conducted according to an in-house protocol that meets the primary requirements for US EPA Guidelines. Standard shell deposition measurements were compared to controls and the LC_{50} calculated by linear regression. Slight growth stimulation (+20%) was noted at the lower two doses (0.47 and 0.80 mg/L) and a significant depression (-27%) at the highest dose of 3.1 mg/L. As the calculated EC_{50} (using linear regression) is above the highest dose used, the EC_{50} is considered as >3.1 mg/L. The author noted that the solubility of azinphos-methyl in seawater is expected to be significantly lower than for freshwater (estimated at 20-50%) and the EC_{50} could exceed the solubility of azinphos-methyl in seawater. However, DEH notes the higher concentrations used in the quahog study below. The study is considered acceptable.

For quahog clams (28000 embryos per treatment) static conditions were used with 48 h exposure of embryos that were assessed for larval survival using microscopic techniques. Mean measured azinphos-methyl concentrations were used to compute the LC_{50} (using linear regression analysis) and effects were only noted at the highest concentration tested (9.3 mg/L). The study is acceptable.

These results rank azinphos-methyl as moderately toxic towards estuarine molluscs. (Acceptable tests)

Literature

The published study (Hardensen and Wratten, 1996) testing toxicity of azinphos-methyl towards two species of New Zealand damselfly larvae, used wild caught nymphs kept singly in glass beakers for an adaptation period of at least 48 h and fed *ad libitum* with Daphnia *spp*. The nymphs were then exposed to azinphos-methyl for 48 h, without food, and assessed for effects (death). A formulated product was used (Gusathion M35), and presumably nominal concentrations were used, but no details are provided of the range of concentrations used or any chemical analyses conducted. The LC50s determined are of the somewhat higher than the other values listed above, but still rank azinphos-methyl as very highly toxic towards these freshwater invertebrates (for information only).

3.3.2.4 Chronic Tests – Invertebrates

Table 69 summarises the reports provided from chronic toxicity tests with aquatic invertebrates.

Table 69: Chronic toxicity tests of azinphos-methyl to invertebrates. R = reliable study, A = acceptable, I = information only

Organism	Test	MATC ng/L	Test substance	Reference
Daphnia magna	Flow-through 21 d	250-400, R	^{14}C-Tech.	Carlisle, 1984b
Mysid shrimp	Flow-through 28 d	8.3–15, R	^{14}C Tech.	Hoberg, 1990
D. magna	Semi-static 21 d	320–1000, I	Gusathion MS; 25% ai and 7.5% demeton-S-methylsulphon	Heimbach, 1989
Chironomus riparius	Static, water sediment, 28 d	EC_{50} 550, A NOEC 320, A	Tech. 93.4% ai	Heimbach, 1999a
D. magna	Static, water sediment, 28 d	EC_{50} 1020, I	Tech. 93.4% ai	Heimbach, 1999b

Study 1

A chronic study (Carlisle, 1984b) used daphnia to assess the effects of ^{14}C- labelled azinphos-methyl on aquatic crustaceans, during a life-cycle test. The protocol used was based on US EPA guidelines. Day old daphnids (4 replicates X 10 daphnia) were continuously exposed to a range of azinphos-methyl concentrations (solvent control, 0, 70, 120, 240, 420, and 970 ng/L nominal) in a flow-through system over 21 days, during which they achieved sexual maturity and reproduced. Survival and growth of the original daphnids and their off-spring were assessed three times per week with juveniles being discarded. Exposure solutions were assayed by radio-counting on days 0, 4, 7, 14 and 21 days and mean measured concentrations (83, 140, 250, 400 and 990 ng/L) were 95-119% of nominal. TLC analysis of the highest concentration on day 21 showed that 83% of the applied radioactivity was associated with Guthion and therefore the ^{14}C radio-counting was considered a good estimate of actual concentration of azinphos-methyl.

At the two highest test concentrations (420 and 970 ng/L nominal) the parental daphnids all died by day 3 and day 12, respectively. Survival and reproduction was not significantly decreased in the other three treatments. Adverse effects on reproduction were noted at the 420

ng/L level, with ~7 off-spring per female per day, significantly less than controls at 12 per day, but azinphos-methyl toxicity to parent daphnids curtailed this measurement. Based on these data, azinphos-methyl exhibits an 250≥MATC≤400 ng/L for daphnia. The study is considered as reliable.

Study 2

A further study (Hoberg, 1990) used mysid shrimp to assess the effects of longer term exposure to ^{14}C- labelled azinphos-methyl on marine crustaceans, during a single life-cycle, conducted according to US EPA Guidelines. One day old mysids were exposed to a range of azinphos-methyl concentrations in a flow-through system over 28 days, during which they achieved sexual maturity and reproduced. Survival and growth of the original mysids and their off-spring were assessed. The test concentrations were analysed by radio-analysis every 7 days and the highest test concentration was also analysed by HPLC at the same time. The mean measured concentrations were 0, 8.3, 15, 23, 46, and 84 ng/L) and the HPLC results show that the mean concentration of azinphos-methyl was 95 ng/L, taken as evidence that the radio-analysis reflects the true concentration of azinphos-methyl.

At the highest test concentration of azinphos-methyl survival of the parental mysids was significantly decreased (17% v 75% in controls), but not significantly at the other levels (59-77%). Adverse effects on reproduction were the most sensitive indicators of azinphos-methyl toxicity to mysids. Off-spring per female per day ranged from 0.33-0.44 for azinphos-methyl at 15-46 ng/L, which was significantly less than controls (0.84 per day). Even at 8.3 ng/L this rate appears lower at 0.59 per day, but this reduction was not significant (P≤ 0.05). Based on these data azinphos-methyl exhibits a mean MATC of 11 ng/L (0.011 µg/L) for mysid shrimp (8.3≤MATC≤15). The study is considered to be reliable.

Study 3

A semi-static study (Heimbach, 1989) used daphnia to assess the effects of Gusathion MS (containing two OP actives; 25% azinphos-methyl and 7.5% demeton-S-methylsulphone) on aquatic crustaceans, during a life-cycle test. The protocol used was based on OECD guideline No. 202. Daphnids (4 replicates x 5 females) were continuously exposed to a nominal range of azinphos-methyl concentrations (solvent control, 0, 10, 32, 100, 320, 1000, 3200 and 10 000 ng/L as formulation) in a static system over 21 days. Analysis of test solutions noted some degradation of azinphos-methyl, so after every 48 h adult daphnids were transferred to fresh test solution, in conjunction with counting off-spring and affected adults, with juveniles being discarded. Exposure solutions were assayed and ranged from 95-152% of the target concentrations. The additional active, demeton-S-methylsulphone, unfortunately confounds the result as additive toxic effects are possible.

The report claims a NOEC for this test of 320 ng/L (~80 ng/L ai) and a LOEC of 1000 ng/L (~250 ng/L ai), basically in the range of the preceding daphnid test. However, since in both controls and treatments the numbers of off-spring/parent was highly variable and there is the added effect of demeton-S-methylsulphone this result is regarded as for information only.

Study 4

The effects on azinphos-methyl on the development and emergence of midge larvae (*Chironomus riparius*) in a water/sediment system was studied in accordance with the proposed BBA Guidelines 'Effect of plant protection products of the development of sediment dwelling larvae of *Chironomus riparius* in a water sediment system, 1995' (Heimbach, 1999a). This German BBA test is the basis for the proposed OECD test

Guideline 219 'Sediment Chironomid Toxicity Test using Spiked Water'.

Larvae of *C riparius* (1st instar, 25 per replicate) were added to an artificial sediment/water system dosed with azinphos-methyl and exposed for 28 days. The nominal test concentrations were 0.056, 0.10, 0.18, 0.32, 0.56, 1.0 and 1.8 µg/L and the sediment consisted of fine sand (69%), sphagnum peat (10%), kaolin (20%) and calcium carbonate (~1%). There were 3 replicates for the control and 2 for each test concentration. Emergence was used as the end point for the test.

Analysis of the test system occurred using additional parallel replicates, which were sampled at 1 hour, 7 and 28 days after application but only for nominal concentrations of 0.18, 0.56 and 1.8 µg/L. The overlying water and the pore water concentration was analysed but the concentration in the pore water could only be analysed on day 28 due to suspended particles in the pore water (these clogged the solid phase cartridges). There was no analyses of the sediment. The analytical results show that test concentrations were 79 to 106% of nominal 1 hour after dosing and the concentrations decreased during the study. After 7 days the concentrations were <0.1, 0.23 and 0.56 µg/L for 0.18, 0.56 and 1.8 µg/L (nominal) respectively. At the end of the test there was no azinphos-methyl detected in either the overlying or pore water.

No midges emerged from the 1.0 and 1.8 µg/L tests and 70% of the larvae emerged from 0.56 µg/L. All other test concentrations were similar to control with ~90% of the larvae emerging. The EC_{50} was quoted as 0.55 µg/L but no confidence limits could be calculated. DEH has recalculated the results using the raw data (nominal concentrations) and Trimmed-Spearman (Toxcal 5) to give an EC_{50} of 0.63 µg/L (CI 0.58-0.68 µg/L). The NOEC was 0.32 µg/L.

Physical measurements of the overlaying water showed that during the course of the test the temperature and dissolved oxygen were constant and satisfactory but that the pH decreased from 7.7-7.9 on –1 DAT to 4.2-4.7 by 28 DAT. This decrease in pH occurred in the last week of the test, with the pH starting to decrease on 20 DAT (pH 5.7-6.2), while the pH measurements on day 13 were similar to that at commencement (pH 7.5-7.7). As this affected controls and all test systems equally, the decrease in pH does not affect the validity of the test.

As measured concentrations were in parallel replicates and not the test systems, the results are not considered to be reliable and the study is rated as acceptable only.

Study 5

A study was performed to investigate the effects and recovery of *D. magna* in a water/sediment system following the application of azinphos-methyl (Heimbach, 1999b). There are no protocols for this study.

Mixed populations of daphnia (neonates, juvenile and adults) were added to sediment/water systems (2 cm sediment, 15 L water) 3 days before the test substance was added. The nominal concentrations used were 0.2, 0.4, 0.8, 1.6, 3.2, 6.4 and 12.8 µg/L. The sediment used a natural pond sediment characterised as a loam (pH 6.5, sand: 54.4%, silt: 46.4%, clay: 8.2%, o.c 4.1%). There were 3 replicates for control and 2 for each test concentration. In aquaria where all daphnia died, additional neonates (80) were added to determined the recovery of daphnia following exposure.

The numbers of daphnia were determined by taking 3 samples per aquaria (2 from the sides

and one from the centre, approximately 300 mL per aquaria) and counting the number of adults, juveniles and neonates. There was considerable variability in the number of daphnia counted between replicates and within each sample.

Analysis of the test concentrations 3 hours after application gave concentrations of 0.22, 0.27, 0.51, 1.14, 2.24, 3.75, and 8.14 µg/L for nominal concentrations of 0.2, 0.4, 0.8, 1.6, 3.2, 6.4 and 12.8 µg/L respectively. The measured concentration of azinphos-methyl declined and after 7 days averaged 31% of the initial applied dose in all aquaria and 10% after 14 days. The analysis of controls on day 0 showed that there was azinphos-methyl present at 0.14 and 0.34 µg/L in 2 of the control aquaria. While DEH notes that these concentrations are below those that gave a significant response, the potential contamination of the controls is of concern.

The populations of daphnia increased in the controls to reach a peak of 155.9 daphnia per litre 10 DAT, then decreased. After 17 days all organisms were absent from all test concentrations and controls and the study was terminated. After 2 days there were no daphnia in test concentrations of 2.24 µg ai/L or above nor were there any in subsequent samples despite the additional daphnia introduced into these aquaria.

At a concentration of 1.14 µg ai/L, a few daphnia survived, a mean of 6.0 daphnia per litre 2 DAT against 24.6 daphnia per litre for control, and remained at a reduced level for the rest of the test period. When controls reached maximum number of daphnia, 10 DAT, the number of daphnia in the 1.14 treatments averaged 2.1 daphnia per litre. The next lowest test concentration, 0.51 µg ai/L also had reduced number of daphnia, which was statistically significant 10 DAT but a statistically analysis for samples taken on days 2, 4, and 7 was not performed. (The statistical analysis showed that the data was not normally distributed despite transformation of the data.) The NOEC was given as 0.27 µg/L. Pooling all the data gave a dose response curve for the experiment (17 days) and an EC_{50} of 1.02 µg/L was calculated but using nominal concentrations. This study is rated as for information only due to the use of nominal concentrations, the contamination of controls, the high variability between replicates (considered due to the method of sampling used) and the loss of all daphnia before study termination.

In order to test the effect of adding sediment, DEH determined the 48 h EC_{50} as 0.88 µg ai/L using the measured concentrations. This is only slightly less than the acute EC_{50} of 1.1 µg ai/L (see Section 3.3.2.3), an indication that there was minimal mitigation due to the presence of sediment.

3.3.2.5 Non-target vertebrates - Amphibians

A published study tested pacific tree-frogs for toxic effects of azinphos-methyl, exposing tadpoles to azinphos-methyl in solution under flow through conditions for up to 10 days (Nebeker *et al.,* 1998). Both technical grade azinphos-methyl (99% ai) and formulated product (Guthion 2S – 22% azinphos-methyl) were tested, with monitoring of the effects on growth (length), leg development and weight, with mean measured concentrations of azinphos-methyl used to estimate 96 h LC_{50}s. In this trial the formulation appears more toxic than the technical azinphos-methyl alone, and gave an LC_{50} of 1.47 mg ai/L compared to the TGAC with LC_{50} of 4.14 mg ai/L. The results rank azinphos-methyl as moderately toxic to these frogs at the tadpole stage.

The larvae of the Northwestern salamander (*Ambystoma gracile*) and the spotted salamander (*Ambystoma maculatum*) were also tested as above using the Guthion 2S. The 96 hour LD_{50}s were 1.67 and 1.9 mg ai/L for Northwestern and spotted salamanders respectively, again moderately toxic.

The US EPA in their review (US EPA 1999) includes the results for two amphibians, Fowlers toad (*Bufo woodhousei*) and Chorus frogs (*Pseudacris triseriata*), with LC_{50} (96 h) of 109 and 3200 µg/L respectively. There are no Guidelines for these tests, which were conducted using TGAC (93% ai) and the US EPA rated them as supplemental (= acceptable). There was no indication in the report as to the growth stage tested but is likely to have been tadpoles.

3.3.2.6 Aquatic Plants

A test on algae (Heimbach, 1985) was conducted according to OECD Guideline No.201. Stock solutions of *Selenastrum capricornutum* (1.4×10^4 cells) were treated with azinphos-methyl (1-10 mg ai/L) and grown in sterile conditions under artificial light (8000 lux) with cell counts conducted daily. The 96 hour E_bC_{50} (growth biomass) was determined as 3.6 mg/L and the algal growth rate (E_rC_{50}) as 7.5 mg/L. The NOEC was 1.8 mg/L. Azinphos-methyl ranks as moderately toxic to algae from this single test (but see mesocosm results below).

3.3.2.7 Mesocosm Studies

The toxicity of azinphos-methyl to aquatic ecosystems was further examined in an intensive mesocosm study (Giddings, 1989) as part of the US EPA's tier three testing regime, since azinphos-methyl has been detected in surface water/aquatic systems, has demonstrated relatively high toxicity towards aquatic organisms, and has been linked to fish kills in the US. A series of 12 mesocosms (control and 5 treatment rates in duplicate) received eight simulated runoff additions of Guthion 35 WP (29% azinphos-methyl ai), basically on a weekly regime. Existing mesocosm ponds were re-established in November 1987 and monitored for the following 11 months, then dosed with azinphos-methyl during July-August 1988, with residue analysis conducted on water and sediment for the following 3 months. 50 adult bluegill sunfish were stocked in each pond in May 1988, several weeks prior to azinphos-methyl dosing.

Target rates were nominally 0, 0.1, 0.5, 2.4, 12 and 60 µg ai/L based on Guthion at 35% ai and pond volume of 300 m^3, but the test material contained 29% ai and pond volumes were recalculated as 400 m^3. The actual nominal rates used were 0.056, 0.28, 1.3, 6.7 and 34 µg/L. Ponds were dosed weekly for eight weeks with a mixing and re-circulating system delivering dosed water at three points and recirculating around 15% of the total pond volume. This was to simulate the runoff from a 0.4 ha field to a 0.04 ha pond.

Pond water pH values rose gradually from ~pH 8.2 at the week 0, to ~pH 9.2 after 19 weeks, with some replicates reaching a peak of pH 10. Water temperatures averaged <10 °C for the first five weeks, rose rapidly to average >20 ºC for weeks 8-17 and then declined (~14 ºC) at the trial conclusion.

Water analyses were conducted daily for the first two weeks following treatment, then 4 times a week, approximately every 2nd day and continued until azinphos-methyl could no longer be detected in samples (LOD 0.02-0.04 µg/L). The results in Table 70 are for the maximum

weekly concentration in each replicate. The dissipation half-lives for azinphos-methyl in these mesocosms were calculated following each application and were between 0.51 and 2.87 days from a total of 63 half-lives the average was 1.64 days, except for the lowest dosing where the half-lives ranged from 1.98 to as high as 7.75 days (12 half-lives calculated) and averaged 3.95 days. There were 4 applications in the lowest dosing where half-lives could not be determined due to rapid degradation limiting the number of data points (3 measured concentrations greater than limit of detection limit were needed for calculating a half-life). In addition, as all these results were close to the limit of detection, where measurements are often less accurate, these half lives are considered less reliable. The averaged half-lives for each replicate is given in Table 70. Comparison of half-lives against pH showed that with pH <9.5 the average half-life was 1.91 days and pH >9.5 the mean half-life was 1.04 days.

Analysis of the sediment, sampled before treatment then after treatments 3, 5 and 8, showed only traces of azinphos-methyl and only for the highest dose. Interestingly, when the water samples were filtered (0.45 μm filter), the dissolved water concentrations average 61% of the unfiltered samples, indicative of adsorption to suspended particles.

After dosing, azinphos-methyl concentrations in pond water declined rapidly to almost reach baseline levels prior to the subsequent dosing, but in the two higher dose rates these minimum levels were significantly higher than the maximum levels at the lower dose rates. This is especially noticeable in the data for the 60 μg/L, where the minimum in the two replicates mesocosms ranged from 0.30 to 3.1 μg/L and 1.8 to 6.3 μg/L with means of 1.4 and 4.4 μg/L. Therefore the high rate mesocosms were subjected to continuous azinphos-methyl exposure and may not reflect the more sporadic field runoff patterns.

Table 70: Measured peak concentrations in mesocosm water after each addition of Guthion 35 WP for replicates A and B. Nominal levels are corrected for changes to concentration of active in Guthion and to volume of water in the mesocosms.

Application	Corrected nominal level, μg ai/L									
	0.056		0.28		1.3		6.7		34	
1	0.043	0.051	0.23	0.22	0.95	1.2	6.2	5.5	36	25
2	0.049	0.043	0.22	0.13	0.72	0.71	6.3	4.0	37	25
3	0.072	0.058	0.24	0.13	0.87	0.84	6.3	3.3	32	21
4	0.061	0.055	0.27	0.23	0.97	1.2	6.9	4.1	35	27
5	0.050	0.052	0.23	0.12	0.78	0.87	4.8	3.5	28	23
6	0.050	0.075	0.22	0.23	0.86	1.0	5.9	4.3	26	26
7	0.054	0.052	0.24	0.21	0.89	1.0	6.4	4.5	33	31
8	0.060	0.048	0.27	0.21	0.94	1.2	6.9	4.8	35	32
Replicate means	0.055	0.054	0.24	0.19	0.89	1.0	6.2	4.2	33	26
Group mean	0.055		0.21		0.95		5.2		29	
Half-lives (days)	4.46*	3.59*	2.28	1.61	1.13	1.74	2.05	0.77	2.10	1.42

* These results are not considered reliable.

The biota in the mesocosms were monitored using traps for emerging arthropods and general sampling of macrophyte, phytoplankton and zooplankton communities plus fish trapping. The sampling regime was basically monthly for the mesocosm establishment phase (6 months), then fortnightly until azinphos-methyl dosing and weekly thereafter, with zooplankton at least weekly and insect emergence trapping continuous after the initial phase.

There was significant natural variability in the biological assessment which reduced the sensitivity of the statistical analysis plus taking into account any sampling variability it would always be difficult to discern treatment effects in this "OP sensitive" group unless the effects are absolute. The emergent insects samples that would expect to be very sensitive to OP treatment, also show a high background variability in the numbers trapped, plus there was the added unknown effect of adding omnivorous fish around a month before azinphos-methyl dosing.

The results show the pond systems developed a stable physico-chemical structure while biota data are far more variable. Few discernible treatment-related effects were noted in aquatic invertebrates from adding azinphos-methyl, with the only significant differences detected for a few emergent insect species at the two highest treatment rates. When total species numbers were bulked together, the number of emergent insects was significantly depressed at the highest dose only once, 1 month after dosing ceased. These results are surprising given that the two highest treatment levels actually exceeded the laboratory LC_{50} for freshwater invertebrates and fish. This may indicate some mitigation of the toxicity was occurring, this is often noted due to binding to sediment and other substrates. But as there was no evidence of adsorption to sediment, it is likely to be due to rapid degradation limiting the period of exposure and/or the high variability between replicates. Following DEH's concern over the lack of effect at high exposures and that compared with other mesocosm studies, where effects in invertebrates were encountered at levels around 1 µg/L, the company has indicated that another a replacement mesocosm test is being conducted.

No treatment related effects were noted for plants (algae and macrophytes), but survival of fish was clearly decreased at the two higher rates (mean measured maximum concentrations of 5.2 and 29 µg/L). This would correlate with the US EPA review where a number of incidences and reports of fish deaths due to runoff were reported.

While this well conducted trial shows few definitive effects of azinphos-methyl runoff in these aquatic systems, apart from the fairly obvious conclusion that azinphos-methyl will be toxic to fish and insects above certain levels, the trial demonstrates the difficulty in making statistically based conclusions of adverse effects in 'natural' systems. As noted above, the treatments where effects were discernible might well be regarded as having constant exposures of the order of 1-5 ppb azinphos-methyl for around eight weeks. Alternatively, the adverse effects may be due to the spikes of higher azinphos-methyl concentrations (up to 37 µg/L) associated with dosing events, or possibly a combination of both. This model situation appears unlikely to occur with the field uses, where pulses are likely to be more sporadic, and quite possibly at higher concentrations. However, the highest peak azinphos-methyl concentration in mesocosm water was similar to the only measured field runoff value provided from sugarcane usage (Coody, 1992), that is 29 µg/L.

Literature

Study 1

A published report (Sierszen and Lozano, 1998) tested the effects of four concentrations of azinphos-methyl (0.2, 1, 4 and 20 µg/L nominal) in artificial littoral enclosures (5X10 m) constructed on the shore of a 2 ha pond. Each enclosure included 5 metres of natural shoreline and sloped towards the open water. Two blocks of six enclosures were used with two untreated controls and the four treatments in each block and a single treatment

(application method not given) occurred on June 1990. Enclosures were installed in spring and removed the following autumn, with biotic effects and community structures monitored. Zooplankton were sampled 10 times (2 pre-treatment), then 2, 8, 14, 22, 29, 36, 50 and 78 DAT with randomly placed traps, which were sub-sampled to give overall population estimates for the various groups of invertebrates and taxon richness indices.

The measured water column azinphos-methyl levels (presumably soon after dosing) were close to target levels (0.2, 1.0, 4.0 and 20.0 µg/L), being 1.33, 4.72 and 20.4 µg/L, noting the lowest treatment rate was below the LOD (0.28 µg/L). Major taxa peaked at different stages with total numbers of cladocerans reaching 20-55 000/m^2 at ~45 DAT, copepods reached 40-130 000/m^2 at ~5-10 DAT and rotifers reached around 250 000/m^2 at ~0 DAT. As in most "natural" systems, defining significant effects required complex statistical manipulation. Visual examination of taxon richness graphs indicates only slight differences between controls and the three lower treatment levels, but the 20 µg/L treatment appears to decrease the number of species noticeably.

The authors used principal component analysis and ordination plots to decipher population effects, but as there were significant differences between the two blocks, data were assessed separately. The multivariate 95% confidence for the control enclosures was also plotted. These plots show that the two highest treatments significantly affected the populations, with the highest rate during the entire experiment and the 4 µg/L enclosure from 2 to 22 DAT in one replicate and 8 to 36 DAT for the other replicate. Unvariate analysis indicated that cladocerans were the most sensitive group, being affected at <1 µg/L and practically eliminated in treatments >2 µg/L. However, their numbers recovered even in the 20 µg/L treatment to match controls within 42 DAT. Most copepod and rotifers appeared to be unaffected by the pesticide at all concentrations. Within the cladoceran group various species showed responses, with 8 of 11 species depleted significantly in the 4 µg/L treatment and recovering by 36 DAT, but at 20 µg/L effects were more severe and recovery slower. Overall this trial shows the variable harmful effects and recovery rates of different aquatic invertebrates from a single azinphos-methyl treatment.

DEH notes that these results are considerably different from that in the larger mesocosm trial above by Giddings.

Study 2

In a published study adult bluegills were exposed to azinphos-methyl in littoral enclosures at nominal concentrations of 1.0 and 4.0 µg/L (Tanner and Knuth, 1995). Four enclosures were used per treatment with 4 enclosures as controls. Enclosures were built with a natural shoreline as the fourth side and extend out to depth of 1.3 metres (mean water depth of 0.72 m). Depth-integrated samples of the enclosures were taken 1 h after treatment then at 1, 2, 4, 8 and 22 DAT and analysed by gas chromatograph. The half-life of azinphos was 2.3 and 2.4 days for 1.0 and 4.0 µg/L treatments respectively and quantifiable residues remained for 8 days. There was no significant long-term effect on bluegill reproduction, embryo hatchability and larval survival growth or biomass 63 days after the single dosing. Although the aquatic invertebrates such as copepods and cladocerans were significant reduced after 7 days, these recovered to levels equal or greater than controls by 35 DAT. The authors concluded that the lack of long term effects on reproductive success was due to the relatively short half-life of azinphos-methyl.

Study 3

A somewhat older model ecosystem study (Dortland, 1980) in the Netherlands used four segmented pond systems and a range of treatments, which included azinphos-methyl, over two summer seasons. In conjunction with the pond trials a series of standard laboratory 48 h and 21 d toxicity tests were conducted according to US EPA guidelines using four aquatic invertebrates (*Daphnia magna* - cladoceran, *Asellus aquaticus* - isopod, *Cloeon dipterum* - mayfly, *Chaoborus crystallinus* - midge). Their resulting toxicity test values, and that for *Dugesia lugubris* (a flatworm) for azinphos-methyl are listed in Table 71 below. It should be noted that these are nominal and that very limited information was reported, making these results not suitable for regulatory use.

Range finding aquatic half-lives were determined using pond water, to establish the pond dosing frequency, both with and without plants and sediment. The aquatic half-life for azinphos-methyl was around 4 days, with sediment and plants (pH ~7.5), but was around 3 times longer in pond water alone (pH 8.2), possibly due to less biotic degradation in the pond water.

Table 71: Toxicity of azinphos-methyl to non-target invertebrates from Dortland (1980)

Organism	Test	LC_{50} /EC_{50} (µg/L)	NOEC (µg/L)
Daphnia magna	48 h acute	1.6	
Daphnia magna	21 d chronic	0.27	0.2
Asellus aquatica	48 h acute	4.8	
Asellus aquatica	21 d chronic	2.4	0.5
Cloeon dipterum	48 h acute	12.7	
Cloeon dipterum	21 d chronic	3.4	2.0
Chaoborus crystallinus	48 h acute	67	
Chaoborus crystallinus	21 d chronic	10.4	2.0
Dugesia lugubris	96 h acute	>160	

After "natural" populations of biota were established in the four outdoor ponds (mesocosms, 3 X 1 X 1 m) they were divided in two parts by an impermeable barrier with one segment treated with azinphos-methyl (@ 1 µg/L nominal) and the other kept as the untreated blank. As part of this trial adjacent ponds were treated with parathion. Azinphos-methyl levels were monitored twice weekly and re-dosed to keep the concentration constantly near to 1 µg/L average, throughout the two seasons (May-August) and water pH, temperature, dissolved oxygen and biota monitored frequently. The measured azinphos-methyl concentrations in 1977 averaged 0.81 µg/L and in 1978 averaged 0.61 µg/L over the treatment period and the half-lives were estimated as ~7 days in 1977 (average pH 8.1) and ~ 3 days in 1978 (average pH 9.3), noting the likely effect of the higher pH.

Azinphos-methyl at these levels (0.81 and 0.61 µg/L) significantly reduced the numbers of *Daphnia spp* and *Simocephalus vetulus* (both cladocerans) in both seasons, but did not appear to affect the other invertebrates. After treatment was ceased the numbers of *Daphnia* did not recover quickly while *S. vetulus* recovered somewhat, but not to control levels and this may be due to other competing algal grazers. It was noted that effects of azinphos-methyl were slower to occur and recover than in the comparative parathion ponds. No treatments appeared to affect the macrophyte populations, and algae/phytoplankton appeared mainly responsive to grazing pressures/declines when numbers of grazers were depleted. The author concludes that OP NOECs for field situations may be readily calculated as 10% of the daphnid LC_{50}.

Again these results are significantly different to Giddings above, where there was minimal effect on cladocerans despite weekly dosing at high levels (average 29 μg/L) and minimal levels being > 1 μg/L. As noted in the above comments, the company is conducting a new mesocosm study.

Study 4

In another study, similar to Study 2 by Tanner and Knuth (1995), adult bluegills were exposed to azinphos-methyl in littoral enclosures at nominal concentrations of 0.2, 1.0 4.0 and 20.0 μg/L (Knuth, Heinis and Anderson, 2000). The enclosures were identical to those in Study 2. Azinphos-methyl was applied using a hand sprayer to the surface of the enclosures and depth-integrated samples of the enclosures were taken 1 h after treatment then at 1, 2, 4, 8 and 15 DAT and analysed by gas chromatography. The maximum concentration occurred 1 hour after treatment of 1.06, 4.1 and 20.4 μg/L for nominal treatments of 1, 4 and 20 μg/L respectively. The half-life of azinphos in the water column was 1.3 (r^2=1.0, n = 3), 1.2 (r^2=0.73, n=5) and 2.0 (r^2=0.95, n=5) days for the 1.0, 4.0 and 20 μg/L treatments, respectively, and quantifiable residues (0.28 μg/L) remained for 8 days for the two highest concentrations. The DT_{95} was calculated as 5.4, 9.4 and 10.4 days, respectively. There were measurable residues in the sediment, with a maximum of 62.7 μg/kg after 4 days (total of 11.3 mg) in the 20 μg/L but this represented <5% of the applied active (662 mg applied), while there were also measurable residues in the macrophytes and fish (total of 0.057 and 0.032 mg respectively) which these were insignificant to the total mass balance amounts of azinphos-methyl.

These results are similar to the other mesocosm studies showing rapid degradation in the water column. However, this study differs in that is clearly shows degradation as the major dissipation pathway, with adsorption to sediment a minor route of dissipation.

3.3.2.8 Stream microcosms

A series of studies have investigated various aspects of azinphos-methyl contamination in a South African river, arising from runoff and to a lesser extent, spray drift, from stone and pome fruit orchards in the catchment area. The following studies investigated the toxicity to aquatic/benthic invertebrates of azinphos-methyl in simulated runoff or spray drift contamination events, using stream microcosms, The relative importance of runoff (particle-borne) and spray drift to azinphos-methyl contamination in the river, and the effectiveness of a constructed vegetated wetland in reducing insecticide concentrations and toxicity due to runoff or spray drift are referred to in the reports discussed in Section 3.2.5.3.

Study 1

Thiere and Schulz (2004) investigated the acute (5 d) effects of particle-associated azinphos-methyl in multispecies microcosms and assessed the results in the context to data obtained from a parallel field study undertaken in the Lourens River, South Africa. The microcosms consisted of 15 stainless steel stream systems (1.5 × 0.2 × 0.2 m situated indoors at constant temperature (18 ± 2°C) and natural light conditions through a glass wall at one room side. Each stream contained a longitudinal middle wall (1.3 m long) forming two channels (10 cm in width) connected at both ends, enabling the current to circulate around the middle wall. Uncontaminated water and sediment were collected from the Lourens River, and macroinvertebrate fauna and rocks were obtained from an uncontaminated site. The rocks were placed in the microcosms in a similar vertical orientation to that in the field and the test organisms added. The sediment was washed through an 88 μm sieve and allowed to settle for

a period of 24 h, after which the aqueous phase was separated and only the fine organic rich fraction then used to prepare sediment/water application mixtures containing suspended particles bearing azinphos-methyl at a range of concentrations (control and 200, 1,000, 5,000, 20,000 µg/kg).

A runoff simulation was carried out in the microcosms by adding a total of 120 mL (i.e. 30 g dry wt) sediment-water solution, applied evenly along the water surface of each circulating stream (30 L), with three replicates of each dose level. The suspended material was allowed to circulate for 1 h, after which the water was exchanged with fresh water. Measured azinphos-methyl concentrations in filtered microcosm water were found to be not detectable (control) and 0.03, 0.2, 1.1, and 6.9 µg/L, respectively, for the control and 200, 1,000, 5,000, 20,000 µg/kg treatments. The two highest treatments resulted in significantly (analysis of variance [ANOVA]) reduced total numbers of individuals, while the number of taxa was affected in the 20,000 µg/kg treatment only. Particularly affected were six out of 14 macroinvertebrate taxa such as mayfly and stonefly taxa.

A comparison with previous data (study below) suggested that observed effects partly resulted from particle-associated azinphos-methyl, as there were effects at aqeous concentrations of 1.1 µg/L (ie the 5000 µg/kg treatment) similar to those at 5 µg/L in the previous study. The authors therefore suggested that observed effects in the runoff simulation experiment were at least partially caused by particle-associated azinphos-methyl. They suggested possible explanations could include that the toxicity of particle-associated azinphos-methyl results from insecticide sorbed to the fraction of very small organic particles, or that uptake of insecticide by the organisms results in a change of equilibrium between dissolved and sorbed azinphos-methyl in the system, which in turn may cause further desorption into the water column, making it more bioavailable.

In parallel, the distribution of macroinvertebrates at a pesticide-free and a contaminated stretch of the Lourens River was monitored five times during the spraying season in 2001 and 2002. Out of the 14 core taxa found in the microcosm study as well as in the field approach, 10 showed comparable reactions in the microcosm experiment and in their field distribution; they were either classified as affected or unaffected in both studies. The investigators therefore concluded that particle-associated azinphos-methyl has the potential to affect the invertebrate community structure of the Lourens River.

Study 2

In a study preceding that above, Schulz et al (2002) also evaluated the potential effects of the organophosphate insecticide azinphos-methyl in a combined microcosm and field approach. The investigators noted that the upper regions of the Lourens River, South Africa, are free of contamination (control site), whereas the subsequent stretches flowing through a 400 ha orchard area receive transient insecticide pollution (e.g., 0.82 µg/L azinphos-methyl, 344 µg/kg chlorpyrifos) following spray drift and runoff (contaminated site). Stones taken from the control site were transferred to microcosms similar to those described above, which were located in shade houses. This provided 12 core species and approximately 350 individuals per microcosm. Microcosms were contaminated for 1 h with azinphos-methyl applied by temporarily exchanging the 30 L water in each microcosm with contaminated water (control, 0.2, 1, 5, and 20 µg/L; three replicates each). Acute effects on survival were evaluated 6 d following exposure. The two strongest treatments (measured concentrations: 19.2 ± 1.0 and 4.9 ± 0.3 µg/L, respectively) resulted in a significantly (analysis of variance) reduced invertebrate density, attributed mainly to various insect taxa, such as *Demoreptus* sp.,

Castanophlebia sp., Simuliidae, and Chironomidae. In contrast, *Aeshna* sp., *Dugesia* sp., Ceratopogonidae, and *Cheumatopsyche* sp. were unaffected.

In parallel, a quantitative macroinvertebrate survey was conducted at the control site and the contaminated site of the Lourens River after the seasonal pesticide application period. The two sites contained a similar number of species but differed considerably in their species composition and abundances. Five of the eight species that were affected by azinphos-methyl in the microcosm study occurred in the field at significantly lower densities at the contaminated than at the control site or were absent at the contaminated site. All of the four species that were unaffected in the microcosm occurred at significantly higher densities at the contaminated field site. Only 3 of the 12 species reacted differently in the microcosm and the field study. The investigators concluded that microcosm studies employing a field-relevant design could be linked successfully to field studies and that their results suggested that transient pesticide contamination affected the aquatic communities of the Lourens River.

3.3.3 Non-target Terrestrial Invertebrates

The application provides data from a number of studies for azinphos-methyl as various formulations tested on a range of non-target terrestrial invertebrates as shown in Table 72.

Table 72: Toxicity of azinphos-methyl to non-target invertebrates in laboratory studies.

Organism	Test	Test Substance	LC_{50} /LD_{50} (mg/kg)	NOEC mg/kg	Reference
Earthworm (*Eisenia foetida*)	14 d contact	* Gusathion MS – 25% ai	158 I	1	Heimbach, 1990
Earthworm (*Eisenia foetida*)	14 d contact	tech – 92.8% ai	59 R	1	Heimbach, 1986
Earthworm (*Eisenia foetida*)	28 d reprod'n	Gusathion M – 20% ai	significant reduction	< 1 kg ai/ha	Heimbach, 1995
Predatory mite (*Phytoseiulus persimilis*)	IOBC 5/15 d	Gusathion M – 20% ai	65% reduction	slightly harmful	Zoebelein, 1984
Parasitoid (*Aphidius rhopalosiphi*)	IOBC/WPRS	Gusathion M WP 23.9% ai	1.2 g ai/ha (leaf surface)		Moll, 1999
Honey bee (*Apis mellifera*)	72 h oral	Reference standard – 99.0% ai	~0.1 µg	Note: used as Reference Std	Davies, 1987
	72 h contact		~0.1 µg		

Gusathion formulation also contained demeton-S-methylsulphone. Results given as test substance.

3.3.3.1 Earthworms

Several acute tests (Heimbach, 1986 and 1990) are reported using earthworms (*Eisenia foetida* species) and Gusathion MS (active ingredients, azinphos-methyl 25% and demeton-S-methylsulphone 7.5%) and the TGAC (92.8% ai) in an artificial soil according to OECD guidelines. Soils were kept at 40-60% of water holding capacity and between 21-22^{o}C during the 14 day test period and 100% mortality was observed at the highest treatment rate. The 14 days LC_{50}s were determined graphically to be 59 mg/kg (technical) and 158 mg/kg (as test substance Gusathion MS) with the NOECs (14 d) as 1 mg/kg and this ranks azinphos-methyl as moderately toxic under the BBM (Netherlands) system (Mensink et al. 1995). The test using the TGAC is considered reliable, noting there is no analyses, while the test using Gusathion MS is for information only due to the unknown effect of the second active.

In the 28 day reproduction study (Heimbach, 1995), Gusathion M EC 200 (active ingredient, azinphos-methyl 20.2%) was applied to the surface of an artificial soil at 1.0, 1.5 and 6.0 kg ai/ha. Each application was done with 4 replicates and each replicate contained 10 earthworms before application. The worms were fed weekly during the course of the study. After 28 days the number of survivors, their weight and length were determined. After a further 28 days the number and weight of offspring was determined. There were no effects on number of survivors compared to control in any application rates but the weight of the adult worms decreased in all application rates. The number of offspring were significantly reduced at all application rates, by 73% to 97%. The NOEC is given as <1.0 mg/kg. Due to the limitation of the number of treatments used, the result is considered to be for information only.

Field Study

In a field trial (Heimbach, 1988), small plots of pasture were treated with Gusathion M 200 EC twice 2 months apart at 1.5 kg ai/ha (max. German rate) and at an exaggerated rate (6 kg ai/ha, 4 X label rate). The earthworms were sampled 6 weeks after the last application, in autumn of the same year (approximately 11 weeks after the last application) and then in the following spring, approximately 1 year after the initial application. There was a significant reduction in earthworm populations under pasture at the exaggerated rate in the first two sampling periods. At the highest label rate (1.5 kg ai/ha) there was only a slight depression of earthworm populations observed after 6 weeks with soils treated, which was not statistically significant, and this had recovered somewhat at the autumn sampling. At the 12 months post-application observations the populations had recovered at the high label rate to control levels. It was concluded that with two applications of azinphos-methyl at the maximum label rate (for Germany) there could be limited effects on populations of earthworms, which are transient, and the populations of earthworms recover.

3.3.3.2 Beneficial Insects

Trials were conducted in Germany with the predacious mite *Phytoseiulus persimilis* which can be used in IPM with selective acaricides. An application of azinphos-methyl at 0.2% (0.05% ai) to beans, under glasshouse conditions (IOBC protocol) for control of two spotted mite, reduced populations of the predatory species by 65% of unsprayed control levels. This ranks azinphos-methyl as slightly harmful (class 2) according to the IOBC scale.

The effect of azinphos-methyl on parasitic wasps was studied using the recommendations of the IOBC/WPRS (1988) and suggestions of the ring-test group (Moll, 1999). In the test, 48 hour old wasps (*Aphidus rhopalosiphi*) were exposed to dry residues (approximately 2 hour after application) of Gusathion M WP (23.9% ai) on apple leaves at rates of 5, 12.5, 20, 40 and 80 mg ai/L, equivalent to 1.0, 2.5, 5.0, 10 and 20 g ai/ha. (The registered rate in Australia is 380 to 490 mg ai/L.) Effects on mortality and reproduction were evaluated. The 48 h LC_{50} was calculated by probit analysis as 1.2 g ai/ha (1.0–1.6) and the parasitation efficiency in the 1.0 g ai/ha test group was reduced by 22%, which was not statistically significant compared to control. There were insufficient survivors at 2.5 g ai/ha for the effects on reproduction to be conducted. DEH noted that while the rates are expressed in g ai/ha, these are not directly related to field rates (clarification is being sought) but nevertheless the results clear shows that azinphos-methyl residues are extremely toxic to beneficial insects.

In a further study (Schopp, 1985), brief details are provided of an evaluation of the effects of

four chemicals, including Guthion MS, on predatory mites. The report noted "the results on Guthion MS are somewhat confusing" since field treatments gave variable results, but mortalities reached 89% after the second treatment, and this ranks azinphos-methyl as moderately hazardous (class 3) on the IOBC scale.

An old literature report (Motoyama *et al*., 1971) discusses the mechanisms of resistance developed towards azinphos-methyl by predatory mites largely due to induction of non-specific esterase activity that apparently led to more rapid degradation of azinphos-methyl within the resistant mites.

A short report (Davies, 1987) on toxicity to honey bees of a test compound (HWG 1608) used azinphos-methyl as the standard reference toxicant, and notes that Guthion when used routinely as reference compound has an LD_{50} of ~0.1 μg/bee by both oral and contact routes, which ranks as highly toxic under the Netherlands classification. The US EPA report (US EPA, 1999) lists three further results for bee toxicity with one acute oral LD50 of 0.15 μg/bee and two acute contact LD50s of 0.063 and 0.423 μg/bee that support this ranking. Also there is a report on the toxicity of foliar residues to bees noting these are highly toxic for 4-13 days after application.

3.3.3.3 Soil Micro-organisms

Study 1

A trial report (Atwell, 1978a) describes the effect of azinphos-methyl on soil micro-organisms (nitrification and denitrification). It was conducted in a loamy sand soil amended with a nitrogen source and glucose and treated with 20 or 200 μg ai per 10 g soil (2 or 20 ppm), equivalent to 1X and 10X the field rate (4.5 kg/ha). Nitrification soils were amended with 2 mg N (added as ammonium sulphate) and samples were incubated aerobically at 30 ºC, then sampled at 0, 7, 14, 21 and 28 days. For denitrification, 2 mg N (as calcium nitrate) was added to soils plus 4 mg glucose then samples were flooded and incubated anaerobically, with sampling at 0, 7, 14, 21 and 28 days. Results were somewhat variable, but no significant effects on soil nitrification and denitrification were noted even with the elevated levels of azinphos-methyl.

Study 2

In a similar trial (Anderson, 1986) studied the effect of azinphos-methyl on soil micro-organisms (nitrification and ammonification) conducted in two soils (loamy sand and sandy silt). The soils, amended and unamended with a nitrogen source were treated with azinphos-methyl (1.07 or 10.67 mg ai per kg soil) equivalent to 1X and 10X the field rate (0.8 kg/ha). Amended soils had N added as ammonium sulphate (at 1000 mg/kg) and both sets of samples were incubated aerobically at 20 ºC with sampling at 0, 7, 14, 21, 28, 42 and 56 days. Results indicate that nitrification of native soil-N was increased somewhat in azinphos-methyl treated soil in the loamy sand, but was unaffected in the sandy silt, probably due to the higher total-N content of the loamy sand. In the amended soils no significant effects on soil nitrification and denitrification were noted at either treatment level of azinphos-methyl.

Study 3

An older report on the effect of azinphos-methyl on soil micro-organisms was conducted in two soil types - Indiana clay loam and Commerce silt loam (Houseworth and Tweedy, 1972). The soils were treated with 50 or 250 ppm azinphos-methyl and maintained at 50% field moisture capacity for 56 days. After this time the populations of bacteria, fungi and

actinomycetes in the treated soils were determined and compared to controls. Populations of micro-organisms were similar between controls and both treatments indicating no effects of azinphos-methyl on soil microbes.

Study 4

A further trial (Atwell, 1978b) examined the effect of azinphos-methyl on growth, nodulation and acetylene conversion of soybeans in pot cultures that were irrigated with N-free water dosed with Guthion (at 2 ppm ai). Control and treatment pots (6 each) were planted with 12 seeds, then irrigated and grown for 4 weeks before measuring growth and nodulation, with 3 pots subjected to the standard acetylene conversion test. No significant effects on nitrogen fixation rate or growth factors (weight, shoot length or nodule weight) were noted with azinphos-methyl treatment.

Study 5

Another test (Minor and Delphia, 1980) examined the effect of azinphos-methyl on asymbiotic nitrogen fixation by soil micro-organisms that are not associated with legumes. A sandy loam soil was adjusted to pH 7.3, fortified with glucose and treated with 50 µg Guthion per sample (25 g) or water. Samples were sealed in glass jars and 1.5 mL of air was evacuated and replaced with 1.5 mL of acetylene and incubated for 3 days at 30 ºC. The headspace atmosphere was sampled and the amount of acetylene converted to ethylene used to estimate the rate of N-fixation. No effects on nitrogen fixation were apparent with azinphos-methyl treatment.

Study 6

The effects of azinphos-methyl on pure cultures of bacteria, actinomycetes and fungi were tested (Minor and Stankowski, 1978) by placing paper discs impregnated with test substances (azinphos-methyl and reference bactericides) onto the surface of pure cultures of several soil micro-organisms and incubating the agar plates. Growth inhibition was noted as zones of no growth around the discs. Fungal inhibition was determined by placing fungal colonies in the centre of potato dextrose agar plates incorporating azinphos-methyl or captan (as a reference fungicide) and fungal growth was compared to the controls after 1-3 days incubation. No bacterial inhibition was noted from 2 ppm to 10000 ppm Guthion, but 4-18% inhibition of fungal growth was noted for the 2 and 10 ppm levels indicating soil fungi may be slightly inhibited at soil azinphos-methyl concentrations likely to arise from normal use.

3.3.3.4 Other micro-organisms

The effect of azinphos-methyl on sewage sludge amended water was tested according to OECD Guideline 209 (Kanne, 1988). Oxygen consumption was followed in sewage sludge amended water using a range of nominal azinphos-methyl concentrations from 100-10000 mg/L. No inhibition of microbial digestion was noted and the EC_{50} was determined to be >10000 mg/L and the test substance was rated as “not toxic to bacteria”.

3.3.4 Mammals

The toxicity of azinphos-methyl to mammals (see Table 73) is expected to be high given the mode of action and relatively high toxicity of many related OP compounds. Summary toxicity data from laboratory tests have been gleaned from standard texts (Tomlin, 1997) or Bayer’s, Part 1, Summaries, previously submitted for registration purposes.

Table 73: Toxicity of azinphos-methyl to mammals.

Test	Animal	LD_{50} (mg/kg BW)	Reference
Acute oral (14 d)	Rat	~9	Tomlin, 1997
Acute oral (14 d)	Rat	6.7-12.8	Bayer, Part 1, Summary
Acute oral (14 d)	Guinea pig	80	Tomlin, 1997
Acute oral (14 d)	Mouse	11-20	Tomlin, 1997
Acute oral (14 d)	Dog	>10	Tomlin, 1997
Inhalation (1 h)	Rat	310-396 mg/m^3 air	Bayer, Part 1, Summary
Inhalation (4 h)	Rat	0.15 mg/L air	Tomlin, 1997

A US trial (Mount et al., 1988) tested the effect of dietary doses of azinphos-methyl in the off-spring of wild caught deer mice (*Peromyscus maniculatus nebrascensis*). Groups of ten mice were fed a diet containing 0, 295, 596, 1195, 2168 and 4423 ppm Guthion (ai azinphos-methyl) for five days. The mice showed a distinct aversion to the treated feed with significantly lower feed intakes at all treatment levels, and all mice lost significant body weight in all treatment groups. Few mice died in the controls or treatments. Feed intake and weight gain increased rapidly when treatment groups were returned to normal, untreated diet. Given the relatively high dosage rates that caused feed aversion, and the short term nature of this feeding trial (5 days) the results are difficult to relate to a field use situation.

Literature

A comparative study on the toxicity of azinphos-methyl to house and laboratory mice, deer mice and gray-tailed voles was undertaken (Meyers and Wolff, 1994). This was part of a long-term program to field validate the quotient method and further results are summarised below (see Section 3.3.6.3 Literature Reports). The LD_{50} (azinphos administered by oral gavage) as well as the LC_{50} (5 and 10 day) was determined using standard methodology. High purity azinphos-methyl was used (99.1% ai) in the testing. The endpoints were calculated using probits. Nominal concentrations used for the LD_{50} and measured concentrations for the LC_{50}. The results are given in Table 74 and are rated as acceptable as there were only 5 animals at most test concentrations and results of analyses are not given.

Table 74: Toxicity of azinphos-methyl to rodents. From Meyers and Wolff, (1994).

Endpoint	Laboratory mouse *(Mus musculus)*	House mouse (wild) *(M. musculus)*	Gray-tailed vole *(Microtus canicaudus)*	Deer mouse (*Peromyscus maniculatus*)
LD_{50} mg/kg bw	11 (9-12)	10 (9-13)	48 (39-74)	32 (24-38)
5 day LC_{50} ppm	543 (464-683)	-	406 (312-858)	2425 (1856-3245)
10 day LC_{50} ppm	277 (212-317)	-	297 (218-519)	1180 (709-1485)

3.3.5 Phytotoxicity

While no specific studies were presented there is no mention of phytotoxicity in any of the range of field and laboratory trials where azinphos-methyl was applied to a large range of crop plants. Azinphos-methyl is an insecticide/miticide used to protect a range of target crops and phytotoxicity has not been reported from normal use rates.

3.3.6 Field Studies – Wildlife

3.3.6.1 Apple Orchards –1

An extensive field study (Johnson, *et al*., 1989) was conducted in commercial, irrigated apple orchards (11-54 acres) in Yakima County, Washington State (US), where eight replicates were treated three times (7 day intervals with exception of a few replicates due to weather) with 4.3 lbs/ac Guthion 35% WP (or 1.68 kg/ha ai, similar to the maximum rate expected for use in pome fruit in Australia). This is the maximum allowable label rate (USA) and the study notes this is at least double the typical use rate in the area where usual repeat intervals are 14-21 days, and the trial equates to a worst case use pattern.

Wildlife abundance was assessed by avian census, live-trapping of small mammals and general wildlife observations. Residues of azinphos-methyl were measured in the apple foliage and non-crop plants and in invertebrates sampled within 24 h of application to assess wildlife exposure. Effects on wildlife were assessed by searching for "casualties" along transects in each replicate. However, the results were somewhat confounded by the fact that 2 of the 8 replicates were treated with rodenticides near trial initiation, apparently unbeknown to the trial operators. This appeared to cause a disproportionate number of casualties (55% of total and 67% of mammalian) from the entire trial to be found within these two replicates. As well, some other insecticide treatments were carried out prior to trial instigation so wildlife not all effects are attributable solely to the azinphos-methyl treatments.

Forty one species of birds and twelve species of mammals were detected within the treated orchards during the trial. Mean azinphos-methyl residues on apple were barely detectable prior to treatment and on apples leaves and non-target vegetation followed the pattern shown in the Table 75 below. It is noted that the data shows that residues in the trees had declined to approximately half before the next application. As the applications were mostly 7 days apart, this gives an approximate half-life of the residues in orchards of 6-7 days.

Table 75: Azinphos-methyl Residues (ppm) in Washington orchard trials (mean values).

Time and Treatment No.	Apple trees	Non-target vegetation (in orchard)	Non-target vegetation (adj to orchard)	Invertebrates (in orchard)
-1, DAT 0	1.9			
+1, DAT 1	201	87	43	4.9
-1, DAT 2	100			3.5
+1, DAT 2	312	80	50	15.4
-1, DAT 3	143			0.64
+1, DAT 3	328	127	66	4.6
+7, DAT 3	183			2.1

173 casualties (species not stated) were found during the study period, with 21 (12%) directly attributed to azinphos-methyl use, 117 (68%) not definite (that is possible azinphos-methyl link) and 35 (20%) attributed as not azinphos-methyl related. Of the casualties 59 were birds (14 species, 5 before treatment and 54 during treatments) with the largest numbers being robins (34%) and quail (20%) and 109 were mammals with voles (82%) predominant. Only 40 of the 173 casualties were tested for azinphos-methyl residues with 21 (53%) considered treatment related due to the residues found. The rodenticide treatment of two replicates was

unfortunate from the azinphos-methyl trial perspective and caused significant casualties, especially in mammals, but this is clearly a normal cultural practice in these orchards and provides evidence of the cumulative effects likely when orchards are subjected to multiple pesticide treatments.

3.3.6.2 Apple Orchards –2

An identical field study (Sheeley, *et al*., 1989) was conducted in commercial apple orchards (10-85 acres) in Leelanau County, Michigan (US), where eight replicates were treated four times (7-10 day intervals) with 4.3 lbs/ac Guthion 35% WP (1.68 kg/ha ai – expected to be maximum use rate in Australia for pome fruit). This is the maximum allowable label rate and the trial equates to a worst case use pattern. Wildlife abundance was assessed by avian census, live-trapping of small mammals and general wildlife observations.

Residues of azinphos-methyl were measured in four of the replicates in the apple foliage and non-crop plants and in invertebrates sampled within 24 h of application to assess wildlife exposure to azinphos-methyl. Searching for "casualties" along transects in each replicate assessed the effects on wildlife. As some other insecticide treatments were carried out in orchards prior to trial instigation not all effects can be attributed solely to the azinphos-methyl treatments.

Fifty five species of birds and twelve species of mammals were detected within the orchard and adjacent areas during the wildlife censuses. Mean azinphos-methyl residues on apple trees were usually low prior to treatment, but zero time samples from two of the four sites showed levels at 29 ppm and 61 ppm, suggesting site or sample contamination. Residues on apple leaves and non-target vegetation followed the pattern shown in the Table 76 below. Residues on the apple trees decline by approximately half before the next application as noted above. However, the data is not as complete as the previous study and only for the last two applications are there data to show this general half-life in orchards of approximately 6-7 days.

Table 76: Azinphos-methyl Residues (ppm) in Michigan orchard trials (mean values). From one replicate only

Time and Treatment No.	Apple trees	Non-target vegetation (in orchard)	Non-target vegetation (adj orchard)	Invertebrates (in orchard)
-1, DAT 0	5.5	<0.10		
+1, DAT 1	236	112	39	2.9
+1, DAT 2	429	147	36	9.5
-1, DAT 3	70*			
+1, DAT 3	536	180	68	9.9
-1, DAT 4	272			4.4
+1, DAT 4	480	147	53	10
+7, DAT 4	305			7.2

29 casualties (species not stated) were found during the study period, with 14 (48%) directly attributed to azinphos-methyl use, 6 (21%) not definite (that is possible azinphos-methyl link) and 9 (31%) attributed as not azinphos-methyl related. Of these attributed casualties 2 were birds and 11 were mammals. Overall, this trial showed lower numbers of affected animals, notwithstanding the extra spray application and higher animal frequencies observed, in comparison with the previous study. Clearly some animals are at risk of severe effects and

death when exposed to commercial orchard spray regimes, with the authors noting the use rates were at the maximum label rate, to create a worst case situation.

3.3.6.3 Literature Reports

Study 1
The study investigated the impact on cholinesterase (ChE) in wild birds from use of in orchards of a number of OP, including azinphos-methyl (Burgess *et al.*, 1999). Nesting boxes for tree swallows and eastern bluebirds were placed into commercial orchards in Ontario, Canada. The orchards were treated as per normal commercial practices for the area.

One orchard was sprayed with azinphos-methyl twice at 2.1 kg ai/ha (greater than the typical Australian rate), 15 days apart. Blood samples collected from adults tree swallows showed the plasma ChE was not significantly different to controls following the first application 2 or 13 days post-spray. However, 12 h after the second application, plasma ChE levels were significantly reduced, mean of 41% (20 birds sampled), with one pair from a nest box showing 68% and 74% inhibition compared to controls, for male and female respectively.

In the treated orchard, tree swallow nestlings were exposed to only one application of azinphos-methyl (or other OPs) because their time in the nests coincided with the time between applications. The only nestlings with greater than 20% brain ChE inhibition compared to control nestlings of the same age after OP applications, including azinphos-methyl, were the youngest sampled at 3 and 5 days old. Mean plasma ChE was not significantly different in the nestlings compared to controls but for one sample with 55% inhibition.

For nesting bluebirds, there was a significant difference between exposed and control brain ChE 24 h after application of azinphos-methyl to the orchards. The greatest percentage change in mean brain ChE was 19% for 5 day old nestlings (n = 17) following azinphos-methyl application, with again the greatest being in the youngest nestlings. Yet there was no difference between plasma ChE levels between control and the exposed nestlings. The adult bluebirds were not tested as previous experience had shown that adult bluebird were prone to abandon their nest if handled.

No birds died due to chemical exposure during the study. It was concluded by the authors that the results were consistent with other such studies in showing that while there was depressed ChE level, there was no indication that OP exposure due to agriculture spraying adversely effected the survival of the birds monitored. DEH notes this is strongly dependent on the OP used but agrees that for azinphos-methyl the study does show that while there is an effect on the ChE in the birds, it is not sufficient to cause mortalities.

Study 2
In a follow-up study to that above, the effect of pesticide spraying, including azinphos-methyl, on chick growth, behaviour and parental care was examined by field observations (Bishop *et al.*, 2000). The study was conducted similarly to that above with one orchard treated as per commercial practice and two control sites. There was only one application of azinphos-methyl during the season.

Following the application of azinphos-methyl there was a significant increase in hunger calling by the swallow chicks, which did not occur at the control sites. In the second year of

the study there were also significant reductions in number of feeding sorties by parent birds. There were low densities of invertebrates in the sprayed orchard compared to non-sprayed but these did not correlate with spraying events. Despite the behavioural changes noted, there was no difference in fledging time or mass of chicks at fledging in the treated compared to the control sites.

Study 3

Gray tailed voles were used to test the assumption that non-target wildlife does not move to avoid contaminated areas, a key assumption of the quotient method (Edge *et al.*, 1996). Twelve voles (6 male and 6 female) were placed into 0.2 ha enclosures containing pasture grasses, similar to the natural habitat of gray-tailed voles. Two enclosures were treated with 5 applications of azinphos-methyl (Gusathion 2S), 0, 0.88, 1.65, 2.63 and 4.48 kg ai/ha as determined by analysis of the spray tanks. In all enclosures the animals were trapped over a 4 days period ever 2 weeks.

Vole population in the enclosures treated at 1.65 kg ai/ha or above were lower than the control but this effect was only statistically significant for one sample (~6 weeks after application). While survival rates in these higher treatments were reduced compared to controls, the size of the populations remained constant. In the controls the populations increased. After ~9 weeks the treated enclosures were starting to recover.

The authors concluded that while the study shows only a short-term depression in the population of the voles, there could be different responses among other species in the small mammal community. Also, the responses to multiple applications, including other pesticides, in unknown but could be more pronounced and prolonged. DEH agrees but notes that there was minimal effect on voles at the maximum Australian rate.

Study 4

Gray tailed voles were used to further test the assumption that non-target wildlife does not move to avoid contaminated areas, a key assumption of the quotient method (Wang *et al.*, 1999). Twelve voles (6 male and 6 female) were placed into 0.2 ha enclosures containing pasture grasses, similar to the natural habitat of gray-tailed voles. Two enclosures were treated with full spray (all habitats sprayed at 1.5 kg ai/ha, maximum Australian rate), 5 with half-spray (half the enclosure sprayed at 1.5 kg ai/ha) and 5 as control (sprayed with water). 47 animals (44 females and 3 males) were radio-collared and their positions were determined (to within 1 metre) 4 days before and 4 days after treatment at 5:00 and 19:30 hours.

None of the 47 animals moved from their established home ranges after treatment and there was no difference in their home ranges between treated and non-treated areas. The authors concluded that the results suggest that small mammals are unlikely to reduce exposure by moving to uncontaminated areas and this supports the quotient methods. The authors also note that behavioural responses are important in the exposures and these may be chemical, species and habitat specific. DEH notes that the experiment was conducted during the breeding season for the voles, with 35 of the females either pregnant or lactating and movement of the voles from their homes ranges would not be expected, except under extreme conditions. There was also no measurement of the actual exposures that the voles experienced and no indication of adverse effects, despite previous experiments (see above) in which the authors state that there were decreased survival and population effects at this rate. If the actual exposures were not sufficient to cause any adverse effects, changes in behaviour are unlikely unless there is a repellent effect from the chemical.

3.3.7 US Incidents Reports

The US EPA review of azinphos-methyl (US EPA 1999) summarised a number of incidents involving azinphos-methyl as the known toxicant and lists these incidents by crops, with sugar cane and cotton being the two crops were most incidents have occurred. These are briefly reported below:

3.3.7.1 Sugarcane

A number of these incidents relate to use of azinphos-methyl in sugarcane in the US, where it was aerially applied (rate not given) to sugar cane then rain occurred shortly afterwards in the years 1991-1997. In 37 incidents reported, the total number of fish affected was estimated by the US EPA at 444,000, with >29 species being involved. There were another 51 fish kills reported where the cause was attributed as low dissolved oxygen but there was no analysis performed to confirm this. The US EPA review questions whether low dissolved oxygen was the cause and not pesticide runoff, with one example given where the initial cause was given as low dissolved oxygen but following water analysis, spray drift was given as the cause.

In some these incidents other species were also affected, including birds and reptiles. Dead ducks were observed in one incident and birds have been observed feeding on the dead and dying fish in other incidents. At one fish kill, an alligator (4 ft, 1.2 m long) was dead and at others incidents alligators, turtles and snakes have been observed feeding on dead and dying fish. The US EPA concluded that these organisms are feeding on dead or dying fish and this is leading to adverse effects in these organisms (secondary effects).

3.3.7.2 Cotton

The US EPA review reports a total of 82 incidents that occurred in Georgia over a two month period, where a total of 100,000 fish were estimated to have been killed. As the reports indicates that precipitation only occurred in one incident and water bodies were within 300 m (1000 ft) of the application site, these incidents could be due to spray drift (note aerial application was used). In 3 other cotton growing regions (Tennessee, Mississippi and Texas), the review gives some details on 5 other incidents involving fish, one with 5000 dead. Interestingly there was one incident where a horse was affected following aerial application to cotton.

3.3.7.3 Orchards

The US EPA review gives 5 fish kill incidents that occurred from the use of azinphos-methyl in orchards, one of which involved 3000 dead fish. The orchards involved were apples, nuts, citrus and peach. The details for one incident shows that runoff was implicated, with rain (50 mm) occurring within hours of application to peach orchard, with a rate stated to be as per label (US maximum rate for peaches (eastern) 1.25 kg ai/ha). No details were given for the other incidents.

3.3.7.4 Alfalfa

One incident involved use on alfalfa where 13 birds and 1 fish died following azinphos-methyl application.

3.3.8 Summary of environmental effects

3.3.8.1 Avian Toxicity

Results indicate that azinphos-methyl is very highly toxic to birds. The only species tested in the acute oral tests, conducted to US EPA requirements, was bobwhite quail, with two tests giving LD_{50}s of 33 and 34 mg/kg bw using technical material and one test using formulated product (20% ac) with LD_{50} of 271 mg/kg bw (54 mg ac/kg bw). There were no 5 day dietary tests presented but the US EPA has reviewed such tests that meet their requirements and the LC_{50}s ranged between 488-1940 ppm for 4 species. The bobwhite quail was the most sensitive. Two 21 weeks single generation reproduction studies were presented for bobwhite quails and mallard ducks and the NOEL was 15.6 and 10.5 ppm respectively.

Field surveys within apple orchards detected wildlife casualties attributed to azinphos-methyl, however, it was not clear from the data what proportion of these casualties were birds. In one of these trials the results were confounded by rodenticide treatments, which clearly increased casualties, but apparently mostly in the small mammal category.

While literature reports on field studies in Canada using nesting birds in orchards showed there were effects on brain and plasma cholinesterase after 2 applications of azinphos-methyl (2.1 kg ac/ha, 15 days apart), the level of these were not sufficient to cause mortality. The results for nestlings were the same, with brain and plasma cholinesterase affected and no mortality due to the chemical treatment. A follow-up study showed minimal effect on the behaviour of the nesting birds when sprayed and no difference in fledging time or mass of chicks at fledging. A similar result was obtained when quail were exposed to azinphos-methyl up to 3.1 kg ac/ha in plots of alfalfa.

3.3.8.2 Aquatic Toxicity

Fish

Acute studies on a range of fish species, conducted to US EPA or Organisation for Economic Co-operation and Development (OECD) requirements, indicated that azinphos-methyl is very highly toxic to fish. The LC_{50}s were between 1.86-3.2 µg/L for technical material and 21.5 to 40.1 µg/L for a number of formulations, which when converted to active material content correspond to between 5.4–8.8 µg ac/L. In the 4 chronic tests, conducted to US EPA or OECD requirements, the maximum acceptable toxicant concentration (MATC) ranged between 0.29 and 0.66 µg/L using technical material. The most sensitive species for both acute and chronic tests was sheepshead minnow.

Aquatic invertebrates

Azinphos-methyl shows very high acute toxicity to daphnia and mysid shrimp with 48 hour LC_{50}s of 1.1 µg/L and 0.12 µg/L respectively using technical material. The formulated product was less toxic to daphnia, with EC_{50}s of 2.2 to 2.9 µg ac/L. Literature results for two species of damselfly native to New Zealand using formulated product show that these are less sensitive, with LC_{50}s of 16 and 44 µg ac/L.

The test reports for molluscs, oysters and quahog, conducted to US EPA requirements using shell growth as the end point gave LC_{50}s of >3.1 and 7.5 mg ai/L respectively, which can be rated as moderately toxic.

In chronic tests conducted to standard protocols the MATC for daphnia and mysid shrimp were 0.25-0.4 µg/L and 0.0083-0.015 µg/L ,respectively using technical material. Tests using sediment/water systems showed there was little mitigation in toxicity, with EC_{50}s of 1.02 and 0.55 µg/L for daphnia and chironomids, respectively.

Amphibians

A published study tested the toxicity of azinphos-methyl to Pacific tree-frog tadpoles using both technical grade azinphos-methyl (99.5% ac) and formulated product (Guthion 2S – 22% azinphos-methyl). The EC_{50}s were of 1.47 mg ai/L for formulated (expressed as active) and LC_{50} of 4.14 mg /L for the active constituent (ac). The larvae of the Northwestern salamander (*Ambystoma gracile*) and the spotted salamander (*Ambystoma maculatum*) were also tested using Guthion 2S. The 96 h LD_{50}s were 1.67 and 1.9 mg ac/L respectively. These results rate azinphos-methyl as moderately toxic to these amphibians.

Algae

The single aquatic plant toxicity test with azinphos-methyl using green algae gave an EC_{50} value (growth) of 3.6 mg/L showing this insecticide may exhibit moderate toxicity to these plant groups.

Mesocosms

The toxicity of azinphos-methyl to aquatic ecosystems was further examined in an intensive mesocosm study under US EPA's tier three testing regime, since azinphos-methyl had been linked to fish kills in the US. A series of mesocosms (control and 5 treatment rates in duplicate) received eight simulated runoff additions of Guthion 35 WP (29% azinphos-methyl) on a weekly regime. The nominal rates used were 0.056, 0.28, 1.3, 6.7 and 34 µg/L and the mean measured concentrations were within 70% of these target concentrations.

After dosing, azinphos-methyl concentrations in pond water declined rapidly to almost reach baseline levels prior to the subsequent dosing, except in the two higher doses. The dissipation half-life of azinphos-methyl in these mesocosms was between 0.51 and 7.75 days, calculated following each application.

Sampling of the aquatic fauna showed no treatment related effects for plants (algae and macrophytes) and there were few discernible treatment-related effects with the aquatic invertebrates, with the only significant differences being at the two highest rates. (This result is surprising given that the two highest treatment levels actually exceeded the LC_{50} for freshwater invertebrates and may indicate some mitigation of the toxicity was occurring.) By contrast survival of fish was clearly decreased at the two higher rates, which correlates with the laboratory results and the US EPA review, where a number of incidences and reports of fish deaths due to runoff were reported.

In a recent literature report, artificial enclosures in a pond were treated with single doses of azinphos-methyl, measured at 1.33, 1.72 and 20.4 µg/L, with the enclosures at nominal concentration of 0.2 µg/L that could not be measured. Principal component analysis and ordination plots were used to decipher effects in the natural populations within each enclosure. These plots showed that highest rate significantly affected the populations during the entire experiment and in the 4 µg/L enclosure from 2 to 22 DAT in one replicate and 8 to 36 DAT for the other replicate. Univariate analysis indicated that cladocerans were the most sensitive group, being affected at <1 µg/L and practically eliminated in treatments >2 µg/L.

However, their numbers recovered within 42 days after treatment in all enclosures. Most copepods and rotifers appeared to be unaffected by the pesticide at all concentrations. Overall this trial shows the variable harmful effects and recovery rates of different aquatic invertebrates from a single azinphos-methyl treatment.

In another literature report adult bluegills were exposed to azinphos-methyl in littoral enclosures at nominal concentrations of 1.0 and 4.0 µg/L. The half-life of azinphos-methyl was determined as 2.3 and 2.4 days respectively and quantifiable residues remained for 8 days. There was no significant long-term effect on bluegill reproduction, embryo hatchability, larval survival growth or biomass 63 days after the single dosing. Aquatic invertebrates such as copepods (cf to previous studies) and cladocerans were significantly reduced after 7 days and recovered to levels equal or greater than controls after 35 days. The authors concluded that the lack of long term effects on reproductive success was due to the relatively short half-life of azinphos-methyl. A follow-up paper on the persistence and distribution of azinphos-methyl in similar mesocosms showed that half-life was between 1.2 and 2 days with 95% dissipation within 10 days. Residues were found in the sediment, macrophytes and fish. Only the residues in sediment were significant to the overall mass balance, the biota contained only trace levels of the applied active.

In an older literature report, four segmented ponds were given a range of treatments, including azinphos-methyl. Azinphos-methyl levels were monitored twice weekly and re-dosed to keep the concentration constantly near to 1 µg/L average, throughout the two seasons (May-August). The measured azinphos-methyl concentrations averaged 0.81 and 0.61 µg/L respectively and the half-lives were estimated as ~7 days in 1977 (average pH 8.1) and ~ 3 days in 1978 (average pH 9.3). At these levels significantly reduced numbers of cladocerans occurred but other invertebrates did not appear to be affected. After treatment was ceased the numbers of *Daphnia* did not recover quickly while *Simocephalus vetulus* recovered somewhat. It was noted that effects of azinphos-methyl were slower to occur and recover than in the comparative parathion ponds.

Stream microcosms

A series of studies were reported investigating aspects of azinphos-methyl contamination in a South African river, arising from runoff and to a lesser extent, spray drift, from stone and pome fruit orchards in the catchment area. In a runoff simulation study, acute effects of particle-associated azinphos-methyl were determined in stream microcosms containing macroinvertebrate fauna from a South African river. Treatments with the two highest particle contamination levels (5000 and 20,000 µg/kg at 1 g/L suspended solids for 1 h exposure) resulted in significantly reduced total numbers of individuals, and the highest treatment reduced the number of taxa. The measured azinphos-methyl concentrations in filtered water at these concentrations were 1.1 and 6.9 µg/L, respectively. In a previous study with aqueous-phase application, toxicity to similar macroinvertebrate communities was observed at ≥ 5 µg/L. This suggests that toxicity in the second study may have partly been due to particle bound azinphos-methyl. Particularly affected taxa included mayfly and stonefly taxa. There was a large degree of consistency between the taxa affected in this study and those observed to be affected in monitoring studies of the river.

3.3.8.3 Non-target Terrestrial Invertebrates

The test results for bees show that azinphos-methyl is highly toxic to bees (oral/contact LD_{50} ~1 µg/bee). The US EPA report lists three further results for bee toxicity with one acute oral

LD_{50} of 0.15 µg/bee and two acute contact LD_{50}s of 0.063 and 0.423 µg/bee that support this ranking. Also, there is a report that plant residues are highly toxic to bees for 4-13 days after application.

The 14 day LC_{50} for earthworms was 59 mg/kg soil using technical active and 158 (equivalent to 39 mg ac/kg soil) for Gusathion MS, which ranks azinphos-methyl as moderately toxic under the Dutch system. Field tests noted significant reductions in worm populations under pastures treated with Gusathion M (20% ai EC) at 6 kg ac/ha (exaggerated rate) and short term reductions when the highest label rate was used (1.5 kg ac/ha).

Tests using azinphos-methyl formulations applied to plants found that when it was slightly harmful (30-80% mortality) to predatory mites on the IOBC scale. Dried residues of azinphos-methyl on leaves were toxic to parasitic wasps, with an EC_{50} of 1.2 g ac/ha of leaf surface.

There was little effect noted on the soil respiration and nitrification activity of the soil micro-organisms at 1X or 10X the field rate of 0.45 kg ai/ha, but some inhibition of fungal growth was noted in one test. When azinphos-methyl was added to pot cultured soybeans in irrigation water at 2 mg/L, no effects were discernible on plant growth, nodulation or nitrogen fixation rates. In sewage sludge azinphos-methyl did not affect oxygen consumption nor microbial digestion.

3.3.8.4 Mammals

The toxicity of azinphos-methyl is very high to laboratory mammals with 14 days acute oral LD_{50}s ranging from 6.7 to 20 mg/kg. In orchard monitoring studies at maximum label rates and minimum re-treatment intervals it caused deaths ("casualties") and presumably other detrimental effects on mammals.

Gray tailed voles in grassed enclosures were treated with five applications of azinphos-methyl (Gusathion 2S) at 0, 0.88, 1.65, 2.63 and 4.48 kg ac/ha. Vole populations in the enclosures were statistically significantly reduced at 1.65 kg ac/ha and above for one sample (~6 weeks after application). While survival rates were reduced compared to control in these higher treatments, this did not affect the size of the populations, which remained constant.

In another study, voles in grassed enclosures were treated with all habitat sprayed or half-sprayed (half the enclosure sprayed) at 1.5 kg ac/ha together with control (sprayed with water). There were no mortalities in any treatment and none of the monitored animals moved from their established home ranges after treatment. The authors also noted that behavioural responses are important in the exposures and these may be chemical, species and habitat specific. However, DEH notes that as the actual exposures were not sufficient to cause any adverse effects, changes in behaviour are unlikely unless there is a repellent effect from the chemical.

3.3.8.5 Phytotoxicity

Azinphos-methyl is not expected to show phytotoxicity in normal use patterns.

3.4 PREDICTION OF ENVIRONMENTAL RISK

3.4.1 Application and Use Pattern

In Australia azinphos-methyl is registered for use in pome and stone fruit orchards, citrus, macadamia nuts and grapes, with further minor uses in crops such as litchis, kiwifruit and blueberries.

Currently azinphos-methyl is mainly used on pome and stone fruit orchards for the control of a range of invertebrate pests (moths, mites, aphids, scale, root borer, beetles and weevils). The use rates stated on the labels correspond to 36-49 g ai/100 L, but the maximum rate for application to tree butts and soil is 98 g ai/100 L. However, overall application rates (L/ha) will vary considerably between crops and planting density (low, medium or high density), between growth stages (immature v mature trees) and application target (foliage versus soil drenching).

Traditionally application to orchards is by orchard air blasters using high volume equipment. However, many orchardists are now using low volume sprayers, and in some cases ultra low volume equipment, although this is not very common due to its higher costs. The directions on the label for such equipment specify that growers should apply the same amount of azinphos-methyl to the target crop using a low volume rate as by the high volume rate. Thus, the rate of active constituent applied to trees should remain constant whatever the method of spraying. In addition, for citrus, oscillating horizontal booms are also used as well as high volume application equipment but current use in citrus is minor.

The labels state that aerial spraying in Tasmania requires the specific approval of the Registrar of Pesticides, but does not add any clarification to the aerial application situation elsewhere. However, it is not widely used due to the requirement to thoroughly wet the entire tree canopy and the increasing use of hail/bird netting in orchards to protect the fruit.

Normal practice in orchards is to spray to the point of runoff, requiring 1500-3000 L/ha of spray solution for mature pome and stone trees, but this could be a high as 4000 L/ha for larger trees. The normal rate corresponds to application rates of between 735 g ac/ha and 1470 g ai/ha for most pests at 49 g ac/100 L. The maximum use rate stated on the labels is for curculio beetles and Fullers rose weevils in pome and stone fruit and is for application to tree butts and soil at 98 g ac/100 L. It is expected that this will be done as a spot treatment around the base of the trees. (A similar use pattern is used to control fig longicorn beetles and elephant weevils in grapes (NSW only) but at the typical rate of 49 g ac/100 L.) For citrus the maximum application rates correspond to 2.9-4.9 kg ac/ha, based on 49 g ac/100 L spray and 6000-10,000 L/ha.

The major uses are in pome fruit and stone fruit industries, with minor quantities used in macadamias, grapes and other minor crops. Use is declining with the introduction of IPM in most orchard systems, particularly for grapes and citrus, but remains a significant chemical for pome and stone fruit to establish IPM and to control break-outs of pest problems in IPM.

3.4.2 Risk Evaluation Approach

The following risk evaluation follows the US EPA approach (Urban and Cook 1986) to

establish a Q-value from the ratio of the Estimated Environmental Concentration (EEC) and lowest effect concentration, such as an LC_{50}. DEH has no formal framework for assigning levels of risk for a given Q, but considers that the following as an appropriate guide in this assessment. As a first step, DEH makes an estimate of the risk based on the relatively crude basis of assuming direct over-spray or 10% spray drift. However, if a low risk is posed from these levels then no further assessment is required.

For the estimation of risk from acute toxicological end points under the various scenarios (ie direct over-spray and 10% spray-drift), if:
$Q>0.5$ then risk is unacceptable,
$0.1 \leq Q \leq 0.5$ risk may be able to be mitigated by some form of risk management, such as label restraints for a specific use, and
$Q<0.1$, risk is considered low (and may or may not require some form of risk management, such as general label restraints).

For the establishment of risk for chronic exposure under the various scenarios,

- if using chronic data, $Q>1$ is unacceptable, and
- if using acute data, $Q>0.1$ is unacceptable.

3.4.3 Terrestrial organisms

3.4.3.1 Mammals

Terrestrial animals may be at risk from azinphos-methyl when applications of the chemical are made directly over them or from contact with sprayed surfaces, such as from orchard tree leaves or inter-row cover crops. It is expected that over-spray by tractor powered equipment is unlikely as larger animals will move some distance from the area where spray operations are occurring, while smaller mammals will be undercover, often underground. Most mammals are not expected to be directly over-sprayed.

It is difficult to assess the risk to terrestrial organisms, such as possums, that enter sprayed areas and are exposed to residues (dermal or dietary). Animals that enter recently sprayed areas are at some risk of exposure. Two field trials in US apple orchards did note "casualties", which included mammals, with 12 and 48% directly attributed to azinphos-methyl use and a further 68 and 21% possibly linked, but it was difficult to ascertain the breakdown of numbers of mammals/birds/etc involved, or at what stage exposure occurred (direct over-spray or post-spraying) plus confounding effect of other chemicals used including in one case, rodenticides.

Tests using gray-tailed voles (LD_{50} of 32 mg/kg BW and LC_{50} of 406 ppm) showed that when oversprayed at the maximum Australian rate of 1.5 kg ai/ha, and remaining in the sprayed area (long-grass, their normal habitat), there were no mortalities. When the same test animal was sprayed at higher rates, up to 4.48 kg ai/ha, there were effects on the populations, with reduced recruitment but the effects were of limited duration (9 weeks). While these voles are not the most sensitive mammals tested, the result does indicate that a significant risk to small mammals is unlikely.

It is concluded that while there are unlikely to be significant effects on mammal populations from orchard spraying, some individuals, especially those living and feeding in orchards, could be affected.

3.4.3.2 Birds

Birds feeding on sprayed fruit could be exposed to residues of azinphos-methyl. There are a number of bird species that are pests in orchards, grapevines etc. These species include silvereyes, parrots, lorikeets, rosellas, cockatoos, starlings, miners, currawongs, etc.

Incidents of azinphos-methyl poisoning of birds in Australia have not been noted in literature or press reports. However, in the US there have been reports of azinphos-methyl implicated in bird deaths associated with field/orchard uses of azinphos-methyl (see Section 3.3.6). In field studies (apple orchards) where azinphos-methyl was used with 7 days between applications and at maximum use rates, there were a number of avian casualties, 54 in one study with 3 applications (Johnson *et al* 1989) but only 2 in the second study with 4 applications (Sheeley *et al*, 1989). While these studies indicate the potential risk, it must be noted that the use pattern is atypical for Australia usage and use of a rodenticide confounded the results in the former. The two field studies from Ontario, Canada, where birds were oversprayed at higher rates than that used in Australia, there were no mortalities and detectable effects were limited to moderate inhibition of cholinesterase and minor behavioural changes.

For fruit sprayed at 1.5 kg ai/ha, the maximum rate expected for pome and stone fruit trees, the concentration of azinphos-methyl on the fruit is calculated as 19.5 mg/kg wet weight (99 mg ai/kg dry weight) from the modified Kenaga nomogram (Fletcher *et al.*, 1994). There were no acute dietary results presented by registrants but using the acute oral test value for birds (bobwhite LD_{50} = 33 mg/kg) and converting to a LC_{50}, assuming that a bird consumes a third of it body weight as food per day, then the LD_{50} is approximately 107 ppm in the diet. Assuming that approximately 50% of the dietary intake is treated, then the Q = 0.18 and the risk is minimal. Using the LC_{50} of 488 ppm from the US EPA review (see Section 3.3.1), the quotient is 0.04 and the risk is again minimal.

Effects on birds are possible from birds eating insects that are dead or dying from contact with azinphos-methyl. Using the EPA food chain (Kenaga) nomogram, the concentration of residues on large insects from applications at 1.5 kg ai/ha is 19.5 mg ai/kg (wet weight, Fletcher *et al.,* 1994). A bird consuming 70% of its diet as large insects and 30% as forage crops and all food is contaminated (worst case), would receive 58 mg ai/kg in the food, noting higher application rates are certainly used in mature orchard trees. Assuming that approximately 50% of the dietary intake is treated, considered a reasonable assumption, then the Q = 0.27 using the estimated LC_{50} of 107 ppm and the risk is minimal. Using the LC_{50} of 488 ppm the quotient is 0.06 and the risk is again minimal.

The Kenaga nomogram is worst case and it would be expected that the actual exposures from food items are likely to be somewhat lower. However, it must be noted that food items are not the only route of exposure. In the semi-field study of Matz et al (1998) it was clearly shown that other routes of exposure are potentially significant (see Section 3.3.1.3). In the field studies conducted in orchards with treatments every 7-10 days, ie program spraying, and at the maximum rate, there were effects on birds in and around the orchards with treatments every 7-10 days, ie program spraying, and at the maximum rate. On the other hand, the studies conducted in orchards with infrequent applications showed minimal effects on birds, even birds with nests in the treated orchards treated at higher rates. These studies indicate that effects on birds cannot be ruled out and with multiple applications, the effects could be

more significant.

The duration of any possible effects on birds is expected to be of relatively short duration. The half-life of degradation on apple leaves in the orchard field studies was approximately 7 days (see Section 3.3.6). In addition, the photolysis studies showed that there was significant degradation of azinphos-methyl on leaves (and presumably fruit), with 20-40% degradation after 8 hours of sunlight (Liang and Lichtenstein, 1976). Under Australia conditions with stronger and more intense sunlight, significant degradation of azinphos-methyl is anticipated, thus reducing the period when residues are toxic to birds.

In conclusion, while the Q values indicate there could be a slight risk from a single treatment to birds frequenting and feeding azinphos-methyl treated orchards, there are a number of uncertainties and there are also reports from overseas of adverse effects in a variety of situations, especially with multiple applications. Risk from Australian usage of azinphos-methyl under certain circumstances cannot be ruled out, since birds were "casualties" in the US orchard trials reported above. Applications are expected to be greatly limited under IPM programs, but to ensure a risk to birds does not result from repeated/program use, use should be restricted on the label to no more than two applications a year.

3.4.3.3 Bees

Bees are at risk if spraying occurs when they are present in the crop and most labels include a precaution - "dangerous to bees, do not spray flowering plants while bees are foraging". Bees are very important to the yield potential of orchard crops and most orchardists are well aware of the harmful effects of OP sprays (and other chemicals) on bees. In addition, azinphos-methyl is used after fruit set, ie 2-3 weeks after flowering, and as such exposure to bees is unlikely. Nevertheless, if bees were oversprayed at the lowest application rate expected in orchards (750 g ai/ha), the estimated dose is 0.68 µg ai per bee (Thompson and Hunt, 1999 and references therein), and from the EC_{50} of 0.1 µg ai per bee, the Q = 6.8. If bees are over-sprayed it is expected 100% kill rates would occur and to limit the exposure of bees to the pesticide, the crop should not be sprayed when there are bees present. In addition, the information from the US EPA review indicates that residues on foliage could be toxic to bees for 4-13 days after application.

Spray drift could also expected to be extremely toxic to bees. Spray drift studies show that worst case (early bud swell) application by orchard air blaster sprayers results in spray drift of 1.04% and 0.3% of the application rate at 30 and 50 metres respectively (Rautmann *et al* 2001). Using these figures, the quotients at 30 and 50 metres are 0.1 and 0.01 respectively and the risk acceptable at 30 metres away. For application in full leaf, the more likely usage, the quotient for 30 metres away is 0.03 (drift = 0.54%) and the risk low. It should be noted that the conditions from which these results were derived are those considered ideal to minimise spray drift – under more adverse conditions the spray drift could increase substantially and likewise the risk.

It is clear that there is a significant risk to bees from aerial application of azinphos-methyl, but as noted above, aerial application in orchards is not regarded as widespread, and should be prohibited, to avoid any likely increased non-target risk.

3.4.3.4 Soil Invertebrates

Earthworms and other soil dwelling invertebrates could be exposed to the pesticide, and at an application rate of 1.5 kg ai/ha, the top 5 cm of soil would contain azinphos-methyl residues at 0.04 mg/kg of soil (assumes no crop cover, density of soil 1300 kg/m^3). This is significantly below the LD_{50} and the NOEC for worms (see Section 3.3.3.1), but in the reproduction test, effects on earthworms were noted for an EC 200 formulation (20% ac) applied at 1 kg/ha, with a NOEC < 1 kg/ha. Some adverse effects on worm populations were noted in German field trials, but these were apparent at extremely high application rates (6 kg/ha direct to pasture).

Soil arthropods may be significantly affected unless they can move away from contact with the sprayed areas or have become resistant to azinphos-methyl from past use. There are no toxicity data available for these organisms and the risk cannot be determined.

The toxicity data available for soil micro-organisms indicate the risk is likely to be low as soil-N metabolism was not affected. Some growth inhibition (4-18%) was noted for soil fungi at 2 and 10 ppm on paper discs but it is unclear as to how this relates to soil concentrations.

3.4.3.5 Conclusions

Mammals were not expected to be significantly exposed to direct overspray of the chemical unless they enter an area recently sprayed. Overseas studies show that mammals in orchards could be affected, with some studies showing a number of casualties. It is concluded that while some individuals living and feeding in orchards could be affected, there is unlikely to be significant effects on mammal populations from orchard spraying.

While the overall risk to birds appears relatively low, the risk is greater with repeated spraying, and there have been reports from overseas of adverse effects in a variety of situations, especially with multiple applications. Applications are expected to be greatly limited under IPM programs, but to ensure a risk to birds does not result from repeated/program use, use should be restricted on the label to no more than two applications a year.

The risk to bees is high if spraying occurs when they are present in the crop and foliar residues may remain highly toxic to bees for 4-13 days after application, To limit the exposure of bees to the pesticide during spraying, the crop should not be sprayed when bees are foraging and users should be warned of the risk from spray drift. To avoid exposure to residues, trees or vines should not be sprayed while they are flowering.

Effects on earthworms and soil micro-organisms are unlikely at normal field rates. There is a possible risk to soil arthropods, but there are no toxicity data for these organisms.

3.4.4 Aquatic organisms

3.4.4.1 Direct over spray

Direct application of azinphos-methyl to a body of water 15 cm deep at a rate of 1.5 kg ac/ha

(corresponding to 3000 L/ha at 49 g ac/100 L, considered a maximum rate for pome and stone fruits) is calculated to give a concentration in the water of 1.0 mg/L. Application by orchard air blasters is unlikely to result in direct over-spray of waterbodies. However, aerial applications might lead to such direct over-spray and because of this of concern, aerial application should be prohibited. Concentrations of 1.0 mg/L in shallow water from direct application (as above) result in water levels that are likely to cause mortalities in the majority of fish species, based on the tests reviewed (LC_{50}s of 1.86 to 8.8 µg ai/L, see Section 3.3.2.1).

Effects on daphnia and other aquatic insects/invertebrates from direct over-spray are likely to be severe (LC_{50} = 1.1 µg/L). Similar effects are likely on other aquatic invertebrates. However, as noted above, DEH regards direct over-spray as being a rare occurrence with ground application and the following risk assessment for spray drift as being more realistic for Australian use patterns.

3.4.4.2 Spray Drift – First Tier Assessment

Spray drift is of major concern for aquatic organisms. Using the US EPA worst case assumption that 10% spray drift reaches water (Urban and Cook, 1986), this would result in a concentration of 100 µg/L for a shallow pond 15 cm deep (rate 1.5 kg/ha). This is above the LC_{50} for all fish tested (Q from 11.5 to 54) and well above the EC_{50} for daphnia and mysid shrimp, the most sensitive organism tested with a reliable endpoint (EC_{50} = 0.12 µg/L) and indicates an extreme risk to aquatic invertebrates. This concentration is also likely to be a significant risk to freshwater crayfish, with the US EPA review (US EPA 1999) listing an EC_{50} for a crayfish species as 56 µg/L, but there are no endpoints for Australian freshwater macro-crustacea.

The risk to aquatic organisms from this crude calculation of 10% spray drift is therefore considered to be unacceptable, but DEH accepts that 10% is an arbitrary, high figure for most spray drift situations and further refinements to more accurately determine the risk are required.

3.4.4.3 Spray drift – Aerial Application

Aerial application is the not regarded as the normal practice for applying pesticides to orchards. However, it is not prohibited on the azinphos-methyl labels, and based on the above the principal registrant has agreed to add a label statement to prohibit aerial application.

3.4.4.4 Spray Drift - Ground Based Spraying

Orchard Air-Blast Spray Drift

The Spray Drift Task Force, set up to undertake trials to measure the spray drift, including that from orchard spraying in several orchard crops: grapes, apples (foliated and dormant), oranges, grapefruits, almonds and pecans. Due to the limited number of applications made to any given crop, the results for crop/situation giving similar levels of drift were pooled into three groups: normal (grapes wrap-around sprayer, pome fruit and grapes with air blast), dense (citrus [airblast and mister] and nut trees) and sparse (small trees and dormant trees). The information was used to develop a model for spray drift, AgDRIFT, but the model was not refined to equipment and nozzles types etc for ground rig applications and is only considered as Tier 1 (US EPA 1997). The results of this modelling are given in Table 77 for

normal (pome and stone fruit trees with full foliage), dense (macadamia nuts etc) and sparse (dormant trees), with results as EECs (@ 1.5 kg ac/ha, maximum Australian rate) in water (15 cm deep, 3 m wide pond) and quotients for fish (EC_{50} = 1.86 µg/L), daphnia (EC_{50} = 1.1 µg/L) and mysid shrimp (EC_{50} = 0.12 µg/L).

Table 77: Concentrations of azinphos-methyl in water 15 cm deep following application to orchard at 1.5 kg ac/ha and quotients for fish, daphnia and mysid shrimp based on LC_{50}s of 1.86, 1.1 and 0.12 µg/L respectively.

Distance from	Concentration (µg/L) and quotients (fish, daphnia and mysid)		
orchard, metres	normal	dense	sparse
10	1.61 (0.87, 1.47, 13.5)	21.9 (11.8, 19.9, 182)	58.4 (31.4, 53.1, 487)
20	0.89 (0.48, 0.81, 7.42)	10.2 (5.50, 9.30, 85.3)	20.4 (11.0, 18.5, 170)
50	0.36 (0.19, 0.32, 2.96)	3.26 (1.75, 2.97, 27.2)	3.38 (1.82, 3.07, 28.2)
100	0.16 (0.09, 0.15, 1.34)	1.46 (0.79, 1.33, 12.2)	0.73 (0.39, 0.66, 6.04)

The AgDRIFT results clearly show that with 'normal' orchard spraying (pome and stone fruit trees with full foliage) there is a limited risk to fish and daphnia at 50 metres, but using the salt water mysid shrimp, a surrogate for sensitive invertebrates, the risk extends to beyond 100 metres. However, for other orchard trees such as macadamias and dormant spraying (or bud swell/green-tip) there is a high risk to all aquatic organisms at 100 metres from the orchards and beyond. It should be noted that the depth of water used to generate Table 76 is considered shallow. This is addressed below under the heading of further refinement.

In addition to the AgDRIFT results, there are German studies (Ganzelmeier, *et al*., 1995; Rautmann *et al*, 2001) that specifically trialed orchard airblast sprayers according to strict protocols and standard conditions to test spray drift in grapes, fruit crops and hops, at both early and later growth stages, under GAP. Results give mean values for statistically treated data from repeated application trials on grapes, fruit trees and hops. Several groups cooperated and applied chemical (copper or a dye) at various rates, with various types of airblast sprayers, but all according to the standard protocol. Estimates for drift are given as the 90th percentile of mean values, quoted as % of the application rate, whereas AgDRIFT Orchard Airblast modelling is for the 50th percentile.

The multiple trials on fruit trees appear useful in comparison with equivalent Australian crops. Apart from Australian weather conditions, where air temperatures are likely higher and humidity lower, the results should be useful in estimating drift in orchard situations under typical usage.

Pome and Stone Fruit

In Table 78 and Table 79 the estimated spray drift for pome and stone fruit are shown at a given distances from crops, both early and late growth stages using the Rautmann et al (2001) tables. Again the EECs and worst case Q-values are shown for fish, daphnia and mysids based on an azinphos-methyl application rate of 1.5 kg ai/ha.

Table 78: 90th percentile spray drift estimated from airblast sprayers in fruit crops, early growth stage (after Rautmann et al, 2001) and aquatic Q–values when sprayed at 1.5 kg ac/ha.. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

Distance	Spray drift, (% of applied)	EEC (µg/L) in water, 15 cm	Q, Fish	Q, Daphnia	Q, Mysid
10	11.8	118	63.5	107	983
20	2.77	27.7	14.9	25.2	231
30	1.04	10.4	5.59	9.45	86.7
50	0.30	3.0	1.61	2.73	25.0

Table 79: 90th percentile drift estimates from airblast sprayers in fruit orchards (trees ~3m), late growth stage (after Rautmann et al, 2001) and corresponding EECs and quotients when sprayed at 1.5 kg ac/ha. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

Distance metres	Spray drift, (% of applied)	EEC (µg/L) in water, 15 cm	Q, Fish	Q, Daphnia	Q, Mysid
10	3.60	36.0	19.4	32.7	300
20	1.09	10.9	5.86	9.91	90.8
30	0.54	5.4	2.90	4.91	45.0
50	0.22	2.2	1.18	2.00	18.3

Clearly the amounts of spray drift likely to exist up to 30-50 m from these orchard scenarios result in Q-values in water indicating there is still likely to be an acute risk to all the above groups of aquatic biota. Where orchards are directly juxtaposed with natural watercourses, that is trees within 20-50 m of water, these aquatic toxicities are likely to cause concern. The water depth in permanent streams/rivers is expected to be greater than 15 cm and in the range 30-40 cm, therefore the risk in Table 78 and Table 79 is considered to be too high for a realistic Australian situation.

The use of insecticides for dormant and green leaf usage to control insects is declining and is no longer the recommended practice in NSW (personal communication, Graham Thwaites, NSW Agriculture). Bayer Australia has clarified the current usage, confirming that there is minimal use during dormancy and green tip, with principal use from post flower/fruit set to harvest for both pome and stone fruit. Therefore the focus of the assessment of the risk will be for trees sprayed in full foliage, eg Table 79 and normal in AgDRIFT (Table 80).

For inland irrigation areas the risk to aquatic animals is regarded as relatively low as orchard areas are usually some distance from rivers and water is delivered through irrigation channels. In the wetter, cooler orchard areas the adequate separation of pome and stone fruit orchards (and spraying) from water courses is less likely to occur, due to the general terrain and the need for supplementary irrigation that is often supplied from pumping direct from creeks, rivers or dams within farmland catchments. Ground-based sprayers no doubt frequently traverse within 10-50 m of the smaller watercourses that lead into the larger creeks and rivers. These areas tend to be older and have not been planted using modern methods (trellises or high densities plantings) with the result that the trees are larger and consequently the spray volumes are correspondingly higher. However, some of these older orchards have been replanted (or re-grafted) to modern orchard practices.

Further Refinements

In refining the risk further the physical properties of azinphos-methyl are considered as well as a more realistic assumption concerning the environment where most pome and stone fruits are grown.

The physical properties of azinphos-methyl clearly indicate moderate binding to soil, with Koc ranging from 472 to 3396 (see Section 3.2.4.1) and therefore significant binding to sediment in streams may be expected. However, no results from aquatic metabolism studies are available to show if there is any adsorption to sediment following application to water. The mesocosm studies did not show such binding, with minimal levels of azinphos-methyl recorded in the sediment, although one study showed there was a mean of 40% adsorption of total active associated with the suspended material in the water column. The chronic daphnia and midge larvae studies using sediment showed little if any mitigation of the toxicity of azinphos-methyl. The stream microcosm studies also suggested that azinphos-methyl adsorbed to particles could contribute to toxicity in addition to dissolved azinphos-methyl (Section 3.3.2.8). Therefore it is unlikely there will be any moderation of the toxicity due to the presence of sediment in natural systems.

Degradation of azinphos-methyl is expected to commence once spray drift reaches water, potentially reducing concentrations of the order of 50% by 48 h after application. However, due to the acute nature of toxicity from azinphos-methyl (eg evident from the 1-hour exposure studies conducted in stream microcosms by Thiere and Schulz, 2004 and Schulz *et al*, 2002), diminishing concentration due to degradation or adsorption to organic matter or other surfaces has not been considered as a mitigating factor.

The depth of water is a significant factor in determining the concentration in water from spray drift. For more permanent streams and those with high ecological values a depth of 30 cm is assumed. Using this, Table 80 is generated for late season spraying of stone and pome fruit trees using Rautmann *et al* (2001) and Table 81 using AgDRIFT.

Table 80: 95th percentile drift estimates from airblast sprayers in fruit orchards (trees ~3m, 1.5 kg ac/ha), late growth stage (after Rautmann *et al*., 2001) in water 30 cm deep. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

Distance metres	EEC (µg/L) in water 30 cm	Q, Fish	Q, Daphnia	Q, Mysid
10	18.0	9.68	16.4	150
20	5.5	2.93	4.95	45.4
30	2.7	1.45	2.45	22.5
50	1.1	0.59	1.00	9.17
	0.3	0.16	0.27	2.50

Table 81: Spray drift estimates from airblast sprayers in normal orchards from AgDRIFT at 1.5 kg ac/ha in water 30 cm deep. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

Distance metres	EEC (µg/L) in water 30 cm	Q, Fish	Q, Daphnia	Q, Mysid
10	0.81	0.43	0.73	6.73
20	0.45	0.24	0.40	3.71
50	0.18	0.10	0.16	1.48
100	0.80	0.04	0.07	0.67

The results in Table 80 and Table 81 are considerably different, with the Rautmann *et al* (2001) results showing a considerable risk to aquatic organisms to 50 metres at least and the AgDRIFT indicating a minor risk to fish and daphnia 10 metres away from the edge of the orchard. However, it should be noted that the AgDRIFT results (normal) are 50th percentile data modelled on data pooled from applications to grapes (both conventional and wrap around sprayers) and apple orchards while the Rautmann *et al* (2001) data are for fruit crops in Germany.

Using the Rautmann *et al* (2001) results as 'worst case', Table 80 indicates a high risk at 50 metres. At 100 metres risk is estimated to be approximately 1/3 that at 50 metres, and the Q values are 0.16 for fish and 0.27 for daphnids, but still 2.5 for mysids. These results are for the maximum expected rate in Australian pome and stone fruit orchards. At typical rates the risk reduces accordingly, and at 1.0 kg/ha (2000 L/ha, typical rate for pome and stone fruit), quotients at 50 metres are 0.40, 0.67 and 6.1 for fish, daphnia and mysid respectively using the Rautmann et al (2001) tables, or approximately 0.11, 0.18 and 1.67 at 100 m. Thus, depending whether the Rautmann et al (2001) tables or the AgDRIFT tables are used, at 100 m the risk is mitigable or acceptable for fish and daphnids, but still remains high for mysids. Note that the US EPA review (US EPA 1999) also contains two EC_{50}s (48 h) for *Gammarus fasciatus* of 0.16 and 0.25 µg/L (ie more comparable to the mysid result), both rated as core studies (= reliable).

In the major mesocosm study (Giddings 1989) there were no detectable effects on aquatic invertebrates at a mean concentration of 0.95 µg/L (comparable to the 48 h EC50 of 1.1 µg/L used for daphnids in the above assessments), despite multiple applications, and only limited effects at 5.2 and 29 µg/L. In contrast, the 3 other literature studies showed that at around 1.0 µg/L there were significant effects on cladocerans. In the study of Sierszen and Lozano (1998) univariate analysis of littoral enclosures showed that cladocerans were affected at <1.0 µg/L and practically eliminated at >2.0 µg/L. As the cladocerans and other affected organisms recovered after 5 weeks in all the studies to the levels in the controls, any sensitive invertebrates that are effected from spray drift are expected to recover. Overall these 'real world' mesocosms tend to indicate a risk to daphnia at approximately 1 µg/L and support Table 80 and Table 81 that a likely risk exists to these organisms.

Considering the current use pattern of azinphos-methyl in orchards and that most pome and stone fruit orchards are somewhat away from water, use once or twice per season is unlikely to present a significant risk, as affected organisms could recover. However, program spraying could represent a significant risk to aquatic organisms due to the increase in the frequency of spray and therefore the probability of spray drift. Program spraying is most likely to still be used by older orchardists (Frank Page, Primary Industries of Queensland, personal communication), whose properties tend to be in the older apple growing areas and are closer to waterways, increasing the level of concern. With the high level of concern regarding single and multiple applications, a buffer of 100 metres from aquatic environments is recommended for orchard applications of azinphos-methyl, based on the Rautmann et al (2001) results, in order to reduce the environmental impacts to an acceptable level. The issue of program spraying is further addressed under Multiple Applications (below).

Macadamias

The above analysis mainly focused on pome and stone fruits, the major use of azinphos-methyl. While azinphos-methyl is used in macadamias and represents approximately 10% of

all the active sold, it is not considered the principal insecticide for control of pests, with its use in macadamia orchard being more occasional (Neil Treverrow, NSW Agriculture, personal communication). The AgDRIFT model included nut trees in the grouping 'dense', but Rautmann *et al* (2001) does not have data specifically for nuts.

For macadamias a high application rate would be approximately 2 kg ai/ha corresponding to 4000 L/ha of spray at 49 g ai/100 L. Using AgDRIFT for dense trees, Table 82 gives the EEC and quotients for fish, daphnia and mysid allowing for 30 cm deep water, as above.

Table 82: Spray drift estimates from airblast sprayers in macadamia orchards from dense AgDRIFT at 2 kg ac/ha in water 30 cm deep.

Distance metres	EEC (µg/L) in water 30 cm	Q, Fish	Q, Daphnia	Q, Mysid
10	14.6	7.83	13.2	121
20	6.82	3.67	6.20	56.9
50	2.18	1.17	1.98	18.1
100	0.98	0.52	0.89	8.12
150	0.64	0.34	0.58	5.29

Table 82 indicates a very high risk to most aquatic organisms, with the risk for fish extending to 100 metres and for daphniato over 150 m. However, in the regions where macadamias are grown, the streamside vegetation is expected to be luxuriant and should act as a buffer, reducing the risk. While it is not possible to model the effective capture rate for a stream side buffer, a paper by Salyani and Cromwell (1992) showed that the last two rows (rows 1 and 2) captured between 70-80% of the spray from rows 3 and 4. If a forested gully intercepts the spray drift similarly, then the risk would be significantly reduced and at 100 metres the quotients are 0.13, 0.22 and 2.03 (assuming 75% capture) for fish, daphnia and mysid respectively. The hazard for fish and daphnia is acceptable to mitigable, but still high for mysid. Again this indicates the need for a 100 buffer from aquatic systems, although the need for a buffer is moderated by the infrequent use. Another possibility to reduce the hazard further would be not to spray the last two downwind rows, as recommended by Salyani and Cromwell (1992), but such an approach is not consider practical by growers.

As use is limited, with most macadamia growers using azinphos-methyl infrequently (the principal registrant indicates usage only once per season), the probability of a harmful drift event occurring is expected to be low and therefore the risk is unlikely to be environmentally significant. However, it should be noted that most growers currently would apply azinphos-methyl as low volume spray, which is not considered above (however, see Other Spray Equipment below).

Citrus

For citrus use, with very high application volumes (6-8000 L/ha, 3-4 kg ai/ha) and scale as the principal targeted pest, the risk to aquatic invertebrates from spray drift is high, approximately twice that in Table 83 (ie using AgDRIFT for dense foliage, as the German studies did not include citrus). While it is recognised that this is a worst case scenario and that use in citrus is infrequent, this use represents a high risk for aquatic invertebrates. This was not mitigated further as several citrus areas rely on irrigation and therefore could be close to drainage systems and natural streams. Further, in a number of citrus growing regions there is only pasture/grasses between the orchard and natural water courses and little stream side vegetation to intercept any spray drift that does occur. As an impracticably high buffer would

be required, and due to the greater risk from runoff at these application rates, it is recommended that use on citrus should be deleted from the label.

Other orchard crops

The other orchard crops on the labels are quinces and lychees. Quinces are a pome fruit and these have been extensively examined above. Lychees are a tropical fruit with the trees being dense and up to 10 metres in height. As this is somewhat similar to the macadamia nut trees above and grown in similar areas, a similar risk is likely.

Non-orchard crops

The other minor crops where azinphos-methyl is registered are grapes, kiwifruit and blueberries. Given that kiwifruit are vine crops, they will be considered with grapes. It should be noted that the major use of azinphos-methyl in grapes is for control of elephant weevil and fig longhorn, with application to the trunk and arms of the vines as well as foliage application at 49 g ai/100 L.

The following risk assessment uses the Rautmann *et al* (2001) data for application to grapes, both early season and late growth stage. As grapes are normally a smaller plant than orchard crops, the volume of spray used is commonly ~1000 L/ha and often less, depending on the trellises used. Assuming a volume of 1200 L/ha as maximum, the application rate is 588 g ai/ha. Table 83 gives the percentage spray drift from Ganzelmeier, the EEC in water 30 cm deep (@ 600 g ac/ha) and calculated risk quotients.

Table 83: Spray drift estimates from airblast sprayers in grapes, early and late season application at 600 g ai/ha in water 30 cm deep. From Rautmann et al (2001).

Distance metres	Percentage spray drift	EEC (µg/L) in water 30 cm	Q, Fish	Q, Daphnia	Q, Mysid
Early season					
10	0.39	0.78	0.42	0.71	6.50
20	0.13	0.26	0.14	0.24	2.17
30	0.07	0.14	0.08	0.13	1.17
50	0.03	0.06	0.03	0.05	0.50
Late season					
10	1.23	2.46	1.32	2.24	20..5
20	0.42	0.84	0.45	0.76	7.0
30	0.22	0.44	0.24	0.40	3.67
50	0.10	0.20	0.11	0.18	1.67

The results in Table 83 (and noting the above comments on mesocosm data) indicate that to protect aquatic organisms in a 15 or 30 cm deep pond, a buffer of at least 50 m is required, particularly with late season application. Hence the proposed 100 m buffer for other crops will be protective for use on grapes and other vine crops, and also for blueberries.

Other Spray Equipment

Orchardists are increasingly using spray equipment other than the high volume conventional sprayers, with low volume methods being the main alternative to the traditional sprayers. The LV equipment that are increasingly being employed have smaller droplet sizes (vmd [volume median diameter] = 30-50 µm, Matthews, 1992) than the spray used to generate the AgDRIFT model or Rautmann et al (2001). Non-electrostatic ULV applications are of particular concern due to the higher potential for spray drift from the smaller droplet size.

The spray drift from low volume applications to citrus orchards has previously been studied and modelled (Salyani and Cromwell, 1992). The experimental data used for the model was obtained from low volume spraying in an orange orchard in Florida. There were three trials and the average spray drift was used to fit a quadratic equation to the spray drift curve. The high volume application was also tested and similarly modelled. (Fit to these equations of the data was good, $r^2 > 0.88$.) Table 84 is generated to show the comparison for high and low volume applications spray drift from citrus trees.

Table 84: Comparison of spray drift as % of application rate, for air blaster spraying and low volume applications to citrus. From Salyani and Cromwell (1992).

Distance downwind, m	25	50	100	150	200
High Volume	0.91	0.21	0.053	0.024	0.014
Low Volume	0.72	0.25	0.083	0.043	0.027

Table 84 shows that the low volume spraying gives less drift than from high volume spraying close to the spray site but higher drift further away. However, for distances ≥50 metres, the results shown from Salyani and Cromwell are lower than the AgDRIFT results for dense trees and therefore the low volume spraying is unlikely to significantly increase the risk compared to high volume applications. However, care is necessary in making such comparsions on the limited data available.

The principal registrant has indicated that macadamias are sprayed using 'spray towers'. These are low volume equipment that direct the compressed air in a tube so it can be directed into the trees, especially the top canopy. When set up and used correctly, it is likely that such equipment could reduce drift, but there are currently no spray drift studies that clearly show this. Therefore while the hazard for spray towers could be less than for normal air blast sprayers, DEH can only consider the hazard for spray towers the same as for orchard air blast.

Flowing Water

While all of the above risk calculations are for ponds, a 'pulse' of contaminated water is likely in flowing streams and the acute risk calculations are used as an approximation of this 'pulse'. For ponds receiving runoff from orchards or from streams near orchards, further dilution is expected and as these ponds are likely to be significantly deeper, the risk should be reduced. As this depends on the other land uses in the area, risk calculations for such situations are site specific and a general case is difficult to derive. However, it is expected that the risk will be less than that calculated for natural lentic ponds etc receiving water only from streams near orchards.

Risk to Algae

Azinphos-methyl is rated as moderately toxic to algae (E_bC_{50} of 3.5 mg/L, see Section 3.3.2.5). As direct application to water is not expected and assuming 10% spray drift the concentration in shallow water is 100 µg/L, approximately an order of magnitude below the algae EC_{50} and effects on algae are unlikely. In the mesocosm study, there were no effects noted on algae at concentrations of up to 30 µg/L.

Risk to Amphibians

Azinphos-methyl is rated as moderately toxic to a tree frog and two species of salamanders with LC_{50}s of 1.47 and 1.9 mg/L (see Section 3.3.2.5). Using the same argument as above for algae, the risk from 10% spray drift is minimal. However, the US EPA reports a LC_{50} for

Fowlers toad of 109 µg/.L. Using the EEC's calculated for macadamias in 30 cm deep water at 10-20 m of 14.6-6.82 µg/L (Table 84) as a worst case, the risk quotient for Fowlers toad is 0.14-0.06 and the risk is expected to be acceptable.

Multiple Applications

The Agricultural Assessment indicates the current usage is limited, with use on pome and stone fruit being the principal uses but mainly as a clean-up spray to start IPM or when IPM system breaks down. In addition, this report indicates that the current use pattern is of intermittent use in response to insect pressure rather than program spraying, thus multiple applications within weeks of each other are not likely, although with high insect pressure multiple applications are more likely (under these conditions it is hoped that alternative sprays would also be used to avoid insect resistance). The other major users of azinphos-methyl are macadamia growers but again the use is relatively low. Other minor crops could use azinphos-methyl as a mainline chemical. In contrast the principal registrant indicates that program spraying occurs in Queensland for pome fruit and very frequent applications (4-8 per season) in NSW for both pome and stone fruit.

The interval between applications is 10 to 14 days for program spraying in Queensland as indicated by the principal registrant. For other minor crops, the label recommendations are for at least 14 days between sprays for litchis, macadamia and blueberries and 3-4 weeks for Kiwifruit and grapes. From the mesocosm studies (see Section 3.3.2.7) the half lives in water ranged from 0.34 to 7.775 days with an average of 1.64 days for the higher concentrations. Assuming a half-life in water of 2 days, then the increase in concentration after 10 days due to carryover is approximately 3.1%, ie >95% dissipation has occurred. A significant increase in concentration in water is not expected or increased acute toxic effects on aquatic organisms from multiple applications, provided there is at least 10 days between applications. The mesocosm study clearly shows that even with just 7 days between each application, the concentration in the water column only increased slightly, if at all. In addition, the mesocosm studies of Knuth *et al.* (2000) showed that the DT_{95} was, at worst, 10.4 days, with most of the dissipation due to degradation. There is unlikely to be a significant increase in concentration from multiple applications, even under worst case conditions with a high level of multiple applications.

However, the main problem is repeated effects on organisms and 10 days between sprays may not allow affected populations to recover, especially if this is repeated for up to 14 times a season, as could occur with program spraying. In the study of Sierszen and Lozano (1998) affected organisms fully recovered after 5 weeks following a single application. Thus program spraying represents a high risk to aquatic organisms, and as it increases the likelihood of adverse spray drift events occurring, program spraying using azinphos-methyl should be actively discouraged. Hence, it is recommended that use be restricted to no more than two applications per production season.

Chronic effects

Once in the aquatic environment, azinphos-methyl is expected to degrade. In the mesocosm study, the half-lives ranged from 0.57 days to 2.87 days for the three highest mesocoms concentrations, with a mean half-life of 1.64 days. After 21 days, corresponding to ~13 half-lives (using a half-life of 1.64 days), the concentration in water would be very low and the chronic hazard minimal. As an example, using the result for macadamias at 20 metres of 6.8 µg/L (application in 30 cm deep water from Table 83above), further degradation of 20 days and a half life of 2.0 days (~10 half lives) gives an EEC of 6.64 ng/L, below the 21 day

MATC for daphnia (250-400 ng/L) and near the 28 day NOEC for mysid shrimp (8.3 ng/L). However, the risk to organisms present in exposed waterbodies is from acute, rather than chronic exposure.

Similarly, the spray drift risk from multiple applications is from repeated acute impacts, rather than chronic exposure, though a closer spraying interval than 21 days may maintain concentrations above chronic toxicity NOEC levels.

3.4.4.5 Runoff

Runoff from areas where azinphos-methyl has been used is not expected to be significantly contaminated, provided rain or irrigation does not occur shortly after application. The K_{oc} indicates at least moderate binding to soil particles, which was confirmed in the column leaching studies. The degradation in soil half-life of between 5.3 and 10.9 days (see Section 3.2.3.1) will limit the time when erosion of soils treated with adsorbed azinphos-methyl is likely to be problematical. Further, significant erosion of contaminated soil is not expected due to modern orchard and vineyard management practices of including cover crops between rows.

However, the US EPA review clearly indicates that azinphos-methyl has accounted for more aquatic incidents in their ecological incidents database than any other pesticide, and there have been some major fish kills. These incidents were mainly associated with use on sugarcane and cotton crops, in areas where intense and frequent rainfall favoured runoff into nearby water. These uses were therefore prohibited or restricted in the USA. There have also been aquatic incidents associated with the use of azinphos-methyl in US orchard crops, but such incidents have been less common than for cotton and sugarcane, despite greater use on orchards. Reasons suggested for this included climatic differences affecting runoff likelihood, use of aerial application in field crops (hence greater spray drift risks), the presence beneath orchards of at least a partial sod to intercept run-off, and greater proximity to water with sugarcane and some cotton production areas.

In Australia there are districts, such as the MIA, with significant numbers of tile drains from which pumped effluent drains into areas such as creeks and swamps which could be affected by runoff.

As a first tier analysis, the following assumptions are made: a treated area of 10 hectare drains to form a pond of 15 cm deep, 1 hectare in area (volume = 1.5 ML) and 5% of the applied product runs off (5% X 10 X 1000 g ai/ha] = 500 g ai), then the concentration in the pond is 500 g/1.5 ML, ie 330 µg/L. This shows that there is likely to be significant effects on aquatic organisms with the quotients >100 indicating a potential risk. Using a more realistic assumption that only 10% of the catchment area is treated, the concentration in receiving water is 33 µg/L and quotients for fish and daphnia are 18 and 30 respectively. Allowing for 2 days of degradation before exposure and assuming a half-life of 2 days, the quotients remain high, 9 and 15 respectively, and the risk remains high and unacceptable.

While the above relatively crude analysis shows that there is potential for runoff to cause significant contamination of aquatic areas, most orchardists limit runoff in order to reduce erosion by such strategies as maintaining grass between rows and inter-row mulching. In addition, orchards on sloped-land are contoured so that the rows of trees are across the slope minimising runoff down the slope. While it is difficult to derive a general scenario, these

factors being site specific, they do reduce the risk of runoff occurring. In addition, the current use pattern of using azinphos-methyl as a clean-up spray to establish IPM or re-establish IMP conditions would minimise the frequency of use and therefore the probability of runoff occurring.

Evidence for significant contamination by azinphos-methyl in runoff is lacking in Australia, in part due to lack of studies.

However, run-off has been a major cause of aquatic incidents with azinphos-methyl overseas. South African studies (Section 3.2.7.6) showed runoff (rather than spray drift) from azinphos-methyl application to pome fruit orchards was the major source of azinphos-methyl contamination in the Lourens River and stressed the need for mitigation measures to address this source of contamination. As noted, US water monitoring studies also show contamination of aquatic ecosystems and there are reports from the US of runoff from orchard applications causing fish kills and presumably other aquatic organisms (see US incidents, Section 3.3.7) at rates comparable with those used in Australia.

Azinphos-methyl is no longer used in cotton or sugarcane production in Australia. With other uses, there is a need for users to ensure that azinphos-methyl is not used if rain is expected in order to reduce the risk of contamination of surface runoff. Hence a label statement restricting use if heavy rainfall is expected within 48 hours has been proposed. Restriction of use to once or twice per production season and not using azinphos-methyl at the high rates required for citrus will also minimise the risk from run-off.

3.4.4.6 Conclusion-aquatic risk

Overall the major risk to aquatic organisms from spray drift is moderate to high, with fish likely to be the least affected and sensitive invertebrates significantly affected. There is also a moderate to high risk due to runoff from treated areas.

Calculation of the risk using the first tier analysis at 1.5 kg ai/ha (10% spray drift) showed that there was a high risk to most fish species and a very high risk to aquatic invertebrates.

Aerial Application
There is currently little if any aerial application of azinphos-methyl, as this is not regarded as the normal practice for applying pesticides to orchards, but it is not prohibited on the azinphos-methyl labels. Due to the high estimated risk, based on previously assessed chemicals, it is recommended that a prohibition on aerial application of azinphos-methyl should be added to the label.

Orchard Air Blast Equipment
Calculations show the hazard to fish in shallow water is moderate from use of orchard air blast equipment. Based on the US EPA AgDRIFT model for spray drift, the hazard to fish and daphnia is acceptable for pome fruit and stone fruit at 1.5 kg ai/ha (2000 L/ha @ 49 mL/100 L of spray), when these trees are in full leaf. However, the Rautmann *et al* (2001) tables, generated from multiple applications to fruit trees in Germany and considered to be scientifically sound, showed there was a higher hazard. Therefore, it is recommended that a 100 metre buffer to aquatic areas is used to reduce the environmental hazard.

As azinphos-methyl is currently not normally used for dormant spraying for scale, a detailed

separate analysis for dormant spraying was not performed, but the hazard was shown to be significantly higher than in the full leaf case from AgDRIFT and is considered unacceptable. Therefore, as this use represents a potential hazard to aquatic invertebrates and this use is not significant, it is recommended that consideration be given to removing uses involving dormant or early season spraying from the label.

Multiple applications were considered and shown to increase the hazard, especially program spraying as it does not allow affected populations to recover. Therefore program spraying is considered to present a high risk to the aquatic environment near orchards and should be discouraged. Hence, it is recommended that use be restricted to no more than two applications per production season.

The risk to aquatic organisms from application to grapes was determined to be lower than that from use on pome and stone fruit trees, based on the Rautmann et al (2001) tables. Hence the proposed 100 m buffer for other crops will be protective for use on grapes and other vine crops such as kiwifruit, and also for blueberries.

For macadamia orchards, there is a moderate risk to fish and a high risk to daphnia at 100 metres away from typical drift levels at 2.0 kg ai/ha (49 g ai/100 L at 4000 L/ha) from the AgDRIFT model. However, noting that the growing areas often abut forested gullies that are likely to intercept spray drift (75% interception was assumed), the risk was considered as acceptable at 100 metres with use at most twice per year, noting that growers predominantly use equipment not well modelled by the AgDRIFT model used. .

For citrus use, with very high application volumes (8000 L/ha) and scale as the principal targeted pest, the risk to aquatic invertebrates from spray drift was calculated to be high. As an impracticably high buffer would be required, and due to the greater risk from runoff at these application rates, it is recommended that use on citrus should be deleted from the label.

It should be noted that the conditions from which these results were derived are those considered ideal to minimise spray drift – under more adverse conditions the spray drift could increase substantially and likewise the risk.

Modern LV equipment used by some growers is of concern due to the higher potential for spray drift from the small droplet size used. However, comparative calculations based on literature results indicate that the spray drift from this type of equipment is somewhat lower than from conventional sprayers. Therefore the risk should be similar to (if not less than) that for conventional orchard airblast equipment.

Runoff

Calculation based on simplistic model for runoff showed that was a very high risk to aquatic organisms from runoff. While this analysis showed that there is potential for runoff to be problematical, most orchardists limit runoff in order to reduce erosion by such strategies as maintaining grass between rows, inter-row mulching and contour plantings. These factors reduce the risk of runoff occurring. In addition, the current use pattern reduces the frequency of use and therefore minimises the probability of runoff occurring.

While the above analysis suggests that azinphos-methyl could cause significant contamination due to runoff from treated areas, there is no evidence for this in Australia. However, run-off has been a major cause of aquatic incidents with azinphos-methyl overseas. South African

studies (Section 3.2.7.6) showed runoff (rather than spray drift) from azinphos-methyl application to pome fruit orchards was the major source of azinphos-methyl contamination in the Lourens River and stressed the need for mitigation measures to address this source of contamination. US water monitoring studies also show contamination of aquatic ecosystems and there are reports from the US of runoff from orchard applications causing fish kills and presumably other aquatic organisms (see US incidents, Section 3.3.7) at rates comparable with those used in Australia.

Azinphos-methyl is no longer used in cotton or sugarcane production in Australia. With other uses, there is a need for users to ensure that azinphos-methyl is not used if rain is expected in order to reduce the risk of contamination of surface runoff. Hence a label statement restricting use if heavy rainfall is expected within 48 hours has been proposed. Restriction of use to once or twice per production season and not using azinphos-methyl at the high rates required for citrus will also minimise the risk from run-off.

3.4.5 Desirable terrestrial vegetation

Azinphos-methyl is stated to be non-phytotoxic with some russetting possible on some fruits (Tomlin, 1997). There were no phytoxicity studies presented. Effects on non-target plants are expected to be minimal.

3.4.6 Risk arising from formulation, handling and disposal

The risk from formulation of the active constituent in Australia is expected to be minimal. This is expected to be done in suitable facilities, with relevant environmental controls to limit environmental exposure. Wastewater expected to be treated before discharge to the sewer and environment. With dilution and adsorption, the environmental risks are expected to be minimal. Any spills are expected to be cleaned up and treated according to the MSDS.

3.5 CONCLUSIONS

Azinphos-methyl has a recent history of fish and other wild life kills in the US. However, this is largely from application by air to sugarcane and cotton and the lack of similar incidents in Australia likely reflects the restriction of its use to ground application to orchards at lower rates and a lower general level of use.

Azinphos-methyl degrades in natural systems by abiotic and biotic pathways, with a half-life of dissipation of 0.5 to 7 days in mesocosms studies. It degrades in laboratory soils with a half-life between 21-49 days. Data from field studies show the half-life in soil as between 5.3 to 15.5 days and there was not evidence of leaching. Azinphos-methyl is moderately bound to soil and together with the rapid degradation leaching is not expected. However, the some of the metabolites could leach.

It is rated as very highly toxic to birds, mammals, fish and aquatic invertebrates. As noted above incident reports from the US involving azinphos-methyl as the known toxicant indicate that environmental effects from its use are possible.

3.5.1 Terrestrial

Mammals were not expected to be significantly exposed to direct overspray of the chemical unless they enter an area recently sprayed. Overseas studies show that mammals in orchards could be affected, with some studies showing a number of casualties. It was concluded that

while some individuals living and feeding in orchards could be affected, there is unlikely to be significant effects on mammal populations from orchard spraying.

While the overall risk to birds appears relatively low, the risk is greater with repeated spraying, and there have been reports from overseas of adverse effects in a variety of situations, especially with multiple applications. Applications are expected to be greatly limited under IPM programs, but to ensure a risk to birds does not result from repeated/program use, use should be restricted on the label to no more than two applications a year.

The risk to bees is high if spraying occurs when they are present in the crop and foliar residues may remain highly toxic to bees for 4-13 days after application. To limit the exposure of bees to the pesticide during spraying, the crop should not be sprayed when bees are foraging and users should be warned of the risk from spray drift. To avoid exposure to residues, trees or vines should not be sprayed while they are flowering.

Effects on earthworms and soil micro-organisms are unlikely at normal field rates. There is a possible risk to soil arthropods, but there are no toxicity data for these organisms.

3.5.2 Aquatic

Aerial Application
There is currently little if any aerial application of azinphos-methyl, as this is not regarded as the normal practice for applying pesticides to orchards, but it is not prohibited on the azinphos-methyl labels. Due to the high estimated risk, based on previously assessed chemicals, it is recommended that a prohibition on aerial application of azinphos-methyl should be added to the label.

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As azinphos-methyl is currently not normally used for dormant spraying for scale, a detailed separate analysis for dormant spraying was not performed, but the hazard was shown to be significantly higher than in the full leaf case from AgDRIFT and is considered unacceptable. Therefore, as this use represents a potential hazard to aquatic invertebrates and the agricultural assessment indicates that this use is not significant, it is recommended that consideration be given to removing uses involving dormant or early season spraying from the label.

Multiple applications were considered and shown to increase the hazard, especially program spraying as it does not allow affected populations to recover. Therefore program spraying is considered to present a high risk to the aquatic environment near orchards and should be discouraged. Hence it is recommended that use be restricted to no more than two applications per production season.

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3.6 REFERENCES

ABGA (2006) Australian Blueberry Growers Association (Incorporated): Website - http://www.abga.com.au/about.htm accessed September 2006.

ABS (2005) 1329.0.55.002 - Vineyards Estimates, Australia, 2004-05. Australian Bureau of Statistics. Website - http://abs.gov.au/

ABS (2006) 7121.0 Agricultural Commodities Australia. 2004-05. Australian Bureau of Statistics. Website - http://www.abs.gov.au/

ACG (2006) Australian Citrus Growers: Website - http://www.australiancitrusgrowers.com/aspdev/industry/aus_citrus.asp accessed September 2006.

Anderson, J.P.E. (1986) Influence of Gusathion M (azinphos-methyl) on the microbial mineralization of nitrogen in soils. Bayer AG., Agricultural Chemicals Div., Report No. AJO/21586. (Unpublished)

Anonymous (1983) Ecosystem responses to alternative pesticides in the terrestrial environment a system approach. Report prepared for US EPA by Corvallis Environmental Research Lab., MSU, East Lansing. NTIS Rpt No. PB84-162726.

APAL (2006) Apple & Pear Australia Limited: Website - http://www.apal.org.au/research.htm accessed September 2006.

Atwell, S.H., and Close, C. (1976) Leaching characteristics of Guthion on aged soil. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 48466.(Unpublished)

Atwell, S. H. (1978a) Effects of Guthion on Nitrification and Denitrification in Soil. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 544833.(Unpublished)

Atwell, S. H. (1978b) Effects of Guthion on Nitrogen Fixation. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 65613. (Unpublished)

AMS (2006) Australian Macadamia Society, website http://macadamias.org/index.php?p=8 accessed September 2006.

Beavers, J. B (1989) GUTHION Technical Insecticide: A One-Generation Reproduction Study with the Bobwhite (*Colinus virginianus*). Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 98490. (Unpublished)

Bishop, C A; Ng, P; Mineau, P; Quinn, J S and Struger, J (2000). Effects of Pesticide Spraying on Chick Growth, Behavior and Parental Care in Tree Swallows (Tachycinet bicolor) Nesting in an Apple Orchard in Ontario, Canada. Environ. Toxicol. Chem. 19, , 2286-2297. Published.

Boeri, R.L. (1989a) Flow-through, acute toxicity of Guthion 2L to Sheepshead Minnows, *Cyprinodon variegatus.* Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 99204. (Unpublished)

Boeri, R.L. (1989b) Flow-through, acute toxicity of Guthion 2L to Mysids, *Mysidopsis bahia.* Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 99205. (Unpublished)

Bowmer, K.H., Korth, W., Scott, A., McKorkelle, G. and Thomas, M. (1998) Pesticide

monitoring in the irrigation areas of south-western NSW, 1990-1995. CSIRO Land and Water, Technical Report 17/98, 112p.

Burgess, N M; Hunt, K A; Bishop, C and Weseloh, D V (1999). Cholinesterase inhibition in tree swallows (*Tachycinet bicolor*) and Eastern bluebirds (*Sialias sialis*) exposed to organophosphorus insecticide in apple orchards in Ontario, Canada. *Environ. Toxicol. Chem.* **18,** , 708-716. Published.

Burns. L.A., Allen, B.W., Barber. M.C., Bird, S.L., Cheplick, J.M., Fendley, M.J., Hartell, D.R., Kittner, C.A., Mayer, F.L., Suarez, L.A. and Wooten, S.E. (1992) Pesticide and Industrial Chemical Risk Analysis and Hazard Assessment – Version 3.0. US EPA, Environmental Research Laboratory, Athens, GA

Bushway, R.L., Litten, W., Porter, K. and Wertam, J. (1982) A survey of azinphos-methyl and azinphos-methyl oxon in water and blueberry samples from Hancock and Washington counties of Maine. *Bull. Env. Contam. & Toxicol*., 28, 341-347. Published

Carlisle, J.C. (1985) Toxicity of Azinphos-Methyl (Guthion technical) to rainbow trout early life stages. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 578. (Unpublished)

Carlisle, J.C. (1984a) Acute Toxicity of Azinphos-Methyl (Guthion technical) to rainbow trout. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 491. (Unpublished)

Carlisle, J.C. (1984b) Chronic Toxicity of ^{14}C-Guthion to *Daphnia magna* under flow-through test conditions. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 558. (Unpublished)

Chukwudebe, A., March, R.B., Othman, M. and Fukuto, T.R. (1989) Formation of trialkyl phosphorothioate esters from organophosphorus insecticides after exposure to either ultraviolet light or sunlight *J. Agric. Food Chem*., 37, 539-545. Published

Coody, P.N. (1991) Field measurement of Azinphos-methyl fate and runoff from a cotton field in Georgia. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 101333 (**Not provided). (Unpublished)

Coody, P.N. (1992) Field measurement of Azinphos-methyl fate and runoff from a cotton field in Benoit, Mississippi. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 102619. (Unpublished)

Coombs, R. (ed.) (1995) Horticulture Australia: the complete reference of the Australian Horticulture Industry, Morescope Publishing P/L, Hawthorn East, Victoria, Australia. Published

Cope, H and Forsyth, J (1995). "Horticultural Australian." National Farmers' Federation/Morescope Publishing Pty Ltd, Camberwell, Vic. (1995), pp 333-340

Dabrowski JM and Schulz R (2003) Predicted and measured levels of azinphosmethyl in the Lourens River, South Africa: Comparison of runoff and spraydrift. Environ Toxicol Chem. 22:494–500. Published

Davidson, D (1992). *A Guide to Growing Winegrapes in Australia*. Dianne Davidson Publishing Services Pty Ltd, Leabrook, South Australia. Published

Davies, L.G. (1987) Report on a laboratory investigation into the toxicity of HWG 1608 to honey bees (*Apis mellifera).* Mobay Chemical Corp., Agricultural Chemicals Div.,

Report No. 8701. (Unpublished)

Dionne, E. (1991) GUTHION - The chronic toxicity to the Sheepshead Minnow *(Cyprinodon variegatus)* Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 101297. (Unpublished)

Dogerloh, M. (1995) Gusathion M WP 25 - Acute toxicity (96 hours) to rainbow trout (Oncorhynchus mykiss) in a static test. Bayer AG., Agricultural Chemicals Div., Report No. DOM 95057. (Unpublished)

Dogerloh, M. (1997) Gusathion M SC 200 - Acute toxicity (96 hours) to rainbow trout (Oncorhynchus mykiss) in a static test. Bayer AG., Agricultural Chemicals Div., Report No. DOM 96070. (Unpublished)

Dortland, R.J. (1980) Toxicological evaluation of parathion and azinphos-methyl in freshwater model ecosystems. Dept of Toxicology, Agricultural University, Centre for Agricultural Publishing and Documentation, Wageningen. Report No. 5265

Dry, P R and Smart, R E (1988). The grape growing regions of Australia. *In* Coombe, B G and Dry, P R (Eds.) *Viticulture. Volume 1: Resources in Australia*. Australian Industrial Publishers, Adelaide. Chapter 2, pp 37-60. Published

Edge, W D, Carey, R L, Wolff, J O, Ganio, L M and Manning, T (1996). Effects of Guthion 2S on *Microtus canicaudus*: a risk assessment validation. *Journal of Applied Ecology* **33,** 269-278. Published

Engelhardt, G., Ziegler, W., Wallnofer, P.R., Oehlmann, L. and Wagner, K. (1981) Degradation of azinphos-methyl by isolated *Pseudomonas fluorescens* DSM 1976. *FEMS Microbiology Letters*, 11, 165-169. Published

Engelhardt, G., Oehlmann, L., Wagner, K, Wallnofer, P.R., and Wiedemann, M. (1984) Degradation of the insecticide azinphos-methyl in soil and by isolated soil bacteria. *J. Ag. & Food Chem*., 32, 102-108.

Fletcher, J S; Nellessen, J E and Pfleeger, T G (1994). Literature Review and Evaluation of the EPA Food-Chain (Kenaga) Nomogram, An Instrument for Estimating Pesticide Residues on Plants. *Environ. Toxicol. Chem.* 1994, **13**, 1383-1391. Published.

Flint, D.R., Church, D.D, Shaw, H.R. and Armour, J. (1970) Soil runoff, leaching and adsorption, and water stability studies with Guthion. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 97434. (Unpublished)

Frank, R. and Klöpffer, W. (1985) Untitled, UBA Research Report No. 10602046.

Fritz, R. (1988) Leaching behaviour of azinphos-methyl aged in soil. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. PF 3099. (Unpublished)

Ganzelmeier, H., Rautmann, D., Spangenberg, R., Streloke, M., Herrmann, M., Wenzelburger, H-J. and Walter H-F. (1995) Studies on the spray drift of plant protection products – Results of a test program carried out throughout the Federal Republic of Germany. Mitteilungen aus der Biologischen Bundestalt fur Land- und Forstwirtschaft. Report 305. Blackwell Scientific, Berlin. Published

Giddings, J.M. (1989) Guthion 35 WP (Azinphos-methyl): Mesocosm Test for Environmental Fate and Ecological Effects. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 99633. (Unpublished)

Granovsky, A V., Ma, L., Ricaud, R., Bengtson, R L. and Selim, H M (1996). Fate of Azinophos methyl is a sugar cane Field: Distributions in Canopy, Soil and Runoff.

J. Environ. Qual. **25** 1210-1216. Published.

Grau, R. (1985a) Bird toxicity, oral: Canary (*Serinus canarius*), males and females. Bayer AG., Agricultural Chemicals Div., Report No. VK-248. (Unpublished)

Grau, R. (1985b) Bird toxicity, oral: Japanese quail (Coturinix cotumix japonica), males and females. Bayer AG., Agricultural Chemicals Div., Report No. VW-101. (Unpublished)

Grau, R. (1989) Toxicity of Gusathion M tech. to rainbow trout *(Salmo gairdneri)* with prolonged exposure (21 days). Bayer AG., Agricultural Chemicals Div., Report No. FF-234. (Unpublished)

Grimes, J. and Jaber M. (1988) Azinphos-methyl technical: the acute oral toxicity with the bobwhite quail. Wildlife International Lab., Maryland, USA. Makhteshim-Agan (America) Inc., Lab. Report No. 234-01. (Unpublished)

Gronberg, R.R. (1989) Photolysis of azinphos-methyl on soil - Abbreviated Study.

Gronberg, R.R., Pollock, R.J., and Wargo, J. P. (1979) The metabolism of Guthion in sandy loam soil. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 68030A. (Unpublished)

Hardensen, S. and Wratten, S.D. (1996) The sensitivity of the nymph of two New Zealand damselfly species (Odonata: Zygoptera) to azinphos-methyl and carbaryl. *Australian Journal of Ecotoxicology*, 2, 55-60. Published

Heimbach, F. (1985) Growth inhibition of green algae (*Scenedesmus subspicatus*) by Azinphos-methyl (technical). Bayer AG, Agricultural Centre, Leverkusen, Report No. HBF/A110. (Unpublished)

Heimbach, F. (1986) Acute Toxicity of Azinphos-Methyl to Earthworms. Bayer AG, Agricultural Centre, Leverkusen, Report No. HBF/Rg 58. (Unpublished)

Heimbach, F. (1988) Influence of Gusathion M 200 EC on the Earthworm fauna of a grassland area. Bayer AG, Agricultural Centre, Leverkusen, Report No. HBF/RgF 12. (Unpublished)

Heimbach, F. (1989) Influence of Gusathion MS on the Reproduction Rate of *Daphnia magna*. Bayer AG, Agricultural Centre, Leverkusen, Report No. HBF/RDM22. (Unpublished)

Heimbach, F. (1990) Toxicity of Gusathion MS to Earthworms. Bayer AG, Agricultural Centre, Leverkusen, Report No. HBF/RG 121. (Unpublished)

Heimbach, F. (1995) Influence of Gusathion M 200 EC on the reproduction of Earthworms *(Eisenia fetida)*. Bayer AG, Agricultural Centre, Leverkusen, Report No. HBF/Rg 206. (Unpublished)

Heimbach, F. (1997) Acute toxicity of Azinphos-methyl SC 200 to water fleas (*Daphnia magna*). Bayer AG, Agricultural Centre, Leverkusen, Report No. HBF/DM 176. (Unpublished)

Heimbach, F. (1999a) Influence of Azinphos-methyl (tech.) on Development and Emergence of Larvae of *Chironomus riparius* in a Water Sediment-System. BAYER AG, Institute fore Environmental Biology, Germany. Report No. HBF/Ch 29 Unpublished.

Heimbach, F. (1999b) Extended laboratory study on the effects and recovery of a *Daphnia*

magna population in a water-sediment system after application of azinphos-methyl (tech.). Report No. HBF/eDm 02, Bayer AG, Crop Protection. Unpublished.

Hellpointner, E. (1994) Determination of the quantum yield and assessment of the environmental half-life of the direct photodegradation of azinphos-methyl in water. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. PF 3990. (Unpublished)

Hermann, G. (1973a) Fish Toxicity Tests, Guthion (product 1630): Red Feather. Report No. FR-17. Bayer AG, Agricultural Centre, Leverkusen, (Unpublished)

Hermann, G. (1973b) Fish Toxicity Tests, Guthion (product 1630): Guppy. Report No. FGu-1. Bayer AG, Agricultural Centre, Leverkusen, (Unpublished)

Hermann, G. (1973c) Fish Toxicity Tests, Guthion (product 1630): Goldfish. Report No. FG-88.. Bayer AG, Agricultural Centre, Leverkusen, (Unpublished)

Hermann, G. (1973d) Fish Toxicity Tests, Guthion (product 1630): Mirror Carp. Report No. FK-15.. Bayer AG, Agricultural Centre, Leverkusen, (Unpublished)

Hermann, G. (1978) Fish Toxicity (R1582): Rainbow Trout. Bayer AG, Agricultural Centre, Leverkusen, Report No. FF-52. (Unpublished)

Hermann, G. (1979) Fish Toxicity: Azinphos-methyl, Golden Orfe. Bayer AG, Agricultural Centre, Leverkusen, Report No. FO-236. (Unpublished)

Heuer, B., Yaron, B. and Birk Y. (1974) Guthion half-life in aqueous solutions and on glass surfaces, *Bull. Env. Contam. & Toxicol*., 11, 532-537. Published

Hoberg, J.R. (1990) Azinphos-methyl chronic toxicity to mysid shrimp *(Mysidopsis bahia*) under flow-through conditions. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 100104. (Unpublished)

Houseworth, L.D., Tweedy, B.G.(1972) Effect of Guthion on Microbial Populations. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 35134. Published. (Unpublished)

Iwata, Y., Düsch, M.E., Westlake, W.E. and Gunther, F.A. (1975) Behaviour of five organophosphorus pesticides in dust derived from several soil types. *Bull. Env. Contam. & Toxicol*., 14, 1-8. Published

Jerie P & McNab S (1994) The significance of nutrient movement and soil acidification in perennial horticulture. In: Nutrient and fertiliser management in perennial horticulture. Proceedings of a workshop held June 15-16, 1994, Institute of Sustainable Irrigated Agriculture, Tatura, Victoria. Occasional Paper 07/94. Land & Water Resources, Research & Development Corporation, Victorian Department of Agriculture. Published

Jobling Ph, Schneider H, McNab S & Travis K (1994) Soil acidity survey of orchards in the Goulburn Valley. In: Nutrient and fertiliser management in perennial horticulture. Proceedings of a workshop held June 15-16, 1994, Institute of Sustainable Irrigated Agriculture, Tatura, Victoria. Occasional Paper 07/94. Land & Water Resources, Research & Development Corporation, Victorian Department of Agriculture. Published

Johnson, G., Frey, L., Kruger, H. and Jaber, M. (1989) Guthion 35 % WP: An Evaluation of its effects upon wildlife on and around apple orchards in Washington State. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 99244. (Unpublished)

Kanne, Dr. (1988) Bacterial toxicity of Gusathion M 92.4 %. Bayer AG., Agricultural Chemicals Div., Report No. BA-878251. (Unpublished)

Knuth, M L; Heinis, L J and Anderson, L E (2000). Persistence and Distribution of Azinphos-methyl Following Application to Littoral Enclosure Mesocosms. Ecotoxicology and Environmental Safety, 47, 167-177. Published

Kuhr, R.L., Davis, A.C.; Bourke, L.B. (1973) Dissipation of Guthion, Sevin, Polyram, Phygon and Systox from apple orchard soil. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. M 363. (Unpublished)

Lamb, D.W., and Roney, D.J. (1976) Accumulation and persistence of residues in channel catfish exposed to Guthion-14C. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 48221. (Unpublished)

Lamb, D. W. (1980) Azinphos-methyl (Guthion) technical – acute toxicity to *Daphnia magna*. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 68678. (Unpublished)

Lenz, M.F. (1979) Soil adsorption and desorption of Guthion, Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 66848. (Unpublished)

Leoni, V., Cremisini, C., Giovinazzo, R., Puccetti, G. and Vitali, M. (1992) Activated sludge biodegradation test as a screening method to evaluate persistence of pesticides in soil. *Sci. Total Environ*., 123/124, 279-289. Published

Liang, T.T. and Lichtenstein, E.P. (1972) Effect of light, temperature, and pH on the degradation of azinphos-methyl. *J. Econ. Entomology*, 65, 315-321. Published

Liang, T.T. and Lichtenstein, E.P. (1976) Effect of soils and leaf surfaces on the photodecomposition of ^{14}C-azinphos-methyl. *J. Agric. Food Chem*., 24, 1205-1210. Published

Lin, J.C., (1995) Guthion Use on Almonds: an Aquatic Exposure Assessment with Consideration of Mitigation Measures. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. M 106930. (Unpublished)

Matthews GA (1992) Pesticide application methods. 2nd edition. Longman Scientific and Technical, Essex, England.

Martin, M. J. S., and Camazano, M. S. (1984) Aspects of the adsorption of azinphos-methyl by smectites. *J. Agric. Food Chem*., 32, 720-725. Published

Matz, A C, Bennett, R S and Landis, W G (1998). Effects of Azinphos-methyl on Northern Bobwhite: A Comparison of Laboratory and Field Results. *Environ. Toxicol. Chem.* 1998, **17**, 1364-1370. Published.

Mensink BJWG, Montforts M, Wijkhuizen-Maslankiewicz L, Tibosch H & Linders JBHJ (1995) Manual for summarising and evaluating the environmental aspects of pesticides. Report No. 679101022. National Institute of Public Health and the Environment, The Netherlands. Published

Meyers, S.M. and J. O. Wolff. 1994. Comparative toxicity of azinphos-methyl to house mice, laboratory mice, deer mice, and gray-tailed voles. *Environ. Contam. Toxicity*, **26**, 478-482. Published. Not reviewed by DEH.

Minor, R.G., and Strankowski K.J. (1978) Effects of Guthion on Isolated Soil Microorganisms. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 66401. (Unpublished)

Minor, R.G., and Delphia, L.M. (1980) Effect of Guthion on Asymbiotic Nitrogen Fixation. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 69083. (Unpublished)

Mitchelmore N & Morenos N (1995) Pome fruit: pears. In: Coombs B ed, Horticulture Australia: the complete reference of the Australian horticultural industry. Morescope Publishing Pty Ltd, Hawthorn East, Victoria. pp.313-316. Published

Moll, M (1999). Effects of Gusathion M WP 25 on the Parasitoid *Aphidius rhopalosiphi* (Hymenoptera, Aphidiidae) Extended Laboratory Test-Dose Response Test. Institut fur Biologische Analytik und Consulting IBACON GmbH, Rossdorf, Germany. Proj. 6750002. Owner: BAYER AG, Monheim Germany. (Unpublished)

Morenos N (1995) Pome fruit: apples. In: Coombs B ed, Horticulture Australia: the complete reference of the Australian horticultural industry. Morescope Publishing Pty Ltd, Hawthorn East, Victoria. pp. 305-309. Published

Morgan, J.G. (1987a) The aqueous photolysis of GUTHION-phenyl-UL-^{14}C. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 94709(Unpublished)

Morgan, J.G. (1987b) The photodecomposition of GUTHION-phenyl-UL-^{14}C on soil. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. NM 94708 (Unpublished).

Motoyama, N., Rock, G.C. and Dauterman, W.C. (1970) Studies on the mechanism of azinphos- methyl resistance in the predacious mite, *Neoseiulus (T.) fallacis* (Family: Phytoseiidae). *Pesticide Biochemistry and Physiology*, 1, 205-215. Published

Mount, D. R., Bergman, H., and Bobbit, J. (1988) Guthion Technical: Subacute Dietary LC_{50} to Deer Mice. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 98333. (Unpublished)

Muschal, M. (1997) Central & North West Regions Water Quality Program - 1996/97 Report on Pesticide Monitoring. Department of Land & Water Conservation (NSW), Report No. CNR97.063. Published

Muschal, M. (1998) Central & North West Regions Water Quality Program - 1997/98 Report on Pesticide Monitoring. Department of Land & Water Conservation (NSW), Report No. CNR98.038. Published

Nebeker, A.V., Schuytema, G.S., Griffis, W.L. and Cataldo, A. (1998) Impact of Guthion on survival and growth of the frog *Pseudacris regilla* and the salamanders *Ambystoma gracile* and *Ambystoma maculatum*. *Arch. Environ. Contam. Toxicol*., 35, 48-51. Published

Nelson, D.L. (1978) Acute toxicity of Guthion 2 S to Bluegill and Rainbow trout. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 66046.(Unpublished)

QDPI (2006) World production and marketing, Issue 9. Queensland Department of Primary Industries, Website - http://www2.dpi.qld.gov.au/lychee/14313.html accessed September 2006.

Rautmann D, Streloke, M, and Winkler, R (2001). New basic drift values in the authorisation procedure for plant protection products. In Forster, R., Streloke, M. Workshop on Risk Assessment and Risk Mitigation Measures in the Context of the Authorization of Plant Protection Products (WORMM). Mitt. Biol. Bundesanst. Land-Forstwirtsch. Berlin-Dahlem, Heft 383.

Read, D.C. (1976) Soil pest management as influenced by method of application of

insecticides. *Proc. Annual Meeting – Agric. Pestic. Soc*., 22, 37-42. Published

Red, L., Nutter, W.L., Bush, P.B., Neary, D.G., and Taylor, J.W. (1984) Progress report: Computer simulation of pesticide runoff - Erambert, Ouachita and Stuart seed orchards. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 88973. (Unpublished)

Reduker, S., Uchrin, C.G., and Winnett, G. (1988) Characteristics of the sorption of chlorothalonil and azinphos-methyl to a soil from a commercial cranberry bog. *Bull. Env. Contam. & Toxicol*., 41, 633-641. Published

Reus, J, Lenndertse, C, Bockstaller, C, Fomsgaard, I, Gutsche, V, Lewis, K, Nilsson, C, Pussemier, L, Trevisan, M, van der Werf, H, Alfarroba, F, Bluemel, S, Isart, J, McGrath, D and Seppaelae, T (1999) Comparing environmental risk indicators for pesticides. Results of the European CAPER Project, CLM 426. Centre for Agriculture and Environment, Utrecht, The Netherlands. Published

Salyani, M and Cromwell, R P (1992). Spray Drift from Ground and Aerial Applications. *Transactions of the ASAE* [American Society of Agricultural Engineers], 1992, **35,** 1113-1120. Published

Schafer, H., and Borchers, H. (1995) Predicted environmental concentration of azinphos-methyl in ground water recharge based on the calculation of PELMO. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. M 9367.(Unpublished)

Schmuck, R. (1997) Acute Oral LD50 of Gusathion M SC 200 to Northern Bobwhite Quail. Bayer AG, Agricultural Centre, Leverkusen, Report No. SXR/VB 60 (Unpublished)

Schopp, A. (1985) Results from laboratory and field testing on the influence of different fungicides and insecticides on predatory mites. Bayer AG, Agricultural Centre, Leverkusen, Report No. N176. (Unpublished)

Schulz, K.R., Lichtenstein, E.P., Liang, T.T., and Fuhremann, T.W. (1970) Persistence and degradation of azinphos-methyl in soils, as affected by formulation and mode of application. *J. Econ. Entomology*, 63, 432-438. Published

Schulz, R and Peall, SKC (2001) Effectiveness of a constructed wetland for retention of nonpoint-source pesticide pollution in the Lourens River Catchment, South Africa. Environ Sci Technol. 35:422–426. Published

Schulz, R, Thiere, G and Dabrowski, JM (2002) A combined microcosm and field approach to evaluate the aquatic toxicity of azinphosmethyl to stream communities. Environmental Toxicology and Chemistry 21(10):. 2172–2178. Published

Schulz, R, Hahn, C, Bennett, ER, Dabrowski, JM, Thiere, G, and Peall SKC (2003) Fate and effects of azinphos-methyl in a flow-through wetland in South Africa. Environ. Sci. Technol. 37: 2139–2144. Published

Sheeley, D., Dingledine, J., Palmer, D.A., Krueger, H. and Jaber, M. (1989) Guthion 35 % WP: An evaluation of its effects upon wildlife on and around apple orchards in Michigan. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. M 99615. (Unpublished)

Sierszen, M E and Lozano, S J (1998). Zooplankton population and Community responses to the pesticide Azinphos-methyl in Freshwater Littoral Enclosures. *Environ. Toxicol. Chem* **17,** 907-914. Published.

Smith, S., Reagan, T E., Flynn, J L. and Wills, G H (1983). Azinphosmethyl and Fenvalerate

Runoff from a Sugarcane-Insect IPM System. *J. Environ. Qual.* **12**, 534-537. Published

Staiff, D.C., Corner, S.W., Armstrong, J.F. and Wolfe, H.R. (1975) Persistence of azinphos-methyl in soil. *Bull. Env. Contam. & Toxicol*., 13, 362-368. Published

Stegh, R. and Wilmes. R. (1982) Light-induced degradation of pesticides on silica gel as a model system for photodegradation on soil. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. PF 1666. (Unpublished)

Stubblefield, W.A. (1987) GUTHION (Technical Grade) - Acute LD50 to Bobwhite Quail. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 878. (Unpublished)

Surprenant, D. C. (1987a) Acute Toxicity of Guthion 50 WP to Daphnids, *Daphnia magna*, under flow- through conditions. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 925. (Unpublished)

Surprenant, D. C. (1987b) Acute Toxicity of technical grade Azinphos-methyl (trade name Guthion) to eastern oysters (*Crassostrea virginica*) under flow-through conditions. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 95074. (Unpublished)

Surprenant, D. C. (1988a) The toxicity of technical grade azinphos-methyl (trade name Guthion) to rainbow trout *(Salmo gairdneri)* embryos and larvae. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 95662. (Unpublished)

Surprenant, D. C. (1988b) Acute Toxicity of technical grade Azinphos-methyl (trade name Guthion) to mysid shrimp *(Mysidopsis bahia)* under flow-through conditions. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 95003. (Unpublished)

Surprenant, D. C. (1989a) Acute Toxicity of Azinphos-methyl to sheepshead minnow *(Cyprinodon variegatus)* under static conditions. Makhteshim-Agan (Australia) P/L., Report No. R-4937. (Unpublished)

Surprenant, D. C. (1989b) Acute Toxicity of Azinphos-methyl to mysid shrimp *(Mysidopsis bahia)* under static conditions. Makhteshim-Agan (Australia) P/L., Report No. R-4936. (Unpublished)

Surprenant, D. C. (1989c) Acute Toxicity of Azinphos-methyl to embryos-larvae of the quahog clam *(Mercenaria mercenaria)*. Makhteshim-Agan (Australia) P/L., Report No. R-4938. (Unpublished)

Tanner, D K and Knuth, M L (1995). Effects of Azinphos-methyl on the Reproductive Success of the Blue gill Sunfish, *Lepomis macrochirus*, in Littoral Enclosures. *Ecotoxicol. and Environmental Safety*, **32**, 184-193. Published

Taylor BK, Emmett RW, Jamieson G, Leamon KC, Peggie ID & Thompson WK (1990) Fruit crops. In: Reid RL ed, The manual of Australian agriculture, fifth edition. Butterworths Pty Limited, Sydney, pp 151-202. Published

Thiere, G and Schulz, R (2004) Runoff simulation with particle-associated azinphosmethyl in multispecies stream microcosms: implications for the field. Environmental Toxicology and Chemistry: Vol. 23(8): 1984–1990. Published

Thompson, H M and Hunt, L V (1999). Extrapolating from Honeybees to Bumblebees in Pesticide Risk Assessment. *Ecotoxicilogy*, **8:3**, 147-166. Published.

Thornton, J.S., Hurley, LB., and Obrist, J.J. (1976) Soil thin-layer mobility of twenty four pesticides chemicals. Mobay Chemical Corp., Agricultural Chemicals Div., Report

No. MR 51016. (Unpublished)

Toll, P.A. (1988) Effects of Technical GUTHION on Mallard Duck Reproduction. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. 98328.(Unpublished)

Toll, P.A. (1993) Monitoring stream water for Azinphos-methyl applied to sugarcane fields in Louisiana. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 106223. (Unpublished)

Tomlin, C. D. S. (ed) (1997) The Pesticide Manual, British Crop Protection Council, Surrey, UK. Published

UBA, (1990) Test Guideline - The Phototransformation of Chemicals in Water – Part A: Direct Phototransformation. UBA, Saphir Verlag, Ribesbuttel. (in German)

Urban DJ & Cook NJ (1986) Hazard Evaluation Division Standard Evaluation Procedure: Ecological risk assessment. EPA 540/9-85-001. Office of Pesticide Programs, United States Environmental Protection Agency, Washington, D.C. Published

US EPA (1982). Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate. EPA-540/9-82-021, § 162-1

US EPA (1997). A user's guide for AgDRIFT 1.0: a tiered approach for the assessment of spray drift of pesticides (8th draft). Spray Drift Task Force Modelling Subcommittee, Version 1.05.

US EPA (1999) At US EPA Website: http://www.epa.gov/pesticides/op/azinphos/azm_01.pdf

Wang, G; Wolff, J O and Edge, W D (1999). Gray-tailed voles do not move to Avoid Exposure to the Insecticide Guthion 2S. *Environmental Toxicology and Chemistry*, **18**, 1824-1828. Published

Wagner, K., (1974-79) Pesticide residues in the leachate - Active ingredient: Azinphos-methyl / Gusathion NIS (E 1582 + E 158) Spritzpulver Soil types: Sand (Standard soils: 2.1 and 2.2) and Sandy loam (Standard soil: 2.3). Bayer Leverkusen., Agrochemicals Div., Report Nos. RR 4219B/1/74-RR 4306/79.(Unpublished)

Wagner, K., Jozefowski, P., and Oehlmann, L. (1982) Metabolism of azinphos-methyl (Guthion) in the soil. Bayer Leverkusen., Agrochemicals Div., Report No. RA 221/82A. (Unpublished)

Wieneke, J. and Steffens, W. (1975) Degradation of 14C-labelled azinphos on glass plates as compared to the metabolism on plant leaves. *Environ. Qual. & Safety - Conference on Pesticides- Supp III.* 544-548. Published

Wilkes, L.C., Wargo, L.P. and Gronberg, R.R . (1979a) Dissipation of GUTHION in buffered aqueous solution. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR67983. (Unpublished)

Wilkes, L.C., Wargo, L.P. and Gronberg, R.R. (1979b) Photodegradation of GUTHION in aqueous solution. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR67980A. (Unpublished)

Wilmes, R (1982a) Properties of pesticides in water. Active ingredient: Azinphos-methyl (Guthion). Mobay Chemical Corp., Agricultural Chemicals Div., Report No. M1039. (Unpublished)

Wilmes, R (1982b) Guthion Preliminary light stability. Mobay Chemical Corp., Agricultural

Chemicals Div., Report No. M1059. (Unpublished)

Yaron, B., Bielorai, H. and Kliger, L. (1974) Fate of insecticides in an irrigated field: Azinphos-methyl and tetradifon cases. *J. Environ. Quality*, 3, 413-417. Published

Zepp, R.G. and Cline, D.M. (1977) Rates of direct photolysis in aquatic environment. *Environmental Science and Technology*, 11, 359ff. Published

Ziegler, D.A. and Hallenbeck, S.A., (1987) Adsorption of Guthion to silt loam, sandy loam, sand, and clay loam. Mobay Chemical Corp., Agricultural Chemicals Div., Report No. MR 95084. (Unpublished)

Zoebelein, G. (1984) Effects of Gusathion M 25 WP on the predatory mite *Phytoseilus persimilis.* Bayer AG, Institute for Applied Zoology, Leverkusen, Report No. Zoe/Pp 6/84. (Unpublished)

Back to Review of Azinphos-Methyl