Section 5

OCCUPATIONAL HEALTH AND SAFETY ASSESSMENT

1. INTRODUCTION

The sources of information Worksafe Australia used in this review include industry registrants, NRA Performance Questionnaires, Agricultural Assessment, Toxicological Assessment, Environmental Assessment and the published literature.

2. TOXICOLOGY

2.1 Toxic end points

A detailed review of mammalian toxicology and toxicokinetic/metabolism data of atrazine is available in the Toxicology Assessment.

Atrazine is of low oral and dermal toxicity and very low inhalation toxicity. It is a slight eye irritant in rabbits and a skin sensitiser in guinea pigs but not in humans. It is not a skin irritant in rats or rabbits.

Repeat dose studies of atrazine in animals showed reduced bodyweight and food intake in males and females and an earlier onset and increased incidence of mammary tumours in females. There are substantial physiological and endocrine differences between rats and humans. The toxicology assessment concluded that "it would appear that the atrazine response in Sprague Dawley (SD) rats is not an appropriate surrogate for the assessment of human risk for mammary tumour development".

Selection of the most appropriate lowest no-observable-effect-level (NOEL) for the occupational health and safety risk assessment, considered short-term repeat-dose, subchronic, chronic, reproductive and developmental studies. The lowest NOEL is 0.5 mg/kg bw/day, based on the statistically significant increase in mammary tumour incidence in female rats at the next dose (2.8 - 4.5 mg/kg bw/d) in a two-year rat dietary study. This NOEL is used to set the ADI.

In selecting a NOEL of most relevance to occupational exposure, the occupational health and safety (OHS) report has considered the nature of the effects observed in chronic studies as well as the seasonal and limited frequency of use of atrazine by Australian end users. Taking this into account, the NOEL of 4.1 mg/kg bw/day, based on the earlier onset of mammary tumours in a one-year female rat dietary study, is considered the most appropriate for the occupational health risk assessment.

Genotoxicity of atrazine technical was studied in a variety of tests such as gene mutation assays, chromosomal effects assays, other genotoxic effects and cell transformation assays. The toxicology assessment concludes that atrazine does not pose a mutagenic hazard.

A study of the immunotoxicology of the atrazine AAtrex formulation in female mice following sublethal single doses, conducted by Fournier *et al*. (1992), was summarised in the toxicology assessment. The study concluded that there was no evidence of direct atrazine related effects on the mouse immune system. However, the authors could not discount the possibility of effects after long term exposure.

The toxicology assessment reported on several *in vitro* and *in vivo* studies on dermal absorption of atrazine in rats and humans. In a recent study, Chengelis (1994) studied *in vivo* percutaneous absorption in the rat using the 4L formulation. The 4L formulation is composed of approximately 45% technical atrazine, 5% ethylene glycol, antifoaming and preservatives at 0.1% each, small amounts of other ingredients and water at 47%. As such it is similar to formulation details provided for Ciba-Geigy Flowable Gesaprim 500 FW Liquid Herbicide (Australian formulation), Nufarm Limited Nufarm Flowable Nu-Trazine Liquid Herbicide and Davison Industries Davison Atrazine 500 Flowable Herbicide. Doses tested were 9.13 $\mu g/cm^2$, 94.3 $\mu g/cm^2$ and 936 $\mu g/cm^2$. After 24 hours exposure and allowing absorption for a further 72 hours, most radioactivity was present in the skin wash (61.06 - 90.8%). Combined excretion in the urine and faeces was 21.23%, 22.52% and 4.89%, from the lowest to the highest dose, mostly in the urine. Skin residue was 4.90%, 2.73% and 2.6%, from the lowest to the highest dose. A comparison of rat and human *in vitro* absorption using the Gesaprim 500FW formulation (Jack, 1994) showed at 48 hours, a higher penetration through rat than human epidermis. The species difference was 7-fold at the lowest dose of 0.4 mg/cm^2 and 2-fold at higher doses. The value(s) used in the risk assessment are derived from the human *in vivo* percutaneous absorption study of Hui *et al*. (1995). Estimated absorption is the average radio-label excreted in urine and faeces of 4 or 6 volunteers per dose at 168 hours (including a surface wash at 24 hours) after application of ^{14}C atrazine. The labelled atrazine was added to a blank 4L formulation and applied to the forearm at 6.7 $\mu g/cm^2$ and 74 $\mu g/cm^2$. Excretion values of 5.63% and 1.18% were achieved at the low dose and high dose, respectively. In the risk assessment, the value used will be that most closely approximating the anticipated atrazine skin contamination for the atrazine users in the study concerned. The toxic end points relevant to occupational health and safety are listed in Table 1.

Table 1: The toxic end points, percutaneous absorption and NOEL for OHS assessment of atrazine

	Atrazine
Oral LD_{50} (mg/kg)	1869 (rat)
Dermal LD_{50} (mg/kg)	>3100 (rat)
Inhalation LC_{50} (mg/m^3)	>710 (rat, 1h, mist, one study) > 5000 (rats, 4h, dust, three studies) (no deaths)
Eye irritation	none or only a slight irritant (rabbit)
Skin irritation	non irritant (rat, rabbit or human)
Skin sensitisation	negative in humans; positive in guinea pigs (2/3 studies)
Percutaneous absorption (%)	5.63% or 1.18% (dose-dependent) (human)
NOEL for OHS assessment (oral, mg/kg bw/day)	4.1

Kinetic and percutaneous absorption studies in humans provide information on urinary metabolite excretion of relevance to biological monitoring. Kinetic studies indicate that small amounts of atrazine metabolites are excreted in the urine, but free atrazine is not found. Following single oral doses of 0.1 mg/kg in human volunteers, the three metabolites desethylatrazine (G-30033, 2-amino-4-chloro-6-isopropylamino-s-triazine), desisopropylatrazine (2-amino-4-chloro-6-ethylamino -triazine) and diaminochlorotriazine (G-28273, 2, 4-diamino-6-chloro-s-triazine) were detected at 5.4, 1.4 and 7.7%, respectively over 168 hours. Small amounts of atrazine were recovered in the blood, but 85% of the dose was unaccountable. This contrasts with findings in rats where atrazine undergoes almost complete absorption from the gastrointestinal tract after oral administration and is rapidly eliminated, predominantly in the urine.

In the human percutaneous absorption study described above, desethylatrazine, diaminochlorotriazine and atrazine mercapturate (trace), were detected in the urine. Levels were difficult to quantify as they were so low. Breckenridge (1996) in the Ciba-Geigy submission to USEPA special review states that G-30033 was 3.94% and G-28273 was 5.94% of the total radioactivity in the urine. Atrazine and desisopropylatrazine were not detected. In biological monitoring studies of workers exposed to atrazine, diaminochlorotriazine, desisopropylated and desethylated atrazine and unchanged atrazine have been detected (see Section 3.3). Catenacci *et al*. (1993) suggested diaminochlorotriazine atrazine was the main urinary metabolite in man following occupational exposure. Loosli (1994) recommended it for biological monitoring. Recent Ciba-Geigy studies are available that assist in the selection of appropriate atrazine metabolites for biological monitoring. In the seven days following oral dosing of ^{14}C-atrazine in Rhesus monkeys (three doses, 1, 10 and 100 mg/animal), most label is excreted in the urine (56%) and the rest in the faeces (27%) (Hui *et al*., 1996a). As with intravenous dosing (Hui *et al*., 1996b), most urinary metabolites are in the form of chlorotriazine residues. After oral dosing, chlorotriazine residues accounted for 8.46%, 14.43% and 10.52% (average of 11.14%) of the administered dose in the low-, mid- and high-dose groups, respectively, over the first 24 hours. G-28273 (6-chloro-1,3,5-triazine-2,4-diamine) and G-30033 (6-chloro-N-(1-methyl ethyl- 1,3,5-triazine-2,4-diamine) were the major chlorotriazine metabolites detected at any time or dose. Unchanged atrazine was found in a small number of samples. Atrazine mercapturate accounted for <1% of label in any one urine sample.

The authors concluded that total urinary chlorotriazine residues would be the best biomarker for atrazine exposure, given their predictable proportion in urine over a range of internal doses. Urinary excretion of these residues was subsequently used by Selman and Rosenheck (1996) in an assessment of exposure and internal dose in a Ciba-Geigy worker exposure study (Honeycutt *et al*., 1996).

Lucas *et al*. (1993) focussed attention on the urinary mercapturic acid metabolite of atrazine in analysis following occupational exposure. Atrazine mercapturate can be detected by enzyme-immunoassay (EIA) techniques using commercial test kits (EnviroGard Triazine Plate Kit, Millipore Corporation) (Brady, 1995) or assays developed in-house (Gilman *et al*., 1996, UC Davis, reported in Hui *et al*., 1996). Some unidentified cross-reactivity occurs in atrazine mercapturate EIA, but the method is believed to be a useful tool in identifying atrazine exposure.

Exposure of individuals to mixtures of chemicals, including atrazine, by contamination of ground water used for drinking water supplies, is causing concern in cropping areas of the mid-west USA. The concerns relate primarily to public exposure, but the implications for workers using a range of chemicals as well as ingesting mixtures via drinking water are unclear. Some toxicological testing of mixtures has occurred. The toxicological assessment reported on rat teratology studies with mixtures of pesticides, including atrazine and nitrogenous fertiliser (ammonium nitrate), at concentrations representative of 1-, 10- and 100-fold underground water concentrations. There were no significant effects on any parameters measured even at the 100 fold levels.

A study using a mixture of atrazine and linuron (found in groundwater supplies in the mid west USA, found that atrazine and linuron together induced greater chromosomal damage in human lymphocytes in vitro, than either agent alone (Roloff *et al*., 1992).

2.2 Summary of human health effects

2.2.1 Topical effects

Patch tests of 50 human volunteers with an 80W atrazine formulation (0.5% in water) did not produce irritation or contact sensitivity in humans during the 15 consecutive exposures or upon challenge 14 days after the last exposure.

Some literature reports indicate that atrazine may on occasion be a sensitiser in humans. The US Department of Health and Human Services and US

Department of Labor *Occupational Safety and Health Guideline For Atrazine (1992)* cites a 1982 report of Hayes where a farmer spraying an atrazine formulation developed severe contact dermatitis and was later shown to be sensitised to atrazine by patch testing.

English *et al*. (1986) described a weed control operator with a 6-month history of dermatitis. The current herbicide contained aminotriazole (9.5%) and atrazine (19%). Patch testing with the herbicide was positive and subsequent tests with aminotriazole (98% pure) and atrazine (99.8% pure) gave a strong reaction to aminotriazole and a very weak reaction to atrazine. The 20 controls were negative to both actives in this study.

Stevens & Sumner (1991) report on one case of slight eye irritation following accidental splashing with an atrazine formulation released under pressure from a clogged vent hose and another case of a farmer developing a rash and swelling around the eyes following use of an atrazine wettable powder.

A report by The Generics Group (1991) cites a published study of a single case of contact dermatitis in a farm worker (Schlicher & Beat, 1972), but comments that exposure to other chemicals was not controlled in this study. Stevens & Sumner (1991) also comment on this study. They note that the farmer had a history of dermatitis from another chemical but were in no doubt that the high degree of exposure to the atrazine formulation, with a strongly positive patch test result, was responsible for this episode.

2.2.2 Epidemiological studies

2.2.2.1 Environmental contamination

A review of studies investigating atrazine and birth defects was undertaken for Ciba-Geigy Ltd by Johnson (1993). The issue of a confounding between atrazine and nitrogenous fertiliser residues in groundwater and birth defects was discussed but there was insufficient data to reach a meaningful conclusion on this.

2.2.2.2 Manufacturing workers

Six reports on atrazine production workers and health effects are available. Two of these (Cronan, 1988; Chartres, 1989) are internal Ciba-Geigy correspondence. One epidemiological study was conducted at the Ciba-Geigy Schweizerhalle plant by Gass and Stalder (1990/1993). Three epidemiological studies were conducted at Ciba-Geigy production plants in Louisiana and Alabama, USA by the University of Alabama (Delzell *et al*., 1989; Sathiakumar *et al*., 1992; Delzell & Sathiakumar, 1992). Part of the assessed information was provided by Ciba-Geigy Australia Limited. A brief summary of the findings is given below.

The correspondence from medical officers, Cronan (1988) and Charters (1989), certified that no cases of skin irritation or other illness due to atrazine had been seen in Ciba-Geigy Corporation plants at St Gabriel and McIntosh, USA.

Delzell *et al*. (1989) conducted a follow-up study of Ciba-Geigy triazine herbicide manufacturing workers in Louisiana. Overall mortality of workers was lower than the general population and cancer rates were normal. In the toxicological assessment, it was noted that the limited exposure information and the small number of deaths limited the capacity of the study to determine cause and effect.

Sathiakumar *et al*. (1992) and Delzell and Sathiakumar (1992) studied epidemiological data from agricultural chemical production workers at Ciba-Geigy Corporation plants in St Gabriel and McIntosh. The studies showed an increase in observed-over-expected levels of Non-Hodgkins lymphoma (NHL) and soft tissue sarcoma. Some affected workers had been employed for short periods and for others specific exposure could not always be quantified. The toxicology assessment concluded that the findings were based on small numbers and a causal relationship between soft tissue sarcoma and employment at the McIntosh plant could not be established or discounted.

Stalder (1993) commented on the findings of the Gass (1990) epidemiological study conducted by Ciba-Geigy at the Schweizerhalle plant. He concluded that there was no indication of a causal relationship between atrazine and gastritis, diagnosed in a higher number of workers since 1975 but independent of duration of atrazine exposure.

2.2.2.3 End users

Four published epidemiological studies concerning the use of atrazine by agricultural workers are available. Three studies investigate health effects in male farmers in the mid-west USA (Hoar *et al*., 1986; Brown *et al*., 1990; Hoar Zahn *et al*., 1993) and one looks at health effects in women in Italy with some exposure to triazine herbicides (Donna *et al*., 1989). A brief summary of the findings is given below. Additional information was provided by Ciba-Geigy Australia Limited and is included where appropriate.

Hoar *et al*. (1986) investigated white male Kansas residents aged 21 or older from 1982 to 1986. They reported that NHL was associated with farm herbicide use and the relative risk of NHL increased significantly with duration or frequency of herbicide use. The conclusion was based on the comparison of exposed farmers with non-farmers. However, no difference was found in comparisons with unexposed farmers.

Donna *et al*. (1989) compared Italian women with primary malignant epithelial tumours of the ovary (1980-1985) with randomly selected referents, for atrazine exposure and reproductive risk factors. Subjects in the study were defined as definitely exposed, possibly exposed and unexposed to triazine herbicides. Considering all subjects, the risk factor for unexposed subjects was one, and the factors for possibly exposed and definitely exposed subjects were 1.8 and 2.7, respectively. Considering agricultural workers alone, the risk factor for unexposed subjects was one, and the factors for possibly exposed and definitely exposed subjects were 2.1 and 2.8, respectively. The toxicology assessment noted that triazine exposure in this study was not quantified and other known non-reproductive factors were uncontrolled. This conclusion reflects those of others. Minder (1990) in a critique of the study, reported concerns with statistical aspects, classification of exposed women and possible confounders and biases. He concluded that the case for an association between ovarian cancer and triazine was weak, and even weaker for a casual link. A Personal Communication from Watson (1991), from the Medical Research Council in the UK, to Ciba-Geigy also pointed out concerns with the study. These related to data collection methodology, determination of exposure, statistical methods and other possible confounders. He concluded that a direct cause and effect could not be substantiated.

Brown *et al*. (1990) conducted a case-controlled study of 578 white men with leukaemia and 1245 controls living in Iowa and Minnesota. They concluded that there was no evidence of a linkage between atrazine and leukaemia in white males.

Hoar-Zahm *et al*. (1993) investigated the role of atrazine in the development of NHL in three case-referent studies conducted in four mid-western states of USA. The authors concluded that the data provided little evidence that atrazine use is associated with NHL in white males.

2.2.2.4 Conclusions from epidemiological studies

Meaningful conclusions on exposure to the combined effects of atrazine and nitrogenous fertiliser degradation products in groundwater have not been reached.

Epidemiology studies of manufacturing workers are unable to completely discount any association between atrazine exposure and human cancers.

An epidemiology study in Italian women reports a positive association for triazine herbicide exposure and ovarian tumours. This finding has been questioned because of concerns with methodology, exposure quantification, statistics and study confounders. The finding remains inconclusive. Epidemiology studies conducted in the USA provide insufficient evidence to link atrazine use and NHL or leukaemia in farm workers.

2.3 Hazard classification

Atrazine

Atrazine is included on the List of Designated Hazardous Substances (NOHSC, 1994a). The updated EU classification lists it as a class III carcinogen and class III mutagen and allocates the following risk and safety phases:

R20/22	Harmful by inhalation and if swallowed.
R36	Irritating to eyes.
R40	Possible risk of irreversible effects.
R43	May cause sensitisation by skin contact.

S2	Keep out of reach of children.
S36/S37	Wear suitable protective clothing and gloves.
S46	If swallowed, contact a doctor or Poisons Information Centre immediately and show this container or label.

End use products

End use products are hazardous substances with respect to atrazine when it is present at the cut-off concentration of $\geq$1%.

The atrazine products under review are hazardous substances.

3 OCCUPATIONAL EXPOSURE

Product labels were seen for most of the 34 registered atrazine products. Atrazine products are available as liquids (223-500 g/L atrazine), granules (forestry use only, one product, 150 g/kg atrazine), wettable powders (800-900 g/kg atrazine) and water dispersible granules (900 g/kg atrazine). Some atrazine products are mixtures with amitrole, ametryn, dicamba, hexazinone and metolachlor. The mixtures contain lower concentrations of atrazine than products containing atrazine alone.

Container sizes for liquid products include 5L, 20L, 200L and 1000L. The granular product is a 20 kg bag. The wettable powder is in 2.2 kg and 25 kg lots and the water dispersible granules are in 2.2 kg, 10 kg and 15 kg lots. Container sizes for Home Garden products include 100g, 200g and 1L packs.

3.1 Handling prior to end use

Technical grade active constituent (TGAC) atrazine is imported. The following companies formulate atrazine products in Australia: Novartis Crop Protection Australasia Limited, Crop Care Australasia Pty Ltd, Davison Industries Pty Ltd, Sipcam Pacific Australasia Pty Ltd and Macspred Pty Ltd.

Formulators are potentially exposed to both atrazine TGAC and the product(s). Transport and storage workers and retailers would only handle the packaged TGAC or products.

3.2 Use pattern of the end use products

3.2.1 Use pattern

Atrazine is a broad spectrum, residual herbicide with major agricultural uses on sorghum, saccaline (forage sorghum), lucerne, grass seed crops, lupins, fallows, maize, sweetcorn, potatoes, broom millet and sugar cane. A major emerging non-label use is on canola and one registrant reports non-registered use in vineyards. The only non-agricultural uses allowed are in the establishment of pine and eucalypt plantations and for Parthenium weed control in Queensland. Since December 1995, restrictions on atrazine have been in effect. These include maximum allowable application rates of 3.0 kg/ha/year for agricultural uses and 4.5 and 8.0 kg/ha/year (soil type-dependent) for plantation uses. Apart from the treatment of Parthenium weed in Queensland, atrazine is not registered for use in industrial and non-agricultural situations. Atrazine is also available in Home Garden Products.

Atrazine may be applied more than once per year as long as the total amount applied per hectare given above is not exceeded. It may be applied by air (fixed wing or helicopter), ground rig or by hand-directed means. Individual operators or contractors may apply atrazine products. The equipment used depends on the nature of the dispensed product, ie whether it is diluted in water or dispensed in solid form.

Atrazine product labels indicate a range in application rates per hectare, covered in detail in the NRA Atrazine Agricultural Assessment. In order to estimate exposure, the occupational health and safety report uses the following sources of information. Allowable application rates and working strength spray volumes are derived from the labels or industry submissions and routine work patterns are obtained from industry submissions or end uses via the NRA Performance Questionnaires (PQs). It is noted that certain uses will not approach the maximum application rate, for instance, established lucerne, lupins and certain fallows.

Atrazine uses - home garden

Home garden products are mixture of atrazine and amitrole. Weed control areas in the home garden include driveways, footpaths, fencelines, paved areas and tennis courts. Workers employed as gardeners or engaged in small scale maintenance of public or private areas may use home garden products. Label application rates are given as product (g) per m^2 and correspond to 2.5 and 5.0 kg atrazine /ha. Working strength solutions range from 0.03 to 0.17% atrazine. The largest package size for atrazine home garden use would enable treatment of 0.04 ha. Use would be by hand directed spraying, for instance from a knapsack or other pressure device, or watering can.

Atrazine uses - broadacre crops and sugar cane

The NRA indicates that one application is given for lucerne, maize, sweetcorn, fallow and sorghum (two if combined with fallow application). There may be up to three applications in sugar cane over a six-month period (spring, summer, autumn). The phytotoxicity of atrazine to sensitive crops introduces further restrictions on the frequency of use on the same ground.

The maximum allowable application rate is 3.0 kg/ha/year, via ground or aerial spray. Representative labels for liquid and solid products, for example Ciba-Geigy Australia Ltd Flowable Gesaprim 500 SC Liquid Herbicide and ICI Atradex 900 WG Herbicide, recommend spray volumes for ground spraying of 50-100 L/ha. This corresponds to a working strength solution of 3-6% atrazine.

The Ciba-Geigy Australia Ltd submission provided similar estimates of spray volume to those above (range 50-200/400 L/ha). The exceptions are sugar cane (250-400 L/ha with flood jet nozzles), established lucerne and grass seed crops (140-170 L/ha) and potatoes (100-500 L/ha).

Estimates of ground coverage range from 15-20 ha/day for sugar cane and 50 ha/day for potatoes, up to 200 ha/day for broadacre use.

Atrazine products are used in more concentrated working strength solutions for aerial spraying. The representative labels above recommend spray volumes of 20-40 L/ha (corresponding to 10-15% atrazine at 3.0 kg/ha) for the liquid product. Slightly lower volumes are recommended for the solid product, 15-22 L/ha (corresponding to 14-20% atrazine at 3.0 kg/ha).

Forestry

The NRA indicates that for softwoods, herbicides are used in the first 1-3 seasons in new plantations. Atrazine may be used in *Pinus radiata* and Eucalyptus plantations at pre-planting or immediately after planting. It may be applied annually in plantations up to three years of age, depending on the amount of grass competition.

Maximum application rates in plantations are 4.5 and 8.0 kg/ha/year. Application methods include helicopters and fixed wing aircraft, hand directed sprays, and boom sprays from tractors, motor bikes or 4-wheel drive vehicles. It is broadcast or applied in approximately 1.5 m wide strips or 1 m diameter circles around treated seedlings.

The Ciba-Geigy Australia Ltd submission indicates that for liquid and solid products requiring dilution, the spray volume ranges from 50-1000 L/ha (0.8-16% atrazine at 8.0 kg/ha). Label-recommended spray volumes are as given above.

Supplementary information from the forestry industry indicates work rates of about one hectare per day for knapsack sprayers.

The granular formulation, Macspred Forest Mix Granular Herbicide 150 g/kg, is not diluted in water but applied directly from the air or ground, using specialised nozzles or equipment. Spot treatments are applied in a 50-60 cm radius around the tree. The area treated per day for granules is estimated in the submission as approximately 20-30 ha (ground), 200-300 ha (air) and 5 ha (hand dispenser).

3.2.2 NRA performance questionnaires

NRA PQs were sent to state coordinators, commodity and industry organisations, users and registrants to gather data on current use patterns. Information relevant to the occupational health and safety assessment is summarised in Table 2 and in the subsequent description. A full summary of the occupational health and safety aspects appears in Attachment 1.

Table 2: Relevant use information from NRA performance questionnaires (pq no 1 large scale users, pq no 5 chemical industry and PQ no 6 commodity/grower)

Crops or situation	Atrazine (kg/ha)	Method of application	Agriculture or forest area treated (ha/hr) [(1)] [(2)]	No. applications per year
Agriculture:				
Broadacre, (e sorghum, broom millet, saccaline, forage sorghum, maize, sweetcorn, fallow, seed bed preparation and grass seed crops)	0.315-3.3	ground boom:	unknown; 2-10; 5; 10; 10; 12-15; 20; 20-30; up to 30	1 or 2
		aerial:	20-500; 25-30; 80	
Lucerne [(3)]	0.55	ground boom:	2-10; up to 30	1
		aerial:	20-500; 80	
Canola [(4)]	0.5-1.25 L (up to 1.25 kg/ha) (in 50-100 L water)	ground boom:	not provided; current off-label use	1-2
Potatoes [(5)]	1.15 (in mixture with amitrol and ammonium thiocyanate)	ground boom:	2-10	1
Sugar cane [(6)]	2-3	high clearance boom:	4	3 over a 6 month period
		ground boom with flood jet nozzles generating large droplets:	2-10; 5-10	
		aerial:	20-500	
Lupins	0.25-0.5 (in mixture with simazine)	ground boom:	2-10; 10; 45	1

Crops or situation	Atrazine (kg/ha)	Method of application	Agriculture or forest area treated (ha/hr) (1) (2)	No. applications per year
Roadside & rights of way (Qld only) (5)	3	ground boom:	2-10	1
Forestry	4.5-8	hand spray:	1 (liquid); 10 (granules)	1 in first one, two or maybe three years of a 25-30 year tree growing cycle
		hand spot spray:	0.75 (liquid)	
		ground boom:	1-1.5; 2; 2-10; 3, 4-5; 5-10; 6 (strip); 10-12; up to 30; 40	
		aerial:	20-500, 30-40, 40; 50; 80; 150; 200	

(1) Individual responses are provided to indicate the variation
(2) Chemical Industry responses may cover a variety of crops
(3) PQ N0 5 Crop Care Australasia Pty Ltd and Ciba-Geigy Australia Ltd
(4) PQ N0 6 Commodity/Growers
(5) PQ N0 5 Ciba-Geigy Australia Ltd
(6) PQ N0 5 Crop Care Australasia Pty Ltd, Ciba-Geigy Australia Ltd and Nufarm Limited

The use pattern information is used to set the parameters to estimate exposure and risk in Section 3.

PQs revealed that in agriculture, atrazine products may be tank mixed with ametryn, amitrole, ammonium thiocyanate, 2,4-D, dicamba, fluroxypyr, glyphosate, metolachlor, paraquat, pendimethalin, picloram/2,4-D or simazine. In forestry, atrazine products may be tank mixed with amitrole, glyphosate, hexazinone or sulfometuron-methyl.

Mixing/loading

End users indicate a variety of mixing/loading methods. Liquid formulations can be added directly to the spray tank. However, for an increasing number of new machines, mixing is done by a self-mixing device via venturi or other metering device from hopper into mixture.

Some users premix suspension concentrates in a bucket before adding to the spray tank.

Powder products are mixed with water before being added to the spray tank.

Granular products are added directly into tanks half-filled with water with agitator running, or washed through the filter screen. The Macspred granular product used in forestry is not diluted or mixed before application.

For aerial application, the mixers either pour product into a vat connected by hose to the sprayplane tank, or aspirate the product directly from the drum.

Application

Both aerial and ground application may be used depending on the crop and conditions. However, the large scale agriculture users favoured ground boom spraying, with spraying in the range of 2 to 45 ha/hour reported.

In sugar cane, high clearance tractors, spraying at 4 ha/hr are increasingly replacing aerial spraying. Supplementary information from sugar cane areas indicates that most growers would not spray throughout the day and would rarely cover more than 8 ha per day.

In forestry, methods include boom spraying by broadcast or strip spraying, aerial spraying by helicopter or fixed wing aircraft and hand directed spot or strip spraying. In strip spraying, 1.5 metre wide strips 3 metre apart are treated using vehicle (tractor or four wheel drive) mounted equipment or hand directed methods. Hand directed spraying occurs in forestry but is not common. Hand directed spot or strip spraying covers 0.75-1 ha/hr and may take place from motor bikes. A separate submission from a large tree grower in WA indicated that atrazine was used for plantation preparation and firebreaks, at average rates of 2.1 kg/ha and 3.0 kg/ha (public submission, 1995).

Forestry uses of diluted liquid or granular products indicate treatment at 1-12 ha/hr (boom spray) and 30-150 ha/hr (aerial).

The Macspred granular product is applied directly by hand, ground or air, using equipment with specialised nozzles. Hand application uses the specially designed Weed-A-Metre (developed by NZ Forest Research Institute). This device automatically scatters a pre-determined dose through a spreader cone, for a diameter of 1.2 m around the seedling. Macspred provided a technical document on the Weed-A-Metre (Davenhill, 1990). Macspred indicates that the particles can be applied by hand held equipment, the Weed-A-Metre at 10 ha/hr, and ground application by pneumatic blowers at 40 ha/hr, and aerial application using pneumatic equipment at 200 ha/hr.

Most but not all, information regarding the use of atrazine was consistent with the product labels.

3.3 Exposure information

There is no atrazine exposure information about chemical industry, agricultural or other workers in Australia.

Loosli (1995) reported on some cases of deliberate (plus one undefined) ingestion, using information provided by Ciba-Geigy and in the published literature.

Overseas studies reported in the literature and conducted by the chemical industry, have attempted to quantify atrazine exposure for workers by direct measurement or in combination with examination of urinary metabolites. These studies, covering both chemical industry workers and agricultural and non-agricultural workers are summarised below. Where possible, defined exposures for workers are subsequently used to estimate risk in the Risk Assessment. Loosli (1994) has reported on means for biological monitoring of triazines, including atrazine, using urinary excretion of metabolites. However it is not possible yet to estimate absorbed dose by this method.

A summary of the relevant information is given below.

3.3.1 Poisoning in humans

Loosli (1995) describes instances of acute and possible subchronic poisoning in humans. Two cases of deliberate ingestion involved 500 g atrazine in a wettable powder formulation and 1000 g in an aqueous formulation with ethylene glycol. Another case involved ingestion of a mixture of atrazine (amount not known) and barium silicofluoride. All individuals were hospitalised but there appeared to be no clinical effects resulting from the atrazine even though ingested at high doses. One fatal case (Pommery *et al*., 1993, cited by Loosli 1995) resulted from ingestion of atrazine product containing 100 g atrazine plus the constituents, aminotriazole, ethylene glycol and formaldehyde. The patient was treated for ethylene glycol poisoning, however the authors considered the clinical picture not typical for this and speculated on the role of the active ingredients and formaldehyde. Loosli does not share this view, suggesting that the clinical picture and pathological findings are compatible with ethylene glycol poisoning. The final case (Gallois and Dereux, 1979, cited by Loosli 1995) involved a worker engaged in weed control along railway tracks. He used a product containing atrazine, tebuthiuron and aminotriazole. The worker was diabetic with a history of alcoholism. The worker was hospitalised with neurologic and other signs. The authors speculated that the peripheral signs were associated with atrazine. Loosli commented on the lack of exposure information and the fact that the authors had implicated the active ingredients in the absence of other causes.

3.3.2 Manufacturing workers

Catenacci *et al*. (1990) investigated atrazine exposure in industrial workers using exposure measurements and determination of free atrazine in urine. Workers involved were the baggers and control board operator.

Dermal exposure on skin via skin pads and inhalation exposure via personal sampling were conducted according to the 1982 standard protocol of Field Surveys of Exposure to Pesticides, WHO Division of Vector Biology and Control. Hand contamination was determined by hand washing in water. Subjects were monitored for consecutive workshifts. Urine was collected before, during and after exposure. Samples were analysed by GC or GC-MS.

Airborne atrazine during production and bagging varied from 0.07 to 0.53 mg/m^3 (8 h time weighted average (TWA)). Skin deposition on the whole body varied from 4.11 to 10.66 mg/h.

Free atrazine in the urine showed a pattern consistent with exposure, with higher amounts during the work shift (0.1-0.3 μg/h) and lower amounts at 12 h after the end of the shift (0.01-0.04 μg/h).

The authors estimated the combined dose from inhaled and skin residues to be in the order of mg. In comparison, free atrazine represented only a small proportion of the possible absorbed dose and the authors concluded it would best serve as a qualitative rather than quantitative indicator of exposure.

Catenacci *et al*. (1993) extended the findings above by conducting a similar study and determining atrazine dealkylated metabolites in urine.

The site for this study was a plant producing technical atrazine (30-70 μm granular size). Six workers were monitored. Two were box operators and monitored the synthesis process from a ventilated room and four were baggers.

The baggers wore extensive protective clothing, including an ori-nasal paper mask. The box operators wore the ori-nasal paper mask only when outside the box.

Dermal and inhalation exposure was determined as in the former study, over 12 workshifts. Urine was monitored for two consecutive workshifts over a 5-day period. Samples were analysed by GC for diaminochlorotriazine, desisopropylated, desethylated and unmodified atrazine.

Results of the atrazine exposure are presented in Table 3.

Table 3: Exposure data from Catenacci study (1993)

Exposure route	Box operator(1) µmol/workshift (range)	Baggers(2) µmol/workshift (range)
Dermal exposure	28 (7-240)	190 (174-275)
Inhalation exposure	0.3 (0.1-51)	104 (11-419)
Total exposure	28 (12-291)	356 (201-675)

(1) mean (range) from 4 subjects, 8 monitored workshifts
(2) mean (range) from 2 subjects, 4 monitored workshifts

Baggers had higher dermal and inhalation exposure than box operators.

Urinary metabolites accounted for 1-2% of exposure and although there was a positive trend, metabolites were not significantly correlated with exposure. Diaminochlorotriazine accounted for approximately 80% of metabolite excretion; unmodified atrazine was 1-2%.

The authors concluded that measurement of dealkylated metabolites in urine collected 8 hours after the end of the workshift may represent a valid biological monitoring method.

3.3.3 End users - non-agricultural workers

Ikonen *et al*. (1988) investigated atrazine exposure in 6 workers mixing and loading a tank wagon used to spray railway lines for weeds. Inhalation exposure and urinary atrazine metabolites were measured.

Inhalation exposure to atrazine dust was determined using personal air samplers with a flow rate of 2-3 L/min and filters of pore size 0.2-10 µm. Sampling time varied from 7-240 min. Urine samples were collected at the end of the 8 hour shift and assayed for metabolites by GC.

Equal amounts of 2-chloro-4-amino-6-(ethylamino)-*s*-triazine and 2-chloro-4, 6-diamino-*s*-triazine were found and the sum of the concentrations (30-110 µmol/L) correlated with inhaled dust (1.1-4.1 µmol/m^3).

However, as the concentration of urinary metabolites was high, the authors concluded that dermal exposure had made a substantial contribution. Dermal exposure was not measured in the study.

3.3.4 End users - agricultural workers

Reed *et al*. (1990) conducted this study to determine atrazine exposure for those spraying from an all terrain vehicle (ATV) towed sprayer. Atrazine residues were measured by an enzyme linked immunosorbent assay (ELISA). The study was performed at Ohio Agricultural Research & Development Center, USA, using workers experienced in using spray equipment. The paper contains only limited experimental detail.

Four workers were monitored for dermal and inhalation exposure during mixing/loading, ATV boom application and spraygun operation. Workers wore protective clothing, comprised of a DuPont Tyvec coverall, butyl rubber gloves and boots and a respirator fitted with a filter paper disc behind the respirator filter. Atrazine was applied at 4.5 kg a.i./ha. Exposure monitoring time was 20 minutes.

The atrazine 4L formulation was used, at 4.5 kg a.i./ha. Potential dermal exposure was determined from square patches (112 cm^2 on thigh, chest and forearms) cut from the coveralls and adjusted for body part area. Respiratory exposure was determined by extraction of the filter paper discs.

The results were quoted as μg/kg a.i. and are given in Table 4. The ELISA technique is quoted at a sensitivity of 1 ppb.

Table 4: Exposure per task (Reed *et al*., 1990)

Operation	Dermal exposure (μg/kg a.i.)	Inhalation exposure (μg/kg a.i.)
Mixing/Loading	272	12
Spray gun	54	4
Boom spray	3	11

Respiratory exposure was not significantly different between operations. Highest dermal exposure was found during mixing/loading and lowest during boom spraying. These values were significantly different. Spray gun exposure was intermediate and does not differ significantly from the other two tasks.

Table 5: Exposure per body part per task (Reed *et al*., 1990)

Operation	Sample area	Dermal exposure (µg/kg a.i.)
Mixing/Loading	Thigh	108
	Chest	33
	Forearm	686
Spray gun	Thigh	0
	Chest	1
	Forearm	161
Boom spray	Thigh	1
	Chest	5
	Forearm	4

For mixing/loading and spray gun operation, most contamination occurred on the forearms.

This study does not measure atrazine contamination beneath the protective coverall or through the gloves onto the hands.

Lucas *et al*. (1993) pursued the search for an effective biomarker for atrazine by developing an ELISA for atrazine and the urinary atrazine mercapturate metabolite. The study measured dermal and inhalation exposure of one worker using atrazine, with urinary analysis by ELISA. The worker made four applications of atrazine over a ten day monitoring period. Pre-exposure and daily post-exposure urine was collected. Dermal exposure during mixing/loading and application was measured via an inner cotton dosimeter (long sleeved T shirt) and inner cotton gloves, beneath protective coverall and gloves. Inhalation exposure was monitored by personal air sampling. Mixing/loading was semi-enclosed and application was by boom spray from a vehicle with an enclosed cab. Total atrazine exposure ranged from 1-22 mg/monitoring period over the four days. Inhalation exposure was $\leq$ 0.075% of the total. Hands accounted for 0.8-12.3 mg/monitoring period. Total exposure equates to 20-324 ug/kg a.i. applied (dermal exposure 19.59 - 324.32 ug/kg a.i. applied; inhalation exposure 0.11 - 0.32 ug/kg a.i. applied) and 592-6487 ug/h. Pre-exposure urine was free of atrazine and the metabolites. Atrazine metabolites were found in post-exposure urine, with atrazine mercapturate being most prevalent in frequency and amount. Excretion continued beyond 24 hours after exposure. External exposure and internal dose cannot be correlated at this stage.

Rosenheck *et al*. (1993) measured exposure to workers applying atrazine to turf, under the direction of the Ciba-Geigy Corporation. The study was conducted under USEPA data requirements: Dermal passive dosimetry exposure, Subdivision U 133-3 and Inhalation passive dosimetry exposure, Subdivision U 133-4.

The study investigated mixer/loader and applicator exposure during commercial and home owner turf treatment with AAtrex Nine-O (water dispersible granules) and Scotts Bonus S (dry granules). Application rates for AAtrex Nine-O and Scotts Bonus S on turf and lawn were 2.24 kg a.i./ha and 2.13 kg a.i./ha, respectively. Study sites in the USA included commercial turf grass farms at Goldsboro and Burgaw, North Carolina, a commercial golf course at Hawkinsville, Georgia, and the Georgia Agricultural Scientific Research Facility.

This study is summarised here because, although turf use of atrazine is not permitted in Australia, atrazine granules (undiluted) and powders and water dispersible granules (diluted for use) may be used in forestry. There may be similarities between hand dispensing or spraying methods in the turf use described by Rosenheck *et al*. (1993) and Australian forestry operations.

Three types of application equipment were used; a hand gun for AAtrex Nine-O and a push cyclone spreader and hand cyclone spreader for Scotts Bonus S.

Hand gun mixer/loaders and applicators wore long-sleeved shirts, long pants, socks, rubber boots and chemical-resistant gloves. Goggles were added by the mixer/loader. The water dispersible granules were mixed in the spray tank (100 or 175 gallons) with a hose (100 or 75 feet) attached, located on the back of a turf cart or truck. The applicator dragged out the hose to the desired length, then walked backwards, spraying in an approximately 10 foot arc. When the application was complete, the applicator rolled up the hose.

Workers using the hand cyclone spreader and push cyclone spreader wore short sleeved T-shirts, long pants, shoes or boots, and socks. The push cyclone spreader operator poured the granules directly into the hopper and pushed the spreader along the turf at approximately 3 miles per hour. The hand cyclone spreader operator poured the granules from a bucket or directly from the bag into the canvas bag and zipped it closed. The worker’s face was within 2 feet of the canvass bag when he was filling it. In some cases, a second worker held open the canvass bag for filling. During application, the worker walked forwards cranking a handle to dispense the granules. Workers performing this task became visibly covered in dust and granules during application.

Dermal exposure was determined from cotton whole-body dosimetry (long underwear located directly beneath the workers clothing), hand washes and facial swipes. Inhalation exposure was monitored by personal air-sampling pumps at 1.5 L/min. It was adjusted for a breathing rate of 45 L/min (moderate work), judged by the study authors as appropriate for activity of this kind. Samples were maintained frozen until time for analysis by gas chromatography. A full report of the analytical procedures was provided. Results are summarised in the Table 6.

Table 6: Exposure data from Rosenheck *et al*. (1993)

Method	Task	Duration (min)	Replicate	Exposure (mg/kg a.i. handled) GM ± S.D.(1) Dermal	Inhalation
AAtrex Nine-O					
Hand gun	1 M/L(2) per application	45±10	15 (M/L) 14 (app)(3)	0.74±1.7 0.95±0.9	0.055±0.062 0.014±0.033
Scotts Bonus S					
Push cyclone spreader	minimum 2 cycles loading per application	30±5	15	7.3±7.8	0.028±0.034
Hand cyclone spreader	minimum 3 cycles loading per application	30±5	15	46.5±72	0.14±0.45

(1) GM ± S.D.: geometric mean ± standard deviation
(2) M/L: mixer/loader
(3) app: applicator

Workers dispensing the dry granular formulation (Scotts Bonus S) had higher exposure than those using the water dispersible granules (AAtrex Nine-O).

Among the workers dispensing the dry granules, the hand cyclone spreader had the higher dermal exposure (46.5 vs 7.3 mg/kg a.i. handled), located mainly on the hands and forearm (23760 μg).

Among the workers diluting the water dispersible granules and spraying via the hand gun, exposure was higher for the applicator than the mixer/loader (0.95 vs 0.74 mg/kg a.i. handled). The applicators had higher exposure on the arms (184 vs 69.7 μg) while the mixer/loaders had higher exposure on the hands (173.9 vs 74 7 μg).

Hofherr (1994) from Ciba-Geigy Limited, provided a field operator exposure study using a liquid atrazine product The study comprised 10 ground application trials measuring worker exposure using Gesaprim 500 FW Herbicide in maize fields in Switzerland and fallows in France. The study was conducted under OECD GLP and FAO guidelines. The study utilised best practice rather than routine farm conditions.

Gesaprim 500 FW Herbicide was applied at 1.42-1.53 kg a.i./ha (about 3 L of formulation/ha) in a final spray volume of 186-205 L/ha. The area treated in each trial was 4.8-5.27 ha except for trial 5, terminated because of heavy wind. This application rate is lower than the maximum amount of atrazine per hectare (3 kg) allowable for agriculture use in Australia. The concentration of atrazine in working strength spray was 7.5 mg a.i./mL or 8.0 mg a.i./mL

Trials 1-5 were conducted in Switzerland. Workers used the 1 L container and tractors with an open cabin.

Trials 6-10 were conducted in France. Workers used the 5 L container and tractors with closed cabins, except for trial 10 where the back of the cabin was open.

In each trial, mixing/loading and spraying were performed by separate workers. Each trial consisted of 2 mixing/loading and 2 spraying operations (except 1 of 10 trials). Exposure times for mixing/loading ranged from 15-30 min (trials 1-5) and 15-45 min (trials 6-10). Exposure times for spraying ranged from 80-95 min (trials 1-4; trial 5 was terminated) and 40-85 min (trials 6-10). Over the monitoring period, workers mixed and sprayed 9, 15 or 16 L of product, averaging out at about 7.4 kg atrazine per worker. They covered about 5 ha, at an average spray volume of 196 L/ha (7.5 mg a.i./mL). Workers wore a cotton coverall and cap, nitrile outer gloves and rubber safety boots.

In trials 1-8, the spray tank and swath was mounted on the back of the tractor and water and test substance was filled in from the top. In trial 9 tank and swath was mounted on a trailer, water was filled in from the top of the tank and the product was filled via an induction hopper with bottle rinsing device. In trial 10 the tank and swath were mounted on a trailer and water and test substance were filled in from the top.

Ciba-Geigy staff performed trials 1-5 and all but three operations in trials 6-10. Commercial equipment was used in all trials; in trials 1-5 it was owned by Ciba-Geigy; in trials 6-10 it was owned by the farmers.

Body exposure at different parts was measured from the sectioned coverall (six sections, lower leg inside the rubber boot was not measured), cotton undergarments, cotton head protection and cotton inner gloves. Hand and glove washes were also collected. Personal air samplers at 2 L/min were used for inhalation exposure. Field recovery and control samples were collected.

Samples were analysed by GC or HPLC by Ciba-Geigy Ltd.

The risk assessment uses 75th percentile data so this is given in Table 7. Total dermal unprotected exposure includes the contamination from coverall, outer gloves, glove wash and cap. Dermal exposure includes residues from undergarments, inner gloves and hand washes. Exposure is as per the monitoring time.

Table 7: Average dermal exposures from Hofherr (1994)

Exposure per monitoring period	Mixing/Loading/Application 75th percentile
Trials 1-5 (1)	
Total dermal unprotected exposure (μg)	88,283
Dermal exposure (μg)	9,245
Inhalation exposure (μg)	10.56
Exposure per monitoring period	**Mixing/Loading/Application 75th percentile**
Trials 6-10 (2)	

Total dermal unprotected exposure (µg)	39,077
Dermal exposure (µg)	1,178
Inhalation exposure (µg)	1.90

(1) mixer/loaders used the 1 L container; sprayers used open cabs
(2) mixer/loaders used the 5 L container; 4/5 sprayers used a closed cab; in 1/5 cab was partially closed

Dermal exposure at mixing/loading was higher in trials 6-10 (498 µg) than in trials 1-5 (212.8 µg). Apart from the difference in container size, there are no apparent reasons for this. Sprayer exposure in trials 1-5 was higher than in trials 6-10, most likely because open cabs were used.

The distribution of unprotected exposure across body parts was shown for mixing/loading and spraying. Mixer/loaders in trial 1-5 had higher average exposure than those in trials 6-10, but for both groups, outer gloves followed by front torso, had the highest proportion. Similarly, applicators in trial 1-5 had higher average exposure than those in trials 6-10. Outer gloves again had the highest proportion, followed by front and back torso and upper leg (trials 1-5, open cab) and front torso (trials 6-10, 4/5 closed cabs).

Penetration of atrazine through protective clothing was presented for each worker. For mixer/loader coveralls, the percentage of inner to outer residue was in the range 0.13-10.4%, with one high value of 84.6% ascribed to cross-contamination from outer to inner clothing. For mixer/loader gloves, the percentage of inner to outer residue was in the range 0.1-18.7%. For sprayers the percentage of inner to outer residue on coveralls ranged from 0.72-20.46%. Findings demonstrate that even under best practice conditions, transfer from outer to inner clothing can be high.

Novartis Crop Protection Australasia submitted an additional study on simazine as a candidate surrogate study for of atrazine. **Tack (1995)** assessed potential exposure of Gesatop 500 SC (500g/L simazine) to farm operators when applied through a knapsack sprayer. The author considered the study representative of knapsack spraying of strawberries or other plantation crops. Simazine residues were measured on personal protective equipment (PPE), underclothing, face masks and gloves. The study was accepted as a surrogate for atrazine use by knapsack sprayer in forestry operations, as both chemicals have similar chemistry including vapour pressure, formulation and application methods and comparable PPE requirements. The study was conducted in the UK under UK Principles of GLP in 1994.

Gesatop 500 SC was applied to 9 ha of stubble (cut stalks of cereal plants) on 3 separate days by 10 experienced spray operators. The product was applied according to label instructions using a commercial 20 L knapsack sprayer with a Fluid Control Valve and Green Floodjet nozzles. Each operator was responsible for mixing/loading and spraying. Gesatop 500 SC was applied at 3 L per hectare (approximately 1.5 kg a.i./ha) in a spray volume of 200 L. Workers used normal work practices.

The operators applied the product to approximately one hectare over one day using 10 mixing/loading/spraying cycles. The times taken for mixing/loading and spraying were recorded. Workers washed the equipment at the end of the day. Operators wore a dust/mist respirator, eye protection, nitrile outer gloves, cotton overalls and rubber safety boots. The outer coverall was worn inside the rubber (wellington) boots.

Dermal and inhalation exposure were measured. Total unprotected exposure (TUDX) was measured from sectioned cotton overalls, nitrile outer gloves and cotton head protection. Total dermal exposure (TDX) was determined by analysis of cotton undergarments (long trousers and long sleeves), cotton head protection and inner cotton gloves. Respiratory exposure (REX) was determined by a analysis of dust/mist respirator for residues. This is an unconventional method of measuring respiratory exposure. Personal air monitoring is required in exposure guidelines, for example US EPA (1996) OPPTS 875-1300 Inhalation Exposure - Outdoor. There is no indication given how the method used would compare with personal air sampling.

After each mixing/loading and spraying replicate, the mask, inner and outer gloves were collected for analysis, and fresh items provided. Fresh items were given for clean up at the end of the day. In this respect, exposure is not measured under typical field conditions.

Spray tank liquor samples were taken for analysis. The average of 94 samples was 7.39 g a.i./L, compared to the theoretical value of 7.5 g a.i./L. Field recoveries of simazine were determined on cotton overalls and the respirator. Recoveries were lower than expected, at 67.2% in cotton overalls (mean) and 58.1% in mask (mean). Recoveries were not measured on inner clothing. The study authors considered a number of reasons for the low recoveries and suggested the most likely reason was an insufficient extraction time.

Individual exposure results are presented in the study. Values at the 75th percentile are given in Table 8.

Table 8: Operator dermal and respiratory exposure at 75th percentile (range)

Operator	TUDX µg	TDX µg	TDX µg/kg bw(1)	REX µg	REX µg/kg bw(1)
M/L/A(2)	30555 (5129-40008)	2737.5 (234.5-3657.5)	45.6	8.7 (7.5-11.0)	0.15

(1) Converted to an average 60 kg worker
(2) M/L/A: mixer/loader/applicator

In calculating the 75th percentile values, certain replicates were discarded. They included 5 cycles amongst the 4 workers on day 3, and all results from one operator who contaminated himself with spray mix by not properly replacing the sprayer lid. This operator had TUDX and TDX of 134,142 µg and 159,963 µg, respectively, in contrast to other workers where the 75th percentiles for TUDX and TDX were 30,555 µg and 2737.5 µg, respectively. Leaking lids not only contaminate the operator but also the sprayer itself and the carrying straps.

The distribution of simazine residues across outer body parts showed that most residues fell on the back, upper legs and lower legs (13,400 µg, 4640 µg and 2550 µg, respectively at 75th percentile). This trend was seen in the inner clothing where inner top residues (1950 µg) exceeded inner bottom residues (436 µg), at 75th percentiles. Sprayers walked into spray drift on windy days. Outer gloves became more contaminated during filling (1110 µg) than spraying (100 µg) or cleaning (162 µg). Most inner glove samples were at the limit of detection.

REX was below the limit of determination (5.0 ug) for all except two replicates. One of these belonged to the self contaminated worker and was discarded. The other registered 88 ug during filling, ascribed to accidental spillage.

Finally, the study **"Evaluation of the Potential Exposure of Workers to Atrazine during Commercial Mixing, Loading, and Spray Application to Corn (EPA-Subpart U) Biological Field Phase" (Honeycutt *et al.*, 1996)** plus the associated results and evaluation volume **"Evaluation of the Potential Exposure of Workers to Atrazine during Commercial Mixing, Loading, and Spray Application to Corn" (Selman and Rosenheck, 1996)** was provided by Ciba Geigy Limited. The study was performed under USEPA Pesticide Assessment Guidelines Subdivision U.

Worker exposure using eight atrazine formulations (AAtrex 4L, AAtrex Nine-O, Biocep, Biocep II, Extrazine II 4L, Harness Xtra, Surpass 100 and Guardman) containing 10.4-85.5% atrazine was measured during ground spraying in corn fields in the US mid west in spring 1995. The commercial atrazine products are normally sold in the USA in bulk, mini-bulk, open pour or bagged containers. In this study, bulk, open-pour (2.5 gallon containers) and 25 kg bags were used.

Nineteen experienced pesticide handlers (5 in Illinois and 5 in Indiana (cold weather applications), and 9 in Ohio (warm weather applications)) were monitored over the entire work day for two or three full working days. The tasks monitored were mixing/loading, applying and truck tending, under actual use conditions. The application rate averaged 1.40 lb a.i./acre (1.57 kg a.i./ha). Mixer/loaders, truck tenders and mixer/loader/truck tenders handled an average of 647 lb atrazine/day (294 kg/day). Applicators treated an average of 271 acres/day at 1.4 lb/acre, equating to 380 lb atrazine/day or 173 kg/day at 1.6 kg atrazine/ha. Applicators used closed cabs.

The study comprised:

mixer/loader	4 workers
truck tender	1 workers
mixer/loader/truck tender	3 workers

applicator	7 workers
mixer/loader/applicator	1 workers
mixer/loader/applicator/truck tender	3 workers

Truck tending included driving the truck, coupling/uncoupling of hoses on the tender truck at the commercial spray company and the applicator rig and some maintenance of the truck and spray rig.

Mixer/loaders dispensed atrazine into tender trucks or spray rigs using metering devices or valves and waited between loads. Occasionally a mixer/loader loaded atrazine from a 25 lb bag or 2.5 gallon container into the tender truck or spray rig.

Applicators drove to the application site, applied the spray, waited during loading, conducted any maintenance on the spray rig and drove back at the end of the day. They occasionally coupled hoses or washed the spray rig at the end of the day.

Workers wore typical clothing for the season and location. It comprised long sleeved shirt (60% cotton/40% polyester), long trousers (100% cotton) and sweatshirt (50% cotton/50% polyester) in Illinois and Indiana and similar long sleeved shirt and long trousers in Ohio, over 100% cotton T-shirt and briefs. In addition, they wore chemical resistant nitrile gloves, leather work boots, socks, goggles (mixer/loader and truck tenders only) and a cap. Protective clothing was provided new for each dosimeter day.

Outer dosimeters for the Illinois and Indiana workers were the long pants and sweatshirt and inner dosimeters were the T-shirt, briefs and long sleeved shirt. Outer dosimeters for the Ohio workers were the long pants and long sleeved shirt and inner dosimeters were the T-shirt and briefs.

Dermal exposures were calculated from values representing exposure to the skin. A clothing penetration factor of 10% was used for estimate inner exposure for legs, arms and torso of Ohio workers. Dosimeter data was converted to the whole body using the body surface areas specified in Submission U guidelines. Hand rise and head patch data was added in. Inhalation values were corrected for pump flow and light work for male workers at 29 litres per minute. Head and neck exposure was determined from a head patch on the front and back of the cap. Hand exposure was measured using hand rinses in soap (0.01% sodium dioctyl sulfosuccinate) and distilled water. Inhalation exposure samples were collected by Chromosorb 102 air sorbent tubes with Gelman mixed cellulose-ester filter attached to a personal air sampling pump, calibrated at 1 litre per minute. Urine was colleted for biological monitoring. Several discrete consecutive samples were collected at least one day prior to handling atrazine and for up to 3 days when atrazine was handled. The study also recorded each workers history of prior handling of atrazine (days and amount handled) and simazine over the 1995 season. Chlorotriazine residues in urine were used as indicators of atrazine dose (Hui *et al.*, 1996a). This involved extrapolating from oral data where approximately 12% of the atrazine ingested dose was accounted for by total chlorotriazine in the 0-24 h post treatment urine.

All samples were placed in frozen storage at the end of each sampling day and shipped to Ciba-Geigy Corporation for analysis. Quality control samples, including standards and field fortifications of collection media, were collected. Field and laboratory recoveries were considered acceptable. The study also documented individual worker tasks and any spills and splashes and weather conditions. Full details are provided in the study volumes. Urinary excretion of atrazine and the three chlorotriazine metabolites (G-30033, G-28279 and G-28273) was analysed by gas chromatography/mass selective detector. Atrazine mercapturate in urine was detected by EIA. Composite urine samples were prepared for each workers by the analytical laboratory prior to analysis. The cloth dosimeters, inhalation media and hand washes were analysed for atrazine by ion chromatography with a mass spectometric detector.

The ranges of dermal and inhalation exposure (geometric mean (GM), range) for workers and internal doses by biological monitoring are listed in Table 8. Workers using open mixing are not included in the means in the original report. Dermal and inhalation exposure were higher for these than for other workers. They are included separately for mixer/loader/applicators in Table 9, as this is relevant to Australian workers likely to perform all tasks and use open mixing.

Table 9: Dermal and inhalation exposure and dose for workers handling atrazine exposure from Honeycutt *et al*. (1996) and Selman and Rosenheck (1996)

Work tasks	Atrazine exposure (GM (range), mg/lb a.i. handled)		Atrazine dose (GM (range), mg/lb a.i. handled)	
	Dermal	Inhalation	D+I (1)	Biological monitoring
Application (2)	$1.21x10^{-2}$ ($3.06x10^{-4}$ - 1.14) n=14	$3.23x10^{-5}$ ($3.83x10^{-6}$ - $4.30x10^{-4}$) n=14	$2.93x10^{-4}$ ($7.44x10^{-6}$ - $1.38x10^{-2}$) n=14	$6.05x10^{-4}$ ($8.61x10^{-5}$ - $7.87x10^{-3}$) n=22
Mixer/loader/truck tender (3)	$8.76x10^{-3}$ ($1.42x10^{-4}$ - $2.81x10^{-1}$) n=14	$8.34x10^{-5}$ ($6.9x10^{-6}$ - $1.68x10^{-3}$) n=14	$2.31x10^{-4}$ ($8.60x10^{-6}$ - $3.87x10^{-3}$) n=14	$3.77x10^{-4}$ ($2.76x10^{-5}$ - $8.70x10^{-3}$) n=26
Mixer/loader/applicator (closed mixing) (4)	$2.12x10^{-2}$ ($2.59x10^{-3}$ - $2.96x10^{-1}$) n=6	$5.81x10^{-5}$ ($9.92x10^{-6}$ - $1.80x10^{-4}$) n=6	$3.40x10^{-4}$ ($4.05x10^{-5}$ - $3.67x10^{-3}$) n=6	$2.18x10^{-3}$ ($1.03x10^{-3}$ - $4.59x10^{-3}$) n=9
Mixer/loader/applicator (open mixing) (5)	$7.62x10^{-1}$ ($1.90x10^{-1}$ - 3.06) n=2	$3.91x10^{-4}$ ($2.83x10^{-5}$ - $5.41x10^{-3}$) n=2	$9.71x10^{-3}$ ($2.27x10^{-3}$ - $4.15x10^{-2}$) n=2	$2.25x10^{-2}$ n=3

(1) Dermal plus inhalation, using 1.18% dermal absorption and 100% inhalation absorption.
(2) All but one applicator used closed cabs; three applicators experienced spills.
(3) All but two mixer/loader/truck tender experienced spills.
(4) All three used closed cabs and closed mixing; two experienced spills.
(5) One only, using open mixing and experienced spills.

Certain increases in urinary chlorotriazine levels could be linked to spills or splashes on the previous day. Inhalation samples above the limit of quantification (1.0 μg/sample) were detected on days when spills occurred.

3.3.5 Penetration through protective clothing

Atrazine has been one of a number of chemicals used to test the barrier effectiveness of various fabrics used in protective clothing (Raheel, 1988; Oakland *et al*., 1992). Raheel (1988) tested fabrics under laboratory conditions. One mL of 1.25% atrazine was pipetted dropwise onto a fabric square at 199.7 ug/cm^2 and allowed to dry at ambient temperature for 12-14 h. This was followed by analysis of the amount transmitted to a secondary fabric underneath. Fabrics tested with atrazine were cotton (100%), PET/cotton (50/50), PET/cotton (65/35), polyester (100%), nylon (100%), acrylic (100%) and olefin (Tyvek). In the first test, the fabrics had no special functional finishes. The secondary layer was T-shirt knit made of cotton or PET/cotton (50/50).

Olefin gave the best protection and polyester gave the least. High to low barrier protection was olefin (0.2% transmission), cotton (10% transmission), polyester (PET)/cotton (50/50, 14% transmission), PET/cotton (65/35, 33% transmission), nylon (41% transmission), acrylic (62% transmission) and polyester (88% transmission).

The author also tested materials with the special functional finishes of durable-press or consumer applied water and soil repellent. The water and soil repellent treated cotton and PET/cotton (50/50 and 65/35) conferred the best and statistically similar barrier properties to olefin (0.3%, all four fabrics). Next best protection was afforded by 100% cotton and durable-press 100% cotton (9%).

Results overall indicated that cotton and cotton/polyester fabrics had better barrier properties than nylon, acrylic or polyester fabrics.

Oakland *et al*. (1992) investigated fabric penetration by spray mist comprised of pesticide and fluorescein dye at varying volumes and pressures. Atrazine was sprayed at 1.25% onto three test materials in a spraybox. The spray solution was applied for 1.25 minutes at 45 mL/min and 50 psi and 65 mL at 70 psi. Penetration was measured at 2, 5, 7, 10 and 15 min.

The fabrics tested were Tyvek 1422, Sontara FC (polyester staple and a layer of wood tissue paper) and SMS (laminates of spunbonded/ meltdown/spunbonded webs of polypropylene) with a repellent finish. The study did not measure woven fabrics, such as cotton or cotton/polyester. No penetration of atrazine or dye was seen through Tyvek 1422 over the times measured (up to 15 mins). Results are not discussed further as the fabric types are not likely to be readily available to Australian end users. The authors conclude the method may be useful for prescreening nonwoven fabrics.

Stone & Stahr (1989) analysed cotton coveralls worn by a farmer in the midwest USA worn over at least three years, for pesticide residues. The coveralls had been washed after each wearing. Results showed that home laundering did not remove all pesticide residues from the coveralls, however, atrazine one of the chemicals the farmer reported using, was not detected.

3.3.6 Re-entry and re-handling

No information or worker exposure studies covering re-entry into atrazine-treated areas were submitted for review.

Current product labels do not include a re-entry period for atrazine.

3.3.7 Public submissions

Public submissions were sent to the NRA as part of the atrazine review program. Most submissions were not related to occupational exposure. Relevant literature reports referred to in certain submissions are covered in the review. One report claimed a link between birth defects and parental occupation as a pesticide sprayer (public submission to the NRA, 1995).

4. RISK ASSESSMENT

End users may be contaminated with atrazine when mixing/loading, applying spray, cleaning up spills and maintaining equipment. Workers entering treated areas may become contaminated with sprayed foliage.

The main route of contamination is most likely to be through dermal exposure to the concentrate, spray mist and contaminated surfaces. As the vapour pressure of atrazine is low (3.7×10^{-8} KPa at 25^{o}C), inhalation of vapour from the concentrates is unlikely. However, as some atrazine products are formulated as wettable powders, granules or water dispersible granules, breathing in of product dust is possible. Sprayers may inhale spray mist.

It is possible for farm operators to be exposed to atrazine for periods of a few days in one or two episodes per crop in the early season. Workers treating sugar cane may have more regular exposure, depending on the number of crops and treatment cycles. Contract sprayers for all crop types and forestry uses would have regular exposure to atrazine over the treatment season. The duration would depend upon the crop area being serviced.

4.1 Dermal absorption and respiratory absorption

The risk assessment used percutaneous absorption of 1.18% derived from a human *in vivo* study.

The risk assessment assumes a default respiratory absorption of 100%. Catenacci *et al*. (1990) used inhalation absorption of 20% but an explanation for this choice was not given.

4.2 Acute toxic potential

The dermal LD_{50} of atrazine is >3100 mg/kg. This is an equivalent dose for an average 60 kg worker of > 186 g atrazine. Using the highest atrazine concentration of 500 g/L in SC or LC formulations and 900 g/kg in WG or WP formulations, this equates to > 372 mL SC or LC product, and > 207 g WG or WP product.

The most concentrated end use sprays are 6% atrazine (agriculture use, ground spray), 20% atrazine (agriculture use, aerial spray) and 16% atrazine (forestry). At these concentrations, contamination with spray volumes exceeding 3.1 L, 0.9 L and 1.2 L, respectively, are needed to reach the dermal $LD_{50.}$ These calculations do not include a safety factor.

Literature reports suggest than on occasion, atrazine may cause irritation or contact dermatitis in workers.

4.3 Repeat dose toxic potential

The repeat dose assessment covers workers repeatedly handling atrazine products.

The NOEL of 4.1 mg/kg bw/day, from a one-year female rat dietary study and percutaneous absorption of 1.18%, is used in the risk assessment. The amount of daily skin contamination with atrazine and product needed to exceed this dose for an average 60 kg worker is 21 g atrazine, 42 mL 50% SC or LC product and 23 g 90% WG or WP product. At the most concentrated spray of 6% atrazine (agriculture use, ground spray), 20% atrazine (agriculture use, aerial spray) and 16% atrazine (forestry), this equates to volumes exceeding 350 mL, 105 mL and 130 mL, respectively. These theoretical calculations do not include a safety factor.

4.4 Assessment of end-use exposure

Information provided in the NRA PQs (Table 2) is used to define the parameters needed to assess worker exposure, from measured studies or prediction model, and risk. The data relevant for the worker exposure studies is given in Table 10. In considering risk, the highest application rates from the labels are used and the range in spray volumes and treatment areas revealed in the NRA PQs. It is noted that atrazine may be used at lower rates, either alone or in combination products or tank mixes with other products.

Table 10: End use parameters derived from NRA PQs used to estimate worker exposure and risk

Situation	Model	Application rate		
		kg a.i./ha (maximum per year)	**spray L/ha (range)**	**ha/day (range)**
Broadacre except lucerne/lupins	boom spray	3	50 - 400	12 - 270
Lucerne/lupins	boom spray	0.55	50; 140	12 - 270
Potatoes	boom spray	1.15	100	5 & 50
Sugar cane	boom spray	3	50 - 250	20
Forestry	hand spray	8	50 - 200	6[(1)]; 1[(2)]
Forestry	boom spray	8	50 - 1000	6 - 72

(1) Used for hand spraying from a trailer-mounted tank
(2) Based on supplementary information from the forestry industry for knapsack sprayers

Actual exposure is estimated where possible (ie contamination transmitted through outer clothing). Absorbed dose accounts for skin and respiratory absorption. As no exposure information is available for forestry uses of atrazine, extrapolations are made from similar uses. Margins of exposure (MOE) are calculated using the oral NOEL of 4.1 mg/kg bw/day.

4.4.1 Measured worker exposure

Manufacturing workers

Catenacci *et al*. (1990, 1993) studied dermal and inhalation exposure in industrial workers manufacturing atrazine. Some atrazine products are formulated in Australia but atrazine itself is imported. It is not possible to assess worker risk during formulation using the studies.

Non-agricultural workers

Ikonen *et al*. (1988) studied inhalation exposure and urinary excretion for workers spraying atrazine along railway tracks from railway cars. The study is not used in the risk assessment because the use pattern is not sufficiently similar to Australian uses and dermal exposure is not measured.

Agriculture and forestry workers

The various worker studies allow an estimate of worker exposure using atrazine in agriculture. There are no worker exposure studies that investigate atrazine use in forestry. Where possible, extrapolations are made from similar use patterns to forestry uses.

Reed *et al*. (1990) measured exposure on the outside of protective clothing and through a respirator for four workers mixing/loading a liquid atrazine product and spraying via an ATV and boom spray or a hand spraygun. This study is of limited assistance only in the risk assessment, for atrazine applications by boom spray (as in agricultural uses) and hand spray (as in forestry uses). Experimental detail is limited, the inhalation method is questionable, hand exposure is not measured and results are quoted as µg/kg a.i. (see Table 4). Accepting the limitations at face value and assuming results refer to µg/kg a.i. handled, the exposure can be standardised against the Australian use pattern. This assumes, for boom spray, 3 kg a.i. per hectare, 12 - 270 hectares per day (range), 10% penetration through protective clothing, dermal absorption of 1.18%, inhalation uptake and absorption of 100% and 60 kg body weight. Hand gun operation assumes 8 kg a.i. per hectare (maximum for forestry), 6 hectares per day (hand held forestry use) and other parameters as above. Exposure is estimated for mixing/loading plus application. Estimated exposure and risk, using the oral NOEL of 4.1, is shown in Table 11. It does not include any contribution from the hands.

Table 11: Estimated exposure and risk for boom spray and hand gun operators, derived from Reed *et al*. (1990)

Estimated exposure M/L/A	Spray gun Forestry	Boom spray Agriculture (12 - 270 ha/day)
Dermal exposure (mg/day)	1.5648	0.9900 - 22.2750
Inhalation exposure (mg/day)	0.7680	0.8260 - 18.5850
Dermal dose (mg/kg bw/day)	0.0003	0.0002 - 0.0045
Inhalation dose (mg/kg bw/day)	0.0128	0.0138 - 0.3105
Total dose (mg/kg bw/day)	0.0131	0.014 - 0.315
MOE	313	293 - 13

MOE are 313 for spray gun operators and within the range 13 - 293 for boomspray operators. Given that hand exposure could not be included and the other limitations of the study for this purpose, the MOE *per se* are insufficient to indicate the risk associated with the use patterns.

The mixer/loader/applicator (M/L/A) monitored four times over a ten day period by **Lucas *et al*. (1993)** provides some basic data to estimate risk for workers using semi-enclosed mixing/loading and spraying atrazine by boom spray from a vehicle with an enclosed cab. It is noted that only one worker is monitored and only summary information is provided in the paper. The method measured atrazine residues inside clothing on the upper body, inside gloves and by personal air sampling. The range of exposure and risk over the four monitoring days is given in Table 12. It is adjusted for the Australian use pattern, assuming, for boom spray, 3 kg a.i. per hectare and 12 - 270 hectares per day (range). Previous assumptions and NOEL are used.

Table 12: Estimated exposure and risk for one boom spray mixer/loader and applicator, derived from Lucas *et al*. (1993)

Estimated exposure M/L/A	Boom spray (12 - 270 ha/day)
	Agriculture
Dermal exposure (mg/day)	0.705 - 262.699
Inhalation exposure (mg/day)	0.004 - 0.262
Dermal dose (mg/kg bw/day)	0.0001 - 0 0517
Inhalation dose (mg/kg bw/day)	0 000 - 0.004
Total dose (mg/kg bw/day)	0.0001 - 0.0557
MOE	41,000 - 74

High MOE (74 - 41,000) were obtained with this worker, noting the limitations above where exposure to the lower body or exposed head and neck is not included. Despite the low exposure estimates, urinary excretion of atrazine metabolites was detectable.

Rosenheck *et al*. (1993) investigated applications of atrazine to turf using various application techniques. The techniques included spraying of diluted water dispersible granules and hand or automatic dispensing of dry granular product. Turf use is not included on the Australian atrazine product labels, however estimated exposures from the study are used to extrapolate to forestry use. The methods selected are hand gun sprayers, using a vehicle mounted spray tank and hand held hose and hand spreaders carrying granules and dispensing them by cranking a handle. Dermal exposure (actual) and inhalation exposure were measured (see Table 6).

The review does not have an estimate of hectares treated per day for hand gun sprayers using a vehicle mounted spray tank and hand held hose. Rosenheck *et al*. (1993) have provided handgun mixer/loader and applicator exposure in mg/hr. For combined tasks this is 4.874 mg/hr dermal exposure and 0.2588 mg/hr inhalation exposure. This is extrapolated to an eight hour day for the risk assessment. Exposure and risk for the hand granule dispenser is estimated at 8 kg a.i./ha (maximum forestry use) and 6 ha/day. Assumptions for body weight and percutaneous and inhalation absorption are given previously. Results are presented in Table 13 and derive from the geometric mean exposure.

Table 13: Estimated exposure and risk for hand gun operators and hand spreaders derived from Rosenheck *et al*. (1993)

Estimated exposure M/L/A	Hand gun (8 hr day) Forestry	Hand Spreader (6 ha day, 8 kg a.i./ha) Forestry
Dermal exposure (mg/day)	38.9920	2232
Inhalation exposure (mg/day)	2.0704	6.528
Dermal dose (mg/kg bw/day)	0.0077	0.439
Inhalation dose (mg/kg bw/day)	0.0345	0.109
Total exposure (mg/kg bw/day)	0.0422	0.548
MOE	97	7

Contamination using the hand spreader was the higher of the two methods for both skin and respiratory tract. The study noted that workers using the hand spreader became visibly covered in dust and granules during use. The MOE for this method (7) is low and indicates that filling the bag and dispensing this way would not be acceptable. MOE for the hand sprayers was high (97), indicating that under these conditions atrazine would be safe to use. The hand gun operators in the study wore rubber boots and chemical resistant gloves, as well as long trousers and long sleeves. Similar protection would be needed for forestry workers using the hand gun.

An exposure study covering some of the major agricultural uses of atrazine, maize and fallows, was conducted for Ciba Geigy by **Hofherr (1994)**. The study was conducted under best practice. It utilised the 50% atrazine liquid product with open mixing/loading. Trials using boom sprays were conducted in Switzerland (trials 1-5, 1 L container, open cabs) and France (trial 6-10, 5 L container, closed cab (4/5 trials)).

Dermal unprotected exposure (outer clothing), dermal exposure (inner undergarment, inner gloves and hand wash) and inhalation exposure were measured and summarised in Table 7. Dermal exposure on inner dosimeters, and inhalation exposure are used to estimate the risk for these workers. Workers wore a cotton coverall and cap, nitrile outer gloves and rubber safety boots. Exposure and risk for mixer/loader/applicators at 3 kg a.i./ha (maximum agriculture use) and 12 - 270 ha/day. Assumptions for body weight and percutaneous and inhalation absorption are given previously. Results are presented in Table 14 and derive from the 75th percentile data.

Table 14: Estimated dermal exposure beneath protective clothing and inhalation exposure and risk for agriculture boom sprayers, derived from Hofherr (1994)

Estimated exposure M/L/A 75th percentile	Trials 1-5 Open cabs 12 - 270 ha/day	Trials 6-10 Closed cabs 12 - 270 ha/day
Dermal exposure (mg)/trial 7.4 kg a.i.	9.245	1.178
Inhalation exposure (mg)/trial 7.4 kg a.i.	0.011	0.002
Dermal exposure (mg/day)	44.976 - 1011.953	5.731 - 128.943
Inhalation exposure (mg/day)	0.054 - 1.204	0.010 - 0.219
Dermal dose (mg/kg bw/day)	0.009 - 0.199	0.001 - 0.025
Inhalation dose(mg/kg bw/day)	0.001 - 0.020	0.000 - 0.004
Total dose (mg/kg bw/day)	0.010 - 0.219	0.001 - 0.029
MOE	410 - 19	4,100 - 141

Mixing/loading is pooled across the trials because the container sizes used (1 L and 5 L) are too small to be of practical use in broadacre uses. It is noted that in the study, there was higher exposure for mixer/loaders using the larger container. MOE are high (141 - 4,100) for all users with the closed cabs. When open cabs are used, MOE become low when large areas are treated (19). It is expected that under Australian conditions, those with large cropping areas would have enclosed cabs.

Tack (1995) reported on worker exposure during knapsack spraying of simazine in crop stubble. This study is used as a surrogate for knapsack spraying of atrazine in forestry, in the absence of specific data.

The study followed ten M/L/A over three days. Operators sprayed approximately one hectare per day, using 1.5 kg a.i. per hectare, over 10 mixing/loading and spraying cycles.

Workers wore extensive PPE, namely wellington boots, cotton overalls, rubber gloves, eye protection, a dust/mist mask and a hat.

Potential and actual dermal and inhalation exposure to simazine were measured. Exposure at 75th percentile and risk are estimated at 8 kg a.i./ha (maximum atrazine forestry use) and 1 ha/day.

Assumptions for body weight and percutaneous and inhalation absorption are as given previously for atrazine. Results are presented in Table 15.

Table 15: Estimated dermal exposure beneath protective clothing and inhalation exposure and risk for knapsack sprayers in forestry, derived from Tack (1995)

Estimated exposure M/L/A 75th percentile	Knapsack sprayers 1 ha/day
Dermal exposure - mg/kg a.i.	1.825
Inhalation exposure - mg/kg a.i.	0.006
Dermal exposure - mg/day	14.600
Inhalation exposure - mg/day	0.046
Dermal dose - mg/kg bw/day	0.003
Inhalation dose - mg/kg bw/day	0.001
Total dose - mg/kg bw/day	0.004
MOE	1025

A high MOE (1025) is obtained from this surrogate study. It is noted that workers in the study have lower leg protection (wellington boots) and wear other extensive PPE. In addition, residue recoveries from outer overalls and the mask were low and hand exposure was not measured strictly under field conditions. The use of mask residues instead of personal air sampling for respiratory exposure is not validated. Recoveries from inner clothing were not tested, so it is not known if they were also low. One operator in this study experienced substantial contamination from a spill from an incorrectly lidded sprayer. His exposures are not incorporated above, but taken in isolation result in an MOE of 24. This demonstrates the importance of well designed lids that do not allow leakage. Under normal conditions where leakage does not occur, the MOE are sufficiently high to be acceptable for knapsack sprayers given the limitations of the study.

Honeycutt *et al*. (1996) and **Selman and Rosenheck (1996)** reported on worker exposure during routine ground spraying of atrazine in the US mid west corn belt. The tasks measured were mixing/loading, truck tending and spraying for up to 3 days per replicate. The study measured potential dermal and inhalation exposure and estimated the internal atrazine dose from atrazine metabolites in the urine.

Dermal and inhalation exposure and internal dose (GM and range) are converted according to kg atrazine handled by workers treating similar crops in Australia. Exposure and risk for all work groups are calculated at 3 kg a.i./ha (maximum agricultural use) and 12-270 ha/day. Assumptions for body weight and percutaneous and inhalation absorption are given previously. Results are presented in Table 16.

Table 16: Estimated dose and risk for agricultural boom sprayers derived from Honeycutt *et al*. (1996) and Selman and Rosenheck (1996)

	Applicator	M/L/TT(1)	M/L/A(2) (closed mixing)	M/L/A (open mixing)
Dermal and inhalation dose from measured exposure (GM, range)				
Total dose (mg/lb a.i. handled)(3)	$2.93x10^{-4}$ ($7.44x10^{-6}$ - $1.38x10^{-2}$)	$2.31x10^{-4}$ ($8.60x10^{-6}$ - $3.87x10^{-3}$)	$3.40x10^{-4}$ ($4.05x10^{-5}$ - $3.67x10^{-3}$)	$9.71x10^{-3}$ ($2.27x10^{-3}$ - $4.15x10^{-2}$)
MOE (12 ha/day)(4)	10600 (230 - 417500)	13400 (800 - 361200)	9100 (850 - 76700)	320 (75 - 1400)
MOE (270 ha/day)(4)	470 (10 - 18600)	600 (36 - 16100)	410 (38 - 3400)	14 (3 - 61)
Biological monitoring data (GM, range)				
Atrazine dose (mg/lb a.i. handled)(3)	$6.05x10^{-4}$ ($8.61x10^{-5}$ - $7.87x10^{-3}$)	$3.77x10^{-4}$ ($2.76x10^{-5}$ - $8.70x10^{-3}$)	$2.18x10^{-3}$ ($1.03x10^{-3}$ - $4.59x10^{-3}$)	$2.25x10^{-2}$
MOE (12 ha/day)(4)	5100 (390 - 36100)	8200 (360 - 112500)	1400 (680 - 3000)	138
MOE (270 ha/day)(4)	230 (18 - 1600)	370 (16 - 5000)	63 (30 - 134)	6

(1) Mixer/loader/truck tender.
(2) Mixer/loader/applicator
(3) Data from Table 8.
(4) At maximum application of 3 kg atrazine/ha.

For applicators and mixer/loader/truck tenders, the internal atrazine dose is similar when derived from measured exposure or biological monitoring of chlorotriazine residues. For workers performing all tasks, dose derived from measured exposure is underestimated by almost an order of magnitude. Some workers appeared to have pre-existing urinary residues at the start of the trial. Some workers also handled simazine during the trial. Simazine interferes with the quantitation of atrazine and its metabolites in the urine. Using both estimation methods, MOE are high and acceptable for workers performing separate or combined tasks, including closed and open mixing, at 12 ha/day.

At 270 ha/day, MOE based on GM measured exposure are acceptable for all workers, except mixer/loader/applicators using open mixing. At 270 ha/day, MOE based on GM biological monitoring are acceptable for workers performing separate tasks, are becoming low for mixer/loader/applicators with closed mixing (MOE of 63) and are low and unacceptable with open mixing (MOE of 6).

There is a wide range in dose and MOE using both estimation methods. At 270 ha/day the highest doses in the range for applicators and mixer/loader/truck tenders and M/L/A (closed mixing) result in low MOE, indicating some unacceptable exposure for workers. MOE are unacceptable across the range for M/L/A (open mixing). Applicators used closed cabs; gloves were worn during mixing/loading and truck tending.

The Ciba-Geigy submission included data submitted to the USEPA special review of atrazine and simazine (Breckenridge, 1996). Included in the risk assessment for the USEPA (as Table 9) are exposure values taken from PHED version 1.1 (μg/lb a.i.). These are presented as absorbed dose using 5.6% and 1.2% percutaneous absorption (human data) (incorporating an additional 10% reduction in percutaneous absorption for granular products) and 100% inhalation absorption. The OHS report has used the combined dose (at 1.2% percutaneous absorption), reconverted μg/lb a.i. to μg/kg a.i. and standardised absorption and risk for Australian conditions (Table 17). Parameters used are 3 kg a.i./ha for ground spraying (12-270 ha/day) and aerial spraying (480 ha/day; 80 ha/h x 6 h) and 8 kg a.i./ha and 6 ha/day for forestry manual operations.

Table 17: Atrazine exposure (μg/lb a.i. handled) from PHED (Breckenridge, 1996) extrapolated to exposure, dose and risk under Australian conditions

Estimates from Table 9 in Breckenridge (1996) (μg/lb a.i. handled)

Use	Dermal exposure	Absorbed dermal dose		Inhalation dose	Total dose	
		5.6%	**1.2%**		**5.6%**	**1.2%**
Mixer/loader 4L	41.5	2.32	0.50	1.2	3.52	1.70
Mixer/loader WDG	67.5	3.77	0.81	0.77	4.54	1.58
Closed system mixer/loader	9.6	0.54	0.12	0.13	0.67	0.25
Open-cab boom applicator	16.0	0.90	0.19	0.63	1.53	0.82
Enclosed-cab boom applicator	4.0	0.22	0.05	0.043	0.27	0.09
Pilot	4.4	0.25	0.05	0.018	0.27	0.07
Flagger	11.5	0.64	0.14	0.19	0.83	0.33
Granular handspreader	21100	118.2	25.3	40	158.2	65.3
Handgun mixer-loader	335	18.7	4.0	16.1	34.8	20.1
Handgun applicator	432	24.2	5.2	3.9	28.1	9.1

Exposure and risk under Australian conditions

	Task	Dose (µg/lb a.i. handled)	Dose (mg/kg bw/day)[(1)]	MOE
			12-270 ha/day	
Broadacre ground spray	open mixing/open cab[(2)]	2.52	$3.33x10^{-3}$ - $7.49x10^{-2}$	1200 - 55
(3 kg a.i./ha)	open mixing/closed cab[(3)]	1.79	$2.37x10^{-3}$ - $5.32x10^{-2}$	1700 - 77
	closed mixing/closed cab[(4)]	0.34	$4.49x10^{-4}$ - $1.01x10^{-2}$	9100 - 400
			480 ha/day	
Broadacre aerial spray	open mixing	1.77	$9.36x10^{-2}$	44
(3 kg a.i./ha)	closed mixing	0.25	$1.32x10^{-2}$	310
	pilot	0.07	$3.70x10^{-3}$	1100
	flagger	0.33	$1.74x10^{-2}$	240
			6 ha/day	
Forestry	granular handspreader	65.30	$1.15x10^{-1}$	36
(8 kg a.i./ha)	handgun[(5)]	29.20	$5.15x10^{-2}$	80

(1) Daily work load is standardised to 12-270 ha (ground spraying), 480 ha (aerial spraying) and 6 ha (manual forestry operations).
(2) Mixer/loader 4L and open-cab boom applicator.
(3) Mixer/loader 4L and enclosed-cab boom applicator.
(4) Closed system mixer/loader and enclosed-cab boom applicator.
(5) Handgun mixer-loader and handgun applicator.

PHED generated exposure for broadacre ground spraying indicates high MOE when only 12 ha/day is treated. At 270 ha/day, MOE are highest for closed mixing/closed cab (400), followed by open mixing/closed cab (77) and open mixing/open cab (55). Under large scale use in Australia, sprayers would commonly use an enclosed cab and bulk containers.

MOE obtained for broadacre aerial spraying at an intermediate rate of 480 ha/day, indicate that closed mixing is preferable to open mixing (MOE of 310 and 44). Pilots are at low risk only (MOE, 1100), as are flaggers (MOE, 240). Under large scale use in Australia, aerial spraying operators would commonly use bulk containers of atrazine.

MOE obtained for manual operators in forestry indicate low MOE (36) using a granular handspreader. Details of the equipment design are not provided, but it is likely to be a cyclone type spreader. Workers using a handgun had higher and adequate MOE (80).

Details of protective clothing worn by workers is not provided. The risk assessment assumes dermal exposure is that available for uptake, with workers wearing normal work clothing.

4.4.2 Predicted worker exposure

The **UK Predictive Operator Exposure Model (POEM)** was used to estimate atrazine exposure for the Australian use pattern. Two application methods were chosen:

- boom spray, ie vehicle mounted (with cab) hydraulic nozzle boom spray (V-nozzle), and
- hand spray (knapsack), ie hand held outdoors hydraulic nozzles (H-nozzles).

The application rates, spray volume and work rate per day are based on the information from products labels and NRA PQs (see Table 2). The work rate used is 6 hours or 3 hours spraying per day. Table 18 summarises the parameters used.

Table 18: End use parameters derived from NRA PQs used to estimate worker exposure and risk using UK POEM

Estimate No	Situation	Model	Application kg a.i./ha	spray L/ha	ha/day
1-8	Broadacre except lucerne/lupins	V-nozzle	3	50 & 400	12 & 270
9-16	Lucerne/lupins	V-nozzle	0.55	50 140	12 & 270
17-20	Potatoes	V-nozzle	1.15	100	5 & 50
21-24	Sugar cane	V-nozzle	3	50 & 250	20
25-32	Forestry	H-nozzle	8	50 & 200	1
33-40	Forestry	V-nozzle	8	50 & 1000	6 & 72

The percutaneous absorption of atrazine used is 1.18%. Two product types are included, namely a liquid formulation (SC or LC) containing 500 g atrazine/L with a 20 L container (L500), and the solid formulation (WG or WP) containing 900 g atrazine/kg with a 15 kg container (S900). Both formulations are tested in each scenario. Other parameters used were within POEM.

Results

Predicted dermal and inhalation dose and MOE for Estimates 1 - 40 are given in Attachments 2 and 3. The tables provide mixer/loader, applicator and M/L/A exposures, for workers wearing one layer of protective clothing plus or minus gloves. An additional layer of body protection was also factored into the model. The most relevant information on dose and MOE from the tables is summarised in Table 19. Contamination during mixing/loading is about 3 times higher with the liquid product than with the solid. Applicator exposure is not influenced by the formulation. The effect of adding the second layer of protective clothing did not result in substantial increases in MOE.

Table 19: End use scenarios and margins of exposure (MOE) from predicted exposure using POEM

Estimate	EUP	Crop type	Application rate			Margin of Exposure	
			kg ai/ha	spray L/ha	ha/day	no gloves (M/L/A)(1)	gloves (M/L/A)
1. V-nozzle	S900		3	50	12	7	30
2. V-nozzle	L500		3	50	12	5	28
3. V-nozzle(2)	S900		3	50	270	3	28
4. V-nozzle(2)	L500	Broadacre	3	50	270	<1	12
5. V-nozzle	S900	except	3	400	12	33	228
6. V-nozzle	L500	lucerne	3	400	12	15	152
7. V-nozzle(2)	S900		3	400	270	4	146
8. V-nozzle(2)	L500		3	400	270	1	19
9. V-nozzle	S900		0.55	50	12	34	164
10. V-nozzle	L500		0.55	50	12	27	152
11. V-nozzle	S900		0.55	50	270	14	152
12. V-nozzle	L500	Lucerne/lupins	0.55	50	270	5	66
13. V-nozzle	S900		0.55	140	12	76	456
14. V-nozzle	L500		0.55	140	12	48	373
15. V-nozzle	S900		0.55	140	270	18	373
16. V-nozzle	L500		0.55	140	270	5	89
17. V-nozzle	S900		1.15	100	5	33	158
18. V-nozzle	L500	Potatoes	1.15	100	5	26	141
19. V-nozzle	S900		1.15	100	50	21	152
20. V-nozzle	L500		1.15	100	50	10	100
21. V-nozzle	S900		3	50	20	6	30
22. V-nozzle	L500	Sugar cane	3	50	20	5	27
23. V-nozzle	S900		3	250	20	21	146
24. V-nozzle	L500		3	250	20	10	98
25. H-nozzle(3)	S900		8	50	1	1	2
26. H-nozzle(3)	L500	Forestry	8	50	1	1	2
27. H-nozzle(3)	S900	(knapsack)	8	200	1	4	9
28. H-nozzle(3)	L500		8	200	1	3	8
29. H-nozzle	S900		8	50	1(4)	2	4
30. H-nozzle	L500		8	50	1(4)	2	4
31. H-nozzle	S900		8	200	1(4)	6	17
32. H-nozzle	L500		8	200	1(4)	4	15
33. V-nozzle	S900		8	50	6	3	11
34. V-nozzle	L500		8	50	6	2	11
35. V-nozzle(2)	S900		8	50	72	2	11
36. V-nozzle(2)	L500	Forestry	8	50	72	<1	8
37. V-nozzle	S900	(boom)	8	1000	6	28	216
38. V-nozzle	L500		8	1000	6	13	137
39. V-nozzle(2)	S900		8	1000	72	5	158
40. V-nozzle(2)	L500		8	1000	72	1	25

(1) M/L/A: mixer/loader/applicator.
(2) Number of mixing/loading operations exceeds 20 per day.
(3) MOE are similar at 3 ha/day.
(4) Applied for three hours only.

MOE indicate that with few exceptions, M/L/A require the use of gloves and body protection. Unless the product is used at 0.55 kg a.i./ha with a final spray volume of at least 140 L/ha, gloves and body protection are required for all tasks.

Below is a discussion of each use pattern.

Inhalation exposure over all uses ranged from 0.004 to 0.32 mg/kg bw/day. For M/L/A using gloves and body protection, inhalation exposure was 0.2 - 0.9% of the dermal and inhalation exposure available for absorption.

Estimates 1 - 8 Broadacre excluding lucerne/lupins

MOE are high for all uses at 400 L spray/ha (Estimates 5 - 7) except for 270 ha/day with the liquid formulation (Estimate 8). Other uses at 270 ha/day, including the exception above also have low MOE, however, the number of mixing/loading operations exceeds 20/day (Estimates 3, 4). Under these circumstances it is more likely that large (> 20 L, > 15 kg) containers would be used, so contamination with the concentrate would possibly be less than predicted with the model. MOE are still low however, for farmers using final spray volume of 50 L (Estimates 1, 2).

Estimates 9 - 16 Lucerne/lupins

MOE are high in most cases and are acceptable overall for atrazine use at 0.55 kg/ha. The minimum spray volume of 50 L/ha should not be further reduced, however.

Estimates 17 - 20 Potatoes

MOE are high for all atrazine uses on potatoes at 1.15 kg/ha and a minimum spray volume of 100 L/ha.

Estimates 21 - 24 Sugar cane

Similarly with broadacre use, a low spray volume on sugar cane at 3 kg a.i./ha results in low MOE (Estimates 21, 22). Supplementary information from sugar cane areas indicates that low volumes would not be used. Applications range from 180 - 300 L/ha with most being 230 - 250 L/ha. At volumes of 250 L/ha, MOE are high (Estimates 23, 24). Submitted data indicates that flood jet nozzles generating large droplets may be used. These would have lower potential for drift than the nozzle types used in the model.

Estimates 25 - 32 Forestry - hand held - knapsack

The model incorporates the maximum application rate of 8 kg a.i./ha. MOE are low for all workers using the hand held knapsack equipment (hydraulic nozzles) using a final spray volume of 50 or 200 L/ha.
MOE are low, irrespective of whether workers spray one hectare over a full day or half a day. MOE for workers treating 3 hectares over a full day are similar (low) for those treating one hectare (data not presented).

Hand directed spraying from a vehicle mounted spray tank cannot be estimated using POEM.

Estimates 33 - 40 Forestry - boom spray

Findings here are similar to those for broadacre spraying.

MOE are high for all uses at 1000 L spray/ha (Estimates 37 - 39) except for 72 ha/day with the liquid formulation (Estimate 40). Other uses at 72 ha/day, including the exception above, have low MOE, however, the number of mixing/loading operations exceeds 20/day (Estimates 35, 36). Under these circumstances it is more likely that large (> 20 L, > 15 kg) containers would be used, so contamination with the concentrate would possibly be less than predicted with the model. MOE are still low, however for workers using a concentrated final spray (50 L) (Estimates 33, 34), even if they treat only a few hectares per day.

4.5 Conclusions on worker exposure and risk - ground spraying

The review was unable to locate any substantiated reports of atrazine causing acute systemic health effects in end users. Experimental testing on animals and humans reports that atrazine is not a skin irritant or a skin sensitiser and at most a slight eye irritant. However a small number of published studies describe irritation, contact dermatitis and positive patch testing in farm workers using atrazine (see Section 2.2.1).

The potential for long term health effects forms the basis for assessing the risk to atrazine end users.

Home Garden Products

Workers engaged in small scale weed control may use home garden products. Only small areas could be treated with the contents of one package, making use of this type of product impractical for large areas. Use would be infrequent because atrazine gives residual weed control and concentrations of atrazine in the final spray are low (maximum of 0.17%). Considering these factors, the protective clothing specified in the toxicological assessment will offer sufficient protection for any workers also using home garden products.

Broadacre - all agriculture uses

Predicted exposures using POEM and the worker exposure studies extrapolated to Australian conditions, indicate acceptable risk for the majority of users. This takes into account the fact that large crop growers would use enclosed cabs and that bulk liquid product containers would be used if large areas required treatment. Where a large amount of product is needed and bulk containers are not an option, solid formulations should be used in preference to liquid formulations.

Scenarios falling outside the above are broadacre excluding lucerne/lupins using the minimum volume of 50 L/ha, and sugar cane using the minimum volume of 50 L/ha. Predicted applicator exposure is high in both cases.

Considering the broadacre use, the Hofherr (1993) study measured applicator exposure under similar conditions to the Australian use (closed cabs). Comparing POEM exposure for applicators beneath protective clothing and the measured exposure (at the 75th percentile, converted to 6 hour spraying and corrected for a 10-fold concentration difference), indicates that predicted exposure overestimates measured exposure by a factor of 5.5. On this basis, the risk at minimum spray volumes would be acceptable.

Honeycutt *et al*. (1996) and Selman and Rosenheck (1996) measured exposure under conditions similar to the Australian ground spraying situation. In most instances, MOE (GM and range) for workers performing separate tasks were high. Open mixing was acceptable only for M/L/A using closed cabs and treating small areas. M/L/A treating large areas would need to use atrazine from bulk containers as well as closed cabs.

Similar conclusions are reached using MOE generated from PHED exposures provided by Breckenridge (1996). Workers treating small areas may use open mixing and open cabs. In large areas however, closed mixing and closed cabs are preferred.

Considering the sugar cane use, the application equipment used in POEM is not completely appropriate for sugar cane treatment and a spray volume below 180 L/ha would not be used. Therefore sugar cane use is acceptable.

<u>Forestry</u>

Predicted exposure for knapsack use from POEM indicate low and unacceptable MOE.

The surrogate study of Tack (1995) for simazine application by knapsack spraying indicates high and acceptable MOE when extrapolated to the Australian forestry use pattern. Operators wore extensive protective clothing, including lower leg protection. The study demonstrated the importance of well maintained knapsack equipment, in protecting workers from spills and excessive contamination.

One worker exposure study (Rosenheck *et al*., 1993) involving some extrapolation across use patterns to cover forestry operations, indicates high MOE for hand directed spraying from a vehicle mounted tank. The operator wore extensive personal protective clothing and this needs to be taken into account in the safety directions.

PHED exposures of Breckenridge (1996), standardised for handgun use in forestry, indicate acceptable MOE. Details of mixer/loader or spray tank size are not provided, but the description does not imply knapsack use.

Rosenheck *et al*. (1993) indicated visible contamination and low MOE for a worker hand dispensing atrazine granules via a hand operated cranking handle. PHED exposures for the granular handspreader, taken to be a similar dispenser, indicate low MOE. The same high risk is unlikely to apply to the Weed-A-Metre, where the plastic granule holder and dispensing method should not involve the same amount of exposure.

Predicted or measured exposure was not available to assess granular use by direct application from specialised ground application equipment. Given that no mixing is needed and application is controlled, this use is acceptable.

Forestry boom spray use was assessed using POEM and the findings are similar to those for broadacre use. Results indicate acceptable risk, in some cases by taking into account that large areas would be treated from enclosed cabs and that bulk liquid product containers would be used if large areas required treatment. Where a large amount of product is needed and bulk containers are not an option, solid formulations should be used in preference to liquid formulations.

Boom spraying at the maximum atrazine concentration and using the minimum volume of 50 L/ha results in high predicted exposure and low MOE, even when a small number of hectares per day is treated. The findings from Hofherr (1993) may again be used under the rationale used to discuss a similar outcome for broadacre applications by boomspray with closed cabs. Comparing POEM exposure for applicators beneath protective clothing and the measured exposure (at the 75th percentile, converted to 6 hour spraying and corrected for a 23-fold concentration difference), indicates that predicted exposure overestimates measured exposure by a factor of 6.4. On this basis, the risk at minimum spray volumes would be acceptable.

4.6 Aerial spraying and human flagging - assessment and conclusions

The NRA PQs (Table 2) show that hundreds of hectares may be treated per day by air in both agriculture and forestry operations. The working strength atrazine concentration is higher in aerial sprays than ground sprays (20% vs 6%). There were no worker studies submitted for aerial sprayers, apart from PHED exposures. The predictive model is not designed for aerial spraying.

The PQs reported that atrazine products were either poured into vats and pumped to the plane or directly pumped to the plane. An open pour method would not be possible with liquids in containers > 20 L. To treat the required areas, bulk supplies of atrazine would be needed as using many small (ie 20 L) container sizes would be impractical. Direct transfer of bulk product should enable more effective control of exposure, ie spillage. Hand and body protective clothing will be needed for mixer/loaders.

Atrazine is sprayed from fixed-wing aircraft and helicopters. Spray pilots are protected against direct exposure to spray mist.

Atrazine granules may be applied undiluted from aircraft fitted with specialised nozzles. Exposure during transfer will be limited and pilots should not be contaminated during application.

Exposure generated from PHED (Breckenridge, 1996) and standardised for Australian conditions using liquid products, indicates acceptable MOE for closed mixing and aerial spraying. Open mixing is not acceptable.

Flaggers involved in aerial spraying would become contaminated with spray mist. Exposure was quantified through PHED. MOE are high. However the OHS assessment cannot rely solely on this figure as there is no supporting information describing if the flaggers were protected by control measures, for example by sitting in vehicles.

In conclusion, existing aerial application uses of atrazine are supported. The use of human flaggers is not supported, unless protected by engineering controls such as enclosed cabs.

4.7 Personal protective equipment indicated by the risk assessment

Personal protective equipment (PPE) for atrazine products from the Handbook of First Aid Instructions and Safety Directions (1996) is listed in Table 20.

Table 20: Current PPE for atrazine from the Handbook of First Aid Instructions and Safety Directions

Formulation	Code	PPE
WP, SC, WG all strengths except where specified	294	elbow-length PVC gloves
GR 170 g/kg or less with hexazinone 50 g/kg or less	294 299	elbow-length PVC gloves, face shield or goggles
HG SC 350 g/L or less with amitrole 350 g/L or less	312	rubber gloves
SC 250 g/L or less with dicamba 135 g/L or less	292 294	cotton overalls buttoned to the neck and wrist and a washable hat, elbow-length PVC gloves

The study of barrier effectiveness of various woven fabric types (Raheel, 1988), demonstrated the best barrier protection was afforded by olefin (Tyvek), 100% cotton and polyester (PET)/cotton (50/50). Atrazine residues do not persist in home laundered cotton coveralls (Stone & Stahr, 1989). The specification of cotton overalls in Safety Directions statements remains appropriate.

The exposure and risk assessment for atrazine indicates that elbow length PVC gloves, hat and cotton overalls are needed for workers handling the concentrate (liquid, wettable powder, granule, water dispersible granule) and spray.

Hand directed liquid sprayers require in addition, waterproof trousers and boots.

Hand directed granular applicators require in addition, chemical resistant footwear.

Some atrazine products are mixtures with amitrole, ametryn, dicamba, hexazinone or metolachlor. Current Handbook entries do not cover all the mixed chemical products.

To overcome the above deficiencies, the existing personal protective equipment specifications on current atrazine products should be revised in accordance with the OHS risk assessment.

There is no conflict in specifications for personal protective clothing for atrazine when it is tank mixed with amitrole, diquat, fluroxypyr, glyphosate, hexazinone, metolachlor, paraquat, pendimethalin, picloram, simazine or sulfometuron-methyl.

4.8 Re-entry and re-handling

No information or worker exposure studies covering re-entry into atrazine-treated areas were submitted for review. The use pattern for atrazine indicates that for broadacre use, it is applied some time prior to or in the early stages of crop growth, with essentially no dislodgeable residues on growing plants. Applications to sugar cane may occur within the first few months of crop growth but frequent entry for crop maintenance is not necessary and any whole crop activities, including harvest, are carried out mechanically. In forestry, atrazine is used some months prior to tree planting with follow up applications around the base of trees up to two years old if necessary. For none of these uses would entry into treated areas be required for crop tending activities or other activities of long duration. Atrazine is used to kill weeds in potato crops prior to harvest. However, as any treated weeds will have died by harvest, and harvesting is a mechanical operation, any residual atrazine will be low. Workers handling harvested potatoes may come into contact with atrazine soil residues. The EA atrazine report summarised field dissipation data where extractable atrazine residues peaked at 2.9 mg/kg in the 10-20 cm soil layer 60 days after application. Workers contaminated with soil at this concentration would need to completely absorb atrazine residues from more than 7000 kg soil to exceed the NOEL. This situation is not possible.

Current product labels do not include a re-entry period for atrazine.

The qualitative risk assessment indicates that a re-entry period for atrazine treated areas is not required.

5 OCCUPATIONAL CONTROLS

Atrazine is classified as a hazardous substance according to National Occupational Health and Safety Commission (NOHSC) criteria. Hazardous substances are subject to the workplace controls outlined in the NOHSC Control of Workplace Hazardous Substances (NOHSC, 1994b).

5.1 Safety Directions

The exposure and risk assessment for atrazine indicates that elbow length PVC gloves, hat and cotton overalls are needed for workers handling the concentrate (liquid, wettable powder, granule, water dispersible granule) and spray.

Hand directed liquid sprayers require in addition, waterproof trousers and boots.

Hand directed granular applicators require in addition, chemical resistant footwear.

Some atrazine products are mixtures with amitrole, ametryn, dicamba, hexazinone or metolachlor. Current Handbook entries do not cover all the mixed chemical products.

To overcome the above deficiencies, the existing PPE specifications on current atrazine products should be revised in accordance with the OHS risk assessment.

5.2 Education and Training

No special training is indicated on the basis of this assessment.

5.3 Information provision

5.3.1 Labels

Atrazine is a hazardous substance. Atrazine labels should be in accordance with the NOHSC code of practice for labelling of hazardous substances (NOHSC, 1994c).

All atrazine products assessed are hazardous substances. All product labels require a reference to the Material Safety Data Sheet.

5.3.2 Material safety data sheet

A Material Safety Data Sheet is required for atrazine, where it is handled by Australian workers.

A Material Safety Data Sheet is required for all atrazine products reviewed in this assessment, in accordance with the NOHSC code of practice (NOHSC, 1994d).

5.4 Occupational exposure monitoring

5.4.1 Atmospheric monitoring

There is a NOHSC Exposure Standard for atrazine of 5 mg/m^3 TWA (NOHSC, 1995).

Formulators of atrazine products in Australia will need to control exposure in accordance with the NOHSC Exposure Standard.

5.4.2 Health surveillance

NOHSC has not placed atrazine on the Schedule for Health Surveillance (Schedule 3 Hazardous Substances for which Health Surveillance is Required).

6 RECOMMENDATIONS

Worksafe Australia has reviewed the current uses of atrazine under the Existing Chemicals Review Program and makes the following recommendations. These do not apply to Home Garden products.

Registration

All existing uses of atrazine are supported, with the following restrictions to go on the product labels:

(1) No hand dispensing of atrazine via dust-prone methods e.g. hand-operated cranking handle. Only use with applicators specifically designed to dispense granular products with minimum dust e.g. the Weed-A-Metre granular dispenser, the Swissmex manual applicator, the Forest Mac applicator.

(2) No human flaggers in aerial spraying, unless protected by engineering controls such as enclosed cabs.

(3) A minimum ground spray volume of 50 L water per hectare (without supporting data for specific uses).

Other

(4) When a large amount of product is needed and bulk containers are not an option, solid formulations should be used in preference to liquid formulations. A mechanism for the distribution of this advice should be determined by the NRA.

(5) All registrants formulating atrazine products in Australia need to label technical grade atrazine and produce a material safety data sheet for atrazine, in accordance with hazardous substances regulations.

(6) All registrants of current atrazine products need to produce a product material safety data sheet.

(7) All existing atrazine product labels require a reference to the material safety data sheet.

(8) Deficiencies exist in the current atrazine entries in the Handbook of First Aid Instructions and Safety Directions (1996) on the basis of this occupational health and safety review. Safety directions should be revised in accordance with this assessment.

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ATTACHMENTS

Attachment 1: **Summary of National Registration Authority Performance Questionnaires**
Attachment 2: **Results from POEM Estimates 1-40**
Attachment 3: **Dose and MOE from POEM Estimates**

Attachment 1: National Registration Authority Performance Questionnaires No 1: Agricultural Chemical Users (large scale)

End use	State	Frequency	Application rate	Use pattern	Tank mix pesticides
Forestry	TAS	once a year	4.5-8 L/ha	150 ha/hr (aerial); 6 ha/hr (ground spray, 1.5 m strip, 3-4 m apart); 2 ha/hr (ground broadcast spray); 1 ha/hr (hand strip spray); 0.75 ha/hr (hand spot spray).	glyphosate, hexazinone
Wheat, barley and lupins	WA	once a year	0.5 L/ha	45 ha/hr (boom spray)	glyphosate
Lupins	VIC	once a year		10 ha/hr (boom spray)	simazine
Grain sorghum and fallows	NSW	once a year		10 ha/hr (boom spray)	knockdown herbicides
P. Radiata plantation	SA	twice in first 2 years of 30 year rotation	4.5 kg ai/ha	direct mixing in ground spray tank or mixing vat (aerial). 3 ha/hr (tractor with boom spray), 50 ha/hr (aerial micronair)	hexazinone, amitrol
Forestry	SA	once in first 2 years of 35 year rotation	4.5 kg ai/ha	30-40 ha/hr (aerial), 1-1.5 ha/hr (ground boom). Hand directed is limited only to granules.	amitrol, hexazinone
Not provided	QLD			20 ha/hr (mixed in tank, boom spray)	
Sorghum, corn and maize	QLD	once a year	1 L/ha	20 ha/hr (mixed in spray tank, air assisted hydraulic boom with flat fan nozzles)	
Eucalyptus plantation	WA	once a year	1.5-2.5 kg ai/ha	4-5 ha/hr (boom spray from motor bikes, 4 wheel drives and tractors, 1.5-2 m strip over 4-5 m row).	glyphosate, sulfometuron-methyl
Maize and sorghum	WA	once a year	1.8 kg ai/ha (maize/sorghum); 9-10.8 kg ai/ha (irrigation channels)	pre-mix in agitated tank. 12-15 ha/hr (boom spray), 25-30 ha/hr (aerial)	metolachlor, paraquat, glyphosate
Maize grower	NSW	once a year		5 ha/hr (boom spray).	metolachlor.
P. radiata and Eucalyptus plantation	Tas		8 kg ai/ha, pre and post emergent spray	10-12 ha/hr (mixed in tank, boom spray); 40 ha/hr (mixed in tank, helicopter via hydraulic nozzles); 1 ha/hr (mixed in tank, hand spray).	
Sorghum crops and fallows	QLD	once a year	2 L/ha,	10 ha/hr (mixed in tank with agitation, boom spray).	picloram, fluoxypyr, glyphosate
Pest control	SA			non-crop, application using hand spray	

National Registration Authority Performance Questionnaire No 4: State chemical coordinators

State	Comments
NSW	Nothing of relevance to occupational health and safety.
QLD	Nothing of relevance to occupational health and safety.
NT	Projected increase in use as more agricultural land is available.
TAS	Nothing of relevance to occupational health and safety.
VIC	Nothing of relevance to occupational health and safety.
WA	Projected increase in use in forestry and agriculture (canola and lupins).

National Registration Authority Performance Questionnaire No 5: Chemical industry survey

Company	Use pattern	Mixing/Loading	Application method
Chemical Recovery Co Pty Ltd	25 g/8 L water/40 m^2 - home garden		
David Gray & Co Pty Limited	6 kg/ha boom spray in railway, forests and vineyards		Knapsack, boom and power spray
Davison Industry Pty Ltd	not provide	not provide	not provide
Macspred Pty Ltd	4.5 kg ai/ha (1.5 kg/ha hexazinone). 10 ha/hr (hand application), 40 ha/hr (ground boom spray) and 200 ha/hr (aerial application for both fixed wing and helicopter)	No mixing equipment used with the granular product.	Applied by hand held equipment (Weed-A-Metre), pneumatic blowers for ground application and pneumatic equipment (Simplex VLW) for aerial application of dry granules.
Ciba-Geigy Australia Ltd		Contents of bags and drums are poured directly into spray vat. Aerial operators either pour product into vat connected via a hose to the tank in the plane, or aspirate the product directly from the drum.	Most common application methods are by tractor or 4WD mounted boom spray (2-10 ha/hr). In forest situations, helicopters are used (80 ha/hr). Knapsack sprayers and fixed wing aircraft are rarely used.
Crop Care Australasia Pty Ltd	Lucerne and fallow are usually one application per year. Maize/sweet corn is one application per season. Sorghum, when combined with fallow application, is maximum of two applications per year. Sugar cane is up to three applications per year over a six month period during spring/summer/autumn. 20-500 ha/hr(aerial), 30 ha/hr (ground spray), 4 ha/hr (high clearance tractor)	For an increasing number of new machines, mixing is self mixing via venturi or other metering devices from hopper into mixture. For machines without self-mixing, product is added to the spray vat when half filled with water and the agitator is running. Suspension concentrate is usually premixed in a bucket, while the granular product is introduced directly into the half-filled tank with agitator running or washed through the filter screen. For aerial application, product is mixed in a similar way to ground rig application. Aircraft is loaded with required volume using GPS calibrated log sheets.	Both aerial and ground application are used depending on the crop and conditions. Aerial application is commonly used for fallows and sugar cane, and may be used for sorghum. High clearance tractors are increasingly being used for sugar cane in lieu of aerial application. Ground rig sprayers use a boom spray; Aerial operators would use hydraulic nozzles; most use GPS systems. Hand held equipment may be used for spot spraying.
Nufarm Limited	2-3 kg/ha (sugar cane), 1-3 kg/ha (sorghum/maize/canola), 1-4 kg/ha (*P radiata*), 1.8-3 kg/ha (fallow) Boom spray 20-30 ha/hr Row crop 5-10 ha/hr		

National Registration Authority Performance Questionnaire No 6: Commodity/Grower Group Survey

State	Use pattern	Mixing/loading	Application equipment	Tank mix pesticide
NSW	maize 2 L/ha, once a year	mix in premix or sprayer tank prior to use	12 m boom spray	pendimethalin
Victoria			boom spray	diquat and paraquat, glyphosate
NSW	canola 1-2 L/ha, 1-2 times per year	mixed in spray tank.	boom spray with 110^{o} flat fan nozzles	simazine
Victoria	canola crops 2 L/ha, once a year, 50-100 L water/ha		boom spray	simazine
WA	canola 2.5 L/ha , 1-2 times per year. Lupins, 2 L/ha, 1-2 times per year.	mixed in spray tank	boom spray	simazine
WA	tree lines, canola, lupins, 2 L/ha	powder products are pre-mixed with water. Liquid products are mixed directly in the spray tank.	boom spray	

Results from POEM Estimates 1-40

Applicaton	Product	Application rate kg ai/ha	spray L/ha	ha/day	Dermal dose (mg/kg bw/day) M/L (no PPE)	M/L (gloves)	Application (no PPE)	Application (gloves)	Application (gloves & overalls)	Inhalation (mg/kg bw/day)
1. V-nozzle	S900	3	50	12	0.053	0.001	0.490	0.076	0.049	0.060
2. V-nozzle	L500	3	50	12	0.197	0.010	0.490	0.076	0.049	0.060
3. V-nozzle	S900	3	50	270	0.062	0.011	0.490	0.076	0.049	0.060
4. V-nozzle	L500	3	50	270	3.983	0.199	0.490	0.076	0.049	0.060
5. V-nozzle	S900	3	400	12	0.053	0.001	0.061	0.010	0.006	0.007
6. V-nozzle	L500	3	400	12	0.197	0.010	0.061	0.010	0.006	0.008
7. V-nozzle	S900	3	400	270	1.062	0.011	0.061	0.010	0.006	0.007
8. V-nozzle	L500	3	400	270	3.983	0.199	0.061	0.010	0.006	0.008
9. V-nozzle	S900	0.55	50	12	0.018	<0.001	0.090	0.014	0.009	0.011
10. V-nozzle	L500	0.55	50	12	0.049	0.002	0.090	0.014	0.009	0.011
11. V-nozzle	S900	0.55	50	270	0.195	0.002	0.090	0.014	0.009	0.011
12. V-nozzle	L500	0.55	50	270	0.738	0.037	0.090	0.014	0.009	0.011
13. V-nozzle	S900	0.55	140	12	0.018	<0.001	0.032	0.005	0.003	0.004
14. V-nozzle	L500	0.55	140	12	0.049	0.002	0.032	0.005	0.003	0.004
15. V-nozzle	S900	0.55	140	270	0.195	0.002	0.032	0.005	0.003	0.004
16. V-nozzle	L500	0.55	140	270	0.738	0.037	0.032	0.005	0.003	0.004
17. V-nozzle	S900	1.15	100	5	0.018	<0.001	0.094	0.015	0.009	0.012
18. V-nozzle	L500	1.15	100	5	0.049	0.002	0.094	0.015	0.009	0.012
19. V-nozzle	S900	1.15	100	50	0.089	0.001	0.094	0.015	0.009	0.012
20. V-nozzle	L500	1.15	100	50	0.295	0.015	0.094	0.015	0.009	0.012
21. V-nozzle	S900	3	50	20	0.089	0.001	0.490	0.076	0.049	0.060
22. V-nozzle	L500	3	50	20	0.295	0.015	0.490	0.076	0.049	0.060
23. V-nozzle	S900	3	250	20	0.089	0.001	0.098	0.015	0.010	0.012
24. V-nozzle	L500	3	250	20	0.295	0.015	0.098	0.015	0.010	0.012
25. H-nozzle	S900	8	50	1	0.071	0.001	3.210	1.558		0.320
26. H-nozzle	L500	8	50	1	0.197	0.010	3.210	1.558		0.320
27. H-nozzle	S900	8	200	1	0.248	0.002	0.802	0.389		0.080
28. H-nozzle	L500	8	200	1	0.688	0.034	0.802	0.389		0.080
29. H-nozzle	S900	8	50	1 (3 h)	0.071	0.001	1.605	0.779		0.160
30. H-nozzle	L500	8	50	1 (3 h)	0.197	0.010	1.605	0.779		0.160
31. H-nozzle	S900	8	200	1 (3 h)	0.248	0.002	0.401	0.195		0.040
32. H-nozzle	L500	8	200	1 (3 h)	0.688	0.034	0.401	0.195		0.040
33. V-nozzle	S900	8	50	6	0.071	0.001	1.307	0.203	0.131	0.160

Applicaton	Product	kg ai/ha	spray L/ha	ha/day	M/L (no PPE)	M/L (gloves)	Application (no PPE)	Application (gloves)	Application (gloves & overalls)	(mg/kg bw/day)
34. V-nozzle	L500	8	50	6	0.246	0.012	1.307	0.203	0.131	0.160
35. V-nozzle	S900	8	50	72	0.761	0.008	1.307	0.203	0.131	0.160
36. V-nozzle	L500	8	50	72	2.852	0.143	1.307	0.203	0.131	0.160
37. V-nozzle	S900	8	1000	6	0.071	0.001	0.065	0.010	0.007	0.008
38. V-nozzle	L500	8	1000	6	0.246	0.012	0.065	0.010	0.007	0.008
39. V-nozzle	S900	8	1000	72	0.761	0.008	0.065	0.010	0.007	0.008
40. V-nozzle	L500	8	1000	72	2.852	0.143	0.065	0.010	0.007	0.008

Estimate	EUP	Application rate			Dose (mg/kg bw/day)				Margin of Exposure (MOE)			
		kg ai/ha	spray L/ha	ha/day	no PPE	gloves (M/L)	gloves (M/L/A)	gloves & overalls (M/L/A)	no PPE	gloves (M/L)	gloves (M/L/A)	gloves & overalls (M/L/A)
1. V-nozzle	S900	3	50	12	0.603	0.551	0.137	0.11	7	7	30	37
2. V-nozzle	L500	3	50	12	0.747	0.56	0.146	0.119	5	7	28	34
3. V-nozzle	S900	3	50	270	1.612	0.561	0.147	0.12	3	7	28	34
4. V-nozzle	L500	3	50	270	4.533	0.749	0.335	0.308	<1	5	12	13
5. V-nozzle	S900	3	400	12	0.122	0.069	0.018	0.014	33	59	228	293
6. V-nozzle	L500	3	400	12	0.265	0.079	0.027	0.023	15	52	152	178
7. V-nozzle	S900	3	400	270	1.131	0.079	0.028	0.024	4	52	146	171
8. V-nozzle	L500	3	400	270	4.051	0.268	0.216	0.213	1	15	19	19
9. V-nozzle	S900	0.55	50	12	0.119	0.101	0.025	0.02	34	41	164	205
10. V-nozzle	L500	0.55	50	12	0.15	0.103	0.027	0.022	27	40	152	186
11. V-nozzle	S900	0.55	50	270	0.296	0.103	0.027	0.022	14	40	152	186
12. V-nozzle	L500	0.55	50	270	0.838	0.138	0.062	0.057	5	30	66	72
13. V-nozzle	S900	0.55	140	12	0.054	0.036	0.009	0.007	76	114	456	586
14. V-nozzle	L500	0.55	140	12	0.085	0.038	0.011	0.01	48	108	373	410
15. V-nozzle	S900	0.55	140	270	0.231	0.038	0.011	0.009	18	108	373	456
16. V-nozzle	L500	0.55	140	270	0.774	0.073	0.046	0.044	5	56	89	93
17. V-nozzle	S900	1.15	100	5	0.123	0.106	0.026	0.021	33	39	158	195
18. V-nozzle	L500	1.15	100	5	0.155	0.108	0.029	0.023	26	38	141	178
19. V-nozzle	S900	1.15	100	50	0.194	0.106	0.027	0.022	21	39	152	186
20. V-nozzle	L500	1.15	100	50	0.4	0.12	0.041	0.036	10	34	100	114
21. V-nozzle	S900	3	50	20	0.639	0.551	0.137	0.11	6	7	30	37
22. V-nozzle	L500	3	50	20	0.845	0.565	0.151	0.124	5	7	27	33
23. V-nozzle	S900	3	250	20	0.199	0.111	0.028	0.023	21	37	146	178
24. V-nozzle	L500	3	250	20	0.405	0.125	0.042	0.037	10	33	98	111
25. H-nozzle	S900	8	50	1	3.600	3.530	1.878		1	1	2	
26. H-nozzle	L500	8	50	1	3.726	3.539	1.887		1	1	2	
27. H-nozzle	S900	8	200	1	1.130	0.885	0.472		4	5	9	
28. H-nozzle	L500	8	200	1	1.571	0.917	0.504		3	4	8	
29. H-nozzle	S900	8	50	1 (3 h)	1.836	1.766	0.940		2	2	4	
30. H-nozzle	L500	8	50	1 (3 h)	1.961	1.775	0.949		2	2	4	
31. H-nozzle	S900	8	200	1 (3 h)	0.689	0.444	0.237		6	9	17	
32. H-nozzle	L500	8	200	1 (3 h)	1.130	0.476	0.269		4	9	15	
33. V-nozzle	S900	8	50	6	1.538	1.468	0.364	0.291	3	3	11	14
34. V-nozzle	L500	8	50	6	1.713	1.48	0.375	0.303	2	3	11	14
35. V-nozzle	S900	8	50	72	2.229	1.475	0.371	0.298	2	3	11	14
Estimate	**EUP**	**Application rate**			**Dose (mg/kg bw/day)**				**Margin of Exposure (MOE)**			
		kg	spray	ha/day	no PPE	gloves	gloves	gloves &	no PPE	gloves	gloves	gloves &

		ai/ha	L/ha			(M/L)	(M/L/A)	overalls (M/L/A)		(M/L)	(M/L/A)	overalls (M/L/A)
36. V-nozzle	L500	8	50	72	4.319	1.61	0.506	0.433	<1	3	8	9
37. V-nozzle	S900	8	1000	6	0.144	0.074	0.019	0.015	28	55	216	273
38. V-nozzle	L500	8	1000	6	0.319	0.086	0.03	0.027	13	48	137	152
39. V-nozzle	S900	8	1000	72	0.834	0.081	0.026	0.022	5	51	158	186
40. V-nozzle	L500	8	1000	72	2.925	0.216	0.161	0.157	1	19	25	26

Estimate No: 1

Estimate No: 2

Estimate No: 3

Estimate No: 4

Estimate No: 5

Estimate No: 6

Estimate No: 7

Estimate No: 8

Estimate No: 9

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