Section 6

ENVIRONMENTAL ASSESSMENT

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1. INTRODUCTION

Atrazine has a history of aquatic contamination that contributed to its selection for review.

Atrazine is a widely used herbicide for control of grassy and broadleaf weeds in maize, sorghum, sugarcane, timber plantations (pines and eucalypts), established lucerne, grass seed crops and potatoes. Atrazine is also used for weed control in conservation tillage farming systems, for seed bed establishment prior to planting sorghum, or for fallow maintenance prior to wheat, peas or lupins. The NRA announced in July 1994 that previous uses in non-crop situations such as fencelines, rights of way and irrigation channels would be discontinued by December 1995 because of concerns for aquatic contamination. These discontinued uses generally involved much higher rates of application in situations conducive to off target movement to water.

2. CHEMICAL IDENTITY AND PROPERTIES

Atrazine is a herbicide from the s-triazine group. It is a crystalline solid with significant water solubility (30 mg/L) and a relatively low partition coefficient. See Section 2 (Chemistry assessment) for details.

3. FORMULATION OF END-USE PRODUCT

Atrazine is available as dry flowable, flowable liquid, soluble concentrate, wettable powder, granular and water dispersible granule formulations, either alone or as a mixture with other herbicides (amitrole, metolachlor, ametryn, hexazinone).

4. ENVIRONMENTAL EXPOSURE

4.1 Environmental release

4.1.1 Volume

Atrazine use in the Condamine-Balonne-Culgoa catchment of Queensland has been estimated at 264 tonnes annually, with less than a tonne used in non-crop situations (Rayment and Simpson, 1993). Annual use on sugarcane has been estimated at 331 tonnes (Hamilton and Haydon, 1996) which would translate to about 2200 tonnes across all crops based on sales distribution figures provided by Ciba-Geigy. Note that earlier estimates by the Bureau of Sugar Experimental Stations, reported to the NRA by the Queensland Department of Primary Industries in September 1993, were much lower at 57-83 tonnes. Annual

consumption of atrazine in the USA exceeds 30 000 tonnes (Solomon *et al*, 1996).

4.1.2 Application and use pattern

Note that the revised conditions of use for atrazine introduced by the National Registration Authority in late 1994 (to take effect by December 1995) include the following restrictions:

- no mixing/loading or application within 20 m of any well, sink holes, intermittent or perennial stream;
- no application within 60 m of natural or impounded lakes or dams;
- no use in industrial and non-agricultural situations; and
- maximum annual rate of application to be 3 kg/ha in all crops except plantation forestry.

Performance Questionnaires returned by users and registrants during 1996 indicate that the above restrictions have yet to be fully observed. For example, a user at Kununurra, WA, reports continued use in irrigation channels at 10-12 kg/ha. A South Australian pest control business reports continued use in non-crop situations, and that no alternative chemicals are available to replace this use. As noted below, one registrant reports seasonal use on sugar well in excess of the above restriction. Another registrant reports that use continues on railways, and that application rates to 6 kg/ha remain current.

It has also been reported recently that some aerial contractors in northern NSW remain unaware of the current prohibition on use of atrazine for irrigation channel hygiene (O'Brien, 1996).

In general, ground based application predominates, but aircraft are commonly used in fallow situations and sugar cane, and helicopter application is widely used in plantation forestry.

Except where otherwise specified, the following details of how atrazine is applied were provided by Ciba-Geigy. They are assumed to be generally representative of atrazine use patterns in Australia. Cropping details are taken from Australian Agriculture (National Farmers Federation, 1995).

4.1.2.1 Sorghum, Broom Millet, Sacchaline and Forage Sorghum, Maize and Sweetcorn

Atrazine is applied to these summer crops mostly pre-emergence, with some post-emergence application, in such products as Gesaprim 500SC, Atrazine Granules 900WG and Primextra. Use may occur between September and December. Use also occurs in the fallow before planting, especially in conservation farming systems, in order to maintain soil moisture. Application is mostly by tractor or 4WD vehicle mounted boom spray, with some aerial application (fixed wing) when soils are wet. Pre-emergence applications use between 1.8 and 3.0 kg/ha active, depending on soil type, or 1.25 kg/ha in combination with metolachlor. Post-emergence rates are 0.5 kg/ha (with added 2,4-D or dicamba).

The area planted to sorghum, the main crop in this group, has fluctuated between about 400 and 600 thousand ha in recent years, with Southern and Central Queensland accounting for some 60-80% of production and most of the rest grown in the Northern and Liverpool Plains areas of NSW. Production is expected to increase in the medium term with a return to more normal seasonal conditions and increased demand for beef lotfeeding. Maize production occupies some 10% of the area planted to sorghum, again mostly in Queensland. Sorghum is generally a rainfed crop, apart from the southern plains area where it is mostly irrigated.

NSW Agriculture advised in September 1995 that some 75% of its last sorghum crop (147 thousand ha) and 90% of maize (22 thousand ha) were treated with atrazine. Assuming an average application rate of 2 kg/ha, this equates to 260 tonnes atrazine.

Performance questionnaires returned by growers indicate a general preference for pre-emergence applications for effective weed control, a view endorsed by NSW Agriculture. The need for post application rainfall with this soil active herbicide is noted, as is a reduction in efficacy and residual control when rains are heavy. Note that pre-emergence applications are not universally favoured. A grower from Clermont in Central Queensland applies at the 3-4 leaf stage at a much lower rate than required pre-emergence, arguing that this helps retain farm flexibility in areas of unreliable rainfall by not tying up country should adequate rains fail to arrive. The lower rate only provides control for 3 months but this is adequate for the use pattern, and avoids the risk of atrazine tie up in the following season. Importantly, the risk of aquatic contamination is reduced in situations of lower soil residue levels.

4.1.2.2 Sugarcane

Use is mostly post-emergence in combination with ametryn and paraquat, at rates of 2-3 kg/ha active, applied as large droplets (mostly floodjet nozzles) by tractor

mounted boom sprayer, or by aircraft. Application may occur between April and November.

Crop Care has indicated that 3 applications may occur to sugar over a 6 month period, each at about 2-3 kg/ha active ingredient. Such use would exceed the maximum annual rate of application of 3 kg/ha required by the NRA.

Sugarcane is grown in small areas of mainly alluvial soils along the Queensland coast, on river flats of the Clarence, Tweed and Richmond Rivers in northern NSW, and increasingly in the Ord River Irrigation Area in WA. In Queensland, some 264 thousand ha of cane was harvested during 1994. Queensland cane growing areas occupy about 457 thousand ha, or about 2% of their catchment areas (Hamilton and Haydon, 1996).

4.1.2.3 Plantation forestry

Use may occur within 2 weeks before planting, or post-planting. Weed control during the first two years of establishment is critical to the success of plantation forestry. Application is made by air (mostly helicopter), boom spray, spot gun or granule spreader, generally during the months of May to July, but including summer applications in Queensland to coincide with weed growth stimulated by summer rainfall. Annual application rates are restricted to 4.5 kg/ha active for sandy soils and those defined as highly erodible, and 8 kg/ha for clay loams and heavier textured soils, the higher rate being mainly used in Tasmania. Practices vary widely between States.

Off-target movement following winter applications is favoured by high rainfall and the prevailing high moisture levels. A number of respondents to performance questionnaires indicated that heavy rainfall reduces the residual activity of atrazine.

The States of Victoria, New South Wales, South Australia, Western Australia and Tasmania support 1 million ha of plantation forest, 91% of which is softwood. Plantation eucalypts are generally grown as monocultures for pulpwood on 15-25 year cycles, within which herbicides are necessary for the first one or two seasons.

In Western Australia, one organisation operates minimum rotations of 25 years for pines and 11 years for eucalypts. Application rates do not exceed 2.33 kg/ha active, significantly less than recommended for sandy soils, as the herbicide is applied in strips. Under the most intense conditions of use, a total of 4.66 kg/ha could be applied every 11 years to eucalypt plantations in WA (it is understood that this use has now been replaced by simazine, with atrazine retained only for pines).

The Queensland Department of Primary Industries indicated in September 1993 that second rotation hoop pines in Queensland are treated with atrazine three

times per season, each at 5 kg/ha. Information provided to the Forest Herbicide Research Management Group indicates that this use pattern may be continuing. Some 10 tonnes of atrazine was used for hoop pine production during 1992/93, primarily in the south-east corner. Simazine can also be used for hoop pine production.

While plantation forestry is a minor use for atrazine across Australia, in Tasmania it is the dominant use, with eucalypt plantations consuming some 40 tonnes during 1990 (Davies *et al*, 1994). Application occurs generally between May and November, usually after rain when soils are at field capacity. One forestry organisation in this State indicated it had embargoed the use of atrazine pending completion of the review, but expected to have difficulties with site access and reduced growth rates because of woody weed competition, with increased use of alternative herbicides possible following establishment. Atrazine was used at rates of 5-8 kg/ha, with most applications at the lower end of this range. The organisation has since indicated to the Forest Herbicide Research Management Group that it is unlikely to resume use of chlorinated triazines until the NRA ECRP review had been concluded, due to community and political opposition in Tasmania. A voluntary embargo was applied but this will be reviewed upon official release of the NRA report.

4.1.2.4 Minor uses

Established lucerne may receive a ground-based atrazine treatment (0.55 kg/ha) between May and July.

Grass seed crops may receive a ground-based atrazine treatment (0.9-1.1 kg/ha) during May or June.

Queensland pastures may receive a ground-based atrazine treatment (0.9-3.0 kg/ha) in May.

Western Australian lupins may be treated at 0.25-0.5 kg/ha (in combination with simazine). Application is mainly pre-emergence, with some very early post-emergence.

Atrazine is applied to potato crops at 1.15 kg/ha, in combination with amitrole and ammonium thiocyanate, as a harvest aid after the haulms have dried off and weeds are at the seedling stage.

A single non-agricultural use, control of Parthenium weed (pre- and post-emergence) along roadsides and rights of way, has been retained in Queensland, but at a reduced rate (from 4 to 3 kg/ha, consistent with the restrictions introduced by the NRA). The Queensland Department of Primary Industries advised in late 1993 that little had been used during the preceding years of drought, but an average 46 tonnes per annum was applied during the late 1980s along roadsides and in industrial situations. Roadside spraying was estimated to

occur over about 1600 ha, which would consume about 6 tonnes atrazine at 4 kg/ha. Atrazine is also regarded as an essential chemical to control Parthenium weed along railways in Central Queensland, but volumes of use are lower (estimated in 1993 at about 5 tonnes per annum, including control of volunteer cereals and broad leafed weeds).

Agriculture Victoria reports that atrazine is the most widely used herbicide for weed control in chickpeas (an off-label use). Use also occurs on faba beans, and is increasing on triazine resistant canola. Performance questionnaires returned by canola growers in NSW, Victoria and Western Australia indicate use to be mainly pre-emergence. The importance of clean seed lines is highlighted by recent experience in Western Australia where a number of growers planted seed contaminated with various weeds including species that have developed triazine resistance in New Zealand, from where the seed was sourced. In response, post-emergence atrazine applications at the 2-3 leaf stage have been recommended as specific chemical control measures for all Karoo canola crops in 1996 (Agriculture Western Australia, 1996).

One registrant reports use of its product in vineyards.

4.1.3 Environmental monitoring

Ciba-Geigy provided results of aquatic monitoring commissioned in Queensland (Simpson, 1988), Western Australia (Sheridan, 1991) and South Australia (Fennell and Stadter, 1991).

Queensland

No atrazine was found in samples from 28 bores in Queensland (Atherton Tablelands, Darling Downs and Lockyer Valley) but detections (0.7-12.4 µg/L) occurred in all six samples of surface water analysed (all collected from ring dams on the Darling Downs, where atrazine had been used on irrigated maize and sorghum). The date of sampling is not specified. It was stated that residues were slightly higher than would normally be expected because of dry conditions and a low water level in the dams (Simpson, 1988). Published sources (Simpson *et al*, 1988) cite a slightly broader range of detections in the ring dams (0.4-14.4 µg/L). Atrazine was not detected in water samples from the Condamine-Balonne catchment during 1991-1993, but detection limits were variable and ranged up to 10 µg/L (Rayment and Simpson, 1993).

The Queensland Department of Primary Industries (Central Region) indicated in a letter dated July 1995 that atrazine was found at low ppb levels in 43% of 133 surface water samples taken during 1994 from streams of the Fitzroy system. Data for the Fitzroy catchment are currently being compiled (Noble *et al*, 1996). Atrazine is by far the most abundant surface water contaminant, being present over the last 2-3 years in some 35% of samples (51% of those taken during flow

events) with a median concentration of 0.27 µg/L and a number of detections above 2 µg/L. Atrazine was absent, however, from upper catchment sites.

Western Australia

In Western Australia, atrazine was found (limit of detection 0.01 µg/L) at 16 of 47 wells where unconfined groundwater sources were sampled. Two wells at Esperance returned readings above 2 µg/L, as did a shallow sump at Vaughan. Sampling occurred in the Perth metropolitan area, the north-west of the State, the wheatbelt, the south-west coast and the south coast, with the majority of sites located in areas where atrazine may have been used (Sheridan, 1991).

Severe atrazine contamination of groundwater (up to 2000 µg/L) has been observed at one location in Perth, Western Australia. Contamination of the 10 m deep aquifer resulted from infiltration of equipment washwater into a soakaway at the residence of a pest control operator. Grab samples of soil indicated residues of 72 mg/kg atrazine in the soakaway (Appleyard, 1995).

One forestry business, operating in WA, indicated in its submission of July 1995 that atrazine may be detected at concentrations above 2 µg/L in intermittent streams draining sites with sandy soils. This contamination occurred during mid-winter when streams were in peak flow, and had subsided below 2 µg/L by early spring.

The Western Australian Department of Conservation and Land Management found atrazine in approximately half of all stream samples taken from sprayed plantation forestry areas during 1990 and 1991 (limit of determination 0.5 µg/L). The highest recorded level was 94 µg/L, with an average of 9.8 µg/L for samples recording over 1 µg/L atrazine.

South Australia

The South Australian investigations deliberately targeted vulnerable sites (shallow water tables and known use of atrazine). Atrazine was found in groundwater samples, at concentrations between 0.3 and 2.0 µg/L, at three of four sites where irrigated agriculture is practised and atrazine had been used for 10 years to suppress weeds in irrigation channels. Contamination was highest where atrazine had been most heavily used for the longest period, and the metabolite desethylatrazine (DEA) was also found at this site. Plantation forestry activities were also suspected of giving rise to groundwater contamination, with atrazine found (0.16-0.75 µg/L) at 1 of 4 sites where it had been used at 5 kg/ha in consecutive years for establishment of pine forests (Fennell and Stadter, 1991).

New South Wales

Atrazine remains the most commonly detected pesticide in many parts of Australia. Residues are found in the Gwydir, Namoi and Border Rivers of NSW,

but have been absent from the Macquarie basin in recent years, perhaps reflecting better flows and improved farm management practices (Cooper, 1995). Atrazine can be found throughout the river basins including their headwaters, with levels approaching 10 µg/L occurring within irrigated agriculture sites. Detailed investigations at one site on the Gwydir revealed that the contamination arose via irrigation supply channels, notwithstanding that no applications of atrazine to the channels had been made for at least 12 months. It was noted that some 25% of cotton growers used atrazine for irrigation channel hygiene during the 1994-95 season, and that only 45% of growers were aware of the proposed removal of this use, to take effect by December 1995.

Detection of moderate to high concentrations of atrazine continued to be a common feature of monitoring in the Gwydir, Namoi and Border river basins during the 1995-96 season, but with no clear temporal pattern. The Macquarie basin, where impacts from the drought continued to be felt, was again free of this contaminant (Cooper, 1996). Detections occurred upstream of and within irrigation areas, with 19% of samples taken within irrigated areas between November and March recording more than 0.5 µg/L. Peak concentrations approached 5 µg/L in Coxs Creek and exceeded 4 µg/L in the Mooki River following storm events during January, with peak instantaneous loads of 120 and 100 kg/day, respectively. The Liverpool Plains in the Upper Namoi valley, where dryland farming of cotton, sorghum, sunflowers and maize predominates during summer, was identified as a problem area due to a limited capacity to harvest storm runoff and store the water on-farm. Atrazine loads were considerably increased from the previous season when planting was reduced by drought and peak instantaneous loads during January storms were relatively low at 29 kg/day.

Recent surveys of cotton and other farmers in the Namoi basin help illuminate the aquatic contamination issue. Some farmers in the upper reaches, particularly on Coxs Creek, reportedly sprayed their fields only hours before heavy rain was expected, including in situations where pest pressure was low. These poor practices were motivated by the apprehension that some time may elapse after the rain before spraying could again be undertaken without violating the *Clean Waters Act* (O'Brien, 1996).

Persistent atrazine contamination of irrigation drainage water is also apparent in the Murrumbidgee and Coleambally Irrigation Areas of southern NSW (Korth *et al*, 1995). Samples from a drainage channel common to a catchment area of five rice farms and a maize farm contained detectable levels of atrazine throughout the 1993-94 summer cropping season, with peak levels in the order of 100 µg/L in early November. This peak level coincided with the appearance of metolachlor, perhaps reflecting post-emergence use of a metolachlor/atrazine combination on maize. The paper notes that atrazine may also have been used for weed control in one of the small on-farm drainage channels. A distinction has been made between atrazine and the more hydrophobic insecticides, such as endosulfan, that are used in the area, in that sorptive influences reduce concentrations in the water column as hydrophobic

contaminants travel through the drainage systems, whereas reductions in atrazine concentration require the passage of time rather than distance.

A submission to the NRA from an irrigation company confirmed that atrazine can be detected in irrigation drainage water, sampled from September 1994 to June 1995. However, residues were generally low, and only exceeded the environmental guideline of 2 µg/L proposed by the NSW EPA during the hot dry months of December and January when spraying and irrigation are frequent.

Victoria

Monitoring of surface waters in the Gippsland region of Victoria indicated the widespread presence of atrazine, but generally at levels below 1 µg/L. The exceptions were from a drain entering the Snowy River near Orbost (4.90 µg/L) and a stream near Bairnsdale (3.2 µg/L), both sampled after heavy rain. In each case, the source of contamination appears to have been irrigated sweetcorn (Chapman and Stranger, 1995).

Tasmania

In contrast to the widespread low-level aquatic contamination associated with the use of atrazine in cropping, significantly higher peak levels are associated with forestry practices, with residues on the day of application spanning over six orders of magnitude to 53 mg/L with a median concentration of 8.1 µg/L (Davies *et al*, 1994). The extreme value of 53 mg/L, significantly above atrazine's water solubility, is clearly an outlier. Unusual conditions may have contributed, but the underlying factors are unclear. It is expected that new restrictions, introduced by the NRA, should prevent a recurrence.

A key factor contributing to the higher residues appears to be timing of application. Herbicide maintenance in plantation forestry may occur from late autumn to late spring in temperate zones. Winter application in plantation forestry situations occurs when soils are already at field capacity, increasing the risk of runoff compared with the main use on summer crops.

A government organisation submission of September 1995 to the NRA details of drinking water contamination incidents associated with plantation forestry operations. In 1993, contamination of Olivers Creek, from which the residents of the small community of Lorinna in northern Tasmania draw their drinking water, occurred following use of atrazine in the catchment headwaters. The submission reports that contamination in excess of EC drinking water guidelines (0.1 µg/L) occurred despite the best efforts of operators, who responded to local opposition to the use of atrazine by observing a buffer of 170 m around the headwaters, applying by tractor mounted boom spray rather than aircraft, and avoiding use of atrazine in one third of the area to be sprayed. It is understood that these precautions may have been rendered ineffective by waterlogging on the site. Atrazine was still detectable in the creek a year and a half after spraying.

Monitoring by State authorities on 13 May 1993 (immediately after application) found atrazine at only one site, adjacent to the reforestation parcel that had been treated, at a concentration of 0.11 µg/L. Higher detections occurred at two sites on 9 July after heavy rainfall. The Tasmanian Director of Public Health indicated in a media release on 23 July 1993 that the highest detection was 2.9 µg/L.

The other well publicised incident involved contamination of the town water supply for Derby in northern Tasmania after exposure of two creeks in the catchment of the Cascade River during plantation forestry operations in June 1994. Media articles reported that tap water contamination in ensuing months ranged up to 0.3 µg/L atrazine.

The above incidents were also highlighted in submissions to the NRA from community groups

Groundwater

Apart from the studies commissioned by Ciba-Geigy, only limited information on atrazine contamination of Australian groundwater is available. Sampling of shallow groundwater near Shepparton, Victoria, found atrazine (range 0.022-0.063 µg/L) in 7 of 13 samples (Bauld *et al*, 1992). One well also contained the metabolite desisopropylatrazine (DIA; 0.16 µg/L). Similar frequencies of detection (50-80%) occurred in samples from Berriquin-Denimein (NSW), Padthaway (SA) and the Burdekin Delta (Qld). The highest recording at Padthaway was 0.785 µg/L, and 70% of positive samples also contained DEA, at levels to 1.013 µg/L. Only one negative sample contained this metabolite. For the Burdekin, atrazine concentrations ranged up to 0.806 µg/L, with 46% of positive samples also containing up to 0.42 µg/L DEA (Bauld, 1994). DEA is the most commonly found metabolite in groundwaters overseas.

The Queensland Department of Primary Industries (Central Region) indicated in a letter dated July 1995 that atrazine was found at low levels (ppb) in about 20% of samples from observation bores in the Fitzroy catchment during 1992-4. However, it was not detected in production bores in the Callide Valley, sampled in late 1994. These detections are confirmed in reports currently in draft (Noble *et al*, 1996).

A recent review of atrazine reports its detection in groundwater down to 30 m during the early 1990s in areas where broadacre use is common, particularly in the alluvial aquifers underlying the Liverpool Plains. Some 6% of samples tested positive for atrazine, generally at levels below 10 µg/L (Boey and Cooper, 1996).

4.1.4 Summary of environmental exposure

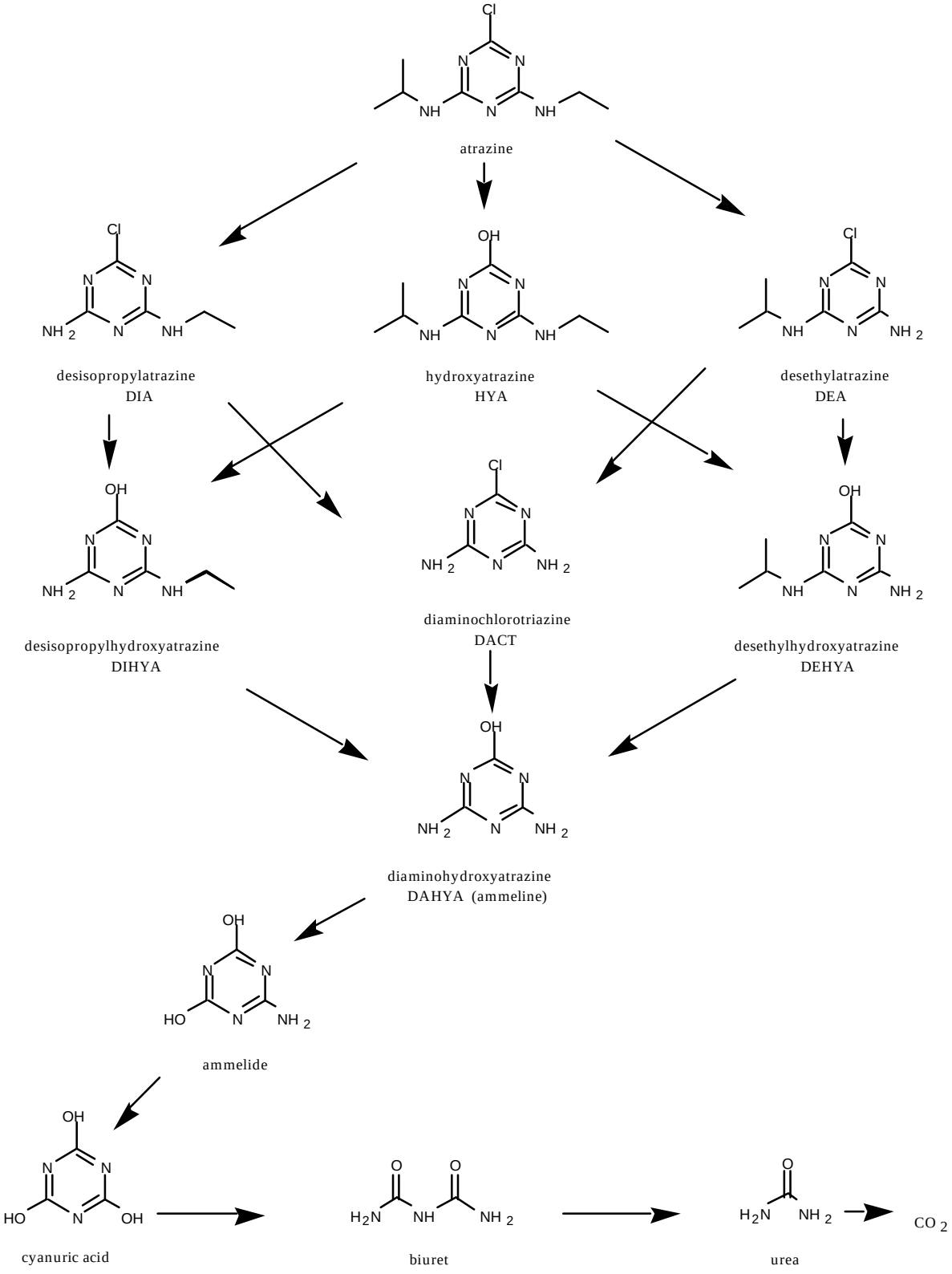
Atrazine is used in high volumes (probably a few thousand tonnes per annum) in Australia, predominantly for coarse grains and sugarcane. Some of its minor uses, notably plantation forestry and legumes, involve winter applications in temperate southern regions of Australia. Annual application rates are restricted to 3 kg/ha in all situations except plantation forestry, which receives less frequent but heavier treatments (4.5 kg/ha for sandy soils and those defined as highly erodible, and 8 kg/ha for clay loams and heavier textured soils).

Because of its widespread use and environmental properties, atrazine is a commonly found contaminant of surface and ground waters in Australia, particularly within irrigated agriculture and plantation forestry areas. Use patterns have been revised to counter this contamination, with the phase out of use for irrigation channel hygiene, and reduced rates in plantation forestry. Atrazine has been found at concentrations in the order of 100 µg/L in irrigation drainage water from a rice growing area with some maize, and occurs commonly in natural surface waters, generally at concentrations below 10 µg/L and, in most cases, below 1 µg/L. A median concentration of 8.1 µg/L was found in Tasmanian streams draining forestry plantations on the day of application. Only limited monitoring of groundwater has been conducted, but atrazine is commonly detected at concentrations in the order of 1 µg/L, accompanied at some sites by the metabolite DEA.

4.2 Environmental chemistry and fate

A large number of published papers are available for atrazine. This report focuses on published studies provided by Ciba-Geigy, and on unpublished work provided by Ciba-Geigy and Makhteshim-Agan. Selected recently published studies are included where their findings add to the report, particularly for work carried out in Australia. Note that a wide variety of methods has been used to investigate the environmental chemistry and fate of atrazine, including recognised test guidelines and less formal procedures designed to study specific aspects. Only the more recent among the unpublished studies have been conducted according to good laboratory practice.

Atrazine undergoes dealkylation and dechlorination reactions to form a range of metabolites in the environment. Deamination and ring cleavage reactions are involved in later stages of its degradation, which is outlined schematically below. The significance of the various degradation routes is detailed in the following text:



4.2.1 Hydrolysis

4.2.1.1 Sterile aqueous buffers

Hydrolysis in aqueous buffers was investigated at pH 1.3, 2.2, 3.1, 11.1, 11.9 and 12.9, and found to depend on pH. The calculated half-lives at pH 5 and pH 9 were 1000 and 6600 days, respectively. Atrazine was stable at neutral pH. Hydrolysis of atrazine produced hydroxyatrazine (HYA), probably by direct nucleophilic displacement of the chloro substituent. A nearly tenfold increase in the rate of hydrolysis was observed at pH 4 in the presence of sterile soil (Armstrong *et al*, 1967).

Studies on radiolabelled atrazine dissolved at about 5 mg/L in aqueous buffers (pH 5, 7 and 9) found no degradation over a 30 day period at 25^{o}C (Spare, 1986).

4.2.1.2 Low concentrations

More recent studies (Lartiges and Garrigues, 1996) have investigated the hydrolysis of atrazine at more environmentally realistic concentrations, in the order of 1 µg/L. No degradation was observed over a 6 month period in ultrapure water. Half-lives in river water were 235 days at 6^{o}C and 164 days at 22^{o}C, declining to 59 days in open systems (temperatures fluctuating with ambient and solutions exposed to natural sunlight). Degradation was only observed at the higher temperature in filtered river water (half-life 130 days) and sea water (half-life 200 days, declining to 169 days in open systems). The relatively short half-life under sunlight in river water may reflect photosensitisation by humic acids.

4.2.1.3 Soil catalysed hydrolysis

As indicated by the above findings of rate increases in the presence of sterile soil, abiotic hydrolysis of atrazine and similar chlorotriazines is also important in soils. Early results in this area have been reviewed. Hydrolysis of atrazine is catalysed in soil solution, as well as in the sorbed state. Mechanistically, adsorption is believed to result from hydrogen bonding between carboxyl groups on the adsorbent and the nitrogen atoms of the triazine ring, leading to protonation of ring or side-chain nitrogens followed by cleavage of the carbon-chlorine bond by water. A number of studies have found that the rate of degradation increases with increasing adsorption, consistent with catalytic hydrolysis at sorption sites.

Studies on simazine, atrazine, propazine and terbuthylazine found increasing strength of sorption in three soils, with the increase particularly marked for terbuthylazine. Hydrolytic half-lives in soil also increased along this series of

compounds, suggesting that the concentration in soil solution is the main factor governing hydrolysis of atrazine in these soils (Burkhard and Guth, 1981).

4.2.1.4 Hydrolysis in dissolved and sorbed states

More recently, soil hydrolysis has been studied using an HPLC technique that monitors reactant and product (HYA) in both solution and reversibly sorbed states, together with material balance loss (non-extractable residues). Sorption equilibrium required 5 days, during which atrazine was removed by hydrolysis from the sorption sites more quickly than from solution (half-lives for hydrolysis are shorter than those for sorption). After 7 days of stirring in an aqueous slurry (15 mL) of a peat soil (50 mg) containing 37.7% organic carbon and acidified to 10^{-4} M with hydrochloric acid, some 55% of atrazine (initial concentration 21.6 mg/L) remained free in solution, with 19% reversibly sorbed. Corresponding figures for HYA were 3.9 and 8.4%, with 14% lost from the material balance.

HYA formation represented some 64% of total atrazine losses, the remainder attributed to sorption at sites with very slow sorption and desorption rates. Formation of these non-extractable residues was correlated with losses of reversibly sorbed atrazine and production of reversibly sorbed HYA (Gamble and Khan, 1990).

4.2.1.5 Summary of hydrolysis studies

Atrazine is transformed to hydroxyatrazine by hydrolysis, but the reaction is very slow in sterile water. Transformation is more rapid in soils, where hydrolysis is believed to be catalysed by acidic groups within the soil organic matter to which atrazine adsorbs.

4.2.2 Photolysis

4.2.2.1 Aqueous solution

- Theoretical predictions

The ultraviolet absorption spectrum of atrazine in aqueous solution exhibits maxima at 222 and 263 nm and overlaps only slightly with the spectral irradiance of sunlight. Earlier findings of a weak absorption in the 300-350 nm range were not confirmed in this study, even using methanol as solvent to improve sensitivity. Assuming a quantum yield of one (unrealistically high) and clear skies, estimated annual mean half-lives for direct photolysis are 198, 333 and 611 days at 30^{o}, 40^{o} and 50^{o} of latitude, respectively. This equates to

approximately 800 days, with considerable seasonal variation, under typical central European conditions (Abildt, 1995).

- **Natural summer sunlight**

Exposure of radiolabelled atrazine solutions (10 mg/L) for 358 hours to natural summer sunlight at temperatures between 12 and 45^{o}C resulted in slow degradation (projected half-life about 335 days). The main products observed were HYA and DEA, accompanied by lesser amounts of DIA, DACT and desethyl- and desisopropylhydroxyatrazines (DEHYA and DIHYA). No photoproduct exceeded 4% of applied (Spare 1988a).

- **Artificial light**

A half-life of 17 hours continuous irradiation was obtained under artificial conditions (medium pressure mercury arc with 290 nm cutoff). The main product (65% yield after 48 hours) was HYA, accompanied by lesser amounts (< 10%) of other products as listed above (Spare 1988b).

The half-life under irradiation through Solidex glass (λ > 270 nm) from a high pressure mercury lamp was 2 hours. Dealkylated atrazines (DEA, DIA and DACT) and corresponding hydroxytriazines [DEHYA, DIHYA and diaminohydroxyatrazine (DAHYA, common name ammeline)] formed as photoproducts (Burkhard, 1972).

- **Sensitised photolysis**

The experimentally determined half-life at 60^{o}C of atrazine solutions (mg/L levels, below solubility limit) exposed to xenon lamp irradiation (340 nm cutoff) was 700 hours. The main product identified after one half-life was HYA, accompanied by lesser amounts of DACT, DAHYA, and miscellaneous unidentified compounds comprising 75% of the yield. Photodegradation in an aqueous soil extract containing 10 mg/L organic carbon was more rapid (half-life 290 hours) and generated the same suite of products after one half-life in addition to the dihydroxytriazine known as ammelide (indicating an effect of humic acid on deamination) and miscellaneous unidentified compounds representing 35% of the yield (Minero *et al,* 1992).

- **Catalysis by metal oxides**

Photocatalytic processes operating in the presence of titanium dioxide reduced the half-life dramatically to a few minutes under the above conditions. Other metal oxides also catalysed the photolysis, but less efficiently. DIA formed as main product after one half-life, accompanied by HYA, DEA, and alkyl oxidised products comprising 38% of the yield. Further irradiation gave rise to DACT, the corresponding hydroxytriazine DAHYA and its deaminated derivative,

ammelide. After 70 hours of irradiation, cyanuric acid was produced in 90% yield (Pelizetti *et al*, 1993).

Ferric ions have also been found to enhance the rate of photodecomposition of atrazine in moderately acidic aqueous solution, apparently through electron transfer processes that generate hydroxyl radicals. This process is unlikely to be significant in natural waters where dissolved organic matter scavenges hydroxyl radicals (Larson *et al*, 1991).

4.2.2.2 Soil

- **Bulk soil**

An early study involved mixing atrazine with silt loam soil (pH 6.1) to a level of 10 mg/kg and irradiation for 24 hours with a xenon lamp having spectral characteristics similar to natural sunlight. Degradation amounted to 29% in moist soils (12% moisture) and 18% in dry. After correction for dark controls, photodegradation accounted for 11 and 5% of applied. The main extractable degradation product was HYA (Burkhard, 1978a).

- **Thin film**

Exposure of ring radiolabelled atrazine adsorbed to the surface of a thin film of sandy loam soil (pH 6.1) to natural sunlight (39^{o}N, November/December) for 168 hours at temperatures between -4 and 24^{o}C resulted in formation of the dealkylated atrazines DEA, DIA and DACT (7.9, 17.4 and 4.3% after 168 hours) together with unidentified products, non-extractable residues and small amounts of HYA. The half-life was about 12 days. Under artificial irradiation (mercury arc in pyrex filter with 290 nm cutoff) on thin strips of the same soil (replacing silica on tlc plates) the half-life was about 3 days continuous exposure at temperature between 32 and 45^{o}C, leading to the same range of products but with HYA predominant (Spare, 1987a). It may be noted that this hydrolysis product was already present at a few percent before artificial irradiation, whereas the naturally irradiated samples prepared from the same atrazine solution assayed at 99.6% atrazine before exposure to sunlight.

A more detailed study was conducted at 25ºC on soil plates (sandy loam, pH 7.5) spiked at 10 mg/kg and irradiated for 30 days (alternating 12 hour light and dark cycles) with artificial sunlight (xenon arc with 290 nm cutoff). Evolution of volatiles and carbon dioxide was monitored in this study but found to be insignificant. Two main degradation products were identified, DEA and DIA, reaching respective maxima of 13.3 and 11.9% by the end of the study. Estimated half-lives with and without irradiation were 38 and 267 days, respectively, with a net half-life attributable to photodegradation of 45 days (Das, 1989).

4.2.2.3 Summary of photolysis studies

Atrazine degrades under the influence of sunlight to a range of dechlorinated and dealkylated products, but the reaction is slow with an estimated half-life in water of about a year. Degradation is faster in the presence of humic acids as sensitiser, giving rise to an additional product (ammelide) from deamination. Half-lives of a few weeks on soil surfaces exposed to natural sunlight appear typical.

4.2.3 Metabolism in laboratory soils and aquatic systems

A broad range of studies was submitted, including standard metabolism and biodegradation studies conducted according to recognised test guidelines, and published papers examining specific issues such as increased mineralisation in the presence of enriched microbial cultures. The key points to emerge are that bioavailable atrazine is moderately persistent in the environment. Furthermore, atrazine tends to become non-bioavailable by forming non-extractable residues rather than degrading, with very limited mineralisation under normal environmental conditions.

4.2.3.1 Soil studies

- **Aerobic/anaerobic**

Early laboratory studies on sandy loam soil (pH 6.5, 2.2% organic carbon) that had been activated by cultivating maize for 8 weeks before fortification with radiolabelled atrazine to a level of 10 mg/kg found a rapid decline, from 93% to 59.6% of applied, over a 4 week period. The main metabolite observed was DEA (8%), accompanied by HYA, DIA, DACT and DEHYA (each below 5%). Formation of the four minor metabolites was apparent during preparation and mixing. Non-extractable material accounted for 15.6%, and carbon dioxide 0.3% after 4 weeks of incubation at 25^{o}C. Degradation continued, but at a slower rate, when conditions were rendered anaerobic by flooding after the first sampling, with increasing formation of non-extractable residues but only HYA among the identified metabolites increasing, to 7.5% of applied after 12 weeks. The estimated half-life under combined aerobic and anaerobic conditions was 10-11 weeks (Keller, 1978).

- **Effects of temperature and moisture**

A further laboratory study on loamy soil (pH 6.8, 3.7% organic carbon) examined the effects of temperature and soil moisture on the degradation of atrazine. The soil was spiked at 10 mg/kg and incubated at 10 or 20^{o}C at 75% field capacity, with a further study at 20^{o}C and 50% field capacity. The study was conducted for 180 days at the higher temperature, and 269 days at the lower. A dramatic effect of temperature was evident from half-lives of 175 and 56 days

at 75% field capacity. Low moisture levels also favour increased persistence, with the half-life increasing to 79 days at 50% field capacity. Non-extractable residues accounted for some 43% of applied at the end of the two warmer studies, compared with 25% after 269 days at 10^{o}C (Abildt, 1991).

- **Non-extractable soil residues and atrazine half-life**

Half-lives reported for atrazine appear generally to have been calculated based on the assumption that formation of non-extractable residues represents loss of atrazine. An alternative approach would be to assume that the non-extractable residues contain the same proportions of atrazine and metabolites as the extractable portion.

Metabolism data from 80 day studies conducted in full sunlight at ambient air temperature on two soils (sandy loam, pH 5.5 and silt loam, pH 6.4, both with 0.91% organic carbon) were treated according to both assumptions. Formation of non-extractable residues reached 35% of applied in the sandy loam and 80% in the silt loam. Extrapolated half-lives in the sandy loam were 110 days based on the former assumption, and 330 days based on the latter. Corresponding estimates for the silt loam were 36 and 385 days (Jones *et al*, 1982).

The half-life of atrazine in soils can clearly be significantly longer than generally reported when non-extractable atrazine residues are accounted for in calculations, particularly for soils in which such residues are formed in abundance.

- **Characterisation of non-extractable soil residues**

Further studies were conducted on an additional loam soil (pH 7.6, 0.8% organic carbon) under aerobic, sterile aerobic, and aerobic/anaerobic conditions in order to characterise the non-extractable soil residues. In the active aerobic study, atrazine had a half-life of 146 days, degrading to 21% of applied dose during 300 days of incubation with the formation of 63% non-extractable residues and 6% organosoluble metabolites. Degradation was slow in the sterile samples, with a projected half-life from poorly correlated data in the order of 600 days and limited formation of non-extractable residues (17% after 94 days). Atrazine had declined from 67% of applied after 32 days of aerobic incubation to 51% after a further 62 days under anaerobic conditions, with the formation of 41% non-extractable residues and 0.8% organosolubles. The calculated half-life under anaerobic conditions was 159 days.

Of the non-extractable residues, some 3-20% remained with the soil following reflux with methanolic hydrochloric acid, associated with humin, fulvic acids and humic acids. Analysis of the extracts by HPLC revealed the presence of atrazine (5-11.9%), HYA (10.6-14.5%) and lesser amounts of DIA, DEHYA and DIHYA, and an unknown metabolite thought to have an oxidised alkyl

substituent. More detailed analysis using TLC and HPLC revealed that all three chloro metabolites (DEA, DIA and DACT) and four hydroxy metabolites (HYA, DEHYA, DIHYA and DAHYA) were present in the extracts. Metabolism occurs through substitution of the chloro by a hydroxy substituent, and oxidative reactions resulting in dealkylation of the side chain amino groups (Nelson and Schabacker, 1991).

Three soils incubated for 6 months with atrazine and exhaustively extracted with methanol were separated into size fractions using physical methods. Non-extractable atrazine residues, estimated at 40% in an organic rich forest soil and 15% in two arable soils that had been previously cultivated with maize, were mainly located in the 20-2 and 2-0.2 µm fractions that contained the bulk of the organic matter as well humified material. Atrazine was also found in high concentrations in the coarse fraction (200-50 µm) which contained a minor proportion of soil organic matter, but as coarse plant residues. The authors suggest that retention of atrazine in the coarse fraction may reflect an interaction with decomposing plant material (Barriuso *et al*, 1991).

- **Significance of non-extractable soil residues**

Ciba-Geigy has provided a proprietary statement on bound triazine residues, based on literature studies. Bound residues are defined by Ciba-Geigy as those firmly attached to soil organic matter. This report will use the term non-extractable residues. Formation of non-extractable residues is described as a process occurring predominantly within soil organic matter (humin, humic and fulvic acids). Covalent bonding is not involved as released residues contain only atrazine and known soil metabolites, with no new structures. Hydrogen bonding is believed to be the main mode of attachment, with kinetic factors (slow diffusion from holes and voids within the organic microstructure) also retarding release.

The bioavailability of non-extractable residues is low because prior release from the substrate is required. This may occur through a number of mechanisms (microbial release, metabolism by plant roots and degradation of soil humic matter, with or without prior incorporation through the formation of covalent bonds). None of these mechanisms is expected to release more than about 1% of the non-extractable residues annually (Egli, 1993).

The formation of non-extractable soil residues has recently been reviewed, with a distinction drawn between non-extractable residues (those that resist solvent extraction) and bound residues (only extractable under strongly forcing conditions, such as vigorous hydrolysis, that break bonds and change the nature of the sorbed residue). Formation of non-extractable residues is described as a sequestration within particulate matter, and is much slower than the readily reversible sorption that occurs to particle surfaces. Essentially, fast and slow sorption gives rise to labile and residual fractions, respectively. Sequestration is believed to involve a slow and continuing diffusion to remote internal sites,

resulting in essentially irreversible sorption, although gradual release is possible as outlined above (Alexander, 1995).

- **Degradation in deep and saturated soil**

As noted earlier in this report, DEA is generally the main metabolite detected in groundwater. Laboratory studies on degradation of atrazine and DIA have been conducted using soils from different depths down to 120 cm, including under saturated conditions, in order to understand this behaviour. Soils were a sandy clay loam (pH 5.7) in the surface 30 cm, a loam (pH 6.2) in the 30-65 cm fraction, and sandy clay loam (pH 6.2) in the 65-90 and 90-120 cm fractions. They had no previous pesticide history, and were stored at 4^{o}C for 90 days before fortification with radiolabelled atrazine (5 mg/kg) or DIA (1 mg/kg).

Atrazine was most persistent in the 90-120 cm fraction, with 77 and 58% remaining after 60 and 180 day incubations, compared with 33-48% and 4-15% for the fractions nearer the surface. Estimated half-lives under unsaturated conditions were 41 days in the surface fraction, 231 days in the 90-120 cm fraction, and 69 days in the intervening fractions. The half-life decreased to 87 days in the deepest fraction under saturated conditions.

All three dealkylated metabolites (DEA, DIA and DACT) were detected, with DEA predominant. This metabolite only increased in concentration between 60 and 180 days in the 90-120 cm fraction. Only small amounts of HYA were found, presumably because pH was close to neutral. DEHYA and DIHYA were only seen in trace amounts. Non-extractable soil residues accounted for most of the radiolabel, being found in higher proportions near the surface, and increasing between 60 and 180 days in all samples. Hydrophilic polar metabolites were also seen in significant amounts, particularly between 0 and 90 cm, but evolution of carbon dioxide remained below 1%.

DIA was found to be more labile than atrazine in all samples, including in saturated soil from 90-120 cm where the half-life reduced to 58 days. The relative degradability of DIA may explain its very low detections in groundwater compared with atrazine and DEA (Kruger *et al*, 1993a).

- **Degradation by *Pseudomonas***

Soil samples were taken randomly from four different areas of a maize field with a 14 year history of atrazine use, including an application 9 weeks before sampling, and used as inocula for enrichment in culture media supplemented with atrazine (50 mg/L). The dilution method was used, with or without cycloheximide to suppress fungi, as well as the soil percolation technique, in which the percolation medium included inhibitors selective for *Pseudomonas* isolation.

Preliminary experiments had shown no measurable degradation after 5 weeks incubation in soil never before exposed to the herbicide, and only limited

breakdown over this period in soil from a maize field that had received numerous atrazine applications. Degradation in the inoculated enrichment media was much more pronounced, reaching 45% of applied in the dilution method (reduced to 31% by cycloheximide) and 17% using the soil percolation technique. Metabolism occurred through dealkylation to DEA and DIA.

Eight different Pseudomonas isolates from three different species were obtained, and found to have the ability to utilise atrazine as sole source of carbon and energy (although populations need to build up before significant metabolism occurs). Concentrations of DIA after 16 days in glucose amended culture media were considerably higher than those of DEA (4.2-7.2 vs 0.08-0.3 mg/L). Two of these strains were also found to be effective in dechlorinating the three dealkylated atrazines DEA, DIA and DACT, with conversion rates of 49-68% and 15-24% after 5 weeks in glucose amended culture media supplemented with 40 mg/L triazine, but only marginally effective in dechlorinating atrazine itself. The rate of dechlorination appeared fastest for DACT. Dehalogenation was determined by the formation of hydroxymetabolites (Behki and Khan, 1986).

- **Microbial mineralisation**

As noted above, the atrazine dechlorination reaction in soils is generally accepted to be a soil catalysed chemical process. Recent results show that a mixed bacterial culture, isolated from soil on the basis of its ability to utilise atrazine as sole nitrogen source, rapidly hydrolyses atrazine to HYA (80% conversion in 24 hours in clay loam, and 95% in silica sand). The transformation was also effected at neutral pH by a cell free, crude protein extract, but this activity was lost after boiling for 10 minutes, indicating that heat labile components are responsible. A hydrolytic mechanism was confirmed using $H_2{}^{18}O$. The isolate was able to liberate atrazine ring carbons as CO_2, but dealkylated atrazines were not detected apart from brief traces of DIA in the sand. Dechlorination occurred under both aerobic and oxygen limited conditions. The authors report that over 30 atrazine degrading cultures have been isolated from 100 soil samples taken from three atrazine contaminated sites, and suggest that biological dechlorination of atrazine may be widespread in soils, and may also occur in oxygen limited environments such as groundwater and subsoil (Mandelbaum *et al*, 1993).

Other workers have found high rates of atrazine mineralisation in soil inoculated with an atrazine mineralising consortium (*Clavibacter michiganese*, *Pseudomonas* sp and *Cytophaga* sp) isolated from an agricultural soil having prior long term exposure to atrazine. For example, 71% of atrazine added at 3 mg/kg to sandy loam soil (pH 6.8) was mineralised in 5 weeks, compared with 2.4% over the same period in unamended soil (and about 0.1% in sterile soil). When the soil microcosms were planted to maize, the mineralisation rate increased to 84%, apparently assisted by initial plant metabolism to HYA, which is more susceptible to microbial attack than atrazine. It would appear that mineralisation occurs rapidly under microbial influence after the initial breakdown of atrazine as more than half the extractable residue was unchanged

atrazine. However, bacteria capable of mineralising atrazine do **not** appear to be abundant in agricultural soils given the documented environmental persistence of atrazine (Alvey and Crowley, 1996).

4.2.3.2 Aquatic studies

- **Anaerobic pond water**

Anaerobic aquatic metabolism was studied in water and sediment from a farm pond. Test systems contained 25 g of sandy clay sediment (pH 7.2, 0.2% organic matter) and 50 mL of pond water dosed at 10 mg/L with radiolabelled atrazine, and were incubated at 25°C under nitrogen for a year without prior equilibration. Approximately 80% of radiolabel in aqueous and sediment fractions was identified as unchanged atrazine at the end of the incubation, with the bulk of the radiolabel remaining in the aqueous phase.

Sediment data appear to show an initial sorption in the order of 10% (although this may reflect freezing of the 1 and 3 day samples prior to analysis) with subsequent desorption in early weeks, before sorption recurred at low levels (<10%) after 30 days. Non-extractable residues gradually increased through the study, but extractable atrazine in the sediment had declined to 4% of applied by study end. Three products were identified in each phase, being HYA, DEA and, in smaller amounts, DIA. Non-extractable residues reached about 10% of applied, and production of volatiles remained below 1%. The projected half-life in this aquatic system was 608 days. Similar results were obtained in sterile systems, except that atrazine was more persistent (Spare, 1987b).

- **Aerobic/anaerobic pond and river water**

These studies utilised Rhine River sediment (220 g, equivalent to 144 g dry weight) or Swiss pond sediment (200 g, equivalent to 60 g dry weight) together with the overlying water (550 mL). The river sediment was a loamy sand (pH 7.1, 0.8% organic carbon) and the pond sediment a silt loam (pH 6.9, 5% organic carbon). Systems were equilibrated for 3 weeks in the dark before treatment with radiolabelled atrazine (0.54 mg/L in the water, equivalent to an application of 1.6 kg/ha direct to 30 cm water) dissolved in acetone. The pH of the systems was around 8. Aerobic, anaerobic and sterile/aerobic systems were studied for a year at 20°C or 9°C.

Atrazine degraded in both systems with the formation of up to 10 metabolites, of which three were identified as HYA, DEA and DIA. HYA was found in highest amounts (maximum 16.2% of applied after 238 days at 20°C in the anaerobic river system) followed by DEA (maximum 5.2% of applied after 238 days at 9°C in the aerobic river system) and a slightly more mobile unidentified metabolite (maximum 4.8% of applied after 363 days at 20°C in the anaerobic river system). DEA was accompanied in many systems by smaller amounts of DIA.

Mineralisation was poor (CO_2 formation reached a maximum of 1.9% in the river and 0.7% in the pond).

Loss of atrazine was most rapid under aerobic conditions at 20^{o}C, with respective first half-lives in river and pond systems of 80 and 35 days, based on total extractable atrazine in water and sediment phases. Dissipation from the water was more rapid, with corresponding half-lives of 20 and 14 days. Note that these half-lives reflect loss of bioavailable atrazine and do not include non-extractable residues in their derivation. Dissipation was slightly slower under anaerobic conditions, and markedly so at the lower temperature or in sterile systems. Dissipation generally slowed after the first half-life, although some systems exhibited pseudo first order kinetics.

Atrazine partitioned to sediment in river and pond systems, particularly at the beginning of the incubation period, with non-extractable residue formation the main route for its disappearance. Sediment evidently has a capacity to sorb atrazine in both labile and residual forms, but the capacity would appear limited given that atrazine largely remained in the aqueous phase in the previously described study, conducted at higher concentration. Others have concluded that atrazine is not expected to strongly adsorb to sediment and may only moderately partition from the water column (Howard, 1991).

Extractable radioactivity in the sediment peaked at 25-39% of applied after 1-2 months. Some 42-66% of applied radioactivity was found to be non-extractable after a year in the river system, and 66-77% in the pond. Total residues in the river and pond sediment at the end of the study were 64-79% and 84-91%, respectively (Mamouni, 1994).

An earlier study using water and sediment taken from the River Rhine and a Swiss pond and an initial atrazine concentration of 1 mg/L found much slower degradation, with more than half the applied atrazine remaining in the pond water after 77 days, and very little lost from the Rhine water. The slowness of degradation and sorption may reflect the low levels (1%) of sediment present. Radiolabel extracted from sediment was mainly unchanged atrazine. DEA was the main metabolite detected, with smaller amounts of DIA and unidentified polar metabolites (Ellgehausen, 1985a).

- **Estuarine water**

Estuarine systems consisted of 600 g of wet sediment (40% water) and 500 mL of the overlying water from two locations in Upper Chesapeake Bay. Radiolabelled atrazine was added as a methanolic slurry with 1 g of the sediment to give a theoretical concentration in water and sediment of 0.1 mg/L. A loamy sediment (pH 5.4, 0.55% organic carbon) from an open bay (15‰ salinity) and a sandy loam (pH 4.4, 0.85% organic carbon) from a more protected estuary (8‰ salinity) were studied for 80 days at 12-35^{o}C in full sunlight under aerobic or low oxygen (stoppered flask) conditions.

Radiolabel was initially found in the water, but became increasingly associated with the sediment with the passage of time, leaving 37% extractable from the loam after 80 days and 29% from the sandy loam. Removal of radiolabel from water followed pseudo first order kinetics. The decline in extractability occurred in parallel with formation of HYA, the main metabolite (90% of extractable residues by study end in the sandy loam) in these low pH systems. Small amounts of dealkylated atrazines were also formed. Respective half-lives were 20 and 15 days, based on the assumption that non-extractable and extractable residues had the same composition (Jones *et al*, 1982). Atrazine appears much less persistent in estuarine systems than in soils.

- **Salt marsh**

Partitioning of atrazine to suspended solids and degradation were studied at a concentration of 20 µg/L in fresh and saline waters with river, mud flat and vegetated marsh sediment. Negligible sorption to suspended solids was observed under fresh and saline conditions, even at fairly high concentrations of suspended solids. Atrazine is a common sediment contaminant, however, and may partition by entrapment in sediment flocs or accumulation in the organic rich surface microlayer. Dealkylated metabolites DEA and DEA were first detected in the sediment 8 days after application of atrazine to the water, but were never detected in the water, nor in separate 20 day metabolism tests on water without sediment. This suggests that degradation occurs only after sorption to sediment. After 71 days, atrazine was still detectable in sediment, but DEA and DIA were no longer found and are assumed to have undergone further degradation. The half-life of atrazine in this system can not be determined as concentrations are not disclosed, but would appear to be in the order of a few weeks (Meakins *et al*, 1995).

- **Groundwater**

Stability of atrazine in aerobic groundwater (100-600 µg/L) was studied in the laboratory in vials containing 60 mL groundwater and 20 g (dry weight) of aquifer material. No degradation was found over a 74 day period.

Investigations also occurred under field conditions by weekly injections (400 µg/L) into an aquifer (pH neutral) and monitoring of the plume using multilevel piezometers downgradient from the injection well. Atrazine was mobile in the aquifer, with a retardation factor relative to chloride of 1.2, and appeared stable over a 96 day period. Subsequent analysis (limit of detection 0.1 µg/L) for metabolites found none (Agertved *et al*, 1992).

- **Sewage treatment**

A modified Sturm test found 14.7% degradation (based on evolution of carbon dioxide) in 28 days at a concentration of 10.7 mg/L over sludge from a Swiss sewage treatment plant, and 7% at a concentration of 21.3 mg/L. Atrazine proved not to be biodegradable in this test, consistent with its general

recalcitrance in the environment (Bader, 1990a). Separate testing found no significant inhibition of respiration for activated sludge exposed to nominal concentrations of atrazine up to 100 mg/L for 3 hours (Bader, 1990b).

4.2.3.3 Summary of metabolism studies

The laboratory investigations outlined above indicate that atrazine degrades in soils through a combination of soil catalysed processes and microbial and plant metabolism, with the main reactions being hydrolytic dechlorination, side chain dealkylation, and subsequent deamination, as represented schematically above. The hydrolytic reaction, which is soil catalysed, appears to be favoured in acidic soils. Half-lives are variable, generally a few months but extending to over a year in some soils, particularly at depth where microbial populations are low.

Half lives from laboratory metabolism studies are tabulated below. These data should be interpreted as half-lives for loss of bioavailable atrazine as non-extractable residues have been excluded from their derivation. Non-extractable residues generally include significant proportions of unchanged atrazine, which considerably increases the half-life when considered in calculations. For example, the half-lives reported by Jones *et al* (1982) extend to about a year when calculated on this basis.

Soil	pH	%	Conc (mg/kg)	Temp °C	Metabolites	Non-extractable	DT50 (day)	Reference
Sandy loam	6.5	2.2	1.0	25	HYA, DEA, DIA, DACT, DEHYA	40% after 12 weeks	70-77	Keller, 1978
Loam	6.8	3.7	1.0	20	Not investigated	43% after 180 days	56	Abildt, 1991
Loam	6.8	3.7	1.0	10	Not investigated	25% after 269 days	175	Abildt, 1991
Sandy loam	5.5	0.9	6.4	12-42	HYA, DEA, DIA	77% after 108 days	110	Jones *et al*, 1982
Silt loam	6.4	0.9	5	12-42	HYA, DIA, DEA	85% after 108 days	36	Jones *et al*, 1982
Loam	7.6	0.8	10.2	25	HYA, DEA, DIA, DACT, DEHYA, DIHYA, DAHYA	63% after 300 days	146	Nelson and Schabacker, 1991
Sandy clay loam	5.7	1.6	5	25	HYA, DEA, DIA, DACT, DEHYA	58% after 180 days	41	Kruger et al, 1993
Loam	6.2	1.6	5	25	HYA, DEA, DIA, DACT, DEHYA	41% after 180 days	69	Kruger et al, 1993
Sandy clay loam	6.2	1.0	5	25	HYA, DEA, DIA, DACT, DEHYA, DIHYA	53% after 180 days	69	Kruger et al, 1993
Sandy clay loam	6.2	0.9	5	25	HYA, DEA, DIA, DACT, DEHYA, DIHYA	20% after 180 days	231	Kruger et al, 1993

Loss of atrazine from soils is mainly accompanied by the formation of non-extractable residues. Non-extractable residues may be extracted under forcing conditions, and have a similar metabolite profile to extractable residues. Release under environmental conditions may occur at a few percent per year through microbial or plant metabolism or decomposition of soil organic matter.

Mineralisation of atrazine in soils is a very inefficient process, except where soils have been artificially fortified with atrazine-mineralising bacterial consortia. Intermediate metabolites such as cyanuric acid and ring opened products such as biuret and urea are not isolated.

Degradation in aquatic systems follows similar pathways, with the hydrolytic reaction apparently catalysed by sediment. Aquatic sediment appears to have only limited capacity to sorb atrazine. At low atrazine concentrations, half-lives of 2 months or more appear typical of freshwater systems, while degradation in estuarine systems appears to proceed with half-lives of less than a month.

4.2.4 Mobility in soil.

A broad range of studies was submitted, including standard batch adsorption and column leaching studies conducted according to recognised test guidelines, and published articles dealing with mechanistic aspects and using less standard

methods. It is evident from the papers submitted that atrazine undergoes only limited sorption to soils, although increasing amounts become associated with the soil over time. The mechanism of sorption has been closely investigated over short and long terms but remains incompletely understood.

4.2.4.1 Adsorption/desorption studies

- **Batch equilibrium studies on four soils**

Batch equilibrium studies were conducted on four soils with varying organic matter and texture (see table). Radiolabelled atrazine solutions (0-11.6 mg/L) were added to soils (5:1 ratio) and shaken for 4 hours before analysis of the supernatant. Range finding studies indicated that solution equilibrium was achieved within 2-4 hours. Data obtained were well correlated with the Freundlich equation, and returned soil organic matter partition coefficients between 39 and 155, indicative of weak sorption and high mobility.

Soil type	pH	% oc	% sand	% silt	% clay	CEC	Koc
Clay	5.9	2.8	25.2	32.8	41.2	24.3	87
Sand	6.5	0.5	95.6	2.2	2.2	1.8	39
Sandy loam	7.5	1.1	63.2	20.0	16.8	6.1	70
Loam	6.7	0.5	44.0	47.0	9.0	4.3	155

Desorption was studied over a 4 hour period at the same ratio of soil to supernatant and also found to be well correlated with the Freundlich equation. Corresponding desorption coefficients (based on organic carbon) were 323, 286, 651 and 1012, indicative of moderate to strong binding and low to moderate mobility. Although atrazine undergoes only limited sorption to soil, that portion that sorbs is more strongly retained, particularly in some soils.

Analysis of the strongest solution concentrations following adsorption/desorption found between 77 and 91% atrazine (Spare, 1989a).

- **Adsorption of metabolites**

A second adsorption study on four Dutch arable soils, conducted under similar conditions but with a 24 hour equilibration step and no desorption, returned a similar range of soil organic carbon partition coefficients (see table). The study also examined the behaviour of dealkylated metabolites and found increased mobility, with soil organic carbon partition coefficients of 53-107 for DIA and 41-79 for DEA.

Soil type	pH	% oc	% sand	% silt	% clay	CEC	Koc
Clay	5.0	8.1	93	4	3	-	176
Sand	4.9	2.3	90	7	3	-	112
Sandy loam	4.3	1.3	84	11	5	-	109
Loam	7.3	0.6	45	44	11	-	76

The metabolite HYA was also studied, but at a single concentration of 4 mg/L. The pH of the solution was adjusted to 4.2 to ensure dissolution of this weakly acidic compound (pKa 5.1). The authors argue that sorption at more acidic pH (below 5) would mainly involve the monocation form (note that HYA may exist in phenolic and quinoid structures).

The results obtained indicate that HYA sorbs more strongly than the chlorotriazines, with soil organic carbon distribution coefficients between 177 and 293, increasing to 1028 in the organic rich sand, in which the organic matter is derived from peat (Brouwer *et al*, 1990).

- **Desorption of metabolites**

Batch equilibrium adsorption/desorption studies were conducted by adding solutions of ring radiolabelled atrazine metabolite (0.2-5 mg/L) to soils (5:1 ratio) and equilibrating by shaking for 24 hours. Additional studies (last four entries in table) used shorter equilibration times (2 hours for DIA, 8 hours for DEA and HYA, 4 hours for DACT) and maximum concentrations of about 10 mg/L, for DIA and HYA, and 2 mg/L for DEA. Desorption was studied over the same time frames as adsorption.

Soil type	pH	% oc	% sand	% silt	% clay	CEC
Sand	5.6	0.5	90.0	8.0	2.0	1.0
Sandy loam	6.1	1.8	58.0	32.0	10.0	6.0
Silty loam	7.0	1.2	13.0	64.0	23.0	15.0
Clay loam	6.6	1.5	24.0	42.0	34.0	14.7
Sand	6.5	0.5	95.6	2.2	2.2	1.8
Sandy loam	7.5	1.1	63.2	20.0	16.8	6.1
Loam	6.7	0.5	44.0	47.0	9.0	4.3
Clay	5.9	2.8	25.2	32.8	42.0	24.3

Adsorption results for the chloro metabolites DIA, DEA and DACT indicate weak sorption and high mobility. Desorption results are generally indicative of weak to moderate sorption, but with strong retention of sorbed material in some soils as indicated by the desorption coefficients above 1000. The significantly increased desorption coefficients reflect contributions from non-extractable soil residues for these weakly sorbing compounds. Desorption could not be determined in the second sand listed because of very low levels of sorption.

The hydroxy metabolite HYA sorbs moderately to most soils, with desorption coefficients indicative of strong sorption. Sorption is strong in two soils. The

particularly strong sorption in the clay soil suggests that the clay component of soils is important to sorption of this weakly acidic metabolite (Yu, 1986a-c, Spare, 1989b-e).

Metabolite	DIA		DEA		DACT		HYA	
Soil type	Koc ads	Koc des	Koc ads	Koc des	Koc ads	Koc des	Koc ads	Koc des
Sand	48	2655	25	1681			350	1174
Sandy loam	35	366	13	584			360	727
Silty loam	82	149	67	1073			680	1355
Clay loam	76	186	64	540			391	1486
Sand	30	na	12	na	31	na	374	1704
Sandy loam	45	1367	32	1001	58	721	583	1330
Loam	58	1484	45	833	76	1640	2573	2398
Clay	97	438	36	288	55	276	13797	18271

- **Role of humic materials**

Adsorption data are also available for three French soils differing mainly in clay and organic matter content. Studies were conducted similarly to those described above, but at concentrations to 20 mg/L and with a 48 hour equilibration. Soil organic carbon partition coefficients were between 80 and 110, consistent with studies described above. The strength of sorption did not correlate with clay content. Organic matter played an important role, with strength of sorption appearing to increase with the degree of humification as measured by the proportion of extractable organic carbon (Dousset *et al*, 1994).

Soil type	pH	% oc	% sand	% silt	% clay	CEC	Koc
Loamy clay	8.2	1.1	3.6	64.7	31.7	-	110
Calcareous clay	8.0	1.5	29.2	19.5	51.3	-	80
High clay	8.0	1.1	24.5	13.0	62.5	-	89

- **Batch equilibrium studies on five soils**

Similar results were obtained from more recent studies on five soils equilibrated for 6 hours with 5 volumes of radiolabelled atrazine solution (0-2.5 mg/L). Atrazine accounted for 92.5-99% of the radioactivity in the aqueous phase, and 96.8-98.5% on the soil after equilibration. Data obtained were well correlated with the Freundlich equation and returned soil organic carbon partition coefficients between 64 and 150, indicative of weak sorption and moderate to high mobility.

Soil type	pH	% oc	% sand	% silt	% clay	CEC	Koc
Loamy sand	7.0	0.8	78.7	17.1	4.2	6.4	93
Sand	5.7	0.4	96.5	1.0	2.5	3.4	150
Silty loam	7.3	2.1	31.8	54.3	13.9	14.0	82
Silt loam	7.1	4.4	18.4	56.8	24.8	30.7	64
Silt loam	6.6	19.3	21.0	55.4	23.6	113.7	96

Partition coefficients followed a gradually increasing trend in two successive desorption steps, apart from the loamy sand where a slight decline was evident at the second desorption. The highest coefficient obtained, from the second desorption from the silty loam, was 269. The increasing coefficients are thought to reflect formation of non-extractable residues (Flückiger, 1995).

- **Sorption to soil and subsoil**

Studies on six sandy and loamy soils from the Atlantic coastal plain of the USA found that isotherms obtained after 24 hours equilibration at supernatant/soil ratios of 4 and atrazine concentrations to about 12 mg/L were best described by linear equations. Significant losses by sorption to centrifuge tubes were observed, and corrected for. A total of 26 soil samples from different horizons to a depth of 2 m was tested. Mean soil distribution coefficients ranged between 0.64 and 2.15 (generally equivalent to soil organic carbon distribution coefficients slightly above 100) in the surface 33 cm. Coefficients were somewhat reduced in deeper soil horizons, although significant sorptive capacity was retained despite dramatic declines in soil organic matter (Johnson and Sims, 1993). The mobility of atrazine increases as it penetrates deeper into the soil, with the concomitant increase in persistence exacerbating the leaching potential.

- **Significance of non-extractable soil residues**

Soil sorption coefficients are generally calculated based on measured solution concentrations, using the assumption that the balance is associated with the soil. As noted above, fast and slow processes give rise to labile and residual fractions in the soil. The sorption coefficients listed above may be thought of as the sum of fast and slow processes, with the much higher coefficients for desorption reflecting significant contributions from the slowly sorbing/desorbing residual fraction.

The contribution of non-extractable residues to the measured sorption becomes evident when sorption coefficients are calculated based on measured concentrations in solution and in the soil. Such studies have been conducted on sandy loam (pH 6.05, 0.43% organic carbon) and loamy sand (pH 6.30, 0.33% organic carbon) equilibrated at 25^{o}C on an electrical shaker for 24 hours with ten volumes of atrazine solution (one-eigth to one-half of aqueous solubility). Aqueous phases were extracted with hexane, and soil with hexane and acetone in a Soxhlet. Soil concentrations were corrected for aqueous solution retained by the soil.

Soil organic carbon coefficients calculated using the Freundlich equation were 142 in the sandy loam and 112 in the loamy sand, based on measured solution concentrations only. When measured soil concentrations were included in the calculations, coefficients declined to 63 and 45, respectively. The authors suggest that atrazine not accounted for in the measured concentrations, which amounts to more than half the atrazine not found in the aqueous phase, was probably lost through degradation or other means (Singh *et al*, 1990). Given results obtained from other studies, it would appear more likely that the missing atrazine remains in the soil, but as non-extractable residues.

The average soil organic carbon partition coefficient from the preceding studies (a total of 16 soils) is slightly below 100, classifying atrazine as highly mobile according to the McCall scale (McCall *et al*, 1980). It would appear that atrazine would be classified in many soils as very highly mobile on the same scale (Koc < 50) if sorption coefficients were calculated based on extractable soil residues. Available evidence indicates that atrazine forms two fractions in soils, a residual fraction being non-extractable and essentially immobile (although gradual release and remobilisation appears possible) and a labile fraction being very highly mobile. The overall mobility of atrazine in soils decreases with time as increasing proportions enter the residual fraction.

- **Possible cooperative binding mechanisms**

Atrazine is able to donate and accept hydrogen bonds. Nuclear magnetic resonance studies have been conducted, using the chemical shift of the amino nitrogen on the isopropylamino side chain to determine by titration the formation constants in organic solvents of complexes with model compounds (pyrrolidine, cyclopentanone, pyrrole, N-methylpyrrolidinone, pyrrolidinone, acetone, ethanol, phenol, methyl acetate and acetic acid). In general, complexation was moderate, but strong complexation was observed with some compounds (pyrrolidinone and acetic acid) that can both donate and accept hydrogen bonds and have molecular geometry favourable for orbital overlap and cooperative interaction. The authors suggest that atrazine would interact with these strong complexing agents even in aqueous solution, and that similar interactions may occur in the field with urea applied as fertiliser, potentially increasing the amount of atrazine in soil solution. Conversely, cooperative hydrogen bonding with soil organic matter would reduce the amount of atrazine in soil solution (Welhouse and Bleam, 1993).

- **Interactions with soil organic matter**

Atrazine sorption to the clay and organic matter fractions separated by sedimentation from a silt loam soil was studied with and without various solvent extractions and chemical treatments. The untreated clay fraction adsorbed twice as much atrazine as the clay fraction from a soil sample treated with hydrogen peroxide and extracted with ether to remove organic matter. Sequential extractions of the untreated clay fraction with ethyl ether and ethanol caused small increases in sorption, suggesting unmasking of binding sites and a limited

contribution to sorption from the ether soluble fats, oils and waxes, and the ethanol soluble resins in the soil. Sorption declined after hot water extraction to remove polysaccharides, suggesting that these components contribute to the retention of atrazine by soil. Atrazine could be almost completely recovered from the soil fractions by sequential desorption. Addition of competitors for hydrogen bonding sites (urea or guanidine salts) increased the desorption of atrazine. Tests on model substrates found particularly high sorption to quinizarin, lignin and humic acid (Dunigan and McIntosh, 1971).

- **Interactions with humic substances**

Humic substances were isolated from three soils (volcanic soil, Leonardite and oxidised coal) by caustic extraction under a nitrogen atmosphere. Humic samples (100 mg) were equilibrated for 1, 2, 4 or 16 hours with 20 mL atrazine solution (25 mg/L) either with or without prior hydrolysis using hydrochloric acid. Supernatants were assayed, and the residue extracted twice with 90% acetonitrile in water. For the unhydrolysed samples, sorption was strongest with the coal extract (49% after 1 hour, 84% after 16 hours) but this pattern was reversed in the hyrolysed samples (sorption reduced to 5% and 27% in corresponding samples). Sorption in the Leonardite sample changed little with hydrolysis, while the volcanic extract became much more strongly sorbing after hydrolysis.

Nuclear magnetic resonance spectroscopy revealed that the coal extract was richest in aromatic carbon and the volcanic extract richest in aliphatic carbon. Levels of carboxylic carbon were highest in the Leonardite sample, but similar in all unhydrolysed samples. The strength of sorption correlates with the degree of aromaticity.

This relationship was not evident for the hydrolysed materials. In these samples, the strength of sorption correlated with molecular size and absorbance. The volcanic extract appeared to undergo condensation on hydrolysis, with an enhanced concentration of chromophores, while the coal extract underwent a reduction in molecular size.

The authors conclude that ion exchange and hydrogen bonding mechanisms, while probably contributing to the sorption of atrazine to humic substances, can not be dominant as hydrolysis of the coal extract reduced its sorptive capacity despite an increase in total, carboxyl and phenolic acidities. The dominant sorption mechanism appears to involve a charge transfer interaction between electron poor groups such as quinones in the humic acid, and electron rich groups such as the various nitrogen atoms in atrazine. This mechanism appears to be favoured in humic extracts of high molecular dimensions, with complex molecular structure, high aromaticity, and a high concentration of electron acceptor groups (Piccolo *et al*, 1992).

- **Sorptive mechanisms**

A recent review of herbicide interactions with humic substances cites electron-spin resonance studies that show increased free radical concentrations in the humic acid/*s*-triazine interacting system relative to unreacted humic acid. It is assumed that electron transfer occurs from atrazine's electron rich amine and aromatic nitrogens to electron deficient quinone like substructures within the humic acid, with the charge transfer complex stabilised through conjugation with the humic molecular structure. No evidence exists for enzyme mediated covalent bonding and incorporation into humic material, as occurs for some herbicides (Piccolo *et al*, 1996).

- **Time dependence and nonideal behaviour**

Testing on a range of soils with differing levels of organic matter indicated soil organic matter to be a dual mode sorbent, in the same way as model glassy polymers. Sorption can be modelled by a partition mechanism and a hole filling mechanism, the latter accounting for about one third to a half of total atrazine sorption. The hole filling mechanism is slower than the partition mechanism as the holes are within the soil organic matter and not immediately accessible to atrazine in solution. The hole filling component also exhibits a degree of chemical specificity. The nonideal sorptive behaviour observed in soils can be attributed to the dual mode sorption to soil organic matter, particularly the limited number of sorption sites in the internal hole filling domain, with no need to invoke sorption to mineral surfaces (Xing *et al*, 1996).

- **Interactions with polymeric humic-like substances**

Polymeric humic-like substances were prepared by oxidising catechol in the presence of atrazine and its dealkylated metabolites DEA, DIA and DACT. An initial red quinoid pigment preceded development of a brown colour. The dark reaction solutions were separated after 5 days into fulvic acids and humic acid type polymers. The study demonstrated that atrazine can become associated with humic like polymers by reacting during the oxidative polymerisation of phenols. The main proportion was associated with fulvic acids or chloroform soluble catechol derivatives, probably through non-covalent processes such as ion exchange or charge-transfer complexation. In contrast, dealkylated atrazines with their free amino group were mainly associated with the humic acid type polymers, probably through covalent bonding with oxidised polyphenols (Andreux *et al*, 1992).

- **Sorption to soil clay components**

Surface properties of soil components are more important to soil sorption than absolute amounts. This has been studied for the clay fraction where the vast majority of organic and inorganic sorption sites reside. Clay components were separated from a fine loamy soil by sedimentation, fractionated into coarse, medium and fine fractions (0.2-2, 0.02-0.2 and <0.02 µm) by centrifugation, and flocculated. Some samples were treated with hydrogen peroxide (to remove organic matter) and subsequently with a dithionite/citrate/bicarbonate buffer (to remove free iron compounds). Distribution coefficients were determined at a single concentration (10 mg/L) by equilibrating the soil fractions for 24 hours with 5 volumes of atrazine solution. Soil residues were calculated by subtraction of amounts measured in the supernatant. Five sequential desorption steps were also performed on each sample.

Sorption was strongest in the coarse fraction, which was found by differential FTIR spectroscopy to be relatively enriched in the more reactive functional groups (carbonyl compounds such as carboxylate, ketone and aldehyde) compared with the fine fraction, where less reactive functional groups (aliphatic carbon, bound hydroxyl, amine) were predominant. The relative abundance of amine functionality was also evident from the lower carbon to nitrogen ratios in finer fractions, characteristic of highly humified material. Note that these findings contradict results obtained by others showing increased strength of sorption with increased humification. This apparent inconsistency may reflect different sorption mechanisms, with hydrogen bonding dominant in these studies but charge transfer complexation the main mode of sorption in others.

Distribution coefficients were 13.7 in the whole clay, and 21.4, 14.5 and 9.8, respectively, in the coarse, medium and fine fractions (corresponding to organic carbon partition coefficients of 500-1000). Peroxide treatment reduced these coefficients to 4.3 in the whole clay and 1.3, 6.4 and 8.4, respectively, in the fractions, indicating the dominant influence of organic matter on sorption. Coefficients increased slightly in most of the additionally treated samples (6.8 in whole clay, 6.4, 8.2 and 6.8 in the fractions) indicating that free iron compounds reduce the affinity of the the inorganic soil components for atrazine, particularly in the coarse fraction. Desorption coefficients followed an increasing trend in all samples, indicative of contributions from non-extractable residues, with the rate of increase highest in samples containing organic matter.

Organic matter represented some 11% of the untreated whole clay and contributed 68% of its affinity for atrazine, but with much stronger contributions from the coarse fraction reflecting its more reactive functionality. Sorption hysteresis associated with organic matter was much more pronounced for the coarse fraction. The cation exchange capacity of the organic matter was also substantially higher in the coarse fraction. Based on these observations, the authors suggest chemisorption as a major sorption mechanism for atrazine with organic matter in the coarse clay fraction.

The inorganic fraction represented 89% by mass and contributed the remaining 32% of soil affinity. Scanning electron micrography indicated that free iron compounds that suppress the affinity of the inorganic components appear to coat quartz particles in the coarser fractions, but not smectite nor illite surfaces in the finer fractions. The less pronounced sorption-desorption hysteresis after removal of organic matter and free iron compounds suggests that binding to inorganic surfaces is less tight than to organic and involves mainly physical sorption. The small variation of distribution coefficient with particle size in these samples appears to reflect a balance of opposing influences. The coarse fraction is dominated by quartz particles with low surface area and low surface charge density, while silicate minerals in the finer fraction have greater surface area, favouring sorption, but higher surface charge densities more conducive to solvation by water (Laird *et al*, 1994).

- **Sorption to clay minerals**

Sorption kinetics and equilibrium have been studied for the labile and reversible but kinetically slow processes that occur between atrazine and clay minerals, using on-line microfiltration and HPLC. Labile sorption is thought to reflect interaction with active sites on the surfaces of soil particles. It is suggested that the non-extractable residues (reversible but kinetically slow fraction) arise from diffusion from the surface into the interior of soil particles.

It was found that the fast labile sorption generally reached equilibrium within minutes, but that the reversible but kinetically slow fraction may require some days or weeks. At low atrazine concentrations, the coverage of labile sites is low, and sorption followed pseudo first order kinetics. The labile sorption capacity of montmorrillonite, kaolinite and illite clays increased qualitatively with increasing surface area and cation exchange capacity. Sorption of the labile fraction was stronger to sodium saturated montmorrilonite than to calcium saturated montmorrilonite, suggesting that the higher charge density of the latter, both at the mineral surface and between layers, leads to stronger and more ordered hydration and weaker sorption of the weakly hydrophilic atrazine, which may be excluded from the interlayer sorption sites (Gilchrist *et al*, 1993).

- **Desorption from field soils**

The above studies were generally conducted over short equilibration times that may offer a poor model for behaviour in the field. To investigate such possibilities, desorption of atrazine residues from three field soils with a history of atrazine use, including within 2-15 months of sampling, was studied over a 24 hour period and compared with batch adsorption coefficients obtained for fresh samples over the same time frame. Atrazine residues in the field soils were between 17.8 and 236 µg/kg.

Only a fraction of total residues in field samples was labile in these studies. The size of this fraction varied inversely with time since the last treatment. Apparent desorption coefficients for field samples exceeded the sorption coefficients for

fresh samples, which were in the normal range for atrazine, by factors of 2.3-22. Larger ratios were obtained in the less recently treated soils. The age dependence of desorption may reflect diffusion into more remote binding sites to form a slowly desorbing phase, or losses of labile chemical through leaching or biodegradation (Pignatello *et al*, 1991).

- **Leaching indices**

The potential for pesticides to leach can be readily estimated from the nomogram of Gustafson (1989) provided that soil adsorption and persistence data from the field are available. As outlined below, the mobility of atrazine, the diversity of its metabolites, and the tendency to form non-extractable residues, preclude ready estimation of field half-lives. Application of the soil organic carbon partition coefficients (39-176) and the laboratory half-lives (56-385 days) tabulated above identifies atrazine as a probable leacher with GUS values above 3.

The above analysis is confirmed in recent work using sorption data determined chromatographically (soil organic carbon partition coefficients of 111 for atrazine, 38 for DEA and 28 for DIA) and first half-lives determined in the laboratory at concentrations in the low ppm range on an Italian loam (DEA, 72 days, DIA, 40 days and atrazine, 37 days). Note that the cited half-lives are likely to be underestimates as they are based on methanol extractable material. DEA and DIA have higher GUS indices than atrazine, indicating a greater susceptibility to leaching (Bottoni *et al*, 1996).

4.2.4.2 Thin layer chromatography

The mobilities of atrazine, HYA and the three dealkylated metabolites DEA, DIA and DACT were studied on thin layer plates of sand, sandy loam, silt loam and silty clay loam. Atrazine and its dealkylated metabolites were generally found to meet criteria recommended by the US EPA (Hitch, 1982a) for chemicals in the intermediate mobility to highly mobile class. Estimated soil sorption coefficients were in the order of one. The exception was desisopropylatrazine, which had low mobility in the sandy loam and silt loam (soil sorption coefficients in the order of five). These triazines generally had similar or lower mobility than standard herbicides (amiben, 2,4-D and prometon) but greater mobility than ethion. DEA was the most mobile metabolite, with the other two dealkylated products appearing slightly less mobile than the parent. The weakly acidic metabolite HYA was immobile in the sandy and silt loams and had low mobility in the sand and silty clay loam. The relative mobilities are broadly consistent with the results from adsorption studies (Blair, 1986a-e).

More recent studies on soils and subsoils from Iowa examined the mobilities of the same suite of metabolites, and DAHYA. Metolachlor and simazine were used as standards. Four mobility classes were evident, albeit with indistinct boundaries. DEA was the most mobile compound, followed by an intermediate

group containing atrazine, DIA and DACT. Metolachlor and simazine formed a less mobile group, while HYA and DAHYA were nearly immobile. Mobility was greatest in subsoils with low organic content (Kruger *et al*, 1996).

4.2.4.3 Column leaching

- **Fresh samples**

Early column leaching studies found the depth of leaching in sand to be proportional to the applied rainfall (Guth, 1972). Atrazine, at rates equivalent to 5 kg/ha, was slightly more mobile than monuron, a moderate leacher, reaching depths of 10, 18, >30 and >30 cm after elution through sandy loam (pH 6.7, 3.2% organic matter), silty loam (pH 6.1, 2.1% organic matter) and two sandy soils (pH 6.6, 0.2% organic matter and pH 7.8, 1.2% organic matter) with 200 mm artificial rain (Guth, 1973).

- **Aged samples**

Atrazine was added to loamy sand and silt loam soils at rates equivalent to 3 kg/ha and aged aerobically for 90 days before application to columns of the same soil as a 2 cm layer and elution for 16 days with 12.5 mm artificial rain per day.

Radioactivity in the leachate represented 7% of applied from the loamy sand and 4.8% from the silt loam. Radiolabel retained on the column was about 40% extractable with aqueous methanol, reduced from a little above 50% before elution. Approximately 60% of applied radioactivity was retained within the surface 10 cm of the columns. The extractable radiolabel included atrazine as main component, HYA and the three dealkylated atrazines DEA, DIA and DACT as main metabolites, and smaller amounts of dealkylated hydroxytriazines DEHYA, DIHYA and DAHYA.

Atrazine was only found in leachate from the loamy sand, in small amounts (0.1% of applied) and accompanied by DEA (2.9%) and DACT (1.1%) together with smaller amounts of the four triazinols (HYA, DEHYA, DIHYA and DAHYA). For the silt loam, no atrazine was found in the leachate, which contained only the dealkylated hydroxytriazines (DEHYA, DIHYA and DAHYA) and an unknown metabolite (Ellgehausen, 1985b).

A more recent study on the same two soils utilised aging periods in metabolism flasks of 57 days on the loamy sand and 43 days on the silt loam, an application rate equivalent to 1.5 kg/ha, and 200 mm artificial rain over a 2 day period.

Almost 80% of the radiolabel was extractable from the soils after aging and found to contain up to 12 radioactive fractions, with atrazine (up to 45%) the main component, DEA (up to 22%) the main metabolite, and DIA (up to 4.3%),

HYA (up to 8.8%) and DAHYA (up to 12.8%) also identified. Evolution of carbon dioxide reached 3.9% in the loamy sand and 1.5% in the silt loam.

Extractability remained above 70% after leaching, with atrazine (up to 52.4%) remaining predominant and DEA (up to 19%) the main metabolite. Radiolabel was distributed throughout the column, but with the bulk (84-85%) remaining in the surface 16 cm. The main component in extracts from deeper fractions was DEA. Leachates also contained this metabolite, together with similar levels of the hydrophilic metabolites HYA and DEHYA and traces of DAHYA, DIA, and various unknown components. Atrazine was only detected in the leachate from the silt loam, at trace levels. Total radioactivity in the leachate reached 2.7% of applied from the loamy sand and 2.4% in the silt loam (Müller-Kallert, 1995).

- **Field samples**

Freshly applied atrazine was found to be much more mobile than residues in long contaminated field samples, taken 7 months after the most recent application and containing 212 µg/kg atrazine, approximately half the predicted residue from a single application. The apparent desorption coefficient was some 13 times higher than the adsorption coefficient obtained from a 24 hour equilibration, indicating a substantial proportion of non-extractable soil residues.

Leaching from soil columns of the field samples under low flow rates was initially rapid but then entered a protracted tailing phase. Only 43% leached from the column in 66 pore volumes, collected over 3.5 months, compared with 75% of freshly injected samples in 20 pore volumes. Concentration peaks were noted following interruption of the flow through the field sample, suggesting that wet-dry cycles may cause pulse inputs to the subsoil from the sorbed herbicide pool at the surface. Field residues remained uniformly distributed along the column after elution, indicating that desorption was slow relative to the eluent residence time of about a day. Leaching losses from field samples appeared to depend on soil organic matter content rather than particle size, suggesting intraorganic matter diffusion from microstructures of <1 µm.

The differential mobility of fresh and aged atrazine in this soil was well described by a two compartment diffusion sorption model, in which sorbed atrazine undergoes rapid exchange with water in the fast compartment, and depends on radial diffusion kinetics for gradual release from the slow compartment. As discussed earlier in this report, soil organic matter behaves as a dual mode sorbent, with sorption occurring by a partition mechanism and a slower hole filling mechanism. Fresh samples remained primarily in the fast compartment, and exhibited pseudo first order kinetics. For field samples, an estimated 91% resided in the slow second compartment at equilibrium, but attainment of this equilibrium required many months. The two compartment model also qualitatively simulated the effect of flow rate interruptions and predicted the uniform distribution on the column after leaching. Results highlight the caution that must be exercised in extrapolating from short term laboratory studies to long term field behaviour (Pignatello *et al*, 1993).

- **Undisturbed soil columns**

Atrazine movement and degradation was studied in undisturbed columns (15 x 60 cm) taken manually from a conventionally tilled field with no previous atrazine use. Radiolabelled atrazine was applied at a rate corresponding to 2.2 kg/ha and leached once per week with 38 mm artificial rain under outdoor conditions for 12 weeks at 25^{o}C, after an initial delay of 3 weeks.

Approximately 0.1% of radiolabel was recovered each week from the leachate, suggesting preferential flow through macropores. The cumulative recovery of 1.2% from leachate corresponded to a concentration of 7.6 µg/L atrazine and metabolites. Most of the radiolabel (77%) remaining on the column was retained by the top 10 cm, mainly as non-extractable residues (57%) but with some atrazine (9%) and DEA (3.6%, the main metabolite). These two components were found, together with DIA, in all soil fractions. DEHYA was found to 20 cm, HYA to 30 cm, and DACT to 50 cm (Kruger *et al*, 1993).

4.2.4.4 Modelling studies

The GLEAMS model (Groundwater Loading Effects from Agricultural Management Systems) was used to predict the fate of atrazine applied pre-emergence to irrigated maize on a clay soil typical of the Murrumbidgee Irrigation Area, and as a pre-plant treatment to sandy soil typical of pine plantations in the south-west of Western Australia. While the results should be treated with some caution because of the inability of GLEAMS and other models to simulate macropore flow, they reinforce the importance of avoiding application if heavy rain is likely to follow within a day or two.

The maize simulation used an application rate of 1.2 kg/ha (reflecting use of the product Primextra containing atrazine and metolachlor) incorporated through the surface 5 cm. Virtually all the atrazine leaving the field was found to be dissolved in surface runoff. The maximum concentration, based on an overland flow model, was 183 µg/L. Modelling the flow through irrigation furrows as channel flow increased losses by 260%. In the absence of soil incorporation, runoff losses increased by 180%. A 30 mm rainfall event on the day following application increased runoff losses by 340% and caused 7.5% of the applied atrazine to be lost from the field, with a maximum concentration of 2300 µg/L from surface application. No leaching losses were apparent, but this may reflect the inability of GLEAMS and other models to simulate preferential flow through cracks and macropores.

The plantation forestry simulation used an application rate of 1.5 kg/ha as a surface spray. No runoff losses were predicted from these permeable soils, but leaching occured below 2 m depth, with some 0.46% of applied atrazine being lost in the three years following application, at a maximum concentration of 5.7 µg/L. Leaching losses were sensitive to the soil organic carbon partition

coefficient, reducing to zero when this parameter was increased from 100 to 500, and to the half-life. A 30 mm rainfall event on the day following application increased leaching below 2 m by 68%. Atrazine metabolites (DEA and HYA) were also predicted to leach in this situation (Scott *et al*, 1996).

4.2.4.5 Volatility

The calculated Henry's law constant of atrazine is low at about 2.6×10^{-9} atm/m^3/mole and volatilisation from water is not expected to be significant (Howard, 1991).

Laboratory volatilisation studies were conducted for 48 hours in volatilisation chambers on a sandy soil spiked at 80 mg/kg with atrazine and maintained at 35^{o}C and 2% moisture. A flow rate of 30 L/hour resulted in an air change every 36 seconds. The daily volatilisation rate was determined to be 0.012 kg/ha, allowing estimation of 0.21% volatilisation in the first 24 hours following application at 5 kg/ha and penetration to 0.5-1 cm. Increasing the temperature by 10^{o}C caused a 4.3 fold increase in volatilisation rate (Burkhard, 1978b).

Volatilisation from sand and peat soils was studied in 1 cm layers under laminar flow rates of 4.2 m^3/hour by cold trapping of volatile emissions. Atrazine volatilisation followed first order kinetics in longer term studies conducted in a climate controlled room over a few weeks, with projected half-lives of 2248 to 8632 days. Volatilisation appeared more rapid over short timeframes, but results were highly variable. Air dried sand was more retentive of atrazine than sand at 40% field capacity, consistent with hydration of mineral binding sites that reduces the sorption of atrazine and favours its volatilisation. In contrast, and for reasons that are not elaborated, atrazine volatilised more rapidly from dry peat soil than at 40% field capacity, perhaps because moisture uptake reduces porosity and air flow through the peat soil (Schneider *et al*, 1992).

Volatilisation from an acidic sandy soil treated at 1.5 kg/ha and exposed to air velocities corresponding to 60 and 21 000 air changes per hour was low (between 0 and 4.9% of applied during 24 hours (Schulze-Aurich, 1994).

4.2.4.6 Summary of mobility studies

A broad range of studies has been conducted to determine the mobility characteristics of atrazine, including standard batch adsorption and column leaching studies conducted according to recognised test guidelines, and published articles dealing with mechanistic aspects and using less standard methods. Considerably more data exist for atrazine than for other herbicides, and the above review is not comprehensive. Results from the studies described are broadly consistent and allow the following conclusions to be drawn.

Atrazine undergoes limited sorption to soils (reported soil organic carbon partition coefficients in the order of 100) and has high mobility. A significant proportion of sorbed chlorotriazine residues is slow to desorb, and desorption coefficients are indicative of moderate to strong binding and low to moderate mobility. The dealkylated metabolites DEA and DIA exhibit similar behaviour, but have slightly lower sorption coefficients than atrazine.

Sorption is well described by a two compartment diffusion sorption model incorporating a rapidly reversible fraction sorbed to soil surfaces and a kinetically slow fraction associated with interior voids in the soil structure. Although often referred to as bound residues, the kinetically slow fraction is not covalently bound to the substrate and undergoes slow desorption therefrom. Tests on field soils indicate that this kinetically slow fraction can be a source of protracted low level leaching following an initial surge from the labile surface adsorbed fraction.

Sorption occurs predominantly to soil organic matter, particularly if well humified (with large molecular size, high aromaticity and an abundance of electron acceptor groups). Consistent with the sorption model outlined above, soil organic matter behaves as a dual mode sorbent having partitioning and hole filling domains, the latter occupied more slowly and accounting for the bulk of residues in soils with a history of atrazine applications. There may be a lesser but significant contribution from clay minerals.

Sorption was originally thought to mainly involve hydrogen bonding, which can be particularly strong when it occurs cooperatively, but is currently believed to occur mainly through charge transfer interactions between ring and side chain nitrogens and electron deficient quinoid substructures within humic macromolecules. The relative significance of these two modes of sorption appears to vary across different soils, with hydrogen bonding important in some soils and charge transfer complexation dominant in others. Although not documented, covalent bonding via primary amino groups would appear possible for dealkylated metabolites DEA, DIA and DACT.

Chromatographic studies indicate DEA to be the most mobile metabolite, followed by atrazine, DIA and DACT, with hydroxytriazines significantly less mobile.

Consideration of persistence and mobility data identifies atrazine as a probable leacher. Similar analysis finds the dealkylated metabolites DEA and DIA to be more prone to leaching than atrazine.

Leachability is confirmed by column leaching studies. While atrazine and metabolites are largely retained on soil columns, significant amounts (in the order of 5% of applied) are recovered from leachate. As noted above, atrazine forms a kinetically slow fraction in soils that can act as a source of chronic, low level leaching.

Atrazine is not particularly volatile, with losses of a few percent to volatility to be expected in the few days following application.

4.2.5 Field dissipation.

4.2.5.1 Residues in field soils

- **Bare ground applications**

Early field studies on two soils (silt loam, pH 7.7, 7.4% organic matter; loamy sand, pH 8.1, 2.5% organic matter) treated in spring at 5 kg/ha, apparently as a bare ground treatment, found that residues were largely dissipated in the year following application. The location of the trials is not specified, but rainfall occurred throughout the year, generally at more than 50 mm monthly.

Methanol extractable residues in the surface 10 cm of the silt loam were 4.9 mg/kg 31 days after application, declining to 0.19 mg/kg after 311 days and below 0.02 mg/kg after 406 days. Residues in the 10-20 cm layer peaked at 2.9 mg/kg 60 days after treatment. Only minor residues were found deeper in the soil, and residues in leachate collected at a depth of 1.2 m remained at or below the detection limit of 2 µg/L (Büttler, 1979a).

Atrazine was more persistent in the loamy sand, being still present in the surface 10 cm at 0.06 mg/kg 566 days after application. Atrazine appeared 9 days after application at levels of 0.034 mg/L in leachate collected at a depth of 80 cm, and remained above 0.01 mg/kg for about 4 months before declining to near the limit of detection (Büttler, 1979b). Atrazine undergoes limited sorption, allowing easy passage through the soil in soil solution. In addition to this initial surge, the persistence of atrazine enables leaching to continue as the labile surface adsorbed fraction desorbs, with protracted low level contamination in the longer term as the residual fraction slowly desorbs.

- **Non-extractable residues in field soils**

The above studies provide no information on levels on non-extractable residues in the soils. Radiolabelled studies have shown that as much as 83% of the original radiolabel can still be found in soil nine years after application, with a considerable portion (50%) in the non-extractable form (non-extractable during two hours with hot methanol). Humic acid, fulvic acid and humin fractions were separated and subjected to high temperature distillation to recover radiocarbon. Recoveries were 95, 84 and 95%, respectively, and 91% from whole soil, albeit with significant decomposition to $^{14}CO_2$ (15-20% from reference standard, >50% from soil residues). Non-extractable radiocarbon in the three fractions amounted to 13, 33 and 44%, respectively, with 10% retained by nonhumic and mineral components. Analysis of the distillates revealed the presence of atrazine in whole soil, together with hydroxytriazines HYA, DEHYA and DIHYA and

traces of DEA and DIA. Most of these residues were found in the humic acid fraction, although significant levels of hydroxyatrazine were also associated with the base insoluble humin fraction (Capriel *et al*, 1985).

- **New South Wales studies**

Two trials were conducted on self mulching grey clay soils around Tamworth. Atrazine residues were determined by methanol extraction. Laboratory metabolism studies found a half-life of about 50 days when soil water content exceeded 25%, but no significant degradation when moisture dropped below 7%. Residues measured in the soil were lower than those predicted by modelling. The discrepancy may reflect volatilisation losses or the formation of non-extractable residues. Significant leaching was observed, with some 26% of applied atrazine recovered from the 50-150 cm layer at 98 days after treatment (1.6 and 3.2 kg/ha) at one site, increasing to 57% by 380 days. At the other site, residues in this soil segment reached 50% by 280 days after application at 1.8 kg/ha. Leaching exceeded model predictions, perhaps reflecting transport on colloids or by preferential flow (Haigh and Ferris, 1991).

- **Queensland studies**

Only low levels of atrazine (20-80 µg/kg) could be extracted from the surface 20 cm of a range of Queensland soils following 2-8 annual atrazine applications. A grey clay near Dalby also contained 2-9 µg/kg atrazine in the 20-50 cm horizon after 4 applications, but no residues were detected deeper in the profile at any site. A red-brown earth near Goondiwindi contained less than 1% of total atrazine applications over the previous 8 seasons as extractable residues. Low levels (0.1 µg/L) were also found in surface water at this site. Approximately 25% of groundwater samples contained atrazine, at concentrations of 0.1-2.0 µg/L with no discernible pattern. Reported half-lives were between 7 and 47 days, calculated on the basis of extractable residues. The detection of residues in groundwater, but not in the 50-100 cm soil horizon, suggests that the soils sampled would also have contained significant amounts of atrazine in the residual form, potentially providing a chronic source of leaching to groundwater. Crop response to the atrazine residues ranged from no effect to total crop death, with the extent of damage related to plant available (water extractable) residues, in turn dependent on a range of factors such as rainfall during the fallow or after sowing, soil pH, and clay content (Walker *et al*, 1994).

- **Western Australian studies**

Samples of acidic sandy Western Australian soils used for lupin production were studied in the laboratory to determine the factors that influence atrazine dissipation. Residues declined sharply in the first day following application at rates in the order of 2 mg/kg, and then more slowly according to first order kinetics. Excluding the first day data, half-lives were between 57 and 131 days at 20^{o}C. Soil sterilisation with gamma irradiation had no influence on degradation kinetics, suggesting acid catalysed hydrolysis as the main

degradation pathway in these acidic soils. Half-lives increased with an increased proportion of atrazine sorbed to the soil, which in turn increased with pH. The authors suggest that the initial rapid loss probably reflects high herbicide concentrations in the soil water immediately after application (Walker and Blacklow, 1994).

Movement and persistence in Western Australian soils used for lupin production were also studied at a field site that received 76-105 mm rain over 100 days following application at 1 kg/ha in late autumn/early winter. One site was treated with lime, raising the surface pH from 4.8 to 6.4. After 100 days, 25% of applied atrazine remained in the acidic soils, and 40% in the limed soils, mainly in the surface 25 mm. Residues were only found in the 150-200 mm horizon in the limed soil, at less than 2% of applied, notwithstanding several leaching rains. A simulation model predicted that most residues would be in the adsorbed state after the initially high dissolved concentrations soon after application, with sharp declines in dissolved concentrations following leaching rains before desorption restored the equilibrium (Walker and Blacklow, 1995).

5.2.5.2 Field volatility

The vertical flux of atrazine was monitored using polyurethane foam (for vapour) or glass fibre filters (for particulates) over a 24 day period following spring application as wettable powder to a cultivated silt loam soil at a rate of 1.68 kg/ha. Maize was planted the day before application.

Volatilisation followed a clear diurnal pattern with peaks at midday or in the early afternoon, particularly when soils were moist. The estimated flux peaked at 0.46 g/ha on the afternoon following application, declining to around 30% of this level at the same time on the following day, and 10% on day 24. Soils were warm and dry for the first two days after application. Flux increased to 0.27 g/ha/h on day 4, following 15 mm rain on day 3. Fluxes of similar intensity were also observed the day after rain on day 10 and day 17. Soil moisture is known to favour pesticide volatilisation, and increased flux from dry soils can often be detected in the early morning under the influence of dew. Such behaviour was not observed in this study, leading the authors to suggest that wind erosion is a significant loss process for the particulate formulation from dry soils. Estimated total losses over the study period amounted to 2.4% of applied (Glotfelty *et al*, 1989).

In the Netherlands, it has been estimated from volatility data that some 178 g/ha of atrazine volatilises from areas of maize production each year. This is 23% of annual applications, but the estimate contains a number of uncertainties. Redeposition of atrazine from the atmosphere is believed to occur mainly through dry deposition, with phytotoxic side effects possible for up to 500 m from the source based on calculation. These predictions have not been confirmed by monitoring (de Jong *et al*, 1995).

Atrazine has been detected in rainwater (up to 1.5 µg/L) and fog (0.3-0.8 µg/L) near agricultural areas in the USA (Richards *et al*, 1987, Glotfelty *et al*, 1987) and elsewhere. Volatilisation after application is thought to be the main source of this contamination.

More recently, atrazine has also been found in remote and pristine areas. Although not a widespread contaminant, atrazine was found in some samples taken during summer and autumn of 1993 from the Bering and Chukchi marine ecosystems. An air sample taken from near the Alaskan peninsula contained 1.1 $pg.m^{-3}$, probably reflecting local use during the late Alaskan growing season. In addition, a sample of marine ice recently separated from the ice edge contained 400 pg/L, probably reflecting long range transport. Atrazine was not found in seawater, however. The failure to find atrazine more commonly in air samples may reflect the time of sampling, after the main use of atrazine in late spring and early summer (Chernyak *et al*, 1996).

4.2.5.3 Runoff and leaching from a 5 year study under maize

Runoff and leaching losses from a silty clay loam planted annually to maize with a pre-emergence atrazine treatment (1.7 kg/ha) were investigated over 5 seasons under conventional tillage (CT) and no-tillage (NT). Three soil pits were excavated within each tillage area and framed to allow access to three pan lysimeters in each pit. Leachates were collected at a depth of 122 cm, and runoff evaluated in flumes constructed at the natural drainage "outlet" of each tillage area. The silty clay loam was well drained with moderate permeability and contained 1.2% organic carbon in the surface 15 cm, and 0.2% in the 15-60 cm horizon.

Leachate volumes were higher under NT management but with no apparent dilution of residues, apparently as a result of preferential flow through macropores under the undisturbed conditions. The higher moisture levels in mulched NT systems may also favour release of atrazine into interstitial water in micropores, providing a ready reservoir of leachable atrazine that can flow into macropores when rain occurs.

In general, smaller losses occurred when the first leaching event was delayed. Leaching losses in this first event and through the season were substantially higher under NT conditions. CT plots lost around 0.5% of applied atrazine to leaching in each of two wet seasons, while the NT plots lost 3.4-4.7%.

In the final year, conditions were unusually dry in the 2 months following application and no residues were detected in leachate from the CT plot when the first event occurred 57 days after application. In contrast, significant losses were observed under NT, including of cyanazine, a chemical that should have largely degraded over this timeframe. Results indicate that triazine persistence in soils is likely to be greater under drought conditions than generally reported.

Runoff volumes and herbicide losses were much less from NT than from CT, with peak seasonal losses from CT in the order of 0.35%, and from NT in the order of 0.1%. Losses through leaching were more significant than in runoff, and total losses were greater under NT (Hall *et al*, 1991).

4.2.5.4 Groundwater contamination

Movement of atrazine to groundwater was studied in 3.1 m monitoring wells beneath continuous irrigated maize grown under no-till and conventional tillage on a loamy sand. Application rates were 1.12, 2.24 and 4.48 kg/ha pre-emergence for the no-till plots, and 2.24 kg/ha for conventional tillage. A combination of low slope and permeable soils precluded any runoff from the plots. Considerable rainfall followed application after the first and third treatments in a three year study, but the intervening year was extremely dry in the month of application.

Atrazine was found in 5 of 9 wells 24 days after the first application to no-till plots, and reached 54 µg/L beneath the high rate plot 59 days after treatment before disappearing (except for one well with a reading of 2.0 µg/L at day 305) by 200 days after treatment. In the second season, atrazine was not detected until 183 days after application. Preferential macropore flow was not evident in these permeable soils. Half-lives during 1985 were 60 days under no-till and 84 days under conventional tillage (without correction for leaching losses). Atrazine was found in groundwater throughout the following winter and spring, with use in 1985 probably contributing to the detection in groundwater (10.7 µg/L under conventional tillage but 1-4 µg/L under no-till) 24 days after the 1986 application. Half-lives during 1986 were 57-62 days under no-till and 151 days under conventional tillage. The apparent longer half-life and more pronounced leaching under conventional tillage may reflect interception by organic residues at the surface under no-till. Concentrations reaching groundwater appeared independent of application rate (Ritter *et al*, 1994).

4.2.5.5 Leaching of atrazine and metabolites on unperturbed soil columns

The following compounds were loaded onto unperturbed columns (60 x 9.5 cm) of a loamy soil, equipped for leachate recovery and buried in the ground: atrazine, 1.6 kg/ha; DEA, 2.9 kg/ha; DIA, 2.4 kg/ha; DACT, 1.4 kg/ha; and HYA, 6.6 kg/ha. A total of 850 mm rain fell evenly over the study period of 1 year. The following percentages of undegraded compounds leached through the columns: DEA, 11.5%; DACT, 4.2%; atrazine, 1.9%; DIA, 1.3% and HYA, 0.06%. Total leached radiocarbon followed a slightly different trend: DEA, 12.1%; atrazine, 5.6%; DIA, 5%; DACT, 4.5% and HYA 0.06% (Schiavon, 1988a).

The above study also investigated the potential for atrazine and metabolites to form non-extractable residues. Dealkylation favoured such formation, while hydroxylation hindered it. Non-extractable residue formation was most pronounced for DACT, but this was also the metabolite that exhibited the most rapid decline in total residues. Radiocarbon losses to volatilisation or mineralisation over the year were as follows: DACT, 63.5%; DIA, 51.5%; DEA, 39.8%, atrazine, 25.2% and hydroxyatrazine, 21%. Radiocarbon was found throughout the columns, but with the bulk (83% for DEA, >99% for HYA) retained in the surface 24 cm (Schiavon, 1988b).

4.2.5.6 Lysimeter studies

- **Bare ground in Canada**

Field lysimeters were constructed using about 18 kg sandy soil containing 0.4% organic carbon, producing a 70 x 15 cm soil core packed to within 5 cm of the top of a stainless steel cylinder equipped for leachate recovery. Lysimeters were conditioned with 6-8 L water over a 2 week period before treatment in spring with atrazine at 2.25 kg/ha. Six pairs of lysimeters received normal rainfall, and another six were supplemented with two 50 mm events on days 2 and 8, followed by 25 mm applications at specified intervals following rain. One lysimeter from each pair was retrieved and frozen after 1, 2, 4, 8, 12 and 21 weeks. Residues were extracted with methanol.

A single detection of atrazine (0.2 µg) occurred in leachate from the columns that received only natural rainfall (380 mm over the study period). For the lysimeters receiving supplementary irrigation, leaching losses ranged between 1.9 and 32.4 µg (<0.8% of applied) beginning at 12 weeks after application. Traces that eluted after the first supplementary irrigation were thought to reflect incomplete equilibration with the soil, rather than macropore flow, as losses to leachate were much less pronounced after the second simulated storm event. Results indicate a particular vulnerability to leaching in the few days following application (Bowman, 1989).

- **Corn (conventional tillage) in USA**

These studies were conducted in Kansas on experimental plots planted with maize and treated in spring at planting with 3.4 kg/ha atrazine incorporated to a depth of 5 cm. Groundwater occurred at 4 m below the clay loam plot, and 5 m below the silt loam. Each plot contained 7 suction lysimeters lined with bentonite to minimise edge effects and placed to depths of 0.3, 0.6, 0.9, 1.2, 1.8, 3.7 and 4.6 m. Leachate samples were obtained by suction at intervals following application. Soil residues were determined by methanol/water extraction and GC/MS analysis.

Atrazine and DEA were below 0.4 and 0.7 µg/L at all depths in the clay loam plot before application. These levels increased to 33.2 and 4.7 µg/L at a depth of 0.3 m 2 days after application. These peak concentrations were found at increasing depth as the summer progressed, reaching the underlying aquifer in concentrations of 4.1 and 5.0 µg/L 120 days after application. DIA levels were consistently below 18% of DEA concentrations. In contrast to the leachate, atrazine was found in higher concentrations than DEA in soil samples, indicating stronger sorption for atrazine. Note that the ratio of DEA to atrazine in leachate increased with time, consistent with formation of DEA during passage of atrazine through the surface soil layers. The authors propose that non-point source contamination is indicated when this ratio exceeds unity in an aquifer (Adams and Thurman, 1991).

Further studies were conducted on the silt loam plots to investigate the relative removal rates of ethyl and isopropyl groups from atrazine, DIA, DEA, propazine and simazine. Results indicated propazine and DEA to be most resistant to degradation, consistent with relatively slow removal of isopropyl groups. Desethylation is thought to proceed some 2-3 times faster than desisopropylation. The authors hypothesise that the low levels of DIA found in this and other studies reflect the relative ease of further dealkylation in the unsaturated zone, rather than low production, thus implying the likely presence of DACT deeper in the soil (Mills and Thurman, 1994).

- **Maize (no till) in USA**

Atrazine was found at concentrations between 1.3 and 5.1 µg/L in tile drainage (depth 122 cm) from a no till maize plot treated with atrazine pre-emergence at 1.68 kg/ha some 43-110 days previously, the higher detections apparently due to preferential flow through macropores. In the absence of further treatment, residues declined to about 1 µg/L in the following season. Total losses of atrazine DIA and DEA reached some 9-18 g/ha in the first season, with an additional 3-4 g/ha in the following season. DEA was more abundant than DIA, and became more abundant than atrazine in the second season. The maximum loss over two seasons was 1.3% of applied, from the plot that received the most rainfall.

The maximum concentration obtained from suction lysimeters was 20.5 µg/L at a depth of 90 cm 7 weeks after application. Total residues (atrazine, DEA and

DIA) were 23.8 µg/L at this time. The ratio of DEA to atrazine followed an increasing trend over the following year in the plots where preferential flow was not apparent (Jayachandran *et al*, 1994).

- **Maize in Switzerland**

This study utilised undisturbed soil monoliths (1.2 m x 1.0 m2) of sandy soil with low organic content, installed in outdoor testing facilities and surrounded by untreated areas planted to maize, followed after harvest by winter cereals. Radiolabelled atrazine was applied at planting at 1.0 kg/ha. Rainfall and irrigation totalled 950 mm in the first year after treatment and 1130 mm in the second. A total of 2.92% of applied radiocarbon leached through the soil during 2 years, mainly (80%) in the second season. Mean leachate concentrations, expressed as atrazine equivalents, were 1.65 µg/L in the first season, increasing to 4.3 µg/L in the second, with a peak concentration in the order of 8 µg/L 549 days after application. More than 90% of the applied radiolabel could be accounted for, with 6% taken up by the crop, 49% retained on soil (mostly near the surface) and 42% lost to volatilisation and mineralisation. Most of the radiolabel remaining on soil was extractable with methanol/water, particularly deeper in the profile.

Mean atrazine concentrations in leachate remained below 0.05 µg/L. Atrazine was accompanied by slightly higher levels of DEA and DIHYA and by four unknown metabolites. DEA and HYA were the main components found in soil (Burgener, 1995).

Similar results were obtained from this lysimeter system following application of unlabelled atrazine at 0.75 kg/ha. Atrazine recovered in leachates over a two year period represented less than 0.05% of applied, even in this low organic sandy soil, and DEA appeared to represent less than 0.1% (Urban and Egli, 1995).

4.2.5.7 Overview of field studies

A wide range of overseas field studies was submitted, with atrazine persistence determined by residue analysis and leaching determined in lysimeters or using monitoring wells or analysis of tile drainage. Monitoring of runoff used flumes. The overseas data submitted have been supplemented by local studies conducted in NSW, Queensland and Western Australia.

Atrazine residues were largely confined to the surface 20 cm of soils, declining from a few ppm soon after application to the low-mid ppb range over the course of a year. Note that these are extractable residues, and may be accompanied by significant amounts (over 80% of applied in one case some 9 years after application) of non-extractable residues. Atrazine concentrations in leachate collected at depths in the order of a metre generally remain below 10 µg/L, although detections up to 54 µg/L have been recorded. Atrazine was found at

34 µg/L in leachate at 80 cm depth some 9 days after bare ground application at 5 kg/ha. Losses from conventional tillage appear generally to be smaller than from no till plots, particularly the leaching component, because of preferential macropore flow under the latter conditions.

Half-lives of about 2 months appear typical but there is wide variation above and below this figure. Note that these half-lives reflect loss of extractable atrazine, including through the formation of untransformed but nonextractable residues, rather than confirmed degradation. In local studies, no degradation is apparent when when soils are dry.

DEA is the most abundant and mobile metabolite. Dealkylation appears to favour non-extractable residue formation, but dealkylated metabolites are also more susceptible to mineralisation. Hydroxylation hinders the formation of non-extractable residues, and HYA appears to be the most persistent metabolite. However, it is also the least mobile primary metabolite.

Lysimeter studies gave similar results, with around 1% of applied radiolabel leaching to depths in the order of 2-4 m over the course of a year, at concentrations in the low ppb range (peak levels in the order of 20 µg/L at 90 cm depth).

Pesticide transport through field soils has recently been reviewed (Flury, 1996). Many pesticides leach through field soils even though laboratory leaching studies indicate that they should be retained by the soil matrix. Preferential macropore flow can be a significant contributor to this behaviour. The largest annual losses recorded into subsurface drains are for atrazine, at 2.6-3.6% of applied, but this may reflect an abundance of studies rather than a unique leaching potential (herbicides have a general tendency to be mobile). A worst case single runoff event of 17% of applied has been recorded. Worst case leaching events include 9.6% of applied atrazine below 1.22 m after 1000 mm rainfall. High losses may occur with high intensity rain to dry soil soon after application, with conventionally tilled plots conducive to runoff and no till soils more prone to leaching. Delays between application and the first storm mitigate losses. Respective delays of 1 hour, 1 day, and 1 and 2 weeks before a simulated storm event (30 mm in 30 minutes) resulted in 4.5, 3, 2 and 1.1% of applied atrazine percolating through earthworm burrows in undisturbed 30 cm cubes of silt loam soil taken from a plot planted continuously for 24 years to no-till corn.

Volatility losses appear to represent a few percent of applied, although higher estimates exist. Because of its widespread use, atrazine is a commonly detected contaminant of fog and rainwater.

4.2.6 Accumulation and bioaccumulation.

Atrazine evidently has the potential to accumulate in soils as non-extractable residues (a reversible but kinetically slow fraction) in soils, given that as much as

83% of the original radiolabel can still be found in soil nine years after application. However, the rate of release of these accumulated non-extractable residues is thought to be low (no more than a few percent annually).

Bioaccumulation in bluegill sunfish exposed under flow-through conditions for 28 days to 0.10 mg/L radiolabelled atrazine was low, with a bioconcentration factor of 13 in whole fish and 90% of steady state achieved within 2 days. The depuration half-life was about half a day. Residues were 70-100% extractable with acetonitrile/dichloromethane. Atrazine was predominant in all extracts, with traces of a metabolite thought to be DIA found in two samples (Forbis, 1987).

Bioconcentration factors in juvenile fathead minnows are also low, as noted later in this report (Dionne, 1992).

4.2.7 Summary of environmental fate.

Atrazine is applied as a spray at moderate rates (typically 1-3 kg/ha) to a range of summer grain crops, sugarcane, pasture and legumes (principally lupins). Application occurs during winter at slightly higher rates but less frequently for pine and eucalypt plantation establishment. Following application, residues that are not retained by the crop are expected to become associated with the soil and interstitial water, although the strength of the association with soil is likely to be relatively weak in the few days after application, and the risk of runoff or leaching relatively high.

Atrazine is a well studied herbicide, with extensive environmental fate data available for the following areas.

4.2.7.1 Hydrolysis

Atrazine is transformed to HYA by hydrolysis, but the reaction is very slow in sterile water. Transformation is more rapid in soils, where hydrolysis is believed to be catalysed by acidic groups within the soil organic matter to which atrazine adsorbs.

4.2.7.2 Photolysis

Atrazine degrades under the influence of sunlight to a range of dechlorinated and dealkylated products, but the reaction is slow with an estimated half-life in water of about a year. Degradation is faster in the presence of humic acids as sensitiser, giving rise to an additional product (ammelide) from deamination. Half-lives of a few weeks on soil surfaces exposed to natural sunlight appear typical.

4.2.7.3 Metabolism

Laboratory investigations indicate that atrazine degrades in soils through a combination of soil catalysed processes and microbial and plant metabolism, with the main reactions being hydrolytic dechlorination, side chain dealkylation, and subsequent deamination. The hydrolytic reaction, which is soil catalysed, appears to be favoured in acidic soils. Half-lives are variable, generally a few months but extending to over a year in some soils, particularly at depth where microbial populations are low, or during drought when soils are dry.

Loss of atrazine from soils is mainly accompanied by the formation of non-extractable residues. Note that reported half-lives are commonly underestimates as non-extractable residues are generally excluded from their derivation. Non-extractable residues may be extracted under forcing conditions, and have a similar metabolite profile to extractable residues. Release under environmental conditions may occur at a few percent per year through microbial or plant metabolism or decomposition of soil organic matter.

Mineralisation of atrazine in soils is a very inefficient process, except where soils have been artificially fortified with atrazine-mineralising bacterial consortia. Intermediate metabolites such as cyanuric acid and ring opened products such as biuret and urea are not isolated.

Degradation in aquatic systems follows similar pathways, with the hydrolytic reaction apparently catalysed by sediment. Aquatic sediment appears to have only limited capacity to sorb atrazine. At low atrazine concentrations, half-lives of 2 months or more appear typical of freshwater systems, while degradation in estuarine systems appears from limited data to proceed with half-lives of less than a month.

4.2.7.4 Mobility in soil

Atrazine undergoes weak sorption to soils (reported soil organic carbon partition coefficients in the order of 100) and has high mobility. A significant proportion of sorbed chlorotriazine residues is slow to desorb, and desorption coefficients are indicative of moderate to strong binding and low to moderate mobility. The difference between adsorption and desorption means that atrazine tends to be highly mobile soon after application. However, once adsorbed, the mobility of atrazine is highly influenced by soil desorption processes. The dealkylated metabolites DEA and DIA exhibit similar behaviour, but have slightly lower sorption coefficients than atrazine.

Sorption is well described by a two compartment diffusion sorption model incorporating a rapidly reversible fraction sorbed to soil surfaces and a kinetically slow fraction associated with interior voids in the soil structure. Although often referred to as bound residues, the kinetically slow fraction is not covalently bound to the substrate and can undergo slow desorption therefrom.

Tests on field soils indicate that this kinetically slow fraction can act as a source of protracted low level leaching following an initial surge from the surface adsorbed fraction.

Sorption occurs predominantly to soil organic matter, particularly if well humified with large molecular size, high aromaticity and an abundance of electron acceptor groups. Soil organic matter behaves as a dual mode sorbent having partitioning and hole filling domains, the latter occupied more slowly and accounting for the bulk of residues in soils with a history of atrazine applications. There may be a lesser but significant contribution from clay minerals. Sorption was originally thought to mainly involve hydrogen bonding, which can be particularly strong when it occurs cooperatively, but is currently believed to occur mainly through charge transfer interactions between ring and side chain nitrogens and electron deficient quinoid substructures within humic macromolecules. The relative significance of these two modes of sorption appears to vary across different soils, with hydrogen bonding important in some soils and charge transfer complexation dominant in others. Although not documented, covalent bonding via primary amino groups would appear possible for dealkylated metabolites DEA, DIA and DACT.

Chromatographic studies indicate DEA to be the most mobile metabolite, followed by atrazine, DIA and DACT, with hydroxytriazines significantly less mobile.

Consideration of persistence and mobility data identifies atrazine as a probable leacher. Similar analysis finds the dealkylated metabolites DEA and DIA to be more prone to leaching than atrazine. Leachability is confirmed by column leaching studies. While atrazine and metabolites are largely retained on soil columns, significant amounts are recovered from leachate. As noted above, atrazine forms a kinetically slow fraction in soils that can act as a source of chronic, low level leaching.

Atrazine is not particularly volatile, with losses of a few percent to volatility to be expected in the few days following application. Because of its widespread use, atrazine is a commonly detected contaminant of fog and rainwater.

4.2.7.5 Field dissipation.

Atrazine residues are largely confined to the surface 20 cm of field soils, declining from a few ppm soon after application to the low-mid ppb range over the course of a year. Note that these are extractable residues, and may be accompanied by significant amounts (over 80% of applied in one case some 9 years after application) of non-extractable residues. Atrazine was found at 34 µg/L in leachate at 80 cm depth some 9 days after bare ground application at 5 kg/ha. Losses from conventional tillage appear generally to be smaller than from no till plots, particularly the leaching component, because of preferential macropore flow under the latter conditions.

DEA is the most abundant and mobile metabolite. Dealkylation appears to favour non-extractable residue formation, but dealkylated metabolites are also more susceptible to mineralisation. Hydroxylation hinders the formation of non-extractable residues, and HYA appears to be the most persistent metabolite. However, it is also the least mobile primary metabolite.

Lysimeter studies gave similar results, with around 1% of applied radiolabel leaching to depths in the order of 2-4 m over the course of a year, at concentrations in the low ppb range (peak levels in the order of 20 µg/L at 90 cm depth).

Many pesticides leach through field soils even though laboratory leaching studies indicate that they should be retained by the soil matrix. Preferential macropore flow can be a significant contributor to this behaviour. The largest annual losses recorded into subsurface drains are for atrazine, at 2.6-3.6% of applied, but this may reflect an abundance of studies rather than a unique leaching potential (herbicides have a general tendency to be mobile). A worst case single runoff event of 17% of applied has been recorded. Worst case leaching events include 9.6% of applied atrazine below 1.22 m after 1000 mm rainfall. High losses may occur with high intensity rain to dry soil soon after application, with conventionally tilled plots conducive to runoff and no till soils more prone to leaching.

4.2.7.6 Accumulation and bioaccumulation.

Atrazine evidently has the potential to accumulate as non-extractable residues (a reversible but kinetically slow fraction) in soils, given that as much as 83% of the original radiolabel can still be found in soil nine years after application. However, the rate of release of these accumulated non-extractable residues is thought to be low (no more than a few percent annually).

Bioaccumulation in fish is low, and accumulated residues are rapidly depurated when fish are returned to clean water.

4.2.7.7 Conclusion

Considerably more data exists for atrazine than for other herbicides as it has been very intensively studied. The above review is not exhaustive but based mainly on data provided by the principal registrant, together with key selected papers from the recent scientific literature. Data submitted are considered complete with no significant data gaps, although a number of aspects remain incompletely understood. In particular, understanding of sorptive mechanisms remains incomplete with some results apparently in conflict, although this probably reflects the existence of a variety of mechanisms the significance of which varies with soil properties.

Although precise mechanisms are not fully understood, it is evident that the persistence of atrazine in the environment, together with its limited sorption to soil, significant water solubility and widespread use, are disadvantageous from the environmental perspective as they lead to chronic low level contamination of surface and groundwater. This is exemplified by contamination of irrigation drainage water in the Murrumbidgee Irrigation Area at levels above 1 µg/L throughout the summer cropping season, with peak levels in the order of 100 µg/L. High peak levels have also been reported in streams draining forestry plantations in Tasmania, reflecting a combination of moderate to high application rates, steep terrain, heavy rainfall, cool winter temperatures, application to wet soils, and particularly weak soil sorption in the few days following application.

The use of atrazine requires careful management and strict adherence to good farming practice if levels of aquatic contamination are to be maintained within acceptable bounds. It is particularly important that new restrictions on use introduced by the NRA are adhered to. Some registrants and users appear to remain unaware of the restrictions and continue to promote or use atrazine in situations conducive to aquatic contamination, such as for weed control in irrigation channels and non-agricultural situations.

4.3 Environmental effects

Results for the following tests are available. Most of the data were provided by Ciba-Geigy. Makteshim-Agan provided some studies, including recent work in the developing area of terrestrial arthropod testing. Selected recently published papers from the scientific literature have also been included. Some of the older tests were conducted more than two decades ago, but results are generally consistent. Except where specifically noted, it would appear that tests have been conducted satisfactorily according to accepted international guidelines such as those of the US EPA (Hitch, 1982b) and OECD. With the exception of the aquatic multi-species studies, test reports have generally not been published.

4.3.1 Avian toxicity

4.3.1.1 Acute oral

Test	Species	Result	Reference
Acute oral	Japanese quail	LD50 > 2000 mg/kg	Leopold and Daamen, 1994
Acute oral	Mallard duck	LD50 > 2000 mg/kg	Daamen, 1994

Recent acute oral results indicate atrazine to be practically nontoxic to Japanese quail and mallards. Sporadic mortalities occurred at doses above 125 mg/kg, particularly in male birds. Symptoms of intoxication included depressed food consumption, lethargy and uncoordinated movement, with some regurgitation observed in mallards. No observed effect levels were 15 mg/kg in Japanese quail and 31 mg/kg in mallards.

Ciba-Geigy also provided a range of older acute oral studies in ducks, quail and chickens that returned similar results as tabulated below, indicating atrazine to be no more than slightly toxic. The relative insensitivity of Peking ducks appears to reflect regurgitation, which occurred just after administration in adult ducks and within 10 minutes in ducklings at higher doses.

Test	Species	Result	Reference
Acute oral	Bobwhite quail	LD50 = 4237 mg/kg	Sachsse and Ullman, 1974
Acute oral	Bobwhite quail	LD50 = 940 mg/kg	Fink, 1976
Acute oral	Peking duck	LD50 > 10000 mg/kg	Sachsse and Ullman, 1975a
Acute oral	Peking duckling	LD50 = 10000 mg/kg	Sachsse and Ullman, 1975b
Acute oral	Chicken	LD50 = 828 mg/kg	Sachsse and Ullman, 1975c
Acute oral	Japanese quail	LD50 = 1660 mg/kg	Sachsse and Ullman, 1976

The metabolite DEA was moderately toxic (LD50 = 464 mg/kg) when administered orally to bobwhite, with mortality generally occurring within a day of dosing (Fletcher, 1971).

4.3.1.2 Dietary toxicity

Dietary studies (5 days exposure and 3 days recovery) in Japanese quail chicks found atrazine to be practically nontoxic (LC50 > 5000 ppm). Birds exhibited symptoms of intoxication (depressed food consumption, lethargy and hunched posture) above the no observed effect level of 1250 ppm (Leopold, 1994).

Older studies returned similar results as tabulated below. Food consumption was significantly depressed, particularly in Japanese quail at higher doses.

Test	Species	Result	Reference
7 day dietary	Bobwhite quail	LC50 > 10000 ppm	Gough and
8 week dietary	Bobwhite quail	NOEC > 2000 ppm	Shellenberger, 1972
8 day dietary	Japanese quail	LC50 > 10000 ppm	Sachsse and Ullman, 1975d

4.3.1.3 Reproduction

Atrazine technical (0, 75, 225 and 675 ppm) was administered in the diet for 20 consecutive weeks to 18 week old bobwhite quail, with a 3 week recovery period. A few parental mortalities occurred but were not dose related. No other clinical symptoms of intoxication were observed. No dose related effects on the number of defective, cracked, broken or infertile eggs were observed at laying.

An increase in mid-term eggs (embryos not showing life at 18 days) was noted at the highest dose during the test period, together with increases in full term eggs (fully developed embryos that did not liberate from the shell) at the two higher doses. Similarly, full term eggs were more abundant during the recovery period at the highest dose relative to controls. These adverse effects on egg viability were considered to be treatment related.

Variations in body weight among the offspring were attributed to normal biological variation rather than to ingestion of atrazine by the parent. The no observed effect level was 225 ppm based on egg viability (Pedersen and DuCharme, 1992a).

Similar results were obtained from an analogous test in mallards. Food consumption was depressed in parent birds at the highest dose. An increase in numbers of one week eggs (embryos not showing life at 14 days) was also noted at this dose. No treatment related effects were observed in the offspring. The no observed effect level was 225 ppm based on reduced feed consumption in adults and a higher incidence of one week eggs at the highest dose tested (Pedersen and DuCharme, 1992b).

4.3.2 Aquatic Toxicity

4.3.2.1 Fish

- **Acute toxicity**

Acute toxicity results for atrazine are tabulated below.

Test	Species	Result	Reference
96 hour acute	Rainbow trout	LC50 = 11 mg/L	Rufli, 1989a
96 hour acute	Common carp	LC50 = 19 mg/L	Rufli, 1989b
7 day acute	Fathead minnow	NOEC = 4.9 mg/L	Jop, 1991a
96 hour acute	Sheepshead minnow	LC50 = 13 mg/L	Machado, 1994a

Trout and carp were tested under static conditions with results expressed as nominal concentrations (but confirmed by analysis) and sheepshead minnow under flow-through conditions with results expressed as mean measured concentations. No observed effect concentrations were 1.8 mg/L in trout (based on erratic swimming, loss of equilibrium and pigmentation), 3.2 mg/L in carp

(based on loss of equilibrium) and 3.2 mg/L in sheepshead minnow (based on lethargy and erratic swimming). The fathead minnow test used static conditions with daily renewal of about 80% of the test medium and found no effects on survival or growth of freshly hatched larvae. Results indicate that atrazine has slight acute toxicity to fish.

- **Metabolites**

The toxicity of DIA to rainbow trout (96 hour LC50 = 17.2 mg/L) is similar to that obtained for atrazine under similar conditions (Vial, 1991a). The completely dealkylated metabolite DACT is practically nontoxic (96 hour LC50 > 100 mg/L) to this organism (Vial, 1991b).

- **Renal effects**

Reduced motility, balance disturbances and darkening of the body surface, together with morphological effects (necrosis of endothelial cells and renal hemopoietic tissue) on the kidneys, have been reported in published work involving acute exposure of rainbow trout to sublethal concentrations (1.4-2.8 mg/L) of atrazine. Minor alterations of renal corpuscles and renal tubules were apparent at much lower concentrations (5-40 µg/L) following chronic exposure, together with an increase in cells with mitotic features in renal hemopoietic interstitium (Fischer-Scherl *et al*, 1991).

- **Chronic toxicity**

Rainbow trout fingerlings (mean weight 0.6 g) experienced 40% mortality when exposed for 21 days under flow-through conditions to 1.0 mg/L atrazine. The no effect concentration based on mortality was 0.06 mg/L (Ritter, 1989). The ratio of acute to chronic no observed effect concentrations is relatively high at 300.

- **Lifecycle testing**

Fathead minnows were continuously exposed under flow-through conditions for 274 days, initially as embryos, to atrazine (mean measured concentrations between 0.15 and 2.0 mg/L) with exposure of progeny continued for 30 days post-hatch. No effects on hatching success or survival to 60 days were noted, but there was a slight reduction in growth rate at the three highest concentrations (0.46-2.0 mg/L) and reduced survival after 274 days at the two highest concentrations (82% at 0.99 mg/L and 86% at 2.0 mg/L compared with 95% in controls). Reproductive parameters (eggs per spawn, total eggs, spawns and eggs per female) remained unaffected.

Hatching success for the offspring appeared compromised at concentrations of 0.25 mg/L and above (74-82% compared with 86% for controls) when analysed using the Cochrane-Armitage Trend Test. However, a second statistical comparison (Williams' Test) that recognises inter-replicate variation when determining significance found no such effect.

As for the parent generation, growth of the offspring was reduced at the three highest concentrations relative to controls and the two lowest test concentrations. The no observed effect level based on these growth reductions in both generations was 0.25 mg/L.

An initial flow-through acute study in juveniles returned a 96 h LC50 of 20 mg/L. Tissue analyses found bioconcentration factors ranging from 3.75 in day old first generation embryos to 8.5 for adult parents (Dionne, 1992).

4.3.2.2 Aquatic invertebrates

- **Acute toxicity**

Acute toxicity results for atrazine are tabulated below:

Test	Species	Result	Reference
24 hour acute	*Daphnia magna*	LC50 = 87 mg/L	Rufli, 1989c
48 hour acute	*Ceriodaphnia dubia*	NOEC = 4.9 mg/L	Jop, 1991b
96 hour acute	*Chironomus tentans*	LC50 > 28 mg/L	McNamara, 1991a
96 hour acute	*Mysidopsis bahia*	LC50 = 5.4 mg/L	Machado, 1994b
96 hour acute	*Acartia tonsa*	LC50 = 94 µg/L	Hollister, 1979a
96 hour acute	*Acartia tonsa*	LC50 = 4.3 mg/L	McNamara, 1991b
96 hour acute	*Neopanope texana*	LC50 > 1000 mg/L	Bentley, 1973
96 hour acute	*Uca pugilator*	LC50 > 29 mg/L	Heitmuller, 1979

The *Daphnia magna* test used static conditions, with results expressed as nominal concentrations. Atrazine was solubilised in the 100 mg/L stock solution with 4 mg/L alkylphenol ethoxylate, and test solutions assayed as close to nominal, notwithstanding some precipitation at test concentrations above 32 mg/L. The no effect concentration was 18 mg/L. Results indicate atrazine to be slightly toxic to this cladoceran species. Similarly low toxicity is apparent in the other cladoceran tested (*Ceriodaphnia dubia*), although an LC50 could not be obtained as no effects were noted at the highest test concentration.

The midge test (*Chironomus tentans*) used flow-through conditions, and deviated from the protocol in that the test organisms were fed to allow survival through 96 hours. The no observed effect concentration was 5.5 mg/L based on 15% mortality at 10 mg/L. Atrazine appears slightly toxic to midge.

The result for the marine species, mysid shrimp (*Mysidopsis bahia*), indicates moderate toxicity. The no observed effect level was 1.7 mg/L based on sub-lethal effects (darkened pigmentation, lethargy, erratic swimming behaviour).

The importance of feeding the marine copepod (*Acartia tonsa*) to ensure adequate survival through 96 hours in controls is noted in the more recent of the two tests listed, conducted under flow-through conditions. Test organisms were cultured in the laboratory and approximately 17 days old when testing

commenced. Results are expressed as mean measured concentrations at initiation and termination of exposure. Solubility of atrazine in the sea water used for testing was about 20 mg/L. Dose dependent mortality was observed at all treatment levels, and the no observed effect concentration in the second test was below 2.9 mg/L. Atrazine is moderately toxic to this marine copepod based on the more recent test.

Dose and time dependent mortality was also observed in the older test, conducted under static conditions using adult copepods taken from a Florida estuary and acclimatised to laboratory conditions for 48 hours prior to testing. Survival through 96 hours in seawater and solvent controls was acceptable (>90%). Results need to be treated with suspicion as they are inconsistent with those from later testing under flow-through conditions, and with data for other aquatic invertebrates. Reasons for the anomalous results are unclear, but errors in preparing the test solutions appear possible. The report states that weighed amounts of atrazine were dissolved in acetone and pipetted into 100 mL seawater. This would have required the accurate weighing of a few micrograms, which is not a simple task.

Adult crabs are insensitive to atrazine. Mud crabs (*Neopanope texana*; mean carapace width 15 mm) and fiddler crabs (*Uca pugilator*; 11-14 mm) were tested under static conditions with results expressed as nominal concentrations. No effects are apparent within atrazine's solubility limit.

- **Metabolites**

The toxicity of DIA to *Daphnia magna* (48 hour EC50 = 126 mg/L) is similar to that obtained for atrazine under similar conditions (Vial, 1991c). The completely dealkylated metabolite DACT is also practically nontoxic (48 hour EC50 > 100 mg/L) to this organism (Vial, 1991d).

- **Reproductive testing**

A 21 day static reproduction test was conducted in *Daphnia magna*, using surfactant to solubilise the test article in the stock solution as for the acute test, and with renewal of the test medium three times per week. The no effect concentration, based on increased number of progeny at 7 and 14 days, was 0.012 mg/L. No effects were noted on adults, or on cumulative number of progeny at 21 days, at the highest test concentration of 0.12 mg/L (Rufli, 1989d). The ratio of acute to chronic no effect concentrations is 1500 based on increased progeny at 7 and 14 days, reducing to 150 or less based on observations at 21 days.

A 7 day static renewal test in *Ceriodaphnia dubia* found a significantly reduced number of offspring per female at concentrations of 2.5 and 4.9 mg/L. The no observed effect concentration was 1.2 mg/L. Adult survival was unaffected (Jop, 1991c).

4.3.2.3 Aquatic vegetation

- Algae

Algal growth was determined by direct cell counts. Results for the first 8 species listed below (3 freshwater and 5 marine) are expressed as nominal concentrations, and indicate high toxicity of atrazine to algae. *M aeruginosa*, *S costatum*, *I galbana*, and *P cruentum* grew faster than controls during a 9 day recovery phase following exposure. Lowest observed effect concentrations were generally about a quarter of the minimum algistatic concentrations (concentrations that allow no net growth during exposure but with at least partial recovery in clean media).

The three algal results obtained more recently by Hoberg, also indicative of high to very high toxicity, are expressed as mean measured concentrations that cause 50% growth inhibition.

Algal results reported by Hughes for freshwater blue-green algae, freshwater diatoms and marine chlorophytes respectively confirm the high toxicity of atrazine to such organisms. Growth inhibition was determined by direct cell counts, with prior sonication for the blue-green alga to break up filaments. No observed effect concentrations were below 100 µg/L. This study also included a 9 day recovery phase, allowing estimation of algistatic concentrations (4.9, 1.73 and 1.43 mg/L, respectively). The algicidal concentration (at which no recovery occurred) was 3.2 mg/L (the highest test concentration) for the marine chlorophyte and above this concentration for the two freshwater algal species. The author comments that the EC50 may be an overly conservative predictor of environmental effects as it does not allow for recovery, and a 50% growth deficit is easily accommodated in a logarithmically growing population.

Test	Species	Result	Reference
72 hour	*Scenedesmus subspicatus*	EC50 = 43 µg/L	Rufli, 1989e
120 hour	*Microcystis aeruginosa*	MAC = 440 µg/L	Hollister, 1979b
120 hour	*Selenastrum capricornutum*	MAC = 200 µg/L	Hollister, 1979b
120 hour	*Chlorella pyrenoidosa*	MAC = 520 µg/L	Hollister, 1979b
120 hour	*Dunaliella tertiolecta*	MAC = 1100 µg/L	Hollister, 1979b
120 hour	*Skeletonema costatum*	MAC = 85 µg/L	Hollister, 1979b
120 hour	*Isochrysis galbana*	MAC = 88 µg/L	Hollister, 1979b
120 hour	*Porphyridium cruentum*	MAC = 780 µg/L	Hollister, 1979b
96 hour	*Selenastrum capricornutum*	EC50 = 130 µg/L	Hoberg, 1991a
120 hour	*Selenastrum capricornutum*	EC50 = 55 µg/L	Hoberg, 1993a
96 hour	*Skeletonema costatum*	EC50 = 55 µg/L	Hoberg, 1993b
120 hour	*Anabaena flos-aquae*	EC50 = 230 µg/L	Hughes, 1986
120 hour	*Navicula pelliculosa*	EC50 = 60 µg/L	Hughes, 1986
120 hour	*Dunaliella tertiolecta*	EC50 = 170 µg/L	Hughes, 1986

Low dose toxicity to *Selenastrum capricornutum* was revisited using a more sensitive bioassay, termed step-wise growth balance dilution, in which fixed volumes of cell suspension were replaced by sterile nutrient after each counting, so as to maintain a constant cell density in controls. Growth rates were reduced, by 7% at 10 µg/L to more than 50% at 50 µg/L. The low dose effect was not

detected using eight consecutive conventional static bioassays. A reduction in cell size was apparent at 29 and 50 µg/L with visible cell necrosis. Rapid recovery in growth rates was observed following acute exposures, and no additional sensitivity was evident from chronic low dose (32 days at 10 µg/L) exposures (Benjamin *et al*, 1996).

- **Metabolites**

The toxicity of DIA to *Scenedesmus subspicatus* (72 hour EC50 = 1.39 mg/L) indicates moderate toxicity, compared with the high toxicity recorded for atrazine under similar conditions (Vial, 1991e). The completely dealkylated metabolite DACT exhibits no phytotoxicity (72 hour EC50 > 100 mg/L) to this organism (Vial, 1991f).

- **Macrophytes**

Test	Species	Result	Reference
120 hour	*Lemna gibba*	EC50 = 170 µg/L	Hughes, 1986
168 hour	*Lemna gibba*	EC50 = 180 µg/L	Hoberg, 1991b
336 hour	*Lemna gibba*	EC50 = 50 µg/L	Hoberg, 1993c
24 hour	*Potamogeton perfoliatus*	IC50 = 80 µg/L	Jones *et al*, 1986

The floating freshwater vascular plant duckweed exhibited similar sensitivity as algae in 5 day static and 7 day static-renewal exposures, as may be expected given that atrazine inhibits photosynthesis. The 5 day phytostatic concentration (frond counts) was 1.72 mg/L, and the 7 day no observed effect level 57 µg/L. Increased toxicity is apparent over 14 day static exposures, with a no observed effect concentration of 8.3 µg/L, but it should be noted that results are expressed conservatively as final measured concentrations, which were a little over half the initial measured concentrations.

The estuarine submersed vascular plant *Potamogeton perfoliatus* appears to be similarly sensitive based on inhibition of photosynthesis as determined from measurements of dissolved oxygen. Atrazine uptake into shoot tissue was rapid in this species, reaching equilibrium at about ten times the dissolved concentration within 15 minutes. Depuration and photosynthetic recovery were rapid in clean water, but depuration remained incomplete, with some residual photosynthetic depression even after 77 hours.

4.3.2.4 Multi-species studies

Ciba-Geigy provided the following four published studies with its submission. Two very recently published studies simulating exposure of surface waters to atrazine in runoff have also been reviewed, together with a mesocosm study investigating whether atrazine acts synergistically with a synthetic pyrethroid.

- **Microbial communities**

Naturally derived microbial communities comprised of bacteria, fungi, protozoa, algae and micrometazoans were collected on polyurethane foam substrates and used to evaluate the toxicity of atrazine. The most sensitive indicators of adverse effects were oxygen production and ability to sequester magnesium and calcium, with a no observed effect concentration of 10 µg/L. Species richness and production of biomass were adversely affected at concentrations of 337 µg/L and above, but stimulated at concentrations below 10 µg/L. Effects of atrazine on ecosystem function are observed at lower concentrations than alterations to ecosystem structure (Pratt *et al*, 1988).

- **Lotic algal communities**

Algal spores and cells from the genera *Anabaena*, *Nitzschia*, *Rhopalodia* and *Navicula* were allowed to colonise artificial streams, where they were exposed to atrazine as wettable powder. Oxygen production was significantly depressed at 100 µg/L, and markedly so at higher concentrations (Moorhead and Kosinski, 1986).

- **Lentic algal communities**

Effects of atrazine (20-5000 µg/L) on algal communities taken from various stock cultures developed for at least 2 months in aquaria were investigated in Leffler microcosms (1 L beakers inoculated weekly with 50 mL stock culture). Seven genera (*Scenedesmus*, *Oedogonium*, *Anabaena*, *Hyallella*, *Cyclops*, *Lecane* and *Philodina*) were prominent in each microcosm after acclimation. Net primary productivity was significantly reduced at 100 µg/L atrazine and above in 3 of 4 cultures studied during the first 14 days of exposure, and generally did not recover (Stay *et al*, 1989).

- **Lentic flora and fauna**

Atrazine (20, 100 and 300 µg/L maintained over 8 weeks) was added after a 2 year stabilisation period to divided artificial ponds (3.94 x 1 x 0.9 m) planted with aquatic macrophytes (*Myriophyllum spicatum*, *Potamogeton natans* and *Chara* sp). Effects on resident organisms (the macrophytes, and phytoplankton and zooplankton introduced with natural sediment) were monitored over 2 years. Atrazine concentrations in the ponds remained stable, after an initial loss from the water column of 30-40% on the day of application, and were still between 50 and 80% of the original amount at the end of the first year.

Macrophyte cover was reduced during the contamination period at the two higher rates, but phytoplankton and zooplankton appeared unaffected in the year of treatment. In the second year, atrazine decreased generally to 20-30% of the original value. The charophytes developed well, but higher plants did not recover and remained sparse at the two higher concentrations. The most striking effects occurred in phytoplankton, with the Chlorophyceae decreasing with increasing atrazine concentration. Cryptophycea (and Cyanophyceae in one system) became dominant in affected systems. Zooplankton were unaffected during the first year but densities declined therafter, particularly at the highest dose, because of population declines in cladocerans and ostracods. The authors comment that others have found daphnids to be more sensitive to atrazine exposure under outdoor conditions than in the laboratory, and suggest that the observed effects on cladocerans may relate to ingestion of contaminated food. No significant impacts were apparent at 20 µg/L (Neugebaur *et al*, 1990).

- **Lotic flora and fauna (microcosm)**

Recirculating laboratory microcosms (120 L) were established using attached algae and benthic invertebrates collected from a clean site, and used to study the effects of a single dose (5 µg/L) of atrazine over a 14 day period. Periodic water replacement reduced this initial concentration to 1 µg/L after 7 days of exposure.

Treatment had no effect on algal biomass as monitored by chlorophyll a absorbance. Similarly, there were no significant differences between treated microcosms and controls in functional group classification or taxonomic composition of the invertebrate community. The authors comment that effects may have been masked by a general decline in algal biomass in treated and untreated microcosms, but that this possibility is balanced by the increased sensitivity conferred by isolation, with no impacts on community structure from new colonists as would occur in natural streams. The only observable difference in these laboratory microcosms was a greater rate of insect emergence soon after treatment (Gruessner and Watzin, 1996).

- **Wetland flora and fauna (mesocosm)**

This study simulated a wetland system (freshwater emergent marsh). The 230 m long mesocosms were fed by water from the Mississipi River (control wetlands contained 0.69 µg/L atrazine from this source). Each contained four pools and four "riffles" and was colonised by emergent aquatic plants, submersed water weeds, floating aquatic plants, and vertebrate grazers including tadpoles and fathead minnows. Fauna were caged for toxicity testing. A stepped exposure regime (2 weeks at a nominal concentration of 15 µg/L, 2 weeks at 25 µg/L, 1 month at 50 µg/L and 2 weeks at 75 µg/L) was applied to the mesocosms.

Atrazine levels leaving the mesocosms were 78-96% of influent concentrations. Partitioning of atrazine into sediments could be detected. Atrazine had an estimated half-life of 8-14 days in the mesocosms.

The only significant impacts were on periphyton colonies, which had depressed gross productivity at the lowest exposure level. This effect in turn reduced the capacity for nutrient uptake in these aquatic ecosystems, with increased ammonium and dissolved nitrogen in treated wetlands after 14 days. Macrophytes were generally unaffected, but wild rice senesced prematurely at 50 and 75 µg/L.

No significant effects on fathead minnow growth or tadpole growth or development were detected. *Daphnia magna* had decreased survival, but only in the first bioassay at 15 µg/L, with no apparent effect in the second bioassay at 25 µg/L. Daphnid bioassays were conducted in sunlight, which was found independently to reduce survival but did not enhance the toxicity of atrazine. The apparent toxicity in the first test may reflect a combination of atrazine exposure and limited food as it was conducted early in the season when primary productivity was low and maximum dissolved oxygen levels depressed (Detenbeck *et al*, 1996).

- **Possible synergistic effects**

The effects of simultaneous exposure to atrazine and bifenthrin, a synthetic pyrethroid, were studied in 5500 L tanks colonised by natural plankton assemblages and bluegill sunfish. Pesticides were introduced as a soil slurry on sandy loam to simulate runoff, and tanks were mixed continuously throughout the experiment. Concentrations were measured after 1 hour and 10 days in the initial low dose phase, and after 1 hour and 14 days in the subsequent high dose phase, and are expressed as mean measured concentrations across 6 tanks. Measured concentrations were generally reasonably consistent.

Chlorophyll was reduced after 7 days at low atrazine concentrations (15 and 150 µg/L) but had recovered by 14 days. Primary productivity and algal cell density appeared unaffected, but some dose related reductions in cladoceran populations may have been related to diminished food supply. These reductions were only apparent at low concentrations of bifenthrin (0 and 0.39 ng/L). At higher concentrations (290 ng/L) the direct toxic effects of bifenthrin overwhelmed any indirect effects from atrazine.

Effects were more marked during a subsequent exposure phase at higher atrazine concentrations (390 and 2200 µg/L) with significant reductions in several algal parameters including chlorophyll, primary productivity and green algal colonies. No significant declines in diatoms or green algal unicells were noted, however. While a number of interactive effects with bifenthrin were apparent, closer analysis revealed that effects from ecologically realistic concentrations of atrazine were only significant when bifenthrin was absent, or present at low concentrations. The observed interactive effects did not indicate that atrazine and bifenthrin acted synergistically (Hoagland *et al*, 1993).

4.3.3 Non-target terrestrial invertebrates

- **Earthworms**

According to Dutch criteria (Mensink *et al*, 1995) atrazine was moderately toxic (LD50 = 78 mg/kg) to the earthworm *Eisenia foetida* in a 14 day artificial soil test (OECD Guideline 207). Significant weight loss was observed at the lowest test concentration of 60 mg/kg. The 7 day LD50 (nominal concentration) was 110 mg/kg (Rufli, 1989f).

- **Bees**

Atrazine was found to have low toxicity to honey bees (48 hour LD50 > 100 µg per bee) exposed by contact and oral routes (Hadházy, 1988). A subsequent study conducted according to EPPO guidelines (European and Mediterranean Plant Protection Organisation, 1982) confirmed these results (Bew, 1993). A soluble concentrate formulation (500 g/L) was slightly more toxic (48 hour oral LD50 = 168 µg whole formulation per bee) than the active ingredient (Nengel, 1995).

- **Carabid beetles (*Poecilus cupreus*)**

The principles of this study were based on a recently published guidance document for testing of non-target arthropods (Barrett *et al*, 1994). Survival and feeding were unaffected by exposure to atrazine application as an aqueous spray at a rate equivalent to 1.5 kg/ha. Beetles were kept in moist silica sand and placed on the surface immediately before spraying. The toxic standard pyrazophos (0.8 kg/ha) caused almost complete mortality, with symptoms of paralysis evident within 4 hours (Kühner, 1995a).

- **Predatory mites**

The principles of this study were based on a recently published guidance document for testing of non-target arthropods (Barrett *et al*, 1994). Survival and fecundity of 1 day old protonymphs of *Typhlodromus pyri* maintained in groups of 20 on glass plates to adulthood (about a week) following exposure to atrazine as an aqueous spray at 0.015 $mg.cm^{-2}$ (equivalent to 1.5 kg/ha) were both reduced. The overall reduction of beneficial capacity derived by combining data on mortality and fecundity according to the method of Overmeer and van Zon (1982) was 61%, indicating atrazine to be slightly harmful to this species based on Dutch criteria (Mensink *et al*, 1995). The toxic standard dimethoate (0.001 $mg.cm^{-2}$) left no survivors after 3 days (Kühner, 1995b).

- **Microorganisms**

No inhibitory effects were noted on respiration and ammonification/nitrification in sand and silt soils containing 6 or 60 mg/kg atrazine, with or without prior amendment with 0.5% lucerne meal. Results indicate that the use of atrazine

should have no adverse effect on organic matter turnover in soils or on their fertility (Ellgehausen, 1984).

As noted earlier in this report, sewage microorganisms are similarly insensitive with no significant inhibition of respiration for activated sludge exposed to nominal concentrations of atrazine up to 100 mg/L for 3 hours (Bader, 1990b).

4.3.4 Mammals

Acute mammalian toxicity appears slight, with reported rodent LD50s in the same order as those tabulated above for birds.

While the acute mammalian toxicity of atrazine is low, questions have been raised concerning its possible effects on reproductive health. For example, atrazine has been reported to cause reproductive impairment (abnormal development, hormone disruption and reduced growth) in laboratory animals, with disfunction of ovaries, and of pituitary and prostate glands. These effects are reported in a review of possible links between adverse effects due to hormone disruption and exposure to chemicals in the environment, an issue that is currently arousing great interest (Colborn and Clement, 1992).

Synthetic chemicals that affect the balance of sex hormones (modulate the endocrine system) have been suggested as causal agents in changes observed in the reproductive physiology of wildlife populations, particularly in areas of high pollution. Persistent organochlorines such as DDT metabolites, PCBs and dioxins feature prominently in these concerns. As a chlorinated triazine, atrazine is frequently included among the organochlorines that are under suspicion.

A more recent review of the endocrine modulation issue (Harrison *et al*, 1995) reports recent findings of reduced bodyweight, reduced ovarian and uterine weight, and decreased circulating levels of oestradiol in female rats dosed orally with atrazine for two weeks. However, dosing levels were very high (100 mg/kg/day). Atrazine appears to have weak anti-oestrogenic activity, rather than intrinsic oestrogenic activity. The review also reports findings that atrazine disrupts oestradiol metabolism, an effect hypothesised to increase the risk of breast cancer in women.

Note that endocrine disruption by atrazine has been invoked only in the mammalian and particularly the human context. Atrazine does not appear to be of concern with respect to endocrine disruption in aquatic organisms based on the current state of knowledge (Harrison *et al*, 1995).

4.3.5 Phytotoxicity

The effects of atrazine on the germination of soybean, lettuce, carrot, tomato, cucumber, cabbage, oat, ryegrass, corn and onion seeds were studied on blotters over a 7 day period. No significant effects on germination success or radicle

length were found following exposure to 12 mg/L atrazine (equivalent to 4.5 kg/ha). The most sensitive plant for germination effects was soybean (EC50 equivalent to 63 kg/ha). For radicle length, cucumber (EC50 equivalent to 5.5 kg/ha) was most sensitive (Chetram 1989a).

Seedling emergence and early growth of soybean, lettuce, carrot, tomato, cucumber, cabbage, oat, ryegrass, corn and onion was studied over 21 days in pots of pasteurised soil. Atrazine applied at 4.5 kg/ha only affected the emergence of lettuce and carrot seedlings, but reduced plant height and dry weight in all species other than corn. No effect concentrations were less than 30 g/ha in all other crops studied (Chetram, 1989b).

Vegetative vigour in the same suite of crops was studied over 21 days in pots by applying atrazine when seedlings were at the 1-3 true leaf stage. Only corn exhibited no phytotoxic effects at 4.5 kg/ha. Corn and cabbage were most sensitive, with no-effect concentrations less than 30 g/ha for phytotoxicity, and less than 10 g/ha for plant dry weight (Chetram, 1989c).

The dealkylated metabolites DEA and DIA retain the phytotoxicity of atrazine, but hydroxy metabolites are herbicidally inactive.

4.3.6 Summary of environmental toxicity

Environmental toxicity data submitted for atrazine are considered complete with no significant data gaps, and allow the following conclusions to be drawn.

Atrazine is slightly toxic to practically nontoxic to birds under conditions of acute and dietary exposure. The metabolite DEA has moderate acute oral toxicity. No avian reproductive effects were found, even at high levels (225 ppm) in the feed.

Atrazine is slightly toxic to fish, but sub-lethal effects such as reduced motility and pigmentation are evident in the low ppm range, and structural alterations were evident in kidneys at autopsy following exposure to 5-40 µg/L. The no observed effect level in life cycle studies on fathead minnow was 0.25 mg/L based on reduced growth of offspring.

Atrazine is slightly to moderately toxic to a range of marine and freshwater invertebrates. Reproductive capacity of *Ceriodaphnia dubia* is impaired by exposure to atrazine in the low ppm range.

Aquatic flora are more sensitive to atrazine than are fauna. Atrazine is highly toxic to algae and aquatic macrophytes. Dealkylated metabolites DEA and DIA are also phytotoxic.

The effects of atrazine in mesocosms and microcosms are mostly manifested through impacts on vegetation and reduced primary productivity. Zooplankton

populations may be reduced at higher concentrations. The threshold for effects in multi-species tests appears to be about 20 µg/L.

Atrazine has slight to moderate toxicity to a range of terrestrial invertebrates.

No mammalian data were submitted for environmental assessment, but the acute toxicity of atrazine to mammals appears slight (similar to avian toxicity).

Atrazine is toxic to a broad range of terrestrial vegetation.

5. PREDICTION OF ENVIRONMENTAL HAZARD

Atrazine is applied as a pre- or post-emergence spray at moderate rates for control of a broad range of weeds. The main use is in coarse grains, with application occuring mainly in late spring and early summer. A notable exception is plantation forestry, where atrazine is mostly applied during winter, usually after rain when soils are at field capacity.

Atrazine is expected to become mainly associated with the soil and interstitial water following application, but significant amounts are likely to be lost to surface and groundwater through runoff and leaching.

5.1 Terrestrial hazard

Application at the maximum rate for field crops of 3 kg/ha would leave predicted residues of 640 ppm on short grass and 360 ppm on broadleaf vegetation (Fletcher *et al*, 1994). These residues are not expected to present an acute toxic hazard to birds or mammals that may ingest them given the low toxicity (recorded dietary LC50s above 5000 ppm and NOECs above 1000 ppm).

The higher rates for plantation forestry of 4.5-8 kg/ha would leave predicted residues of 960-1700 mg/kg on short grass and 540-960 ppm on broadleafed vegetation. These levels are below those found to be acutely lethal in laboratory tests, but above the NOEC for some species. This suggests a slight potential hazard to birds feeding exclusively on short grass in plantation forestry areas, but the scenario is unrealistic given avian feeding habits and the anorexic effects noted in dietary studies.

A review by the US Fish and Wildlife Service found that atrazine is not acutely lethal to birds at realistic environmental concentrations, but that indirect effects through reductions in food supply may be occurring. The review found mammals to be comparatively resistant, based on data for domestic and small laboratory mammals, with no evidence of carcinogenicity, mutagenicity or teratogenicity. Risk from feeding on atrazine treated crops were found to be limited, with mitigating factors including metabolism within the plant and the

formation of bound residues in plants with limited bioavailability to fauna (Eisler, 1989).

The agricultural rate of 3 kg/ha equates to 0.03 $mg.cm^{-2}$. The amount of atrazine landing on 1 cm^2 is more than three orders of magnitude below the LD50 for bees, indicating a very low hazard to these organisms.

If dispersed through 10 cm of soil (density 1.2) the above rate equates to 2.5 mg/kg, well below the LD50 for earthworms of 78 mg/kg.

The increased application rates in plantation forestry areas increase the hazard to earthworms and bees slightly but not to significant levels.

Overall, the hazard of atrazine to terrestrial fauna appears low. However, atrazine is highly toxic to a range of plants, and may impact on non-target vegetation if used carelessly. In its notice of initiation of the special review (US EPA, 1994) the US EPA noted that non-target plants in the corn belt would be periodically exposed through spray drift, as well as from the widespread presence of atrazine in soil, water and the atmosphere, and may suffer some adverse effects.

5.2 Aquatic hazard

A worst case scenario of direct application to 15 cm of standing water at 3 kg/ha would result in a concentration of 2 mg/L, which approaches the LC50 for some aquatic invertebrates, and would be expected to have a disruptive effect on aquatic vegetation. In plantation forestry situations where rates of 4.5-8 kg/ha may be used, such an overspray would leave estimated concentrations of 3-5 mg/L. Atrazine from direct overspray is clearly hazardous to aquatic ecosystems.

A more realistic exposure scenario is for contamination through runoff or spray drift, which may deliver around 10% of a direct application. In this situation, the predicted environmental concentrations reduce to 0.2 mg/L in agricultural situations (0.3-0.5 mg/L for plantation forestry) easing concerns for direct toxicity to aquatic fauna, but still sufficiently high to disrupt aquatic vegetation and impact indirectly on aquatic fauna. Furthermore, any detections at or above this level are expected to be transient, and prolonged exposure to concentrations that may damage the ecosystem is not anticipated.

The above estimates represent worst case peak concentrations at discrete sites immediately following pollution events, rather than general levels in the aquatic environment. Monitoring data for Australia indicate that most aquatic exposures to atrazine are likely to be in the low ppb range, around two orders of magnitude below the estimated level. General historical levels in natural surface waters are less than 10 µg/L, and revisions to use patterns such as the cessation of most non-crop use including in irrigation channels should help reduce contamination

of Australian waterways. Higher exposures may occur in irrigation drainage systems, and in streams draining forestry plantations. Contamination of groundwater appears from limited data to be widespread, with concentrations generally in the order of 1 µg/L.

In its notice of initiation of the special review (US EPA, 1994) the US EPA concludes, based on the review by the US Fish and Wildlife Service (Eisler, 1989), that atrazine concentrations below 5 µg/L are adequately protective of the most sensitive flora, and concentrations below 11 µg/L protective of most aquatic plants and animals. It is noted that risks to aquatic fauna tend to be indirect due to loss of food and habitat.

A recent review of the aquatic ecotoxicology of atrazine concludes that no permanent damage will be caused to aquatic ecosystems at concentrations up to 20 µg/L (Huber, 1993).

A detailed probabilistic risk assessment, focusing on watersheds in the Midwest of the USA where most use occurs, concluded that atrazine does not pose a significant risk to that aquatic environment. The analysis found that concentrations rarely exceeded 20 µg/L, although brief excursions may occur in lower order streams receiving storm runoff, and that effects in field studies were only significant at concentrations above 50 µg/L (Solomon *et al*, 1996).

In most situations, atrazine exposures will be below the threshold for ecosystem effects of about 20 µg/L determined in multi-species aquatic toxicity testing and in literature reviews. However, safety margins may be narrow, and there is clearly a need to minimise concentrations of atrazine leaving the site of application in runoff or as spray drift. This need is particularly acute in plantation forestry situations where atrazine may enter streams in concentrations likely to be damaging to aquatic ecosystems if heavy rain occurs soon after application to wet soils. There is also a need to publicise the cessation of use in irrigation channels, as atrazine appears to remain the product of choice in such situations and many users appear unaware that such use is now prohibited.

The Australian Drinking Water Guidelines state that steps should be taken to determine the source and stop further contamination when pesticides in drinking water exceed the limit of determination, which for atrazine is 0.5 µg/L. The Guidelines also include a health value of 20 µg/L, being the concentration of atrazine that could safely be consumed over a lifetime without adverse effects.

No Australian guideline has been proposed for protection of aquatic life from atrazine, but the Griffith Office of the NSW EPA has proposed an interim guideline of 2 µg/L. This is the same as the value adopted by Canada. The Canadian guideline (CCREM, 1989) includes a tenfold safety factor based on the concentration of about 20 µg/L shown to be the threshold for adverse effects in various aquatic ecosystem studies, as noted above.

The National Registration Authority has established a broadly based taskforce to conduct a three year program of trials and monitoring to establish whether revised conditions of use in plantation forestry will reduce aquatic contamination to acceptable levels (see NRA News of July 1994). A number of trials are in progress.

Other countries have introduced similar restrictions on the use of atrazine as adopted in Australia by the NRA. For example, a ban on the use of atrazine on non-cropped land came into force in the UK in September 1993. Monitoring by the National Rivers Authority has indicated that, while atrazine detections in surface water have declined, those for diuron, the main alternative to atrazine for non-cropped land, increased during 1993. Atrazine levels in groundwater had yet to decline, but there were indications that diuron was beginning to contaminate groundwaters (Eke, 1996).

Based on its monitoring results, the National Rivers Authority formulated a range of recommendations that aim to minimise the impact of pesticides on water quality. A key recommendation is that governments should examine the case for no-spray zones of 6 m adjacent to all watercourses for all pesticides not approved for use in or near water. The current Australian restrictions on atrazine include a 20 m no spray zone adjacent to all intermittent or perennial streams, exceeding the UK proposal.

5.1 Controls/labelling

Atrazine must not be allowed to contaminate water, either accidentally or as a result of normal use. It is acknowledged that low level aquatic contamination is unavoidable, but every effort should be made to minimise its occurrence.

The need to minimise aquatic contamination is particularly acute in plantation forestry situations where atrazine is likely to be applied under cold and wet conditions. A number of restrictions have been introduced, including reduced application rates and buffer zones to protect waterways consistent with those in force in the USA. However, it should be noted that plantation forestry applications do not occur in the US, apart from limited use on small scale conifer plantations, primarily Christmas trees (Ciba-Geigy, 1995). The different use pattern in plantation forestry suggests that additional restraints to those operating in the USA may be necessary, depending on the results of trials being undertaken by the task force noted above.

5.1.1 Formulation/packaging

No special controls are necessary.

5.1.2 Transport

The material safety data sheets should contain adequate instructions for containing and disposing of material spilt as a result of accident during transport, with particular reference to the importance of avoiding aquatic contamination.

5.1.3 Use

All draft labels should be upgraded without further delay to include the restrictions introduced by the National Registration Authority in late 1994 (to take effect by December 1995). The current level of compliance is clearly incomplete given that David Gray reports continued use on railways, and that application rates to 6 kg/ha remain current.

The draft labels should contain the following warning and additional restraints:

Atrazine is a mobile chemical with the potential to contaminate surface and groundwater. In order to minimise this possibility, the following conditions must be adhered to:

- Do NOT apply under meteorological conditions or from equipment which could be expected to cause drift of this product or spray mix onto adjacent areas, particularly wetlands, waterbodies or watercourses.
- Do NOT apply to waterlogged soil.
- Do NOT apply if heavy rain is forecast within two days of application.
- Do NOT irrigate to the point of runoff for at least two days after application.

5.1.4 Disposal

The draft labels are satisfactory.

6. CONCLUSIONS AND RECOMMENDATIONS

Atrazine is a mobile chemical that is likely to contaminate water at low levels as a result of normal use. This is a general property of most herbicides. Unlike many herbicides, however, atrazine is persistent in soils and aquatic systems. As noted by the US EPA (1994) the pervasiveness of the triazines in the environment is the result of their massive use combined with their mobility and persistence.

At the present time, exposure of the Australian environment to atrazine generally occurs at levels below those that may cause ecosystem damage. Evidence reviewed indicates this threshold to be in the order of 20 µg/L, with current exposures in natural surface waters generally below 10 µg/L. However, safety margins are clearly narrow.

Notwithstanding that atrazine is one of the most heavily used herbicides and a documented aquatic contaminant, Australia has yet to establish a water quality guideline for protection of aquatic ecosystems. The Australian Water Quality Guidelines for Fresh and Marine Waters are currently being reviewed by the Environmental Research Institute of the Supervising Scientist (ERISS) with guidance from a broadly based Project Committee. The need for a guideline for atrazine has been brought to the attention of ERISS. A copy of this report should be provided to aid deliberations.

Overseas jurisdictions have set such a guideline at 2 µg/L, a level that applies a tenfold "safety" factor to the chronic no effect concentration of 20 µg/L. This approach is sound, and a guideline of 2 µg/L has been proposed locally. A guideline of 2 µg/L would be violated from time to time at current Australian exposure levels. If the continued use of atrazine is to be defended, it is clear that every effort must be made to minimise aquatic contamination. This should involve both source reduction and management of off-target movement through improvements to agricultural practice.

The need to carefully manage the use of atrazine to avoid undue off-target impacts has been noted by others with recommendations framed accordingly. A number of the recommendations that follow are simple endorsements of those that have been made elsewhere (for example, Korth, 1996, Boey and Cooper, 1996, O'Brien, 1996).

In general, management of risks is more efficient than simplistic approaches that attempt to eliminate them. In the specific case of atrazine, attempts to eliminate risk by banning the chemical are unlikely to be fruitful as atrazine would inevitably be replaced by other chemicals, and the risks of one substance substituted by the risks associated with others. The increasing diuron levels in British waterways illustrate this concept.

Source reduction

Steps have already been taken to eliminate some sources of aquatic contamination by atrazine. As noted earlier in this report, the NRA has restricted maximum annual application rates of atrazine and deregistered certain uses with a high potential for aquatic contamination, notably high rate applications to irrigation channels and in non-agricultural situations, with effect from December 1995. A number of registrants and users appear to remain unaware of, or are ignoring these restrictions, which must be fully implemented and enforced. The prohibition on use in irrigation channels needs to be publicised widely within the irrigated agriculture industry. The industry needs to be made aware that use of atrazine in irrigation channels can contribute significantly to broader aquatic contamination, and that such contamination needs to be avoided if registrations of atrazine for crop uses are to be retained.

Avoidance of weed problems is more efficient than management after they have arisen. Recent experience in Western Australia with contaminated Karoo canola seed, as noted earlier in this report, highlights the importance of sowing clean seed lines if additional applications of herbicide, including atrazine, are to be avoided. Careful attention to equipment cleaning, and to weed management along boundaries and channels, can help maintain clean paddocks.

At a general level, source reduction needs to be achieved through agricultural methods that reduce reliance on synthetic chemical inputs by including herbicide use in integrated weed management programs that make maximum possible use of mechanical and biological methods, and crop rotation and competition. Crop competition can be a valuable contributor to weed management, but is reliant on conditions that favour vigorous crop growth, such as soil fertility, moisture, and depth and time of planting.

Management of off target movement

Management practices to minimise off-target movement of atrazine will differ between irrigated and dryland agriculture. For irrigated agriculture, the principal objective must be to improve irrigation efficiency in order to minimise contamination of drains by tailwater. As one component, drainage recirculation systems should be installed to capture irrigation tailwater and at least the first flush of storm runoff. The practice of irrigating until tile drains begin to flow should be discouraged, particularly soon after atrazine application, as runoff with subsequent rain will be much more likely from soils that are saturated, and available evidence indicates that atrazine is not attenuated significantly as it travels through irrigation drainage systems.

Additional measures to improve the effectiveness of weed control are relevant to both irrigated and dryland situations. Timing of application is particularly important. Growers of sorghum and maize should consider whether pre-emergence applications can be replaced by post-emergence applications, given

reports that this can increase farm flexibility, particularly in areas where rainfall is unreliable, while at the same time reducing application rates and attendant risks of aquatic contamination by atrazine contained in runoff. The risk of runoff decreases as application rates are reduced, and with the passage of time after application. While recognising that some rain is necessary to carry atrazine into the soil where it becomes active, farmers should avoid using atrazine if heavy rain or storms are forecast within 48 hours. This is particularly important for dryland farms which are unable to contain storm runoff. The mobility of atrazine is such that runoff from just a few farms may be sufficient to contaminate an entire catchment.

Storm runoff appears to be the main route for aquatic contamination by atrazine, but spray drift can also contribute. Application, particularly by aircraft, should not occur in high winds or under inversion conditions. Growers should consider planting trees along boundaries to help intercept any spray drift that may arise.

Label restrictions

A number of restrictions to atrazine use patterns have been introduced in Australia, based on US restrictions. Trials to determine the effectiveness of these restrictions in plantation forestry situations have commenced, under the oversight of the Forest Herbicide Research Management Group. Decisions concerning whether revised atrazine use patterns may continue in plantation forestry should await the outcome of those trials.

In the interim, we strongly recommend that the following additional restrictions be included on the label to minimise the risk of aquatic contamination from storm runoff:

- Do NOT apply under meteorological conditions or from equipment which could be expected to cause drift of this product or spray mix onto adjacent areas, particularly wetlands, waterbodies or watercourses.

- Do NOT apply to waterlogged soil.

- Do NOT apply if heavy rains or storms that are likely to cause surface runoff are forecast within two days of application.

- Do NOT irrigate to the point of runoff for at least two days after application.

Environmental monitoring

Information on use patterns is the essential basis for assessment of environmental exposure to chemicals. As noted in this report, information on volumes of use of atrazine in Australia has not been disclosed, except by the principal registrant. Provision on an annual basis of current and projected sales volumes should be made a condition of continued registration for all atrazine registrants. This should include information on geographical areas in which atrazine products are sold and used, and estimates of use on individual crops. Information on use patterns allows specific management practices to be developed in response to any contamination issues that may arise, which in turn helps deflect the inevitable calls for a complete cessation of atrazine use. Such information is also essential as a basis for determining the acceptability for registration of new uses, such as for triazine resistant canola.

Monitoring of atrazine levels in the environment needs to continue in order to determine trends in atrazine contamination of Australian surface and groundwaters, and whether current and proposed restrictions are effective in maintaining or improving current safety margins. In some areas, monitoring efforts need to be expanded. For example, monitoring of storm runoff from dryland farms needs to be conducted to determine the significance of this source to general aquatic contamination. In addition, future monitoring needs to investigate levels in natural waterways as well as the irrigation drainage systems that have been the main focus to date in the Murrumbidgee Irrigation Area, for example. Monitoring of residue levels should be linked to biological monitoring to determine the ecological significance of atrazine levels found in Australian waterways. Responsible registrants will commit resources to such environmental monitoring as a demonstration of their commitment to product stewardship.

Should this not occur, or should monitoring demonstrate that safety margins continue to be narrow, Environment Australia strongly recommends that further restrictions be implemented.

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