local government are not required to hold a licence. Contract work for councils or government departments is considered to be a commercial activity and requires the contractor to be registered and licensed with this department if the work is the control of weeds on urban, industrial, municipal or public lands.

There has been some confusion as to what constitutes 'public' land. To assist in handling inquiries about where the Department of Health and Community Services licence is required a list of specific examples is available from officers of the Pest Control Unit. Pest Control Operators who are contracted to control weeds on agricultural lands are not required to have a licence with this department as they are considered to be regulated by the Department of Agriculture.

The Pest Control Unit is concerned with issues relating to the health of pesticide users as well as public health. As well as ensuring that operators are adequately trained and experienced, the Pest Control Unit is developing a targeted inspection program of pest control operators to enable high risk operators to be given inspection priority and to improve compliance with regulations and departmental guidelines. An inspection will involve checking of storage and record keeping of chemicals, inspection of vehicles and equipment as well as an assessment of practical skills.

Pest control businesses are required to keep records of all pesticides used in their business. Licence holders are required to provide their employer with the following information:

- date of application
- name of pesticide used
- address where it was used
- location of treatment (i.e., roof void, sub-floor, fence)
- purpose of treatment
- applicators name and licence number Licensed pesticide users are required to operate from vehicles using equipment to the standard specified in the Department

of Health and Community Services Vehicle and Equipment Guidelines.

The regulations do not apply to anyone who only applies a herbicide which is exempted, with hand-pumped equipment that has a tank capacity of 10 litres or less. Exempted herbicides are:

- ethidimuron
- ethofumesate
- glyphosate
- karbutilate
- propyzamide
- siduron
- copper salts

As well as its administrative role, the Pest Control Unit also provides advice and assistance to the public, industry and local government on matters regarding health and technical information and pesticide usage. A number of pamphlets are available to assist with these inquiries.

For further information contact Environmental Health Program. Tel: (03) 616 7766. Fax: (03) 616 7347.

# The triazine herbicide atrazine – are you effectively adopting risk minimization practices?

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#### Introduction

DDT controversies of the 1960s, phenoxy herbicide controversies of the 1960s, 1970s and 1980s. Will it be the triazine herbicide controversies of the 1980s, 1990s and into the year 2000? Investigations in the next few years in Australia may prove this to be the case. This paper is about the herbicide atrazine and recognition of the need to develop and utilize sustainable agricultural and horticultural practices which will have minimal impact on the environment. Sustainable urban space management programs, as well as agricultural and horticultural weed control programs must always endeavour to minimize the risks to both the end user, the community and the environment as a whole. But first to raise a number of issues by way of introduction.

Herbicides happen to be one group of chemicals which have played a valuable role in vegetation management. They have also been the focal point, particularly in urban areas, for expressions of concerns about agrochemical usage. Since the bulk of agricultural chemicals used in urban areas consists of herbicides, it is an interesting exercise to reflect on the parallels between the controversy surrounding the phenoxy herbicides 2,4-D and 2,4,5-T, and human health effects which ran for almost 20 years and the triazine herbicides, particularly with respect to atrazine and ground water contamination. Fortunately, the issue is not clouded with any problems with contamination of the commercial product as was the case with 2,4,5-T. But attempts to link atrazine with human health problems appear as tenuous as with 2,4,5-T at present.

Atrazine, like the phenoxy herbicides, in some respects has been in use for more than 30 years providing excellent weed control within selected crops and forest species and is efficacious on a range of difficult weed species, notwithstanding the contribution to minimum tillage practices designed to improve soil moisture retention and avoid the structural degradation of cropping soils.

If there was a serious problem with atrazine, one would have expected a problem to have emerged by now. However, since the 1980s studies (Hallberg 1989) on chemicals generally in ground water have been steadily emerging, mainly concentrating on mobile compounds, volatile soil fumigants, nematicides, herbicides, including atrazine and nitrate fertilizers. The focus of such studies has tended to be on leaching from potential routine point sources normally

associated with intensive agriculture production, but does not exclude potential non point sources concerned with the storage and manufacturing of agrochemicals. Such sites would be where high concentrations of herbicide have occurred in well defined areas through mishandling or storage problems.

Concerns about atrazine primarily began to be raised when water quality reports (Hallberg 1989) in the 1980s conducted in a number of countries revealed the presence of atrazine. This was not particularly startling news since in the mid 1970s investigations concerning organochlorine insecticide reported by Richard et al. (1975) also analysed for atrazine successfully. Water quality reports conducted in studies in Wisconsin and Iowa, for example, in the USA indicated that atrazine was the most commonly detected herbicide in ground water. However, in a nationally conducted EPA study in the USA, almost 99% of all wells across the USA recorded no detectable level of atrazine. The focus of these earlier studies appears to be on hot spots or non point sources in high use areas associated with intensive agricultural production and chemical usage.

It should also be pointed out that extrapolation from information generated in areas such as the prime corn belt growing areas of the USA and specific areas such as the Columbia basin needs to be done, if at all, with extreme caution since soil conditions are quite different in terms of soil profiles in these areas. Intensively cropped loams are often underlaid by beds of gravel and sand connected to ground water supplies. Such conditions are linked with glacial activity and quite

different to soil profiles experienced in Australia.

The facts are, that despite the use of atrazine for more than 30 years, no longterm deleterious effects on humans or environmental health have been documented in a manner directly associating atrazine with these types of problems. Nevertheless, misuse or mishandling of this herbicide could easily lead to the media spotlight focusing on atrazine, followed by further regulation or possible deregistrations as the end product of a chemophobic popular reaction which has decided to target atrazine. This is not to say that there should be no concern in the long-term about the possibility of chronic exposure to contaminated water supplies by any chemical.

It is worth noting that atrazine's registration status already varies considerably in different countries around the world. In Holland existing registrations were to be valid until January 1992, in France registrations were renewed for rates up to 1.5 kg a.i. ha-1 alone or in mixtures and coupled with plans for more extensive ground water monitoring. In North America, Ciba-Geigy label restrictions on 'Minimization Strategy' were accepted by the EPA in January 1990 with rate limits for selected crops and recommended buffer zones of 15 m between treated areas and drainage channels being established. The main concern in many of these countries, including the USA, is due to the fact that ground water supplies the bulk of the drinking water in the USA.

So where do we go from here? What I wish to do is to take a realistic look at atrazine and reflect on the need for an improvement in our understanding of the nature of specific agrochemical tools. Just as any other chemical or non chemical tool requires an understanding about appropriate uses and use limitations today. Atrazine just happens to be a useful case study, equally another herbicide which is persistent and relatively insoluble in water could be reviewed.

Current economic conditions and the costs associated with the development of alternative chemicals demand better methods of managing the use of agrochemicals, apart from critical application issues and the need to strive towards a total reduction in the quantities of chemicals used. Of course agrochemicals need to be understood and managed to minimize their impact on the environment. However, information about the risk minimization procedures involved needs to be more effectively communicated to the general public to counter the criticisms that are levelled periodically from a partially informed public bearing limited scientific evidence of a problem.

# Historical perspective

Atrazine is a member of a broad class of herbicides described collectively as aminotriazines. They were initially used in 1956 in the United Kingdom following the release of simazine by the Geigy Company, later to become Ciba-Geigy. The sequel to simazine was atrazine, released in 1958 following registration for use in the United States for weed control in corn.

Today there are a large number of related herbicides employed as either preemergent or post-emergent herbicides described as heterocyclic nitrogen compounds, but with different substitutions of chloro, methoxy or methylio groups to their ring structures .

Figure 1. Atrazine structure

Atrazine (Figure 1) is a member of the chloro-substituted triazines:

molecular weight 215-7 melting point 176°C water solubility 30 mg (at 293°K) (70 ppm)

vapour pressure 0.04 m Pa at 20°C. Trade names include Gesaprim, Atradex 900 WG, Atramet Combi, Atrazine Flowable, Crop King Atragranz Herbicide, Crop King Flowable Atrazine 500, SC, Erase Granular, Flowable Gesatop A, Fyrbar, Fyrbar Flowable, Gesapax Combi 500 FW, Gesaprim 500 FW, Nu-Trazine, Nutrazine Liquid, Nu-Zinole AA, Primextra 500 FW, Vorox AA Liquid and Atrazine Flowable.

Manufacturers include Ciba-Geigy, Compania Quimica, DuPont, Griffin, MakhteshimAgan, Rallis India and Schering.

Formulation methods are suspension concentrate, wettable powder, granules or water dispersible granules. The opportunity to select formulations such as water dispersible granules, offers a particularly significant method of avoiding non point source contamination of ground water through storage leakages due to the ease of containment.

Atrazine is described (British Crop Protection Manual 7th Edition) as a colour-less crystalline compound stable in neutral, weakly alkaline and weakly acid media. Triazines generally are described as solids with relatively low vapour pressures at room temperatures, therefore not prone to volatility problems and of low solubility, with simazine being one of the least soluble, atrazine more soluble and prone

to movement in water, compared with simazine.

It is worth noting that the herbicide atrazine has been subjected to extensive laboratory and field studies concerning the chemistry, toxicology, environmental fate process and uses. It is important also to appreciate that such studies are not only conducted by the patent company, but also normally involves independent testing authorities, as well as contracted laboratories in these studies. This is the normal course of events prior to Federal clearance and State Registration in Australia, although registrations vary from state to state in Australia.

#### Mode of action

Atrazine is a selective systemic herbicide. Atrazine acts as both a soil applied preemergent herbicide and foliar applied knockdown herbicide. Uptake of the herbicide is primarily by roots with minor uptake at the leaf surface through stomatal cavities. Translocation occurs in plants through the apoplast system. Selectivity expressed by different plants is attributed to differences in degradation rates amongst other factors. Atrazine inhibits photosynthesis and disrupts other enzymic processes.

The site of action in plants is particularly associated with the interruption of photosynthetic and enzymic pathways in plants, in particular, the Hill reaction and Photosystem II consequently causing chlorosis and eventual death of the plant. In sensitive plants atrazine accumulates causing chlorosis and death, while in tolerant plants the herbicide is metabolized to hydroxyatrazine and amino acid conjugates. Further decomposition of hydroxyatrazine follows. This high degree of specificity in terms of action sites is a particularly desirable feature in terms of avoiding unwanted affects on non target organisms.

## Atrazine uses

Atrazine is used as a pre-emergent and post-emergent herbicide to control certain annual grasses and a wide range of broad leaf weed species, some of which are difficult to control satisfactorily using other herbicides. Atrazine is largely associated with pre-emergent weed control where residual activity is required, usually in the vicinity of five to seven months when applied at rates of approximately 3 kg ha-1. This herbicide has been particularly useful within the agricultural food production industries and has widespread usage where crops such as maize, linseed, sugar cane, sweet corn and lucerne are grown. In addition, the herbicide has been widely used in Pinus radiata plantations. Apart from direct usage with crops, atrazine has been used on drainage channels and fallow areas. Normally application in New Zealand and Australia is not advocated for use in water channels if passage of water is expected within two months from the time of the last application. Maximum residual activity is normally achieved on moist, smooth, clod free soil.

Application is not advised if heavy rainfall is expected within three hours of application. Atrazine is also compatible with a range of different knockdown herbicides.

# **Toxicity**

# Toxicity to mammals

Acute Oral LD<sub>50</sub> for:

1869 (or 3080) mg kg<sup>-1</sup> rats 1750 mg kg-1 mice

rabbits 750 mg kg

Acute Dermal  $LD_{50}$  for: rats 7500 mg kg<sup>-1</sup> rabbits 7500 mg kg<sup>-1</sup>

#### Chronic toxicity

Reports of feeding 50% atrazine to rats at 2, 20 and 200 mg kg<sup>-1</sup>, body weight in two year feeder studies, produced no symptoms of illness. The highest dose without effects NOEL is 100 mg kg-1 in rats and 15 mg kg<sup>-1</sup> in dogs over a two year period. In mammals after oral administration (after British Crop Protection Manual), atrazine is rapidly and completely metabolized (The Agrochemicals Handbook).

#### Toxicity to other animals

LC<sub>50</sub> for rainbow trout 10 mg L-1 LC<sub>50</sub> for carp 100 mg L-1 (48 hours)

LC<sub>50</sub> (ppm) for earthworms 4 4 4

Not toxic to bees

## **Bio-Magnification**

The USDI (1989) 'Review of Atrazine Hazards to Fish, Wildlife and Invertebrates' stated that "bio-accumulation of atrazine from freshwater is limited and food chain bio-magnification is negligible".

Data from laboratory experiments reported by Generics indicates the maximum bio-accumulative factors ranged from four times in annelids to  $480 \times in$ mayfly nymphs, but that these accumulation events were followed over several days by loss of atrazine from the animal following the removal of atrazine from the local environment.

Hazards to humans, if it were to occur, is most likely related to either ingestion through water or diet or related to handling and usage in an inappropriate manner. It should be noted that factory workers in atrazine manufacturing plants are not reported as suffering from adverse effects linked to this herbicide.

In the United States, the EPA Office of Drinking Water (ODW) has established

what is described as a life time Health Advisory Level or Maximum Contaminant Level (MCL) of 3 ppb atrazine. Individuals who drink water at that level of contamination should be able to do so without ill effects for a life time. The ten day Health Advisory Level is set at 200 ppb and the longer-term Health Advisory Level (7 year term) is at 48 ppb for children and 168 ppb for adults. It is worth highlighting that in MCL value of 3 ppb we are talking about an equivalent of one drop of water in 21 700 gallons (82 000 litres). Dietary exposure appears to be virtually non existent and applicator or handling exposure minimal if correct handling mixing and application procedures are adhered to.

Of course atrazine is toxic if ingested at a significant dose level as are all chemicals. The  $LD_{50}$  Acute Oral for male rats = 1869 mg kg $^{-1}$  has a similar Acute Oral toxicity value to aspirin with an LD<sub>50</sub> value = 1750 mg kg<sup>-1</sup>. Of course few people are concerned about aspirin usage while many are dependent on it for management of a wide range of medical conditions.

Chronic toxicity tests to date suggest atrazine should be classified as a weak oncogen, but humans are not considered to be a risk at levels of exposure known to normally occur. The EPA review of atrazine in 1988 in the USA classified atrazine as a Group C substance 'a possible human carcinogen' based on limited evidence of carcinoginicity in specific test populations of animals and in the absence of human data. It is worth noting that attempts to link triazine herbicides with ovarian cancer reported in the Journal of Work Environmental Health in 1989 has been disputed and appears not to stand up to statistical scrutiny by others reported Journal of Work Environmental Health 1990. Parallels could be drawn with 2,4,5-T case in Victoria and associated statistical problems in terms of pinning down 2,4,5-T and birth abnormalities.

Atrazine is not reported as having fungicidal or insecticidal properties, although evidence exists that soil related organisms, including mites, nematodes and springtail populations may be affected.

### **Environmental issues**

Environmental issues might include:

- Contamination of soil in proximity to the root zone of desirable plant spe-
- Prolonged and unwanted residual activity in soil.
- Off target damage to plants through poor application techniques.
- Leaching or lateral shift caused by water movement.
- Movement of contaminated soil by wind, water or human activity.

It could be argued that most of these undesirable effects can be avoided or minimized if label instructions are adhered to and a clear understanding of the fate processes for chemicals is gained. The fate processes are the issues which I wish to concentrate on and they can be summarized as follows in a broad sense.

Adsorption process:

soil texture soil structure moisture content soil pH

Transfer process:

volatilization leaching run-off

absorption - plant transfer

Degradation process: photo degradation microbial action

chemical action/hydrolysis

Degradation rates for atrazine vary according to different literature sources and provides weight for the need for local studies to be supervised by National Authorities in Australia.

Half life figures for atrazine vary from 30-40 days in soil under certain conditions (Generics) and up to 300 days in fresh water and less than 72 hours in vertebrate animals.

Rates of degradation are related to differences in microbial activity, pH, temperature, light exposures and moisture content. For example, the half life could be up to 385 days for atrazine in sandy alkaline soils under conditions of low temperature and low levels of microbial activity.

It would seem logical that given the chemical properties of atrazine and including the residual activity of atrazine that under certain conditions movement from the point of application is likely to occur. Hence atrazine has been detected at low levels in ground and surface water in a number of different locations in studies conducted in the USA. Atrazine contamination to date, however, has been at low ppb and well below any level thought to be of toxicological significance. There is also some doubt as to whether triazine substances identified are in fact entirely from herbicide applications. Nevertheless, the fate processes are complex and again highlight the need for closer scrutiny of the situation under local conditions in Australia.

It is, therefore, suggested that as with many chemical tools and other mechanical devices there is a potential for harm to the user, community at large or the environment if label instructions are not followed. Before contemplating dispensing of the baby with the bath water, we should demand that in the first instance application procedures and conditions are understood and adhered to. Steps such as those listed below are meant to achieve that end:

- Read the label before purchase.
- · Read the label before handling.
- Read the label before application.
- · Read any pre-cautionary statements.
- · Apply at the correct rate.
- Locate bulk storages over impervious materials.
- Store over impervious sites or areas designed to contain spillages.
- Mix on impervious sites.
- · Capture all rinsate.
- Prevent contamination of wells or bores.
- Prevent contamination of waterways.
- Do not allow back-siphoning to occur when filling spray carts.
- · Dispose of carefully.

## Atrazine clearance information

There is a clearance issued by the Australian Bureau of Animal Health, Department of Primary Industry, Canberra for atrazine dated 13 July 1984.

This states that it can "provide longterm control of a wide range of weeds and grasses in non agricultural situations, irrigation channels and drains". This is still one of the registered uses for atrazine.

The clearance also states that the lower rate should be used on light sandy soil. N.B. Not recommended in the MIA.

Currently registered labels state "Heavy rains immediately following an application tend to result in excessive concentrations of herbicide in the seed furrow, thus encouraging possible crop injury. This is most likely to occur when a pre-plant or pre-emergence application is made using rates in excess of 3.6 litres per hectare. In the northern irrigation areas of WA do not use as a pre-emergence application during the wet season. The product

requires rainfall or irrigation to move it down through the soil into the weed root zone to make it effective. Sufficient rain or irrigation to thoroughly wet the soil through the weed root zone should occur or be made within 10 days after spraying".

The clearance protection statement "DO NOT apply, or drain, or flush equipment on or near desirable trees, or other plants, or on areas where their roots may extend, or in locations where the chemical may be washed or moved into contact with their roots. Do not contaminate dams, waterways, or drains with the product or used containers", is still current.

There is no mention on currently registered labels warning the user specifically about ground water contamination. It is conceivable that in the future additional information may be incorporated in label information required in Australia.

Appropriate label instructions have been identified in this case, but are a small part of the total strategy required to minimize any risk. Adoption of better integrated methods of weed control and more efficient application systems designed to reduce total amounts of chemical applied are all part of the resolution of this issue. It is then a matter of ensuring through effective communication that risk minimization is achieved through widespread adoption of such practices and that at the same time factual information is presented to the community at large about the steps being taken. Otherwise we run the risk of losing a valuable herbicide in environment where replacement chemicals are tending to be few and far between due to the high costs of development and information demands required to meet clearance and registration proce-

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