Best Management Practices for Atrazine in Broadacre Crops.

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Key Messages

Thirteen practical guidelines for use of atrazine in broad acre crops can reduce atrazine contamination of surface and ground waters to insignificant levels.

Summary

Contamination of water sources is most likely where there is direct application of atrazine to surface water or water, clay and organic matter move from treated areas into rivers, lakes or other areas that recharge aquifers. Movement of atrazine vertically through the soil is not likely to be a significant contributor to ground water contamination in Western Australia.

Introduction

Atrazine is a herbicide that is registered to control a wide range of weeds in many broadacre crop and pasture situations as well as in fallows and plantations (Moore & Moore). It is absorbed through the roots and foliage and inhibits photosynthesis in susceptible plants or is metabolised in tolerant plants. The widespread adoption of varieties of canola that are tolerant to atrazine and an increase in plantation areas has led to increased usage over the last ten years. Concerns over its potential to contaminate ground water have led to a number of reviews, restrictions on use and recording protocols for high volume users (NRA, 2002; APVMA, 2004).

Rates up to 3kg a.i./ha are registered for broad acre crops and up to 8 kg a.i./ha in plantations.
If approximately 1% of the applied atrazine enters the ground water then the NHMRC guideline values for drinking could be exceeded.
This paper provides research based guidelines for applying atrazine and will reduce the risk of atrazine causing significant environmental impact.

Planning

Atrazine is a very cost effective herbicide in many situations and restrictions on its use will increase production costs in many cases. Misuse resulting in water contamination is likely to lead to further restrictions being applied. Help to keep national usage levels low by only using it and only planting triazine tolerant crops where they are the most profitable option.

Guideline 1: Plan your use of atrazine for the areas where it is more profitable than other weed control methods.

Rate of application

As the rate of application increases so does the amount of atrazine entering ground and surface water reservoirs. Detectable ground water contamination is likely if excessive rates are used or there are multiple applications within the season exceeding the guidelines.
Where there is limited mixing of ground water, high application rates could lead to localised contamination that may result in sporadic detectable levels of atrazine in the water.
Atrazine at around 1 kg a.i./ha is usually enough to provide pre-emergence weed control for 2-4 weeks. For longer term weed control, split applications are more effective than applying a single larger dose because the breakdown of atrazine in the soil is approximately exponential. Two applications at 1 kg a.i./ha about 4 weeks apart provides similar weed control as a single application of 3 kg a.i./ha. In crops, such as lupins that don’t tolerate post-emergence atrazine, use simazine for the second application.
Atrazine and simazine have similar weed spectrums and are generally additive in their activity. In most cases, a mixture at one half of each herbicide will provide similar control to a full application of either herbicide by itself for pre-emergence applications. Simazine is less soluble than atrazine and is less likely to contaminate water.

Time of application

The timing of atrazine application will be determined largely by the crop and weed situation. In bare-area situations or where no post emergence weed control is required consider using simazine or a mixture with simazine.

For susceptible weeds with less than 2-3 leaves atrazine at an application rate of 1 kg a.i./ha generally provides adequate control. For larger weeds, add a companion herbicide that targets those weeds rather than increasing the atrazine rate.

Multiple applications at lower rates reduce the risk of localised areas of ground water contamination.

Guideline 2: Use split applications rather than increased rates to increase the residual control of weeds in triazine tolerant crops.

Guideline 3: Use the minimum rate required to achieve weed control.

Guideline 4: Use mixtures with simazine (or other herbicides) to reduce the amount of atrazine being applied without compromising weed control.

Guideline 5: Don’t exceed the maximum label rate.

Weather conditions

Most of the atrazine in water comes from surface water flows carrying dissolved atrazine or atrazine adsorbed on the suspended clay and organic matter. Large rainfall events soon after atrazine application that cause significant run off will carry atrazine to rivers and lakes. Small rainfall events carry atrazine into the soil where it is bound and less likely to move off site. In waterlogged soils, atrazine movement into the profile is limited and the associated anaerobic conditions reduce the rate of breakdown. Following rains also result in larger run off where the soil is saturated.

High winds may carry up to 10% of the herbicide off-target. Most is deposited within 10 metres down wind and less than 1% will move more than 60 m for boom spraying. Herbicide does not drift up wind so spray-drift onto water bodies or catchment areas can be avoided by spraying when the wind is blowing away from the sensitive area.

When low level inversions occur with low wind and high humidity, herbicides may drift many hundreds of metres. In these situations, the quantities of herbicide that move are also low and are of more consequence to sensitive species than from a water contamination point of view. As atrazine is a water-based suspension it is not as susceptible to drift as oil based products.

Guideline 6: Don’t apply atrazine when large rain events that could lead to surface water flows or erosion are expected.

Guideline 7: Avoid application to waterlogged soils and areas that regularly carry surface water flows.

Guideline 8: Avoid spraying within 50-100 m of the upwind side of water bodies or catchment areas.

Soils and topography

Atrazine may leach into water tables that are close to the surface. GRDC funded research at Geraldton and Esperance has shown that direct leaching from the paddock surface into water tables more than 2 metres deep will not result in significant water contamination.

Atrazine contamination of water bodies is more likely on steep slopes, where there is little filtering vegetation and where it has been applied close to the water body. Similarly, use of atrazine on raised beds should be minimised as these tend to be located in wet areas and there may be significant movement of water from the sprayed areas to local drainage lines.

Atrazine degradation is generally slower in soils with high pH, though there are some references indicating it is slowest at a neutral pH.

Guideline 8: Avoid application on sandy or cracking clay soils that have shallow water tables (especially if they are alkaline and in high rainfall zones).

In these situations atrazine may be transported to the ground water more quickly. In cracking clays atrazine laden water my travel down the cracks directly to the water table. In sandy soils the lack of clay and organic matter means atrazine travels through the soil faster and has less time to breakdown before entering the ground water. Under alkaline conditions the rate of breakdown is slower and under high rainfall conditions there is simply more water passing through the soil to carry atrazine.

Guideline 9: Avoid spraying within 60 m of water courses where run-off may carry atrazine, clay or organic matter into the water course.

On bare or steep areas this distance should be increased and where good filtering vegetation is present this distance is conservative.

Climate

In Mediterranean environments, low temperatures and waterlogging will reduce the rates of degradation in winter and lack of soil moisture will reduce degradation rates in summer. At registered use rates there is little carryover from one season to the next. 90% of the atrazine is expected to have dissipated within 13 to 36 weeks (Bos et al, 1995) in broad acre cropping regions of WA.

Atrazine degradation depends on moisture, temperature and aerobic soil conditions. In areas with sporadic and high intensity rainfall, atrazine movement to ground water, streams and reservoirs is more likely.

Guideline 10: Avoid handling concentrate or mixing herbicide close to water courses or on impermeable surfaces where storm water may carry herbicide into streams or water bodies.

Guideline 11: Avoid handling concentrate near bores or on permeable recharge areas.

Guideline 12: Apply adequate fertiliser to ensure good crop growth and don’t over fertilise with nitrogen.

Plants absorb atrazine from the soil in proportion to their water usage or growth. Applying high levels of nitrogen may lead to microbes preferentially using the fertiliser as a source of nitrogen rather than atrazine and consequently reducing microbial breakdown rates.

Guideline 13: Use liquid rather than granular applications in marginal situations such as steep clayey sites or where runoff is more likely to occur.

Granules are more likely to carry more atrazine in storm water flows than soil sprayed with atrazine.

Acknowledgments

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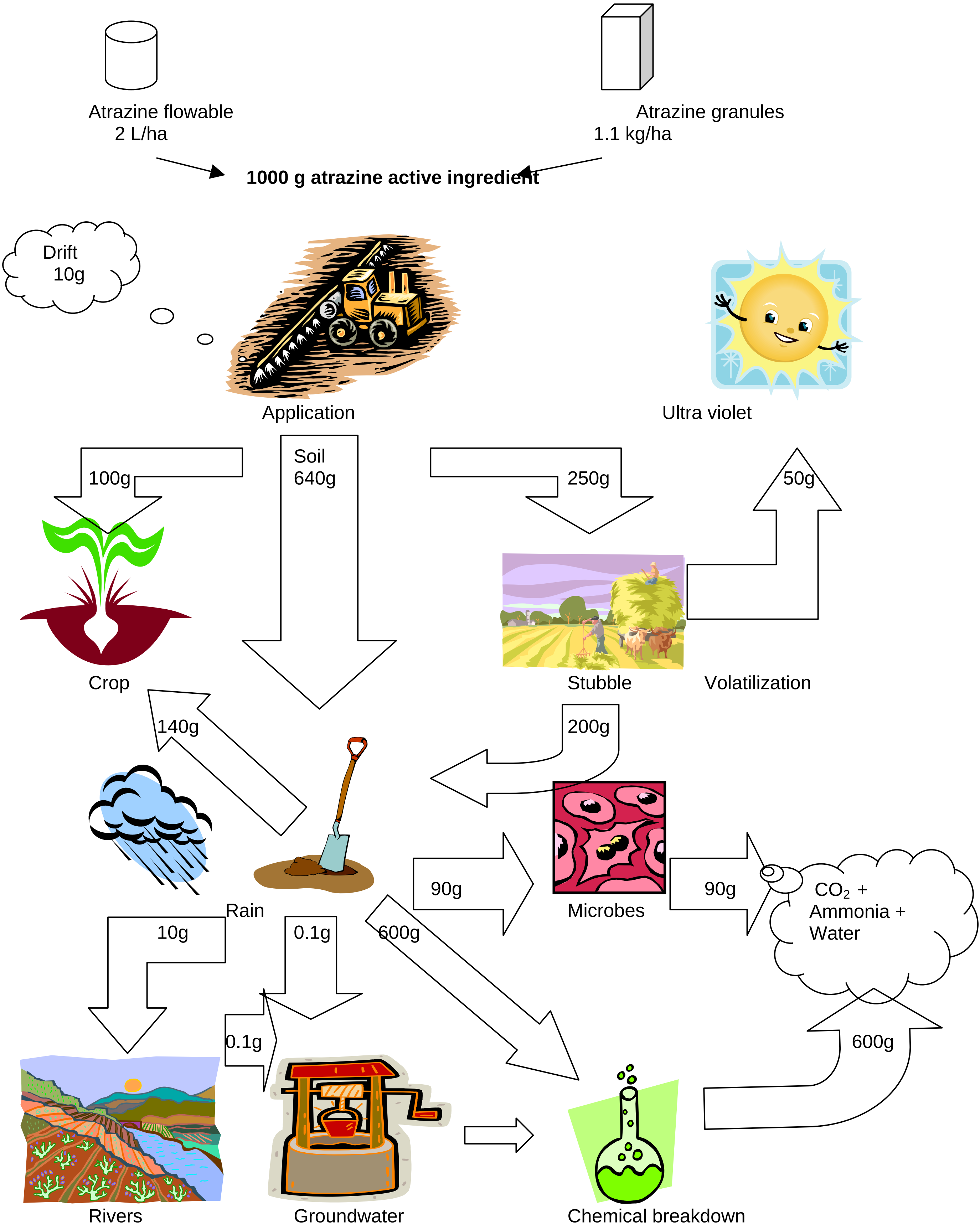
What happens to the applied atrazine applied to fields.



Appendix 1

What happens to the atrazine applied to the field.

Concentration

The amount of atrazine applied depends on the concentration of atrazine in the product. Products vary from10% to 90% active ingredient. Most agricultural products have 50-90% active ingredient.

Degradation in storage

There is little loss of active ingredient in storage over a period of 3-5 years. Some suspension formulations tend to settle. Granular formulations lose virtually no activity if they are kept dry.

Degradation after mixing with water and other pesticides in the spray tank

Hydrolysis is slow and little degradation occurs over a period of months, however settling in the tank may occur and vigorous agitation may be required to resuspend the product. When mixed with other products such as paraquat and diquat the atrazine can settle considerably within an hour if not constantly agitated. This may result in very high rates of application occurring at the beginning of the spray run as the settled atrazine is sucked from the bottom of the spray tank.

Drift

Most sprayers produce some fine droplets that may drift. Typically this is 1 to 10% of the applied product and most settles within 100 m of the sprayed area. It is rare for more than 1% of the applied product to drift more than 250 m downwind even under adverse conditions.

Interception

The applied product may land on bare soil, vegetation or water.
On soil, it is exposed to UV radiation from the sun and losses of 5% per day can be expected until it is washed into the soil by rainfall where it attaches to clay and organic matter and is then exposed to chemical breakdown mainly along with some microbial breakdown with about half of the product degrading every 1-6 months in agricultural soils. In dry soil, degradation is very slow. Virtually none evaporates.
On vegetation, some is lost each week due to UV breakdown. About 10% is absorbed by green plants and nearly all of this is broken down within the plants. Dead plants or stubble absorb lesser quantities and it is more prone to being washed off and into the soil by following rains. Typically about 65% of the atrazine applied to areas covered by stubble or plants will reach the soil.
On water, atrazine usually simply dissolves. At a solubility of 33 ppm, about 30,000 litres of water is required to dissolve 1 kg of active ingredient. This is equivalent to water 3 mm deep over a hectare. Atrazine applied to inundated areas will probably go wherever the water is flowing to.

Runoff, erosion and leaching.

On water logged soils, additional rainfall causing runoff will transport a significant amount of the applied atrazine in solution.
On drier soils, rainfall penetrates and soil carrying atrazine which is stripped from solution and attaches to clay and organic matter. Subsequent erosion of the clay and silt may lead to movement of atrazine but this is generally minor. Similarly, wind transporting clay or organic matter may move attached atrazine but it is generally minimal.
Leaching vertically through the soil profile is minimal (Rothnie et al, GRDC report 2006) in agricultural soils. Even in wet years, on sandy soils where the water table is close to the surface ground water contamination is not likely with normal use rates. Less than 0.1 ppb (the drinking water guideline value) or one millionth of the applied atrazine is likely to enter the water table by leaching. Localised contamination is usually associated with disposal of herbicide, mixing operations or spills.

Fate in soil

Crops and other plants take atrazine up through their roots and break it down within the plant.
Most (>95%) of the atrazine that is washed into the soil is tightly bound to organic matter or clay in the top few centimetres.

Dissociation constant

In WA soils, most of the breakdown is due chemical hydrolysis producing hydroxy-atrazine and desethyl-atrazine and finally carbon dioxide and ammonia. Microbes break the atrazine into desethyl-atrazine and desisopropyl-atrazine which are then broken down into cyanuric acid and finally to carbon dioxide, ammonia and water. The chemical breakdown, activity of microbes and the amount of water passing through the soil in combination with the clay content determines the amount of atrazine that moves to deeper soil horizons and then into the water table. One of the breakdown products of atrazine is very insoluble and doesn't move through the soil while the other is soluble and can move through the soil quite quickly.
In culture solutions, atrazine is broken down into carbon dioxide and water within a few days but in soil it may take many months for atrazine to break down. The main reasons for this are lack of bio-availability and regulation of breakdown rates by the microbes. In soil there are 1000-10000 organisms per gram of soil that can break down atrazine and these live in the 100 million or so soil pores. Each molecule of atrazine has to pass 1000 or more pores to find an organism that will break it down. The levels of atrazine that are normally present in soil are generally too low to cause a build up in the microbe population and the microbes usually use atrazine as a nitrogen (rather than energy) source. When fertiliser nitrogen sources are available they tend to use these rather than break down atrazine{Sims 2004 2843 /id}.

Fate in the water table

Atrazine that ends up in the water table is broken down more slowly by chemical hydrolysis (and other reactions?).

Properties of atrazine that affect its potential to contaminate the environment.

Atrazine and its decomposition products

Atrazine
Atrazine CASRN - 1912-24-9.

Physical Properties

Solubility –

Atrazine - 33 mg/L at 22^{0}C. (31.9 mg/L at 20^{0}C) This is considered moderately soluble.
The neutral form of atrazine is present at pH>1.6 so field pH of 4-10 should have little effect on solubility.
pKa = 1.56-1.6 pKa at 25^{0}C.
Degradation products are more and less soluble than atrazine.

Volatility

Vapour Pressure of 0.04mPa at 20˚C.
Up to 2% of the applied atrazine may escape to the atmosphere by volatilization.
A few percent may be lost in spray drift.

Mobility

Mobility decreases as the clay and organic matter content of soils increase.
It has leaching index of 10 and the LogPow is 2.34 (2.59 at 20^{0}C, 2.5 at 25^{0}C).

Degradation

In Soil

Half life varies from 30 to 180 days in soil. In Europe and the US the DT50 was 43 days with a range of 16-77 days as the realistic range. The DT90 was 135 days with a range of 52-256 days. (DT = Dissipation time). In German soils the DT50 was 50 days in aerobic conditions and 230 days in anaerobic conditions at 25^{0}C with an initial concentration of 10 mg/kg. When comparing aerobic and anaerobic conditions the DT values vary considerably between studies.
Break down is more rapid in moist, acid {pH($CaCl_2$)<6.5} soils, at higher temperatures, with higher organic carbon levels under aerobic conditions.
Absorption is mainly onto organic carbon in the soil. Humic acids have the highest affinity followed by lignine and quinizarine. Water soluble polysaccharides can also absorb atrazine (which could be significant in sugar cane areas).
Wind erosion – losses by wind erosion are usually negligible.

In Water

Half life varies from 80 to 260 days.
Half life at pH7, 70^0C = 200 days.
Half life at pH9, 70^0C = 22.5 days.
Half life at pH5, 20^0C = 86 days.
In buffered solutions at pH 5, 7 and 9 and 25^0C with a concentration of 5 mg/L, atrazine was not hydrolysed over a 30 day period.
Atrazine degradation in aquatic systems follows similar pathways to those found in soils.

In Air

In the atmosphere, atrazine breaks down with a half life of 0.9-39 hours due to OH radical oxidation. The half life due to direct photolysis is 198, 333 and 611 days at 30^0, 40^0, and 60^0 latitudes respectively. In artificial sunlight the half life was 2 hours. The breakdown product is mainly deethylatrazine with some deisopropylatrazine and diamino-chloro-triazine.
Rainfall also removes atrazine from the atmosphere.
Atrazine will not be transported to the stratosphere but can be transported in minute quantities by wind over long distances.

Bioaccumulation

Atrazine has a low bioaccumulation potential in fish. The risk of it entering the food chain and harming predators or humans is negligible.

Government guidelines

National Health and Medical Research Council

Drinking water

Level at which atrazine contamination should be reported is 0.1 ppb atrazine. If these levels are exceeded the drinking water supply authorities are required to investigate reasons for the contamination.
Level at which no expected adverse impact on health is expected is greater than 40 ppb atrazine.

EPA

Decreased bodyweight gain was found in rats fed 70 ppm or 0.35 mg/kg/day
In a 2 year rat feeding study the no effect level was 500 ppm or 25 mg/kg/day
In a 1 year dog feeding study the no effect level was 1000 ppm or 34 mg/kg/day.

Questions
leaching index of hydroxy atrazine and desethyl atrazine