NRA Special Review of

Glyphosate

June 1996

NRA Special Review Series 96.1

by the

Chemical Review Section
National Registration Authority
for Agricultural and Veterinary Chemicals

Canberra
AUSTRALIA
## Contents

Executive Summary 1

1. Introduction 2

2. Scope of Review 2

3. Reasons for the Review 3

4. Notification of the Review 4

5. Responses from Participants in the Review 4

6. Evaluation of Submissions and Conclusions 5

7. Recommendations 7

8. PRRD Status 8

Attachments

Attachment 1: Glyphosate Products Affected by the NRA Review 10

Attachment 2: Environment Protection Agency Australia Report 12
EXECUTIVE SUMMARY

Because glyphosate is a recognised low-risk active ingredient, the NRA is taking this opportunity to improve the environmental safety margin for glyphosate products still further by amending use patterns and labels to reduce the potential for aquatic toxicity.

The review of glyphosate was initiated following advice from the Commonwealth Environment Protection Agency that the safety margins for aquatic uses of particular glyphosate formulations were too narrow. This advice is based on a study commissioned by the Western Australian Department of Environmental Protection detailing the results of an acute toxicity study on selected frog species from the south west of Western Australia. These results suggest certain surfactants in glyphosate formulations are acutely toxic to tadpoles at concentrations that are likely to occur in shallow water.

Seventy five products were placed under review covering 27 registrants. All registrants were given the opportunity to provide information to the NRA relating to the scope of the review which involved:

- reviewing application methods adjacent to aquatic environments for glyphosate formulations;
- including a warning statement on all agricultural glyphosate product labels precluding use on or adjacent to waterways (ie ditches, drains, lakes etc.) unless authorised; and
- only allowing use in sensitive aquatic situations where it can be demonstrated the glyphosate formulation does not pose a significant risk to the aquatic environment.

From the information received, and the re-evaluation of existing data, the NRA concluded that the aquatic toxicity of currently registered glyphosate formulations is undesirably high and is mainly due to the surfactants in the formulations. Accordingly, the current conditions of registration of all agricultural glyphosate products will be refined to describe more clearly the situations in which these products can be used to avoid the risk of significant aquatic contamination. Use of these products will be restricted to dry drains and channels, and dry margins of dams, lakes and streams and amendments to the labels will be made to minimise any possible aquatic contamination. Where a need does exist to control weeds growing in or over water, only formulations with an acceptable margin of aquatic safety will be registered.

Registrants will be given twelve months (until 30 June 1997) to make the necessary changes to their registered products. No changes will be made to products registered solely for use in the home garden.
1. **Introduction**

Glyphosate is a broad-spectrum, non-selective, post-emergence herbicide with high activity on virtually all annual and perennial plants. When applied post-emergence it shows no pre-emergence or residual activity. This is because glyphosate binds strongly to soil particles and is readily metabolised by soil microorganisms. The rapid translocation of glyphosate from the foliage of treated plants to the roots, rhizomes and apical meristems results in the total destruction of hard to kill perennial weeds and is one of the main reasons for glyphosate’s effectiveness and popularity. Many other herbicides kill only the above ground parts of plants allowing re-emergence of new shoots from the underground storage organs.

Glyphosate is present as the isopropylamine, trimesium, diphenylamine and mono-ammonium salts and the free acid in products, with the isopropylamine salt the most common. Each is used exclusively, with no mixtures of salts registered. Concentrations of glyphosate in products are usually 360g.L\(^{-1}\) or 450g.L\(^{-1}\) in products approved for agricultural use and 100g.L\(^{-1}\) or 3.6g.L\(^{-1}\) (ready to use) in products approved for home garden use.

In Australia, glyphosate is approved for the control of a wide range of annual, perennial, tree, brush and woody weeds. Application is via boom, knapsack, hand spray and wiper equipment. It is used in many different situations including:

- Croplands for the control of emerged weeds prior to crop and fallow establishment, minimum tillage farming;
- Non-cultivated land such as industrial, commercial, domestic and public service areas, and rights of way;
- Aquatic areas such as drains, channels, edges of dams, lakes and streams
- Forests, orchards, vines and plantations; and
- Home garden use on rockeries, garden beds, driveways, fencelines, firebreaks, around buildings and prior to planting new lawns and gardens.

2. **Scope of the Review**

The review was limited to the use of glyphosate formulations in and around aquatic areas with particular reference to the toxicity of surfactants to aquatic organisms.

In particular, the review covered the three following areas:

- Review of application methods adjacent to aquatic environments of all agricultural products containing glyphosate (not home garden products);
- Proposal to include a warning statement on all agricultural glyphosate product labels precluding use on or adjacent to waterways (ie ditches, drains, lakes etc.) unless authorised; and
- Proposal to only allow use in sensitive aquatic situations where it can be demonstrated the glyphosate formulation does not pose a significant risk to the aquatic environment.

The review focused on glyphosate formulations approved for use near streams, waterways etc. and other formulations where use may result in the contamination of waterways (ie agricultural uses). A total of 75 products, distributed amongst 27 registrants, were placed
under review when the review was initiated. A full listing of products is available at Attachment 1. This listing also includes additional glyphosate products, registered since the initiation of the review. These products are also subject to the review outcomes.

3. Reasons for the Review

In June 1995, Bidwell and Gorrie, on behalf of the Department of Environmental Protection, WA (WA DEP), published a report on the acute toxicity of Roundup® to selected frog species. Their investigation was initiated after a proposal was referred to the WA DEP in 1994 for aerially spraying a glyphosate based herbicide over substantial areas of Lake Kununurra to control the emergent water weed, Cumbungi. The WA DEP had also received anecdotal reports of frogs being killed or frog chorus being “silenced” after the application of herbicides (including glyphosate) in or adjacent to aquatic areas.

The results of the study led the authors to conclude that tadpoles were many more times sensitive to the glyphosate formulation than adult frogs and that tadpoles were approximately ten times more sensitive to the formulation than to technical grade glyphosate. Calculations based on recommended application rates for the control of emergent aquatic weeds predicted that concentrations of the formulation in shallow water (<5cm) could be similar to the LD_{50} for tadpoles.

A copy of this report was forwarded to the NRA, in June 1995, from the WA DEP together with a request that the NRA consider reviewing the label warnings and application methods over or adjacent to aquatic environments (particularly spraying) for glyphosate formulations containing surfactants.

An assessment of the WA DEP report by the Commonwealth Environmental Protection Agency (EPA) indicated that the safety margins for aquatic uses of glyphosate formulations are narrow. However, the EPA also pointed out that the same conclusion had been reached from its assessment of data previously provided by product registrants. The EPA support for these products was based on a number of mitigating assumptions, such as application by hand spraying would minimise contamination of water and allow dilution of any contamination that did occur; advice from State authorities that glyphosate is a vital aquatic herbicide for reasons of superior efficacy and reduced environmental impact, and that no adverse effects were known from its use in aquatic situations at that time.

However, the suggestion of adverse effects in WA, together with other suggestions that the use of a glyphosate formulation in drainage channels in Griffith, NSW impacts on aquatic invertebrates, led the EPA to recommend the review of previous data with a view to reducing the risks associated with the large scale spraying of aquatic weeds to an acceptable level. The EPA noted that the option of improving the aquatic safety of glyphosate formulations appeared feasible.

Based on this evidence, the NRA determined that a review of glyphosate would be initiated under section 31(1) of the Agricultural and Veterinary Chemicals Code (Agvet Code) because the NRA was not satisfied that the requirements for the continued approval of agricultural products containing glyphosate could be met. The reason being that the NRA was concerned the surfactants in these products did not conform with the requirements for continued registration stated in section 31(2) of the Agvet Code and
clause 20 and 21 of the Agvet regulations in that they may be “likely to have an unintended effect that is harmful to animals, plants or things or to the environment.”

4. Notification of the Review

All registrants of agricultural products containing glyphosate were notified of the review, its scope and given the opportunity to provide any information, of which they were aware, that was relevant to the review, particularly any relating to the aquatic toxicity of glyphosate formulations or surfactants. State Departments of Agriculture were also asked to comment on the review. A press release ‘Action on herbicide threat to frogs’ was issued by the NRA on 14 September, 1995 publicly announcing the review of glyphosate.

5. Responses from Participants in the Review

The NRA received 21 responses on the review. All were in favour of continuing the registrations of glyphosate, but very few contained data to support the continued use of currently approved surfactants in aquatic situations. All data submitted were referred to the EPA for evaluation.

Several respondents suggested that the NRA publish lists of surfactants suitable and unsuitable for incorporation into agricultural chemical products used in aquatic situations. Two respondents stated they had already suffered a decrease in sales due to the publicity surrounding the WA DEP report on glyphosate. Several registrants indicated their willingness to include more detailed warning statements relating to aquatic use on their labels. However, one registrant stated it did not support a general review of application methods as it was of the opinion that existing application methods and glyphosate use patterns do not pose a significant risk to frog habitat and that any decisions regarding the definition of significant risk to the aquatic environment should be decided by the NRA on the basis of a risk/benefit analysis. Another registrant commented that the WA DEP study confirmed the toxicity values generated by the study are within the EPA’s slight to moderate range and stated that it did not believe the margins of safety had been reduced as there have been no changes in the glyphosate herbicide formulations, or the labelling of products for use on waterways.

The State Departments of Agriculture were in favour of retaining as many glyphosate uses as possible because of the importance of the chemical. One commented that glyphosate has long been regarded as a “safe” herbicide to use in and near watercourses and several States thought it important that this reputation not be lost when it is chemical additives that appear to be causing the problem. They commented that it would be very detrimental to industry, to support sustainable agricultural practices if glyphosate were deregistered, and that alternative chemicals may be more toxic and have possible residual effects. However, they recognised that the recent concerns over the potential for aquatic contamination should be addressed and that more data on surfactants were needed. Several also recommended that formulations suitable for aquatic use should be introduced which are efficacious and safe for aquatic fauna and that the impacts and costs of the required changes to the glyphosate formulations should be minimised for uses away from aquatic situations.

One registrant (Rhone-Poulenc Rural Australia Pty Ltd) advised the NRA the two glyphosate products registered to them were no longer sold and requested they be deleted.
from the review. In response to this request, the product registrations have been cancelled by the NRA.

All responses from participants in the review were evaluated and taken into account when preparing this report on glyphosate.

6. Evaluation of Submissions

The NRA requested the EPA to review the data and information submitted on the aquatic uses of glyphosate products. The EPA is a Commonwealth agency the NRA refers to for specialist advice. The EPA evaluates the environmental implications and recommends measures to avoid or minimise adverse environmental effects. A full copy of the EPA’s final report, *Reconsideration of Glyphosate Formulations with Aquatic Use Patterns* is at Attachment 2.

The principle objective of the EPA review was to identify formulations that do not pose a significant risk to the aquatic environment.

In its report the EPA recommends that such formulations should exhibit no toxicity to aquatic organisms at concentrations of at least 100mg.L\(^{-1}\) (when comparing the toxicities of different chemicals, the US EPA categorises those with aquatic end-points above 100mg.L\(^{-1}\) as practically non-toxic).

Details provided for many of the formulations were brief. None of the data submitted by registrants showed the formulations had aquatic end-points above the threshold level of 100mg.L\(^{-1}\). From the data available it was apparent that concentrations (total formulation) following application of glyphosate products over shallow water would be likely to exceed concentrations shown to be toxic to aquatic fauna in laboratory testing.

The EPA report concludes that the aquatic toxicity of currently registered glyphosate formulations is undesirably high and is mainly due to the surfactants in the formulations or those that are recommended to be added to the tank mix. One exception is Touchdown®, where it appears the toxicity to certain invertebrates is conferred by the active ingredient (the trimesium salt of glyphosate) rather than the surfactant. However, for many products the aquatic toxicity could not be defined due to a lack of information from registrants on the aquatic toxicities of surfactants or formulations and, therefore, they are presumed to be of similar toxicity to the others.

The EPA report recommends that all glyphosate products registered for use in aquatic situations (including perimeter treatment of water bodies) refine their labels to more clearly describe the situations in which they can be used and avoid the risk of significant aquatic contamination. Given the strong retention of glyphosate and the polyoxyethylene amine (POEA) surfactant by soil, it is considered that careful application adjacent to waterways should not give rise to significant aquatic contamination.

With regard to use in irrigation channels, this should occur when irrigation channels are dry and a delay of four days should occur before water is returned to the channel. The EPA estimate that the predicted environmental concentration (PEC) in the overlying water if channels are filled four days after spraying is acceptable and should not impact significantly on aquatic fauna and downstream aquatic flora (see EPA report for calculations).
It should be noted, however, that narrow safety margins derived through calculation do not necessarily equate to impacts under conditions of use. It may be argued that toxicity will be rapidly attenuated in natural environments by factors such as interception of spray by the weed canopy, sorption by soil and dilution by water thus reducing the impact of the formulation. There is also no direct evidence to link the use of glyphosate products with toxic impacts in the field, even after decades of widespread use, but anecdotal reports continue to be received.

Due to the recognised low risk of the active ingredient and the availability of alternative formulations with much more favourable aquatic toxicity profiles, the NRA has taken this opportunity to improve the margin of safety for glyphosate products still further by amending use patterns and labels to reduce the potential for aquatic toxicity.
7. Recommendations

A. Glyphosate products with registered aquatic uses (including on the margins of water bodies) for which aquatic toxicity data have been provided:

Unless these products can be reformulated to afford an acceptable margin of aquatic safety, the conditions of registration for use in aquatic situations will be restricted to dry drains and channels, dry margins of dams, lakes and streams. Labels will be required to carry the following amended:

In the Directions for Use table, the use situation for aquatic areas will be amended to:

USE SITUATION - Dry drains and channels, dry margins of dams, lakes and streams.

The Critical Comments accompanying this use will be amended to:

CRITICAL COMMENTS - Do NOT apply to weeds growing in or over water. Do NOT spray across open bodies of water, and do NOT allow spray to enter the water. Do NOT allow water to return to dry channels and drains within 4 days of application.

Under the heading PROTECTION OF WILDLIFE, FISH, CRUSTACEA AND ENVIRONMENT the following phrases will appear:

Do NOT contaminate dams, rivers or streams with the product or used container. When controlling weeds in aquatic situations, refer to label directions to minimise the entry of spray into the water.

B. Glyphosate products with registered aquatic uses (including on the margins of water bodies) for which no aquatic toxicity data have been provided:

Unless aquatic safety can be demonstrated by submission of data, either for current or reformulated products, the above label amendments will apply.

C. Glyphosate products with no registered aquatic uses:

Under the heading PROTECTION OF WILDLIFE, FISH, CRUSTACEA AND ENVIRONMENT the following phrases will appear:

Do NOT contaminate dams, rivers or streams with the product or used container. Do NOT apply to weeds growing in or over water. Do NOT spray across open bodies of water.
D. Home Garden products:

Labels for products intended solely for home garden use will not be amended as the risk of significant aquatic contamination from home garden use of products is very low.

E. Future Approvals for Aquatic Use

Where a need exists to control weeds growing in or over water, only formulations with a superior margin of aquatic safety (no toxicity to fish, daphnids and tadpoles at concentrations in excess of 100mg.L\(^{-1}\) whole formulation) will be registered.

F. Time-frame for the introduction of label changes and restrictions of use:

Registrants will be given twelve months to amend their labels and aquatic uses will be withdrawn as from 30 June 1997.

8. PRRD Status

The objectives of the NRA’s PRRD (Proprietary Rights in Registration Data) scheme are:

- to grant protection to providers of certain information relating to agricultural and veterinary chemicals to provide an incentive for the development of products and data applicable to Australian or local conditions;
- to encourage the availability of overseas products and data; and
- to provide reciprocal protection for Australian products and data under overseas PRRD systems.

In general, the NRA designates information as “protected registration information” for a “protection period” of two to seven years if it:

- is requested by the NRA for the purposes of reconsidering (reviewing) a product;
- is relevant to the scope of the review; and
- relates to the interaction between the product and the environment of living organisms or naturally occurring populations in ecosystems including human beings.

If the NRA proposes to use the same information to determine whether to register, or continue registration, of another chemical product, the NRA must not use the information until the parties come to an agreement as to terms for compensation, unless the NRA is satisfied that it is in the public interest to use the information or the protection period has expired.

With reference to the glyphosate review, registrants were requested by the NRA to provide information of relevance to the scope of the review, particularly information relating to the aquatic toxicity of surfactants present in glyphosate formulations. Several new studies were submitted which are covered by the PRRD scheme and are now designated as protected registration information. These protected studies are identified in the reference list accompanying the EPA report.

This information was considered protected because it:

- was submitted in response to the NRA’s request;
• was relevant to the review because it was required to make the decision to withdraw certain aquatic uses due to unacceptable safety margins; and
• related to the interaction between the product and living organisms.

Although this information is designated protected registration information, registrations for products involved in this review will continue without the need for registrants to access the protected registration information from the providers of such information. This is because it was not necessary to use any of this information to make the decision to continue the registrations for the remaining uses (ie non-aquatic) of the primary or any other currently registered products.

For more information on how the PRRD Scheme operates, please refer to the NRA’s booklet: *The NRA’s Scheme for Proprietary Rights in Registration Information (PRRD)*.
## Glyphosate Products Affected by the NRA Review:

1. 48552 4 FARMERS GLYPHOSATE 450 HERBICIDE
2. 46737 ACRES GLYPHOSATE 360 HERBICIDE
3. 46736 ACRES GLYPHOSATE CT HERBICIDE
4. 48136 AGCHEM GLYPHOSATE 450 CT HERBICIDE
5. 46733 AGSPRAY 100 WEEDSPRAY
6. 47273 AGSPRAY GLYPHOSATE 450 HERBICIDE
7. 46704 AGSPRAY GLYPHOSATE HERBICIDE
8. 39276 APL GLYPHOSATE 360 HERBICIDE
9. 39277 APL GLYPHOSATE 450 HERBICIDE
10. 39265 APL INDUSTRIAL GLYPHOSATE 360 HERBICIDE
11. 41685 AITALA GLYPHOSATE 360 NON-RESIDUAL HERBICIDE
12. 46637 AUSGEN GLYPHOSATE 360 HERBICIDE
13. 46638 AUSGEN GLYPHOSATE 450 HERBICIDE
14. 46846 BROAD SPECTRUM HERBICIDE TRIGGER
15. 46747 CHEMSPRAY GLYPHO 360 TOTAL WEEDKILLER
16. 40521 COUNTRY GLYPHOSATE 360 HERBICIDE
17. 40522 COUNTRY GLYPHOSATE 450 HERBICIDE
18. 47848 CM GLYPHOSATE 360 HERBICIDE
19. 47847 CM GLYPHOSATE 450 CT HERBICIDE
20. 31378 CRG NO-GROW 450 WEED SPRAY
21. 47203 CRT GLYPHOSATE 360 KNOCKDOWN HERBICIDE
22. 47202 CRT GLYPHOSATE 450 KNOCKDOWN HERBICIDE
23. 46086 CYNDAN GLYPHOCYDE 450 WEEDKILLER
24. 47234 DAVID GRAYS GLYPHOSATE 360 HERBICIDE
25. 31386 DAVISON GLYPHOSATE 300D HERBICIDE
26. 31384 DAVISON GLYPHOSATE 450 HERBICIDE
27. 40209 DAVISON GLYPHOSATE 700 WSP HERBICIDE
28. 31385 DAVISON GLYPHOSATE 360 HERBICIDE
29. 47540 DUPONT CUT-OUT BRUSH CONTROLLER
30. 46767 ELDERS GLYPHOSATE CT BROADHECTARE HERBICIDE
31. 31401 FARMCO GLYPHOSATE 360 HERBICIDE
32. 31400 FARMCO GLYPHOSATE CT BROADHECTARE HERBICIDE
33. 39263 FARMOZ WIPE-OUT 360 NON-RESIDUAL HERBICIDE
34. 39264 FARMOZ WIPE-OUT 450 NON-RESIDUAL HERBICIDE
35. 48068 GENEREX GLYPHOSATE 450L
36. 48070 GENEREX GLYPHOSATE 360L
37. 45289 GLYCEL 360 HERBICIDE
38. 45288 GLYCEL 450 HERBICIDE
39. 46485 GLYFOS CT HERBICIDE BAYER
40. 45043 GLYFOS HERBICIDE
41. 46672 GLYFOS HERBICIDE BAYER
42. 45419 OZTEC RURAL GLYPHOZ 450 NON-SELECTIVE HERBICIDE
43. 46004 GLYPHOZ 450 NON-SELECTIVE HERBICIDE
44. 46021 HARPOON 360 HERBICIDE
45. 46015 HARPOON HERBICIDE
46. 46017 HONCHO HERBICIDE
47. 48082 LIEF GLYPHOSATE 450
48. 48081 LIEF GLYPHOSATE 360
<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>46732 MASTRA 100 WEEDSPRAY</td>
</tr>
<tr>
<td>50</td>
<td>46711 MASTRA GLYPHOSATE HERBICIDE*</td>
</tr>
<tr>
<td>51</td>
<td>46847 MASTRA GLYPHOSATE 450 HERBICIDE</td>
</tr>
<tr>
<td>52</td>
<td>45264 MJ ENTERPRISES GLYFOSATE 100 HERBICIDE</td>
</tr>
<tr>
<td>53</td>
<td>45266 MJ ENTERPRISES GLYFOSATE 360 HERBICIDE</td>
</tr>
<tr>
<td>54</td>
<td>46686 NATIONAL GLYPHOSATE 360 HERBICIDE</td>
</tr>
<tr>
<td>55</td>
<td>46685 NATIONAL GLYPHOSATE CT BROADHECTARE HERBICIDE</td>
</tr>
<tr>
<td>56</td>
<td>31399 NUFARM GLYPHOSATE 360 HERBICIDE</td>
</tr>
<tr>
<td>57</td>
<td>31398 NUFARM GLYPHOSATE CT BROADHECTARE HERBICIDE</td>
</tr>
<tr>
<td>58</td>
<td>39117 PACER HERBICIDE BY MONSANTO</td>
</tr>
<tr>
<td>59</td>
<td>40410 PACER SOL-TECH HERBICIDE</td>
</tr>
<tr>
<td>60</td>
<td>47697 PIVOT GLYPHOSATE CT HERBICIDE</td>
</tr>
<tr>
<td>61</td>
<td>47382 POWER GLYPHOSATE 360 HERBICIDE</td>
</tr>
<tr>
<td>62</td>
<td>46020 RANGER 360 HERBICIDE</td>
</tr>
<tr>
<td>63</td>
<td>46014 RANGER HERBICIDE</td>
</tr>
<tr>
<td>64</td>
<td>46019 RICOCHET 360 HERBICIDE</td>
</tr>
<tr>
<td>65</td>
<td>46013 RICOCHET HERBICIDE</td>
</tr>
<tr>
<td>66</td>
<td>31394 ROUNDUP CT BROADACRE HERBICIDE BY MONSANTO</td>
</tr>
<tr>
<td>67</td>
<td>48482 ROUNDUP DRY HERBICIDE BY MONSANTO</td>
</tr>
<tr>
<td>68</td>
<td>31393 ROUNDUP HERBICIDE BY MONSANTO</td>
</tr>
<tr>
<td>69</td>
<td>46018 RUSTLER HERBICIDE</td>
</tr>
<tr>
<td>70</td>
<td>46016 SADDLE HERBICIDE</td>
</tr>
<tr>
<td>71</td>
<td>47063 SANDOBOAN HERBICIDE</td>
</tr>
<tr>
<td>72</td>
<td>39309 SANDOZ SANDOBOAN HERBICIDE</td>
</tr>
<tr>
<td>73</td>
<td>46064 SANOS 360 NON-SELECTIVE HERBICIDE</td>
</tr>
<tr>
<td>74</td>
<td>47204 SANOS 450 NON-SELECTIVE HERBICIDE</td>
</tr>
<tr>
<td>75</td>
<td>31396 SQUADRON HERBICIDE BY MONSANTO</td>
</tr>
<tr>
<td>76</td>
<td>46673 SUPERWAY GLYPHOSATE 360</td>
</tr>
<tr>
<td>77</td>
<td>47743 SUPERWAY GLYPHOSATE CT 450 HERBICIDE</td>
</tr>
<tr>
<td>78</td>
<td>31263 TILLMASTER CT HERBICIDE</td>
</tr>
<tr>
<td>79</td>
<td>31261 TILLMASTER CT HERBICIDE BY MONSANTO</td>
</tr>
<tr>
<td>80</td>
<td>31262 NUFARM TILLMASTER HERBICIDE</td>
</tr>
<tr>
<td>81</td>
<td>45855 TOUCHDOWN BROADACRE HERBICIDE</td>
</tr>
<tr>
<td>82</td>
<td>39672 TOUCHDOWN HERBICIDE</td>
</tr>
<tr>
<td>83</td>
<td>47017 TROUNCE BRUSH-PACK HERBICIDE BY MONSANTO</td>
</tr>
<tr>
<td>84</td>
<td>45816 WEEDMASTER CT HERBICIDE</td>
</tr>
</tbody>
</table>
Introduction

On 13 September 1995, the National Registration Authority (NRA) instigated a special review of glyphosate formulations used in aquatic situations, with specific reference to the following points:

• application methods adjacent to aquatic environments;
• inclusion of a warning statement on all glyphosate product labels precluding use on or adjacent to waterways unless authorised; and
• use in aquatic situations only to be allowed where it can be demonstrated that the formulation does not pose a significant risk to the aquatic environment.

The impetus for this review was a report (1) commissioned by the Western Australian Department of Environmental Protection (DEP) that showed the surfactant in Roundup® to be significantly more toxic to frogs than the active ingredient, glyphosate. Unconfirmed anecdotal reports of the impact of glyphosate formulations on frogs had been circulating in Australia for some years. The toxicity to aquatic fauna of the surfactant, a polyoxyethylene amine (POEA) derivative, had been known for some time, but the Western Australian report was the first to deal specifically with frogs. Calculations by the DEP, confirmed by the EPA, found the safety margin for frogs and other aquatic fauna exposed to Roundup® following application to shallow water to be undesirably narrow.

Rationale for Review

The questions surrounding aquatic uses of glyphosate products are important as glyphosate products are preferred for use in sensitive aquatic situations because of the recognised low risk of the active ingredient, and dominate this sector of the market. Close scrutiny of the environmental characteristics of glyphosate products is justified given their widespread use.

It should be noted that narrow safety margins derived by simple calculation do not necessarily equate to impacts under conditions of use. A variety of natural processes, such as sorption, dilution and biodegradation, operate in open environments to mitigate any hazards that may be predicted based on laboratory toxicity data. The US EPA has found glyphosate to be eligible for reregistration, noting that some end-use products intended for direct application to aquatic environments must be labelled "Toxic to fish" because of the presence of a toxic inert ingredient (2). There is no evidence in the scientific literature to link the use of glyphosate products with toxic impacts on aquatic fauna in the field, even after decades of widespread use, but anecdotal reports continue to be received. Such reports are difficult to refute while theoretical safety margins remain narrow and scope exists to improve them.

Aquatic Use Patterns

A number of glyphosate products are registered for use in aquatic situations, such as "AQUATIC AREAS: Drains and channels, Margins of dams, lakes and streams" or "aquatic areas such as drains, channels, edges of dams, lakes and streams". Boom, handspray or wiper equipment are recommended for various weeds likely to be found in such situations, with aerial application not recommended for aquatic situations. Product labels contain restraints against contaminating waterways, such as dams, streams or rivers.
It has been noted that the current labels for glyphosate products appear contradictory in allowing use in (or adjacent to) aquatic areas but proscribing contamination of such areas. Margins/edges of waterways may be understood to extend for unspecified distances into the waterway in question.

The need also arises in Australia to control floating aquatic weeds across bodies of water, a situation where glyphosate products are often used under Permit.

There is clearly an opportunity to improve the aquatic safety of glyphosate products, by clarifying labels with respect to the modes and situations of application, and reformulating to reduce the aquatic toxicity associated generally with the surfactants in their formulations. This opportunity calls for swift action given the large volumes in which glyphosate products are used and the sensitive environments to which they may be applied.

### Review Objective

It is important to note that the focus of this review is on the surfactants in glyphosate formulations, rather than on glyphosate itself. Glyphosate has been the subject of numerous reviews that attest to its favourable ecotoxicological profile. A recent example is the Environmental Health Criteria document of 1994 (3). This report will therefore deal mainly with data for glyphosate formulations, and for the surfactants contained in them.

The principal objective of the review will be to identify formulations that satisfy the NRA’s third criterion (use in aquatic situations only to be allowed where it can be demonstrated that the formulation does not pose a significant risk to the aquatic environment).

According to the US EPA's standard evaluation procedure (4) no acute risk to aquatic fauna is presumed where the estimated environmental concentration (EEC) is less than 10% of the LC50 or EC50 for the most sensitive organism tested. Where the EEC exceeds 50% of this threshold, acute risk is presumed to be significant. At intermediate concentrations, the presumption is that the acute risk can be mitigated by precautionary label statements or use restrictions. In the first instance, the EEC is calculated based on a worst case scenario of direct application to 15 cm standing water.

Glyphosate formulations (360g.L⁻¹) may be applied at rates up to 9 L.ha⁻¹ (10.6 kg.ha⁻¹ whole formulation) which would leave residues of 7.1 mg.L⁻¹ in a 15 cm pond. The methodology described above would require that the LC50s or EC50s for aquatic organisms exposed to this and similar products be consistently above 71 mg.L⁻¹ whole formulation. As noted in this report, a broad range of aquatic fauna exhibit greater sensitivity and fail to meet this criterion.

A conservative hazard assessment, based on concentrations following application to 5 cm water, is justified by the use pattern around margins of water bodies, which entails direct application to shallow water environments where non-target fauna such as frogs may be found. The maximum rate would leave residues of 21.2 mg.L⁻¹ of the glyphosate formulation (360g.L⁻¹) if applied directly to 5 cm standing water. A tenfold safety margin would require that the LC50s or EC50s for aquatic organisms exposed to this and similar products be consistently above 212 mg.L⁻¹ whole formulation. However, a fivefold safety margin should suffice to ensure that residues following direct application to 5 cm of standing water are nontoxic. The US EPA categorises chemicals with aquatic end-points above 100 mg.L⁻¹ as practically nontoxic when comparing the toxicities of different chemicals.
**Fate and Toxicity of Glyphosate Formulations**

None of the responses from registrants were able to satisfy the objective outlined above of leaving nontoxic residues following direct application to 5 cm of standing water. Accordingly, a need to refine all labels is indicated.

**Fate and Toxicity of Glyphosate Surfactants**

Only Monsanto has provided information on the environmental fate of the surfactant in its formulation, a POEA derivative with the trade name MON 0818 obtained from a number of sources. Fate studies were conducted on $^{14}$C-MON 0818 and toxicity studies on pure MON 0818. Crop Care provided aquatic toxicity data for the alkylpolysaccharide surfactant in its Touchdown™ formulation, and summary data for analogues of accompanying POEA surfactants.

- **Shake flask study**

  The fate in soil of MON 0818 (prepared from radiolabelled ethylene oxide) was studied under aerobic conditions in shake flask experiments on three soils (see table for properties) maintained at the somewhat elevated temperature of 30°C in a gyratory incubator in the presence of some 20 volumes of water (5). The test material was added to the shake flask systems at a level equivalent to 20 mg.kg$^{-1}$ on the soil.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>pH</th>
<th>% organic C</th>
<th>% Clay</th>
<th>% Silt</th>
<th>% Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silt loam</td>
<td>6.5</td>
<td>0.6</td>
<td>10.0</td>
<td>82.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Silty clay loam</td>
<td>7.0</td>
<td>3.5</td>
<td>36.8</td>
<td>55.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Sandy loam</td>
<td>5.7</td>
<td>0.6</td>
<td>2.3</td>
<td>11</td>
<td>86</td>
</tr>
</tbody>
</table>

Very little radiolabelled carbon dioxide was evolved from studies on steam sterilised soils. Most of the radiolabel was found to have partitioned to soil after 7 days. Around 20-30% was recovered from the supernatant, predominantly as chloroform soluble material suspected to be unchanged test substance. As the surfactant is water soluble, significant binding to soil is indicated.

In contrast to the lack of degradation observed under sterile conditions, considerable evolution of carbon dioxide (24-31% of applied radiolabel over seven weeks) occurred from non-sterile soils, particularly during the first week of incubation (18% of applied from the silt loam). Again, the bulk of the radiolabel partitioned to soil, with only minor amounts (8% after 1 week, declining to about 3% after 7 weeks) recovered from the supernatant from the silt loam.

Evidence for degradation is provided by chloroform extractability data showing the extractability of the supernatant to be around half that of pure MON 0818 (thereby suggesting the formation of more polar metabolites). Similarly, only minor amounts were extractable from non-sterile soil using chloroform, indicating considerable degradation or binding of parent material. A strong contribution from degradation is evident from the evolution of $^{14}$CO$_2$.

Results indicate that the surfactant sorbs readily to soils, particularly those that are biologically active, and degrades with a half-life of less than a week. For the silt loam, less than 5% of applied radiolabel was chloroform extractable from soils and supernatant after 1 week, indicating a half-life for dissipation as short as 1-2 days. Given the large volumes of water used, the results can be considered indicative of the likely fate in aerobic aquatic environments, and particularly to the use pattern in farm channels. Desorption of the surfactant from soils, such as may occur when water is returned to dry channels that have been sprayed, is expected to be a minor process as less than 8% of applied radiolabel, containing significant levels of metabolites in addition to unchanged surfactant, was found in the supernatant a week after treatment. When applied direct to dry surfaces (rather than to soil/water mixtures as in this study) subsequent release to water should be even less pronounced.
• **Aquatic metabolism study**

The aquatic fate of the surfactant was studied in samples of surface water and bottom sediment from a lake (sphagnum bog) in Wisconsin, a pond in Missouri, and the Mississippi river upstream from metropolitan St Louis (6). These waters had respective pHs of 4.6, 7.4 and 7.8. Biometer flasks contained radiolabelled surfactants (0.05 or 0.1 mg.L\(^{-1}\)) dissolved in 150 mL of the natural waters, and were maintained at 30\(^{\circ}\)C in the dark for 14 weeks. Considerable evolution of \(^{14}\)CO\(_2\) occurred over this period, representing about 50% of applied radiolabel in the lake water and about 40% in the pond and river water. Some 7-15% of applied was so released during the first 2 weeks of incubation. This contrasts with sterilised samples where \(^{14}\)CO\(_2\) evolution remained below 0.3% over a 2 week period.

In contrast to the shake flask study, between 21 and 53% of applied radiolabel remained in the aqueous phase, and 7-29% became bound to suspended sediment during 14 weeks of incubation. Losses of 5-32% during evaporation of filtrates were thought to reflect formation of volatile metabolites other than \(^{14}\)CO\(_2\). The higher recoveries of radiolabel from the aqueous phase compared with the shake flask study may reflect lower amounts of soil/sediment and associated binding sites.

The estimated half-life was about 3-4 weeks using the conservative assumption that results from anion exchange chromatography represent only the parent surfactant. This assumption was shown subsequently to be misplaced: high voltage electrophoresis revealed acidic material, thought to be carboxylic acid metabolites, coeluting with the surfactant. Less than 10% of applied radiolabel could be identified as unchanged surfactant after 7 weeks of incubation, declining to 2-6% by study end, suggesting a half-life in the order of 2 weeks. High rates of mineralisation indicate that primary and intermediate metabolites do not persist.

In summary, the POEA surfactant would be expected to be lost from the water column following application by a combination of sorption/binding to sediment and microbial metabolism. Dilution would also rapidly reduce concentrations in the water.

• **Aquatic Toxicity**

Results from test reports provided by registrants, together with those from relevant published studies, are tabulated below as concentrations of the stipulated test materials..

<table>
<thead>
<tr>
<th>Test</th>
<th>Test Material</th>
<th>Species</th>
<th>Result</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>96 h acute</td>
<td>MON 0818</td>
<td>Rainbow trout</td>
<td>LC50 = 4.2 mg.L(^{-1})</td>
<td>7</td>
</tr>
<tr>
<td>96 h acute</td>
<td>MON 0818</td>
<td>Bluegill sunfish</td>
<td>LC50 = 1.3 mg.L(^{-1})</td>
<td>8</td>
</tr>
<tr>
<td>48 h acute</td>
<td>MON 0818</td>
<td>Daphnia magna</td>
<td>LC50 = 2.0 mg.L(^{-1})</td>
<td>9</td>
</tr>
</tbody>
</table>

Static testing of rainbow trout, bluegill sunfish and *Daphnia magna* exposed to MON 0818 indicated moderate toxicity. Endpoints measured at 24 h were the same as those recorded at 96 h for fish.

One glyphosate registrant has provided information on a new formulation with improved aquatic toxicity characteristics. No effect levels for aquatic fauna (fish, daphnids and tadpoles) are well above 100 mg.L\(^{-1}\). The NRA's intention to register this new formulation was advertised in the NRA Gazette of 2 April 1996.

• **Published studies**

The Monsanto results are consistent with published data (10) indicating the surfactant to be clearly the dominant contributor to the toxicity of Roundup® and similar glyphosate formulations. Toxicity did not
Results from testing of Roundup® on sockeye salmon, rainbow trout and coho salmon fry and Daphnia magna equate to 4-6 mg.L⁻¹ MON 0818. The authors suggest that the higher toxicity observed in testing on the surfactant alone indicates that glyphosate antagonises the toxicity of the surfactant in the lake water used for the bioassays since testing of the surfactant alone gave results in the range of 2-3.5 mg.L⁻¹ (11).

The LC50 of 19 mg.L⁻¹ whole formulation recorded for Litoria moorei tadpoles (1) indicates the sensitivity of tadpoles to be similar to that recorded for fish, as expected given that the main toxicant is a surfactant that would be expected to interfere with oxygen transport across gills. Tadpoles were much more sensitive than adult frogs.

- **Crop Care studies**

Crop Care provided summary data on two ethoxylated alkylamines analogous to one of the surfactants in its formulation, showing slight to moderate toxicity to rainbow trout (96 h LC50s of 3.6 and 22.5 mg.L⁻¹). All fish that died did so within 24 h in testing of the more toxic surfactant (Atlas G-3780A). Testing of the alkylpolysaccharide surfactant (AL2575W) contained in Crop Care's Touchdown® Herbicide indicated it to be practically nontoxic to Daphnia magna (12), with no adverse effects noted at a nominal concentration of 100 mg.L⁻¹.
Testing of the Touchdown® formulation (code name 4 LC-E) indicated it to be practically non-toxic to fish (13-15). No effect concentrations were at least 100 mg.L\(^{-1}\) whole formulation. It appears that the ethoxylated alkylamine surfactant is the dominant contributor to the limited fish toxicity of the Touchdown® formulation as Crop Care reports a 96 h LC50 of 10 mg.L\(^{-1}\) towards rainbow trout. Reports of this testing may be made available on a confidential basis, to the NRA, from ICI surfactants if required. This is not considered necessary as the result appears typical of this class of compound, and as noted below the active appears to be the dominant contributor to the toxicity of the formulation to daphnids.

In contrast to the lack of effects on fish, the 4 LC-E formulation proved slightly to moderately toxic (respective 48 h EC50s of 15.6 and 10.1 mg.L\(^{-1}\) whole formulation, equivalent to 6.9 and 4.1 mg.kg\(^{-1}\) active) to adult and first instar *Daphnia magna* (16 and 17). Separate testing of the technical active indicated it to be the main contributor to the overall toxicity of the formulation.

The previous assessment of Touchdown® Herbicide (89/2347 dated 23 June 1993) identified a hazard to *Daphnia magna* based on the above laboratory data but recognised that a number of mitigating factors should operate to reduce this hazard in natural environments. It was considered that to withhold registration would not at that time have been justified as the environmental characteristics of Touchdown® were similar to those of the registered glyphosate (360g.L\(^{-1}\)) formulations. Similar reasoning leads to the conclusion that any restrictions that may now be imposed on the currently registered glyphosate (360g.L\(^{-1}\)) formulations should apply equally to Touchdown® Herbicide.

**Submissions from State Authorities**

A common feature of the views expressed by State agricultural authorities was the need to preserve the uses of this important herbicide, particularly when used away from water. For aquatic uses, the risks of herbicide use must be balanced against the loss of amenity and disruption to natural habitat associated with weed infestations.

Some States expressed a view that data on surfactants should be collated with a view to issuing a list of surfactants safe to use in sensitive aquatic environments. It is argued that this could be of assistance to users when applying products, such as Pacer®, to which surfactants must be added. Such an exercise falls outside the scope of this review, but may be useful in the longer term.

An option suggested by some States is to introduce formulations suitable for aquatic use, that are both efficacious and safe for fauna. Any such changes should not impact adversely on the costs of weed control away from aquatic situations.
Aquatic Hazard from Current Practices

It is evident that the aquatic toxicity of currently registered glyphosate formulations is undesirably high and that improved formulations exist.

The undesirable aquatic toxicity is generally conferred by the surfactants that currently registered glyphosate formulations contain or that are recommended to be added to the tank mix. One exception is Touchdown®, where it appears the toxicity to certain invertebrates is conferred by the active ingredient. For many products, the aquatic hazard could not be defined because of a lack of information provided regarding the aquatic toxicities of the formulations or the surfactants that they contain, but must be presumed to be of similar magnitude. Data available indicate that concentrations (total formulation) following application of glyphosate products over shallow water exceed concentrations shown to be toxic to aquatic fauna in laboratory testing.

It may be argued that toxicity will be rapidly attenuated in natural environments and that significant impacts should therefore not be expected, and have not been recorded during widespread use around the world. However, the widespread use of glyphosate products, including in sensitive environments, and the possibility of developing formulations with improved safety margins for aquatic fauna, requires that action be taken to address this issue.

Accordingly, it is recommended that all glyphosate products currently registered for use in aquatic situations (including perimeter treatment of water bodies) refine their labels to more clearly describe the situations in which they can be used and avoid the risk of significant aquatic contamination. Generic label amendments are listed below.

The views of registrants and some State authorities that the use of glyphosate products adjacent to aquatic environments should be continued have been noted. Given the strong retention of glyphosate and the POEA surfactant by soil, it is considered that careful application adjacent to waterways should not give rise to significant aquatic contamination.

The other situation that merits specific comment is the control of weeds in irrigation channels. Clearly, this should occur when channels are dry. The critical issue is the time that should elapse before water is returned.

Taking the worst case of a 50 cm deep farm channel sprayed with a glyphosate (360g.L⁻¹) formulation at the maximum rate of 10.6 kg.ha⁻¹, the estimated environmental concentration (EEC) in the overlying water if channels are filled and all is released from soil and vegetation would be 2.1 mg.L⁻¹ whole formulation. This approximates the LC50s for fathead minnow and Daphnia magna recorded by Folmar et al (9) but is an order of magnitude below end-points recorded by other researchers for aquatic fauna, including tadpoles. An additional order of magnitude reduction in the EEC would be desirable given the recorded sensitivity of fathead minnows and daphnids.

Fate studies on the MON 0818 surfactant that is mainly responsible for the aquatic toxicity of formulations indicate a half-life for degradation in the order of days, and a tendency to sorb rapidly to soils. Concentrations in the supernatant were 8% of applied at 1 week after application.

Data to indicate the degree of desorption of the surfactant when the time between application and return of water to farm channels is varied are not available. For glyphosate itself, 7% of the applied dose was found in irrigation water returned to a dry channel 4 days after spraying (18).
Given that the EEC should also be reduced below the above estimate by the flow of water, a delay of 4 days before returning water to sprayed farm channels should afford the desired order of magnitude decrease in the EEC. While these arguments are fairly qualitative, use of glyphosate (360g.L\(^{-1}\)) formulations (and other currently registered glyphosate formulations) in dry channels to which water is not returned for 4 days should not impact significantly on aquatic fauna. Downstream aquatic flora should not be impacted as glyphosate is generally only effective as a herbicide when applied direct to foliage.

It is therefore considered that such use patterns are acceptable for currently used glyphosate formulations.
Conclusions and Recommendations

Glyphosate based products included in this review appear to fall into four categories, for which we offer the following label amendments to ensure that unacceptable aquatic contamination does not arise.

Note that the recommendations apply equally to dry and liquid formulations at this time. As noted above, further data on surfactant toxicity and efficacy would be required if the use of dry formulations in aquatic situations is to be considered. It may be argued that ready to use liquid formulations should be preferred in sensitive aquatic situations as greater scope for error exists when the user must add a specified rate of a specialist surfactant.

- **Glyphosate products with registered aquatic uses (including on the margins of water bodies) for which aquatic toxicity data have been provided**

  Unless these products can be reformulated to afford an acceptable margin of aquatic safety, situations of use and critical comments should be amended as outlined below to minimise any possible aquatic contamination.

  **Use Situation - Dry drains and channels, dry margins of dams, lakes and streams**

  Critical comments - Do NOT apply to weeds growing in or over water. Do NOT spray across open bodies of water, and do NOT allow spray to enter the water. Do NOT allow water to return to dry channels and drains within 4 days of application.

  In addition, the standard statement "Do NOT contaminate dams, rivers or streams with the product or used container" should be augmented by the sentence "When controlling weeds in aquatic situations, refer to label directions to minimise the entry of spray into the water."

- **Glyphosate products with registered aquatic uses (including on the margins of water bodies) for which no aquatic toxicity data have been provided**

  Unless aquatic safety can be demonstrated by submission of data, either for current or reformulated products, the above label amendments should apply.

- **Glyphosate products with no registered aquatic uses**

  The standard statement for avoidance of aquatic contamination should be augmented as follows "Do NOT apply to weeds growing in or over water. Do NOT spray across open bodies of water."

- **Glyphosate products for which registration no longer required**

  Such product registrations should be discontinued or amended.

  Labels for products intended solely for home garden use need not be amended as the risk of significant aquatic contamination from home garden use of glyphosate products is very low.

  Where a need exists to control weeds growing in or over water, a formulation with a superior margin of aquatic safety (no toxicity to fish, daphnids and tadpoles at concentrations of at least 100 mg L\(^{-1}\) whole formulation) should be used. Labels for glyphosate formulations currently registered for use in aquatic situations (including drains and channels and perimeter treatment of water bodies) should be amended as outlined above unless an acceptable safety profile for aquatic fauna can be demonstrated.

  Some State authorities have recommended that all or a majority of glyphosate formulations should incorporate safer surfactants to ensure that safer products are used in sensitive aquatic situations. Registrants are encouraged to pursue this option, subject to the availability of surfactants.
References


