Australian Pesticides &
Veterinary Medicines Authority

# The reconsideration of approvals of the active constituent 2,4-D, registrations of products containing 2,4-D and their associated labels.

# Preliminary Review Findings (Environment)
# Part 1:
# 2,4-D Esters

## Volume 1: Review Summary

APRIL 2006

This Preliminary Review Findings report contains a preliminary environmental risk assessment for all forms of 2,4-D (acid, salts and esters) and a refined environmental risk assessment for the high volatile esters 2,4-D ethyl ester, 2,4-D butyl esters, 2,4-D isobutyl ester ONLY. This report ONLY proposes regulatory actions for 2,4-D ethyl ester, 2,4-D butyl esters, 2,4-D isobutyl ester and products containing these 2,4-D esters.

The *Preliminary Review Findings (Environment) Part 2: 2,4-D Acids, Salts and Low Volatile Esters* report, will be published once the refined risk assessment of the low volatile esters, acid and salts is completed.

**Australian Pesticides &**
**Veterinary Medicines Authority**

**Canberra**
**Australia**

This preliminary review findings (environment) Part1: 2,4-D esters, report for products containing 2,4-D is published by the Australian Pesticides & Veterinary Medicines Authority. For further information about this review or the Review Program, contact:

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# FOREWORD

The Australian Pesticides & Veterinary Medicines Authority (APVMA) is an independent statutory authority with responsibility for the regulation of agricultural and veterinary chemicals in Australia. Its statutory powers are provided in the Agvet Codes scheduled to the *Agricultural and Veterinary Chemicals Code Act 1994*.

The APVMA can reconsider the approval of an active constituent, the registration of a chemical product or the approval of a label for a container for a chemical product at any time. This is outlined in Part 2, Division 4 of the Agvet Codes.

The basis for the current reconsideration is whether the APVMA is satisfied that continued use of the active constituent 2,4-D and products containing 2,4-D in accordance with the instructions for their use:

- would not be an undue hazard to the safety of people exposed to it during its handling; and
- would not be likely to have an effect that is harmful to human beings; and
- would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

The APVMA also considered whether product labels carry adequate instructions and warning statements.

A reconsideration may be initiated when new research or evidence has raised concerns about the use or safety of a particular chemical, a product or its label.

The reconsideration process includes a call for information from a variety of sources, a review of that information and, following public consultation, a decision about the future use of the chemical or product.

In undertaking reconsiderations (hereafter referred to as reviews), the APVMA works in close cooperation with advisory agencies including the Office of Chemical Safety, the Department of the Environment and Heritage, and state departments of agriculture as well as other expert advisers as appropriate.

The APVMA has a policy of encouraging openness and transparency in its activities and community involvement in decision-making. The publication of review reports is a part of that process.

The APVMA also makes these reports available to the regulatory agencies of other countries as part of bilateral agreements. The APVMA recommends that countries receiving these reports not utilise them for registration purposes unless they are also provided with the raw data from the relevant applicant.

This document sets out the preliminary review findings and proposed recommendations relating to 2,4-D esters only. A subsequent document (Preliminary Review Findings (Environment) Part 2: 2,4-D Acids, Salts and Low Volatile Esters will be published in due course, following refinement of the risk assessment. The preliminary review findings and proposed recommendations are based on information collected from a variety of sources. The information and technical data required by the

APVMA to review the safety of both new and existing chemical products must be derived according to accepted scientific principles, as must the methods of assessment undertaken.

The review summary (Volume 1) and the technical reports (Volume 2) for all registrations and approvals relating to 2,4-D esters are available from the APVMA web site: http://www.apvma.gov.au/chemrev/chemrev.html.

## COMMENT FROM THE PUBLIC IS INVITED

This Preliminary Review Findings report:

- outlines the APVMA review process
- informs interested parties how to respond to the review
- summarises the technical assessment from the Department of Environment and Heritage
- outlines the proposed regulatory action to be taken in relation to the continued approvals of 2,4-D ester active constituents, and products containing 2,4-D esters.

The APVMA invites persons and organisations to submit their comments and suggestions on this Preliminary Review Findings (Environment) Part 1: 2,4-D esters, report directly to the APVMA. Your comments will assist the APVMA in preparing the Review Findings report, which is the second report in the three-stage review reporting process. The final report is the Final Review Report and Regulatory Decision.

## PREPARING YOUR COMMENTS FOR SUBMISSION

You may agree or disagree with, or comment on as many elements of the preliminary review findings as you wish.

When making your comments:

- clearly identify the issue and clearly state your point of view
- give reasons for your comments, supporting them, if possible, with relevant information and indicate the source of the information you have used
- suggest to the APVMA any alternative solution you may have for the issue.

Please try to structure your comments in point form, referring each point to the relevant section in preliminary review findings. This will help the APVMA assemble and analyse all of the comments it receives.

Finally please tell us whether the APVMA can quote your comments in part or in full.

## THE CLOSING DATE FOR SUBMISSIONS IS 31 MAY 2006

Your comments should be mailed to:
Evaluator, 2,4-D Review
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PO Box E240
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# ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| ae | Acid equivalent |
| AR | Applied Radioactivity |
| BCF | Bioconcentration Factor |
| CEC | Cation Exchange Capacity |
| DEH | Department of the Environment and Heritage |
| dw | Dry weight |
| Koc | Organic carbon adsorption coefficient |
| Kow | Octanol-Water partition coefficient |
| LCx/ECx | The concentration of a substance that will be lethal (L) or induce an effect (E) to x% of the test population |
| LDx | The dose of a substance that will be lethal to x% of the test population |
| Log | Logarithm to the base 10. |
| MATC | Maximum Acceptable Toxicant Concentration |
| NOEC | No Observed Effect Concentration |
| NOEL | No Observed Effect Level |
| OM | Organic Matter |
| Pa | Pascals |
| PEC | Predicted Environmental Concentration |
| pH | Potential hydrogen – *logarithm* (to the base 10) of the hydrogen ion concentration ($H^+$) |
| ppb | Parts per billion |
| ppm | Parts per million |
| Q | Quotient value |
| WHC | Water Holding Capacity |

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# EXECUTIVE SUMMARY

## INTRODUCTION

This Preliminary Review Findings (Environment) Part 1, Esters report ONLY considers 2,4-D ethylhexyl, ethyl and butyl esters and products containing these 2,4-D esters. The Preliminary Review Findings (Environment) Part 2: 2,4-D Acids, Salts and Low Volatile Esters, will be published once the refined risk assessment for these chemical forms is completed.

Products containing 2,4-D (a phenoxy herbicide) are used for control of broadleaf and grass weeds in an extensive range of crops and non-cropping situations. Aerial, handheld and ground methods of application are used. Major agricultural uses of 2,4-D include pasture, stubble and fallow maintenance, cereal crops (including wheat, oats, barley, rye, triticale), grain crops (including sorghum, millet, maize) and oilseed crops (safflower, canola, rape). Other agricultural uses include cotton, citrus crops (particularly to inhibit post harvest abscission of buttons), sugar cane, sweetcorn, peanuts and control of banana suckers. 2,4-D is also used extensively for weed control in non-cropping situations, including commercial and industrial areas, turf and aquatic areas.

The active constituent 2,4-D, all products containing 2,4-D and their associated labels were placed under review because of concerns over toxicological, occupational health and safety and environmental issues (including impacts on waterways, non-target animals and plants).

## PREVIOUS REGULATORY ACTION

To address concerns associated with spray drift pending the completion of this review, the APVMA required additional instructions to be included on all 2,4-D labels by 30 November 2005. Other risk mitigation measures may be required when the review is finalised.

In consultation with State and Territory authorities, the APVMA developed additional instructions to strengthen the current label warnings in relation to minimising chemical spray drift. All registrants were required to update their labels so that all products in the market bear the additional instructions by 30 November 2005, as outlined below.

- This is a PHENOXY HERBICIDE that can cause severe damage to susceptible crops such as cotton, grapes, tomatoes, oilseed crops and ornamentals.
- DO NOT use unless wind speed is more than 3 kilometres per hour and less than 15 kilometres per hour as measured at the application site.
- DO NOT apply with smaller than coarse to very coarse spray droplets according to the ASAE S572 definition for standard nozzles.

These changes are not the final outcome of the review of 2,4-D in relation to spray drift management. Further changes to approvals and registrations may be required once the full toxicological, occupational health and safety, and environmental risks have been assessed.

## PRELIMINARY REVIEW FINDINGS (ENVIRONMENT)

This Preliminary Review Report (Environment) Part 1: Esters, is being published ahead of the completion of the toxicological, occupational health and safety evaluations and the refined environmental risk assessment for low volatile ester, acid and salt forms of 2,4-D, in order to address particular environmental concerns relating to the environment for high volatile (short chain) ester forms of 2,4-D.

The APVMA is aware of concerns regarding potential harmful effects of 2,4-D on aquatic organisms and non-target vegetation. Of particular concern is spray drift, volatilisation and movement of the chemical following application, particularly when environmental temperatures are high.

Post-application vapour movement can occur with 2,4-D ester formulations, while spray drift can occur with all 2,4-D formulations.

The criterion that is examined in this report is whether or not the APVMA can be satisfied that the continued use of the 2,4-D esters would not be likely have an unintended effect that is harmful to animals, plants or things or to the environment.

### Environmental Assessment

The Department of the Environment and Heritage (DEH) has undertaken an assessment of the available data provided to the APVMA for the review of 2,4-D and products containing 2,4-D. These data were primarily generated as part of the 2,4-D reregistration process required by the US EPA, by the Industry Task Force II on 2,4-D Research Data.

2,4-D comes in multiple chemical forms and is marketed in numerous end use products, primarily as a sole active ingredient but also in conjunction with other active ingredients. The compound is formulated primarily as an amine salt in an aqueous solution or as an ester in an emulsifiable concentrate. Chemical forms of 2,4-D assessed in this assessment are grouped into the following three categories:

- 2,4-D Acid
- 2,4-D Esters
- 2,4-D Salts

A tiered approach was taken for the assessment of the available data. A preliminary risk assessment conducted under a ‘worst-case’ exposure scenario was for all forms of 2,4-D and is presented in this report. Following the preliminary assessment a refined assessment of identified risks was undertaken. Only the refined risk assessment for ester formulations is presented in this report. The refined risk assessment for 2,4-D esters was undertaken for non-target terrestrial vegetation and for its aquatic risk to fish and aquatic invertebrates. Further refinement of the risk assessment for all low volatile ester, acid and salt forms of 2,4-D is currently being conducted.

The following overview table provides a summary of the environmental toxicity of 2,4-D acid, salts and esters. The environmental fate of all forms of 2,4-D has been reported as generally not persistent.

| Toxicity | Acid | Salts | Esters |
|---|---|---|---|
| AVIAN<br>- acute | practically non-toxic | practically non-toxic | practically non-toxic |
| - short term | practically non-toxic | practically non-toxic | practically non-toxic |
| - reproduction | no effect at 100ppm for bobwhite quail | no data | no data |
| AQUATIC-<br>- fish | practically non-toxic | practically non-toxic | highly toxic |
| - invertebrates | slightly toxic | slightly toxic | moderately toxic |
| - amphibians | practically non-toxic (frog tadpoles) | low toxicity | Undetermined (data gaps) |
| algae/aquatic plants | highly toxic (duckweed) | highly toxic (duckweed) | highly toxic (duckweed) |
| TERRESTRIAL – invertebrates/arthropods | slightly toxic | slightly toxic | moderately toxic |
| - non-target vegetation | highly toxic | highly toxic | highly toxic |

### *Preliminary Risk Assessment*

The preliminary risk assessment for all forms of 2,4-D undertaken by the DEH is summarised below:

### *Terrestrial risk assessment*

*Avian toxicity*

Birds did not appear to be sensitive to 2,4-D through either oral or dietary exposure. Considering the latter route, no definitive LC50 was determined at highest concentrations tested in any test reviewed by DEH or cited in the US EPA Re-registration Eligibility Document (RED) document, 2005. DEH found that the risk to birds through chronic exposure is acceptable.

*Bees and other terrestrial invertebrates*

No standard oral or contact toxicity tests were provided for the free acid form of 2,4-D. Standard oral and contact toxicity tests were performed on the 2-Ethylhexyl ester and Dimethylamine salt forms of 2,4-D with all results showing that 2,4-D is likely to not be toxic to bees. The risk of off-target adverse effects to non-target terrestrial arthropods is considered acceptable for salt formulations at up to 1000 g ae[1]/ha. DEH considers there are insufficient data at higher rates or for ester formulations to be able to quantify risks to non-target terrestrial arthropods.

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[1] 'ae' is the acid equivalent of 2,4-D

### *Soil-dwelling invertebrates*

Earthworms were insensitive to 2,4-D exposure either as the free acid or in its dimethylamine salt form, with LD50s in excess of 300 mg ae/kg dw soil. The lack of persistence of 2,4-D in soils indicates accumulation will not be an issue. There are no data for toxicity of ester forms of 2,4-D to earthworms. However, studies assessed by DEH indicate that in soils, 2,4-D ethylhexyl ester will hydrolyse rapidly. There are insufficient data to rule out short-term effects, but a chronic risk is not expected.

### *Soil micro-organisms*

No data have been provided for 2,4-D acid or any of its ester forms. Two studies, one addressing soil respiration and the other addressing soil nitrification, were provided for a 2,4-D salt formulation. The studies demonstrated that 2,4-D should have no significant impact on soil respiration or ammonification and nitrification of soil when applied at a rate up to 13.3 mg ae/kg soil. Taking this into account along with the lack of persistence of 2,4-D in soil suggest that the risk to soil microorganisms is likely to be low, although a short-term risk from 2,4-D esters cannot be ruled out.

### *Non-Target terrestrial plants*

Seedling emergence test data were received for 2,4-D acid, 2,4-D ethylhexyl ester, 2,4-D butoxyethyl ester and 2,4-D dimethylamine salt. Vegetative vigour test data were received for 2,4-D acid, 2,4-D ethylhexyl ester and 2,4-D butoxyethyl ester. In addition, the US EPA reports data for 2,4-D IPE and 2,4-D diethanolamine. No data are available for the ethyl ester and butyl ester forms.

2,4-D is a plant growth regulator which is absorbed through the roots and foliage within 4-6 hours and distributed throughout the plant via the xylem and phloem. Once in the plant it selectively eliminates broadleaf plants by mimicking the effect of plant growth regulating hormones. This action stimulates growth, which leads to an abnormal growth pattern and death in some plants. Therefore, if even a portion of the surface area of a non-target plant comes into contact with 2,4-D there is a possibility that the plant may be severely damaged or die as a result. Even if the plant only exhibits minor damage, the damage may be sufficient to prevent the plant from reproducing or competing successfully with other plants for resources, including water. The use of 2,4-D could apply selective pressure against non-target vegetation resulting in changes in species composition.

The preliminary risk assessment found an unacceptable risk to non-target terrestrial plants. Risk to non-target terrestrial plants will be considered in more detail in the refined risk assessment.

## ***Aquatic risk assessment***

### *Fish (non-aquatic use patterns)*

Worst-case exposure assumptions included application to a standard pond of 1 ha surface area and an average depth of 15 cm, with modelling based on direct overspray. The fish risk assessment for the acid and salt formulations was found to be acceptable. The preliminary risk assessment found ester formulations currently registered for broadcast applications unacceptable due to acute risk to fish. Therefore the refined risk assessment focused on ester forms of 2,4-D.

*Invertebrates (non-aquatic use patterns)*

Worst-case exposure assumptions included application to a standard pond of 1 ha surface area and an average depth of 15 cm, with modelling Based on direct overspray. The invertebrate risk assessment for the acid and salt formulations was found to be acceptable. The preliminary risk assessment found ester formulations currently registered for broadcast applications unacceptable due to acute risk to aquatic invertebrates Therefore the refined risk assessment focused on ester forms of 2,4-D.

*Algae and aquatic plants*

Worst-case exposure assumptions included application to a standard pond of 1 ha surface area and an average depth of 15 cm, with modelling based on direct overspray. Given the similarities in worst-case results for the 2,4-D acid, esters and salts, a single EC50 of 0.3 mg/L was used for the preliminary risk assessment. All forms of 2,4-D were considered in the preliminary risk assessment and found to be unacceptable. All forms of 2,4-D were considered further in the refined risk assessment.

### *Refined Risk Assessment*

Based on results from the preliminary risk assessment, the refined assessment for ester formulations focussed on:

- *Terrestrial risk assessment*. For non-target terrestrial plants, a single value has been chosen to be protective of 95% of species based on analysis of the full terrestrial plant data set including acid, salt and ester formulations.
- *Aquatic risk assessment.* The risk to fish and aquatic invertebrates from exposure to the ester formulations was estimated
- *Aquatic risk assessment (aquatic uses of 2,4-D.)* The risk to algae/aquatic plants from exposure to 2,4-D esters were estimated.

The refined aquatic risk assessment was conducted first as there are worst-case spray drift calculations performed in this section that need to be used and refined further in the terrestrial assessment.

### *Refined aquatic risk assessment*

The refined aquatic risk assessment considered exposure to fish and aquatic invertebrates, as well as aquatic plants. For the acute assessment, the most sensitive endpoints used were:
Esters – most sensitive toxicity endpoint for fish = 0.23 mg ae/L
Esters – most sensitive toxicity endpoint aquatic for invertebrates = 1.04 mg ae/L
All forms – most sensitive toxicity endpoint for algae/aquatic plants = 0.3 mg ae/L

*Broadcast use patterns*

The predicted environmental concentrations (PEC) were based on the maximum application rates derived from currently approved labels, with exposure considered from spray drift. To predict spray drift, the AgDrift model was used for aerial application, and drift data from Rautmann *et al* (2001) was used for ground based applications.

The refined risk assessment concluded that in order to mitigate the potential risk to algae/aquatic plants from exposure resulting from spray drift of 2,4-D ester formulations applied aerially, products should be applied with a median droplet diameter of 400 µm or more, corresponding to a ASAE S572 coarse droplet size, and a buffer zone of 100 m between field edges and downwind water bodies should be maintained. This was considered to be protective of amphibians and sediment-dwelling organisms, as well as those exposed only through the water column.

The risk to aquatic organisms from 2,4-D ester resulting from drift from ground-based application equipment was considered to be acceptable without a need for a buffer zone.

*Non-broadcast use patterns*

Non-broadcast uses for 2,4-D include spot spraying in all situations, bananas (stem injection), citrus (dipping, one product only), timber regrowth control (eg cut stump application, one product only) and home lawns.

Application in these situations is unlikely to involve significant exposure to aquatic areas. Some drift exposure may occur but this is unlikely to be at levels resulting in adverse impacts to nearby aquatic areas.

*Risk from run-off*

Risks from run-off was considered for 2,4-D acid only due to the rapid conversion of 2,4-D esters to the acid in moist soils. Modelling predictions supported by field measurements following storm events indicated that risk to aquatic organisms through run-off is acceptable. In addition applications of 2,4-D in non-broadcast situations is unlikely to involve significant exposure to aquatic areas through run-off.

### *Aquatic uses of 2,4-D*

The refined risk assessment considered direct application of 2,4-D ester formulations in aquatic situations and concluded 2,4-D esters pose an unacceptable risk to fish and aquatic organisms.

2,4-D esters will pose an unacceptable risk to algae and aquatic plants. However these risks may be mitigated if mechanical removal of aquatic weeds was undertaken prior to application of 2,4-D, thus reducing the amount of 2,4-D needing to be being applied in aquatic situations.

### *Refined terrestrial risk assessment*

The refined risk assessment for the terrestrial environment focussed on the risk to non-target terrestrial plants. A significant database of effects to field crops through seedling emergence and vegetative vigour studies were available, and statistical analysis of these data determined that a representative NOEL of 0.73 g ae/ha should be sufficently protective for 95% of species. This value was used in the risk assessment. Risk to non-target terrestrial vegetation was considered for exposures through several routes including volatilisation, spray drift and run-off for three use pattern types, broadcast, aquatic and non-broadcast. Broadcast use patterns were also assessed for ground and aerial application routes.

### *Runoff*

Risks from run-off was only considered for 2,4-D acid due to the rapid conversion of 2,4-D esters to the acid in moist soils. Risks from run-off were difficult to model in any meaningful way given the range of possible application rates, use patterns and potentially different site characteristics. However, it was demonstrated that a potential risk to non-target plants from this exposure route could exist under certain conditions. For example, sites with larger slopes, less sandy soils or soils with lower organic carbon contents will have more run-off than flatter, sandier and higher organic carbon soils. Some of these may result in sufficient run-off to cause adverse effects in stands of non-target vegetation.

### *Volatilisation*

Off-target movement from areas to 2,4-D application to non-target crops was a major issue raised in submissions received by the APVMA. While there was little in the way of information received for off-target damage to native vegetation, it is unlikely that such damage has ever actually been monitored. With obvious non-target crop damage, damage to exposed native vegetation may also be expected.

Based on direct measurements from Guth *et al* (2004), no noticeable volatility can be expected from compounds with a vapour pressure below $10^{-3}$ Pa from soil and below $10^{-4}$ Pa from crops. The vapour pressures for the long chain ester (ethylhexyl ester), and the short chain esters (ethyl ester and butyl ester) are $4.8 \times 10^{-4}$, $1.47 \times 10^{-1}$ and $5.29 \times 10^{-2}$ to $8.2 \times 10^{-3}$ Pa respectively. This suggests that long chain esters may not volatilise from soil surfaces but may to some extent from crops, while the short chain esters are expected to volatilise from both soil and crop surfaces. Further, the calculated Henry's Law Constants indicate that the three esters may be moderately volatile to volatile from water bodies.

Based on calculations undertaken by DEH a much greater risk is posed to non-target vegetation from the shorter chain esters. Of further concern is their persistence with modelling suggesting the atmospheric half-life in air of 2,4-D ethyl ester is in the order of 2 days, classing it as persistent and meeting this criterion for classification as capable of long range transport in air. The atmospheric half-life in air for 2,4-D butyl ester is around 1.7 days. Both these chemicals may therefore be anticipated to travel long distances in the environment through air.

The issue of persistence in the atmosphere, high volatility and potential to travel long distances in the environment, along with their toxicity to non-target vegetation makes it very difficult to mitigate the risk for the short chain high volatile esters. DEH has recommended the discontinuation of use of 2,4-D ethyl ester, 2,4-D butyl ester and isobutyl ester (both the active constituents and formulated products).

## PROPOSED REVIEW RECOMMENDATIONS RESULTING FROM THE ENVIRONMENTAL ASSESSMENT OF 2,4-D ESTERS

After consideration of all data for the environmental fate and eco-toxicology assessment for the active constituents 2,4-D ethyl ester, 2,4-D butyl ester and isobutyl ester, forms), the APVMA proposes to find that it is NOT satisfied that continued use or any other dealing with these active constituents or products containing these active constituents in accordance with the instructions for their use, would not be likely to have an unintended effect that is harmful to animals, plants or things or the environment.

This finding is based on the propensity of the high volatile (short chain) esters to volatilise and persist in the environment (atmosphere) thereby causing off-target damage. The APVMA proposes the following regulatory actions for 2,4-D high volatile(short chain) esters:

### Cancel approvals of the active constituent

All active constituent approvals for the active constituents (2,4-D ethyl ester, 2,4-D butyl ester and 2,4-D isobutyl ester), as listed in (Attachment A, Table 1) be **cancelled.**

### Cancel product registrations and associated label approvals

As all the active constituent approvals for 2,4-D ethyl ester, 2,4-D butyl ester or 2,4-D isobutyl ester are to be cancelled the Agvet Code requires that all product registrations containing those active constituents and all associated labels, as listed in (Attachment A, Table 2) must also be **cancelled.**

### Proposed registration cancellation as an outcome of review findings

As a consequence of the proposed findings of this review, the APVMA proposes to find that products (containing 2,4-D ethyl ester, 2,4-D butyl ester or 2,4-D isobutyl ester) and associated labels registered subsequent to the review commencement are therefore subject to the outcomes of the review, as listed in (Attachment A, Table 3) also be **cancelled.**

# 1. INTRODUCTION

The APVMA is reviewing the approval of the active constituent, registered products containing 2,4-D and the associated label approvals for products containing 2,4-D. This Preliminary Review Findings (Environment) Part 1: 2,4-D Esters report ONLY considers 2,4-D ethylhexyl, ethyl and butyl esters and products containing these 2,4-D esters. The Preliminary Review Findings (Environment) Part 2: 2,4-D Acids, Salts and Low Volatile Esters report, will be published once the refined risk assessment is completed.

This document summarises the environmental data evaluated for all forms of 2,4-D, the preliminary risk assessment for all forms of 2,4-D, the refined risk assessment for 2,4-D esters ONLY, and the proposed recommendations from the review of the environmental data for the high volatile short chain esters (ethyl ester, butyl ester and isobutyl ester) only.

The assessment of the available information necessary to complete the toxicological, occupational health and safety evaluations is expected to be completed by the end of 2006. Further changes to approvals and registrations may also be required once the full toxicological, occupational health and safety, and environmental risks have been assessed.

## 1.1 REGULATORY STATUS OF 2,4-D IN AUSTRALIA

As at March 2006, there were 36 active constituent approvals for 2,4-D, 136 registered products containing the active constituent 2,4-D. Of these there are 12 (short-chain) high volatile ester active constituents and 39 registered products containing high volatile esters. 2,4-D can be formulated in salt (dimethylamine, sodium, diethanolamine, triisopropylamine, triethanolamine and isopropylamine), ester (ethyl, butyl, isobutyl, and ethyhexyl) and acid forms. Formulation types include aqueous concentrates, dry flowables, emulsifiable concentrates, granular formulations, liquid concentrates, liquids, suspension concentrates, soluble concentrates, soluble powders and wettable powders.

In addition to registration of products, some states including Victoria, Western Australia, Tasmania and Queensland currently have mechanisms whereby the use of specific chemicals (including 2,4-D) are restricted. These restrictions are in place to address the risk of adverse off-target crop or environmental effects.

### 1.1.1 Queensland

The following herbicides are restricted in their respective hazardous areas and a distribution permit is required to carry out ground distribution of these herbicides.

*Hazardous Area No. 1.*The restricted herbicides in Hazardous Area No. 1 requiring a distribution permit if applied other than by an authorised technique are any herbicides containing picloram or an ester formulation of 2,4-D and MCPA.

The restricted herbicides in Hazardous Area No. 2 requiring a distribution permit if applied other than by an authorised technique 2 are any herbicides containing an ester formulation of picloram. Please note that any ester formulation of 2,4-D is totally banned from use in hazardous area No.2.

*Hazardous Area No.3.* The restricted herbicides in Hazardous Area No. 3 requiring a distribution permit if applied other than by an authorised technique2 are any herbicides containing an ester formulation of 2,4-D.

### 1.1.2 **Western Australia** (extract from Farmnote 61/99)

Restrictions on use of the hormone herbicides 2,4-D Under the 'Agriculture and Related Resources Protection (Spraying Restrictions) Regulations 1979' the use of 2,4-D herbicides is controlled within 10km radius of commercial vineyards and tomato gardens (see "Under the Regulations" below). The use of 2,4-D near other sensitive crops are not controlled by the Regulations, but landholders and spray contractors should exercise a 'duty of care' when spraying.

#### *1.1.2.1 Under the Regulation*

Within a 5km radius of commercial vineyards or tomato gardens only amine and sodium and potassium salt formulations are approved for spraying under permit.

Between 5 and 10 km radius of these crops both amine, sodium salt and low volatile ester formulations can be used without permit.

Outside of a 10km radius all formulations, that is amine, sodium salts, low volatile and volatile ester formulations can be used without permit.

**Note:** Landholders and spray contractors in the Geraldton, Swan Valley and Ord Irrigation Districts need to consult the Regulations for more precise information on restricted spraying areas. They vary in these districts from the above.

### 1.1.3 Tasmania

2,4-D products may not be used from Spring to Autumn between 15 September and 15 April unless a 2,4-D Permit is issued to allow its use.

### 1.1.4 Victoria

Certain areas in Victoria have been declared Agricultural Chemical Control Areas (ACCAs). These areas have restrictions on the types and methods of application of certain herbicides and are designed to protect herbicide sensitive and high value crops from potential herbicide damage.

The dates the restrictions apply are as follows:

| ACCA | Start Date | Finish Date |
|---|---|---|
| Melbourne | All year | |
| Lindenow | All year | |
| Orbost | All year | |
| Boisdale | All year | |
| Mallee & Mid Murray | 1st August | 30th April the following year |

| | | |
|---|---|---|
| Goulburn Valley | 1st September | 30th April the following year |
| North Eastern | 1st September | 30th April the following year |
| Rutherglen | 1st September | 30th April the following year |

During this time:
Application of ester formulations of 2,4-D by all methods is prohibited.
Aerial spraying or mister application of any amine formulation is prohibited unless a permit has been granted.

### 1.2 REASONS FOR 2,4-D REVIEW

The active constituent 2,4-D, all products containing 2,4-D and their associated labels were placed under review because of toxicological, occupational health and safety and environmental concerns.

2,4-D (2,4,-dichlorophenoxyacetic acid) is a phenoxy compound used as a post-emergence herbicide. In October 1994 the APVMA (then the NRA) invited the public to nominate active constituents, chemical products or labels for consideration for review. Of the 600 chemical nominations, 80 were prioritised for review, one of which was 2,4-D. 2,4-D was nominated for review by community groups, individual citizens and government agencies. Government agencies nominated 2,4-D on the basis of concerns about a potential risk for chronic toxicity, claims of human birth defects, its potential to be a possible carcinogen, gaps in available data, and international regulatory activity.

### 1.3 SCOPE OF THE REVIEW

The scope of the review covered the following risk areas associated with active constituent approvals, product registrations and associated label approvals including:

- Toxicology
    - potential for carcinogenicity in humans which might pose an undue hazard to human health; and
    - potential for toxicological exposure to humans via the oral, inhalation and dermal routes.
- Occupational health and safety
    - possible risks to workers health associated with short and intermediate term occupational exposure; and
    - potential for hazards to worker safety
- Residues
    - if the Office of Chemical Safety (OCS) sets or modifies an Acute Reference Dose (ARfD) and/or Acceptable Daily Intake (ADI) for 2,4-D, then a dietary exposure assessment might be required.
- Environmental
    - potential for contamination of waterways; and
    - potential hazard to non-target animals and plants

The basis for a reconsideration of the registration and approvals for a chemical in Australia is whether the APVMA can be satisfied that the requirements prescribed by the Agvet Codes for continued registration and approval are being met. These requirements are that the use of 2,4-D products in accordance with there instructions for its use:

- would not be an undue hazard to the safety of people exposed to it during its handling; and
- would not be likely to have an effect that is harmful to human beings; and
- would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

The APVMA also considered whether product labels carry adequate instructions and warning statements. Such instructions include:

- the circumstances in which the product should be used
- how the product should be used
- times when the product should be used
- frequency of the use of the product
- the withholding period after the use of the product
- disposal of the product and its container
- safe handling of the product.

On the basis of these concerns, it was appropriate that the active constituent approvals, product registrations and label approvals for 2,4-D be subject to reconsideration under Part 2, Division 4 of the Agvet Codes.

### 1.4 REGULATORY OPTIONS

There can be three possible outcomes to the reconsideration of the active constituent 2,4-D, registration of products containing 2,4-D and all associated label approvals. Based on the information reviewed the APVMA may be:

- satisfied that the products and their labels continue to meet the prescribed requirements for registration and approval and therefore affirms the registrations and approvals
- satisfied that the conditions to which the registration or approval is currently subject can be varied in such a way that the requirements for continued registration and approval will be complied with and therefore varies the conditions of registration or approval
- not satisfied that the requirements for continued registration and approval continue to be met and suspends or cancels the registration and/or approval.

### 1.5 PREVIOUS REGULATORY ACTION

To address concerns associated with spray drift pending the completion of the review, the APVMA required additional instructions to be included on all 2,4-D labels by 30 November 2005. Other risk mitigation measures may be required when the review is finalised.

In consultation with State and Territory authorities, the APVMA developed additional instructions to strengthen the current label warnings in relation to minimising chemical spray drift. All registrants have been required to update their labels and all products in the market must contain the additional instructions by 30 November 2005, as outlined below.

- This is a PHENOXY HERBICIDE that can cause severe damage to susceptible crops such as cotton, grapes, tomatoes, oilseed crops and ornamentals.
- DO NOT use unless wind speed is more than 3 kilometres per hour and less than 15 kilometres per hour as measured at the application site.
- DO NOT apply with smaller than coarse to very coarse spray droplets according to the ASAE S572 definition for standard nozzles.

These changes in relation to spray drift management are not the final outcome of the review of 2,4-D. Further changes to approvals and registrations are likely to be required once the full toxicological, occupational health and safety, and environmental risks have been assessed.

The assessment of the available information necessary to complete the toxicological, occupational health and safety evaluations is expected to be completed by the end of 2006.

# 2. APPROVED 2,4-D USE PATTERNS

## 2.1 INTRODUCTION

Products containing 2,4-D are used for post-emergent control of broadleaf and grass weeds in an extensive range of crops and non-cropping situations. Aerial, handheld and ground methods of application are used.

Major agricultural uses of 2,4-D include pasture, stubble and fallow maintenance, cereal crops (including wheat, oats, barley, rye, triticale), grain crops (including sorghum, millet, maize) and oilseed crops (safflower, canola).

Other agricultural uses include cotton, citrus crops (particularly to inhibit post harvest abscission of buttons), sugar cane, sweetcorn, peanuts and control of banana suckers. 2,4-D is also used extensively for weed control in non-cropping situations, including commercial and industrial areas, turf, forestry and aquatic areas.

**Table 1. Uses of 2,4-D Products in Australia**

| Situation | Representative crops |
|---|---|
| Winter cereals | Wheat, barley, cereal rye, triticale, (oats included on amine labels only) |
| Fallow, stubble spray prior to direct drilling or sowing | Winter cereals, maize, sweetcorn, potatoes, (canola on some 2,4-D ester labels only) |
| Summer cereals | Maize, sweetcorn, sorghum, millet |
| Sugar cane | |
| Peanuts | |
| Harvest aid or salvage spray | Winter cereals, maize, sorghum |
| Pastures and non-agricultural | Amine labels |
| Improved pasture containing legumes | Ester labels |
| Pastures, rights of way and industrial | |
| Pastures, conservation tillage – direct drilling, surface sowing or fallow maintenance | |
| Pastures, spray graze techniques | Amine labels. |
| Lawns/turf | Includes domestic, golf fairways, commercial etc. |
| Forage crops | Common or Carribean Stylo forage or seed crops |
| Rice | Some ester labels only |
| Preparatory spray[6] | Isoproylamine salt labels only |
| Bananas | Injection or spot spray |
| Potatoes | Two ester labels only. |
| Pears | One label only. Uses 2.3 g ae in 450 L water and applied as spray to individual trees with thorough coverage. No indication of a per hectare rate. |
| Citrus | One label only. 0.1-0.2 ppm ae for tree spraying; 5 ppm ae for dipping. |
| Timber regrowth control | One label only. Stem injection or cut stump. |
| Spot spraying | All weeds – weed table provided with labels. |
| Aquatic | Control of water hyacinth |

## 3. ACTIVE CONSTITUENT

The toxicology of the active constituent 2,4-D is being undertaken by the Office of Chemical Safety (OCS) as part of the full toxicology assessment of 2,4-D.

## 4. SUMMARY OF DATA ASSESSMENTS

### 4.1 TOXICOLOGY

The toxicological assessment for the review of 2,4-D is being undertaken by the OCS whichis considering all the toxicological data and information submitted for the review. The toxicological assessment is expected to be completed by the end of 2006.

### 4.2 OCCUPATIONAL HEALTH AND SAFETY (OHS)

The OHS assessment for the review of 2,4-D is being undertaken by the OCS which is considering all the OHS data and information submitted for the review. The OHS assessment is expected to be completed by the end of 2006.

### 4.3 ENVIRONMENT

The environmental assessment for the review of 2,4-D was undertaken by the Department of the Environment and Heritage (DEH), which considered all the environmental data and information submitted for the review. The environmental findings from the hazard assessment, the preliminary risk assessment for all forms of 2,4-D and the refined risk assessment for 2,4-D esters are summarised below. The refined risk assessment for the non-ester forms of 2,4-D is expected to be completed in the near future.

### 4.3.1 Introduction

In June 2003, the APVMA initiated its reconsideration of the approvals of the active constituent 2,4-D, the registrations of products containing 2,4-D, and the approvals of associated labels. While the scope document stated that approvals of the active constituent were being reconsidered because of toxicological concerns, it is also stated that products containing 2,4-D and all associated labels were being reviewed because of environmental, toxicological and occupational health and safety concerns.

The environmental aspects for consideration as outlined in the scope document are:

- potential for contamination of waterways; and
- potential hazard to non-target animals and plants

In order to assist the environmental risk assessment, large quantities of data have been provided to the APVMA. These data were primarily generated as part of the 2,4-D reregistration process required by the US EPA. Through this process, the Industry Task Force II on 2,4-D Research Data, and registrant companies, conducted soil dissipation studies during 1993 and 1994 on amine and ester formulations. Laboratory data were also provided.

In 1989 the World Health Organization published the IPCS Environmental Health Criteria (number 84) on the environmental aspects of 2,4-D (WHO, 1989). This is considered to be an acceptable internationally peer reviewed document and DEH has used this document to consider relevant 2,4-D data available prior to 1989. Further to this document, the US EPA has made available their environmental assessment of 2,4-

D which includes reviews of available literature. In addition, there are several studies summarised in the US EPA report that were not made available to the APVMA. These studies are relevant in terms of confidently bridging gaps in information on various ester or amine salt forms of 2,4-D. It is unclear why these data were not provided to the APVMA. In this assessment, the US EPA review is relied on for access to this information, but it is only discussed in summary form.

Volume 1 of this PRF report contains the summary of the study and risk assessment for 2,4-D esters. Volume 2 of this PRF contains a series of technical reports addressing the test data. Readers should refer to the respective technical reports to obtain more detailed information on test conditions and findings. A number of metabolites are identified throughout the report. For representative structures, readers should refer to Attachment 2.

2,4-D belongs to the phenoxy or phenoxyacetic acid family of herbicides. It is a synthetic auxin herbicide, causes disruption of plant hormone responses. Endogenous auxins are plant growth regulator hormones. These growth-regulating chemicals cause disruption of multiple growth processes in susceptible plants by affecting proteins in the plasma membrane, interfering with RNA production, and changing the properties and integrity of the plasma membrane. The plant's vascular system becomes blocked due to excessive cell division and the resulting growth crushes the vascular transport system. The most susceptible tissues are those that are undergoing active cell division and growth.

Plant injuries include growth and reproduction abnormalities, especially on new growth. Stem and petiole twisting (epinasty), leaf malformations (parallel venation, leaf strapping, and cupping), undifferentiated cell masses and adventitious root formation on stems, and stunted root growth is experienced by broadleaf plants. Rolled leaves (onion leafing), fused brace roots, leaning stems, and stalk brittleness are observed on grass plants. Disruption of reproductive processes may occur resulting in sterile or multiple florets and nonviable seed production. Symptoms may appear on young growth almost immediately after application, but death may not occur for several weeks (US EPA, 2005).

### 4.3.2 Environmental Exposure

The quantity of 2,4-D used in Australia annually is not known. However, it was reported in 2002 that over 1,000 tonnes of plant cell growth disrupting group of chemicals [including phenoxys (of which 2,4-D is a member), benzoic acids and pyridines] are used annually. The herbicides 2,4-D and its derivatives, along with MCPA, are the major chemicals used in this group (Radcliffe, 2002).

#### *4.3.2.1 End use products*

2,4-D comes in multiple chemical forms and is found in numerous end use products intended for use in a wide range of use patterns. 2,4-D is an ingredient in several agricultural and home use products, primarily as a sole active ingredient but also in conjunction with other active ingredients. The compound is formulated primarily as an amine salt in an aqueous solution or as an ester in an emulsifiable concentrate. Chemical forms covered by this risk assessment are as follows:

**Table 2. Chemical forms of 2,4-D**

| Abbreviated name | Full name | Volatility |
|---|---|---|
| 2,4-D | 2,4-D acid | Essentially non-volatile |
| 2,4-D DMA | 2,4-D Dimethylamine salt | Essentially non-volatile |
| 2,4-D IPA | 2,4-D Isopropylamine salt | Essentially non-volatile |
| 2,4-D TIPA | 2,4-D Triisopropylamine salt | Essentially non-volatile |
| 2,4-D EHE | 2,4-D Ethylhexyl ester[1] | Low volatile |
| 2,4-D EE | 2,4-D Ethyl ester | High volatile |
| 2,4-D BE | 2,4-D Butyl ester | High volatile |
| 2,4-D IBE | 2,4-D Isobutyl ester | High volatile |
| 2,4-D DEA | 2,4-D Diethanolamine | Essentially non-volatile |
| 2,4-D TEA | 2,4-D Triethanolamine | Essentially non-volatile |
| 2,4-D Sodium salt | 2,4-D Sodium salt | Essentially non-volatile |

1) 2-ethylhexyl ester is considered one of three isooctyl esters. For this assessment, labels using the active constituent 2,4-D Isooctyl ester are all referred to as EHE.

Target pests include a wide variety of broadleaf weeds and aquatic weeds. 2,4-D may be applied with a wide range of application equipment including aircraft (both fixed wing and helicopter), backpack sprayer, band sprayer, boom sprayer and injection equipment. Methods of application of 2,4-D may include aerial and ground broadcast application, band treatment, basal spray treatment, spot treatment, stump treatment, tree injection treatment, and water related surface treatment. Timing of 2,4-D application can include pre-plant, pre- and post-emergence, before bud break, and established plantings.

### *4.3.2.2 Application rates and use patterns*

DEH reviewed 122 separate product labels currently registered with the APVMA containing 2,4-D in various amine salt or ester forms, and some with mixtures of other pesticide active ingredients. Three products used 2,4-D in its sodium salt form. The break-up of this is as follows:

**Table 3. 2,4-D products registered in Australia**

| | Form | Number of products |
|---|---|---|
| Esters | Ethylhexyl ester | 6 |
| | Ethyl ester | 13 |
| | Ethyl/Butyl ester | 7 |
| | Butyl ester | 1 |
| | Isobutyl ester | 6 |
| Salts | Dimethylamine | 27 |
| | Isoproylamine | 28 |
| | Dimethylamine/Diethanolamine | 17 |
| | Diethanolamine | 6 |
| | Diethanolamine/Triethanolamine | 1 |
| | Sodium salt | 3 |
| Acid | (Active identified only as 2,4-D) | 7 |

2,4-D is registered for a very large range of uses. Within uses, several forms of application may exist including aerial, ground or spot treatments. The following table provides a summary of the registered uses of 2,4-D in Australia. Application rates are referred to as acid equivalents (ae) which is the equivalent application rate of 2,4-D acid regardless of the parent active constituent:

**Table 4. 2,4-D use patterns in Australia**

| Situation | Representative crops | Maximum registered rate (g acid equivalent/ha) |
|---|---|---|
| Winter cereals | Wheat, barley, cereal rye, triticale, (oats included on amine labels only) | 1220 |
| Fallow, stubble spray prior to direct drilling or sowing | Winter cereals, maize, sweetcorn, potatoes, (canola on some ester labels only) | 1063 |
| Summer cereals | Maize, sweetcorn, sorghum, millet | 880 |
| Sugar cane | | 3640 |
| Peanuts | | 2250 |
| Harvest aid or salvage spray | Winter cereals, maize, sorghum | 1140 |
| Pastures and non-agricultural | Amine labels | 2000[1] |
| Improved pasture containing legumes | Ester labels | 560[2] |
| Pastures, rights of way and industrial | | 2750[3]/4500[4] |
| Pastures, conservation tillage – direct drilling, surface sowing or fallow maintenance | | 1040[5] |
| Pastures, spray graze techniques | Amine labels. | 1040 |
| Lawns/turf | Includes domestic, golf fairways, commercial etc. | 2500 |
| Forage crops | Common or Carribean Stylo forage or seed crops | 1040 |
| Rice | Some ester labels only | 800 |
| Preparatory spray[6] | Isoproylamine salt labels only | 540 |
| Bananas | Injection or spot spray | 10 g ae/L water |
| Potatoes | Two ester labels only. | 1620 |
| Pears | One label only. Uses 2.3 g ae in 450 L water and applied as spray to individual trees with thorough coverage. No indication of a per hectare rate. | |
| Citrus | One label only. 0.1-0.2 ppm ae for tree spraying; 5 ppm ae for dipping. | |
| Timber regrowth control | One label only. Stem injection or cut stump. | 15-200 g ae/L water |
| Spot spraying | All weeds – weed table provided with labels. | 2240[7] |
| Aquatic | Control of water hyacinth | 3300 |

1. One product (2,4-D Acid) has an approved rate of 3000 g ae/ha.
2. Two labels (isobutyl ester active) have registered rates of 3520-4480 g ae/ha for use in Victoria only.
3. The rate is for aerial control of one weed species only. All other weeds are controlled through ground application with a maximum rate of 40 g ae/L of spray mix (hectare rate not always clear)
4. Ester labels have much higher rates than amine labels. The highest rate of 4500 g is found on several EHE labels for boom spray in Victoria only.
5. Ester labels with this use pattern carry an additional application rate of 3200-3360 g ae/ha for aerial or ground application to control one weed species (St. Johns Wort).
6. Preparatory Spray for fallows and seed beds or prior to sowing of the following crops: Balansa clover, Barley, Canola, Chickpeas, Cotton, Faba beans, Field peas, Lentils, Linseed, Lucerne, Lupins, Narbon beans, Navy beans, Oats, Perennial ryegrass, Persian clover, Phalaris, Rice, Safflower, Sorghum, Soybeans, Subterranean clover, Sunflower, Triticale, Vetch, Wheat, White clover.
7. Spot spraying may use high volume spraying where 1/10th of the rate on the labels weed table is added to 150 L water, expected to cover 1000 $m^2$, or knapsack application where 1/100th of the rate is added to 10 L and expected to cover 100 $m^2$. The maximum per hectare rate of application based on the weed tables is expected to be 1050 g ae/ha. Significantly different rates may be found for the same weed depending on the form of 2,4-D used in the formulation.

#### *4.3.2.3 2,4-D monitoring data in Australia*

No monitoring data were provided to the APVMA and no recent data have been found. In their 2002 review of pesticide use in Australia, the Australian Academy of Technological Sciences and Engineering (ATSE) report on several results of monitoring studies as follows (Radcliffe, 2002):

***Irrigation areas in South Western NSW:*** Supply water from rivers was of high quality and generally few pesticides were detected. Just a few channels contained low levels of atrazine, endosulfan sulfate, molinate and 2,4-D. In their report on pesticide monitoring in the irrigation areas of south western NSW over the 1990-1995 period, Bowmer *et al* (1998) note only one detection of 2,4-D in the Murray River at a concentration of 0.5 ppb (which was the detection limit). Over 1994-95, 3 detections of 2,4-D in Murrumbidgee Irrigation Area (MIA) surface waters were found, ranging from 2-5.7 ppb (this is assumed to be in drainage channels). Over the same period, 2 detections of 2.1 ppb were found in surface waters of the Coleambally Irrigation Area (CIA - again assumed to be drainage channels).

***Queensland waterways****:* 2,4-D was reported as being detected in between 9 and 27% of samples from the Johnstone and Daintree rivers. The concentration in the water was not reported. Also in Queensland, 2,4-D is reported as being found in trace amounts in 3 of 52 groundwater samples from the Bundaberg region. Again, the concentration was not reported.

***South Australia****:* Several pesticides including 2,4-D were reported in surface waters around the Mount Lofty Ranges region at levels of 0.04-0.6 ppb.

***Western Australia****:* Following claims of damage to tomato crops, 2,4-D was monitored in air around Geraldton over the 1979-1982 period. While the monitoring was not able to distinguish sources of separate “pulse” and “press” events, it did establish that damage may have occurred from short-distance drift of droplets of 2,4-D amine.

***Sediment****:* Radcliffe (2002) reports on monitoring results from several sampling studies in sediments where various organochlorine pesticides were detected. 2,4-D is not reported as being detected, although presumably it was looked for.

### 4.3.3 Environmental Fate

In support of the assessment for the review of 2,4-D, applicants submitted a full range of laboratory environmental fate data for 2,4-D acid and some bridging laboratory data for the 2-ethylhexyl ester and DMA forms of 2,4-D. In addition a full suite of field dissipation studies were provided for 2,4-D 2-EHE and 2,4-D DMA. No field data were provided for any other ester or amine salt form of 2,4-D. It is known from the US EPA report that some laboratory and field environmental fate data are available for other ester and amine salt forms of 2,4-D. This information is discussed below, based on the US EPA report.

There is a significant weight of evidence from literature and registrant-sponsored data supporting the conclusion that 2,4-D amine salts and 2,4-D esters are not persistent under most environmental conditions, including those associated with most sustainable agricultural conditions. 2,4-D amine salt dissociation is expected to be instantaneous (< 3 minutes) under most environmental conditions. While the data reviewed suggest that de-esterification of 2,4-D esters to 2,4-D acid under all conditions is not instantaneous, they do indicate that 2,4-D esters in normal agriculture soil and natural water conditions are likely to be short-lived compounds (<1 week). Under these conditions, the environmental exposure to 2,4-D esters and 2,4-D amines is expected to be minimal for both terrestrial and aquatic environments.

There are exceptions to these statements. The US EPA notes persistence of 2,4-D Butoxyethyl ester (there are no registered products containing BEE in Australia) in sediments from aquatic field studies that were not provided to the APVMA. Additionally, 2,4-D 2-EHE was shown to persist on foliage and in leaf litter from registrant submitted forest field dissipation studies. No field dissipation data (terrestrial, forest, or aquatic) have been submitted for the amine salts, 2,4-D IPA, 2,4-D TIPA, and 2,4-D DEA, or for the esters 2,4-D BEE and 2,4-D Isopropyl Ester (IPE) to confirm their persistence under field conditions. Additionally, no data on the other esters used in Australia, namely the ethyl, butyl and isobutyl esters, have been provided.

#### *4.3.3.1 Stability in Water*

Direct evidence of the stability of 2,4-D amine salts in soil and aquatic environments is difficult due to the lack of analytical methods. The US EPA point out in their report that based on maximum application rates for 2,4-D amine salts (@ 4.5 kg ai/ha), 2,4-D amine salts are expected to fully dissociate in soil environments because their theoretical concentrations in soil solution does not exceed water solubilities. Additionally, dissociation studies indicate the time for complete dissociation is rapid (< 3 minutes). Reim (1989) considered the dissociation of 2,4-D and 2,4-D DMA in water. Analytical grade 2,4-D and 2,4-DMA, in HPLC grade water had dissociation times of ≥120 minutes and <1 minute, respectively. Complete dissociation was determined through a comparison of theoretical and estimated electrical conductance measurements at infinite dilution. For 2,4-D DMA, plots of equivalent conductance vs. concentration$^{1/2}$ (Onsager equation) are linear indicating it is a strong electrolyte while that for 2,4-D is non-linear indicating it is a weak electrolyte. Conductivity data are consistent with the premise that 2,4-D DMA completely dissociates in aqueous solution to form dimethylammonium ion and the conjugate base of 2,4-D.

Regarding the esters forms of 2,4-D, the US EPA (2005) reports that de-esterification of 2,4-D esters is more difficult to generalize because it is dependent on heterogenous hydrolysis (microbial-mediated and surface-catalyzed hydrolysis) and homogenous hydrolysis (alkaline catalyzed). The de-esterification of 2,4-D ester leads to formation of 2,4-D acid and an associated alcohol moiety. Unlike the physical dissociation mechanism of 2,4-D amine salts, the de-esterification of 2,4-D esters is dependent on abiotic and microbial-mediated processes. Any environmental variable influencing microbial populations or microbial activity could theoretically influence the persistence of the 2,4-D ester. Soil properties including clay mineralogy, organic carbon content, temperature, and moisture content are known to influence hydrolysis rates.

Test data were received addressing the hydrolytic stability of 2,4-D and 2,4-D 2-EHE. The former was stable to hydrolysis at environmentally relevant pH and temperature conditions. However, 2,4-D 2-EHE was hydrolytically unstable in sterile, basic conditions with a half-life of 52.2 hours at pH 9 (compared to 78.3 days and 99.7 days at pH 7 and 5 respectively). Additionally, when this compound underwent hydrolysis testing in natural water (pH 7.8), hydrolysis was rapid with a half-life of 6.2 hours demonstrating the importance of microbial activity in aiding hydrolysis. Hydrolytic rates in soil slurries were even faster with half lives of 1.22-1.45 hours in two soils with pH values of 6.7-6.9.

The US EPA assessed hydrolysis data for 2,4-D BEE and 2,4-D IPE (tests not supplied to the APVMA). They report that in sterile systems, radiolabeled 2,4-D BEE had first-order half-life of 196 days in pH 5 buffer solution, 47.5 hours in pH 7 buffer solution, and 55 minutes in pH 9 buffer solution. The major degradation product was 2,4-D acid. Additionally, the dissipation of 2,4-D IPE appears to be dependent on de-esterification through alkaline-catalyzed abiotic hydrolysis and microbial-mediated or soil surface catalyzed de-esterification processes. The abiotic hydrolysis half-life of 2,4-D IPE was >30 days at pH 5, 89.2 days at pH 7, and 22.4 hours at pH 9. However, in microbially active systems, Isopropyl 2,4-dichlorophenoxyacetate was rapidly de-esterified ($t_{1/2}$ <13 hours) in an aerobic sandy loam soil and aerobic sediment-water test system. The de-esterification of 2,4-D IPE will form 2,4-D and isopropanol.

Modelled data suggest hydrolytic rates for the ethyl, butyl and isobutyl esters would be similar under sterile conditions with predicted half-lives of 1.9, 2.25 and 3.5 days at pH 8, and 19.1, 22.5 and 35 days at pH 7. It could be expected that de-esterification would be more rapid in microbially active systems based on results discussed above for other longer chain esters.

#### *4.3.3.2 Photodegradation*

##### *Air*

The issue of volatility of esters is discussed below. Photodegradation rates in air for the various esters and 2,4-D, based on reaction with hydroxyl radicals, have been calculated using AOPWIN Version 1.91.

The diurnally and seasonally averaged concentration of tropospheric hydroxyl radicals used by the AOP program is 1.5 X $10^6$ $cm^{-3}$. Outputs from the modelling were as follows based on a 12 h:12 h light:dark day:

| Ester | Smiles String | Rate Constant[1] | Half-life (hours) |
|---|---|---|---|
| 2,4-D 2-EHE | Clc1cc(Cl)ccc1OCC(=O)OCC(CC)CCCC | 14.5058 | 17.69 |
| 2,4-D EE | Clc1cc(Cl)ccc1OCC(=O)OCC | 5.2610 | 48.72 |
| 2,4-D BE | CCCCOC(=O)COc1ccc(Cl)cc1Cl | 8.1666 | 31.44 |
| 2,4-D IBE | Clc(cc(Cl)c1OCC(=O)OCC(c)C)cc1 | 8.1582 | 31.44 |
| 2,4-D BEE[2] | CCCCOCCOC(=O)COc1ccc(Cl)cc1Cl | 27.79 | 10.34 |
| 2,4-D IPE[2] | CC(C)OC(=O)COc1ccc(Cl)cc1Cl | 7.0379 | 36.48 |
| 2,4-D | OC(=O)COc1c(Cl)cc(Cl)cc1 | 6.6262 | 38.74 |

1) Rate constant, $K_{OH}$ (X $10^{-12}$ $cm^3$/molecule/second)
2) No product registrations in Australia

The US EPA report that the non-volatile nature of 2,4-D BEE prevented an estimation of the photodegradation rate in air (where less than 1.4% of the applied 2,4-D BEE volatilized). No photodegradates were identified.

### *Water*

Test data were received addressing the photodegradation of 2,4-D and 2,4-D 2-EHE in water. In a sterile aqueous solution with pH of 7, 2,4-D photodegraded with a half-life of 13 days (12:12 hour light:dark regime). This compared to negligible photodegradation where direct photolysis in water was considered based on quantum efficiency. In this test, 2,4-D was stable in water for the 7 day test period.

Photolysis was shown to not be environmentally relevant for the removal of 2,4-D 2-EHE from water bodies. When exposed to natural sunlight in an aqueous pH 5 buffer solution for up to 31 days, less than 15% degradation was observed. The extrapolated photolysis half-life was determined to 128.2 days and the major identified degradation products were 2,4-D and 2,4-DCP.

The US EPA report a study where radiolabeled 2,4-D BEE had a half-life of 74 days in both irradiated and dark control samples. The major degradate identified was 2,4-D acid at less than 17% of applied 2,4-D BEE. The data indicate that 2,4-D BEE does not photodegrade in slightly acid aqueous environments. APVMA did not receive this study.

Aqueous photodegradation of 2,4-D amine salts were not investigated due to the rapid dissociation of these compounds to 2,4-D acid.

### *Soil*

Data indicate 2,4-D is stable to photodegradation on soils with a theoretically calculated half-life of 69 calendar days using linear regression. However, this calculated half-life was not statistically reliable, as degradation did not follow first-order kinetics. The major photodegradate was identified as $CO_2$ (5% of applied). Many unidentified degradates (<10% of applied) also were separated by TLC.

### *4.3.3.3 Volatility*

Volatility of 2,4-D 2-EHE was tested in the laboratory following application to soil pans. The soil was classified as a sandy loam with a pH of 6.5 and 4.17% moisture content at 1/3 bar. The highest losses occurred during the first day. Average volatilisation rates for the 100 and 300 mL/minute air flow rates were $8.06 \times 10^{-4}$ and $3.45 \times 10^{-3}$ $\mu g/cm^3/hour$ respectively with average air concentrations at these rates of 34.84 and 46.06 $\mu g/m^3$ respectively. The conclusion was that volatilisation of 2,4-D 2-EHE from the light textured soils was low.

2,4-D esters with short-chain alcohols are highly volatile. This influences the effectiveness of their application to target crops, their effects on neighbouring crops, and the degree of contamination of the atmosphere. 2,4-D alkali salts or amine salts are much less volatile than esters, and these products are to be preferred when the use of 2,4-D esters might lead to evaporative 2,4-D losses and to crop damage or damage to the surrounding environment (WHO, 1989). As noted in Section 4.3.2.2 above, the majority of ester formulations registered for use in Australia are the short chain forms of ethyl, butyl or isobutyl esters of 2,4-D.

It is further stated in WHO (1984) that the drifting of vapours of the more volatile short-chain 2,4-D esters may result in air pollution and crop damage, and that these products were being replaced by less volatile long-chain esters or by amine salts. However, the report did not state the countries where such replacement is occurring.

**Table 5. Vapour pressure and solubility of 2,4-D salts and esters**

| Compound | Vapour pressure[a] | Solubility |
|---|---|---|
| 2,4-D free acid | 0.4 mmHg (160°C) | 0.09% in water (25 °C), 85% in acetone (25 °C) |
| dimethylamine salt | | 300% in water (20 °C), soluble in acetone |
| isopropyl ester | $1.4 \times 10^{-3}$ mmHg[b]<br>$4.6 \times 10^{-5}$ mmHg[b] | insoluble in water, soluble in most organic solvents |
| butoxyethanol ester | $4.5 \times 10^{-6}$ mmHg[b] | insoluble in water, soluble in most organic solvents |
| ethylhexyl ester | $2.0 \times 10^{-6}$ mmHg[b] | insoluble in water, soluble in organic solvents |
| isooctyl ester | $2.0 \times 10^{-6}$ mmHg[b] | insoluble in water, soluble in organic solvents |
| propyleneglycol butyl ether ester | $3.0 \times 10^{-6}$ mmHg[b] | insoluble in water, soluble in organic solvents |
| methyl ester | $2.3 \times 10^{-3}$ mmHg[b] | |
| ethyl ester | $1.1 \times 10^{-3}$ mmHg[b] | |
| butyl ester | $3.97 \times 10^{-4}$ mmHg[b] | |

[a] 1 mmHg = 0.133 kPa.

[b] Vapour pressures of esters were determined at high temperatures by gas-liquid chromatography, and these values are the result of extrapolation to 25°C. Values vary considerably between authors as a result of this extrapolation; original values at high temperatures agree. Results are presented here as an indication of relative vapour pressure at working temperature.

According to the scale of Mensink *et al* (1995), substances with vapour pressures of $7.5 \times 10^{-6} – 7.5 \times 10^{-3}$ mm Hg are slightly to moderately volatile; this suggests that several of the above esters may volatilise following application. This appears particularly true for the ethyl and butyl esters used in Australia.

This statement is further supported by German research. Guth *et al* 2004 state that, based on direct measurements, no noticeable volatility can be expected from compounds with a vapour pressure below $10^{-3}$ Pa from soil and $10^{-4}$ Pa from crops, and this is fully confirmed by indirect measurements. Converting the above vapour pressures for the EHE, ethyl and butyl esters to Pa gives results of $2.67 \times 10^{-4}$, $1.47 \times 10^{-1}$ and $5.29 \times 10^{-2}$ Pa respectively, indicating the latter two may be expected to volatilise from both soils and crops while EHE is marginal but may volatilise from crop surfaces (supported by data described in the Technical Report – Appendix II).

### 4.3.4 Summary of Environmental Toxicity

#### *4.3.4.1 2,4-D Acid*

When tested in its acid form, 2,4-D was not toxic to birds based on acute oral exposure from one standard test (not reviewed) and two non-standard tests. Short term toxicity was not evident with three tests all resulting in an undefined LD50 due to a lack of mortality at up to 5620 ppm (although 40% mortality at this level was found for the bobwhite quail). A single reproduction test showed no effects on reproductive parameters for the bobwhite quail at 1000 ppm. There was no corresponding reproduction study for the mallard duck. However, given the lack of effects through dietary exposure for both species, and the lack of effects on bobwhite quail through the reproduction study, this test is not considered necessary.

Acute testing on fish showed a range of freshwater and marine fish species to be insensitive to 2,4-D in its acid form. The most sensitive species for which a defined end-point was obtained in acute testing was a 96 h LC50 of 175 mg/L for the marine tidewater silverside. A single acute amphibian test on leopard frog tadpoles resulted in a 96 h LC50 of 359 mg/L. One chronic study on fathead minnow showed a NOEC of 63.4 mg/L.

Aquatic invertebrates (water fleas, pink shrimp and eastern oysters) were variable in their sensitivity to 2,4-D. The most sensitive animal appeared to be *Daphnia magna* with a lowest 48 LC50 value of 25.0 mg/L (slight toxicity). A single chronic test on daphnids gave a 21-day NOEC of 79 mg/L (corresponding EC50 of 235 mg/L).

Two tests on different green algae species showed relatively low toxicity of 2,4-D acid to algae with EC50s between 30-100 mg/L. However, the duckweed *Lemna gibba* appears much more sensitive, and 2,4-D is highly toxic with a reported EC50 of 0.695 mg/L, from a study not assessed within this review.

No standard toxicity tests were performed on terrestrial organisms using 2,4-D in its acid form. This is acceptable as tests were performed with 2,4-D in various ester or salt forms that are used in formulations, and therefore are of more relevance. Data provided for 2,4-D in its acid form to non-target vegetation through seedling emergence and vegetative vigour studies demonstrated that plants were more sensitive in their growth stage rather than at emergence. Monocots tended to be less sensitive than dicots. EC25 values for dicots in the vegetative vigour studies ranged from 8.4 to 25.7 g/ha.

#### *4.3.4.2 Esters*

Acute oral toxicity results were available for 2,4-D EHE, 2,4-D IPE, 2,4-D BEE, 2,4-D BE and 2,4-D EE, although only studies for 2,4-D EHE and 2,4-D EE were reviewed. Of the available results, mallard duck (LD50 = 423 mg ae/kg bw) and the pigeon (LD50 = 346 mg ae/kg bw from a non-standard test) were the most sensitive. Other results where data were not reviewed indicate the 2,4-D esters are moderately toxic to practically non-toxic to birds, with results provided for mallard duck, bobwhite quail and the domestic chicken.

Only two short term toxicity tests were reviewed, both for 2,4-D EHE, with no defined short term LC50 able to be derived up to 3588 ppm ae for either the mallard duck or the bobwhite quail. In addition to these reviewed data, nine other results were reported, confirming this lack of toxicity through the diet. These results covered the 2,4-D EHE, 2,4-D BEE, 2,4-D IPE and 2,4-D BE esters and indicate that in general, 2,4-D esters will not be toxic to birds when consumed in the diet.

No avian reproductive tests were available for any of the 2,4-D esters.

Several acute fish toxicity results were reviewed for 2,4-D EHE and one for 2,4-D EE. Results for the former were often difficult to interpret due to inconsistent recoveries of the test substance. The main conclusion is that 2,4-D EHE is unlikely to be toxic up to its level of solubility. In one test in which the ester was apparently kept in solution at sufficient quantities to obtain a result, rainbow trout appeared the most sensitive, with a 96 h LC50 of 3.12 mg ae/L. The more soluble ethyl ester (2,4-D EE) was highly toxic to the non-standard species Mozambique tilapia, with a 96 h LC50 of 0.63 mg ae/L. Several non-reviewed results for 2,4-D EE, 2,4-D BE, 2,4-D BEE and 2,4-D IPE confirmed the highly toxic nature of the 2,4-D esters to fish, both freshwater and marine. A single acute amphibian test on leopard frog tadpoles for 2,4-D EHE again resulted in a conclusion that this substance was not toxic up to its limit of solubility. One chronic study on fathead minnow with 2,4-D EHE showed a NOEC of 0.079 mg ae/L, indicating moderate toxicity.

Several acute aquatic invertebrate toxicity results were reviewed for 2,4-D EHE and one for 2,4-D BE. Again, results for the former were often difficult to interpret due to inconsistent recoveries of the test substance and the main conclusion is that 2,4-D EHE is unlikely to be toxic up to its level of solubility. Non-reviewed results for other esters included 2,4-D EE, 2,4-D BE, 2,4-D BEE and 2,4-D IPE and covered a range of aquatic invertebrates. Results for 2,4-D BE, 2,4-D BEE and 2,4-D IPE indicate these esters are moderately (approaching highly) toxic, with the most sensitive result being a 96 h LC50 of 1.04 mg ae/L for 2,4-D BE to the stonefly. Two chronic test results, both to *Daphnia magna*, are available. The reviewed study for 2,4-D EHE resulted in a MATC of 0.013 mg ae/L with a 21 d EC50 of 0.036 mg ae/L (moderate toxicity), while the non-reviewed result for 2,4-D BEE showed this ester to be less sensitive with a MATC of 0.31 mg ae/L.

Five standard tests for different algae and the duckweed *Lemna gibba* were available for 2,4-D EHE. There were significant problems interpreting the obtained test results due to very low recoveries of test material. The marine diatom, *S. costatum*, and duckweed appeared to be the most sensitive to this ester with EC50s of 0.15 and 0.33 mg ae/L respectively (highly toxic). Generally, 2,4-D EHE did not appear toxic up to its limit of solubility. The same species were tested with 2,4-D BEE (reports not reviewed), but this ester was less toxic to algae. Again, the marine diatom, *S. costatum* was the most sensitive algae with an EC50 of 1.02 mg ae/L. Duckweed was the most sensitive species overall with an EC50 of 0.4 mg ae/L, indicating that it to have around the same level of toxicity to this species as 2,4-D EHE.

2,4-D EHE was, at worst, slightly toxic to bees through either contact or oral exposure routes with LD50 values of >64.3 and >62.9 µg/bee respectively. A non-standard test using 2,4-D EE on Indian worker bees showed this chemical to have an LD50 of 0.013% v/v, but this value cannot readily be translated to a rate per bee or a rate per hectare. No other bee toxicity data were available for any other esters. 2,4-D EHE was harmless to the predatory mite up to the highest rate tested of 564 g ae/ha. However, at this rate it was harmful to the parasitic wasp, causing 100% mortality of adults. It was harmless to this species at the next lowest rate tested of 28 g ae/ha. No other ester form of 2,4-D was tested on any other beneficial insect.

Additionally, no ester toxicity data to earthworms or soil micro-organisms were available.

Some data were provided for 2,4-D in its EHE and BEE ester forms to non-target vegetation through seedling emergence and vegetative vigour studies with other results reported but not reviewed for this assessment. Terrestrial plants were shown to be very sensitive to 2,4-D. In *in vitro* seedling germination studies, radicle length was the most sensitive indicator. In soil assays, dicots were more sensitive, and plants were generally more sensitive in the actively growing phase (vegetative vigour studies). Results for vegetative vigour studies, particularly for 2,4-D EHE, indicate that 2,4-D esters will have significant impacts on actively growing plants, often at relative low rates (<30 g ae/ha).

#### *4.3.4.3 Salts*

Acute oral toxicity results were available for 2,4-D DMA, 2,4-D DEA, 2,4-D IPA, 2,4-D TIPA and 2,4-D sodium salt, although only studies for 2,4-D DMA and 2,4-D sodium salt were reviewed. The only standard test was with 2,4-D DMA to bobwhite quail and showed this chemical to be moderately toxic, with an LD50 of 415 mg ae/kg bw. The other tests reviewed were non-standard and conducted on the domestic chicken and pigeon. The pigeon was most sensitive to 2,4-D DMA with an LD50 of 334 mg ae/kg bw, but the sodium salt was practically non-toxic to both these non-standard species. Other results (primary data not reviewed) indicate the 2,4-D DMA is practically non-toxic to the mallard duck and only threshold concentrations were obtained for the IPA and TIPA salts to mallard duck (LD50 >314 mg ae/kg bw) and bobwhite quail (LD50 >219 mg ae/kg bw) respectively.

Four short-term toxicity tests were reviewed for 2,4-D DMA salt, with no defined short-term LD50 able to be derived up to 1899 ae ppm in the diet for either species in old, non-standard tests or >4655 ae ppm to either species in standard short-term tests. In addition to these reviewed data, seven other results were reported, confirming this lack of toxicity through the diet. These results covered the 2,4-D DMA, DEA, IPA and TIPA salts, and indicate that in general, 2,4-D salts should not be toxic to birds when consumed in the diet.

No avian reproductive tests were available for any of the 2,4-D salts.

Several acute fish toxicity results were reviewed for 2,4-D DMA salt and one for 2,4-D sodium salt. Results were in good agreement that both these salts were practically non-toxic to fish (96 h LC50s >100 mg ae/L), with the exception of a non-standard test using 2,4-D DMA salt on the non-standard species, Mozambique tilapia, with a 96 h LC50 of 35.6 mg ae/L (slightly toxic). A total of eighteen other non-reviewed results for the 2,4-D DMA, DEA, IPA, TIPA and sodium salts all added to the weight of evidence that 2,4-D in its salt forms will not be toxic to fish, with all definitive results showing 96 h LC50s >80 mg ae/L. A single acute amphibian test on leopard frog tadpoles for 2,4-D DMA salt again resulted in a conclusion of low toxicity with the 96 h LC50 of 188 mg ae/L. Two chronic studies reviewed for 2,4-D DMA resulted in a 28-d NOEC of 100 mg ae/L to rainbow trout and a 31-d MATC of 18.3 mg ae/L to fathead minnow while results of one non-reviewed test showed a MATC of 36.3 mg ae/L. Both indicated very slight toxicity.

Several acute aquatic invertebrate toxicity results were reviewed for 2,4-D DMA salt and all results tended to support a conclusion of this compound being practically non-toxic to aquatic invertebrates, with defined LC50s >100 mg ae/ha. One older study resulted in an EC50 somewhere between 85-131 mg ae/L. In addition, fourteen non-reviewed tests provided results generally supportive of limited toxicity. The most sensitive species tested appeared to be the eastern oyster, with a 96 h LC50 of 49.6 mg ae/L with 2,4-D IPA and 89.1 mg ae/L for 2,4-D TIPA (both slightly toxic). Generally, however, defined LC50s were >100 mg ae/L for non-reviewed studies for

2,4-D DMA, DEA, IPA and TIPA salts. Two chronic test results with *Daphnia magna* were reviewed, resulting in MATC values of 73.1 and 33.6 mg ae/L. This very slight toxicity was supported by a non-reviewed test result with an MATC >16.05 mg ae/L for 2,4-D DEA salt to *Daphnia magna*.

Algae and aquatic plants were the most sensitive aquatic organisms to 2,4-D salts. Seven standard tests for different algae and the duckweed *Lemna gibba* were available for 2,4-D DMA along with supporting results for the 2,4-D DEA, IPA and TIPA salts. Generally, these salts were slightly to practically non-toxic to the simpler freshwater and marine algae. The most sensitive algae species appeared to be the freshwater diatom *N. pelliculosa* with a (unreviewed) EC50 of 4.38 mg ae/L from 2,4-D DMA salt, and the green alga *S. capricornutum,* with an EC 50 of 7.48 mg ae/L to the 2,4-D DEA salt (both moderately toxic). The vascular aquatic plant, duckweed (*L. gibba*) was more sensitive, with 2,4-D DMA and DEA salts being highly toxic to this plant with EC50s of 0.48 and 0.30 mg ae/L respectively. The only other salt for which a result is available to duckweed was 2,4-D TIPA, with an EC50 of 1.3 mg ae/L.

2,4-D DMA was slightly toxic to bees through either contact or oral exposure routes with LD50 values of >83.3 and 78 µg/bee respectively. Non standard tests with 2,4-D DMA and 2,4-D sodium salt on Indian worker bees showed these chemicals to have an LD50 of 0.14% v/v and >3% w/v respectively, but these values can not readily be translated to a rate per bee or a rate per hectare. No other bee toxicity data were available for any other salts.

2,4-D DMA salt was harmless to a range of non-target terrestrial arthropods up to the highest rates tested, which in all cases was at least 1000 g ae/ha. Similarly, earthworms were not affected at rates up to 500 mg ae/kg soil when exposed to 2,4-D DMA salt, making this chemical at worst, only slightly toxic to earthworms. 2,4-D DMA salt was shown to have no significant impact on soil respiration or ammonification and nitrification of soil when applied at a rate up to 13.3 mg ae/kg soil. No other salt form of 2,4-D was tested on any other beneficial insect or soil micro-organisms.

Data were provided for the 2,4-D DMA salt with testing on seedling emergence, while other data for 2,4-D in various amine salt forms to non-target vegetation through seedling emergence and vegetative vigour studies are reported but not reviewed for this assessment. Terrestrial plants were shown to be very sensitive to 2,4-D. In soil assays, dicots were more sensitive, and plants were generally more sensitive in the actively growing phase (vegetative vigour studies) with a non-assessed study for the 2,4-D DEA salt reporting EC25 values fanging from 3.4-50.4 g ae/ha.

### 4.3.5 Preliminary Risk Assessment

When assessing risk, it is not possible to account for every case, so DEH follows an iterative process by considering:

- a ‘worst case’ scenario, and, if needed,
- a series of refinements which account for other factors and results in setting more realistic scenarios at each step.

The worst case estimate is performed in this preliminary risk assessment and should identify the sensitive environmental compartment(s) most at risk from exposure to the chemical. If these environmental compartments are not at risk (ie the Q-value is acceptable), then no further assessment is needed. If at the preliminary stage, insufficient data are available to characterise risk, then no refined risk assessment has been conducted.

DEH uses a quotient approach. In general, where there are sufficient data and acute toxicity endpoints are used for the Q-value, values of 0.1 or less are considered acceptable. Where chronic toxicity values are used, Q-values of 1 or less are considered acceptable. In the case of terrestrial plants, a Q-value of 0.1 or less, based on EC25 data, will be considered in the preliminary assessment. Where further refinement is required, a representative NOEL will be determined based on the range of data, and a Q-value of 1 or less will be considered to be acceptable.

#### *4.3.5.1 Preliminary Terrestrial Risk Assessment*

#### *Avian Toxicity*

Birds did not appear to be sensitive to 2,4-D through either oral or dietary exposure. Considering the latter route, no definitive LC50 was determined at highest concentrations tested in any test reviewed by DEH or cited by the US EPA, 2005. In terms of acid equivalent doses, all birds tested through dietary studies had an LC50 >1899 ppm. The lowest NOEC was 466 ppm to Mallard duck when exposed to 2,4-D in its DMA salt form, but generally, NOECs obtained were 1000 ppm or greater.

Non-standard tests conducted on the pigeon showed this bird to be the most sensitive from acute oral exposure, with acute LD50s of around 350 mg ae/kg bw for esters and salts, and around 1000 mg ae/kg bw for 2,4-D acid. Given that the most probable route of exposure to birds will be through dietary uptake of 2,4-D residues contained in treated plant material or prey, and due to extensive data available for dietary exposure, dietary endpoints will be used in the risk assessment.

Dietary Q values for a single application of 2,4-D at the maximum registered label use rate of 4500 g ae/ha estimated by the updated Kenaga nomogram (Pfleeger *et al*, 1996) have been determined. This nomogram is based on a review of the highest levels of pesticide residues reported from spray application and represents an upper limit to residues likely to be found on various substrates.

| Environmental Compartment | Concentration fresh weight (mg ae/kg) |
|---|---|
| short grass | 964.3 |
| leaves and leafy crops | 542.4 |
| forage crops | 542.4 |
| small insects | 542.4 |
| grain/long grass | 441.0 |
| pods with seeds | 60.27 |
| large insects | 60.27 |
| fruit | 60.27 |

Quail total residues are based on a diet of 30% small insects and 70% grain. Mallard total residues are based on a diet of 30% grain (same as long grass) and 70% large insects.

Based on the application and diet described here, the Kenaga nomogram predicts residues in quail and mallard duck diets of 471.4 and 174.5 mg/kg fresh weight respectively. The dietary LC50s return acute Q values of 0.25 and 0.09 respectively. This indicates a low risk to mallard ducks and a potential risk to bobwhite quail. However, the dietary LC50 used to base this on was a threshold value of >1899 ppm in the diet (2,4-D DMA in the product DMA-4). These were the lowest threshold concentrations obtained from an old study in which the test material was not characterised and acid equivalent concentrations have essentially been estimated based on information in other studies using the same product name. The corresponding NOEC from this study was 879 ppm in the diet (again estimated from other information). The Q value using the 5 day NOEC is 0.54. Even though this is not a chronic NOEC, it is still <1. The NOEC was based on observations of wing droop and lethargy at 1899 ppm (ae), the next highest concentration tested. This was the highest concentration and resulted in 20% mortality.

Corresponding tests on bobwhite quail and mallard duck where the test material (2,4-D DMA) was well characterised showed dietary LC50s >4665 ppm for both species. Using these more valid results for the DMA salt, dietary Q values for quail and mallard are 0.1 and 0.04 respectively. Other forms of 2,4-D for which test results are available all show that no defined LC50 could be calculated due to a lack of mortality at the highest tested rates, all >3000 ppm acid equivalent.

The very high rates of application are prescribed for use in pasture situations including rights of way and industrial areas with ester products. With the exception of one product registered for sugar cane at 3640 g ae/ha, field crop application rates (including sugar cane) are usually below 2500 g ae/ha with all other products. At this application rate, residues in quail and mallard diets are reduced to around 262 and 97 mg/kg fresh weight respectively. Using the threshold dietary LD50 of 1899 ppm results in Q values of 0.14 and 0.05 respectively. Further, it is unlikely that birds would be obtaining all their diet from the treated area consistently and a conclusion of low acute risk to birds is considered acceptable. This conclusion is further supported when considering the reproduction NOEC to bobwhite exposed to 2,4-D acid was 1000 ppm.

Australian labels are generally silent on the issue of repeat applications. There are likely situations where repeat applications may occur e.g. pastures. However, the short half-lives of 2,4-D and its various forms in the environment should preclude the opportunity for chronic exposure. Field half-lives from application to pastures and turf averaged 10 days or less with longer half-lives usually attributed to the use of granule formulations. In this regard, it is important to note that no granule formulations are registered in Australia. The risk to birds through chronic exposure is therefore predicted to be acceptable.

### *Bees and other terrestrial invertebrates*

No standard oral or contact toxicity tests were provided for the free acid form of 2,4-D. Standard oral and contact toxicity tests were performed on the 2-EHE and DMA salt forms of 2,4-D with all results showing that 2,4-D is not likely to be toxic to bees. The highest defined toxicity was exhibited through the oral route to bees with a 72 h LC50 for 2,4-D DMA of 78 µg ae/bee. The more relevant contact route did not result in defined toxicity values. 2,4-D EHE and 2,4-D DMA were both tested through contact routes to bees, with LD50's >64.3 and >83.3 µg ae/bee respectively. In the 2,4-D EHE study, at the highest rate of 64.3 µg ae/bee, 35% mortality was found. Based on the dose/response observed in this study, plotting dose vs mortality, a linear relationship was found ($r^2 = 0.92$), and an LD50 of around 98 µg ae/bee can be extrapolated.

In the 2,4-D DMA experiment, the only mortality observed in the treatment groups was 3% in the 83.3 µg ae/bee group. With the exception of one bee in this group which was immobile on day 0, all other surviving bees in the five treatment groups were normal in appearance and behaviour throughout the test period. This suggests the LD50 will be well in excess of 83.3 µg ae/bee.

Given the insensitivity of bees to the 2,4-D DMA salt through the contact route, the extrapolated value of 98 µg ae/bee from the EHE test will be used as the end point for the risk assessment.

Where the quotient is <1, risk to bees and pollinating insects is considered to be acceptable. Assuming that a honeybee is approximately 1 $cm^2$ in surface area (Davis and Williams 1990), an application rate of 4500 g ae/ha is equivalent to 45.0 $µg/cm^2$. This results in an acceptable Q value of 0.46, since this reference assumes an acceptable risk with a Q value of 1. This very high rate is prescribed for ester formulations used in non-legume pastures, rights of way and industrial areas. Table 29 below provides maximum registered broadcast application rates for other 2,4-D forms. With the exception of improved pastures, sugar cane, lawns/turf and pre-harvest potatoes, application rates tend to be around 1100 g ae/ha or less. The predominant registered rate for improved pastures, sugar cane and lawns/turf are between 2000-2750 g ae/ha (plus 1620 g ae/ha for pre-harvest potatoes). These rates result in a deposition rate of 20-27 $µg/cm^2$ and give Q values of 0.27-0.20, further indicating an acceptable risk to bees. The lower rates for field crops of 1100 g ae/L or less result in deposition of 11 $µg/cm^2$ or less, and Q values of ≤0.11.

Results for terrestrial arthropod toxicity tests suggest that the ester forms are more toxic to insects than salt forms of 2,4-D. The standard parasitic wasp species was tested using the same test system for both 2,4-D DMA and 2,4-D 2-EHE and maximum label application rates for their respective formulations (not Australian). For 2,4-D DMA, reduction in beneficial capacity was such that this chemical is considered harmless up to its use rate of 1800 g ae/ha. However, the maximum rate of 564 g ae/ha for 2,4-D 2-EHE resulted in 100% mortality of adult wasps prior to the reproductive phase of the test. Unfortunately, this was a tier I test performed in the laboratory with exposure from application to glass plates. No higher tier testing was performed to establish the effect mitigating factors in the field may diminish toxicity (eg, interception, conversion of the ester to 2,4-D acid through hydrolysis, degradation or dissipation).

2,4-D EHE was harmless to the predatory mite at it maximum application rate for the test of 564 g ae/ha. 2,4-D DMA was harmless to the predatory mite, spiders and the rove beetle up to 1800, 1056 and 1000 g ae/ha respectively.

Clearly, application rates in Australia can be significantly higher than those tested in laboratory non-target invertebrate tests. Using 2,4-D DMA as a surrogate for all other salt forms of 2,4-D, it can be stated that no in-field adverse impacts on non-target invertebrates should be expected when the application rate of 2,4-D in its salt forms is 1000 g ae/ha or less, which would be the case for the majority of broadcast use patterns in Australia.

Very limited testing is available for 2,4-D EHE and no tests on non-target arthropods are available for other ester forms. At broadcast application rates for 2,4-D EHE uses in Australia, adverse effects in-field to terrestrial arthropods cannot be ruled out. However, limited results in this area are likely to overestimate toxicity and effects in the field are not expected to be as severe, particularly due to the rapid conversion of 2,4-D esters to the acid form in soils. Nonetheless, where non-target arthropods are exposed through plant surfaces rather than from soil exposure, this conversion may not occur as quickly and effects may be expected. Without higher tier testing, risks can not be quantified further.

Off-target adverse effects on non-target arthropods are not expected. The maximum registered application rate of 2,4-D salts is 3640 g ae/ha in sugar cane. Even drift of 10% (highly unlikely) would result in deposition of 360 g ae/ha, well below levels likely to cause adverse effects.

Off-target effects of 2,4-D esters again can not be ruled out due to the low tier level testing and limited results available. However, mitigation factors found in the field as discussed above are expected to limit any effects from drift to non-target areas. A deposition rate of 28 g ae/ha equates to 0.6% drift at the highest ground application rate of 4500 g ae/ha, or 0.9% for the maximum registered aerial application rate of 3200 g ae/ha. Downwind buffer zones are prescribed in the refined risk assessment below for other environmental compartments that will result in drift significantly less than these values. However, without higher tier testing, risks can not be quantified further for the ester formulations.

The risk to off-target adverse effects to non-target terrestrial arthropods is considered acceptable for salt formulations at up to 1000 g ae/ha. There are insufficient data at higher rates or for ester formulations to be able to quantify risks to non-target terrestrial arthropods and adverse effects to these organisms can not be ruled out.

### *Soil-dwelling invertebrates*

Earthworms were insensitive to 2,4-D exposure as both the free acid and in its DMA salt form with LD50s in excess of 300 mg ae/kg dw soil.

An application rate of 4500 g/ha results in residues of 3.46 mg/kg soil if distributed through the top 10 cm of soil (density 1.3 g/cm$^2$).

The lack of persistence of 2,4-D in soils indicates that accumulation will not be an issue. The short term concentration of 3.46 mg/kg results in Q values of 0.01 for 2,4-D acid and salts (using DMA salt as a surrogate).

There are no data for toxicity of ester forms of 2,4-D to earthworms. However, studies assessed in this report indicate that in soils, 2,4-D EHE will hydrolyse rapidly with a half-life of <1.5 hours (Conch *et al*, 1993c; McCoy and Lehman, 1998). Field half-lives for 2,4-D EHE, while not as short as the laboratory values, were still fast. Of the 29 soil results available (not counting granule formulations) for forestry, pasture, wheat, turf and bare ground field dissipation studies, half-lives of 2,4-D EHE ranged from 0.34-12.9 days with an average of 3.1 days. Only two half-lives were >5.2 days.

Conversion was primarily to the 2,4-D acid. Again there was insufficient data to rule out short-term effects, but a chronic risk is not expected.

### *Soil micro-organisms*

No data have been provided for 2,4-D acid or any of its ester forms. Two studies, one addressing soil respiration and the other addressing soil nitrification, were provided for 2,4-D DMA when applied in a formulation containing 500 g/L 2,4-D acid and demonstrated that 2,4-D should have no significant impact on soil respiration or ammonification and nitrification of soil when applied at a rate up to 13.3 mg ae/kg soil.

DEH has used these results as a surrogate for 2,4-D in both its acid and ester forms. 2,4-D DMA along with other 2,4-D salts dissociates very quickly to form 2,4-D acid, so the toxicological properties are expected to be similar. Similarly, the 2,4-D esters have been shown to rapidly break down in soils (not as quickly as the salt forms, but still with short half-lives as discussed in soil-dwelling invertebrates above), again producing the 2,4-D acid.

As shown with soil dwelling invertebrates above, the maximum application rate of 4500 g ae/ha results in a theoretical concentration in the top 10 cm of soil of 3.46 mg ae/L. This is almost 4 times lower than the maximum rate tested which was shown not to impact soil microorganisms. This, along with the lack of persistence of 2,4-D in soil, indicates the risk to soil microorganisms is expected to be low, though again a temporary risk from 2,4-D esters cannot be ruled out from the available data.

### *Non-Target Terrestrial Plants*

Seedling emergence test data were received for 2,4-D acid, 2,4-D EHE, 2,4-D BEE and 2,4-D DMA. Vegetative vigour test data were received for 2,4-D acid, 2,4-D EHE and 2,4-D BEE. In addition, the US EPA reports data for 2,4-D IPE and 2,4-D DEA. No data were available for the EE and BE forms. The most sensitive EC25 (expressed as g/ha) are as follows:

**Table 6: Most Sensitive Terrestrial Plant Toxicity Results (EC 25, g ae/ha).**

| | Seedling Emergence | | Vegetative Vigour | |
|---|---|---|---|---|
| | Monocot | Dicot | Monocot | Dicot |
| 2,4-D Acid | 1640 | 33.6 | <8.4 | 8.4 |
| 2,4-D DMA | 50.7 | 22.3 | No data available | |
| 2,4-D DEA[1] | 426 | 50 | 44.8 | 3.4 |
| 2,4-D EHE | 270 | 33.6 | 244 | 11.2 |
| 2,4-D BEE | 434[2] | 237[2] | 212 | 24 |
| 2,4-D IPE[1] | 11.2 | 0.9 | 226 | 1.4 |

1) The test reports for these chemicals have not been provided to the APVMA.
2) The definitive test also tested seed germination and effects on radicle length. These were *in vitro* studies not considered representative of real exposure. Nonetheless, effects were severe, with EC25 values for monocots and dicots <1 g ae/ha. The relevance of these effects is discussed in the refined assessment below.

By far the most sensitive result in the above table is that for seedling emergence from the 2,4-D IPE test in whiche an EC25 of 0.9 g/ha to the lettuce was found, based on shoot length. These values have to be used as surrogates for EE and BE in the absence of test data. With a maximum ground application rate of 4500 g/ha in pastures, a drift or volatilization rate of 5% moving to a neighbouring field or stand of native vegetation would result in an amount available for deposition of 250 g/ha. This would clearly result in an unacceptable risk and thus risk to non-target terrestrial plants will be considered in the refined risk assessment.

### *Aquatic Preliminary Risk Assessment*

The following assessment is for non-aquatic uses of 2,4-D. Aquatic uses are considered separately.

### *Fish*

**Table 7. Acute Fish Toxicity Endpoints For Risk Assessment.**

| Test species | System | LC50 (mg ae/L) |
|---|---|---|
| **2,4-D Acid** | | |
| Tidewater silverside (*M beryllina*) | 96 h flow through | 175 (m) |
| **2,4-D Esters** | | |
| Bluegill sunfish (*L. macrochirus*)[1] | 96 h static | 0.23 |
| **2,4-D Salts** | | |
| Mozambique tilapia (*T mossambica*)[2] | 96 h static | 35.6 |

1) This is the lowest definitive result obtained through the ECOTOX data base for the butyl ester. Even though the study has not been reviewed by DEH, there is strong weight of evidence from other results from this data base. The lowest definitive result of a study reviewed by DEH was an LC50 of 0.63 ppm (nominal) for ethyl ester, which although obtained from a non-standard test, is still considered valid due to no control mortality and a clear dose-response curve. 2,4-D in its butyl ester and iso-butyl ester form are well represented amongst registered products in Australia. Therefore the use of this value is considered appropriate.
2) Definitive results for 2,4-D salts from tests reviewed by DEH overwhelmingly showed these forms to be practically non-toxic to fish. This is supported by weight of evidence from US EPA (2005). However, the result used for the risk assessment showed higher than usual toxicity, and although the test was performed using non-standard guidelines, it is considered scientifically valid as no control mortality and a clear dose-response curve were observed.

Worst case exposure assumptions include application to a standard pond of 1 ha surface area and average depth of 15 cm. Based on direct overspray, the following Q values are determined:

***2,4-D Acid.*** For an acceptable Q value of 0.1 or less, exposure from 2,4-D acid cannot result in a concentration of more than 17.5 mg/L. The maximum registered rate of 2,4-D in acid equivalent terms resulting from broadcast use for non-ester labels is 3640 g/ha in sugarcane.

Direct overspray: 2.43 mg/L; Q value = 0.01 (Acceptable risk)

***2,4-D Esters.*** For an acceptable Q value of 0.1 or less, exposure from 2,4-D esters cannot result in a concentration of more than 0.023 mg/L. The maximum registered rate of 2,4-D in acid equivalent terms resulting from broadcast use for ester labels is 4500 g/ha in pasture.

Direct overspray: 3 mg/L; Q value = 13 (Unacceptable risk)
Acceptable drift: 0.77% drift would result in an exposure concentration of 0.023 mg/L resulting in an acceptable Q value of 0.1.

***2,4-D Salts.*** For an acceptable Q value of 0.1 or less, exposure from 2,4-D salts cannot result in a concentration of more than 3.56 mg/L. The maximum registered rate of 2,4-D in acid equivalent terms resulting from broadcast use for non-ester labels is 3640 g/ha in sugarcane.

Direct overspray: 2.43 mg/L; Q value = 0.07 (Acceptable risk)

It was concluded that the fish risk assessment should focus on ester forms of 2,4-D as currently registered broadcast applications using salt forms or 2,4-D acid do not result in an unacceptable acute risk to fish under worst-case exposure calculations.

### *Invertebrates – Acute*

**Table 8. Acute Aquatic Toxicity Endpoints For Risk Assessment.**

| Test species | System | LC50 (mg ae/L) |
|---|---|---|
| **2,4-D Acid** | | |
| *Daphnia magna* | 48 h static | 25.0 |
| **2,4-D Esters** | | |
| Stonefly (*Pteronarcella badia*)[1] | 96 h static | 1.04 |
| **2,4-D Salts** | | |
| Eastern oyster (*C. virginica*)[2] | 96 h | 49.6 (m) |

1) This is the lowest definitive result obtained through the ECOTOX data base for the butyl ester. Even though the study has not been reviewed by DEH, there is strong weight of evidence from other results from this data base. While there were several studies reviewed by DEH where lower results were obtained, these were all threshold values where no impacts were found at the highest rate tested and can not realistically be applied in the risk assessment. The lowest definitive LC50 in a test reviewed by DEH was 2.92 mg/L to *Daphnia magna* when exposed to 2,4-D 2-EHE. 2,4-D in its butyl ester and iso-butyl ester form are well represented amongst registered products in Australia and therefore, the use of this value is considered appropriate.
2) DEH reviewed several studies where definitive LD/EC50 concentrations were obtained for 2,4-D DMA salt. These showed this chemical to be practically non-toxic to aquatic invertebrates. The end-point chosen for the risk assessment is reported in US EPA, 2005 and was obtained for exposure to the IPA salt. Based on available data, it is considered a worst case for acute aquatic invertebrate exposure.

Worst case exposure assumptions include application to a standard pond of 1 ha surface area and average depth of 15 cm. Based on direct overspray, the following Q values are determined:

***2,4-D Acid.*** For an acceptable Q value of 0.1 or less, exposure from 2,4-D acid cannot result in a concentration of more than 2.5 mg/L. The maximum registered rate of 2,4-D in acid equivalent terms resulting from broadcast use for non-ester labels is 3640 g/ha in sugarcane.

Direct overspray: 2.43 mg/L; Q value = 0.097 (Acceptable risk)

***2,4-D Esters.*** For an acceptable Q value of 0.1 or less, exposure from 2,4-D esters cannot result in a concentration of more than 0.1 mg/L. The maximum registered rate of 2,4-D in acid equivalent terms resulting from broadcast use for ester labels is 4500 g/ha in pasture.

Direct overspray: 3 mg/L; Q value = 3 (Unacceptable risk)
Acceptable drift: 3.3% drift would result in an exposure concentration of 0.1 mg/L resulting in an acceptable Q value of 0.1.

***2,4-D Salts.*** For an acceptable Q value of 0.1 or less, exposure from 2,4-D salts cannot result in a concentration of more than 4.96 mg/L. The maximum registered rate of 2,4-D in acid equivalent terms resulting from broadcast use for non-ester labels is 3640 g/ha in sugarcane.

Direct overspray: 2.43 mg/L; Q value = 0.05 (Acceptable risk)

It was concluded that the aquatic invertebrates risk assessment should focus on ester forms of 2,4-D as currently registered broadcast applications using salt forms or labelled as 2,4-D acid do not result in an unacceptable acute risk to aquatic invertebrates under worst-case exposure calculations.

## Algae and Aquatic Plants

**Table 9. Acute Algae/Aquatic Plant Toxicity Endpoints For Risk Assessment.**

| Test species | System | EC50 (mg ae/L) |
|---|---|---|
| **2,4-D Acid** | | |
| Duckweed (*L. gibba*)[1] | Assumed 14 d | EC50 = 0.695 |
| **2,4-D Esters** | | |
| Duckweed (*L. gibba*)[2] | 14 days | 0.33 |
| **2,4-D Salts** | | |
| Duckweed (*L. gibba*)[3] | | 0.3 |

1) The APVMA was not provided with this study, reviewed and reported by the US EPA, 2005. The result is significantly more sensitive than other algal results reviewed by DEH so will be used as the endpoint for 2,4-D acid in the risk assessment.
2) The APVMA received several studies for algae and duckweed for 2,4-D 2-EHE. In all tests, there was extremely low recovery of test material and often the NOEC was greater than the EC50, making the results questionable. The US EPA reported a further duckweed result for 2,4-D BEE that approximates that for 2,4-D 2-EHE. Therefore, the 2,4-D 2-EHE result has been chosen as the endpoint for the risk assessment (result is as nominal concentration).
3) The lowest definitive result reviewed by DEH was a 14 d EC50 of 0.48 ppm (measured) for 2,4-D DMA to duckweed. However, the DEA salt is registered in Australia, and the result chosen for the risk assessment is reported by the US EPA, 2005.

Given the similarities in worst case results for the 2,4-D acid, esters and salts, a single EC50 of 0.3 mg/L will be used to assess risk. The difference in risk will therefore be a function of exposure.

Worst case exposure assumptions include application to a standard pond of 1 ha surface area and average depth of 15 cm. Based on direct overspray, the following Q-values are determined:

***2,4-D Acid and salts.*** For an acceptable Q value of 0.1 or less, exposure from 2,4-D acid cannot result in a concentration of more than 0.03 mg/L. The maximum registered rate of 2,4-D in acid equivalent terms resulting from broadcast use for non-ester labels is 3640 g/ha in sugarcane.

Direct overspray: 2.43 mg/L; Q value = 8.1 (Uncceptable risk)
Acceptable drift: 1.25% drift would result in an exposure concentration of 0.03 mg/L resulting in an acceptable Q value of 0.1.

***2,4-D Esters:*** For an acceptable Q value of 0.1 or less, exposure from 2,4-D acid cannot result in a concentration of more than 0.1 mg/L. The maximum registered rate of 2,4-D in acid equivalent terms resulting from broadcast use for ester labels is 4500 g/ha in pasture.

Direct overspray: 3 mg/L; Q value = 10 (Unacceptable risk)
Acceptable drift: 1% drift would result in an exposure concentration of 0.03 mg/L resulting in an acceptable Q value of 0.1.

It was concluded that the algae/aquatic plants risk assessment will focus on all 2,4-D forms.

### 4.3.6 Refined Risk Assessment

Based on results from the preliminary risk assessment, the refined assessment will focus on non-target vegetation and aquatic organisms from exposure to the ester formulations.

#### *4.3.6.1 Aquatic Refined Risk Assessment*

The refined aquatic risk assessment in this report considered exposure to fish and aquatic invertebrates, and exposure to algae and aquatic plants from ester formulations only. For the acute assessment, the most sensitive endpoints were maintained:
Esters – fish most sensitive endpoint = 0.23 mg/L
Esters – aquatic invertebrates most sensitive endpoint = 1.04 mg/L
All forms – algae/aquatic plants most sensitive endpoint = 0.3 mg/L

The current Australian freshwater trigger value for 2,4-D acid for the protection of aquatic ecosystems is 0.28 mg/L. This moderate-reliability trigger value, which was calculated using a statistical distribution approach with an application factor of 10.2, is based on aquatic animal data as no acceptable aquatic plant toxicity data were identified (ANZECC/ARMCANZ, 2000). The data available in this assessment indicate close agreement with the established ANZECC trigger value.

Exposure was considered from two routes, aerial and ground based application. For algae/aquatic plants, while the endpoint is the same for both esters and salt formulations, application rates may vary depending on the type of application. Therefore, risk to algae/aquatic plants was considered based on exposure from the maximum ester application rate.

Registered uses of 2,4-D products and application rates for the ester formulations are summarised in Tables 29 below. Table 29 shows a maximum ground broadcast field rate for ester formulations of 4500 g ae/ha (pastures – non legumes, rights of way, industrial) with a corresponding aerial rate of 3180 g ae/ha.

With the exception of turf/pasture, sugar cane and peanuts, broadcast application rates are 1620 g ae/ha (potatoes, next is 1140 g ae/ha for harvest aid) or less for 2,4-D ester labels.

#### *4.3.6.2 Statement of uncertainties*

There are areas of uncertainty in the terrestrial and the aquatic risk assessments that could potentially cause an underestimation of risk.

1. Several products contain 2,4-D present as a mixture, for example, formulated products may include 2,4-D with other active constituents such as ioxynil, dicamba and/or mecocrop. The risk assessment only focussed on 2,4-D and any additive or synergistic effect from the mixture, or individual toxicity characteristics of other active constituents have not be considered.
2. This assessment accounts only for exposure to 2,4-D, but not to its metabolites. In the event that metabolites are also toxic, the risk may be underestimated.
3. Full data sets were not available for all forms of 2,4-D. While significant information exists on the 2,4-D acid, 2,4-D DMA and 2,4-D EHE, outside these there are significant data gaps in many areas, eg, non-target terrestrial arthropods. While the chemicals tested have been used as surrogates for non-

tested 2,4-D forms, this is an area of uncertainty where the risk may be underestimated.

4. For non-target terrestrial plants, a single value has been chosen to be protective of 95% of species regardless of whether application is through an ester or salt form of 2,4-D. The validity of this assumption may be questioned, particularly for run-off exposure where the extent of run-off is a function of solubility. However, the view has been taken that esters, while significantly less soluble than 2,4-D acid, will hydrolyse quickly to the acid form in moist soils. Where application is made to dry soils, this assumption may be incorrect although it is largely supported by field evidence where soil half-lives for 2,4-D EHE ranged from 0.34-12.9 days with an average of 3.1 days (29 observations). The majority of results (27 observations) resulted in half-lives of 5.2 days or less, and an average of 2.5 days.

The aquatic refined assessment is conducted first as there are worst case spray drift calculations performed in this section that will be used and refined further in the terrestrial assessment.

In the first instance, the predicted environmental concentrations (PEC) will be based on these maximum application rates, with exposure to be considered through spray drift. To predict spray drift, AgDrift will be used for aerial application, and drift data from Rautmann *et al*, (2001) used for ground based equipment.

The following assumptions have been used in running this model based on the label information and in accordance with the work of Woods and Dorr (2000):

**Table 10: AgDrift Input Paramaters**

| | |
|---|---|
| Aircraft type | AT502 |
| Boom height | 3 m |
| Flight lines | 25 |
| Swath width | 20 m |
| Swath displacement fraction | 0.5 |
| Wind speed | 4.2 m/s (15 km/h) |
| Wind direction | 90° |
| Temperature | 30°C |
| Relative humidity | 50% |
| Spray volume | 20 L/ha |
| Surface roughness | 0.0075 |
| Droplet size | BCPC Fine – $Dv_{0.5}$ 183.09 μm |

Labels for the ester suggest 10-90 L water/ha for aerial application. A value of 20 L/ha has been chosen for modelling purposes, and a fine droplet size is expected.
Drift exposure to a stream/water body 3 m wide with a depth of 15 cm is assumed.

**Table 11: Registered Use Patterns by Formulation Type.**

| | **2,4-D Ester Products** | |
|---|---|---|
| | EHE | Short Chain[1] |
| **Broadcast Use Patterns** | | |
| Preparatory spray – fallows & seed beds | No | No |
| Cereals (Barley, Wheat, Cereal rye, Triticale) | Yes | Yes |
| Oats | No | Yes |
| Harvest Aid[2] | Yes | Yes |
| Stubble/Fallow[3] | Yes | Yes |
| Maize, sweetcorn, sorghum, saccaline, broom millet, millet, grain sorghum | No | No |
| Improved Pastures containing clover | Yes | Yes |
| Pasture – Non-legume, Rights of Way, Industrial | Yes | Yes |
| Pasture – direct drilling or surface sowing | Yes | Yes |
| Pasture – spray graze techniques | No | No |
| Sugar cane – post emergence | Yes | Yes |
| Sugar cane – pre emergence | No | Yes |
| Peanuts | No | No |
| Rice | No | Yes |
| Carribean and Common Stylo forage and seed crops | No | Yes |
| Potatoes – Pre-harvest | Yes | No |
| Citrus | No | No |
| Pears | No | No |
| Turf, Lawns, Playing fields | No | No |
| **Aquatic** | No | Yes |
| **Other Use Patterns** | | |
| Spot spraying – all situations | Yes | Yes |
| Bananas | No | No |
| Timber regrowth control | No | No |
| Home lawn | No | No |

1. Includes 2,4-D Ethyl Ester; Butyl Ester; Ethyl/Butyl Ester mixtures and Isobutyl Ester.
2. On Ester labels, includes winter cereals only. Includes maize and sorghum on amine salt labels.
3. On Ester labels, includes winter cereals, Maize, Peanuts, and Sweetcorn.

**Table 12: Maximum Registered Application Rate for Broadcast Use Patterns by Formulation Type (g ae/ha)**

| | **2,4-D Ester Products** | |
|---|---|---|
| | EHE | Short Chain[1] |
| **Broadcast Use Patterns** | | |
| Preparatory spray – fallows & seed beds | | |
| Cereals (Barley, Wheat, Cereal rye, Triticale) | 540[2] | 560 |
| Oats | | 376 |
| Harvest Aid | 1140 | 1120 |
| Stubble/Fallow spray | 540 | 540 |
| Maize, sweetcorn, sorghum, saccaline, broom millet, millet, grain sorghum | | |
| Improved Pastures containing clover | 540 | 560 |
| Pasture – Non-legume, Rights of Way, Industrial | 4500[3] | 4500[3, 4] |
| Pasture – direct drilling or surface sowing | 3180 | 3200 |
| Pasture – spray graze techniques | | |
| Sugar cane – post emergence | 1620 | 2400 |
| Sugar cane – pre emergence | | 3200 |
| Peanuts | | |
| Rice | | 800 |
| Carribean and Common Stylo forage and seed crops | | 1040 |
| Potatoes – Pre-harvest | 1620 | |
| Citrus – to avoid early fruit fall | | |
| Pears – to avoid early fruit fall | | |
| Turf, Lawns, Playing fields | | |
| **Aquatic** | | 3200 |

1. Includes 2,4-D Ethyl Ester; Butyl Ester; Ethyl/Butyl Ester mixtures and Isobutyl Ester.
2. Three labels (56117, 53817 and 54813) have a maximum rate of 2220 g ae/ha while 2 labels (55923 and 42229) have the maximum rate above. The lower value in this case was chosen as the three labels with the higher rate appear less standard and should be reviewed separately.
3. This is the maximum rate for ground application. The maximum rate for aerial spraying is 3200 g ae/ha.
4. A higher rate of 3520 g ae/ha is registered for use in Victoria only on some labels.

Based on calculations for both ester and salt formulations with the parameters from Table 10, AgDrift calculates drift at 20, 50 and 100 m downwind to be around 21, 12 and 7% respectively.

### *Risk from Drift*

#### *Aerial Application (ester formulations)*

The following Q values were obtained for ester formulations:

**Table 13: Q values to aquatic organisms from exposure to ester formulations at the highest aerial field rate of 3200 g ae/ha**

| Buffer zone | Drift (%) | PEC (mg/L) | $Q_{fish}$ | $Q_{aquatic\ invertebrates}$ | $Q_{algae/aquatic\ plants}$ |
|---|---|---|---|---|---|
| 20 | 20.1 | 0.44 | 1.91 | 0.42 | 1.47 |
| 50 | 12.0 | 0.26 | 1.13 | 0.25 | 0.87 |
| 100 | 7.2 | 0.15 | 0.65 | 0.14 | 0.50 |
| 200 | 3.7 | 0.08 | 0.35 | 0.08 | 0.27 |
| 300 | 2.0 | 0.043 | 0.19 | 0.04 | 0.14 |
| 400 | 1.18 | 0.025 | 0.11 | 0.02 | 0.08 |

Fish are the most sensitive aquatic organisms. AgDrift predicts that an acceptable Q value to fish will be achieved with a 400 m buffer zone where drift will be around 1.18%, the PEC will be around 0.025 mg/L, and the Q value around 0.11.

**Impact on reducing application rates**

The next highest application rates for ester formulations potentially applied by air (apart from aquatic uses that are considered separately) are 1620 g ae/ha for pre-harvest preparation for potatoes and 1140 g ae/ha for harvest aid uses.

AgDrift predicts that as the application rate reduces, the level of drift (all other things being equal) increases. For example, at 400 m downwind, the level of drift from the peanuts and the harvest aid/salvage spray rate are 2.1% (PEC 0.023 mg/L) and 2.5% (PEC 0.019 mg/L) respectively. Corresponding $Q_{fish}$ values are 0.1 and 0.08 respectively, suggesting that at application rates above 1000 g ae/ha, a buffer of 400 m would be needed.

**Impact of droplet size**

Increasing droplet size in the AgDrift Model gives a good indication of reduction in drift rate with buffer zones. Revised drift values have been calculated by changing the parameters to a BCPC medium droplet (median diameter 300 µm) and a BCPC coarse droplet (median diameter 402 µm) with application in 30 L water/ha. The following results were obtained for fish:

**Table 14: Q values to aquatic organisms from exposure to ester formulations at the highest aerial field rate of 3200 g ae/ha with medium and coarse droplet sizes.**

| | Medium Droplets | | | Coarse droplets | | |
|---|---|---|---|---|---|---|
| Buffer zone | Drift (%) | PEC (mg/L) | $Q_{fish}$ | Drift (%) | PEC (mg/L) | $Q_{fish}$ |
| 50 m | 4.26 | 0.091 | 0.4 | 1.91 | 0.041 | 0.18 |
| 100 m | 2.4 | 0.051 | 0.22 | 0.93 | 0.020 | 0.09 |
| 150 m | 1.64 | 0.035 | 0.15 | | | |
| 200 | 1.14 | 0.024 | 0.10 | | | |

These results suggest the best way to reduce drift is to increase droplet size. A Q value to aquatic organisms is within acceptable limits at 100 m downwind with a median droplet size of 400 µm at the highest aerial application rate of 3200 g ae/ha.

Modelled values should only be used as a guide. With this type of screening level assessment, alteration of a number of input parameters will impact the result of the model. For example, the water body characteristics used are not representative of water bodies exposed from all the different terrestrial cropping situations for which 2,4-D is registered for. If an exposed stream 3 m wide had a depth of 50 cm, the PEC with a coarse droplet size at 100 m would be 0.006 mg/L (Q = 0.03).

#### Further mitigation arguments

It is worth considering the end-point used for fish toxicity was a non-reviewed result for the butyl ester form of 2,4-D. Based on several non-reviewed results and one non-standard test for the ethyl ester, the BE and EE forms appear much more toxic to fish than the 2,4-D EHE. The latter compound generally showed no treatment related effects up to its level of solubility. One study run for 8 days determined a 96 h LC50 of 3.12 mg ae/L and an 8-day LC50 of 2.03 mg ae/L. Using the 8-day value, the Q value to fish would be acceptable at 100 m with a fine droplet spray. The PEC of 0.21 mg/L and the most sensitive endpoint for fish from 2,4-D EHE of 2.02 mg/L results in a Q value of 0.1. Nonetheless, the 100 m buffer with coarse droplets would still be necessary to protect algae/aquatic plants, based on the derived endpoint of 0.3 mg/L.

#### Conclusion

To mitigate potential risk to algae/aquatic plants from exposure resulting from spray drift of 2,4-D from ester formulations, products should be applied with a median droplet diameter of 400 µm or more, corresponding to a BCPC Coarse droplet size, and a buffer zone of 100 m between field edges and downwind water bodies should be maintained.

This is considered to be adequately protective for amphibians and sediment dwelling organisms as well as those exposed only through the water column.

### *Ground Application (ester formulations)*

There are German studies (Rautmann *et al*, 2001) of drift trials carried out in field crops (including some vegetables) and orchards. Some of these were done on bare ground with other on cereals during late growth stages. In previous trials of this nature (Ganzelmeier *et al*, 1995), the applied amount of fluid was adjusted to be 300 L/ha at a driving speed of 6 km/h and pressure ranging from 2.4-2.5 bar (240-250 kPa). This is assumed to be the case for the latest trials included in this paper.

Estimates for drift are given as the 90th percentile of mean values, quoted as % of the application rate. In the following table (Table 34) these estimated drift percentages are shown at given distances from field crops. The PEC values have been calculated based on the predicted drift entering a water body of surface area 1 ha and depth 15 cm. The rate of application has been defined as 4500 g ac/ha. Table 32 provides drift values along with corresponding PECs and Q-values for a range of buffer zones:

**Table 15: Q values to aquatic organisms from exposure to ester formulations at the highest field rate of 4500 g ae/ha**

| Buffer zone (m) | Drift (%) | PEC (mg/L) | $Q_{fish}$ | $Q_{aquatic\ invertebrates}$ | $Q_{algae/aquatic\ plants}$ |
|---|---|---|---|---|---|
| 5 | 0.41 | 0.012 | 0.05 | 0.01 | 0.04 |
| 10 | 0.20 | 0.006 | 0.03 | 0.006 | 0.02 |

The risk to aquatic organisms from 2,4-D Ester formulations resulting from drift from ground based application equipment is acceptable without a need for a buffer zone.

### *Aquatic Use Pattern*

Several products using the short chain ester forms of 2,4-D are registered for aquatic use. The ester labels have this use pattern; in the Directions for Use under "Aquatic Areas" as a specific use pattern for control of water hyacinth. The maximum registered rate for esters is 3200 g ae/ha.

#### Direct Application

Direct application at the highest rate to water bodies 15 cm deep will result in water concentrations up to 2.2 mg/L. Using the endpoints for aquatic organisms in Tables 13, 14 and 15, the following Q values are obtained for ester formulations:

**Table 16: Aquatic Q-values for direct application to water at 3300 g ae/ha.**

| | Fish | Aquatic Invertebrates | Algae/Aquatic Plants |
|---|---|---|---|
| 2,4-D Esters | 9.6 | 2.11 | 7.3 |

These results show that 2,4-D esters will pose an unacceptable risk to these organisms. DEH have advised that use of esters for aquatic weed control should be discontinued, based on their much higher toxicity to aquatic organisms.

### *Non Broadcast Use Patterns*

Application in these situations is unlikely to involve significant exposure to aquatic areas. Some drift exposure may occur. However, this is unlikely to be at levels resulting in adverse impacts to nearby aquatic areas.

## ***Risk from Run-Off***

### *Broadcast Use Patterns*

Risks from run-off was considered for 2,4-D acid only, due to the rapid conversion of 2,4-D esters to the acid in moist soils through hydrolysis. The amount of run-off is difficult to predict as it is dependent on many factors such as meteorological conditions, agricultural practices, hydrological aspects, rainfall intensity, formulation type and infiltration capacity.

In a review of pesticides in run-off and surface waters, Burgoa and Wauchope (1995) concluded that pesticide losses under "normal" rainfall conditions account for 0.5% of the amount applied. However, in this review, they pointed to literature showing that while losses are typically 0.5% or less, they can be up to 5% or more under worst case conditions.

Table 12 above lists the maximum registered use rates for 2,4-D, and depending on the form of 2,4-D and use pattern, applications range form 300 to 4500 g ae/ha. Q-values based on runoff of 5 and 1% from a ten hectare catchment area to a pond with a surface area of one hectare and depth of 15 cm for algae/aquatic plants are shown below:

**Table 17: Q values to Non-Target Vegetation from Run-off of 2,4-D**

| | 5% run-off | | 1% run-off | |
|---|---|---|---|---|
| Application rate (g ae/ha) | EEC (mg/L) | Q | EEC (mg/L) | Q |
| 500 | 0.17 | 0.57 | 0.03 | 0.1 |
| 1000 | 0.33 | 1.1 | 0.07 | 0.23 |
| 2000 | 0.66 | 2.2 | 0.13 | 0.43 |
| 2200 | 0.73 | 2.4 | 0.15 | 0.5 |
| 2750 | 0.92 | 3.1 | 0.18 | 0.6 |
| 3200 | 1.1 | 3.7 | 0.22 | 0.73 |
| 4500 | 1.5 | 5.0 | 0.30 | 1.0 |

It is clear from these results that even at 1% run-off, a potential risk exists to aquatic organisms from exposure to 2,4-D in run-off. Work has been done to try and quantify the amounts of chemical in run-off. The model described by Birkved and Hauschild (2003) was chosen for this risk assessment as it considers the Koc of the chemical and calculates the fraction of applied chemical likely to run-off with consideration of soil type (based on sand content), slope of fields and rainfall. An additional formula is provided to account for the dissolved fraction of pesticide in run-off waters. Applying this model using the lowest Koc (34) found for 2,4-D, rainfall of 50 mm, a slope of 3%, a medium soil type (sand content between 45-85%) and 1% OC, the model predicts 0.57% will run-off. The majority of this (75%) is predicted to be in solution.

The model uses a 10:1 catchment area (10 ha running off to 1 ha). The volume of receiving water was set at 4500 $m^3$ (4.5 ML) to account for excess runoff entering the previously existing shallow water body. With a maximum application rate of 4500 g ae/ha, the model predicts the concentration in receiving waters will be 0.042 mg/L, resulting in a Q value of 0.14. This is approaching acceptable limits.

Within the confines of this model, application rates of 3200 g ae/ha or less would result in an acceptable Q-value to aquatic organisms. The only use patterns registered at rates higher than this are for the 2,4-D EHE products with application to pastures at 4500 g ae/ha and the 2,4-D Na salt product registered for use on sugar cane at 3640 g ae/ha. These two uses would result in Q values based on the above model of 0.14 and 0.11 respectively, both being considered a marginal risk only.

This model is sensitive to changes in factors such as slope and soil type. For example, a flatter slope of 1% results in total predicted run-off of 0.19% (0.14% in solution) . This low level would result in an EEC of 0.014 mg/L and an acceptable Q value (0.05) even at the highest application rate of 4500 g ae/ha.

Donald *et al* 2005 describes mobilization of pesticides on an agricultural landscape flooded by a torrential storm. The Vanguard area of southeastern Saskatchewan, Canada, was subjected to a torrential storm in July 2000 that produced as much as 375 mm rain in an 8-hour period. In the previous 45 days, some 96 mm had been recorded, so chances were the soil was fairly moist, thereby reducing capacity for infiltration. The majority of herbicides would have been applied to crops in this area during the four weeks preceding the storm. After the storm, 19 herbicides and insecticides were detected in flooded wetlands, with 14 of the detected in 50% or more of wetlands (2,4-D was found in 100% of wetlands tested). Average concentrations of 2,4-D were 362 ng/L, with the authors stating that the pesticides were probably from long-range transport, followed by deposition in rain and from application to crops within the area subjected to the storm (1700 km$^2$). Interestingly, in the following year when only 62 mm of rain fell in the same 45 day period, only five pesticides were detected in 50% or more of wetlands. One of these was 2,4-D, found in 100% of wetlands at an average concentration of 535.6 ng/L (0.00054 mg/L). The higher levels of 2,4-D detection with the much lower rainfall is possibly due to much less dilution than from the large storm event. It is difficult to correlate these values to a percentage of run-off. However, if these values are taken as indicative of concentration levels in Australian receiving waters after run-off events, then an acceptable risk to aquatic organisms is predicted (Q-values to algae/aquatic plants of <0.01 based on a water concentration of 0.00054 mg/L). Modelling predictions supported by field measurements following storm events indicate that risk to aquatic organisms through run-off is acceptable.

*Non-Broadcast Use Patterns*

Application in these situations is unlikely to involve significant exposure to aquatic areas through run-off.

#### 4.3.6.3 Terrestrial Refined Risk Assessment

The refined risk assessment for the terrestrial environment will focus on risk to non-target terrestrial plants.

***Discussion on the end point to be used in the assessment.***

Test data indicate a wide range in sensitivity of plants to 2,4-D in its various forms. The general trend for all studies was that monocots were less susceptible than dicots, although in some cases, monocot species were also extremely sensitive.

As explained in the US EPA report (US EPA 2005), 2,4-D is a plant growth regulator that is absorbed through the roots and foliage within 4-6 hours and distributed throughout the plant via the xylem and phloem. Once in the plant it selectively eliminates broadleaf plants by mimicking the effect of plant growth regulating hormones. This action stimulates growth, which leads to an abnormal growth pattern and death in some plants. Therefore, if even a portion of the surface area of a non-target plant comes into contact with 2,4-D there is a possibility that the plant may be severely damaged or dies as a result. Even if the plant only exhibits minor damage, the damage may be sufficient to prevent the plant from reproducing or competing successfully with other plants for resources, including water. The use of 2,4-D could apply selective pressure against dicots along field edges resulting in changes in species composition.

*Data available for plant germination*

Seedling emergence studies provided for 2,4-D DMA, 2,4-D EHE and 2,4-D BEE tested seed germination by *in vitro* testing where germination was considered as a function of the radicle length. Only the 2,4-D BEE study went on to measure effects on radicle length in the definitive study (still through *in vitro* exposure).

This end-point proved extremely sensitive. Preliminary results from the 2,4-D DMA and 2,4-D EHE test showed both monocots and dicots to have NOELs of 0.07-0.67 g ae/ha, with the exception of two monocot species with NOELs equal or greater to the highest tested rate of 6.7 g ae/ha. The definitive testing for 2,4-D BEE showed radicle length to be affected in both monocots (EC25 values ranging from 0.33-16.8 g ae/ha) and dicots (EC25 values ranging from 0.8-17.6 g ae/ha). For all monocots and dicots, the NOELs were 1 g ae/ha or less with radish being the most sensitive with a NOEL of 0.016 g ae/ha.

Impacts on radicles can potentially have serious consequences for plants. In most dicots the root develops from the radicle (lower end of the embryo). The radicle gives rise to an apical meristem, which continues to produce root tissue for much of the plant's life. By contrast, the radicle aborts in monocots, and new roots arise adventitiously from nodes in the stem. The first indication that the processes of germination have begun is generally the swelling of the radicle. In all cases, the radicle imbibes water rapidly and, bursting the seed coats and other coverings that may be present, starts to grow downward into the soil. This helps to assure that the young seedling has an adequate supply of water and nutrients when the shoot breaks through the surface of the soil (Weier *et al*, 1982). An adverse impact on the radicle could be decisive over longer periods for susceptible plants. For example, more susceptible plants would likely develop weaker initial root systems possibly impacting on their competitiveness and altering population dynamics.

Conversely, it is recognised that the nature of the seed germination tests exaggerates the activity of 2,4-D. The seeds were germinated *in vitro* and exposed constantly to the chemical. Since 2,4-D is taken up by roots and moves systemically in the plant, exposure to a continuous low concentration of the compound can lead to accumulated and resultant plant growth effects. It is accepted that these effects will probably not be as pronounced in the field due to greater chance for dissipation and hence non-continuous exposure. However, drift/volatilisation exposure to non-target susceptible native vegetation is of concern and these effects should not be ignored.

Given the uncertainty associated with extrapolating the *in vitro* results to a realistic exposure concentration in the field, the refined assessment did not include the available data on radicle length. However, the conclusions of the refined assessment were formulated to take into account any possible effects on this end-point.

### *Utilisation of the range of data*

In the preliminary assessment, only the most sensitive results were considered along with a single high drift rate of 5% from the maximum application rate of 4500 g ae/ha. For the refined assessment, given the wide range of data available and the wide range of application rates possible, this is not an appropriate method.

### *Use of a single NOEL value for determining an acceptable deposition from drift*

In total, 110 NOEL values were used for the analysis. Data were log transformed. In many instances, NOELs could not be defined either because there were no effects at the highest treatment rate (17 observations, or 15.5% of observations), or because effects statistically different to the controls were found at the lowest rate tested (9 observations, or 8.2% of observations). These censored data were dealt with as follows:

### *Left Censored Data*

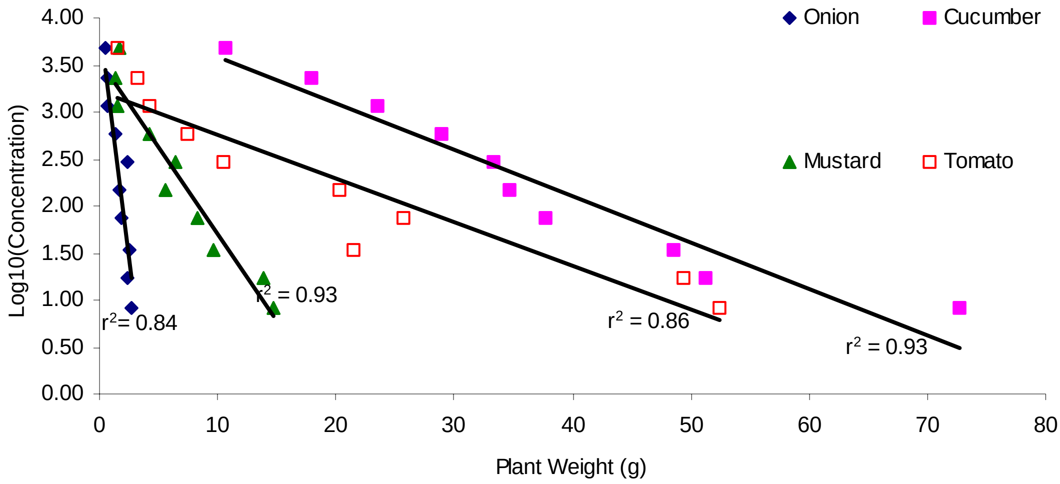
Vegetative vigour tests with 2,4-D acid resulted in four NOEL results being left censored data, that is, a NOEL was unable to be determined due to significant effects even at the lowest tested concentration.

To try and use more meaningful values in the risk assessment for these data, DEH has further analysed the raw data results. In many cases, values were difficult to read in the test report. However, best efforts were made to use the data where possible.

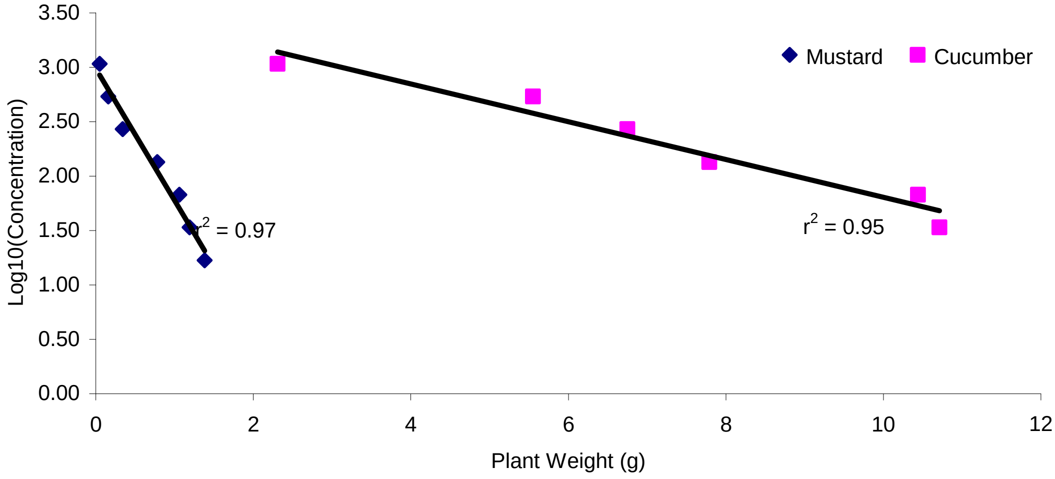
Onion (a monocot), cucumber (dicot), mustard (dicot) and Tomato (dicot) all had NOELs lower than the lowest treatment rate. Similarly for the 2,4-D DMA vegetative vigour studies, results for mustard and cucumber were left censored and were further analysed by considering the raw data.

In all cases, plotting Log[concentration] against weight (g) resulted in good linear dose-response relationships. The pooled control values were used for comparison, and an EC05 value used as the NOEL. The following data plots were obtained:

**EC05 from Left Censored Data - 2,4-D Acid**



**EC05 from Left Censored Data - 2,4-D DMA**



Based on the regression equations, the NOELs were determined as follows.

**Table 18: Extrapolated EC05 values for Left Censored Data**

| | Onion | Cucumber | Mustard | Tomato | Mustard | Cucumber |
|---|---|---|---|---|---|---|
| Pooled control (Weight – g) | 4.05 | 85.02 | 17.83 | 69.9 | 2.28 | 11.5 |
| EC05 (g) | 3.85 | 80.77 | 16.94 | 66.41 | 2.17 | 10.93 |
| **Concentration (g ae/ha)** | **1.3** | **1.2** | **2.8** | **1.3** | **2.3** | **44.1**[1] |
| $r^2$ | 0.84 | 0.92 | 0.93 | 0.86 | 0.97 | 0.95 |

1) This result ignored the apparent outlying results from the 16.8 g ae/ha group. Where these data were included, the NOEL was predicted to be 32.5 g ae/ha, but a much lower correlation co-efficient ($r^2$ = 0.54) was observed.

Additional left censored data were reported for the DEA salt, with 2 values from the seedling emergence study and 1 value from the vegetative vigour study. Unfortunately, no further analysis of these data were possible as the test reports were not provided. All three of these results appeared to have defined EC25 values. The two values from the seedling emergence study were significantly lower than other results available in this study and therefore, should be represented in the overall data set. A representative NOEL for these three results was arbitrarily set at 10% of the value of the defined EC50. This resulted in seedling emergence NOELs of 5 g ae/ha for mustard and buckwheat, and a vegetative vigour NOEL of 0.9 g ae/ha for cucumber.

***Right Censored Data***

A total of 17 NOEL results (15.5%) from the whole data set were right censored data, that is, no effects were found up to the highest level tested. It is not appropriate to disregard the right censored data as they represent the less sensitive results of the distribution. As no definitive value could be assigned to them, it was decided to treat the highest tested rate in each case as the NOEL.

***Analysis of Data Sets***

Data were analysed for the whole data set, and the sub-sets such as plant type, chemical type and test type. The statistical analysis was performed using Microsoft EXCEL to determine the mean and standard deviation of each data set. The NOEL was then determined assuming the data were normally distributed around the mean, and using the 95th percentile as the NOEL (ie, the EC05 of each data set – see Attachment 2 of volume 2, Technical Report). This was based on the formula:
$LOG_{10}NOEL = (z \times \text{Std. dev.}) + \text{mean}$; where $z = -1.645$(95% confidence level).

**Table 19: 95th Percentile NOELs by Data Set (results provided in terms of g ae/ha).**

| | | Test Type | | Chemical Type | | Plant Type | |
|---|---|---|---|---|---|---|---|
| | Whole data set | Seedling emergence | **Vegetative vigour** | Acids and Salts | Esters | Monocots | Dicots |
| No. obs. | 110 | 60 | **50** | 50 | 60 | 40 | 70 |
| Mean | 71.4 | 149.7 | **29.3** | 88.1 | 59.9 | 343.8 | 29.0 |
| Std dev | 9.9 | 8.0 | **9.4** | 15.2 | 6.5 | 6.0 | 7.9 |
| NOEL | 1.6 | 4.9 | **0.73** | 1.0 | 2.7 | 18.2 | 0.97 |

On the basis of this analysis, plants were more susceptible in their post-emergent growth stage. The analysis confirmed the previous observation that dicots were significantly more sensitive than monocots and showed that acid/salt forms of 2,4-D were more toxic to plants at the lower end of the toxicity spectrum than ester formulations.

For the risk assessment from exposure to spray drift, a single representative value will be used. A representative NOEL of 0.73 g ae/ha will be used based on the sensitivity of plants in the vegetative vigour studies. Due to the use of a statistically derived representative NOEL, a Q value (PEC/NOEL) of 1 is considered acceptable. Therefore, an environmentally acceptable level of deposition from drift exposure is 0.73 g ae/ha. This level is not considered too conservative for the following reasons:

1. Full life-cycles of plants including reproductive phases have not been tested. 2,4-D is a plant growth regulator and will therefore impact on the reproductive phase of plants.
2. Potential impacts to seedling germination at levels less than 1 g ae/ha should not be ignored. *In vitro* testing showed NOELs to several species of monocots and dicots of 0.67 and 0.07 g ae/ha based on radicle length. Where seeds are not incorporated into soil (such as expected in native stands of vegetation where seeds more likely remain on the soil surface), impacts on root development can not be ruled out.

### *Risk from Volatilisation*

#### *Broadcast Use Patterns*

Off-target movement from areas to 2,4-D application to non-target crops was a major issue raised in submissions received by the APVMA for this assessment. While there was little in the way of information received for off-target damage to native vegetation, it is unlikely such damage has ever actually been monitored. The reality is that with obvious non-target crop damage, damage to exposed native vegetation may also be expected.

While submissions seem to indicate the damage is through spray drift, it is quite likely that significant damage could actually occur due to volatilization, particularly where the ethyl ester butyl ester and isobutyl ester formulations are used. These shorter chain esters are much more volatile than the longer chain esters and salt forms of 2,4-D. In addition, they persist in the atmosphere for long periods, thereby increasing time and area of exposure.

Guth *et al.* (2004) state that, based on direct measurements, no noticeable volatility can be expected from compounds with a vapour pressure below $10^{-3}$ Pa from soil and $10^{-4}$ Pa from crops, and this is fully confirmed by indirect measurements. The vapour pressures for EHE, EE and BE are $4.8\times10^{-4}$, $1.47\times10^{-1}$ and $5.29\times10^{-2}$ to $8.2\times10^{-3}$ Pa respectively. This suggests that EHE may not volatilise from soil surfaces but may to some extent from crops, while the short chain EE and BE forms are expected to volatilise from both soil and crop surfaces. Further, the calculated Henry's Law Constants indicate the three esters may be moderately volatile to volatile from water bodies.

Australia has no formal model for quantifying volatilization of pesticides from soil or plant surfaces for regulatory use. However, this is an important issue for the short chain volatile esters. There are a number of models available to assess this endpoint.

One such model is the EVA (Exposure Via Air) 2.0 model from Europe, and may have potential for use in a regulatory environment. This model is currently being evaluated through the European Union FOCUS air workgroup, and advice on this model is being sought.
One recent and publicly available model from the Netherlands can be used to give an indication of likely volatilization.

*Volatilization from Crop Surfaces*

In this model, described in van der Linden *et al* (2004), volatilization from plant leaves is calculated as a function of the percentage of the application rate and the fraction intercepted by the crop. Calculations are as follows:

$$\mathrm{Log}(CV_{crop}) = 1.661 + \log(P_{sat})$$

Where:
$CV_{crop}$ = the cumulative volatilization, (% of amount reaching the crop);
$P_{sat}$ = the saturated vapour pressure of the substance, (mPa), $P_{sat} \leq 11.8$ mPa.
Where $P_{sat} > 11.8$ mPa, the cumulative volatilization is taken to be 100%; substances having such a high $P_{sat}$ are not likely to be sprayed on crops.

From this calculation, the total amount of substance volatilized from the crop is calculated according to:

$$E_{crop,\,air} = (CV_{crop} \times f_l \times A)/100$$

Where:
$E_{crop,\,air}$ = the total amount volatilised from the crop (g/ha);
A = the nominal rate for a single application (g/ha)
$f_l$ = the fraction intercepted by the crop, (-); and
100 = factor to convert from % to fraction.
Vapour pressures for the ester forms registered in Australia are as follows:

| 2,4-D EHE | 2,4-D EE | 2,4-D BE |
|---|---|---|
| 0.48 mPa | 147 mPa | 52.9 mPa |

Therefore, $CV_{crop}$ for both EE and BE will be 100% for the calculations.

Calculations on PECs have been performed with the following assumptions. These assumptions are not scientifically based. The results will be used for comparative purposes only between the different ester forms.

1. Crop interception is 50%;
2. The amount of chemical volatilised will be "diluted" in the environment. In this regard, lift-off from one hectare will be assumed to deposit over 10 ha of non-target area.

Based on the above calculations, the $CV_{soil}$ for EHE was calculated to be 7% (100% for EE and BE). The following table shows $E_{crop,\,air}$ values based on different application rates and crop interception of 50%.

**Table 20: Volatilisation from Crops Based on Ester Type and Application Rate.**

| Application rate (g ae/ha) | $E_{crop,\,air}$ - EHE | $E_{crop,\,air}$ - EE | $E_{crop,\,air}$ - BE |
|---|---|---|---|
| 4500 (pastures) | 158 g/ha | 2250 g/ha | 2250 g/ha |

| | | | |
|---|---|---|---|
| 3200 (sugar cane) | 112 g/ha | 1600 g/ha | 1600 g/ha |
| 1620 (potatoes) | 57 g/ha | 810 g/ha | 810 g/ha |
| 1140 (harvest aid/salvage spray) | 40 g/ha | 570 g/ha | 570 g/ha |
| 1040 (forage crops) | 37 g/ha | 520 g/ha | 520 g/ha |
| 800 (winter cereals) | 28 g/ha | 400 g/ha | 400 g/ha |
| 560 (winter/summer cereals) | 20 g/ha | 280 g/ha | 280 g/ha |

### *Volatilization from Soil Surfaces*

2,4-D will often be applied to bare soil. However, evidence indicates the esters will rapidly hydrolyse to 2,4-D acid (half-lives <1.5 hours in laboratory testing) thereby limiting their availability for volatilization from this route.

Given this, only exposure from volatilization from crop surfaces will be considered in more detail below.

### *Calculation of Risk Quotients*

From the calculations in Table 20 above, a Q value for non-target plants can be derived by “diluting” these values over a 10:1 area ratio, and comparing to the generic endpoint of 0.73 g ae/ha discussed above.

The following Q values were derived:

**Table 21: Q values for Different 2,4-D Esters to Non-Target Terrestrial Plants**

| Application rate (g ae/ha) | Q values- EHE | Q values - EE | Q values - BE |
|---|---|---|---|
| 4500 (pastures) | 21.6 | 308 | 308 |
| 3200 (sugar cane) | 15.3 | 219 | 219 |
| 1620 (potatoes) | 7.8 | 111 | 111 |
| 1140 (harvest aid/salvage spray) | 5.5 | 78 | 78 |
| 1040 (forage crops) | 5.1 | 71 | 71 |
| 800 (winter cereals) | 3.8 | 55 | 55 |
| 560 (winter/summer cereals) | 2.7 | 38 | 38 |

These calculations demonstrate the much greater risk posed to non-target vegetation from the shorter chain esters. Of further concern is their persistence, with modelling suggesting the atmospheric half-life in air of 2,4-D ethyl ester is in the order of 2 days. The atmospheric half-life in air for 2,4-D BE is around 1.7 days. For a chemical that migrates significantly through air, its half-life in air should be greater than 2 days (POPs screening criteria). Therefore, both these chemicals may be anticipated to travel long distances in the environment through air.

Characteristic travel distance (CTD) is a useful way of predicting the distance a chemical may travel in an environmental medium (water or air). It uses the concept of overall persistence in the environment ($P_{ov}$), a parameter that needs to be modelled, and considers the fraction of the chemical in the medium of interest. Absolute values are not considered appropriate in this case due to the large number of assumptions made in the modelling. However, the outcome in terms of ranking the chemicals relative to each other for their potential to move through the atmosphere is considered useful. Beyer and Matthies (2002) describe methodology for calculating CTD as:

$\text{CTD} = \mu \text{ X } M_m/M_{tot} \text{ X } P_{ov}$

Where:
$\mu$ = flow velocity of the medium (eg, wind speed);
$M_m$ = mass of chemical in the medium (in this case air);
$M_{tot}$ = total mass of chemical;
$P_{ov}$ = overall persistence in the environment.

The velocity $\mu$ is simply a linear factor transforming the residence time into a measure in units of a length. The aim of this exercise is to demonstrate the propensity of the short chain esters to travel in relation to the longer chain, less volatile ester. Therefore, $\mu$ will simply be taken as 1 in the equation as it is the ranking of the chemicals, not absolute values that are of interest.

For illustrative purposes, the overall persistence of 2,4-D EE, BE and EHE have been modelled by the Level III fugacity model from the US EPA PBT Profiler (www.pbtprofiler.net). Fractions of chemical in the air ($M_m/M_{tot}$) are taken from calculations already described above. Based on this, the following results were found:

| Chemical | 2,4-D EHE | 2,4-D EE | 2,4-D BE |
|---|---|---|---|
| $P_{ov}$ (days) | 168 | 59 | 65 |
| $M_{air}/M_{tot}$ | 0.07 | 1 | 1 |
| CTD (km) | 11.8 | 59 | 65 |

In terms of ranking, it is predicted that 2,4-D EE and 2,4-D BE will move through the atmosphere more than five times the distance of the longer chain, less volatile 2,4-D EHE.

This is of particular concern given the very sensitive nature of non-target terrestrial plants (including both native vegetation and non-target crops) to these substances. The WHO review of 2,4-D (IPCS, 1989) stated that the highly volatile ethyl, isopropyl, and butyl esters are being replaced by low-volatile esters or by amine salts to reduce crop damage resulting from 2,4-D vapour drift, and to decrease atmospheric pollution. This does not appear to have happened in Australia, however, the evidence from this risk assessment suggests this is a highly appropriate course of action. The issue of persistence in the atmosphere, high volatility and potential to travel long distances in the environment along with their toxicity to non-target vegetation makes it very difficult to mitigate the risk from these compounds.

### *Aquatic Use Patterns*

A measure of a chemicals propensity to move from water to the surrounding air may be made by its Henry's Law Constant. Based on the scale provided by Mensink *et al* (1995), chemicals are moderately volatile from water where their Henry's Law Constant is between $2.45 \times 10^{-7}$ – $7.34 \times 10^{-4}$ atm.m$^3$/mol, and highly volatile at $>7.34 \times 10^{-4}$ atm.m$^3$/mol. Henry's Law Constants for the short chain esters are $3.25 \times 10^{-7}$, $4.88 \times 10^{-7}$ and $1.25 \times 10^{-7}$ atm.m$^3$/mol for ethyl ester, butyl ester and isobutyl ester respectively, indicating they may be moderately volatile from water bodies. Henry's Law Constant for 2,4-D EHE is $1.81 \times 10^{-4}$ atm.m$^3$/mol, a value indicative of moderate volatility from water bodies. This is a concern for the use of esters in aquatic situations, including 2,4-D EHE, although in Australia, this chemical is not registered for aquatic uses.

### *Non Broadcast Use Patterns*

No further assessment has been undertaken for this aspect. Volatility aspects of the chemicals discussed above for broadcast use patterns are transferable to non-broadcast use patterns.

### 4.3.7 Conclusions

#### *4.3.7.1 Preliminary Environmental Risk Assessment –2,4-D (all forms)*

Preliminary calculations using worst-case exposure showed that risks to birds, terrestrial invertebrates (2,4-D salt forms), soil dwelling invertebrates and soil microorganisms were acceptable with the registered uses and forms of 2,4-D. Risks to fish and aquatic invertebrates were considered acceptable when exposed to 2,4-D in its acid or salt forms under worst case exposure conditions. There were insufficient data to adequately characterise risk to terrestrial invertebrates from 2,4-D esters.

The preliminary assessment showed an unacceptable risk to non-target terrestrial vegetation and to fish and aquatic invertebrates through exposure to ester forms of 2,4-D. Additionally, risks to aquatic plants and algae were shown to be unacceptable to 2,4-D in all its forms, based on worst case exposure. These end points were therefore considered in more detail in the refined risk assessment.

#### *4.3.7.2 Refined Environmental Risk Assessment – 2,4-D (volatile esters)*

The refined aquatic risk assessment showed an acceptable risk to fish, aquatic invertebrates and algae/aquatic plants from ester forms of 2,4-D where aerial application for terrestrial use patterns used coarse spray droplet sizes (median droplet diameter of 400 μm) and a buffer zone of 100 m between treated areas and downwind water bodies was maintained. This was considered to be protective to amphibians and sediment dwelling organisms as well as those exposed only through the water column. Using ground application, risk to aquatic organisms was considered acceptable without the need for downwind buffer zones.

The refined aquatic risk assessment for aquatic uses identified an unacceptable risk to all aquatic organisms from use of ester products.

Ground application for broadcast uses of 2,4-D esters were modelled for (Physical Spray Drift) and demonstrated that buffer zones of 100 m with the use of coarse droplet sizes should be protective for non-target vegetation for the majority of the use patterns.

An assessment of volatilisation determined that the short chain esters may result in a high risk to non-target terrestrial vegetation through long range transport and their persistence in the atmosphere. The longer chain EHE is less of a risk through this route. Further, the ester forms are expected to be moderately volatile to volatile from water.

Risks from run-off were difficult to model in any meaningful way given the range of possible application rates, use patterns and potentially different site characteristics. However, it was demonstrated that a potential risk to non-target plants from this exposure route could exist in certain conditions. For example, sites with larger slopes, less sandy soils or soils with lower organic carbon contents will have more run-off than flatter, sandier and higher organic carbon soils. Some of these may result in sufficient run-off to cause adverse effects in stands of non-target vegetation.

Risks to non-target terrestrial plants and aquatic organisms from non-broadcast use patterns are considered acceptable.

### 4.3.8 Recommendations

Following the risk assessment, the DEH has made the following recommendation:

1. **Short chain ester forms.** Due to the propensity of the short chain esters to volatilise and persist in the environment thereby causing off target damage, DEH recommends to the APVMA that they NOT be satisfied that continued use of or any other dealings with the constituent or products containing 2,4-D Ethyl Ester, 2,4-D Butyl ester or 2,4-D isobutyl ester in accordance with the instructions for use, would not be likely to have an unintended effect that is harmful to animals, plants or thing or to the environment.

# 5. OVERSEAS REGULATORY STATUS

In recent years, comprehensive reviews of 2,4-D have been conducted internationally. Largely, the data have been generated by the Industry Task Force II of 2,4-D Research Data, an industry funded co-operative that was initially established to satisfy US regulatory requirements.

High volatile esters have not been registered for use in North America or Europe for some time.

## 5.1 UNITED STATES

The United States Environment Protection Agency (USEPA) released its Reregistration Eligibility Document (RED) for 2,4-D (salts and low-volatile esters) in 2005. EPA determined that all products containing 2,4-D as the active ingredient are eligible for reregistration, provided changes specified in the 2,4-D RED are incorporated into the labels. The US EPA has also called for further data in relation to the Agency's Endangered Species Protection Program. There will therefore be a further review of 2,4-D in the near future in relation to risks to specified endangered species.

## 5.2 CANADA

The Pesticide Management Regulatory Authority (PMRA) re-evaluation of 2,4-D (salts and low volatile esters) has been split into two parts: review of the turf uses, which was announced in 2000, and review of the agricultural uses, which was targeted for completion in 2005. The PMRA has not yet finalised its review of 2,4-D of agricultural uses. The re-evaluation of lawn and turf uses of 2,4-D has determined that 2,4-D can be used safely on lawn and turf when label directions are followed, and is therefore proposing continued registration of 2,4-D for these uses.

## 5.3 UNITED KINGDOM

In 1993, the Pesticides Safety Directorate released a review report on 2,4-D and its salts and esters. It is evident from the report recommendations that significant gaps existed in the evaluated data. The report recommended additional data requirements, including toxicity/operator exposure, methods of analysis, physical properties, storage stability, monitoring of toxic impurities (dioxin), residues in food and crop metabolism, as well as studies on environmental fate and impacts on wildlife. Despite the deficiencies in the data, it was recommended that all approvals be allowed to continue while data requirements were generated and evaluated. Currently, the Pesticides Safety Directorate has national regulations that implement the directives and Maximum Residue Limits (MRLs) set by the European Commission in 2002.

## 5.4 EUROPE

The European Commission Standing Committee on Plant Health completed a re-evaluation of the active 2,4-D in October 2001. The effects of 2,4-D on mammalian toxicology, environment fate and behaviour, ecotoxicology and residues were assessed as a part of the re-evaluation process. The evaluation concluded that it may be expected that plant protection products containing 2,4-D will satisfy the safety requirements of the Council Directive. The commission concluded that residues arising from the proposed uses have no harmful effect on human or animal health and no unacceptable effects on the environment subject to conditions outlined in its re-evaluation. The review also identified several acceptable exposure scenarios for operators, workers and bystanders. The findings of the review are subject to the condition that active constituents are manufactured to a standard where the manufacturing impurities dioxins and furans are kept below detectable levels. The use of 2,4-D in Denmark has been restricted for environmental reasons. The registrations for the use of 2,4-D in Sweden and Norway were withdrawn as the market size did not warrant further data investment.

### 5.5 JMPR

The Joint WHO/FAO Meeting on Pesticides Residues (JMPR) conducted extensive reviews of 2,4-D in the 1970s, 1984, 1989 and more recently in 1996, 1997 and 1998. The 1996 review concluded that the toxicity of the salts and esters of 2,4-D was comparable to that of the acid. Accordingly, the ADI and NOEL reflected a combined exposure to the analogues. It also concluded that 2,4-D and its salts and esters do not appear to be genotoxic. The WHO concluded in 1998 that the intake of residues of 2,4-D resulting from the uses considered by JMPR is unlikely to present a public health concern in the long term. The 2000 JMPR meeting concluded that the intake of 2,4-D residues was unlikely to present a risk to consumers in the short-term.

## 6 PROPOSED REVIEW RECOMMENDATIONS

After consideration of all data for the environmental fate and eco-toxicology assessment for the active constituents 2,4-D ethyl ester, 2,4-D butyl ester and isobutyl ester, forms), the APVMA proposes to find that it is NOT satisfied that continued use or any other dealing with these active constituents or products containing these active in accordance with the instructions for their use, would not be likely to have an unintended effect that is harmful to animals, plants or things or the environment.

This finding is based on the propensity of the high volatile (short chain) esters to volatilise and persist in the environment (atmosphere) thereby causing off-target damage. The APVMA proposes the following regulatory actions for 2,4-D high volatile(short chain) esters:

### 6.1 CANCEL APPROVALS OF THE ACTIVE CONSTITUENT

All active constituent approvals for the active constituents (2,4-D ethyl ester, 2,4-D butyl ester and 2,4-D isobutyl ester), as listed in (Attachment A, Table 1) be **cancelled.**

### 6.2 CANCEL PRODUCT REGISTRATIONS AND ASSOCIATED LABEL APPROVALS

As all the active constituent approvals for 2,4-D ethyl ester, 2,4-D butyl ester or 2,4-D isobutyl ester are to be cancelled the Agvet Code requires that all product registrations containing those active constituents and all associated labels, as listed in (Attachment A, Table 2) must also be **cancelled.**

### 6.3 PROPOSED REGISTRATION CANCELLATION AS AN OUTCOME OF REVIEW FINDINGS

As a consequence of the proposed findings of this review to find that products (containing 2,4-D ethyl ester, 2,4-D butyl ester or 2,4-D isobutyl ester) and associated labels registered subsequent to the review commencement and therefore subject to the outcomes of the review, as listed in (Attachment A, Table 3) also be **cancelled.**

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# ATTACHMENT A. ACTIVE CONSTITUENT AND PRODUCTS INCLUDED IN THE REVIEW

## Table 1: Active Constituents under review

| Approval Number | Active Name | Approval holder |
|---|---|---|
| 47187 | 2,4-D-Isobutyl ester | Nufarm Australia Limited |
| 47188 | 2,4-D-N-Butyl ester | Nufarm Australia Limited |
| 47189 | 2,4-D-Ethyl ester | Nufarm Australia Limited |
| 47486 | 2,4-D-Isobutyl ester | Ancom Australia Pty Limited |
| 47549 | 2,4-D-Butyl ester | Dow Agrosciences Australia Limited |
| 51007 | 2,4-D-Isobutyl ester | A H Marks Australia Pty Ltd |
| 51653 | 2,4-D-Ethyl ester | Rotam Australasia Pty Ltd |
| 51903 | 2,4-D-Ethyl ester | Nufarm Australia Limited |
| 52286 | 2,4-D-Isobutyl ester | Rotam Australasia Pty Ltd |
| 52798 | 2,4-D-Isobutyl ester | Binary Chemicals Pty Ltd |
| 59395[#] | 2,4-D Ethyl ester | Agrogill Chemicals Pty Ltd |

[#] Approval granted after the commencement of the review, but is subject to the outcomes of the review

## Table 2: Products under review

| Product Number | Product Name | Registrant |
|---|---|---|
| 31209 | Nufarm Estercide 800 Herbicide | Nufarm Australia Limited |
| 40234 | Farmoz 2,4-D Ester 800 Herbicide | Farmoz Pty Limited |
| 49673 | Generex 2,4-D Ester 800 L Herbicide | Generex Australia Pty Limited |
| 50475 | Ester 800 Selective Herbicide | Nufarm Australia Limited |
| 51110 | Chemag Ester 800 Herbicide | Imtrade Australia Pty Ltd |
| 51815 | Summit Sum-Ester 800 L Herbicide | Summit Agro Australia Pty Ltd |
| 52322 | Sipcam Siester 800 Herbicide | Sipcam Pacific Australia Pty Ltd |
| 52569 | Agcare Biotech 2,4-D Ester 800 Herbicide | Agcare Biotech Pty Ltd |
| 52591 | 4farmers 2,4-D Ester 800 Herbicide | 4farmers Pty Ltd |
| 52634 | Smart 2,4-D Ester 800 Herbicide | Agcare Biotech Pty Ltd |
| 52924 | Country Ester 800 Selective Herbicide | A & C Rural Pty Ltd |
| 53169 | Distribution 2,4-D Ester 800 Herbicide | Grow Choice Pty Limited |
| 53699 | United Farmers Ester 800 Herbicide | United Farmers Cooperative Company Ltd |
| 54595 | Halley 2,4-D Ester 800 Herbicide | Halley International Enterprise (Australia) |
| 54655 | Sekira Herbicide | A H Marks Australia Pty Ltd |
| 54925 | Conquest Ester 800 Selective Herbicide | Conquest Agrochemicals Pty Ltd |
| 54954 | Kenso Agcare Ken-Ester 800 Herbicide | Kenso Corporation (M) Sdn Bhd |
| 55079 | Wsd 2,4-D Ester 800 Herbicide | Rebop Holdings Pty Ltd T/A Western Stock D |
| 55930 | 2,4-D Ester 800 Herbicide By Sanonda | Sanonda (Australia) Pty Ltd |
| 56405 | Agricrop Rubber Vine Spray Herbicide | Agricrop Pty Ltd |
| 56764 | Crop Care Ester 800 Selective Herbicide | Crop Care Australasia Pty Ltd |
| 56895 | Rotam 2,4-D Ester 800 Herbicide | Rotam Australasia Pty Ltd |

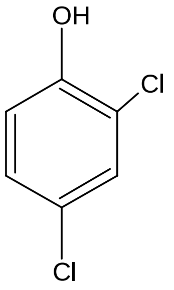
### Table 3: Products registered after the commencement of the review

| Product Number | Product Name | Registrant |
|---|---|---|
| 58444* | Tradewyns Ester 800 Selective Herbicide | Ospray Pty Ltd |
| 58760* | Dow Agrosciences 2,4-D Ester 800 Herbicide | Dow Agrosciences Australia Limited |
| 58919* | Crown 2,4-D Ethyl Ester 800 Selective Herbice | Corona Industries Pty Ltd |
| 59215* | Arm 2,4-D Ester 800 Herbicide | Australian Rural Marketing Pty Ltd |
| 59653* | Genfarm 2,4-D Ester 800 EC Herbicide | Genfarm Crop Protection Pty Ltd |
| 60216* | Esteron LV Herbicide | Dow Agrosciences Australia Limited |
| 60523* | Dow Agrosciences Ester 800 Herbicide | Dow Agrosciences Australia Limited |
| 56117* | 4farmers 2,4-D Ester 600 Herbicide | 4farmers Pty Ltd |
| 58444* | Tradewyns Ester 800 Selective Herbicide | Ospray Pty Ltd |
| 58760* | Dow Agrosciences 2,4-D Ester 800 Herbicide | Dow Agrosciences Australia Limited |
| 58919* | Crown 2,4-D Ethyl Ester 800 Selective Herbicide | Corona Industries Pty Ltd |
| 59215* | Arm 2,4-D Ester 800 Herbicide | Australian Rural Marketing Pty Ltd |
| 59649* | Conquest LV Ester 600 Herbicide | Conquest Agrochemicals Pty Ltd |
| 59653* | Genfarm 2,4-D Ester 800 EC Herbicide | Genfarm Crop Protection Pty Ltd |
| 59709* | Kenso Agcare Abroholos 600 Selective Herbicide | Kenso Corporation (M) Sdn Bhd |
| 60216* | Esteron LV Herbicide | Dow Agrosciences Australia Limited |
| 60264* | Crop Care LV Ester 600 Herbicide | Crop Care Australasia Pty Ltd |

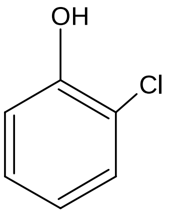
* Products registered after the commencement of the review that are subject to the outcomes of the review

## ATTACHMENT B Metabolite Chemical Structures

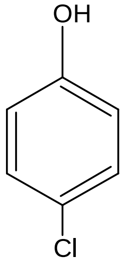
2,4-Dichlorophenol (**2,4-DCP)**



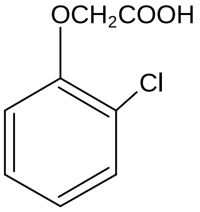
2-Dichlorophenol (**2-DCP**)



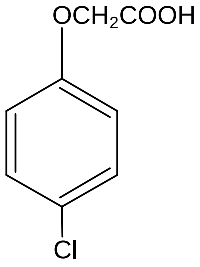
4-Dichlorophenol (4**-DCP**)



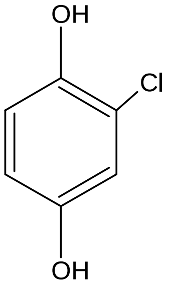
2-Chlorophenoxyacetic Acid (**2-CPA**)



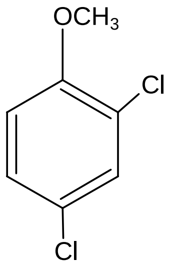
4-Chlorophenoxyacetic Acid (**4-CPA**)



2-Chlorohydroquinone (**CHQ**)



2,4-Dichloroanisole (**2,4-DCA**)



1,2,4-Benzenetriol