Australian Government
Australian Pesticides and
Veterinary Medicines Authority

ANNEX TO THE APVMA'S PRELIMINARY REVIEW FINDINGS (ENVIRONMENT)

PART 1

2,4-D ESTERS

Volume 1

Review Summary

APRIL 2006

This Report was prepared for the APVMA by

Department of the Sustainability, Environment, Water, Population and Communities

May 2013

© Australian Pesticides and Veterinary Medicines Authority 2013

ISBN: 978-1-922188-39-7 (electronic)

Ownership of intellectual property rights in this publication

Unless otherwise noted, copyright (and any other intellectual property rights, if any) in this publication is owned by the Australian Pesticides and Veterinary Medicines Authority (APVMA).

Creative Commons licence

With the exception of the Coat of Arms and other elements specifically identified, this publication is licensed under a Creative Commons Attribution 3.0 Australia Licence. This is a standard form agreement that allows you to copy, distribute, transmit and adapt this publication provided that you attribute the work.

A summary of the licence terms is available from www.creativecommons.org/licenses/by/3.0/au/deed.en. The full licence terms are available from www.creativecommons.org/licenses/by/3.0/au/legalcode.

The APVMA's preference is that you attribute this publication (and any approved material sourced from it) using the following wording:

> *Source: Licensed from the Australian Pesticides and Veterinary Medicines Authority (APVMA) under a Creative Commons Attribution 3.0 Australia Licence. This report was prepared for the APVMA by the Australian Government Department of Department of the Sustainability, Environment, Water, Population and Communities (DSEWPaC).*

In referencing this document the Australian Government Department of Department of the Sustainability, Environment, Water, Population and Communities should be cited as the author and the Australian Pesticides and Veterinary Medicines Authority as the publisher and copyright owner.

Use of the Coat of Arms

The terms under which the Coat of Arms can be used are set out on the Department of the Prime Minister and Cabinet website (see www.dpmc.gov.au/guidelines).

Disclaimer

The material in or linking from this report may contain the views or recommendations of third parties. This material does not necessarily reflect the views of the APVMA, or indicate a commitment to a particular course of action.

There may be links in this document that will transfer you to external websites. The APVMA does not have responsibility for these websites, nor does linking to or from this document constitute any form of endorsement.

The APVMA is not responsible for any errors, omissions or matters of interpretation in this document.

Comments and enquiries:

The Manager, Public Affairs
Australian Pesticides and Veterinary Medicines Authority
PO Box 6182
KINGSTON ACT 2604 Australia

Telephone: +61 2 6210 4701

Email: communications@apvma.gov.au

This publication is available from the APVMA website: www.apvma.gov.au.

Australian Government

Department of Sustainability, Environment, Water, Population and Communities

Annex to the APVMA's Preliminary Review Findings (Environment) Part 1: 2,4-D Esters Volume 1: Review Summary APRIL 2006

May 2013

This Annex to Volume 1: Review Summary of the Preliminary Review Findings report (April 2006) contains summaries of work conducted by the Department of Sustainability, Environment, Water, Population and Communities since the release of the 2006 report. This includes assessments on data provided since 2006 and conclusions on the future registrations of 2,4-D High Volatile Esters (HVE).

FINAL

This report has been prepared by the Environment Protection Branch of the
Australian Government Department of Sustainability, Environment, Water, Population and Communities for the
Australian Pesticides and Veterinary Medicines Authority

Executive Summary

This summary report, presented as an Annex to the APVMA's Preliminary Review Findings [PRF] (Environment) Part 1: 2,4-D Esters Volume 1: Review Summary of April 2006, contains a summary of the 2006 PRF's environmental assessment findings with respect to the 2,4-D high volatile esters (HVE). Based on the PRF's findings, the APVMA suspended the registrations of 2,4-D HVE formulations and called for public comment on the PRF and for data to be presented to address data gaps identified in the assessment for this class of chemicals.

The suspension decision derived from the findings and recommendations of the Commonwealth Department of Sustainability, Environment, Water, Population and Communities (DSEWPaC) that the high volatile (short chain) esters had a propensity to volatilise and persist in the environment (atmosphere) and to cause off-target damage.

Since the 2006 suspension, some environment related data associated with the 2,4-D HVE has been submitted and assessed by DSEWPaC. While Tier I data presented have addressed some of the physico-chemical data gaps for some of the 2,4-D HVE identified in the 2006 PRF, higher Tier testing still remains problematic.

This summary report presents DSEWPaC's conclusions and advice given to the APVMA on 2,4-D HVE data received since 2006, including DSEWPaC's assessment of the public comments received after the release of the PRS in 2006.

Because the data presented since 2006 to support the continued use of the 2,4-D high volatile esters remains either incomplete or has confirmed that volatilisation of the 2,4-D HVE will occur, DSEWPaC's original conclusion that, on the available evidence, the risks of the use of 2,4-D HVE are unacceptable and the risks cannot be mitigated remains unchanged.

As a consequence, the proposed recommendation in the Preliminary Review Findings in 2006 that, "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." stands.

Consequently, DSEWPaC does not support further extensions of use of the 2,4-D HVE under permit PER13339 which was originally granted in October 2006 and renewed in May 2007, October 2010, February 2011 and February 2012.

Table of Contents

Introduction

Purpose

This Annex has been prepared by DSEWPaC at the request of the APVMA to present a compilation of DSEWPaC's assessment of the public comments received on the APVMA's April 2006 Preliminary Review Findings (Environment) Part 1: 2,4-D Esters document and assessments of data submitted since that time to address the deficiencies identified in the 2006 report.

Background

As reported at the APVMA's website dealing with the chemical review of 2,4-D, 2,4-D is a systemic herbicide used post emergence for the control of broadleaf and grass weeds on crops, commercial and industrial areas, turf, forestry and waterways. In 1995 the APVMA began its review of 2,4-D because of concerns over the potential risk of the various chemical forms of this active constituent to public health, occupational health and safety, and the environment (including impacts on waterways, non-target animals and plants).

The published review of 2,4-D was split into two parts:

- Part 1 contains the environmental risk assessment of high volatile (short-chain) ester forms of 2,4-D
- Part 2 will contain the toxicological, occupational health and safety assessments for all 2,4-D forms, and the environmental risk assessment of the low and non-volatile forms (acid, salt, and long-chain esters) of 2,4-D.

Currently only the Preliminary Review Findings (PRF) report for Part 1 is available (together with its associated Technical Report and Appendices (APVMA, 2006).

The PRF's principal conclusion was that the APVMA proposed to find that it was NOT satisfied that continued use of the 2,4-D high volatile esters (HVE or HVE) would not be likely to have an unintended effect that is harmful to animals, plants or things or the environment.".

This decision on the high volatile esters was published by the APVMA in April 2006 and was based on the recommendation of the Department of Sustainability, Environment, Water, Population and Communities (DSEWPaC) [then the Department of the Environment and Heritage, DEH]. The Department had reached this decision after its consideration of data for the environmental fate and environmental effects (ecotoxicology) for the high volatile esters 2,4-D ethyl ester, 2,4-D butyl esters, 2,4-D isobutyl ester.

DSEWPaC's decision was primarily based on the propensity of the high volatile (short chain) esters to volatilise and persist in the environment (atmosphere) thereby causing off-target damage. DSEWPaC also observed that the assessment of the HVE identified significant data gaps with no contemporary data provided for the 2,4-D short chain esters to support their assessment. This lack of data resulted in uncertainties in the risk assessment outcomes.

Consequently, the APVMA proposed:

- All active constituent approvals for the active constituents (2,4-D ethyl ester, 2,4-D butyl ester and 2,4-D isobutyl ester) be cancelled.
- that all product registrations containing those active constituents and all associated labels, must also be cancelled; and
- 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 also be cancelled.

In October 2006 (APVMA Gazette No.10, 3 October 2006) the APVMA suspended the registrations and label approvals of some 24 products containing high volatile ester forms of 2,4-D and issued new instructions for use until such time as further data is generated by registrants.

This suspension has been extended a number of times and continues to the present time.

Subsequent to placing 2,4-D high volatile esters under suspension on 26 September 2006, primarily because of concerns about damage to non-target crops and vegetation, the APVMA required active constituent approval holders to provide new data on the physico-chemical properties of high-volatile (short-chain) esters by end of February 2007.

Following assessment of the data provided, the APVMA extended the suspension period until April 2009 (and since further extended) to allow interested persons to generate and provide new data to allow a refined assessment of risks to the environment. The data to be provided were categorised as follows with further detail contained in Attachment 1:

Tier I data Physical and chemical properties including vapour pressure

Tier II data Environmental fate

Tier III data Environmental effects

Use of the suspended products is still allowed under Permit PER13339 with the intent that new data would allow a refined assessment of risks to the environment.

To address the data gaps identified by DSEWPaC, the new data being sought used a tiered approach in order to allow refinement of the risk assessment of the 2,4-D HVE. The data to be provided, plus explanatory comment, are provided as Attachment 1.

These studies were requested to provide an improved understanding of the likely fate of the short-chain esters and enable higher tier modelling to be performed.

In addition to the call for this new data, the April 2006 Preliminary Review Findings document also requested comment from the public on the document.

In November 2007, a consortium of six companies was established to fund the atmospheric monitoring required for the 2007/2008 summer use permit with the consortium operating under the informal working name, “2,4-D Permit Support Group” (2,4-D Permit Support Group, 2008)

Subsequent to this, information for a number of the data gaps was provided and DSEWPaC assessment reports relevant to these matters are included as attachments to this Annex.

Additionally, this Annex presents DSEWPaC’s conclusions on the future registration of 2,4-D HVE products on the basis of the data submitted to date.

The assessment of data conducted by DSEWPaC for the review of 2,4-D HVE are summarised blow and where relevant, further detail contained in the attachments to this report. Issues considered by DSEWPaC but where no further detail can be provided (due to confidential information) are also discussed.

SUMMARIES OF DATA CONSIDERED BY DSEWPAC

Public comments received on the April 2006 Preliminary Review Findings (Attachment 2)

DSEWPaC's assessment of public comments received on the April 2006 Preliminary Review Findings document is contained in Attachment 2. Fourteen responses were received on fourteen issues.

DSEWPaC's advice to the APVMA contained written responses to the comments received and consideration of a plant toxicity paper.

Additionally, several papers were provided to the APVMA supporting comments received through the public consultation that Australian native plants are more tolerant to 2,4-D than DSEWPaC's risk assessment suggested. DSEWPaC's response on the public comments addressed this issue.

DSEWPaC also identified reports previously provided to the USPEA relating to the effects on terrestrial plants and non–target arthropods as of particular importance and which DSEWPaC had used the reported end points provided in the USEPA report.

Public comments – 2,4-D Review, Short Chain Ester Reports: NFF Submission (Attachment 3)

A late public comments submission from the National Farmers Federation (NFF) following a critique of this assessment by Professor Ivan Kennedy of the University of Sydney was also assessed by DSEWPaC. With respect to the Preliminary Review Findings, this submission addressed:

1. The appropriateness of the methodology
2. The validity of the assumptions (particularly where data gaps exist)
3. The relevance of overseas studies in assessing potential impacts on the Australian natural environment
4. Any scientific work which may have been overlooked
5. Opportunities to mitigate risk
6. The appropriateness of the APVMA's conclusions

DSEWPaC provided the APVMA with five separate documents addressing these issues (all provided within Attachment 3 to this Annex).

- The first provided responses to each of the components of Professor Kennedy's report, to offer further justification for some of these responses,
- Attachment 2 gave an overview of current methodologies relating to assessing environmental risk relating specifically to the atmospheric compartment.
- Attachment 3 discussed more recent atmospheric monitoring data relating to 2,4-D and its detections considered to be a result of medium to long-range atmospheric transport.
- Attachment 4 provided a list of current data gaps identified in DSEWPaC's original report relating to the short chain esters, which will need to be filled should any higher tier assessment for atmospheric transport and potential off target effects be required for these chemicals.
- Finally, Attachment 5 provided suggested amendments to the APVMA report to provide further explanatory text relating to the methodology employed in the assessment, and hopefully increase transparency.

DSEWPaC assessment of the submission on 2,4-D HVE submitted by the West Australian Department of Agriculture and Food (Attachment 4)

This submission consisted of data and argument to address the Tier II environmental fate data gaps and also partly to address the Tier III environmental toxicity data gaps. In addition, DSEWPaC assessed several studies not provided as part of the submission in order to put the various arguments into perspective.

DSEWPaC concluded that the argument and data in the submission did not affect the preliminary review findings and the original conclusions on the potential environmental risks from the continued use of 2,4-D HVE remained unaltered. In some cases, the information provided reinforced the Department’s conclusion that HVE will be sufficiently persistent in the air column to enable atmospheric transport over long (regional) distances. It was also apparent that volatilisation following application to foliage and moist soil is very high. Based on biomonitoring results, off target movement was found to be significant (even for LVE) with evidence showing the distance of movement is dependent on the amount of chemical applied.

Regarding locally available monitoring, the main study cited was Gilbey *et al.* (1984) where several years of monitoring were undertaken around Geraldton in Western Australia. Industry has previously assumed these results showed that HVE were manageable. However DSEWPaC noted that the levels detected were only mean weekly levels. Measurements were all west of the zone where spraying of HVE was permitted indicating that the 2,4-D HVE would only be present in the air collected by samplers at times when the wind direction was coming from the general easterly direction, combined with temperatures being sufficient to allow volatilisation. This meant atmospheric levels were necessarily much higher for shorter periods of time when winds were blowing from the east to lead to the weekly concentrations found in the study. DSEWPaC was concerned that non-target native vegetation to the west of the spray zone would be highly exposed given the findings in the Geraldton study demonstrating movement of at least 35-40 km from the sprayed area.

Some non-standard testing considering plant effects where exposures through the gas phase were provided for DSEWPaC’s assessment. Tomato plants, strawberries, raspberries and grapes, green beans and canola were examples of plants referred to in such work . Results confirmed the potency of 2,4-D to plants, and the evidence was that the HVE were more potent than the LVE and acid/salt formulations, presumably because of the greater vapour levels. The studies confirmed DSEWPaC’s understanding that using the standard vegetative vigour and seedling emergence studies available for LVE and acid/salt in the original assessment are not suitable for measuring reproductive end points such as on fruit set or yield which reproductive toxins such as 2,4-D may exhibit. In the non-standard testing considered in this assessment, adverse impacts were found for germination of several species following exposure to vapours. Short term exposures (several hours) at relatively low air concentrations (0.06 $\mu g/m^3$) were sufficient to induce long term effects on plant dry weight. Exposure of sunflowers to 2,4-D during the reproduction phase of the plants life-cycle was sufficient to reduce seed yield by 96%.

DSEWPaC noted that the 2,4-D Industry Task Force did not generate any contemporary data as these compounds were discontinued in North America and Europe some 20 years ago due to environmental concerns. It was also noted that it was over 12 months since Nufarm provided an undertaking to address the data gaps relating to the use of these compounds and that the West Australian Department of Agriculture and Food submission did not address these data deficiencies.

Based on the then available information, DSEWPaC concluded that an unacceptable risk to the environment posed by the continued use of 2,4-D HVE remained due to the expected high volatilisation rates of these chemicals following application, long residence time in the atmosphere and high plant toxicity.

The DSEWPaC response is provided as Attachment 4 to this Annex.

DSEWPaC's assessment of a 2,4-D HVE AIR MONITORING STUDY - SEPTEMBER 2008 (Attachment 5)

A preliminary study and two large scale trials designed to measure atmospheric dispersion of 2,4-D HVE vapour from recently treated paddocks were conducted by the 2,4-D Permit Support Group (PSG) in Western Australia during March and April 2008 (2,4-D Permit Support Group, 2008). In the large scale trials air was monitored for 2,4-D HVE vapour at the centre and perimeter of the paddock treated with 2,4-D ethyl ester and at 200, 500 and 2000 metres from the perimeter of the treated paddocks. The protocol for the large scale trials had been provided by the APVMA and found acceptable by DSEWPaC.

The report of this work was assessed by DSEWPaC where it was identified that the study addressed the local scenario for application of 2,4-D HVE. It did not, however, address the regional requirements (as acknowledged in the report), because sales volumes were too low during 2007-08 to undertake any meaningful monitoring on this scale.

For the monitoring component of the study, DSEWPaC drew the following conclusions:

- Where favourable conditions exist, off target movement through volatilisation will occur.
- The movement through the vapour phase changes direction with wind changes, thereby potentially exposing a larger area.
- Highest levels of local exposure maybe expected to occur during first two days following a single application.
- Based on an application rate of 560 g ae (acid equivalents) /ha, maximum in-field air concentrations could approach 3 $\mu g/m^3$ (based on 8 hours exposure), with levels up to 0.3 $\mu g/m^3$ (8 hours exposure) predicted at 2 km off-site.

DSEWPaC's rationale on predicted air concentrations (assuming the majority of exposure occurs during 8 hours of the day when temperatures are at their warmest) was provided in its assessment report.

The study report also included a risk assessment conducted by the Permit Support Group which was assessed by DSEWPaC:

DSEWPaC identified that the monitoring study was required to obtain more reliable data on likely vapour concentrations in local and regional use situations and that the monitoring results obtained were for the local situation only, based on application to 70 ha fields. It was never a requirement, DSEWPaC stated, that a risk assessment be conducted as this stage because the available plant toxicity data from gas phase exposure were inadequate for undertaking a risk assessment. Nonetheless, because the Permit Support Group (PSG) had performed both a preliminary and refined risk assessment, DSEWPaC had assessed it.

DSEWPaC concluded that the approach of relating available toxicity data in terms of "total available herbicide" back to monitored levels in the same terms was incorrect and could not be used to assess risk. The toxicity data as referred to by the PSG was reviewed and risk assessment end-points (EC25 and EC05) calculated by DSEWPaC who found are very large discrepancies between its calculated values and those derived by the PSG.

DSEWPaC's preliminary risk assessment, undertaken in a number of different ways with different end points, all indicated a potentially unacceptable risk from the local monitoring trial. DSEWPaC anticipated that the proposed regional trial would only exacerbate this situation, due to the expected much higher levels in situations of significant regional use, and would serve only to confirm the conclusion of an unacceptable risk.

The main deficiencies, DSEWPaC found, in the assessment were the use of end points for vapour phase toxicity based on a single species (although with a spread of results for a relatively sensitive plant), and the need to extrapolate levels from 24 hour time weighted averages to those for shorter periods that might be expected more accurately reflect those during daylight hours when volatility will be highest.

On the available evidence, the risks of the use of 2,4-D HVE were considered by DSEWPaC as remaining unacceptable and not able to be mitigated. DSEWPaC also considered the conduct of regional trials would be unlikely to provide evidence that would allow mitigation of the risks. However, should the trials proceed, DSEWPaC identified monitoring issues that would need to be addressed. It was also noted by DSEWPaC that the monitoring protocols agreed for the local monitoring trial were not followed in all respects.

The DSEWPaC response was sent to the APVMA on 11 December 2008 and contained three attachments. The covering letter and three attachments are provided as Attachment 7 to this Annex.

DSEWPaC's assessment of the 2,4-D HVE REGIONAL MONITORING STUDY. FEBRUARY-MARCH 2009 (Attachment 6)

This study (Hay, 2009) was performed to attempt to address potential regional concentrations of 2,4-D HVE movement that may be found in their use areas.

The study protocol initially requested that regional monitoring be undertaken in the 2007-08 summer period. However, the 2007-08 permit period did not address the regional requirements because sales volumes were too low during this summer to undertake any meaningful monitoring on this scale. Consequently, regional monitoring was re-addressed under the 2008-09 permit.

The report, 2,4-D HVE Regional Monitoring Study, February-March 2009, provided the results of that monitoring program. DSEWPaC concluded, from the report that:

- The regional monitoring study was conducted for a single region situated between Esperance, Salmon Gums and Mount Ridley in Western Australia with three sampling stations within the region. Weekly samples from the southernmost part of the region, Esperance Downs Research Station, did not detect any 2,4-D HVE.
- Detections of 2,4 D ethyl ester (both 12 hourly and weekly) were found at the other two sites.
- 2,4-D ethyl ester was the only HVE found in samplers, and in the 12 h samples, was detected in Salmon Gums more frequently (70.4% of samples compared to 33% at Mt. Ridley), and at higher concentrations (0.001-0.03 µg/m3 compared to 0.001-0.01 µg/m3 at Mt. Ridley).
- Available wind data indicate wind moving predominantly from the south west in the test region.
- Prior to undertaking the regional scale trial, concern was expressed that results would only be meaningful if the trial were conducted under normal use. The report makes no comment on "normal use" in terms of areas sprayed during the trial period compared with historic use, or the total amounts of 2,4-D HVE used compared with historic amounts.
- Spray records are inadequate to properly interpret the sampled data with respect to areas of application or volumes of use, making it difficult to add any further context to the detected levels.

In addition to the regional monitoring, a supplementary study was undertaken to address the issue of post application volatilisation of 2,4-D HVE measured at different time scales. This study was important to allow establishment of exposure time frames for vapour phase plant toxicity testing.

While it was considered that the bulk of volatilisation would occur during daytime hours, the data obtained in this study did not support this, and the following conclusions were drawn from the supplementary study:

- Where direct comparisons were able to be made, the data showed that the concentrations observed over a daytime sampling period (8 to 12 hours), were not remarkably different to those found over a 24 hour continuous sampling period. This further suggests, in the area tested, the rates of volatilisation were not substantially different between day and night time in the test climate.
- These findings allow increased confidence in using a 24 h exposure concentration in vapour phase ecotoxicity testing.

- The use of modelling incorporating the data obtained through this supplementary study indicate cumulative volatilisation of around 15% of the applied amount, with the majority of this being lost in the first 24 hours following application.

Despite the deficiencies in the studies, in particular the lack of evidence that the regional study was carried out under “normal use” conditions and the failure of the pumps in crucial wind directions for the supplementary study, DSEWPaC concluded that no further such studies were necessary.

This was because data provided with these and previous studies established beyond doubt that 2,4-D HVE will volatilise following application, and the combined data allowed both the recommendation of exposure levels and times for the vapour phase toxicity testing.

DSEWPaC also noted that further soil and foliage volatility testing would be carried out using the backward Lagrangian stochastic modelling method.

The DSEWPaC consideration of this study is provided as Attachment 6.

Revised 2,4-D HVE Air Monitoring Study report (Attachment 7)

Submitted with the 4 Farmers Pty Ltd Tier I data was a draft report entitled, 2,4-D HVE Air Monitoring Study. This document was prepared by the 2,4-D Permit Support Group with Biosecurity Queensland identified as providing the peer reviewer.

Examination of the report identified it as essentially the same report assessed by DSEWPaC in 2008 and already discussed under Attachment ?, “DSEWPaC’s assessment of a 2,4-D HVE AIR MONITORING STUDY - SEPTEMBER 2008”.

The principal exception being the inclusion of a revised risk assessment based on the no observed effect level.

Unfortunately, the revised report does not address DSEWPaC’s 2008 advice that the report’s approach of relating available toxicity data in terms of “total available herbicide” back to monitored levels in the same terms is incorrect and cannot be used to assess risk. Similarly, the revised report has not addressed the previously identified main deficiencies of the use of end points for vapour phase toxicity based on a single species and the need to extrapolate levels from 24 hour time weighted averages to those for shorter periods that might be expected more accurately reflect those during daylight hours when volatility will be highest.

The revised report presents no reason to change the original DSEWPaC advice given to the APVMA that, on the available evidence, the risks of the use of 2,4-D HVE are unacceptable and the risks cannot be mitigated.

DSEWPaC’s assessment of the revised study report is provided as Attachment 7 to this Annex.

OTHER CONSIDERATIONS (no associated attachments)

DSEWPaC review of Tier I data provided by Nufarm Australia Limited

In response to the call for additional data, Nufarm Limited provided Tier I data on the 2,4-D ethyl ester (2,4-D EE). DSEWPaC observed that these additional data were performed in Japan and, although available prior to DSEWPaC’s assessment, had not been provided for the original assessment.

DSEWPaC drew the APVMA’s attention to the fact that these physico-chemical data did still not enable a higher tier risk assessment. Rather, they were needed to confirm the values obtained from older literature and formed the first basis of the simple modelling undertaken in the assessment. To that end, the results for water solubility and octanol water partition co-efficient were found supportive of the values used in the original assessment. However, there remained questions about the measured vapour pressure for 2,4-D EE in the test provided. This study (non-GLP) was undertaken in 1988 following an older version of the OECD Test Guideline 104. No reference substance was tested (acceptable to the guideline, but making interpretation of the result somewhat more difficult) and the value obtained was significantly less volatile than other published values for this compound.

In summary, DSEWPaC concluded, the Tier I water solubility and octanol-water partition coefficient data were in agreement with the values already used and therefore did not lead to changes in the assessment.

Pending resolution of the assessment of the vapour pressure, the Department advised that it remained of the opinion that the ethyl ester was significantly more volatile than 2,4-D EHE for which a reliable result was available, and the other issue of persistence in the atmosphere following lift off from application sites still needed to be addressed. DSEWPaC also identified that the Tier II and III data requirements were still outstanding and the Department's original recommendations were unchanged.

The complete assessment was provided to Nufarm and has not been included here as it is considered confidential.

DSEWPaC's September 2009 assessment of Tier I, II and III data provided by Nufarm Australia Limited

Following a second call by the APVMA for Tier I (vapour pressure) data in November 2007, Nufarm Australia Limited presented two Tier I studies for the determination of the vapour pressure of 2,4-D ethyl ester. Also presented were a modelling study for the photooxidation half-life of 2,4-D ethyl ester (EE), which formed part of the Tier II data requirements, and an old literature study for a range of 2,4-D chemicals on bluegill sunfish, which was part of the Tier III data requirements.

DSEWPaC's assessment identified that the data provided focused on 2,4-D EE, and noted it would seem the ethyl ester is the only HVE form that industry were supporting. As a result, DSEWPaC concluded that, with respect to the 2,4-D ethyl ester that:

> Tier I Data Requirements had been fulfilled;
>
> Tier II Data Requirements for photooxidation of the 2,4-D ethyl ester have been met and no further data are required for this particular data requirement. Other outstanding Tier II data were still required; and
>
> Tier III Data Requirements had been partly fulfilled by the supplying of one non-standard, old literature report on various forms of 2,4-D to bluegill sunfish. As a result, no further fish toxicity data are required. However, other outstanding Tier III toxicity data were still required.

Based in DSEWPaC's considerations of this newly provided data, the following conclusions and recommendations were made:

1. The Tier 1 data supplied by Nufarm Australia Limited for 2,4-D EE are considered acceptable for inclusion in the Part 1 report and confirmed the high volatility of 2,4-D EE;
2. The Part 1 report be amended accordingly, specifically the sections relating to sections on physico-chemical properties; environmental fate; effects; and risk characterisation where the new data values can be applied; and
3. Outside the Tier 1 data, there have been significant other data supplied and debated since the release of the Part 1 Report in 2006. These included that from the Department of Agriculture and Food, Western Australia and the field monitoring data supplied through the 2,4-D Permit Support Group and Nufarm Australia Limited. The outcomes from these discussions, along the data supplied and considered, should be included in the Part 1 Report for completeness.

DSEWPaC's assessment was provided to the registrant. It is not included in this report as it is considered confidential.

2,4-D Isobutyl ester (2,4-D IBE) Tier I Data; 4 Farmers Pty Ltd (Vapour pressure, water solubility and partition coefficient

4Farmers Pty Ltd, in response to requests by the APVMA to fill data gaps identified in the APVMA's 2006 Preliminary Review Findings (PRF) on the 2,4-D high volatile esters (2,4-D HVE), presented, in 2012, Tier I studies on the vapour pressure, water solubility and partition coefficient of the 2,4-D HVE, 2,4-D Isobutyl ester or 2,4-D IBE

Although the Tier I study reports submitted contained minimal experimental detail, sufficient information has been provided to indicate the water solubility and octanol/water partition coefficients results presented are acceptable. The failure of the reports to have been signed and (on occasion) not to identify that good laboratory practice had been followed, is a significant protocol aberration and resulted in a “Reliable with restrictions” rating for the water solubility and octanol/water partition coefficients studies.

The data provided and the endpoints determined indicate that 2,4-D IBE has physicochemical properties consistent with those of the other 2,4-D HVE, and because of this, to pose an unacceptable risk to non-target terrestrial plants.

The modelling study for the vapour pressure of 2,4-D IBE provides an endpoint that predicts 2,4-D IBE as being moderately volatile. However, a Tier I experimental result for vapour pressure, which was requested, still has not been supplied for this HVE.

While the reporting of the studies conducted for 4Farmers' data was minimal, the water solubility and log Pow endpoints reported have fulfilled the Tier I data requirements for these two parameters of the 2,4-D isobutyl ester and show that this ester has physicochemical properties consistent with those of the other 2,4-D HVE of concern and to also pose an unacceptable risk to the environment.

The studies presented have resulted in the Tier I water solubility and octanol/water partition coefficient data gaps for 2,4-D IBE being filled. In the absence of experimental data, the Tier I vapour pressure data gap for the 2,4-D isobutyl ester remains.

DSEWPaC's assessment was provided to the registrant. It is not included in this report as it is considered confidential.

2,4-D Isobutyl ester (2,4-D IBE) Tier I Data; Runge Agrichems Pty Ltd (Vapour pressure, water solubility and partition coefficient)

Runge Agrichems Pty Ltd presented, in 2013, Tier I studies on the vapour pressure, water solubility and partition coefficient of the 2,4-D HVE, 2,4-D Isobutyl ester or 2,4-D IBE. This was in response to data calls by the APVMA to fill data gaps identified in the APVMA's 2006 Preliminary Review Findings on the 2,4-D high volatile esters (2,4-D HVE).

DSEWPaC has reviewed these Tier 1 data and finds that the vapour pressure value of 0.741×10^{-3} Pa, the water solubilities of 0.2966 to 0.3092 mg 2,4-D IBE/L over the pH range of 5 to 9 and the log Pow value of 3.43 are acceptable. No further tier I data are outstanding for these three 2,4-D isobutyl ester parameters.

The experimentally determined vapour pressure value of 0.000741 Pa is towards the border of the vapour pressures which predict no noticeable volatility from soil (i.e. vapour pressure is $< 10^{-3}$ Pa), volatility from crops is still expected (i.e. vapour pressure $>10^{-4}$ Pa). However, the methodology used in the determination of this vapour pressure (effusion method, isothermal thermogravimetry) is relatively recent with respect to the OECD methodology use and data on the comparability of results with earlier methodologies were not presented. It is possible the method used underestimates vapour pressure and other considerations are still taken as predicting the 2,4-D isobutyl ester will be volatile.

While the Tier I water solubility study with 2,4-D IBE gave a solubility of 0.2966 to 0.3092 mg 2,4-D IBE/L which classifies this ester as slightly soluble in water, the determinations were conducted in buffer solutions rather than in water as required by the guidelines followed and the results relate to solubility in buffer, not water. Consequently, the Tier I water solubility data requirement has not been addressed by the study.

DSEWPaC's assessment was provided to the registrant. It is not included in this report as it is considered confidential.

Conclusions and recommendations

Since the release of the APVMA's 2,4-D Preliminary Review Findings Report (Environment) Part One: 2,4-D high volatile esters and associated Technical Report and Appendices) in 2006, some of the data gaps associated with the 2,4-D HVE have been addressed, especially with respect to Tier I requirements; But, overall, DSEWPaC finds that data provided in response to the APVMA's data call-in have not adequately addressed the data gaps identified in 2006.   This is despite DSEWPaC's provision of a number of assessments of data submitted and of advice on trial protocols.

Given the failure of those supporting the continued use of the 2,4-D high volatile esters to adequately address the data requirements, the proposed recommendation made by DSEWPaC in the Preliminary Review Findings in 2006 that, "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." stands.

Additionally, DSEWPaC does not support further extensions of use of the 2,4-D HVE under permit PER13339 which was originally granted in October 2006 and renewed in May 2007, October 2010, February 2011 and February 2012.

References

APVMA (2006). 2,4-D Preliminary Review Findings Report (Environment) Part One: 2,4-D high volatile esters (and associated Technical Report and Appendices). Accessible via http://www.apvma.gov.au/products/review/current/2_4_d.php.

2,4-D Permit Support Group (2008). 2,4-D HVE Air Monitoring Study September, 2008. Author: Philip Hay. 2,4-D Permit Support Group.

Gilbey D, Ralph C, Scott A, Ebell G and Horne R, 1984. Airborne 2,4-D and Tomato Damage at Geraldton, Western Australia. Australian Weeds Vol 3(2), pp 57-69.

Guth J, Reischmann F, Allen R, Arnold D, Hassink J, Leake C, Skinmore M and Reeves G. 2004. Volatilisation of Crop Protection Chemicals From Crop and Soil Surfaces Under Controlled Conditions – Prediction of Volatile Losses from Physico-Chemical Properties. Chemosphere, 57 (2004), 871-887. Elsevier.

Hay P (2009). 2,4-D HVE Regional Monitoring Study February – March 2009 Esperance – Salmon Gums, WA. Volume 1: Report. July 2009.

Attachments

1. Tier I, II and III data requirements identified by the APVMA for the 2,4-D HVE
2. Public comments received on the April 2006 Preliminary Review Findings
3. Public comments – 2,4-D Review, Short Chain Ester Reports: NFF Submission
4. DSEWPaC assessment of the submission on 2,4-D HVE submitted by the West Australian Department of Agriculture and Food
5. DSEWPaC's assessment of a 2,4-D HVE AIR MONITORING STUDY - SEPTEMBER 2008
6. DSEWPaC's assessment of the 2,4-D HVE REGIONAL MONITORING STUDY. FEBRUARY-MARCH 2009
7. Revised 2,4-D HVE Air Monitoring Study report

Attachment 1

Tier I, II and III data requirements identified by the APVMA for the 2,4-D HVE

Data/study required	Comments	Study protocol
Tier I: Physical and chemical properties		
Vapour pressure		OECD Test No. 104
Water solubility		OECD Test No. 105
Octanol-water partition co-efficient		OECD Test No. 117 – HPLC OECD Test No. 123 – Slow stirring method
Tier II: Environmental fate		
Photo-oxidation/persistence in atmosphere	Estimated photochemical oxidative degradation – 2,4-D HVE stability in the air, photochemical degradation, identity of breakdown product(s)	
Volatility from range of soils	Environmental fate studies to consider volatility from a wide range of soils and representative exposure conditions (i.e. surface applied without soil incorporation)	
Volatilisation from foliage	Studies on volatilisation from foliage (and to determine persistence on foliage)	
Exposure concentrations in soil and air at point of application. Air monitoring at downwind points.	As presented to the 2,4-D Permit Support Group in November 2007. A pilot study using five samplers from a small point source. This was to ensure integrity of the system, prior to commencing a large scale trial of 70 ha blocks. A regional monitoring study: (1) weekly monitoring of air at 10 locations in the area of 2,4-D HVE use and (2) monitoring at 4 locations daily, collecting air samples for 12 hours per day. Trial must be conducted in a ‘normal’ season.	
Aerobic soil metabolism	Studies to characterise persistence and breakdown in a range of soils.	Protocol based on OECD Test No. 307
Tier III: Environmental effects		
Effects on non-target arthropods and aquatic plants/algae	Non-target arthropods: Tier 1 Lab studies Comments: typically run to IOBC Guidelines covering 2 different species – Typhlodromus and Aphidius). Extended lab (dose response, limit test) Protocols / quotes / timing currently being obtained. Non-target aquatic plants/algae.	OECD Test No. 201

	Comments: Test algae - use OECD 201 – refer to Appendix 3 . Protocols / quotes / timing currently being obtained. This work to be conducted using the formulation.	
Test reports for other aquatic organisms in US EPA ECOTOX database		
Effects on non-target terrestrial vegetation including effects of exposure to gas phase and ground deposition spray	Determination of effects 2,4-D HVE on seed germination, seedling emergence and vegetative vigour of ten plant species. Studies on Australian native species to be included using these protocols. Min. 10 spp. dicot & monocot Also, a conventional vegetative vigour study to be conducted when the most sensitive species is known, and subject it to vapour exposure	OECD Test No. 208A OECD Test No. 227

Attachment 2

Public comments received on the April 2006 Preliminary Review Findings

1 Introduction

This report considers a total of 12 submissions received by the APVMA in response to the Preliminary Review Findings (Environment), Part 1: 2,4-D Esters for the 2,4-D Review. . In this report, submissions are referenced by number only.

2 Issues arising in submissions

Issue	Submission no.
Use of modelling for volatility	1
Volatility (no. 10 also includes benefits of volatility)	1, 5, 10
Toxicity of short chain 2,4-D esters to Australian native plants	1, 5
Validity of aquatic toxicity endpoints	1
Application rates in spray drift modelling	1
Use and impact of short chain 1,2-D esters in Australian agriculture	1, 10
Current use control restrictions on phenoxy products	1, 3, 11, 13, 14
Education and spray management	1, 4, 9
Editorial/amendments to current report	2
Availability of previously unsupplied studies	2
Need for wider scope (costs and benefits; alternative chemicals etc)	3, 4, 5, 6, 7, 9, 10, 11, 13
Use of international data as surrogate values for Australia	3, 6, 7
Use of Australian generated data (including field experience)	3, 4, 7, 10
Focus on Western Australian broadacre use	4, 5, 9, 10, 11, 12

2.1 Other comments on the submissions

Submission no. 8 provides nothing constructive and demonstrates ignorance relating to the report. The author, while referring to 2,4-D esters, provided a fact sheet for 2,4-D acid. His comment on international reviews (USA, Canada and Europe) never leading to a ban of 2,4-D esters may be correct. However, in these reviews, the short-chain volatile esters were not considered as they are not used in these regions. It is difficult to know how to respond (politely) to such correspondence.

Submission no. 2 provided three appendices with suggested amendments to the report and reasoning for these. This aspect will be dealt with separately to this document.

3 Use of modelling for volatility

This submission (NuFarm) is concerned that there is insufficient scientific basis for deregistration of the short chain 2,4-D esters, and lists several concerns about the validity of the models used in the risk assessment.

They state that the risk assessment is based on theoretical modelling and rightly state that the outcome of the modelling is therefore dependent on the parameters used in the model.

With respect to the modelling approach for volatility of these short-chain esters, Nufarm believes that the EVA 2.0.1 model is the most relevant to use in the assessment.

3.1 Current volatility modelling in the risk assessment

It is stated categorically in the report that Australia has no formal model for quantifying volatilization of pesticides from soil or plant surfaces for regulatory use. Given the use of the volatile esters in Australia, it was important that this issue be considered. The US EPA **did not** address the issue of volatility in their risk assessment as it is not currently part of their risk assessment process. Additionally, the short chain, volatile esters were not considered in their risk assessment, presumably because they are not registered in the USA. The USA report makes the following statement on the issue of volatility:

> Based on the physical chemical properties of the ester forms of 2,4-D and on evidence from the open literature there may be a concern for impacts to non-target organisms due to volatilization and off-site deposition of 2,4-D esters. However, EFED (US EPA Environmental Fate and Effects Division) does not currently assess the impact of volatility, long-range transport and deposition as a route of exposure in its risk assessment process. Therefore, the effect of volatility of the 2,4-D esters on non-target organisms has not been quantified in this (US EPA) assessment.

3.1.1 Choice of model in the risk assessment

Given the need for considering this end-point, and noting no formal assessment approach for volatility in Australia, the model used was chosen because it was recent, publicly available, and simple to use. It is stated in the report that this model was used only to provide an indication of likely volatility. This model indicated 100% cumulative volatilization from the short chain esters as the trigger values used were based on vapour pressure, and the model claimed that substances having such a high vapour pressure as the short chain esters (>11.8 mPa or $1X10^{-2}$ Pa) are **not likely to be sprayed on crops**.

While DEH was prepared to be challenged on the modelling used, for these assessments, we need to use the tools available to us. The EVA model proposed by Nufarm is currently been assessed as part of a suite of models to predict volatility within the regulatory context of European Union assessments. We have obtained advice from the EU FOCUS Air Workgroup on this model, and understand it will be recommended as the model of choice for estimating short range transport (SRT) of chemicals within a tiered approach to considering volatility.

However, we have read the proposed guidance on the uses of these models (still not publicly available although we understand EU Member States have largely agreed to the document), and it is stated that, for very volatile pesticides:

> Volatilisation and subsequent deposition of very volatile compounds e.g. fumigants (Vp > 10^{-2} Pa at 20°C) can result in a substantially higher emission and off-site exposure rates than from other exposure routes, even when they are incorporated into the soil. Therefore **these substances would not adequately be assessed** by the given exposure assessment schemes for SRT and **a study would be required** to determine the deposition from this type of substance. The nature of this study would need to be agreed between the registrant and the authority concerned.

While the example is given of fumigants, the vapour pressure of the ethyl ester is $1.47X10^{-1}$ making it amongst the chemicals considered unsuitable for the approach recommended by the EU FOCUS Air Workgroup.

This helps to highlights the problem with modelling overall, but both the proposed EU guidance, and the model chosen for our assessment are at least in agreement that the short chain esters are likely to be very volatile following application.

3.1.2 Movement through the atmosphere

In addition to modelling the potential volatilisation (which was deemed to be very high), DEH considered the potential for the short chain esters to move through the atmosphere. A characteristic travel distance was calculated using a level III fugacity model. We understand the argument that these models are better for long range transport (LRT) rather than SRT. However, it was stated categorically that we were only using the results in terms of ranking, not the absolute values as these can be highly variable depending on the model of choice.

One of the contributing factors in considering this was the expected persistence in air. The ethyl and butyl esters had a predicted half-life in air in the order of 2 days. These predictions were made with an internationally accepted model in the absence of test data measuring the breakdown of these substances by hydroxyl radicals in the troposphere.

A DT50 of 2 days is an alerting factor to other types of assessments (eg, it is considered indicative of persistence in air sufficient for a chemical to undergo LRT in the atmosphere within the POPs convention). The essence of this value is to estimate the distance a chemical can travel in air within 2 days. For example, with a constant wind speed of 5 km/h, a parcel of air could travel 240 km by which time a chemical with a DT50 of 2 days will have halved its concentration.

We recognise that a DT50 of 2 days is a simplistic measure (it really only reflects the residence time of chemicals that partition 100% to air), but again, there are no experimental results available to refine our predictions.

We note that in a farmnote on organic acid herbicides provided as an attachment to the Nufarm submission, it is stated that high volatile 2,4-D esters will volatilise from the soil within a few days and the chemical vapour is quickly broken down by UV light in the atmosphere. If this statement is based on fact, we would be happy to review the data and amend conclusions regarding potential atmospheric transport appropriately.

3.1.3 Further scientific argument

Nufarm state in their submission that there is insufficient scientific basis for the de-registration of the short chain esters. The proposed de-registration is based primarily on arguments relating to the highly volatile nature of these substances and consequently, the likelihood of them moving significant distances off target and causing non-intended impacts.

There is little contention that these compounds are highly volatile. The herbicidal nature of the chemicals means plants may be susceptible, and this is no surprise. The actual effects on plants were assessed extensively using guideline/GLP studies (the actual toxicity to non-target plants is addressed separately in this document)

Also noted in our report are the comments from the WHO assessment of 2,4-D and its ester and salt formulations from 1984 and 1989. This read as follows:

> 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 shown in Section 4.2 above, the majority of ester formulations registered for use in Australia are still in the short chain forms of ethyl, butyl or isobutyl esters of 2,4-D.
>
> It is further stated in WHO, 1984 (EHC 29) that the drifting of vapours of the more volatile short-chain 2,4-D esters may result in air pollution and crop damage, and these products are being replaced by less volatile long-chain esters or by amine salts. However, the report does not state the countries where such replacement is occurring.

It needs to be recognised that these reports (while old now) contain the views of an international group of experts. While we am not aware of regulatory progress in other countries relating to the phasing out of these short chain esters, it does appear from later international, country or region specific reviews (USA, Canada, EU) that they are not used in these countries as the short chain esters are not considered in the reviews.

Other more recent scientific literature is used in our report. 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. The vapour pressures for ethyl and butyl esters are $1.47 X 10^{-1}$ and $5.29 X 10^{-2}$ Pa respectively, indicating these may be expected to volatilise from both soils and crops.

3.1.4 Conclusions for volatility modelling

All available evidence indicates shorter chain esters are much more volatile than the longer chain esters and salt forms of 2,4-D. In addition, they are predicted to persist in the atmosphere for longer periods than the longer-chain esters thereby increasing time and area of exposure. While the modeling used in the risk assessment for volatilization and potential transport in the atmosphere are recognized as being indicative only, they do support the conclusions in the risk assessment for this issue.

Evidence of rapid breakdown of these substances in the troposphere would be valuable in reassessing this end-point and should be provided if available.

Nufarm has provided an alternative model to predict volatilisation. DEH has not evaluated this model however, it is understood it is a regulatory tool in Germany, and in the near future, may be the tool of choice for SRT calculations in the EU regulatory scheme. Nonetheless, proposed guidance for this model specifically states that chemicals with vapour pressures of the order of 2,4-D butyl ester, and lower than 2,4-D ethyl ester, cannot be adequately assessed with this model for the potential for SRT and a study would be required to determine the deposition from this type of substance.

Other issues relating to the risk assessment outcome (specifically the hazard endpoints) are considered elsewhere in this document.

4 Volatility (no. 10 also includes benefits of volatility)

Submission number 5 states, “To our (PGA WA) understanding, no field studies into the volatilisation potential of 2,4-D short-chain esters under Australia (sic) climatic conditions exist.”

We agree and have not identified any Australian generated data for the volatility of these short chain esters. As described above, in the absence of such information, modelling is undertaken. We would welcome any domestic studies if they can be provided.

5 Toxicity of short chain 2,4-D esters to Australian native plants

Two submissions raised the issue of tolerance of native plants to 2,4-D esters, both quoting the Moore (1998) paper on tolerance of direct seeded native species to herbicides. The concern was raised in both submissions that there was no evidence of 2,4-D esters being more toxic to Australian natives (or conversely, 2,4-D being one of the more benign agricultural chemicals on native vegetation).

The whole issue of terrestrial non-target plant (TNTP) risk assessment has been debated internationally for a long time and continues to be so without any strong conclusions on how it should be performed. Standard methodology used here and internationally considers the lowest effects value (EC25 or EC50) from a range of tests on a minimum of 6-10 species, and applies an assessment factor. The use of probabilistic approaches are not widely accepted currently for a number of reasons.

However, given the volume of data for this assessment covering at least 10 species and considering both seedling emergence and vegetative vigour for a range of test substances including 2,4-D acid, amine salts and longer chain esters (no data on short-chain esters were available), a probabilistic approach was adopted to allow a better use of all available data (conducted to US EPA guidelines and following good laboratory practice). Consequently, a NOEL rather than an EC50 was used for protection **without** the application of an assessment factor. If an EC50 were used, an assessment factor of 10 would have been applied.

In this regard, it needs to be recognised that for Australian chemical risk assessment, international studies are routinely accepted in lieu of domestic studies and this issue is explored in greater detail further below in this document.

The results of the analysis of the available data are described in some detail in the assessment report. The Moore paper was provided following the completion of the risk assessment and has since been reviewed by DEH, and the following comments are made:

- The test was performed using 2,4-D amine (50%) on 39 native species following germination, that is, it was comparable to a vegetative vigour study. This is good as 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.

- Observations on effects were categorised three ways, <25% impact on growth/survival; 25-50% impact on growth/survival or >50% impact on growth/survival.
- Observations were only made at 60 and 100 days. This is inadequate to determine any shorter term impacts, and such shorter term adverse effects (if found) would be useful to build arguments relating to a plants ability to recover based on observations at the later times.
- It is noted some species did not survive in sufficient numbers, especially in trays watered from below. As it reads, this is a problem due to the watering method. However, there is no reference to control plants, and it is unclear as to whether this could also be due to the effect of the chemical. It is not known whether such problems were found in the 2,4-D experiment.
- The application rate was stated as 1000 or 4000 g product/ha. A 2,4-D amine 50% formulation was used, therefore, application rates are assumed to be 500 and 2000 g ae/ha. These gave the following broad results:

500 g ae/ha	% of species	2000 g ae/ha	% of species
33 species <25% effects	84.6%	18 species <25% effects	46.2%
3 species 25-50% effects	7.7%	7 species 25-50% effects	17.9%
3 species >50% effects	7.7%	14 species >50% effects	35.9%

General comments on the study:

At the time of application, seedlings were 8 weeks old. Plants in standard vegetative vigour studies are usually younger (application within 7 to 21 days of emergence).

While overall, this study can provide useful insight into the tolerance of the tested native species between different herbicides, it is very difficult to draw real conclusions relating specifically to 2,4-D compared to other studies in the data set. Results of this study are provided in terms of visual observations. There are no measurements of other factors that may point to longer term problems such as measurements of plant height or shoot/root weight compared to control plants.

The end-point used in our assessment in the end was the NOEL. This allowed us to derive a Q value of 1 rather than applying a further conservative factor and using a Q value of 0.1. The results from this study do not provide NOELs (and could not in any event as there were only two rates tested). No statistically derived EC25 value could be obtained either as a dose-response relationship could not be defined.

The measured EC25 values in the assessed data set (n = 104) ranged from <1 to >4700 g ae/ha. The number of tests in the assessed data set with measured EC25 values <500 g ae/ha was around 64% compared with the visually determined “EC25” values in the Moore study being about 15%. Therefore, while on their face value, these results do indicate that the species tested are possibly more tolerant than the standard crop species that we have GLP studies for; they are not directly comparable for reasons outlined above. Also, it should be remembered that this only looks at one stage of a plant’s life. Other stages such as germination, emergence and reproduction are not addressed, and some *in vitro* evidence provided in the US EPA studies, but not considered in the risk assessment due to problems with extrapolating results to the environment, indicate that other life-stages (specifically germination), may be very sensitive.

To be able to undertake a better analysis, standard vegetative vigour studies allowing a dose/response relationship to be determined would be needed. For example, if the most sensitive species found based on the visual approach in the Moore paper were tested for vegetative vigour following the same guideline as other currently available data, this would give a much better indication of the sensitivity of these species. If any testing were to be performed (and to this end it is noted that in the Nufarm submission (No. 1), the company would be prepared to replicate the experiments to expand on the findings), prolonged testing to determine recovery of susceptible plants would be highly desirable.

Unfortunately, in the absence of such information, we are left with the view that the tested species in the Moore paper probably fall within the range of values found in the standard laboratory testing, and given the probabilistic approach taken in the risk assessment and the decision to adopt the 95th percentile from the distribution of NOEL results, it needs to continue to be assumed that this will also be protective of 95% of Australian native species.

6 Validity of aquatic toxicity endpoints

Nufarm (submission no. 1) have strongly questioned the validity of using aquatic toxicity endpoints derived from old non-GLP studies rather than using data from the available newer GLP studies. (We note that this concern is at odds with one of their other concerns that the GLP plant toxicity data are doubtful given the results of a non-standard non-GLP study on tolerance of Australian natives.)

Australia accepts international data where it is available. We do not have our own national test guidelines and consequently rely on internationally generated data as the primary data source to support our assessments. This point is elaborated on further elsewhere in this document.

In the event we receive non-GLP data and also have available GLP data, the former is not automatically dismissed. Where the studies are deemed valid (for example, a good dose/response was obtained, control mortality was within reasonable means and the test was performed in a sound manner), the results should not be precluded from use in the risk assessment.

In the case of the short-chain esters, no test data were provided for toxicity to aquatic organisms with the exception of one test for fish that while considered valid, was performed on a non-standard species and not to a known guideline, and one older study for aquatic invertebrates. However, in the absence of data, a weight of evidence approach was taken using results reported in the US EPA ECOTOX database (noting again that no actual studies were provided to the APVMA). It should be noted that the majority of test data used in the risk assessment was provided by the 2,4-D Task Force.

Given this, we need to use what is available to us, and this means using results from the literature, or non-GLP data where available.

7 Application rates in spray drift modelling

Spray drift modelling for the short-chain esters has only been performed at the higher rate with some consideration (but no refinement of the modelling) given to reducing the application rate.

The tiered approach of the overall risk assessment resulted in an unacceptable risk being determined through the volatilisation of the chemicals, hence it was not considered necessary to further refine the spray drift modelling for the short-chain esters.

8 Use and impact of short chain 2,4-D esters in Australian agriculture

The risk assessment has been performed on behalf of the APVMA by ~~DEH~~ DSWEPaC following standard risk assessment methodology. This methodology does not allow for wider issues such as cost/benefit analysis or total environmental impact resulting from potential regulatory action based on the risk assessment.

9 Current use control restrictions on phenoxy products

Several submissions (numbers 1, 3, 11, 13, 14) point to the current restrictions used in WA (exclusion zones), stating that these have worked well in reducing off target damage from the short-chain esters.

It is our understanding that these restrictions are aimed at the protection of non-target crops, not non-target plants in general (including native vegetation). The use of such controls is a risk management tool that may be considered based on the outcomes of the risk assessment.

10 Education and spray management

Several submission (numbers 1, 4, 9, 13) note that risks are mitigated through use of current spray technology and spray management systems, and educated/accredited applicators. We accept this is highly desirable for limiting likely non-intended impacts resulting from application, however, it is not an issue for the science based risk assessment. This is a risk management issue.

11 Editorial/amendments to current report

Submission number 2 provides a lengthy list of suggested amendments and editorial comments on the body of the report. These will be considered separately to this document.

12 Availability of previously unsupplied studies

The list of non-target arthropod studies provided in Submission 2 should be provided.

13 Need for wider scope (costs and benefits; alternative chemicals; low tillage farm practices etc)

Several submissions (numbers 3, 4, 5, 6, 7, 9, 10, 11, 13) state the need for a wider scope of the assessment requesting such issues as total environmental costs and benefits (value such chemicals provide to low tillage farming, possible increase in use of herbicides if these short chain esters are not available etc.) are considered.

While we are sympathetic to these arguments, the risk assessment in this case has been performed on behalf of the APVMA by DEH following standard risk assessment methodology and in the confines of the APVMA legislation. This does not allow for wider issues such as cost/benefit analysis or total environmental impact resulting from potential regulatory action based on the risk assessment.

14 Use of international data as surrogate values for Australia

Several submissions raised concerns over our use of international experimental data rather than the use of Australian specific data, claiming that the use of the international data should only be accepted when validated against Australian conditions. We understand frustrations readers of the report may have in this area. This is not an uncommon question, however, several issues need to be understood.

- International test guidelines have been established and adopted in specific countries (for example, the USA and European Union), or at a wider level (OECD). Australia has as a matter of policy been prepared to adopt studies performed to these guidelines, and in the case of OECD test guidelines, is involved to a degree in their development.
- While we as the risk assessors would be very welcoming of tests conducted in Australia, it is not an economic reality for us to receive them. If we insisted on such studies, industry would be very unlikely to perform them due to cost restraints, and the consequence may be that no new chemistry would be available in Australia, or for existing chemicals, industry would simply not continue to support their registration due to the relatively small Australian market size.
- In the case of ecotoxicity tests, standard tests are performed with species recognised to be at the sensitive end of the likely toxicity range.
- To account for possible interspecies variation, the risk assessment applies an assessment factor to the international results, an these are taken as surrogate values to be protective of Australian species.
- For environmental fate studies, we recognise that there are variations between Northern Hemisphere climates where these studies are usually performed. If it is considered these variations are sufficiently large (remembering we are talking Tier I or Tier II assessment level only), we may (and have in the past) ask for Australian specific studies.

15 Use of Australian generated data (including field experience)

We agree that the range of available data should be considered. It is very difficult in the actual risk assessment to use anecdotal data (usually the type available from field experience) within the risk assessment framework. This type of information may be used further in developing risk management options or mitigating risk assessment outcomes.

Unfortunately, the submissions received for the 2,4-D review mainly provided anecdotal evidence of adverse off-target effects with no comment or data provided indicating the opposite. Some of this field experience is being shared now following the release of the draft assessment report.

16 Focus on Western Australian broadacre use

Several submissions focus on the adverse impact on farming for Western Australia broadacre uses if these short chain 2,4-D esters are no longer available. These concerns have been noted.

Attachment 3

Public comments – 2,4-D Review, Short Chain Ester Reports: NFF Submission

Responses to National Farmers Federation Submission to APVMA

1. The appropriateness of the methodology

APVMA has commissioned DEH to provide an ecological risk assessment of all forms of 2,4-D, including the 2,4-D esters which are specifically dealt with in Part 1, 2,4-D Esters, This document, including the refined risk assessment for volatile esters, is the main subject of this review prepared for the NFF.

STATEMENT: No response required.

Quoting from the document, "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"

STATEMENT: No response required.

"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 to have an unintended effect that is harmful to animals, plants or things or to the environment".

STATEMENT: No response required.

The methodology used by DEH is as follows:

- A tiered approach was taken for assessment of the available data. In the first level or tier, a 'worst-case' exposure scenario was taken for all forms of 2,4-D, and is presented in the report. In the second tier a 'refined' assessment of identified risks for 2,4-D esters with non-target terrestrial vegetation and for its aquatic risk to fish and aquatic invertebrates was attempted.

STATEMENT: Refined risk assessment was mainly performed in the Part II report (long chain esters, amine salts and acid) that is still to be released.

- Available databases were reviewed for information related to the physicochemical properties of 2,4-D as well as to toxicology data, with a view to determining toxicity endpoints as safe or no-effect concentrations or levels (NOEC, NOEL), a procedure highly dependent on reliable indicators or endpoints of toxicity such as LD50, LC50 or EC50/EC25 values affecting a percentage of the test population species.

STATEMENT: Not entirely correct. Databases were interrogated for test end-points where no data were provided. This was particularly the case for the short chain esters where essentially no test data were provided for any end-point in the assessment.

- In particular DEH uses a quotient approach. In this desktop method, the ratio or quotient (Q) of the predicted environmental concentration (PEC) or exposure and the selected acute toxicity endpoint is calculated; values of 0.1 or less are considered as acceptable and for chronic toxicity, a value of 1 is acceptable. In the case of terrestrial plants, a Q-value of 0.1 or less based on EC25 data was considered as acceptable.

Response: This was the case for the preliminary risk assessment. However, with terrestrial plants, it is stated clearly in the document that "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 acceptable." This was to enable a more full use of available data rather than the very conservative approach adopted in the preliminary risk assessment.

In principle, this methodology does provide a basis for relative estimation of the hazard presented by particular chemicals. However, the approach presents difficulties regarding the following factors:

- Accurate data must be available on which to base the calculations
- The method is suitable for estimation of the relative hazards presented by different chemicals, but is not an estimator of the risk since it does not consider the probability that exposure will occur. Factors affecting probability of exposure include frequency of application, wind direction, temperature, rainfall and the likelihood of runoff and so on. No account is taken in the APVMA review of the probability of exposure, on the basis that a 'worst-case' scenario as a result of a single application is being examined.

Response: This is largely true for the Part I report. The preliminary risk assessment identified the areas more at risk (eg, in-field non-target arthropods, aquatic plants and terrestrial plants for all forms of 2,4-D, and aquatic organisms for the ester forms of 2,4-D). In the refined risk assessment within the Part I report, only one application rate was modeled, namely, the highest rate. These rates were considered acceptable to aquatic organisms provided adequate buffer zones were in place and coarse droplets were used. The buffer zones were considered manageable, so no further refinement was undertaken. The only use pattern showing an unacceptable risk to aquatic organisms was using direct application of esters for aquatic use patterns.

Much more refinement including an in-depth assessment of altering application rates through spray drift modeling were addressed, but in the second part of the report that has not yet been released. Nonetheless, impacts of reducing application rates and changing droplet sizes were still considered and discussed in the refined assessment performed in the Part I report.

Table 1 below outlines the data reported by DEH for assessment of volatility, which we find to be inadequate for effective risk analysis.

The vapour pressures detailed are not referenced to their original sources. The following explanation was given: *"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 temperature agree. Results are presented here as an indication of relative vapour pressure at working temperatures.* " (p31)

Response: The original data for the short chain esters were NOT provided by industry. The references provided in the report are referenced to the source document (EHC report), or available experimental databases (EPI Suite). Vapour pressures were also reported in the appendices to the report (Technical Reports for the acid, salt forms of 2,4-D and ester forms of 2,4-D).

Without detailed referencing of the vapour pressure and other relevant data, peer review of its accuracy is difficult. APVMA policy (p3 Summary) requires transparency of data. Adding to the inadequate reporting of relevant data,

- Solubilities are not reported (m); Henry's Law constants cannot be verified without solubility values.

Response: These values are reported in Appendix II, Technical Report for Esters of 2,4-D, which was made available with the report. Again, no data were provided by industry for the short-chain esters. Therefore, it is clearly described following the Physico-Chemical table in the Appendix that:

"EPISuite was used to calculate all values where experimental data do not exist. Experimental values are available from the US EPA EPISuite experimental database for water solubility and vapour pressure for 2,4-D EE and 2,4-D BE. The vapour pressure result for 2,4-D EE is also reported in WHO (1984 and 1989). However, the vapour pressure result for 2,4-D BE differs between these references. A vapour pressure of 6.16×10^{-5} mmHg is reported in the EPISuite experimental database while 3.97×10^{-4} mmHg is reported in WHO 1984 and 1989."

- Half-life in air is modelled using the model AOPWIN Version 1.91. In the US EPA, this model is only used for screening assessments. This program is available for purchase, but detailed methods are not published so that review of these methods is difficult; however, for screening purposes the method has merit.

Response: This is simply incorrect. The AOPWIN software is publicly available within the US EPA EPIsuite of software and can be downloaded from: (http://www.epa.gov/opptintr/exposure/docs/episuite.htm). Model documentation is available.

The AOPWIN model uses the structure-reactivity relationships approach developed by Atkinson and his collaborators and is accepted as a modelling tool within OECD member countries. The methodology is described in OECD Environment Monograph No 61: The Rate of Photochemical Transformation of Gaseous Organic Compounds in Air Under Tropospheric Conditions. Further information has been added to the assessment report relating to this issue.

While the model is considered screening level, it is an acceptable tool given no experimental data were provided or appear to be available for degradation in air.

Table 1. Physical-chemical properties reported in the APVMA document

Property	Ethylhexyl (EHE) 2,4- D	2,4-D Ethyl ester (EE)	2,4-D Butyl ester (BE)	2,4-D Isobutyl ester (IBE)
Vapour pressure (mm Hg)	2.0×10^{-6}	1.1×10^{-3}	3.97×10^{-4}	Nr
Solubility	Nr	Nr	Nr	Nr
Henry's law constant atm.m^3/mol	1.81×10^{-4}	3.25×10^{-7}	4.88×10^{-7}	1.25×10^{-7}
Half-life (air)	Modelled	Modelled	Modelled	Modelled

nr= not reported;

Given the importance of specific information in risk assessment, we found it surprising that more effort was not made to obtain original data for the more volatile esters (EE, BE, IBE).

Response: It is the responsibility of industry to provide the data. The 2,4-D Taskforce did not generate any contemporary data for the short-chain esters as they DO NOT support their use. Therefore, data were modeled where no test endpoints were available, or were taken from the EPI Suite database of experimental results. The older test data available in the EPI Suite database were not provided for review.

Regarding the standards of environmental protection required, on page 12 the following statement is made regarding hazards from 2,4-D herbicides.

"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".

This statement lacks objectivity and is unhelpful, taking no account of the resilience of most plants. Systemic herbicides like the synthetic auxins are readily translocated to plant meristems where they act and do not cause highly localised damage where they are deposited. It would be preferable to provide endpoints or thresholds involving measurable responses, so that registrants and researchers can have reasonable targets to achieve.

Response: The statement was a quotation from the US EPA report and is referenced as such. The reason that, as stated by Prof. Kennedy, systemic herbicides like the synthetic auxins are readily translocated to plant meristems where they act and do not cause highly localised damage where they are deposited supports the statement in the report that “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.”

The second part of this issue, “it would be preferable to provide endpoints or thresholds involving measurable responses” is fully supported. The actual hazard assessment to non-target plants was performed based on measured responses such as root weight, fresh weight or survival, from a range of standard GLP plant toxicity studies.

DEH' s methodology is not required to consider the efficacy of a product as a herbicide. The 2,4-D esters are popular with farmers mainly because of their greater efficacy, particularly with actively growing weeds and in farming systems with stubble retention requiring herbicides for weed control. The volatile esters are currently in heavy use because they can achieve pest or weed control more effectively per unit cost.

Response: This goes to the scope of the assessment. The risk assessment does not allow for issues such as cost/benefit analysis or comparison with current or new chemistry other than the one being assessed. APVMA may wish to respond in more detail to this statement.

In the refined assessment of the volatile esters, the weakness of the data set is admitted by DEH.

Regarding the use of the Van der Linden equation (p59 Summary) to determine the extent of cumulative volatilisation, DEH states that, "These assumptions are not scientifically based. The results will be used for comparative purposes only between different ester forms." Yet, the values are use to determine PEC's and then used for Q-values in Table 21. This result is then used to argue for their "much greater risk", contrary to previous statement by not referencing a level of concern, and then to bias the "long range persistence/transport" argument (p60, Summary).

Response: This comment is misleading. While the assumptions used to determine the environmental concentrations were not scientifically based, this is not true of the model used to predict volatilisation. A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

Regarding long distance volatile transport, it is stated that the characteristic travel distance (CTD) approach was used to "rank chemicals, not (determine) absolute values..." (p61). And "Absolute values are not considered appropriate in this case due to the large number of assumptions made in modelling." Yet the relative long-range transport result is still used to argue in favour of the final recommendation to withdraw approvals. This is not logical as methodology as there is no absolute reference point, only a relative ranking.

Response: A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

The CTD method was developed to provide estimates of travel distances for persistent organic pollutants (Beyer *et al.,* 2000) not subject to rapid degradation. Even for these persistent pollutants, the CTD estimates are considered as useful only for screening purposes; the opportunities for rapid dissipation of volatile esters of 2,4-D by deposition in water, vegetation or soil and by ultraviolet degradation in the atmosphere reduce the likely accuracy of the method. It is accepted, however, that estimates of many kilometres travel for the more volatile esters by this method do represent a 'worst-case" scenario that applies when factors such as meteorological inversions, lack of turbulence and high temperature favouring volatilisation combine to increase the risk of long distance transport.

Response: This is partially correct. However, there are NO fate data for the short chain esters. While we accept that these chemicals will probably degrade relatively quickly when in contact with the soil through hydrolysis and microbial degradation, the process is by no means instantaneous. The volatility of these compounds mean that significant amounts of the applied substance will lift off prior to these processes, and in the atmosphere, they are considered persistent based on available information. Therefore, the use of CTD calculations are considered appropriate. A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

The question remains whether such events do represent a risk sufficient to justify a complete ban in Australia. In fact, we find that no valid risk assessment showing this has been performed in the "refined" assessment; only a subjective inference of hazard is achieved. No clear evidence is presented that volatile 2,4-D esters would be likely to have "an unintended effect that is harmful to animals, plants or things or to the environment" if carefully managed.

Comment: A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

2. The validity of the assumptions (particularly where data gaps exist)

The assumptions used in the environmental risk assessment include the following:

- In the absence of specific toxicity data for the 2,4-D esters, ethyl 2,4-D and butyl 2,4-D the assumption is made that data related to other esters (e.g. isopropyl-2,4-D) can be used. This is the case for their aquatic risk assessment, where the potential toxicity to the most sensitive fish species is found to be unacceptable.

Response: It is acceptable to use surrogate data where the surrogate chemicals are considered structurally similar and valid data are available for them. However, it remains our preference to have chemical specific data. In this case, no contemporary data were generated for the short chain esters due to the view of the 2,4-D Taskforce that they did not support their use, and they haven’t been used in North America or Europe for more than 20 years. Some toxicity data were available for the short-chain esters that were submitted. These tended to use non-standard test species and non-standard guidelines, but in cases were still deemed acceptable. Other test data were reported in databases (ECOTOX), but these appeared old and the test reports were not provided.

- Critical assumptions are made regarding estimates of PEC values for esters deposited on terrestrial vegetation nearby the areas of application. This includes an estimate of 50% of the application applied will be volatilised and that this will be entirely deposited on ten times the area of nearby terrestrial vegetation.

These assumptions are challenged since they are not supported by data for the products at issue. The theoretical weakness of the assumptions is recognised by DEH as stated above but they are still used in the document to estimate Q-values for comparative purposes regarding the different 2,4-D esters.

Response: A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

However, this approach is potentially misleading. While it is possible that 50% volatilisation of applications for esters may occur, no direct evidence supporting this is available. Uncharged volatile esters are particularly prone to 'absorption through the waxy cuticle of leaves of plants and once in the plant tissues, they may be subject to enzymatic conversion to 2,4-D by esterase activity. Esterases causing hydrolysis of the 2,4-D ester to 2,4-D and a simple alcohol are very widespread in living organisms and a large proportion of the 2,4-D ester absorbed may be converted to the non-volatile acid form more active as a herbicide.

Response: There is little doubt in the international scientific community that the short-chain esters of 2,4-D are highly volatile. There is also little doubt that they have the ability to move long distances off target. A separate document is provided outlining the results of some international work considering the long range transport of 2,4-D, even following application in its low volatile forms (see Attachment 3).

Furthermore, the proposal that all of the 2,4-D ester volatilising will be deposited on 10 times the area of terrestrial vegetation is particularly unrealistic and could be several orders of magnitude in error. Temporary deposition of vapour on nearby vegetation is certainly expected as a result of partial equilibration with a volatile plume of the chemical in air, but this highly reversible process is time dependent and the deposited volatile ester will be reabsorbed into fresh mobile air. Indeed, the assumption of complete transfer to 10 times the vegetation directly conflicts with the assumption of a long transport path estimated for the more volatile esters up to 50 km or more. Better methods for estimating the likely exposure of nearby terrestrial vegetation are available, discussed below in Section 4.

Response: A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

Regarding the treatment of data used to establish threshold values:

- The development of the NOEL value for vegetative vigour (p 62-65 Volume 2 Technical report) is not well described. The treatment of "left-censored data" is not detailed. The data, apparently used for statistical analysis (appearing in Attachment **n,** p88), are not referenced, nor are units provided to enable interpretation. Only minimal review is possible.

Response: All available test data used to determine the NOEL are described in some detail in the appendices to the report, namely, the technical reports for 2,4-D acid, 2.4-D esters and 2.4-D salts. These appendices were provided with the report and were therefore available for review.

- Furthermore, the treatment of the right censored data introduces bias into the determination of NOEL. By assuming that the maximum test dose is the NOEC (when there may be no response at all) will significantly reduce the mean value. The approach also has uncertainty which is not considered; the coefficient of variation is 32.08%, which indicates the low accuracy of the final figure, compounded by the introduced bias.

Response: In order to use all available data, we needed to have some way of dealing with the right censored data. To remove these values from the database would have been improper as they represented the least sensitive species. There was no way of extrapolating out to an actual NOEL as no effect was seen at the highest level tested. Therefore, the decision was made that the highest rate tested would be deemed the NOEL.

We appreciate this introduces some bias. However, the alternative approach, that is, the more conservative deterministic approach of taking the lowest obtained value and applying an assessment factor, seemed inappropriate given the level of data we had available, and would have resulted in a much lower level of protection than that determined statistically.

- This approach was developed to estimate a NOEL when assessing risk in spray drift, not for volatilization. The units given by DEH are consistent with assessing risk to drift, i.e. a rate (g ae/ha.). The mechanism of exposure is not rationalised. For risk from volatilisation a concentration *(mass/volume, rather than mass/area)* and a coefficient of partitioning must be determined, and then related to toxicity effect concentrations. Therefore, the use of this end point for volatilisation assessment is not justified.

Response: This is not correct. The NOEL can be used for exposure from spray drift, or from exposure through atmospheric transport where chemicals are deposited through wet or dry deposition. This aspect is discussed separately in more detail (see Attachments 2 and 3). We would expect the short-chain esters of 2,4-D to be present in the atmosphere either in the gas phase or bound to particulates, so both routes of exposure are available. However, typically no test data were available to determine plant toxicity when exposed through the gas phase, so it was assumed all available chemical in the atmosphere would deposit in a rate of g/ha.

- The derived NOEC of 0.73 g ae per ha would be more useful in Section 8.1.1 Risk for Drift, where levels of concern in buffer zones are described. This indicates that a 200-300 metre buffer zone (see Table 13 in APVMA's Vol. 1) would provide sufficient protection from aerial droplet drift for applications at the highest rate. Considered as a refined assessment predicting exposure, such a buffer zone could be recommended for regulatory purposes.

Response: The NOEC is used much more in the refined risk assessment for exposure through spray drift in the second report that is yet to be released.

- Regarding p 36 Volume II: "There was no *significant difference* between toxicity of the free acid, ester or salt forms of 2,4-D...". Such a statement infers a statistical analysis. What was the analysis, and where are the data? A better justification of the use of the surrogate data is required. It is clear that the toxicity of the esters vary significantly.

Response: No statistical analysis was performed. The statement simply relates to the data described in the tables for algae/aquatic plant toxicity. The only data available for the esters were for the longer-chain compounds.

These assumptions, in part invalid for volatilisation, amount to a significant lack of rigour in the risk assessment conducted for the more volatile 2,4-D esters. In particular, the confusion between aerial drift of spray droplets and volatilisation of the esters needs resolution.

Response: A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

3. The relevance of overseas studies in assessing potential impacts on the Australian natural environment

Overseas data is generally acceptable for first tier risk assessment but local data would be preferable for use in refined risk assessments and regulatory decisions. However, very little overseas data has actually been used, even in the refined risk assessment. The conclusion that the volatile esters are too risky is largely based on qualitative opinions expressed in USA and Europe possibly justified in their highly intensive agricultural systems with close proximity to urban populations. These conclusions were probably made in the context of deciding research priorities at the time (WHO 1984, 1989), but little data was subsequently generated as a result. Australia's far more extensive style of agriculture may reduce the potential for significant risk of toxic exposure.

Response: This statement is largely incorrect. While we don’t want to speculate as to the opinions of the USA and Europe, the WHO reports are scientific documents, not policy documents and they are written by experts in their field. The conclusion that the volatile esters are too risky is based on their unacceptable exposure to the non-target air compartment, persistence in this compartment, and corresponding ability to move large distances off target. We agree that Australian data would be desirable, but this is not always needed to make regulatory decisions. In the case of the short-chain esters, any data would have been appreciated, however, industry chose not to perform any contemporary studies as the 2,4-D task force DO NOT support the use of these chemicals. All available test data provided to the APVMA for this review was considered and used as thought appropriate.

The seedling emergence and vegetative vigour data referred to above is for annual agricultural or horticultural plant species not directly relevant to most native terrestrial vegetation in Australia, which is mostly perennial. As a result, the APVMA may wish to recommend commissioning studies to test the effect of direct applications of various herbicides to Australian native species similar to those conducted by John Moore in Western Australia (Personal communication, 2006). These studies showed that the direct applications of hormone herbicides in Group I in the 2,4-D family were generally tolerated by 40 native species at low rates of application. These tests used 2,4-D amine salts and did not include the more volatile esters but more quantitative studies like these could be useful to determine NOEC/NOEL values.

Response: The assessment in this case was for non-target terrestrial plants, not specifically non-target native vegetation. It is standard procedure to use the species for which the available test data were generated as these are easily cultivated and include representative species from monocot and dicot families. These data are accepted routinely here and are internationally accepted as being representative of non-target plants, regardless of whether they are crop or native species. Any tests performed to dispute these findings with regard to Australian natives should be undertaken using similar methodology with internationally accepted test guidelines to enable a proper comparison with dose/responses found in the standard studies assessed for this endpoint.

We are aware of the Moore paper, and have previously provided comment to the APVMA on its usefulness. A briefer version of these comments are provided here:

- The test was performed using 2,4-D amine (50%) on 39 native species following germination, that is, it was comparable to a vegetative vigour study.
- Observations on effects were categorised three ways, and only visually with observations were only made at 60 and 100 days. This is inadequate to determine any shorter term impacts, and such shorter term adverse effects (if found) would be useful to build arguments relating to a plants ability to recover based on observations at the later times.

- It is noted some species did not survive in sufficient numbers, especially in trays watered from below. As it reads, this is a problem due to the watering method. However, there is no reference to control plants, and it is unclear as to whether this could also be due to the effect of the chemical. It is not known whether such problems were found in the 2,4-D experiment.
- At the time of application, seedlings were 8 weeks old. Plants in standard vegetative vigour studies are usually younger (application within 7 to 21 days of emergence).
- While overall, this study can provide useful insight into the tolerance of the tested native species between different herbicides, it is very difficult to draw real conclusions relating specifically to 2,4-D compared to other studies in the data set. Results of this study are provided in terms of visual observations. There are no measurements of other factors that may point to longer term problems such as measurements of plant height or shoot/root weight compared to control plants.
- No statistically derived NOEL or EC25 value could be obtained as a dose-response relationship could not be defined.
- Also, it should be remembered that this test only looks at one stage of a plant's life. Other stages such as germination, emergence and reproduction are not addressed, and some *in vitro* evidence provided in the US EPA studies, but not considered in the risk assessment due to problems with extrapolating results to the environment, indicate that other life-stages (specifically germination), may be very sensitive.

4. Any scientific work which may have been overlooked

Transport of volatile pesticides

From APVMA's review it is clear that the main cause for the recommendation is the volatility of the 2,4-D esters and their propensity to move as a volatile cloud to nearby terrestrial vegetation. Aerial drift of droplets downwind is not of specific concern as drift will apply equally to other forms of non-volatile 2,4-D such as the amine or other salts or the acid, though these non-volatile forms will tend to remain where they are deposited.

STATEMENT: no response required.

Apart from a simple model involving an equation to estimate the percentage of a product that is expected to become volatile, based solely on its saturated vapour pressure (Van der Linden *et al.,* 2004), no recognised modelling to predict movement as a volatile cloud off-site is employed in the review. However, DEH does refer to a European model for which they are currently seeking more information. "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". This shows that this APVMA assessment of the volatility of 2,4-D esters is incomplete.

Response: Given the lack of data provided to support continuing registration of the short-chain esters, simple modeling was considered appropriate. The compounds in question are highly volatile for crop chemicals and available modeling (using an internationally accepted model) indicates they will persist in the atmosphere thereby allowing them to move long distances. The EVA model has since been considered in more detail and a response provided to the APVMA on its likely applicability. Unfortunately, this model (while in the future is likely to be the model of choice in EU risk assessments) is designed for assessing short-range transport. The documentation of the EU Air FOCUS Working Group (not yet publicly available) explicitly states that for chemicals with a vapour pressure in the order of the short-chain esters, the model is inappropriate and long range transport should be considered.

A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

Furthermore, the DEH admits this saying "Calculations on PECs have been performed with the following assumptions. These assumptions are not scientifically based". As a result, "The results will be used for comparative purposes only between the different ester forms". Despite these statements regarding the weak scientific basis for their approach, Q-values were calculated and characteristic travel distances calculated. As a result of these comparisons, it was concluded as "highly inappropriate" that, despite the advice in a WHO review of 2,4-D (IPCS, 1989) that highly volatile ethyl, isopropyl and butyl esters should be replaced by low-volatile esters or by amine salts to reduce crop damage from 2,4-D vapour drift and to decrease atmospheric pollution, this advice has been ignored in Australia.

Response: A more detailed response to the issue of risk assessment through the volatility end-point is provided separately (see Attachment 2).

A suitable Australian model that should be used

However, there is an Australian model available that could be readily applied to predict the transport of volatile pesticides downwind (Raupach *et al.,* 2001 a, 2001 b); this model was developed for a study on the insecticide endosulfan applied to cotton. Although endosulfan is less volatile than the 2,4-D esters, volatile transport does represent the most significant means for removal of this chemical off the site of application, given it is not metabolised rapidly. More than half of the endosulfan deposited can volatilise from plants during the first week after application.

Response: APVMA has contacted the author of this model who indicates it is probably not suitable for 2,4-D. APVMA/DEH are open to considering higher tier modeling. However, prior to undertaking higher tier modeling, data gaps relating to the chemistry and environmental fate of the short-chain esters are required. These are described separately in Attachment 4.

Raupach links fluxes of contaminants through a mass balance equation (Raupach *et al.,* 2001a) in which the change in contaminant concentration in air and absorbent media with time can be given as a function of various fluxes and transformations.

The vapour transport model invoLVE three sequential processes, post-spray volatilisation from the crop, dispersion of the vapour by wind and turbulence and re-deposition of the vapour to surfaces, in this case water surfaces. The post-spray volatilisation is described by a simple, exponentially-decaying release rate constrained to conserve mass and dispersion by a Gaussian-plume algorithm (Raupach et al., 2001 b). This model enabled the concentration in the air and the concentration in water where re-deposition occurred to be estimated and the predictions then tested against actual measurements in water trays, effectively validating the model. It would be possible to model the same process of volatilisation of 2,4-D esters in air, with reversible dispersion downwind and re-deposition to terrestrial vegetation. Key factors in such a model would be the estimates of the degradation rate in target plants, the capacity to release the remaining volatile ester, the capacity to uptake the ester into soil and into non-target terrestrial vegetation. Such a model could also assess the effect of temperature and wind speed and be modified to include incident radiation.

Response: Prior to undertaking higher tier modeling, data gaps relating to the chemistry and environmental fate of the short-chain esters are required. These are described separately in Attachment 4.

Other data related to atmospheric loading with volatile esters of 2,4-D is available in the WHO 1984 publication referenced in the APVMA review (see Appendix 1). These data, surprisingly not considered in the refined assessment in the APVMA document, include concentrations of volatile butyl 2,4-D ester in ambient air (Table 4) and would be useful for validation purposes in completing the exposure modelling for terrestrial vegetation, as indicated in our footnote to Table 4. Data relevant to risk assessment for 2,4-D esters in surface waters are included in Table 7 in the Appendix, together with our comment in the footnote.

Response: These data were reviewed but not reported. There are several other publications that discuss atmospheric concentrations of 2,4-D, although in its less volatile forms. The issue in question was not so much the loading in air (strongly affected by assumptions relating to mixing height), but the load available in its deposited form. This issue is discussed in more detail in a separate document (see Attachment 3).

5. Opportunities to mitigate the risks

As stated in the APVMA review, modified label conditions to mitigate the risk of drift have recently been introduced. However, these conditions relate to reducing the risk of aerial drift of spray droplets rather than the drift of vapour.

Statement. No response needed.

Factors affecting the rate of volatilisation of chemicals include their inherent vapour pressure, temperature, the degree of saturation of the adjacent atmosphere affected by wind speed, the solubility of the chemical in the material where it is deposited and the intensity of incident radiation. These factors could provide a basis for limiting the magnitude of volatilisation, or the rate at which it occurs and thus the predicted concentration of the chemical that will be reached in other environmental compartments such as terrestrial vegetation and bodies of water. Modelling such as that discussed in (4.) can take some or all of these mitigating factors into account.

Response: Possibly. However, prior to higher tier modeling, reliable test data on endpoints such as vapour pressure and solubility are required. No such data were presented and results were obtained from the EPISuite experimental database. A separated discussion of data requirements needed to refine modeling is provided as Attachment 4.

Despite the opinion expressed in the APVMA review (p. 61) that "persistence in the atmosphere, high volatility and potential to travel long distances in the environment" "makes it very difficult to mitigate the risk from these compounds", this is not necessarily true. The butyl and isobutyl esters have less than one-third the vapour pressure of the ethyl ester and are likely to be vaporised proportionately less rapidly; they could be selectively retained on this basis. The risk from volatile esters can be further reduced by further restricting applications of all three chemicals to conditions of lower temperature or of restricted incident solar energy, such as when shaded within plant canopy, or under dawn, evening or night conditions and by more strictly enforcing buffer zones for susceptible terrestrial vegetation and crops.

Response: We do not dispute that there may be measures taken during application that could result in limiting damage. However, there are significant data gaps relating to the short-chain esters (see Attachment 4) that need to be provided prior to further considering mitigation arguments. Additionally, the range of scenarios for which these compounds are currently registered are extensive, and the ability to adequately mitigate risk from each of these is questionable. For example, when used as a pre-emergent spray for canola in Western Australia, application will probably occur in March, a time of elevated temperatures in this state. The soil will be bare, unshaded and probably dry thereby limiting the ability for the chemical to hydrolyse to the low volatile acid and not having any canopy cover to provide shade.

Applications of volatile esters under conditions restricting volatilisation such as low incident radiation (the primary driver for vaporisation) and consequent lower temperature and saturation vapour pressure will minimise volatilisation, allowing deeper penetration into vegetation and soil and increasing the path length for remobilisation as vapour, allowing conversion into non-volatile metabolites. For example, applications to broad-leaved weeds within sugarcane canopies may allow little risk of significant volatile transport off site, because of the combined effects of shading, lower temperature within the canopy from shading and evapotranspiration, and lower wind speed. Therefore it is likely that management of these factors can strongly mitigate the hazard of transport off-site as a volatile cloud producing a significant risk to other terrestrial vegetation.

Response: To adequately determine the suitability of such management procedures, higher tier testing is required as the suite of data currently available for the short-chain esters is inadequate. It is noted for example that the longer chain 2,4-D BEE was shown to be significantly more persistent on leaves than other forms of 2,4-D for which test data were provided. If this is the case for the short-chain esters, then such mitigation measures may not work. Data requirements are discussed separately.

Another scenario presenting an opportunity for mitigation of risk would be applications of esters to pastures by ground rig under conditions of lower temperature and incident radiation. Risk from volatiles would be least under conditions or low or no wind speed, reducing the concentration of volatile chemical by greater dispersion in an aerial plume; higher wind speed off-site could mean less exposure of nearby terrestrial vegetation.

Response: See above response. It is unclear based on the lack of available information how effective such measures could be.

It would be useful if hazard quotients and levels of concern were analysed for particular registered use scenarios, to estimate the risk for each crop or pasture use, as employed by the US EPA. By contrast, the APVMA document makes its regulatory decisions based on a single worst-case scenario. Because the frequency or probability of exposure of terrestrial vegetation or fish was not considered in the APVMA document, it is stressed that risk was not assessed.

Response: In this case, the regulatory decision is made on the exposure to the non-target air compartment due to their volatile nature, the likely persistence of these chemicals in the air, and therefore the potential for long-range transport and exposure to other non-target areas. This is not something to be assessed using a refined Q approach.

Hazard quotients and levels of concern are analysed for particular registered use scenarios for other forms of 2,4-D in the second report, not yet released.

It would also be possible to restrict use of volatile esters to conditions where there are no efficacious alternatives, where the selective action against broad-leaved species is required and for those weeds with active growth where the volatile esters have greater efficacy. In this context, there could be less need to employ esters for rights-of-way where public authorities are more likely to order applications, or for industrial applications. These uses might be discontinued, retaining the esters for farming uses where mitigation of risk can be demonstrated. A review of all data relevant to mitigation in the literature, or provided from the registrants of chemicals, would be warranted to help define which methods would be most effective.

Response: this is an APVMA issue and outside the scope of the actual risk assessment.

APVMA is requested to consider such opportunities for risk mitigation that may be appropriate for particular applications, rather than cancelling all approvals for the application of these volatile 2,4-D esters.

Response: this is an APVMA issue and outside the scope of the actual risk assessment.

6. The appropriateness of the APVMA's conclusions

In recommending a ban on the approvals for the use of 2,4-D esters, no consideration has been given to the possibility that replacement products may differ in efficacy. Substitute chemicals may be used either more or less often, at greater or lesser total rates of application, possibly raising the environmental risk from another cause. Such an unintended outcome of banning the use of volatile 2,4-D esters may need to be considered by the APVMA. A complete ban of the volatile hormone esters could also impact negatively on strategies designed to prevent the development of herbicide resistant weeds.

Response: this is an APVMA issue and outside the scope of the actual risk assessment.

Partial or complete cancellation of the more volatile 2,4-D esters may be appropriate in the future, following more definitive risk analysis, or if the more restricted conditions of use suggested are found unable to adequately reduce ecological risk.

Statement. No response needed.

However, APVMA should also ensure that alternative methods of weed control with less overall risk to the environment are available. Otherwise, bans on the use of the volatile esters might increase hazards to the environment. Given these unknown results of canceling approvals, the APMVA may consider commissioning studies of the overall risk.

Response: It is considered more appropriate for the APVMA to respond to this.

Attachment 1: Overview of Risk Assessment with respect to the Atmosphere

The assessment of the short chain 2,4-D esters focussed on their likely volatility and potential to result in adverse environmental effects off target due to movement through the atmosphere. The reasons for this included:

- Likely persistence in air for the short chain esters (based on modelling);
- High volatility;
- High toxicity to non-target plants; and
- International action resulting in the discontinued use of these compounds due to their volatility and off-target movement.

Where pesticides partition to the atmosphere due to volatilisation, the area over which the chemicals can be distributed is likely to be much greater than those due to other mechanisms. Unfortunately, methodologies for assessing environmental risk in this area are lacking. The US EPA state categorically in their 2,4-D assessment that “EFED (Environmental Fate and Effects Division) does not currently assess the impact of volatility, long-range transport and deposition as a route of exposure in its risk assessment process. Therefore, the effect of volatility of the 2,4-D esters on non-target organisms has not been quantified in this assessment.”

In Europe, the development of an EPPO (European and Mediterranean Plant Protection Organisation) air scheme has attempted to provide a clear and consistent scientific basis for risk assessment and decision-making. However, this has been subject to significant delays and is likely to be largely overtaken as the primary regulatory basis for assessment of concerns in air by the establishment of the FOCUS Air Working Group (Mackay *et al*, 2004). DEH is aware of activities in this group. However, working documentation is not yet publicly available.

Mackay *et al* (2004) provide a comprehensive report on approaches and tools for higher tier assessment of environmental fate in the United Kingdom. There is detailed discussion on consideration of the air compartment, focussing on volatilisation, atmospheric transformation and atmospheric transport. Some important views directly applicable to the Australian assessment on short chain esters are worth noting:

- The air compartment is increasingly the focus of regulatory interest because of both short-range (local) and long-range transport and exposure issues. At present there is comparatively little regulatory guidance available on how to interpret pesticide behaviour in air, or indeed, estimate exposure, transport or degradation. Unlike the existing environmental risk assessment framework for the aquatic and terrestrial compartments there are no clear protection criteria based upon TER or hazard quotient thresholds. Environmental risk assessment for the air compartment is largely politically driven in the absence of a clear risk assessment framework and the absence of the data necessary to undertake a more comprehensive assessment of potential impacts. At the heart of this discussion is the question of what exposure is considered unacceptable? In the absence of clear scientific criteria the politically driven alternative has been to consider ‘air as the non-target’ and attempt to reduce exposure where possible.

- In Europe, at present there is no formal regulatory guidance on the calculation of air concentrations (pending the completion of the EPPO air scheme and the activities of the FOCUS Air Group). With the exception of concerns surrounding long-range transport and persistent organic pollutants (POPs), therefore, no risk-based regulatory triggers that would require that volatility issues are addressed further.
- At the present time in Europe the regulatory requirements for assessment of the fate of a substance in air is very limited, both at the national and the EU-level. This is because there are a very large number of uncertainties associated with such an assessment. There is an intention to address these regulatory uncertainties through the efforts of EPPO and FOCUS. There is however, a requirement to provide an estimation of the photochemical oxidative degradation (indirect phototransformation) of the active substance within the EU data requirements, and use of AOPWIN to model this endpoint is considered acceptable in the first instance.
- There are currently no regulatory requirements for information addressing the likely transport and deposition of air borne pesticides. However, it would seem reasonable that an attempt be made to ascertain if the pesticide has the potential to be transported significantly off-site. A first-tier assessment can be made based on expected transformation rates.

NOTE: This was performed in the DEH assessment using expected transformation rates in air based on modeling.

The situation in Europe summarized above is largely reflected in Australia. With no formal risk assessment framework available for the air compartment, a screening level approach only is possible in the absence of more detailed information. For the short-chain esters, no more detailed information was available, and in fact, the total data set available for these compounds was alarmingly incomplete. The reason for this as stated by the 2,4-D Taskforce was that this body did not generate any contemporary data for the short-chain esters as they had not been used in North America or Europe for over 20 years, and the Taskforce did not support their use.

Mackay *et al* (2004) further state that in the present regulatory environment even those preliminary assessments for the air compartment presented in their document would be regarded as higher-tier. However, for most pesticides the data required to carry out those assessments are either likely not to be available or significant uncertainty is likely to be associated with them. The processes acting on substances, which determine their transport and deposition from air, are very complicated and not always well understood. Higher-tier approaches to assist in better assessing transport and exposure potential typically involve two methods; monitoring and modeling.

Monitoring

There are no monitoring data available for 2,4-D short chain esters in Australian air. Several research papers have been obtained for such monitoring in Canada, and these are reported separately (Attachment 3). These studies show consistent detections of 2,4-D in the air compartment, and deposited through wet/dry deposition, at sites well removed from the area of application. This is the case where low volatile esters were used for application as short-chain esters are no longer used in Canada. One reference points to concentrations in air up to 13,500 ng/m^3 during monitoring in Canada from 1966 to 1975 that occurred during the use of more volatile butyl ester formulations.

Modeling

As pointed out in Mackay *et al* (2004), attempts have been made to arrive at modeling approaches to the problem, the most prominent being that of the fugacity-based multi-media modeling. This has been developed into a series of models, which attempt to predict the distribution and fate of substances once they are released into the atmosphere. However, these models are essentially dealing with processes over a large (global) scale and so were not considered appropriate for use in the DEH assessment of the short-chain volatile esters where regional exposure is more appropriate.

There are also models that attempt to carry out regional scale predictions, and base their approach on very detailed transport calculations in only one compartment, the atmosphere. Unfortunately, all these models require a range of data about the substance and its interaction with environmental components, which largely is not currently a part of the regulatory requirements. In addition, there are significant uncertainties associated with the process descriptions in the models, and no convincing validation of the models as applicable to pesticides has been carried out. Therefore, this approach was not considered appropriate in the DEH assessment of the short-chain volatile esters.

An alternative approach is to crudely estimate the concentration of an air borne pesticide deposited at a remote location, and then to compare this to relevant ecotoxicity endpoints for species at risk at the remote location. In its approach, this is very similar to the procedures already employed to carry out a risk assessment for a non-target species within the more conventional risk assessment framework (comparing exposure values with ecotoxicity endpoints to arrive at Q-values). This depends upon estimating values for many of the parameters that characterise the volatility, transformation and transport of a pesticide in air, and is quite simplistic in approach. It was this method that was used in the DEH assessment, although exposure was not considered in a remote region, rather in a non-target area surrounding the field of application. Mackay *et al* (2004) state that while this approach has much to commend it, it is doubtful if the uncertainties associated with it in its present form would be acceptable when considering the effects of a pesticide on remote and potentially fragile ecosystems.

Given the screening level assessment performed for the short-chain esters showed an unacceptable risk to the environment (based on exposure to the non-target atmospheric compartment, potential for persistence within this compartment, and potential for longer range transport), the recommendation was that the short-chain ester usage in Australia be discontinued.

If this is an unacceptable decision (as it is made only on a screening level assessment), then a higher tier assessment is possible. However, significant data would be required prior to performing such an assessment, noting again that no data were provided for review of these short-chain esters. Possible studies/data could include:

- Perform under current guidelines, studies investigating water solubility, vapour pressure and octanol-water partition coefficients for the short chain esters (or provide good quality studies if available);
- Additional fate studies considering volatility from a wide range of soils;
- Volatility studies for the short-chain esters from foliage (and to determine likely persistence of these compounds on foliage);
- Development of higher tier studies to investigate how the chemical behaves in the soil and investigate rates of loss from the soil surface;

- Assessment of the likely exposure concentrations in soil and air at the point of in-field application;
- Conduct higher tier photo-oxidation studies on the short chain esters to better determine persistence in the atmosphere.

References:

Mackay N, Terry A, Arnold D, Pepper T, Price O and Mason P, 2004. Approaches and Tools for Higher Tier Assessment of Environmental Fate. Cambridge Environmental Assessments. DEFRA Contract PL0546 & PS2202. January 2004.

http://www.pesticides.gov.uk/uploadedfiles/Web_Assets/PSD/Approaches_and_Tools_for_Higher_Tier_Assessment_of_Environmental_Fate_v2.pdf

Attachment 2: Recent data on Atmospheric Transport and Deposition of 2,4-D

Monitoring data

The issue of 2,4-D movement off target through volatilisation is not new. Felsott (2005 - http://feql.wsu.edu/esrp531/Fall2005ESRP/FelsotCostaRicaDrift.pdf) provides some history in this regard:

> By the early 1950's, the herbicide 2,4-D was commercially introduced and quickly adopted by cereal farmers. Its mode of toxic action was specific to plants but selectively toxic to broadleaf species. Throughout the 1950's engineering of application equipment had improved the precision of delivery and foliar coverage. Ground rigs, airplanes, and helicopters supplanted hand-application equipment in the industrialized countries. While 2,4-D was hailed as a great breakthrough for adequately controlling weeds in cereal crops, its side effects on non-target crops were soon noted. Specifically, in California, USA, where cereal crops were grown in proximity to vineyards, grape growers complained of foliar injury and yield loss. The symptomology was characteristic of 2,4-D injury.
>
> Court records of the time document civil actions taken as a result of drift movement of the herbicide from target to nontarget crops. Pertinently, movement of 2,4-D was recognized both during spraying through drift and after spraying through volatilization losses. In contrast to experiences with DDT movement, where residues could only be detected following chemical analysis of tissues, 2,4-D residues were easily surmised by the easily recognizable morphological changes in foliage.

There is little surprise that recent data relating to non-target impacts of short-chain esters are unavailable. These compounds have not been used for more than 20 years in North America or Europe and in their 1984 review of 2,4-D compounds, the World Health Organisation state:

> Volatilization of 2,4-D products in the air during the spraying operation and from the surface of plants and the soil is difficult to distinguish from the drift of spray droplets. Evaporation occurs to a greater extent with the highly volatile ethyl, isopropyl, or butyl esters; very little occurs with amine salt formulations, and it is greatly reduced when 2,4-D is dissolved in corn oil, cottonseed oil, or diesel oil. In one experiment, no significant amounts of 2,4-D amine, but 20 - 40% of the initially deposited 2,4-D butyl ester, and 10 - 15% of the octyl ester of 2,4-D vapourized within 2 h of spraying; less

> volatilization occurs with the higher esters of 2,4-D. For this reason, the use of the more volatile esters has been discontinued in some countries.

This report further reports that while studies of 2,4-D aerial drift following ground spray operations have shown that only 3-8% of the applied herbicides drift as spray droplets when low volatile preparations are applied as large droplets, ultra-low-volume (ULV) applications by aircraft, or the use of highly volatile esters may cause as much as 25-30% of the 2,4-D sprayed to move off the target

This volatilisation is supported by research in Gile (1983), who evaluated airborne losses of seven commercial 2,4-D formulations from a simulated wheat field. The formulations tested were butyl ester, isooctyl ester, two propylene glycol butyl ether esters, ethanol/isopropyl amine, and two dimethyl amines. The butyl and isooctyl esters exhibited the greatest airborne losses (17.5% and 15.0% respectively compared to <2% for the amine salt formulations).

Reisinger and Robinson (1973) report a sampling study conducted during the spring months of 1973 and 1974 to determine atmospheric 2,4-D levels in Washington State. They claim in their paper that 2,4-D grape damage had been a problem recognised for many years with significant damage to grape vineyards resulting from 2,4-D applied in grain growing regions, even through the two crop areas are separated by many miles. Prior to 1974, the Washington State Department of Agriculture systematically enacted various regulations banning high volatile 2,4-D from most counties where commercial grape vineyards were grown. Also, in May 1974, a total ban on the use of all 2,4-D formulations designated as highly volatile was enacted throughout the state of Washington.

In actual fact, there is significant evidence that even the lower volatile forms of 2,4-D can move long distances through the atmosphere. Atmospheric concentrations and depositions in the Georgia Basin airshed were considered in an Environment Canada report (Beltzer, 2003). In this report, it is claimed that:

> In February 1996, a peak of 2,4-D at both the Abbotsford and Agassiz sites; temperatures rose to approximately 20°C. The week before and the week after this sample period were periods of winter snowstorms. A back-trajectory analysis of the winds showed that the ground level winds (1000 mb) came from southern California, near the Imperial Valley.
>
> Correspondence with growers discovered that 2,4-D was used as a pre-emergent herbicide seed treatment, during the week. This implied that unique packets of air containing pesticides could travel long distances and remain relatively undiluted. Local Fraser Valley sources were not possible during this time period, so the source is quite likely from southern California.

While the form of 2,4-D used initially is unclear, it would not have been a high volatile ester as these compounds have not been used in North America for a long time.

In the WHO 1984 report, some ambient air levels for short chain esters are reported and show maximum levels of the butyl ester in the order of 1.3-13.5 $\mu g/m^3$, generally at a sample time of 24 hours after application. These results are from older research.

Unfortunately, as previously stated, there are no available data assessing effects on plants when exposed through the gas phase. In their assessment of long distance transport of 2,4-D, Reisinger and Robinson (1973) refer to evidence that grapes exposed to 1 $\mu g/m^3$ for 6 h per week for 10 weeks experienced a loss in yield of >50%. This suggests that sensitive species could be at risk from gas phase exposures to short-chain 2,4-D esters.

Much work is published by Waite and co-workers (Waite *et al*, 1995; 2002; 2005) considering atmospheric deposition of pesticides in the Saskatchewan region in Canada. This research consistently shows detections of 2,4-D in the atmosphere, and in samplers measuring deposition resulting from both wet and dry deposition, at areas well removed from the sites of application. For example, in Waite *et al*, 2002, where application was with the lower volatile forms of 2,4-D, the chemical was detected in 63% of atmospheric samples collected at dugouts in 1989 and 53% in 1990. Detections in 1989, when no 2,4-D was applied in the vicinity, are attributed to medium to long-range atmospheric transport. 2,4-D concentrations had maximum levels of 3.9 and 3.59 ng/m^3 in 1989 and 1990 respectively. However, this paper notes in earlier research in Saskatchewan, from 1966 to 1975, air levels as high as 13,500 ng/m^3 were detected at a time when the more volatile butyl ester formulations were currently used.

Waite *et al*, (2002) determined bulk atmospheric deposition rates (total of wet and dry deposition) in 1989 and 1990 and this research showed deposition rates were highest in the month when the majority of the herbicide was applied in the region. The maximum bulk atmospheric deposition rates were 3550 ng/m^2/day in 1989 and 1550 ng.m^2/d in 1990. 2,4-D was detected in 69-75% of samples and median concentrations ranged from 180 ng/m^2/day (1990) to 450 ng/m^2/day (1989). The total amounts of 2,4-D in bulk deposition samples were 101 µg/m^2 in 1989 and 40 µg/m^2 in 1990. Deposition quantities were stated to be comparable with seasonal bulk deposition quantities of 386 mg/ha to 1374 mg/ha reported in Waite *et al* (1995) for 4 years from 1984 to 1987 at a site 10 km north of Regina, Saskatchewan. In this 1995 study, seasonal deposition of 2,4-D ranged from 0.08-0.28% of their application rates. However, this was not for highly volatile esters, which would be expected to move in higher levels off-site.

Waite *et al*, (2002) further considered the relationship between bulk deposition and atmospheric concentration. For 2,4-D, bulk atmospheric deposition rates did not appear to be directly correlated with atmospheric concentrations, however, in this study they did appear to be related to rainfall. For example, in one sampling area in 1989 there was a positive correlation ($r^2 = 0.73$) between weekly rainfall and bulk deposition between the weeks of 18 May to 19 July when most of the bulk deposition occurred. It is noted that the weeks of 18, 24 and 31 May, when 2,4-D was present in bulk deposition, it was not found in atmospheric samples collected at 1 m height. This indicates that long-range transport may have contributed to the bulk deposits.

Further work is reported in Waite *et al*, (2005) where data were obtained at various elevations to determine variability in herbicide concentrations above ground level in order to identify contributions of both local and long-range transport, and to estimate atmospheric loadings. Measurements were taken at 1, 10 and 30 m heights with sampling being conducted within the province of Saskatchewan. Atmospheric concentrations of 2,4-D, used for post-emergence control, tended to be higher at 30 m (maximum mean levels approaching 2 ng/m^3 than at 10 m and 1 m (around 1.4 and 1.3 ng/m^3 respectively) and this is stated to indicate a greater influence of long-range atmospheric transport. This paper further considered the relationship between atmospheric concentrations and dry deposition weights. A strong relationship was shown for 2,4-D (and other herbicides considered in the report). The pattern of dry deposition of the herbicides considered generally followed that of their occurrence in the high-volume air samples. This paper reports 2,4-D to bind relatively strongly to solid particles in the atmosphere.

References:

Belzer W, 2003. Atmospheric Concentrations and Depositions in the Georgia Basin Airshed. *In Proceedings 2003 Georgia Basin/Puget Sound Research Conference*. Environment Canada.

Felsot A, 2005. Evaluation and Mitigation of Spray Drift. *Proc. International Workshop on Crop Protection Chemistry in Latin America*; Harmonized Approaches for Environmental Assessment and Regulation, 14-17 February, 2005, San Jose, Costa Rica

Gile J, 1983. Relative Airborne Losses of Commercial 2,4-D Formulations from a Simulated Wheat Field. *Archives of Environmental Contamination and Toxicology* Vol 12, pp 465-469.

Reisinger L and Robinson E, 1976. Long-Distance Transport of 2,4-D. Journal of Applied Meteorology. Vol 15, pp 836-845

Waite D, Bailey P, Sproull J, Quiring D, Chau D, Bailey J and Cessna A, 2005. Atmospheric Concentrations and Dry and Wet Deposits of Some Herbicides Currently Used on the Canadian Prairies. *Chemosphere*, Vol 58. pp 693-703.

Waite D, Cessna A, Grover R, Kerr L and Snihura A, 2002. Environmental Concentrations of Agricultural Herbicides: 2,4-D and Triallate. *Journal of Environmental Quality*, Vol 31. pp 129-144.

Waite D, Grover R, Westcott N, Irvine D, Kerr L and Sommerstad H, 1995. Atmospheric Deposition of Pesticides in A Small Southern Saskatchewan Watershed. *Environmental Toxicology and Chemistry*, Vol 14 (7) pp 1171-1175.

Attachment : Data Requirements for Higher Tier Risk Assessment of Short-Chain Esters of 2,4-D

No data were provided by industry for assessment of the short-chain 2,4-D esters currently registered in Australia. The 2,4-D Taskforce did not generate any contemporary data for these compounds, as they have not been used in North America or Europe for over 20 years. Consequently, the review possible for these compounds was limited and relied where possible on older values reported in open databases or in some cases of ecotoxicity, obtained from non-standard tests performed internationally.

In order to undertake a more complete assessment of the short-chain esters, significant data will be required for the ethyl ester, butyl ester and iso-butyl ester forms of 2,4-D. While areas data gaps/testing requirements have been provided below, prior to commencing a testing regime, it is very important that industry identify what short-chain esters they are proposing to keep, and what use patterns they wish to defend. This will enable testing to be targeted more effectively. It is therefore recommended the APVMA obtain this information from industry prior to finalizing additional data/testing requirements.

Physical and chemical properties

Current guideline studies on vapour pressure, water solubility and octanol-water partition coefficient.

Environmental fate

Conduct higher tier photo-oxidation studies on the short-chain esters to better determine persistence in the atmosphere.

Additional fate studies considering volatility from a wide range of soils and representing exposure conditions (that is, surface applied without mixing). Such testing should be performed with a range of realistic ambient temperatures to allow assessment of the varied use patterns currently registered;

Volatility studies for the short-chain esters from foliage (and to determine likely persistence of these compounds on foliage). Such testing should be performed with a range of realistic ambient temperatures to allow assessment of the varied use patterns currently registered, or can be targeted to use patterns nominated by industry as being important to maintain;

Adsorption/desorption data may be required depending on other test outcomes;

Assessment of the likely exposure concentrations in soil and air at the point of in-field application;

Aerobic soil metabolism studies. There is currently conflicting evidence in this regard based on the data for longer chain esters and salt forms of 2,4-D as to persistence in aerobic soils. Any testing should characterize the persistence and breakdown of the short-chain esters in a range of soils, and be performed in a manner consistent with the use pattern, that is, surface applied to soils at a range of temperatures and without soil incorporation.

Environmental Effects

Guideline studies on effects on non-target arthropods and aquatic plants/algae are required.

Several results are available for other aquatic organisms in the US EPA ECOTOX data base. Test reports should be provided for these. If they are unsatisfactory in their quality, some additional testing may be required. The need for chronic testing is unclear at this stage and will depend on results found in the environmental fate studies listed above.

No test data for effects of 2,4-D short-chain esters to non-target terrestrial vegetation are available, and test data in this area is required. Such data should include consideration of effects due to exposure through the gas phase as well as ground/deposition exposure.

Prior to any testing commencing, industry should discuss and get agreement from DEH/APVMA on relevant protocols.

Attachment 5: Suggested amendments to current sections of the report.

5.2 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 AOPWIN software is publicly available within the US EPA EPIsuite of software and can be downloaded from: (http://www.epa.gov/opptintr/exposure/docs/episuite.htm). Model documentation is available.

The AOPWIN model uses the structure-reactivity relationships approach developed by Atkinson and his collaborators and is accepted as a modelling tool within OECD member countries. The methodology is described in OECD Environment Monograph No 61: The Rate of Photochemical Transformation of Gaseous Organic Compounds in Air Under Tropospheric Conditions (OECD, 1993).

While the model is considered screening level, it is an acceptable tool given no experimental data were provided or appear available for degradation in air.

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:

Table 5: Tropospheric Hydroxyl Radicals Monitoring.

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) Not registered 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.

8.2.2 Risk from Volatilisation

The air compartment is increasingly the focus of regulatory interest because of both short-range (local) and long-range transport and exposure issues. At present there is comparatively little regulatory guidance available on how to interpret pesticide behaviour in air, or indeed, estimate exposure, transport or degradation Mackay *et al*, (2004).

While standard risk assessment methodology is available in Australia and internationally for performing risk assessments for the aquatic and terrestrial compartments, there is no standard methodology or clear protection criteria (for example, based on the quotient method) in the air compartment.

It is therefore more the case that, in the absence of a risk assessment framework (and indeed the general absence of data required for a higher tier risk assessment for the atmospheric compartment) that risk assessment for the air compartment is more policy driven, that is, through considering air as a non-target receptor compartment, and attempting to reduce exposure where possible.

This certainly is the case in Europe (well described in Mackay *et al*, 2004). In the US, the position for assessing risk through volatilisation movement is described specifically in their 2,4-D Reregistration Eligibility Decision document where it states that “EFED (Environmental Fate and Effects Division) does not currently assess the impact of volatility, long-range transport and deposition as a route of exposure in its risk assessment process. Therefore, the effect of volatility of the 2,4-D esters on non-target organisms has not been quantified in this assessment.”

DEH considers there is a strong need to consider the impacts of off-target movement through the atmosphere resulting from use of the short-chain 2,4-D esters in Australia. This decision is driven by the following facts:

- Short-chain 2,4-D esters are highly volatile;
- Initial modelling using an internationally accepted model by regulators within the OECD suggest these compounds may be quite persistent in air (described in more detail below);
- The 2,4-D Taskforce did not generate any contemporary data for the short-chain esters as they do not support the use of these chemicals and note they have not been used for over 20 years in North America and Europe;
- Previous international scientific evaluations of 2,4-D have concluded that because of the volatility of the short-chain esters, the use of the more volatile esters has been discontinued in some countries

In the absence of clear assessment criteria, DEH has conducted a lower tier assessment for the air compartment resulting from the use of the short-chain esters. This assessment is based on a relatively simple model to predict possible levels of volatilisation, persistence in air, and therefore, the potential to move off-target.

8.2.2.1 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. Given the volatile nature of the short chain esters, risk from volatilization is being considered in more detail for this Part 1 report rather than the more traditional areas of spray drift and run-off.

Ester forms of 2,4-D

While public submissions to the APMVA 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 $4.8X10^{-4}$, $1.47X10^{-1}$ and $5.29X10^{-2}$ to $8.2X10^{-3}$ 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.

As describe above, 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 while public documentation is not yet available, DEH has consulted the FOCUS Air Workgroup and been advised that this model is likely to become the regulatory model of choice in the EU for considering short range atmospheric transport of pesticides. However, it is clear that for pesticides with vapour pressures in the order of those of the short-chain esters (>10^{-2} Pa at 20^{o}C), the model is considered unsuitable and long-range atmospheric transport should be considered.

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:

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

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:

$$E_{crop,\ air} = (CV_{crop} \text{ x } f_1 \text{ x } A)/100$$

Where:

$E_{crop,\ air}$ = the total amount volatilised from the crop (g/ha);

A = the nominal rate for a single application (g/ha)

f_1 = 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 42: 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. It should be stressed that no standard data for the short-chain esters are available in this regard, so this statement may not apply to them. Further, there is experimental evidence provided in the WHO report (EHC, 1984) that 20-40% of applied butyl ester had evaporated within 2 hours of application.

Given this, only exposure from volatilization from crop surfaces will be considered in more detail below. This will be taken to also represent volatilization from soil surfaces, particularly in the short-term following application to soil. To refine this assessment, additional data would be required and this is discussed below.

Calculation of Risk Quotients

In air, a substance can exist in the gas phase, adsorbed/absorbed to particles and dissolved in air borne moisture. Substances with a liquid-phase vapour pressure (P_L) $<10^{-6}$ Pa at ambient atmospheric temperature are primarily present in the particle phase, and those with values of $P_L>1$ Pa exist essentially totally in the gas-phase. Chemicals with intermediate values of P_L are present in both phases and are termed semi-volatile organic compounds (SOC). For the SOCs, the balance between the phases will depend on the temperature. An SOC might be susceptible to different transformation processes depending on which of these forms it finds itself in (Mackay *et al*, 2004). It is anticipated that the short-chain esters would be available in both the gas phase and the particulate phase where they would be available for deposition.

When considering transport of pesticides through the air to non-target areas, there are three distinct phases for consideration, namely, emission to the atmosphere, transport and transformation in the atmosphere, and deposition from the atmosphere. All three stages need different modeling approaches. The processes acting on substances, which determine their transport and deposition from air, are complicated and not always well understood. Higher-tier approaches to assist in better assessing transport and exposure potential can typically involve monitoring and/or modelling. There are no monitoring data for air concentrations of 2,4-D in Australia. Some data are available internationally, and these are discussed further below.

As pointed out in Mackay *et al* (2004), attempts have been made to arrive at modelling approaches to the problem, the most prominent being that of the fugacity-based multi-media modelling. This has been developed into a series of models, which attempt to predict the distribution and fate of substances once they are released into the atmosphere. However, these models are essentially dealing with processes over a large (global) scale and were not considered appropriate for use in this assessment of the short-chain volatile esters.

There are also models that attempt to carry out regional scale predictions, and base their approach on very detailed transport calculations in only one compartment, the atmosphere, for example, Gaussian or Lagrangian type approaches. Unfortunately, the range of data needed for the substance and its interaction with environmental components are not all part of the regulatory requirements, and are not always available. In addition, there are significant uncertainties associated with the process descriptions in the models, and no convincing validation of the models as applicable to pesticides has been carried out (Mackay *et al,* 2004). Therefore, this approach was not considered appropriate this assessment of the short-chain volatile esters.

An alternative approach is to crudely estimate the concentration of an air borne pesticide deposited at a remote location, and then to compare this to relevant ecotoxicity endpoints for species at risk at the remote location. In its approach, this is very similar to the procedures already employed to carry out a risk assessment for a non-target species within the more conventional risk assessment framework (comparing exposure values with ecotoxicity endpoints to arrive at Q-values). This depends upon estimating values for many of the parameters that characterise the volatility, transformation and transport of a pesticide in air, and is quite simplistic in approach.

This method has been chosen for this assessment, although exposure is not considered in a remote region, rather in a non-target area surrounding the field of application.

There are no effects data available for organisms (including plants) exposed through the gas phase, so the assumption has been taken that volatilised chemical is available for wet/dry deposition and will result in an exposure rate in g/ha. While this approach has much to commend it, there are considerable uncertainties associated with it. Consequently, the outcomes are more illustrative than robust, and are designed to show the much greater exposure potential to off-target areas from using the short-chain esters compared to less volatile forms.

From the calculations in Table 37 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 are derived:

Table 43: 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 potential 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:

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

Where:

μ = 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 μ 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, μ 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 are found:

Table 44: Estimated overall persistence, M_{air}/M_{tot} and indicative characteristic travel distance for 2,4-D EHE, 2,4-D EE and 2,4-D BE.

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) states 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.

Monitoring data

The issue of 2,4-D movement off target through volatilisation is not new. Felsott (2005 - http://feql.wsu.edu/esrp531/Fall2005ESRP/FelsotCostaRicaDrift.pdf) provides some history in this regard:

> By the early 1950s, the herbicide 2,4-D was commercially introduced and quickly adopted by cereal farmers. Its mode of toxic action was specific to plants but selectively toxic to broadleaf species. Throughout the 1950s engineering of application equipment had improved the precision of delivery and foliar coverage. Ground rigs, airplanes, and helicopters supplanted hand-application equipment in the industrialized countries. While 2,4-D was hailed as a great breakthrough for adequately controlling weeds in cereal crops, its side effects on non-target crops were soon noted. Specifically, in California, USA, where cereal crops were grown in proximity to vineyards, grape growers complained of foliar injury and yield loss. The symptomology was characteristic of 2,4-D injury.
>
> Court records of the time document civil actions taken as a result of drift movement of the herbicide from target to nontarget crops. Pertinently, movement of 2,4-D was recognized both during spraying through drift and after spraying through volatilization losses. In contrast to experiences with DDT movement, where residues could only be detected following chemical analysis of tissues, 2,4-D residues were easily surmised by the easily recognizable morphological changes in foliage.

There is little surprise that recent data relating to non-target impacts of short-chain esters are unavailable. These compounds have not been used for more than 20 years in North America or Europe and in their 1984 review of 2,4-D compounds, the World Health Organisation state (WHO, 1984):

> Volatilization of 2,4-D products in the air during the spraying operation and from the surface of plants and the soil is difficult to distinguish from the drift of spray droplets. Evaporation occurs to a greater extent with the highly volatile ethyl, isopropyl, or butyl esters; very little occurs with amine salt formulations, and it is greatly reduced when 2,4-D is dissolved in corn oil, cottonseed oil, or diesel oil. In one experiment, no significant amounts of 2,4-D amine, but 20 - 40% of the initially deposited 2,4-D butyl ester, and 10 - 15% of the octyl ester of 2,4-D vapourized within 2 h of spraying; less volatilization occurs with the higher esters of 2,4-D. For this reason, the use of the more volatile esters has been discontinued in some countries.

This report further reports that while studies of 2,4-D aerial drift following ground spray operations have shown that only 3-8% of the applied herbicides drift as spray droplets when low volatile preparations are applied as large droplets, ultra-low-volume (ULV) applications by aircraft, or the use of highly volatile esters may cause as much as 25-30% of the 2,4-D sprayed to move off the target.

In their compilation of air pollution emission factors, the US EPA provides a summary of field tests of pesticide volatilization and includes 2,4-D (assumed to be acid), 2,4-D butyl ester, 2,4-D octyl ester and 2,4-D isooctyl ester (US EPA, 1994). All measurements are from a 1978 report except the 2,4-D isooctyl ester, where the values are taken from a 1985 report. The results reported show that for the acid, 1-8% was lost at application. This compared to 30-40% of the butyl ester within 2 hours of application, 10-15% of the octyl ester within 2 hours of application (assumed to be the same research described in WHO, 1984 above). In addition, 21% of the isooctyl ester with 5 days of application.

This volatilisation is supported by research in Gile (1983), who evaluated airborne losses of seven commercial 2,4-D formulations from a simulated wheat field. The formulations tested were butyl ester, isooctyl ester, two propylene glycol butyl ether esters, ethanol/isopropyl amine, and two dimethyl amines. The butyl and isooctyl esters exhibited the greatest airborne losses (17.5% and 15.0% respectively compared to <2% for the amine salt formulations). In this experiment, only 4 hours after application, the butyl ester formulation resulted in an air concentration of 140 ng/L. This is a high initial rate loss as compared to 24.5 ng/L at 4 hours for the isooctyl ester while the amine salt formulations were not detected in the air at this sampling time.

Reisinger and Robinson (1973) report a sampling study conducted during the spring months of 1973 and 1974 to determine atmospheric 2,4-D levels in Washington State. They claim in their paper that 2,4-D grape damage had been a problem recognised for many years with significant damage to grape vineyards resulting from 2,4-D applied in grain growing regions, even through the two crop areas are separated by many miles. Prior to 1974, the Washington State Department of Agriculture systematically enacted various regulations banning highly volatile 2,4-D from most counties where commercial grape vineyards were grown. Also, in May 1974, a total ban on the use of all 2,4-D formulations designated as highly volatile was enacted throughout the state of Washington.

In actual fact, there is significant evidence that even the lower volatile forms of 2,4-D can move long distances through the atmosphere. Atmospheric concentrations and depositions in the Georgia Basin airshed were considered in an Environment Canada report (Beltzer, 2003). In this report, it is claimed that:

> In February 1996, a peak of 2,4-D at both the Abbotsford and Agassiz sites; temperatures rose to approximately 20°C. The week before and the week after this sample period were periods of winter snowstorms. A back-trajectory analysis of the winds showed that the ground level winds (1000mb) came from southern California, near the Imperial Valley.
>
> Correspondence with growers discovered that 2,4-D was used as a pre-emergent herbicide seed treatment, during the week. This implied that unique packets of air containing pesticides could travel long distances and remain relatively undiluted. Local Fraser Valley sources were not possible during this time period, so the source is quite likely from southern California.

While the form of 2,4-D used initially is unclear, it would not have been a high volatile ester as these compounds have not been used in North America for a long time.

Much work is published by Waite and co-workers (Waite *et al*, 1995; 2002; 2005) considering atmospheric deposition of pesticides in the Saskatchewan region in Canada. This research consistently shows detections of 2,4-D in the atmosphere, and in samplers measuring deposition resulting from both wet and dry deposition, at areas well removed from the sites of application. For example, in Waite *et al* (2002), where application was with the lower volatile 2,4-D iso-octyl ester, 2,4-D was detected in 63% of atmospheric samples collected at dugouts in 1989 and 53% in 1990. Detections in 1989, when no 2,4-D was applied in the vicinity, are attributed to medium to long range atmospheric transport. 2,4-D concentrations had maximum levels of 3.9 and 3.59 ng/m^3 in 1989 and 1990 respectively. However, this paper notes in earlier research in Saskatchewan, from 1966 to 1975, air levels as high as

13,500 ng/m^3 were detected at a time when the more volatile butyl ester formulations were currently used.

In the WHO 1984 report, some ambient air levels for short chain esters are reported and show maximum levels of the butyl ester in the order of 1.3-13.5 µg/m^3, generally at a sample time of 24 hours after application. These results are from older research.

Unfortunately, as previously stated, there are no available data assessing effects on plants when exposed through the gas phase. In their assessment of long distance transport of 2,4-D, Reisinger and Robinson (1973) refer to evidence that grapes exposed to 1 µg/m^3 for 6 h per week for 10 weeks experienced a loss in yield of >50%. This suggests that sensitive species could be at risk from gas phase exposures to short-chain 2,4-D esters.

8.2.2.2 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 2.45X10^{-7} – 7.34X10^{-4} atm.m^3/mol, and highly volatile at >7.34X10^{-4} atm.m^3/mol.

Henry's Law Constants for the short chain esters are 3.25X10^{-7}, 4.88X10^{-7} and 1.25X10^{-7} atm.m^3/mol for ethyl ester, butyl ester and isobutyl ester respectively indicating they may be moderately volatile from water bodies. The Henry's Law Constant for 2,4-D EHE is 1.82X10^{-5} 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 the 2,4-D EHE, although in Australia, this chemical is not registered for aquatic uses.

8.2.2.3 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.

8.3 Conclusions

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, risk to aquatic plants and algae was 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.

The refined aquatic risk assessment showed an acceptable risk to fish and aquatic invertebrates to ester forms of 2,4-D and algae/aquatic plants to all forms of 2,4-D where aerial application used coarse spray droplet sizes (coarse droplet diameter of 400 µm) and a buffer zone of 100 m between treated areas and downwind water bodies was maintained for terrestrial use patterns. 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.

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

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 although all the ester forms are expected to exhibit some volatility from waterbodies.

Ground application for broadcast uses of 2,4-D were modelled 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.

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 the wrong 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.

9 Recommendations

Short chain ester forms. In the absence of higher tier data, 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 active constituents 2,4-D Ethyl Ester, 2,4-D Butyl ester or 2,4-D isobutyl ester or products containing these active constituents 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.

A higher tier risk assessment may be undertaken provided significant data gaps are filled. Possible studies/data should include:

Physical and chemical properties

- Current guideline studies on vapour pressure, water solubility and octanol-water partition coefficient.

Environmental fate

- Conduct higher tier photo-oxidation studies on the short-chain esters to better determine persistence in the atmosphere.

- Additional fate studies considering volatility from a wide range of soils and representing exposure conditions (that is, surface applied without mixing). Such testing should be performed with a range of realistic ambient temperatures to allow assessment of the varied use patterns currently registered;
- Volatility studies for the short-chain esters from foliage (and to determine likely persistence of these compounds on foliage). Such testing should be performed with a range of realistic ambient temperatures to allow assessment of the varied use patterns currently registered;
- Adsorption/desorption data may be required depending on other test outcomes;
- Assessment of the likely exposure concentrations in soil and air at the point of in-field application;
- Aerobic soil metabolism studies. There is currently conflicting evidence in this regard based on the data for longer chain esters and salt forms of 2,4-D as to persistence in aerobic soils. Any testing should characterize the persistence and breakdown of the short-chain esters in a range of soils, and be performed in a manner consistent with the use pattern, that is, surface applied to soils at a range of temperatures and without soil incorporation.

  Environmental Effects

- Guideline studies on effects on non-target arthropods and aquatic plants/algae are required.
- Several results are available for other aquatic organisms in the US EPA ECOTOX data base. Test reports should be provided for these. If they are unsatisfactory in their quality, some additional testing may be required. The need for chronic testing is unclear at this stage and will depend on results found in the environmental fate studies listed above.
- No test data for effects of 2,4-D short-chain esters to non-target terrestrial vegetation are available, and test data in this area is required (including data for Australian native plants). Such data should include consideration of effects due to exposure through the gas phase as well as ground/deposition exposure.

Any further data generated should have test protocols discussed with APVMA/DEH and agreed prior to testing commencing.

References:

Belzer W, 2003. Atmospheric Concentrations and Depositions in the Georgia Basin Airshed. *In Proceedings 2003 Georgia Basin/Puget Sound Research Conference*. Environment Canada.

Felsot A, 2005. Evaluation and Mitigation of Spray Drift. *Proc. International Workshop on Crop Protection Chemistry in Latin America*; Harmonized Approaches for Environmental Assessment and Regulation, 14-17 February, 2005, San Jose, Costa Rica

Gile J, 1983. Relative Airborne Losses of Commercial 2,4-D Formulations from a Simulated Wheat Field. *Archives of Environmental Contamination and Toxicology* Vol 12, pp 465-469.

Mackay N, Terry A, Arnold D, Pepper T, Price O and Mason P, 2004. Approaches and Tools for Higher Tier Assessment of Environmental Fate. Cambridge Environmental Assessments. DEFRA Contract PL0546 & PS2202. January 2004.

OECD, 1993. The Rate of Photochemical Transformation of Gaseous Organic Compounds in Air Under Tropospheric Conditions. Environment Monograph No. 61. OCDE/GD(92)172. Paris, 1993.

Reisinger L and Robinson E, 1976. Long-Distance Transport of 2,4-D. Journal of Applied Meteorology. Vol 15, pp 836-845

US EPA, 1994. Emission Factor Documentation for AP-42. Section 9.2.2. Pesticide Application. Final Report. Office of Air Quality Planning and Standards. EPA Contract No. 68-D2-0159. September 1994 (http://www.epa.gov/ttn/chief/ap42/ch09/bgdocs/b9s02-2.pdf)

Waite D, Bailey P, Sproull J, Quiring D, Chau D, Bailey J and Cessna A, 2005. Atmospheric Concentrations and Dry and Wet Deposits of Some Herbicides Currently Used on the Canadian Prairies. *Chemosphere*, Vol 58. pp 693-703.

Waite D, Cessna A, Grover R, Kerr L and Snihura A, 2002. Environmental Concentrations of Agricultural Herbicides: 2,4-D and Triallate. *Journal of Environmental Quality*, Vol 31. pp 129-144.

Waite D, Grover R, Westcott N, Irvine D, Kerr L and Sommerstad H, 1995. Atmospheric Deposition of Pesticides in A Small Southern Saskatchewan Watershed. *Environmental Toxicology and Chemistry*, Vol 14 (7) pp 1171-1175.

Attachment 4

DSEWPaC assessment of the submission on 2,4-D HVE submitted by the West Australian Department of Agriculture and Food

EXECUTIVE SUMMARY

This report is an assessment of a submission provided by the Department of Agriculture and Food Western Australia, in response to a call for additional information to cover data gaps for the 2,4-D High Volatile Ester (HVE) environmental risk assessment. Data provided were to address the Tier II environmental fate data gaps and also partly address the Tier II environmental toxicity data gaps.

In the original assessment, no data were provided for the 2,4-D HVE. The 2,4-D Industry Task Force did not generate any contemporary data, as these compounds have not been used in North America or Europe for over 20 years. Based on available information, the Preliminary Review Findings are that an unacceptable risk to the environment (particularly non-target terrestrial vegetation) exists from using 2,4-D HVE due to their high volatilization rates following application, long residence time in the atmosphere and high plant toxicity. The first two factors taken together mean that these substances can move significant distances through air and thereby expose non-target plants large distances from the point of application.

The information provided in the Department of Agriculture and Food Western Australia submission has not provided any significant evidence to counter these concerns, and in many cases has reinforced the weight of evidence against the continued use of HVE. No data were provided showing that these substances have a shorter half-life in air than initially estimated. Therefore, the conclusion of persistence in air must be maintained. Limited studies addressing volatilization following application confirm that significant amounts of the HVE do volatilize, particularly following application to plant surfaces, and even the low volatile esters could be prone to significant volatilisation.

Studies with a high volatile ester and several low volatile esters showed off target movement and adverse plant effects at large distances relative to the “application area”, and the distance of damaging off-target movement seemed to be a function of the amount of chemical applied. For example, in one study only 16 g of a 2,4-D HVE allowed to volatilise in the centre of a plot caused visible plant damage to a distance outwards of up to 100 m in all directions. The movement of an atmospheric 2,4-D vapour load resulting from thousands of hectares each treated with hundreds (if not thousands) of grams acid equivalent of 2,4-D in a volatile ester form remains therefore a significant concern.

Overseas monitoring studies showed region-wide distribution of significant atmospheric concentrations of 2,4-D HVE. A 1984 monitoring study in Geraldton WA seems at first to show that measured atmospheric levels of HVE were significantly lower than those found in the international studies. However, these measured values were mean weekly levels and maximum exposure concentrations along with the duration of maximum exposure periods could not be determined from the weekly data values collected. Nonetheless, these data demonstrated that the measured HVE were sourced from application areas 35 to 40 km away and were only that portion of the total volatilized atmospheric load brought to the samplers during that part of the time when the wind was blowing generally from the application area toward the samplers. DEW estimates that the exposure concentrations could have been consistently around 0.06 µg/m^3 (for example, several days at 5 hours per day), and the overall result would still be determined as a relatively low weekly average concentration of 0.008 µg/m^3.

Finally, several studies were provided addressing plant toxicity when exposed to 2,4-D HVE in the gas phase. These results confirmed the potency of 2,4-D to plants, and demonstrated that the HVE were more potent than the LVE or acid/salt formulations as one would expect for a gas phase exposure study. The studies further confirm that our understanding of non-target plant toxicity from reproductive toxins such as 2,4-D is not adequately supported using the standard vegetative vigour and seedling emergence studies available for LVE and acid/salt in the original assessment. In the non-standard testing considered here, adverse impacts were found for germination of several species following exposure to vapours.

Short term exposures (several hours) of plants at relatively low air concentrations were sufficient to induce long term effects on plant dry weight. Exposure of sunflower to 2,4-D during the reproduction phase of the plant’s life cycle was sufficient to reduce seed yield by 96%.

In the light of the additional data provided in this submission, our initial conclusions relating to the potential environmental risk resulting from use of the 2,4-D HVE in Australia are unchanged and the Department concludes that there is an unacceptable risk to the environment posed by the continued use of 2,4-D HVE.

Comments relating to the general submission

The submission received from Dr John Moore, Western Australian Department of Agriculture, consisted of a number of comments and assertions followed by specific consideration of the Tier II data gaps identified for environmental fate and behaviour of 2,4-D HVE.

His initial assertion is the lack of evidence for environmental damage beyond the zone where droplets drift, stating that in the documented cases where HVE have been withdrawn from use, the injury that brought this action has generally continued.

Dr Moore quotes Baskin and Walker (1953) as part of his rationale that volatility of the 2,4-D esters is unlikely to be the main cause of injury (to tomatoes in Geraldton based on the results of Gibley *et al* (1984) below). He states that the main reason for this is that droplets carry the herbicide in a concentrated form more likely to deposit on plants whereas the vapour is in a dilute form. He further states the part of this misconception (on our part) comes from the terminology where high volatile refers to a biological effect rather than the actual volatility of the compound. In the Baskin and Walker (1953) paper, Dr Moore notes their quote that the ester is considered highly volatile, not because of its rate of evaporation, which is relatively low, but because of its formative (biological) effects. It should be pointed out that the reference to the “high volatile esters” being relatively low in their volatility was, in the Baskin and Walker paper, a comment on their volatility relative to ether, alcohol, acetone, dimethylamine and trimethylamine. The authors noted that when these substances were placed in a broad evaporating dish and vaporised in the presence of cotton plants no drastic injury was observed. However, a volatile 2,4-D ester in a similar situation caused drastic injury to the same test object. Therefore, the authors concluded the 2,4-D ester is considered highly volatile, not because of its rate of evaporation (which is relatively low

compared to the very high vapour pressures substances it was compared to), but because of its formative effects.

The conclusion reached in the Moore submission is deficient. There is little doubt the HVE of 2,4-D are classified as such based on their higher vapour pressure relative to other ester forms of 2,4-D, not based on their volatility *per se*. The fact that the vapours have been demonstrated to be highly potent to a range of plants (discussed further below) reinforces the concerns relating to the continued use of these substances.

From the Gibley *et al* (1984) paper, Dr Moore considers that since spraying restrictions around Geraldton didn't reduce damage to tomato crops, this indicates volatility was unlikely to be the main cause of injury. This is also disputable. Despite a 50 km no-spray zone in 1980, HVE still accounted for some 40% of the atmospheric 2,4-D load closer to the township (10-15 km from town). This means that these esters had to move through the air only when the wind direction was favourable, for distances of at least 35 to 40 km. The raises the issue of how much exposure east of the application zone occurred to non-target native plants when winds prevailed from the west as such plant communities could be found significantly closer than 40 km from the spray zones.

The next aspect of Dr Moore's submission addresses the question of how far 2,4-D vapour drifts to cause plant damage. He quotes Sherwood *et al* (1970 - discussed below) to conclude that the injury to a range of species was evident approximately 10-15 m from the source, and that HVE are likely to have effects up to 50-100 m from a source providing continuous exposure. The concern with this simple analysis is that it takes no account of environmental load. In the Sherwood study, 2,4-D (as isopropyl ester) was applied to cheesecloth with a total

16 g ae in the centre of the plot. It was noted that symptoms were of about equal severity in the whole circular test plot (360^o). If 16 g of a 2,4-D HVE caused noticeable damage to a distance outwards of up to 100 m, then the actual area affected is 7,800 m^2. The movement of an environmental load resulting from hundreds to thousands of hectares each being treated with hundreds (if not thousands) of grams acid equivalent of 2,4-D in a volatile ester form is a significant concern.

The above result was not an isolated one. Also discussed below are the results from Day *et al* (1959). In this test, various **low volatile** 2,4-D esters were applied to 10 sq ft plots (0.93 m^2) at rates up 16 lb/ac (18 kg/ha) for the propyleneglycol butyl ether. At the highest applied rate (equivalent to about 1.7 g for the plot), severe damage was noted from the 10 sq ft plot extending out around 33 m, and around 20 m from the plot treated with 8 lb/ac (9 kg/ha or around 0.84 g for the plot). From the 4 lb/ac (4.5 kg/ha; 0.42 g for the plot) rates, severe damage was noted at distances of 12 – 15 m. Even slight effects were recorded hundreds of feet (at least 100 m) away from the small plots. If the effects of such vapour movement are a function of the load of chemical in the air, this analysis suggests again that where hundreds to thousands of hectares are treated with even a moderately volatile ester, effects would be expected at significant distances from the treated areas.

The next part of Dr Moore's submission discusses another worst case (in his view) scenario reported by Lanphear and Soule (1970) in which symptoms of toxicity were observed in a plume up to 3.3 km from industrial sites handling phenoxyacetic acid herbicides and chemicals used in their manufacture. He notes symptoms were due to vapour movement from the site. Dr Moore states the important aspect of this study is that "the pattern of symptoms is not the random damage in all directions for large distances that is postulated by those seeking removal of HVE but is a well defined plume probably associated with particular meteorological conditions." While the Department accepts that any damage caused by vapour movement is a function of wind direction, it is not necessarily a function of wind direction **at the time of application**. If prevailing winds persist in a similar direction during times of vapour lift off from treated areas a consistent pattern of exposure would be expected. However, changes in wind direction after application will result in movement in different directions (note, this happened in the Gilbey *et al* (1984) study – see the aerial spraying component of the study, p 20 below) and this is what leads to short term unpredictability for off-target effects resulting from vapour movement. While this study is discussed in more detail below, it is notable that additional field surveys described in this paper revealed no further damage to plants in the initial survey area, but did indicate injury on redbud (*Cercis canadensis*) extending at least 5 miles (8 km) further west of the original pattern (remembering exposure came from a single point source, not from broadacre application). Redbud trees were absent in the original survey area and this may be coincidental or indicative of damage in previous years that prevented them growing in this area. This is a noteworthy observation and goes to one of the environmental concerns with the 2,4-D HVE assessment, that just because a non-target stand of vegetation may appear healthy, there may over time still have been the removal of the more sensitive species due to a competitive disadvantage, particularly when exposure may occur over many years. It is unlikely such an hypothesis could ever be demonstrated due to a lack of detailed knowledge of plant communities existing prior to widespread use of 2,4-D esters in Australia and the lack of monitoring of the communities over time.

Consideration of Specific Tier II Data Requirements

Following the above comments, Dr Moore addressed the Tier II data gaps relating to environmental fate, and also provided some data relating to the Tier III data gaps, toxicity to plants exposed through the vapour phase. These data gaps and information provided by Dr Moore are discussed below.

The submission is in response to the additional Tier II data required relating to environmental fate, namely:

- *Conduct higher tier photo-oxidation studies on the short-chain esters to better determine persistence in the atmosphere.*
- *Additional fate studies considering volatility from a wide range of soils and representing exposure conditions (that is, surface applied without mixing). Such testing should be performed with a range of realistic ambient temperatures to allow assessment of the varied use patterns currently registered;*
- *Volatility studies for the short-chain esters from foliage (and to determine likely persistence of these compounds on foliage). Such testing should be performed with a range of realistic ambient temperatures to allow assessment of the varied use patterns currently registered;*
- *Assessment of the likely exposure concentrations in soil and air at the point of in-field application;*
- *Aerobic soil metabolism studies. There is currently conflicting evidence in this regard based on the data for longer chain esters and salt forms of 2,4-D as to persistence in aerobic soils. Any testing should characterize the persistence and breakdown of the short-chain esters in a range of soils, and be performed in a manner consistent with the use pattern, that is, surface applied to soils at a range of temperatures and without soil incorporation.*

The submission addresses each of these issues with argument or further information/data. We have considered the information supplied and the following provides our assessment of data contained in this submission.

Conduct higher tier photo-oxidation studies on the short-chain esters to better determine persistence in the atmosphere.

In the assessment report, persistence of various ester forms of 2,4-D were predicted using AOPWIN Version 1.91 based on reaction with hydroxyl radicals.

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

3) Rate constant, K_{OH} (X 10^{-12} cm^3/molecule/second)
4) Not registered in Australia

One paper (Que Hee and Sutherland, 1979) has been provided describing an experiment where the vapour and liquid phase photolysis of the *n*-Butyl Ester of 2,4-D was tested. In short, 10 µL of pure ester was placed in the bottom of the irradiation apparatus and evacuated to around 10 mm Hg. The upper valve was closed and the apparatus allowed to reach thermal equilibrium at 70° or 30°C for half an hour. The bottom valve (between the liquid and gas phase) was closed and irradiation carried out for 94-188 h at a light intensity of 300 nm. Following irradiation, vapour was condensed, dissolved in hexane and analysed while the residual liquid was dissolved in hexane and analysed.

As explained in OECD (1993), the following photochemical processes may contribute to a chemical's reaction and breakdown or degradation in the troposphere:

direct phototransformation, that is, excitation of a molecule through absorption of a photon followed by chemical reaction, usually oxidation through reaction with oxygen;

indirect phototransformation processes including:
- reaction with OH-Radicals
- reaction with ozone
- reaction with other photochemically generated species.

The study described here is one performed to measure direct phototransformation. Irradiations were performed within reactors of the preparative Rayonet Photochemical type RS and a Rayonet Srinivason type, both equipped with 300 nm lamps, which delivered 16 and $4X10^{-17}$ photons/mL/minute.

After 188 h, 79% of the original starting material was characterised as volatile chlorinated organic residues implying that the remainder was inorganic or non-volatile. Of the 79%, 48% remained as unchanged parent in the residual liquid and 18% as unchanged parent in the gas phase. Total volatile residues in the gas phase were ~19.5% (that is, almost all unchanged parent) and total volatile residues in the liquid phase were ~59% (a significant amount being unchanged parent compound). Assuming first order degradation, the half-life for decomposition was around 13 days (continuous irradiation). However, this was for combined liquid and vapour residues. Based on residues found in the vapour phase, it would appear the direct photolysis half-life is significantly longer than this.

This study was conducted at a light intensity of 300 nm, and it is unclear whether 2,4-D even absorbs light at this intensity. In a separate experiment, the degradation of 2,4-D under UV light (>210 nm) was studied under various conditions (Kunda *et al*, 2005). A photoreactor was used for the photochemical reaction. Calibration curves for 2,4-D were generated at two different absorption maxima (230 and 283 nm). The effects of various parameters such as light intensity, exposure time, various solvents and micellar media (cationic and anionic) and the effects of some other parameters such as O_2, wavelength of light, pH, other commonly occurring ions, were studied. The percentage of degradation of 2,4-D was achieved up to 81% in simple aqueous medium. However, percent degradation of 2,4-D using **solar** irradiation (wavelength mainly >290 nm) under similar conditions as that applied for the photoreaction using the photoreactor was compared. Using the solar light the degradation was very negligible. The reaction in general follows zero-order kinetics.

Dr Moore has used the results of this study to calculate a half-life of about 40 hours, or 3.3 days with 12 hours light per day for photo-oxidation in the vapour phase. It is unclear as to how these calculations were undertaken. Of the direct and indirect phototransformation processes possible in the troposphere, reaction with OH-Radicals is generally the most important. This is because reaction with OH-Radicals is the most rapid photo-transformation process for the majority of organic chemicals. Direct phototransformation reactions may also be very rapid but only for a limited number of organic chemicals. The rate of a direct phototransformation reaction depends (1) on the overlap between the solar light emission spectrum under tropospheric conditions and the light absorption spectrum of the compound, and (2) on the quantum yield (OECD, 1992). While there are still no measured data for photo-chemical reactions with hydroxyl radicals, this experiment testing direct photolysis indicates it will be a slower process than indirect photolysis in the atmosphere (based on estimation above).

There is a photolysis study for 2,4-D BEE referenced in Dr Moore's letter that could be sought from the US EPA by the APVMA. The study is:

> Marx, M.; Shepler, K. (1990) Vapor Phase Photolysis of (Carbon 14)-Phenyl} 2,4-Dichlorophenoxyacetic Acid, Butoxyethyl Ester (2D-BEE): PTRL Report No. 195W-1: PTRL Project No. 195W. Unpublished study prepared by Pharmacology & Toxicology Research Laboratories, West. 92 p.

DEW did not have access to this study through the course of our assessment. Further, DEW have checked the final US EPA re-registration eligibility document and it does not discuss vapour phase photolysis at all even though the above reference is found in the list. In a separate assessment performed by the Washington State Department of Ecology, they mention a vapour photolysis half life of 13-20 days, but don't provide a reference.

It seems that these both refer to direct photolysis, not photo-oxidation, which for reasons outlined above, DEW would expect to be a faster process for removal of short chain esters from the troposphere. It does appear from Dr Moore's submission that industry is prepared to accept an atmospheric half-life of 2-3 days without generating further information, and thus the Marx and Shepler (1990) reference does not need to be supplied.

Conclusion relating to Tier II data requirement for higher tier photo-oxidation studies on HVE to better determine persistence in the atmosphere.

When considering movement through the atmosphere, one of the main issues is the chemicals persistence in air. A chemical with a half-life in air >2 days is considered persistent in this medium and therefore, able to move significant distances in air. This is the assertion made in our original assessment, and generation of additional data was only sought if this claim was to be challenged. The estimated half-life was further used in the assessment only insofar as it helped calculate a characteristic travel distance (CTD). These CTDs were not used in a quantitative sense, rather they were used as an illustration of how far short chain esters could potentially travel compared to longer chain esters that were modelled to have significantly shorter atmospheric half-lives.

If no further data are to be generated in this area, DEW will continue to assume that the short-chain esters of 2,4-D are persistent in air, and therefore, potentially capable of moving large distances through the atmosphere, at least in a regional sense (up to several hundred kilometres).

Given this, the issue remains one of how much the HVE are likely to volatilise from foliage or soil following application.

Additional fate studies – volatility from soils.

This requirement was for fate studies considering volatility from a wide range of soils and representing exposure conditions (that is, surface applied without mixing). Such testing should be performed with a range of realistic ambient temperatures to allow assessment of the varied use patterns currently registered.

In responding to this issue, Dr Moore quotes three papers. Gile (1983) measured losses from a simulated wheat field and is discussed in further detail below. This study would have measured losses resulting from both foliage and soil application and it is difficult to determine the extent volatilization from soil would have played in the results.

A second study, Leonard (1961) is reported and only the abstract provided. This seemed to be a bioassay using cotton plants exposed to vapours of various 2,4-D formulations up to 48 h at 93 and 72°F (34 and 22°C respectively) following application to bare soil. Assessment of effects was based on the number and degree of strap-shaped leaves produced in 3 weeks. The abstract notes that the two salt formulations did not cause deformities after exposure for 48 h. Seedlings exposed for the same period to the butoxyethanol ester, emulsifiable acid and alkanolamine salt formulations, applied at 10 lb/ac (11.2 kg/ha) when air temperatures reached 100°F (37.8°C) to dry soil on plots 100 sq ft (30.5 m^2) in area and 30 ft (9 m) apart, all produced strap-shaped leaves including controls. This is noted as possibly being due to plots being too close together. No testing was performed with 2,4-D HVE. Of the seedlings exposed 48 h after the spray was applied, only those from plots treated with the butoxyethanol ester showed deformities. No real interpretation of these results can be made without the full paper to further evaluate the test results. It seems application was to dry soil (which will greatly limit volatilization). The test design seems questionable due to control effects and issues with plot spacing. It is difficult to apply these results at present without the full paper and we note that Dr Moore is seeking this document.

Dr Moore also briefly quotes Grover *et al* (1972). This study is described in more detail below and is considered more representative of volatility from foliage than from soil. In terms of loss following application, the study found 26-30% losses from volatilization within **30 minutes** of application at moderate temperatures of 24-26^{o}C.

Dr Moore concludes based on the above that the vapours from butyl and longer chain esters are expected to fall below the tomato NOEL within 48 hours of post emergent applications to cereal fields. It is unclear as to how he reached this conclusion, which in any event, doesn't actually relate to the purpose of the data requirement. While vapours may well reduce in air within the field of application, where applications are occurring to very large acreages from a number of properties, DEW needs to have an idea of the total likely volatilization from soil (and foliage, but that is dealt with later) to gain an idea of potential total environmental load. It is therefore DEW's opinion that this data requirement is not adequately addressed by Dr Moore's submission. Consequently, we have undertaken further assessment in this area.

The US EPA publishes a document, Compilation of Air Pollutant Emission Factors (AP-42). This has been published since 1972. Supplements to AP-42 have been routinely issued to add new emission source categories and to update existing emission factors. This document considers the issue of volatilization as an emission process for pesticides to reach the atmosphere.

Processes affecting emissions through volatilization of agricultural pesticides applied to soils or plants have been studied in numerous laboratory and field research investigations. The 3 major parameters that influence the rate of volatilization are the nature of the active constituent, the meteorological conditions, and soil adsorption.

Regarding meteorological conditions, the extent of volatilization depends in part on air and soil temperature. Temperature has a different effect on each component relative to its vapor pressure. An increase in temperature can increase or decrease volatilization because of its influence on other factors such as diffusion of the active constituent toward or away from the soil surface, and movement of the water in the soil. Usually, an increase in temperature enhances volatilization because the vapor pressure of the active increases. Wind conditions also can affect the rate of volatilization. Increased wind and turbulence decrease the stagnant layers above a soil surface and increase the mixing of air components near the surface, thus increasing volatilization.

The effects of soil adsorption depend not only on the chemical reactivity of the active but to a great extent on the characteristics of the soil. Increased amounts of organic matter or clay in soils can increase adsorption and decrease the volatilization rate of many actives, particularly the more volatile actives that are nonionic, weakly polar molecules. The soil moisture content can also influence the rate of vaporization of the weakly polar actives. When soil is very dry, the volatility of is lowered significantly, resulting in a decrease in emissions. The presence of water in the soil can accelerate the evaporation of pesticides because, as water evaporates from the soil surface, the active present in the soil will be transported to the surface, either in solution or by codistillation or convection effects. This action is called the "wick effect" because the soil acts as a wick for movement of the active.

DEW accepts that for the HVE of 2,4-D, where application occurs to bare soil, the amount lost through vapour will increase as soil moisture increases and as soil organic carbon decreases. In our original assessment, it was assumed negligible release through soil evaporation due to potential hydrolysis in the soil. However, this is unlikely to be correct. While hydrolysis may occur, the hydrolysis half-life will depend factors such as moisture conditions of the soil or whether the product is incorporated. For surface applied chemicals, hydrolysis is likely to be a slower process particularly where the soil surface is dry, and chemical will be available in unchanged form for some time following application. In the mean-time, volatilization losses (as shown below) could be quite high (up to 30%) within hours of application. In the paper by Gile (1983), he concludes that volatilization of 2,4-D materials from the soil is unlikely (please see below for a fuller description of this study). However, this is further clarified in the report. As noted, there was little mass flow of water through the soil column (the soils could not be considered particularly moist at <17% moisture content). An average of 90 L water was added to each test unit and during that time the leachate removed averaged less than 3 L total for any unit (the soil depth was 40 cm). Application was foliar although it is unclear just how much interception would have occurred. However, Gile notes that with such application, plants can hydrolyse the esters to the acid and it would be expected that the acid would be the primary form reaching the soil. Therefore, it is not surprising that under this experiment, volatilization from soil was not a significant dissipation route.

Conclusion relating to Tier II data requirement – volatility from soils

This issue in our view remains inadequately dealt with. Again DEW reiterates, no data on 2,4-D HVE volatility from soils were available for assessment. As noted above, we accept that application to bare soil may limit volatilization losses where soils are dry. However, time of application is still important, and increased temperatures are likely to increase volatilization. For example, application to bare soil in March in Western Australia may see the soil surface being dry, but temperatures may be high. Additionally, where application is to moist soil surfaces, volatilization from soils may be a significant removal mechanism. There remains insufficient information in this area to refine our assessment.

Volatility studies – foliage.

This data requirement sought volatility studies for the short-chain esters from foliage (and to determine likely persistence of these compounds on foliage). Such testing should be performed with a range of realistic ambient temperatures to allow assessment of the varied use patterns currently registered

In the initial assessment, the model used for estimating volatilization from crop surfaces was that 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.

The model states that where $P_{sat} > 11.8$ mPa, the cumulative volatilization is taken to be 100% as substances having such a high P_{sat} are not likely to be sprayed on crops.

In his submission, Dr Moore makes the assertion that requirement for studies on the volatilization of the short-chain esters from foliage is due to erroneous calculations in the assessment where it was assumed that volatile losses are 100% for HVE's under the Exposure Via Air model (note, this was not the model we used), commenting that it is obvious that losses can't be high and certainly not 100%.

Again, this comment really doesn't relate to the purpose of the data requirement, and in any event, we consider the rationale incorrect. The volatilization of 100% from foliage was **total**

cumulative volatilization. Studies provided by Dr Moore addressing this point are assessed below. In addition, DEW submits evidence provided by Taylor (1978) showing cumulative volatilisation rates from plants can be very large for more volatile compounds. These compounds tested were heptachlor (VP 0.0003 mmHg @ 25%) and trifluralin (VP 0.00024 mmHg @ 25^{o}C). For these chemicals, following moist bare soil surface application, volatilization was measured at 90% in 2-3 days. For heptachlor applied to vegetation, volatilization was measured at 90% after 7 days. Even dieldrin (VP 2.8 X 10^{-6} mm Hg @ 25^{o}C) had a cumulative volatilization of 90% after 30 days following application to vegetation (compared to 20% in 40 days following application to moist bare soil surface and 3.6% after 167 days following incorporation). Air temperatures are not reported, but it is noted application occurred in the summer months.

Converting these vapour pressures to mPa as used in the above model gives results of 39.99, 31.99 and 0.37 mPa for heptachlor, trifluralin and dieldrin respectively (compared to 148 mPa for 2,4-D ethyl ester). The model used for the assessment would therefore assume cumulative volatilization **from the crop** of 100% for heptachlor and trifluralin, which is in fact supported by the measured data.

Bearing in mind that the assessment assumed 50% crop intervention, the actual amount volatilized in total did not equate to the total amount applied, rather, it was half the applied rate as the view was taken that chemical reaching the soil could hydrolyse and volatilization would not be the main route of dissipation. This assumption was probably incorrect as other evidence suggests where soils are moist, volatilization may be a significant dissipation route.

Further, in data presented in Dr Moore's submission, a field study (Grover *et al*, 1972) measured 25-30% loss of 2,4-D butyl ester through vapour in only half an hour following application. This study is evaluated further below, but does lend support for an assumption of 50% cumulative loss through volatilization as assumed in the preliminary assessment (100% through crops and 0% through soil with 50% crop interception).

Maybank *et al* (1978 – not part of the Dr Moore submission) considered pesticide losses from the target area at the time of application, and the amount of volatilized active constituent drifting off in the subsequent hour or two following spraying. Trials were conducted with both groundrig and aircraft. The paper abstract reports results (to date for the time of publication) indicating that some 30-40% of initially deposited butyl ester evaporates and drifts downwind as vapour in the 2 h following spraying. The corresponding figure for the octyl ester is 10-15%.

Grover *et al* (1985 – not part of the Dr Moore submission) provides further support for the use of the simple volatilization model used in the HVE assessment. This study considered dissipation of the 2,4-D isooctyl ester in air, crop and the soil component following application in a wheat field. Drift losses during application were only 0.2% of the amount applied (calculated based on mean horizontal wind speed and herbicide concentration at six heights downwind of the treated field). Air samples collected at six heights ranging from 30 cm to 200 cm above the crop canopy during the first 7 d after application showed distinct ester gradients in the air with concentrations highest in the samples closest to the crop canopy. The highest concentration was measured during the afternoon of day 1 when 1,604 ng/m^3 were recorded 30 cm above the crop canopy. The vertical flux of the ester showed distinct diurnal variations with maxima reached in the early afternoon of day 1 and 2, followed by a rapid decline of the ester flux thereafter, corresponding with the depletion of the ester from the crop canopy. The total or cumulative vapour losses of the isooctyl ester over the 5 d sampling period were estimated to be 93.5 g/ha, or 20.8% of the amount applied.

The crop canopy intercepted 52% of the applied ester and acted as the major source of vapour losses. This suggests a cumulative volatilization from the crop of around 40% of that intercepted. In our initial assessment, DEW estimated cumulative volatilization from the crop of only 7% for 2,4-D EHE. The magnitude of vapour activity was controlled primarily by the atmospheric stability and air temperature following application. On entry into the crop, the ester was hydrolysed to the acid metabolite, which reached its maximum level on day 3. There appeared to be a rapid initial metabolism of the acid followed by a slow decline.

Ester losses from the soil surface occurred only when the soil surface was moist (after a rainfall event or in the early hours of the morning following deposition of dew). In addition, both the hydrolysis of the ester and the subsequent degradation of its acid metabolite in the soil were dependent on the availability of soil moisture. No detectable 2,4-D remained in the soil after 34 days.

Further assessment of volatilization of 2,4-D esters following application:

Gile (1983) determined relative airborne losses of commercial 2,4-D formulations from a simulated wheat field. Formulations included two DMA salt and an ethanol/isopropyl amine salt (deemed nonvolatile), an isooctyl ester and a propylene glycol butyl ether ester (deemed slightly volatile) and a butyl ester (deemed highly volatile). The test microcosm was a glass plexiglass and polyethylene box with dimensions of 1.25 m (height) X 1.0 m (length) X 0.75 m (depth). Each microcosm received 38,000 lumens/m^2 (1 lumen/m^2 = 1 lux) from a single 1000 watt lamp at the soil surface during the 16 h day 8 h night cycle. Airflow through the microcosm was ~400 L/min resulting in 37.6 air changes per hour. Calculated averages for the seven microcosms showed average daytime air temperatures of around 23^{o}C and average night air temperatures around 16^{o}C. Average daytime humidity was 55.5% and soil temperature was around 20.5^{o}C. The soil moisture content was around 16.9% and the soil was a sandy loam (1.2% OC, pH 6.43, WHC 22.9 @ 0.3 bar).

Soil was added to each microcosm in two equal portions to a depth of 40 cm. 160 wheat seeds were planted in each chamber 8 cm apart in rows and covered with 1 cm soil. After 26 days, the formulated 2,4-D was sprayed on the plant foliage at a rate of 1.2 kg/ha acid equivalent. To determine the distribution of 2,4-D within the ecosystem including its transport via air and metabolism, the air, plant and soil samples were prepared and analysed by HPLC. To collect air samples, PUF disks were fitted in the exit air stream. The efficiency of PUF disks for collection of 2,4-D vapours was discussed in Grover and Kerr (1981) where they showed collection efficiencies of 2,4-D butyl ester and iso-octyl ester vapour on 20X50 mm PUF plugs over six h at air flow rates of 4 L/min of 104 and 99% respectively. Samples were collected daily for the first seven days then twice weekly for the remainder of the test (total 28 days following application). Wheat and soil samples were collected at the end of the test for analysis.

The butyl ester volatilized the most to air. Four hours after application this formulation resulted in an air concentration of 140 ng/L. After 48 h this concentration had declined to 2.16 ng/L. Through the 4th day, the ester was the major portion of detected material in the air, then the metabolite 2,5-dichloro-4-hydroxyphenoxyacetic acid became predominant. A cumulative loss to air for butyl ester was 17.5% of the applied amount. What is not known from this experiment is what proportion of the applied amount was intercepted by the wheat crop as opposed to being soil applied, and therefore, what proportion of cumulative volatilization was attributable to soil losses. Given application occurred 26 days after planting, it could be assumed crop interception was not high as the plant cover would not be great at this time as plants would still be small. Therefore, the majority of the applied chemical was likely to be on the soil.

The isooctyl ester also showed significant losses to air. After 4 h sampling, 24.5 ng/L was present in air and 2 days after application the concentration of isooctyl exceeded that of the butyl ester. The parent ester remained the predominant component through the 5th day with the hydroxy metabolite dominating after that. A total of 15% application rate was recovered in the air over the course of the experiment.

Between 5.1-8.3% of the applied amounts of propylene glygol butyl ether ester was recovered in air over the course of the experiment and this compared with <2% of the amine salt formulations tested.

Hydrolysis of the ester products in plant tissues was observed as after 28 days, analysis of wheat tissue revealed a predominance of either 2,4-D acid or the hydroxy metabolite. However, hydrolysis was not complete as the parent ester was still observed in each of the three different ester formulations.

Grover *et al* (1972) performed a field experiment to determine the relative potential of droplet and vapour drift when 2,4-D was applied in the ester (butyl ester) and amine form. Sampling poles were arranged in two concentric arcs, 30 m and 75 m downwind from the target area. While not stated in the report, application appeared to be to a vegetated (pasture) plot with little exposed soil based on a photograph of one of the sample poles, and it is assumed the application area was of a similar nature. If this was so, then measurements in this study from the vapour phase are considered more representative of volatilisation from foliage, not soil. Preliminary experiments showed 2,4-D was not detected at heights greater than 2 m so samplers were set on the poles at heights of 0.5, 1 and 2 m only. Some poles had two rows of samplers. One row was run from 0-3 minutes following application and the second row for 3-30 minutes. It was assumed that the first sampling period would account for vapour and droplet drift while the second would only account for vapour drift. A further set of poles had one row of samplers and collected total dose information over the 0-30 minute period following application. The airflow of the samplers was maintained at about 14.5 L/min and at all sampling sites individual gas operated suction pumps were used to draw air through the samplers. The 2,4-D formulations were radiolabelled and counting efficiencies were shown to be >90%.

The butyl ester and DMA salt formulations were sprayed at 350 g/ha (assumed acid equivalent) in 50 L/ha water using 65015 TeeJet nozzles at 1.76 kg/cm^2. The VMD of this nozzle was 430 microns and the volume fraction of droplets <200 microns was 2.8% of the total spray (@21^{o}C under controlled atmospheric conditions). A 12 m boom sprayer with 26 nozzles was used to apply herbicides. The nozzles at 50 cm apart on the boom were oriented backward at a 45^o angle. The boom was 66 cm from the ground. Experiments were conducted in duplicate for each formulation.

The droplet and vapour recoveries expressed as % mass of material discharged are summarised as follows:

Table 1: Estimated recoveries of 2,4-D as droplets and in vapour form on the 75 m arc in the four experiments:

Form of 2,4-D	Experiment no.	Droplet drift (0-3 minutes)	Vapour drift (0-3 minutes)	Vapour drift (0-30 minutes)
DMA	1	2%	0%	0%
	2	4%	0%	0%
Butyl Ester	1	3.5%	11%	30%
	2	3.5%	14%	26%

It is assumed that all collection of the DMA formulation was as droplet form. Further, assuming a similar amount as droplet for the ester formulation, the vapour drift resulting from the 0-3 minute sampling is taken to be the difference. In the 0-3 minute period, the droplet drift was estimated to be 3-4%. These are reasonably consistent with a value of 2.8% for the fraction of sprayed liquid in droplets <200 microns. The vapour recovered in the same initial period for the butyl ester was 11-14%. In addition, another 12-19% vapour losses from the target area were recovered in the 3-30 minute period for the butyl ester formulation. Vapour movement of the DMA salt was negligible.

Day *et al* (1959) report field tests of **low-volatile** formulations of 2,4-D under summer temperature conditions encountered in the agricultural area of the Coachella Valley of California, designed to explore the volatility of the herbicide under hot conditions. Cotton was used as a test plant purely as a matter of convenience. Butoxyethanol 2,4-D (vapour pressure of 0.32 mPa compared to 148 mPa for 2,4-D ethyl ester) was applied at 16, 8, 4, 2 and 1 lb/ac (~18, 9, 4.5, 2.25 and 1.1 kg/ha). Propyleneglycol butyl ether 2,4-D, tetrahydrofurfuryl 2,4-D, Alkanolamine salts of 2,4-D and a 2,4-D acid emulsion were applied at 4 lb/ac (4.5 kg/ha). Plot sizes were 10 sq feet (0.93 m^2) and cotton plants were about 18" (46 cm) tall and in full bloom. Applications were made with a compressed air knapsack sprayer equipped with a flat-fan nozzle of 0.052" (0.13 cm) orifice diameter using a pressure of approximately 10 lb/sq inch (0.7 kg/cm^2). Materials were diluted with water and sprayed uniformly over the plot areas at a rate of 100 gallons/acre (1120 L/ha) and precautions were taken to avoid drift out of the plots during spraying. The extent of injury to the cotton plants surrounding the plots was recorded 10 days after treatment. Wind direction and velocity and soil surface temperatures were recorded during the trial and provided a basis for calculation of the total miles of wind moving from each of the 16 points of the compass. Only the amine salt formulation failed to produce symptoms outside the plot, although symptoms around the emulsifiable acid plot were slight. All of the ester formulations affected areas extending northwesterly from the plots in a fan shaped pattern roughly proportional in extent to the concentration of the solution applied. The areas affected relative to each plot were only shown graphically in the report. However, for the highest applied rate, severe damage was noted from the 0.93 m^2 plot extending out around 33 m, and around 21 m from the plot treated with 9 kg/ha (**equivalent to around 0.84 g 2,4-D in the test plot**). Even from the 4.5 kg/ha rates (**~0.42 g 2,4-D in the test plot)**, severe damage was noted at distances of 12-15 m. Even slight effects were recorded hundreds of feet away from the small plots. If the effects of such vapour movement are a function of the load of chemical in the air, this analysis suggests that where thousands of hectares are treated with even a moderately volatile ester, it would not be unexpected to see effects at significant distances from the treated areas. Average air temperatures during the first 10 days are stated as 106°F (~40°C). These seem exceptionally hot for average temperatures and may actually reflect the maximum daytime temperature. The pattern of injury suggests the influence of wind. Wind velocities were stated as normally moderate, rarely exceeding 20 miles/h. Night winds were almost opposite in direction than day wind direction. At night, the report states there was insufficient vapour to affect plants, although the pattern of impacts shown still demonstrates minor effects outside the plots in the direction of the night winds.

Conclusions relating to Tier II data requirement for volatility studies from foliage

The end result of assessing these data is that they underline concerns over how the short chain esters of 2,4-D may behave in the environment, that is, they reinforce DEW's expectation that significant amounts of the sprayed herbicides will be lost to vapour following application, particularly where application occurs to foliage, and that the persistence in the atmosphere is sufficient for them to undergo significant environmental transport. Data presented above clearly shows that low amounts of even LVE can move significantly further than their limited area of application, and that the distance moved appears to be a function of the amount of chemical applied.

Given the extra information reviewed, DEW is of the opinion that further research in this area may not provide evidence to the contrary.

It really then comes down to a question of whether these factors will actually result in sufficient concentrations in the air column to cause off target damage. To that end, a range of further information has been provided in Dr Moore's submission on monitoring activities relating to 2,4-D both in Australia and internationally. This research is assessed below.

Assessment of the likely exposure concentrations in soil and air at the point of in-field application

Dr Moore quotes the results of Grover *et al* (1972) where 2,4-D butyl ester vapour concentrations at various heights downwind from the sprayed area were measured. This study is discussed in greater detail above. Dr Moore states that the findings from this study were 1 µg/m^3 (within 2 m height) at around 2 m from the edge of the field and 0.2 µg/m^3 40 m downwind. It appears Dr Moore has misinterpreted these results. The values provided in the paper have not been discussed in terms of µg/m^3. Rather they are provided as a concentration **relative to the concentration at 0.5 m** height. The actual concentration is never provided in the paper. Further, the concentration of 0.2 (or 20% of the 0.5 m height concentration) is modeled to occur at least out to 100 m from the edge of the field. This was following application of about 66 g 2,4-D into the plot area (12.5 m X 150 m length).

Dr Moore states these results are supported by those of Day *et al* (1959 – also described above) where vapours of the lower volatile butoxyethanol ester of 2,4-D affected cotton plants at around 46 m from the source of exposure. DEW disagrees with this analysis. As explained above, the test plots were very small (<1 m^2), yet effects on plants were found at large distances despite the overall very small environmental load, and appeared to move further as application rates increased.

Dr Moore also cites Breeze and West (1987) stating they find 5 ng/L 2,4-D butyl ester for 2.5 h giving tomato symptoms and dry weight losses at 5 h exposures. The Breeze and West paper is discussed in more detail below and is better suited to the issue of plant toxicity when exposed through the vapour phase and is not applicable to the question of edge of field levels. In any event, the data obtained by Breeze and West are more in-depth than suggested in Dr Moore's analysis. Overall, these experiments showed that less than 2.5 h exposure to concentrations of around 5 ng/L 2,4-D butyl was required to produce epinasty in tomatoes and twice this period of exposure produces severe symptoms that eventually reduced the dry weight of the plant, as measured **47 days after the 5 h exposure period**

ceased. This level was calculated by the authors to represent around 2.5% of the saturated vapour pressure.

Environmental Monitoring Studies

Que Hee *et al* (1975) discuss GLC analysis of 2,4-D concentrations in air samples from central Saskatchewan in 1972. Only the abstract and 1st page of the article have been provided. The air sampling procedure is described. Commercial activated silica (60/70 mesh) was treated by Soxhlet extraction for 2 days using boiling methanol. The gel was dried at 200^oC for two days. 5 g of the gel was packed into polyethylene air samplers (sampler characteristics not provided directly) and shielded from moisture. Sampling stations were established in Saskatoon and at weather stations on farms in the Rosetown and Naicam districts. The samplers were placed on the vertical inlet of a vacuum line, 7 ft (~2 m) above ground level. They were encased in a cage of mesh and the air flow maintained at 10 L/min. The samplers were changed daily.

GLC mass spectrometry confirmed the presence of 2,4-D. Mean total daily levels of 2,4-D (as *n*-butyl ester) found for Saskatoon for 33 days were 600 ng/m^3 of air, and for Naicam for 47 days, 142 ng/m^3 of air. Very little 2,4-D was detected at Rosetown.

Results are limited, particularly without the full study. It would be interesting to see the range of daily results (and bear in mind, these are still 24 h averages with no indication of peaks, lengths of peak exposure or wind direction during the 24 h period), compared with distances from the samplers for the likely source of 2,4-D exposure.

Farwell *et al* (1976) discuss survey results of airborne 2,4-D in south-central Washington State from 1973 and 1974. A two stage sampling system consisting of a rotating disk impactor (collection of aerosol droplets down to around 3 μm diameter) followed by a midget impinger to collect the vapour fraction was used. The impactor cup contained a two phase collection solution of 10 mL *n*-decane and 10 mL aqueous $NaHCO_3$. The midget impinger contained 10 mL *n*-decane. This method was first described by Bamesberger and Adams (1965). They explain the functioning of the impactor. Incoming air impinges on the impaction disk, which slowly rotates through a fluid well containing the *n*-decane. The impacted droplets wash off into the collection fluid. The disk then passes through a Teflon squeegee to remove the adhering droplets presenting a smooth surface containing a fluid film upon which the air stream impinges. The collection efficiency of the system for gaseous and aerosol forms of 2,4-D ester was studied under laboratory conditions and used at two field sampling sites for approximately 3 months.

Field monitoring sites were selected to gather factual information on the airborne concentrations of 2,4-D herbicides in the grape growing areas of the lower Yakima Valley and surrounding wheat regions. The concentration data were obtained from integrated 24 h samples. The air flow rate was normally 1 L/min. 2,4-D levels were analysed by gas chromatography.

In 1973, high volatile esters were applied in April and May with very small amount in June. The high volatile *n*-butyl ester of 2,4-D was the predominant compound present in the samples and on average, 57% of this was collected in the rotating disk (aerosol) and 43% in the midget impinger (vapour). In general, the highest daily average 2,4-D concentrations were recorded for 21-23 May (0.49 $\mu g/m^3$ *n*-butyl ester). During this period, the *n*-butyl ester comprised 62% total 2,4-D in the samples. Despite limited application of high volatile 2,4-D esters in June, over 5-7 June, the *n*-butyl ester still comprised 43% total 2,4-D with 84% in the aerosol form and 17% in the vapour form.

In 1974, application of HVE was prohibited from 30 April in Washington State. HVE applications in April were of a similar magnitude to those in April of 1973, and from then, no HVE was legally applied. The 1974 monitoring program was performed during a time when vineyards in the collection network were experiencing the most severe 2,4-D damage recorded in recent years. The atmospheric concentrations were considerably higher than levels measured in 1973 for chlorophenoxy herbicides. The eight-station averages of total 2,4-D for April and May were 0.84 and 0.83 $\mu g/m^3$ respectively. In April, HVE accounted for 66% total 2,4-D and 67% total 2,4-D in May. In June, the average total 2,4-D dropped to 0.52 $\mu g/m^3$, but of this, 92% was HVE despite no legal application since the end of April. As in 1973, the *n*-butyl ester was the dominant 2,4-D formulation, and on average, 53% was detected in the aerosol form and 47% in the vapour form.

Among its conclusions, the report states that the HVE *n*-butyl 2,4-D ester represented 75% of total chlorophenoxy herbicide burden in the representative air samples during 1973 and 1974 even though none was legally applied in the counties adjacent to the vineyards. On at least five different occasions there was a definite correlation between the reported concentrations of airborne 2,4-D and the herbicide related damage to vineyards. The authors concluded the possibility for major source areas of 2,4-D herbicides outside the state of Washington were suggested by both the high levels of HVE found during 1974 despite a ban on their use in Washington State, and an analysis of meteorological conditions identifying the general characteristics of a weather pattern acting as a long distance transport mechanism for airborne 2,4-D.

While this study separated 2,4-D between vapour and aerosol phases, it needs to be emphasised that the aerosol levels were for aerosols less than 50 microns, and down to 3 microns. These are exceptionally small droplets and would probably remain suspended in air indefinitely until they evaporate or are trapped. Therefore, they still should be considered relevant for any discussion on long distance airborne transport of 2,4-D, not simply dismissed as drift in droplet form at the time of application. The latter would not be possible for the 1974 results as there was no legal application in the area.

Gilbey *et al* (1984) report on airborne 2,4-D and tomato damage at Geraldton in Western Australia. The paper reports results from each year between 1979 and 1982 along with results of a study on 2,4-D drift from aerial spraying operations in 1980. The method of collection and analysis of 2,4-D is stated as similar to that described by Robinson and Fox (1978). Based on Robinson and Fox (1978), the collection device used solid adsorbent material. The samplers consisted of glass tubes (15 cm length, 19 mm diameter) filled with 3-4 g of a dry adsorbent resin. Glass wool plugs and a pair of small stainless steel screens served to hold the resin in the glass collection tubes. The solid adsorbent, known as Amberlite XAD-2, is a porous polystyrene divinylbenzene copolymer as 20 to 60-mesh beads. At the sampling site, the cartridge was unstoppered and attached to the sample holder. A critical orifice was incorporated into the hose connector in order to control the flow rate at 5.5 L/min.

In the Gilbey work, vertically oriented air inlets to the sampling tubes were 12 mm in diameter and air flow rates were within the range of 1.18-1.81 L/min (1979 monitoring). This flow rate is lower than the 5.5 L/min described in Robinson and Fox (1978). Robinson and Fox (1978) note the overall collection efficiency of XAD-2 for 2,4-D compounds, as studied in their laboratory, ranged from 84-100%. No separate efficiency testing of the sampling method was performed in the Gilbey work. The flow rates of this work are less than those used by Robinson and Fox. The implications of this are unclear. However, as resin tubes were changed only weekly, a flow rate in the order of 1 L/min over the week will result in an air volume of around 10 m^3 being sampled, compared to around 7.8 m^3 in the Robinson and Fox work where they took daily samples.

Adsorbed 2,4-D was recovered by sequential solvent extraction and analysed by gas chromatography. In 1979, seven sampling units were distributed around Geraldton. One was around 10 km from the town centre, three around 20 km from the town centre and another three around 30 km from the town centre. The sampling units operated continuously for 20 weeks from 25 June and resin tubes were changed weekly. Tomato seedlings at the airport (~10 km from town) were changed each week at the same time as the resin tubes, grown on for at least 4 weeks away from further 2,4-D exposure and visually rated for 2,4-D damage. Thirty commercial tomato gardens distributed throughout the Geraldton district were also inspected for 2,4-D damage during the monitoring period.

In 1979, very little high volatile ester was sprayed onto cereal crops around Geraldton due to drought conditions. Airborne 2,4-D was detected when cereal crops were being sprayed, but mainly in the non-volatile acid/amine form (although this was also detected in the atmosphere). Main detections of this form occurred from week 9 through to week 15 from the start of sampling with mean weekly concentrations (where detected) of 0.01 to 0.06 µg/m^3. 2,4-D damage occurred in six tomato gardens in the Moonyoonooka area, which adjoins the airport. There was no relationship between the damage and 2,4-D levels detected at the airport monitor. Furthermore, wind speed and direction at the airport bore no relationship to either atmospheric 2,4-D levels or crop damage.

Very little can be deduced with regard to the HVE from the 1979 data due to the limited amount applied in this year. In 1980, the sensitivity of the air monitoring procedure was increased to enable results to be reported to 0.001 µg/m^3. Apart from this, the method of collecting and analysing 2,4-D was identical to that for 1979. This year, nine sampling units were operated continuously for 21 weeks from June 10. Most of these were within a 10 to 15 km radius of the centre of town. Two stations were further out with one at 38 km and another at 50 km (from this year, there was a 50 km exclusion zone for application of HVE around Geraldton). Resin tubes and tomato seedlings at the airport, Moonyoonooka and Eradu (50 km from town) were changed weekly and the tomatoes grown on at Perth for observation. Thirty-six commercial tomato gardens distributed throughout the Geraldton district were inspected for 2,4-D damage during the monitoring period.

In 1980, record areas of wheat were sown around Geraldton. Most of the 2,4-D was detected during the period (weeks 6-10), which coincided with cereal crop spraying. 90% of samples collected at this time contained 0.001 µg/m^3 or more of 2,4-D. The following table summarises the findings:

Table 2: Mean weekly aerial 2.4-D concentrations (µg/m^3), including from stations where 2,4-D was not detected.

Sampling station distance from town (km)	No. sampling stations		Weeks from start of sampling				
			6	7	8	9	10
10 to 15	7	LVE	0.001	0.002	0.006	0.010	0.015
	7	HVE	0.003	0.001	0.002	0.008	0.010
38	1	LVE	nd	0.008	nd	0.006	0.009

	1	HVE	0.003	0.003	0.003	0.008	0.009
50	1	LVE	0.003	0.003	0.004	nd	0.002
	1	HVE	0.006	0.018	0.025	0.020	0.031

The highest mean weekly 2,4-D concentration for the low volatile acid/amine was 0.052 μg/m^3 at Moonyoonooka (~10 km from town) in week 10. The next highest for this form of 2,4-D was 0.04 μg/m^3 found in week 8 at a sampling point around 10-15 km from town. For the samplers 10 to 15 km from town, the highest level found as HVE was 0.014 μg/m^3, and this level was detected at several of the seven sampling stations in weeks 9 and 10. Mean weekly levels of 0.025 and 0.02 μg/m^3 HVE were found at the sampling station situated 50 km from town, and this was accompanied by much lower concentrations of the low volatile acid/amine forms of 2,4-D.

Slight distortions of tomatoes were widespread throughout the whole area. Severe 2,4-D damage occurred in commercial gardens at Moonyoonooka and moderate damage occurred in several other gardens. All were located near cereal crops. Of the samplers in the 10-15 km zone, mean weekly levels of both low volatile and high volatile 2,4-D were noticeably higher than their respective concentrations in other sampling locations. It is suggested in the paper that this may be due to restricted dispersion due to the hilly terrain during inversion conditions. Tomato seedling placed near the monitors at this location and the airport each week frequently developed herbicide damage symptoms later in the glass house. No relationship was established with mean weekly 2,4-D concentrations detected at the same monitoring station for the same week and seedlings were damaged on several occasions when no 2,4-D was detected for the corresponding site and week. On other occasions, no damage was recognised when a relatively high level of 2,4-D was detected for the same site and week. These observations are not surprising given concentrations were expressed in mean weekly terms, and symptoms can often take days and weeks to manifest themseLVE as shown in other papers assessed in this report.

In 1981 the study was confined to one air-sampling unit stationed at the airport for 15 weeks from mid-July with 39 commercial tomato gardens being inspected for 2,4-D damage. In 1982 air sampling units were stationed north and west of Geraldton airport with a directional sampling unit at the airport Bureau of Meteorology base. The unit incorporated an anemometer, which directed the air sample to specific XAD-2 resin-filled glass tubes according to the wind speed and direction. Providing the wind speed exceeded 0.6 m/s, the monitor sampled from 6 equal segments between 0-360^o. The air-sampling units were operated for 16 weeks from 6 July and 29 commercial tomato gardens were inspected for 2,4-D damage during the sampling period. The only herbicides detected in 1981 were 2,4-D ester and dicamba (0.003 and 0.002 μg/m^3 maximum mean weekly concentrations respectively) with no low volatile acid/amine detected. Twenty-three gardens were found to contain moderately or severely malformed tomato plants despite the relatively low levels of airborne herbicide detected.

In 1982, the maximum mean weekly concentrations of 2,4-D acid/amine was 0.015 μg/m^3, three times higher than the maximum weekly concentrations of HVE or dicamba. Only six gardens were moderately or severely affected and at three locations, these were in close proximity to undamaged gardens. Information from the directional monitors showed both 2,4-D acid/amine and dicamba were detected coming from all directions and the highest concentration of each was detected from the west sector over a period of 4 hours during the same week. 2,4-D acid/amine was detected during 8 weeks of the 16 week sampling period. By contrast, 2,4-D ester was detected coming from only two sectors (east and south east), in each case during one week out of 16. It was not detected by one of the nearby non-directional monitors during the same weeds. The authors conclude that these results do not support the hypothesis that 2,4-D ester sprayed 50 km or more to the east of Geraldton is the main source of airborne herbicide at the town. The direction of movement of the HVE, however, is not surprising given the exclusion zone around Geraldton thereby limiting the direction from which they could enter the sampling area.

The aerial spraying study was carried out in 1980. On 25 July a 600 ha paddock of wheat 100 km east of Geraldton was aerially sprayed with 448 g ac/ha of the isopropyl ester (to distinguish it from the ethyl ester most commonly used). The aircraft was fitted with nine 0.004 Spraying Systems fan jet nozzles and the herbicide was applied at a pressure of 200 kPa from a height of 7.6 m at 177 km/h in a cross wing of 23.5 km/h. The carrier was distillate and total output was 1.12 L/ha. Air sampling monitors were placed in a line along the wind direction at 0, 0.5, 1, 2, 5, 10 and 35 km from the edge of the sprayed paddock and at a height above ground of 1.5 m. Silica gel coated glass plates were placed on the ground at each of the monitoring stations and were also located within the crop during spraying. Sampling at all stations commenced at the time of spraying except the 35 km station where sampling started 30 minutes later. Unfortunately, a slight change in the wind direction during spraying meant that only the southernmost section of the sprayed area would have contributed to the samples gathered at 2, 5 and 10 km during the actual spray period. On the day after spraying the samplers were placed at the same distances (except 35 km) away from the paddock in line with the wind direction and again run for 4 hours during the afternoon.

Atmospheric 2,4-D was detected up to 10 km from the sprayed area during the 4 hour period after commencement of spraying and ground deposits were detected up to a distance of 5 km. Because the samplers at and beyond 2 km were significantly off the plume centre line during the spraying period it was not possible to assess the highest concentrations at and beyond 2 km. On day 1, mean 2,4-D concentrations at 0, 0.5, 1 and 2 km from the sprayed area were 7.0, 3.6, 2.0 and 0.14 µg/m^3 respectively. At day 2 sampling, detectable levels were found at 0 and 0.5 km (0.012 and 0.007 µg/m^3 respectively) with levels less than 0.004 µg/m^3 at all other distances.

Interpretation of these results:

Aerosols can be collected by a number of methods including filtration, centrifugation, electrostatic precipitation and impaction. Any of these techniques could be used to collect aerosols containing compounds of 2,4-D, simultaneously separating them from concomitantly occurring gases. However, the direct application of these techniques to the collection of a 24-h sample of aerosols containing the more volatile esters of 2,4-D would suffer from continuing loss of the collected esters to the sampled air stream during the remainder of the sampling period (Bamesberger and Adams, 1965).

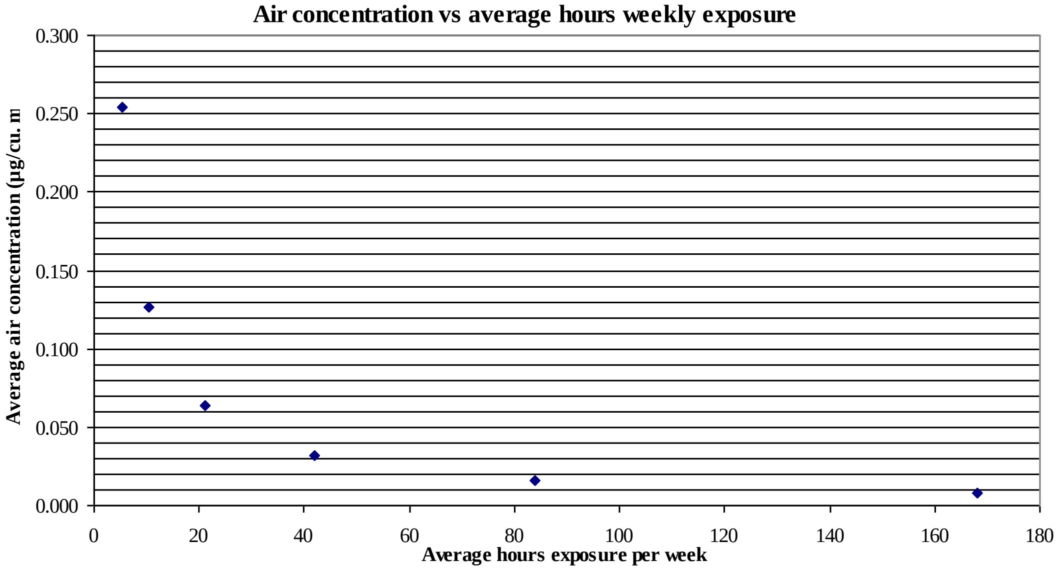
The sampling in this study used a newer (at that time) sampling method of drawing air through adsorbent material. The methodology was based on Robinson and Fox (1978) who claim that the use of adsorbents in air samplers is practicable due to their ability to retain selectively the organic compounds while allowing water vapour and the common air components to pass through the collection column. No concern was expressed by the authors that the more volatile esters of 2,4-D would be underdetected due to loss of the esters with the air stream and this appears a suitable collection method. The main differences in sampling strategy between Gilbey *et al* (1984) and Robinson and Fox (1978) are that the former used an air flow rate of around 1 L/min and collected average weekly samples while the latter used an air flow rate of around 5.5 L/min and collected average daily samples.

The 1980 monitoring data provide the most comprehensive information. In this year, HVE were prohibited from being sprayed within 50 km of the town. The data show that at around 50 km, HVE accounted for the majority of 2.4-D found in air samples. They also show that even closer into the town, (10-15 km), HVE still accounted for some 40% of total 2,4-D detected, and shows transport of at least 35-40 km through the atmosphere as no HVE should legally have been applied closer than this.

The authors note that atmospheric levels are much lower than those reported internationally (see above studies). This may be the case. However, the concentrations here were mean weekly concentrations. There is no way of knowing what peak levels were within the weekly sample, and what duration such concentrations lasted. It is apparent from other information that exposure for only a few hours at effective concentrations can lead to long term damage to susceptible plants (see Breeze and West, 1987 below). **To illustrate this point**, for 2,4-D HVE to be detected in the first place, they had to have moved in a general easterly direction. An analysis of climatic conditions at Geraldton airport over the long term, and during June-August (the sampling months) in 1980 has been performed and is presented in Appendix 1. Briefly, this analysis shows that in the morning (9 am) over June-August, wind directions are generally from the north east. Mean temperatures at this time are cool (<14^{o}C), and supposedly, they are cooler further inland thereby leading to a lower level of volatilisation. This is an important point. As illustrated in the research by Day *et al* (1959 – see p 15), they showed that where night winds were almost opposite in direction than day wind direction, at night there was insufficient vapour to affect plants, with effects mainly being noticed from vapour movement following the day time wind pattern. By 3 pm, the main winds are from a southerly through to north westerly direction, that is, they would generally be blowing from the airport back towards the zone where HVE may have been applied. Mean temperatures at this time were somewhat warmer (18-20^{o}C), so levels of volatilisation could be expected to be higher.

Purely as an example, Table 2 above showed that within 10-15 km of Geraldton, in week 9 of sampling, an average of 0.008 µg/m^3 (not the highest or the lowest weekly value detected during this study). This means, over the course of the week, sufficient HVE had to move at least 35-40 km from the general easterly direction to provide the mean weekly level detected. Assuming HVE are more available for lift off during the warmer times of the day (noting this study was undertaken in winter), and further assuming wind was blowing from the general easterly direction for 3 hours of the day when volatilisation was occurring (that is, prior to the wind direction shifting to the south or west), then maybe a total of 21 hours exposure may have resulted during the week. This means that the average exposure concentration over those 15 hours must have been in the order of 0.06 µg/m^3 to result in the final weekly concentration of 0.008 µg/m^3, or more than an order of magnitude higher than the average weekly value found. This is unlikely to be the case for the LVE or amine/salt formulations as they were applied within the sampling zone often quite close to actual samplers. It therefore stands to reason that at the times HVE were present in the air stream, they would have counted for a much greater proportion than 40% of total 2,4-D load.

Note that this theory is not without support. In the 1982 part of the study where directional monitors were used, the HVE were only detected as coming from the east and south east (as expected given the no-spray zone), and in each case during one week out of 16. It is therefore reasonable to assume that in the more comprehensive 1980 monitoring results, the only available HVE were coming in from the general east direction would therefore be limited to times wind was blowing from this general direction. Conversely, the 2,4-D acid/amine forms were detected coming from all directions (noting that spraying of these forms was allowed in the HVE no-spray zone, so not surprising) and the highest concentration was detected from the west sector over a period of 4 hours during the same week. This provides further support that the overall load of 2,4-D attributable to the HVE when they were actually present, are likely to be significantly underestimated, and weekly averages are simply too dilute to conclude anything further. The following graph illustrates the average hourly concentration of 2,4-D HVE required to result in a weekly (168 hour) concentration of 0.008 µg/m^3, depending on the actual number of hours of exposure through winds against the prevailing westerly winds:



Thus, it can be determined that if exposure of the samplers only occurred for 5 hours (maybe over 1 day of the week), or 10 hours (maybe over 2 days of the week), average exposure concentrations would need to be 0.254 and 0.127 µg/m^3 respectively to result in an average weekly concentration of 0.008 µg/m^3. If the winds blew against the prevailing direction for 5 hours every day of the week (total 35 hours exposure), the average hourly concentration would still need to be around 0.04 µg/m^3 to result in an average weekly concentration of 0.008 µg/m^3.

Damage to tomato plants was observed and generally no relationship existed between levels of damage and levels of 2,4-D in the atmosphere. This is not unsurprising given some effects may take some time to manifest themseLVE.

The authors conclude that the data gives support to the belief that short distance droplet drift from localised spraying with 2,4-D amine and dicamba is the most likely cause of herbicide damage to tomatoes in Geraldton. While the study results by themseLVE may support this (based on higher levels of 2,4-D acid/amine closer into the township than HVE), the overall concern of long-distance movement through the atmosphere of the HVE is not alleviated by the results of this study. Additionally, the point needs to be reiterated yet again, the concern is with environmental protection and non-target terrestrial plants as a whole, not simply neighbouring crops or horticultural crops. With other evidence supporting a conclusion that only short term atmospheric exposure to harmful levels of 2,4-D in the atmosphere are needed to bring about long term impacts (described in Section 3 below), and with the results of this study (as supported by international studies) showing the HVE can indeed move long distances from their point of release, it is difficult to amend the outcomes of the initial risk assessment in this area.

Conclusion relating to Tier II data requirement for Assessment of the Likely Exposure Concentrations in Soil and Air at the Point of In-field Application

The data requirement itself is not adequately addressed. Two literature papers were discussed by Dr Moore specifically addressing air concentrations at the point of application (Grover *et al* 1972; Breeze and West, 1987). The first of these did not provide actual concentrations in air, rather, considered downwind concentrations as a proportion of close in concentrations. The second study was a laboratory study considering vapour phase concentration to plant effects. No information was provided on soil concentrations at the time of application.

A range of environmental monitoring data were provided that address potential concentrations in the atmosphere at points well removed from the point of application. These data (including a major Australian study) provide supporting evidence that HVE do move significant distances from their source. In the Australian study, the HVE were found well west of their application point despite the dominant wind direction being from the south or west during the warmer parts of the day where volatilisation would be higher. Few conclusions on atmospheric levels being correlated to adverse non-target plant exposure can be drawn from this work as the samples were taken weekly so no firm conclusions on peak concentrations or the length of the exposure period to peak concentrations can be made.

Aerobic soil metabolism studies.

Data in this area was sought as again, no HVE data were available for the assessment, and the available data we had on aerobic soil metabolism showed conflicting evidence in this regard based on the data for longer chain esters and salt forms of 2,4-D as to persistence in aerobic soils. Any testing should characterize the persistence and breakdown of the short-chain esters in a range of soils, and be performed in a manner consistent with the use pattern, that is, surface applied to soils at a range of temperatures and without soil incorporation.

Dr Moore asks in his submission what the conflicting evidence is and whether it should be in fact for anaerobic soils. The initial assessment report quite clearly states what the problem is for aerobic soil metabolism:

> Two studies using 2,4-D (in acid form) in aerobic soils resulted in conflicting results. Both followed the same guidelines and microbial viability of the soil was established. In the first study the soil was a silty clay loam with pH 6.9, CEC 10.08 meq/100 g, 3.87% OM and a water holding capacity of 27.16% at 1/3 bar. Degradation was rapid with a half-life of 1.7 days ($r^2 = 0.98$). This compared with the second study where a silty clay loam was also used (pH 7.4, CEC 9.8 meq/100 g, 1.4% OM but no WHC provided). In this study the half-life was much longer at 66.2 calendar days ($r^2 = 0.83$). In both studies, the major degradates was CO_2 with significant amounts of bound residues being found at the end of the respective study periods. 2,4-DCP and 2,4-DCA were found at residues of 3.5% AR or less throughout the first study, but were not identified in the second.

Dr Moore then quotes the aerobic soil half-life of 6.2 days (available in the US EPA RED) and states “Crop effects after ester is much less than crop effect after preplanting amine spraying. That is, esters are less persistent (in biological activity) than amine formulations.” The US EPA bridging strategy for environmental fate data requirements are then quoted.

In response to this, DEW is familiar with the bridging strategy and had to rely on it ourseLVE (that is, using 2,4-D acid data as surrogate for salt forms given their rapid dissociation, and for the LVE due to their eventual hydrolysis to the acid form). However, again it is pointed out, HVE are not used in the USA, and no data were generated for them because the 2,4-D industry taskforce does not support their use. Consequently, the reliance on the bridging strategy to compare 2,4-D acid/DMA forms with HVE is questionable. It is simply not acceptable to state the esters are less persistent in biological activity than the amine formulations. That is one of the main issues we are trying to assess. They are less persistent in the application area because (as demonstrated adequately above), they leave the area through volatilisation at a rapid rate. However, this does not mean they lose their biological potency.

Conclusion relating to Tier II data requirement for Aerobic Soil Metabolism studies.

This data requirement has not been met by the data provided in Dr Moore's submission.

Tier III Data Requirements

The third tier of data related to environmental effects with three areas identified. The third area noted that no test data for effects of 2,4-D short-chain esters to non-target terrestrial vegetation are available, and test data in this area is required. Such data should include consideration of effects due to exposure through the gas phase as well as ground/deposition exposure. Some data in this area have been provided in Dr Moore's submission and are assessed here.

Plant effects with exposure through the vapour phase

Breeze and West (1987) conducted experiments using tomato plants exposed to 2,4-D butyl ester to investigate the relationship between vapour concentration and plant response in the short and longer term based on impacts on photosynthesis rate, leaf movement and the rate of dry matter production. An air flow system was designed with the following specifications: a filtered air stream to the experimental plants; a droplet-free herbicide vapour in an air stream; a means to provide a wide range of vapour concentrations; chambers to contain the experimental plants; and a method to measure the vapour concentrations in air. Plants were grown on mineral wool blocks and watered with nutrient solution. Plants up to about 30 cm tall could be placed in each chamber and the base of each chamber was sealed. An equilibration time of 24 hours was used and during this time clean air was circulated over the plants at around 100 L/min. To expose the plants to herbicide vapour, the airflow was switched through an evaporation column and dilutions set up with flow meters. The evaporation column was shut off following the exposure period. In the first experiment, four 8-week old tomato plants were sealed into each of five chambers. The test temperature was 20^{o}C. Dilutions were set to give nominal vapour concentrations in the plant chambers of 10, 30, 60 and 100% maximum vapour concentrations, along with a vapour free control. Flow rates were between 133 and 150 L/min. The dilutions were maintained for 5 h prior to shutting off the vapour airstream. Plants were then given herbicide free air at 150 L/min for a further 24 h after which the plants were returned to a glasshouse. During exposure, four sets of three samples of herbicide vapour, each set with a blank of air upstream from the evaporation column, were taken. Each sample was taken for at least 1 h, starting about 10 minutes from commencement of exposure. The end of the last sampling period coincided with the end of the exposure period.

In a second experiment, two plant chambers were modified to include a circulation fan with a free airflow rate of 800 L/min. Light intensities were increased to 200 W/m^2 photosynthetically active radiation by fitting reflectors to the mercury vapour lamps and a water bath was fitted to maintain air temperature control. Measurements were made on two occasions. On the first occasion, 6-week old plants were used with 4 plants/chamber and on the second, eight plants each 4 weeks old were used. Each used two chambers, a herbicide free control and a treatment to which herbicide vapour was added. During the second light period (presumably after the first 24 h acclimatisation), 1 h was allowed for steady rates of photosynthesis to be achieved, and about 2 h after this, the plants were exposed to herbicide vapour. On the first occasion an exposure period of 2 h was given and on the second, 1 h. In each case, the concentration of 2,4-D butyl ester vapour was around 50 ng/L. Leaf movement was measured by recording the positions of three of the youngest fully expanded leaves at frequent intervals throughout the light period in both control and treated chambers. At the end of the light period (~10 h), the rates of respiration of the darkened plants were measured.

Concentration of 2,4-D butyl ester in air as measured in the first experiment showed an initial absorption period (probably by the pipework of the sampling system), lasting until at least the end of the first hour of exposure. In the undiluted air stream, the concentration was nominally 50 ng/L with the other three exposure levels being measured as 31 (62%), 14 (28%) and 5 (10%) ng/L. No epinasty or stem bending was observed in the control plants. Symptoms of damage were first observed at the two highest concentrations after 90 minutes exposure and these were rated as moderate at 31 ng/L after 140 minutes and severe after 215 minutes, compared to a severe rating in the undiluted air stream after 155 minutes. Even at 5 ng/L, epinasty was rated as severe after 245 minutes exposure. After 185 minutes the stems of plats at the three highest concentrations had begun to bend with responses clearly related to herbicide concentration. Eighteen hours after plants were returned to clean air, the symptoms were still apparent. Stem bending and epinasty of leaves and petioles showed some recovery during the next 4 days in the glasshouse, but on the fifth day, white swollen areas had developed on the stem. By the tenth day, these areas ranged in size from small regions on the plants from the lowest test concentration to almost complete cover in plants from the highest concentration. These areas of swelling had begun to split longitudinally and around the circumference of the stem in the two highest concentrations. After 47 days following cessation of exposure, when the control plants and those of the lowest treatment had begun to flower and set fruit, the plants were harvested. Both dry weight (p <0.1%) and dry matter content (p <1.0%) were affected by the herbicide treatments. Mean individual plant dry weight in the control was 35 g compared to 28.8, 19.1, 18.1 and 12.0 g in the 5, 14, 31 and 50 ng/L treatments respectively. Considering Log(concentration) to % dry weight decrease, a rough EC25 and EC50 from this experiment of 6.7 ng/L and 23.1 ng/L respectively are derived.

In the second experiment, short periods of exposure of 2 h and 1 h produced decreases in the rate of photosynthesis of about 40% of the initial value within about 3 h of the start of treatment. After this, the rate of photosynthesis began to reach a steady value. During the first 3 h of the next light period, photosynthesis rates increased slightly in control plants while rates in the treated plants declined. Respiration measurements during the dark period following exposure showed only small differences between the controls and treated plants.

Overall, these experiments showed that less than 2.5 h exposure to concentrations of around 5 ng/L 2,4-D butyl ester was required to produce epinasty in tomatoes and twice this period of exposure produces severe symptoms that eventually reduce the dry weight of the plant.

This level is calculated by the authors to represent around 2.5% of the saturated vapour pressure.

Mullison and Hummer (1949) describe an investigation carried out to determine if 2,4-D derivatives were volatile enough to have an effect on dry seeds with respect to viability, rate of germination and seedling characteristics. While seed exposure in this study is longer than would be expected in real world exposure, some interesting results were found. The study consisted of several separate experiments. In brief, 50 or 100 seeds of vegetables or crop species were exposed in a sealed container with the test chemical placed in a petri dish at the bottom of the jar. Small cheesecloth bags containing the seeds were suspended so as to avoid contact with the sides of the jar. Temperature was maintained at around 27^{o}C. Exposure periods were 30, 60 or 180 days. Following this, the seeds were germinated in flats filled with clean, moist sand and seedling counts were made.

Experiment 1 – 30 day exposure data are shown as follows:

Table 3: 10 day % germination of control seeds; % germination inhibition relative to control of test species (following vapour exposure for 30 days).

Species tested	Control (% germ)	Derivative of 2,4-D tested Na salt	Alkanol-amine	methyl ester	ethyl ester	isopropyl ester	n-butyl ester	n-amyl ester
Tomato	86	10.5	1.2	**26.7**	14.0	9.3	19.8	3.5
Bean	98	-2.0	4.1	12.2	6.1	2.0	0.0	0.0
Corn	96	-4.2	-2.1	0.0	-2.1	4.2	2.1	-4.2
Cucumber	64	-12.5	-9.4	**78.1**	**75.0**	**37.5**	**40.6**	-6.3
Rye	44	9.1	-2.3	**68.2**	**77.3**	**68.2**	**40.9**	**31.8**
Wheat	70	2.9	4.3	-1.4	-7.1	4.3	1.4	7.1
Turnip	80	-7.5	-10.0	**85.0**	**97.5**	**62.5**	**72.5**	**45.0**
Cotton	37	0.0	-8.1	10.8	**45.9**	24.3	**32.4**	16.2
Pea	96	0.0	2.1	**66.7**	**85.4**	**58.3**	6.3	-2.1

Germination was generally uninhibited compared to control plants for the non-volatile sodium and alkanolamine salt derivatives with no inhibition of more than 10% (except 10.5% for tomato with the sodium salt). By comparison, the ester derivatives were significantly more toxic with large negative affects on germination for many of the test species. Bold values in the above table show inhibition of germination >25% of control levels. Rye seemed particularly susceptible to the esters, and the methyl and ethyl ester seemed more potent with 5 species each showing >25% germination inhibition.

To extend the scope of the first experiment, seeds of some other common vegetable and field crops were exposed for 30 days to the isopropyl ester of 2,4-D. Species tested and 10 day germination % values for control plants were lima bean (68%), soy bean (76%), spinach (23%), watermelon (92%), sugar beet (73%), peanut (36%), onion (70%) and eggplant (53%). Germination was counted at 15 days for the last three species due to their slower general germination. The inhibition (% of control values) from 2,4-D isopropyl ester was 35, 13, 100, 24, 73, 50, 61 and 60% respectively again showing the potential toxicity of vapours of this ester to non-target plants.

From experiment 1, marked depression of germination was noticed with cucumbers, rye, turnips and peas. The third experiment considered the effect of longer exposure (60 days). The following results were found:

Table 4: 10 day % germination of control seeds; % germination inhibition relative to control of test species (following vapour exposure for 60 days).

Species tested	Control (% germ)	Derivative of 2,4-D tested Na salt	Alkanol-amine	methyl ester	ethyl ester	isopropyl ester	n-butyl ester	n-amyl ester
Tomato	65	-26.2	-15.4	**100.0**	**90.8**	**75.4**	24.6	12.3
Bean	86	-14.0	-2.3	**32.6**	**27.9**	4.7	-9.3	-2.3
Corn	94	-6.4	0.0	6.4	6.4	6.4	14.9	16.0
Cucumber	90	-4.4	-8.9	**100.0**	**86.7**	**26.7**	6.7	0.0
Rye	40	22.5	20.0	**100.0**	**100.0**	**95.0**	**72.5**	**40.0**
Wheat	92	17.4	-4.3	**76.1**	**55.4**	21.7	19.6	6.5
Turnip	81	17.3	-2.5	**100.0**	**100.0**	**100.0**	**98.8**	**92.6**
Cotton	26	-15.4	11.5	**96.2**	**96.2**	**80.8**	0.0	0.0
Pea	98	2.0	4.1	**98.0**	**98.0**	**91.8**	**46.9**	20.4
Squash	68	-44.1	-29.4	**100.0**	**100.0**	**97.1**	**91.2**	20.6
Radish	79	11.4	19.0	**100.0**	**100.0**	**100.0**	**93.7**	**36.7**
Muskmelon	50	8.0	-24.0	**100.0**	**100.0**	**100.0**	**76.0**	-

Again, the non-volatile forms of 2,4-D did not really suppress germination. However, the increased exposure resulted in more severe effects to most crop species for the ester derivatives. In many species for the methyl, ethyl and isopropyl esters, complete inhibition of germination was observed.

Also as part of experiment 3, cucumber seeds were exposed for 180 days, this time to 2,4-D acid, three salt forms (triethanolamine, alkanolamine and sodium salt) and the methyl ester. 100% germination was observed after 10 days for control seeds. For the seeds exposed to all the salt derivatives, germination was >90%. However, no germination was found for seeds exposed to the methyl ester.

The fourth experiment was undertaken to determine whether the volatile esters were entering the seed or adhering to the seed coat surface. Cucumber seeds were exposed to the methyl ester for 180 days. They were then divided into two groups of 50, one of which was put on moist filter paper overnight and the other not. Each of these groups was then subdivided into two more, one of which had the seed coats removed and the other not. Thus, four treatments of 25 seeds each were planted. For those seeds not soaked, peeled control seeds resulted in 72% germination and those not peeled had 80% germination. By comparison, 40% of the exposed peeled seeds germinated compared to no germination for the un-peeled seeds. Similar results were found in those seeds soaked overnight with 92% control germination in both peeled and unpeeled seeds. Germination in the exposed peeled seeds was 32% compared to no germination in the exposed un-peeled seeds. These results indicate that the vapours from the volatile esters do not penetrate the dry seed coats appreciably in a 180 day period.

The authors also considered in their discussion the effect on rates of germination for peas exposed 30 and 60 days (noting from the above information that after 30 days exposure, the germination after 10 days for the amyl and butyl ester were not too different to the control as compared to the other esters). They report, however, a 36-48 h inhibition of germination. The data for the more volatile, lower alkyl esters (methyl, ethyl and isopropyl) showed both an inhibition period (2-4 days after control germination for the 30 day exposure seeds) and a depressed final count. This pattern was repeated in the seeds exposed for 60 days with an inhibition period of 1-2 days after control germination before germination of seeds exposed to the amyl and butyl esters. However, this time, the final count was also depressed. Seeds exposed to the other three esters did not start germinating until 3 days after control seeds, and final numbers were very low compared to control germination.

These results demonstrate that effects other than a visual observation of stress in growing plants can occur following exposure to vapour from the 2,4-D esters to their seeds.

Weigle *et al* (1970) describe a study considering effects of atmospheric 2,4-D on market quality of several horticultural crops. Plastic covered greenhouses were erected over field soil. The greenhouses were 32 x 22 x 9.5 ft. Each was equipped with a 2 input type, wet pad and fan units to modify air temperature. The input type of fans created a slight positive pressure in the houses so air would be forced out through the door when opened and through any openings that may occur in the plastic. The air entering 4 of the greenhouses was filtered through activated charcoal to remove any ambient 2,4-D. The 2 houses without the filters were the “ambient” treatment. In the 2,4-D “added” houses, a measured amount of 2,4-D solution was atomized into the airstream in front of the air inlet during a 6 h period each week for a total of 10 applications in each of the first 2 years. In the 3rd year, only four applications were made. The amount of 2,4-D added was sufficient to maintain a concentration of 1 ppb by weight in the air inside the greenhouse during the treatment period. The remaining two greenhouses were the “clean” treatment. Half of each greenhouse was planted with small fruits (strawberries, raspberries and grapes) and the other half planted with tomatoes and green beans.

No differences in market quality were found with green beans and raspberries. Deformed fruit in strawberries, uneven berry ripening in grapes and blotchy ripening and deformed fruit in tomatoes occurred in the “added” treatment but not in the “clean” treatment while the “ambient” treatment was generally intermediate. The amount of 2,4-D in the atmosphere also influenced yields of grapes and strawberries. The greatest yield reduction was found in grapes. The “added” treatment yielded <50% and the “ambient” <75% of the “clean”.

Lanphear and Soule (1970) describe results from a field survey undertaken to survey injury to city plants within the city of St. Louis. Injury typical of 2,4-D and 2,4,5-T was observed in a large area of St. Louis in the spring of 1969. An exploratory survey of plants for pollution damage revealed the widespread prevalence of this injury was not caused by uncontrolled local spraying. Rather, the presence of industrial firms engaged in the production of these herbicides appeared to be the source of exposure. An extensive survey of damage in the affected area was first made with a series of N-S transects along city streets, spaced about 2 blocks apart until no further injury was observed. This demonstrated a very definite pattern of injury and species were differentially sensitive to the herbicide in the injury area. On the outer edges, only *Ailanthus* and *Ulmus* exhibited injury symptoms. Closer to the pollutant origin other plants (eg *Forsythia* and *Gingko*) were exhibiting symptoms. In the centre, plants such as *Acer saccarum, Syringa* and others described as tolerant were not affected. The injury was characteristic of that caused by phenoxyacetic acids. In some cases the only symptom was curling of leaf margins, but in more severe cases there were stem epinasty, leaf defoliation, and ultimately necrosis of meristematic tissue. At least two industrial plants in the immediate area were noted to produce or handle phenoxyacetic acids for herbicides. Additional field surveys revealed no further damage to plants in the initial survey area, but did indicate injury on *Cercis Canadensis* (redbud) extending at least 5 miles (8 km) further west of the original pattern. The absence of redbud trees in the original survey area may be coincidental or indicative of damage in previous years that prevented them growing in this area. This is a noteworthy observation and goes to one of the main environmental concerns with the 2,4-D HVE assessment, that just because a native stand of trees may appear healthy, this may be because of the removal of more sensitive species due to a competitive advantage, particularly when exposure may occur over many years.

Following this survey, chemical screening experiments were undertaken. Initially, 14 chemicals were tested on *Forsythia intermediai*. These included 2,4-D sodium salt, 2,4-D acid, 2,4-D isobutyl and 2,4-D isooctyl. The chemicals were prepared at 1000, 100, 10 and 1 ppm. Each solution was prepared and placed in an individual bottle with an atomizer attached. The solutions were sprayed on branches exhibiting new growth and these were observed for possible injury after 3 to 15 days. After the results from the screening were obtained, chemicals displaying the herbicide injury symptoms were applied to *Ailanthus altissima* (tree-of-heaven) and redbud, both extremely sensitive in the field survey. The highest concentration was eliminated in this screening and 0.1 and 0.01 ppm were added to those chemicals displaying injury at 1 ppm on forsythia. An additional test was conducted to determine if the volatile esters of 2,4-D would cause injury. A 4” filter paper disk was saturated with 2,4-D isobutyl ester and air was blown lightly across the filter paper into a chamber containing tomato, redbud and tree-of-heaven. Plants were generally exposed to 4-6 h in low light.

In the initial screen, all 2,4-D derivatives above produced symptoms similar to those observed in the field survey. The concentration required for injury to occur varied between 10 and 1 ppm or less with the isobutyl ester of 2,4-D appearing the most active. In the second study, concentrations lower than 1 ppm were not injurious. The final treatment of the isobutyl ester of 2,4-D in the vapour form induced severe epinasty in tomato and the typical leaf curling in redbud and tree-of-heaven. In fact, some sensitive plants growing in the greenhouse above the room where the vapour treatments were conducted showed similar symptoms indicating the potency of this material.

While quantitative results from this paper are difficult to determine given no analytical measurements of 2,4-D in the air were undertaken, the results again show the potency of vapour exposure of 2,4-D, this time to grown trees a long way from the point source. Further, in this case, the point source was limited to industrial buildings, not from broadcast application to agricultural land.

Sherwood *et al* (1970) addressed movement of vapour from 2,4-D isopropyl ester using a diffusion test method. Experiments were begun in 1960 to determine working parameters of volatility, concentrations and diffusion into ambient air as related to gross effects upon sensitive horticultural plants. In 1962, the first diffusion test circle for 2,4-D exposures was established at the Iowa Agricultural Experiment Station Horticultural Farm for testing seasonal responses of representative horticultural plants in regimes of planting and care considered typical for outdoor plants. The first test circle (1962 – 1967) consisted of 17 concentric circular rows each subdivided into 12 arcs and spaced 8 ft (2.4 m) further from the common centre. The first row was 20 ft (6.1 m) from the centre. The first representative horticultural cultivars randomised in each arc were grape, zinnia, geranium, tomato, rose and redbud. As increasing arc length and succeeding years of trials permitted, additional crops of apple, cherry, black raspberry, onion, potato, bean, muskmelon, viburnum, pin oak, elm, black walnut and mimosa were included. The circle in 1968 differed in having a 12 ft (3.7 m) row spacing with discontinuous arcs of equal size throughout. It is not entirely clear from the paper whether the discussion on test methodology applies to every year, or just the 1968 trial. As reported, 10 seasonal exposures to 2,4-D were begun in early June. For each treatment, 8 g ae (as the isopropyl ester) was applied to two 4 ft lengths of doublefold cheesecloth 8” wide (each cheesecloth being 0.25 m^2). These were suspended from a wire stretched horizontally 2 ft above the ground with an open sided sheetmetal cover shielding from sun and rain without preventing evaporation into ambient air. When replaced (in 1 week) the old cloths still smelled of 2,4-D but tests indicated <1% active remained. Estimates, based on the wind velocity for an average week, suggested that the average concentration of 2,4-D at the centre (rows 7 and 8) were in the ppb range.

The results as reported are not that easy to interpret. The findings are summarised as follows:

- Symptoms varied, but were about equal in severity throughout the 360° coverage. Susceptible plants in the rows close to the source were markedly stunted and deformed while those in intermediate rows tended to show apparent stimulation.
- The first noticeable symptoms were increased stiffness of leaves and soft shoots of plants closest to the source (20 ft, ~6 m). These were apparent within a few hours and were readily discernable 2 weeks after exposures began.
- Because growth tended to be excessively delayed, stunted and aborted at the high exposure, plants further from the source often appeared to be more responsive (that is, they suffered less) to sustained exposures. Fewer and smaller flowers were produced on the inner plants.
- In the outer circles, vegetables were larger, less misshapen and earlier ripening. More fruit was produced and the sugar content was higher. The variability between fruits on the same and adjacent plants was accentuated by proximity to the 2,4-D source.
- Peppers tended to produce shorter and thicker fruits, which were unusually waxy in appearance, but the seed content did not seem greatly reduced. Conversely, tomato fruits at higher exposures did tend to be hollow with few seeds; and unusually high proportion exhibited uneven ripening and began to break down and decay prior to full ripening.
- Throughout the test area, bush beans tended to produce curled, slowly developing pods, while the base of the leaves was abnormally large, glossy and even tumour-like in appearance at the higher exposures. Cabbage was markedly stunted at high exposures and such plants usually died before forming heads. At slightly less exposure, outer leaves reflexed abnormally and the raised petiol typically split lengthwise.
- Woody plants appeared unusually waxy and with more obvious lenticils (raised pores on the stems of woody plants that allow the interchange of gas between the atmosphere and the interior tissue) with proximity to the 2,4-D source. During the growing season, both boxelder and redbud frequently lost the growing apex.
- In winter, the plants exposed to the most 2,4-D tended to die back further and subsequent lateral shoots did not as readily yield to the most dominant. Fewer redbud and grape plants survived.
- Plants grown from seed collected from slightly to markedly affected plants showed no correlation with proximity of the seed crop or soil to the 2,4-D source.
- Well-started plants placed in the various exposure rows for 24 h and then returned to the greenhouse gave unexpected information. It was noted that despite symptoms being greater on plants exposed more closely to the source the degree of symptom

expression was not related to the renewal of the 2,4-D source indicating that sufficient potency continued to relate to the cheesecloth.

For some aspects of growth such as plant height, most horticultural plants tended to increase to a maximum with intermediate proximity to the 2,4-D source. This maximum usually was most evident near rows 6-9. In the region of rows 2-3, pronounced stunting of these kinds of plants occurred. These same kinds of plants typically exhibited fewer normal leaves, flowers and fruits from the further to the nearest rows and appeared less well developed or able to withstand stress.

The results of this study again demonstrate movement of a very small load of 2,4-D HVE to a comparatively wide area.

Baskin and Walker (1953) describe a biological method for the determination of extent of volatility of esters of 2,4-D. Rutgers tomato plants grown to 4 or 5 leaf stage in dispensable containers were exposed to vapours of 2,4-D ester formulations in a forced air system to determine the extent of their volatility. Epinasty and more advanced formative responses of the test plants were the measures by which volatility was evaluated. Exposure intervals of 2, 4 and 16 h at room temperatures were used. First observations were made at 0, 24, 48 and 72 h after cessation of exposure. This work was performed to readdress the conception of volatility, away from the physico-chemical sense of the word to being more based on biological effects. The evaluation in terms of plant response (stem bending, epinasty, formative response) was separated into 6 categories with 1 being for no response and 6 being epinasty of 81^o or more and including severe formative effects such as twisting of the main stem and distortion of petioles and leaflets. Responses falling in class 1-2 were considered low volatile and 3-6 being high volatile. Based on this, results showed the low volatile preparations were the sodium salt, the isooctyl, butoxyethanol, butoxyethyl, polypropylene glycol and the tetrahydrofurfuryl ester of 2,4-D. High volatile 2,4-D esters were the methyl, ethyl, propyl, butyl, amyl and pentyl series.

Dr Moore has provided details of pilot trials he undertook in August 2007 considering the effect of 2,4-D and its drift on canola. The experiments are described as follows:

In the first experiment, a logarithmic sprayer was used to spray the 3 formulations at rates from 1000 g ae to 0.00625 g ae/ha over an 80 m long by 5 m wide plot. Herbicides were applied in 283 L/ha water using 110-03 nozzles at 200 kPa with a NW wind at 3.5-8.2 km/hour temperature of 15.8 degrees C and relative humidity of 60% on 3 August 2007. The conditions and equipment are stated as chosen to minimise drift and maximise damage due to vapour movement. The canola was at the 8 leaf stage and approximately 300 mm wide. Plants were rated for visual symptoms on 8 August 2007 and photographed.

The visual rating of damage 5 days after spraying was described. There was severe epinasty of canola at the 1000 g ae/ha rate, which decreased to almost no symptoms at the 50 g ae/ha rate. No visual symptoms were observed on canola sprayed with less than 25 g ae/ha of any formulation.

There was little difference between the dose response of the three formulations, however, at the high rates ethylhexyl ester appeared to have more bare ground showing (due to leaf curl) than the butyl ester or amine formulations.

Symptoms on canola outside the sprayed area were not seen more than 1 m from the leeward edge of spraying.

In the second experiment, a 40 by 40 metre area of canola was sprayed with 2,4-D butyl ester at 1000 g ae/ha in 150 L/ha water using 110-03 nozzles with a north west wind at 4.5-7.3 km/h, temperature of 15.5 degrees C and relative humidity of 62% on 3 August 2007. The wind speed fell to less than 5 km/h in the 2 hours after spraying. The canola was at the 8 leaf stage and approximately 300 mm wide. Plants were rated for visual symptoms on 8 August 2007 and photographed.

Visual rating of damage 5 days after spraying from this experiment are described. Canola showed severe epinasty within the sprayed area. No symptoms were seen on canola 10 m from the sprayed area. One plant had hormone like symptoms 1 m from the sprayed area on the S side. On the east and west side of the sprayed area plants within 2 m of the sprayed area had symptoms, which could be attributed the turn on, and turn off and dripping of the sprayer and the area. No plants showed symptoms more than 1 m from the N side of the sprayed area.

Unfortunately, such testing and results are not particularly helpful for addressing the concerns about HVE. Observations were visual only and made 5 days after spraying. This is probably a bit too early for appreciable results to be determined, and we remain concerned about impacts other than those found from simply observing the plants, such as decreases in plant heights and weights, losses of reproductive capacity and so on (see studies described in Section 3 above).

Further, canola may not represent species at the sensitive end of the 2,4-D toxicity range. An example of the sort of testing that could be appropriate (although this study did not consider gas phase exposure) is described by Fletcher *et al*, 1996. While the focus of this study was really chlorsulfuron, 2,4-D as the isooctyl ester was tested, and endpoints such as growth and yield of a number of non-target plants were considered. It is worth reporting the second part of this investigation, which examined the effects of four herbicides (chlorsulfuron, 2,4-D [isooctyl ester of 2,4-dichlorophenoxyacetic acid], atrazine [2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine], and glyphosate [isopropylamine salt of *N*-(phosphono-methyl) glycine]) on the growth and reproduction of canola, smartweed, soybean, and sunflower. Each herbicide was applied at a rate of $8x10^{-3}$, the recommended field rate for smartweed, soybean, and sunflower, and a rate of $4x10^{-3}$, the recommended field rate for canola, or 8.8 and 4.4 g ae/ha respectively for 2,4-D. Between administration of the different herbicides extreme care was taken to ensure that no cross-contamination occurred.

Briefly, the growing conditions were as follows. Canola and soybean were germinated and grown in 15.5-cm-diameter pots. Smartweed plants were germinated and grown in 10-cm-diameter pots. Sunflowers were grown in two different potting arrangements: for chlorsulfuron testing they were in 10-cm diameter pots and in 15.5-cm pots for other herbicides. All pots were sub-irrigated with water in a greenhouse until germination and shoot emergence (8 to 18 d). The experiment was conducted on 120 uniform plants in individual pots selected from a pool of 130 initial plants. Individual plants were randomly assigned positions on greenhouse benches. Each treatment was replicated with 10 plants per species, and the treatment assignments were random. Plants were irrigated to excess four times daily. Greenhouse temperatures ranged from 15 to 38°C during the day and from 11 to 21°C at night. A shading compound was present on the greenhouse glass during the first months of the study. The compound was removed when appropriate to compensate for the loss of natural light in the winter months. Throughout the study, sunflower plants were grown with supplementary artificial light for 16 h each day. The remaining species were grown under natural lighting until such time that insufficient day length meant artificial lighting was provided for 16 h each day.

The chemical applications were administered with a Mandel RC-5000-100EP track sprayer fitted with a Teejet 8002EVs flat fan-tip nozzle. A single pass at 3 km/h was used to deliver 262 L/ha. Delivery rate was verified gravimetrically prior to chemical applications. The spray nozzle was positioned 16 cm from the surface of the highest fully expanded leaf. All chemical and control applications included 0.05% Unifilm 707 surfactant to reflect the end-use product.

During the course of the individual experiments, plant growth and development were examined by counting and/or observing nodes, buds, flowers, and the number and colour of leaves. Individual experiments were concluded when the fruits on the control plants were mature. At the conclusion of each experiment, plants were harvested and appropriate measurements (described below) were made depending on the growth form of the species tested. Measurements included plant height, the number of pods and seeds, and the dry weight of seeds for canola; on smartweed, shoot and seed dry weight; on soybean, plant height, number of pods and seeds, and seed fresh and dry weights; and on sunflower, plant height, flowerhead diameter, number of seeds, and seed dry weight. Analyses of variance (ANOVAs) were conducted using the SAS Institute GLM procedure and Dunnett’s multiple range test to determine which chemical treatments caused effects that were significantly lower than those of the controls ($\alpha = 0.05$).

This study was primarily concerned with chlorosulfuron so actual numerical results for the other herbicides considered are not provided in the literature paper. However, it is reported that 2,4-D had no influence on canola, smartweed, or soybean but did reduce the yield (seed dry weight) to 4% and the growth (stem height) to 42% of the controls when applied to sunflower. What this helps to illustrate is that at the low rates tested in this experiment, canola was not as sensitive as sunflower, and it may require measurements other than visual observations of plants growing during their vegetative growth phase (such as the pilot trials on canola described above) to characterize impacts. In this study, application was to the reproductive phase of the plants at rates much lower than field application rates and resulted in a 96% yield reduction to sunflower.

Conclusion with respect to Tier III data requirement – Environmental Effects

While not completely addressing the information sought from the Tier III data requirements, the available information does go some way to addressing part of the requirements, namely, consideration of effects due to exposure through the gas phase.

While many of the studies are older in nature, they do show that standard vegetative vigour and seedling emergence studies spraying plants/soil may not encompass some of the likely effects of 2,4-D exposure, and exposure through the gas phase can lead to long lasting effects even at low concentration. Adverse effects have been described for non-traditional end-points such as yield and non-standard test species. It reinforces the need for higher tier testing in this area, for example, considering exposure to the reproductive phase of a plant’s life cycle; measuring growth and reproduction of second generation plants following exposure of parent plants; and considering germination and further growth/reproduction of plants following seed and growing/fruiting plants exposure to 2,4-D HVE vapour to a wide range of plants. Currently, we are unable to alter our conclusions from the original risk assessment.

References:

Baskin D and Walker E, 1953. A biological Method for the Determination of Extent of Volatility of Esters of 2,4-D and/or 2,4,5-T. Proc. 7th North Eastern Weed Control Conference. pp 47-50.

Breeze V and West C, 1987. Long- and Short-Term Effects of Vapour of the Herbicide 2,4-D Butyl on the Growth of Tomato Plants. *Weed Research* Vol 27, pp 13-21.

Day B, Johnson E and Dewlen J, 1959. Volatility of Herbicides under Field Conditions. *Hilgardia* Vol 28(11), pp 255-267.

Decker F and Hennessey J, 1977. Comments on “Long Distance Transport of 2,4-D”. *Journal of Applied Meteorology*. Vol 16, pp1003-1009. (Reviewed, but not used in this assessment)

Farwell S, Robinson E, Powell W and Adams D, 1976. Survey of Airborne 2,4-D in South-Central Washington. *Journal of the Air Pollution Control Association*. Vol 26 (3), pp 224-230.

Gilbey D, Ralph C, Scott A, Ebell G and Horne R, 1984. Airborne 2,4-D and Tomato Damage at Geraldton, Western Australia. *Australian Weeds* Vol 3(2), pp 57-69.

Gile J, 1983. Relative Airborne Losses of Commercial 2,4-D Formulations from a Simulated Wheat Field. *Archives of Environmental Contamination and Toxicology*. Vol 12, pp 465-469.

Grover R, Maybank J and Yoshida K, 1972. Droplet and Vapor Drift from Butyl Ester and Dimethylamine Salt of 2,4-D. *Weed Science*, Vol 20(4), pp 320-324.

Lanphear F and Soule O, 1970. Injury to City Plants from Industrial Emissions of Herbicides. *HortScience*, Vol 5(4), pp 215-217.

Leonard O, 1961. Volatility Studies with 2,4-D. Proceedings 13th Annual California Weed Conference, pp 93-99. (Abstract only received – partially assessed in this response).

Mullison W and Hummer R, 1949. Some Effects of the Vapour of 2,4-Dichlorophenoxyacetic Acid Derivatives on Various Field Crop and Vegetable Seeds. *Botanical Gazette*, September 1949, pp 77-85.

Que Hee *et al*, 1975. ES&T. GLC Analysis of 2,4-D Concentrations in Air Samples from Central Saskatchewan in 1972. Still to receive full paper – Partially assessed in this response.

Que Hee S and Sutherland R, 1979. Vapour and Liquid Phase Photolysis of the n-Butyl Ester of 2,4-Dichlorophenoxyacetic Acid. *Archives of Environmental Contamination and Toxicology*, Vol 8, p 247-254.

Reisinger L and Robinson E, 1976. Long-Distance Transport of 2,4-D. *Journal of Applied Meteorology*. Vol 15, pp 836-845. (Reviewed but not used in this assessment).

Sciumbato A, Chandler J, Senseman S, Bovey R and Smith K, 2004. Determining Exposure to Auxin-Like Herbicides. II. Practical Application to Quantify Volatility. *Weed Technology*, Vol 18, pp 1135-1142.

Sherwood C, Weigle J and Denisen E, 1970. 2,4-D as an Air Pollutant: Effects on Growth of Representative Horticultural Plants. *HortScience* Vol 5(4) pp211-213.

van der Linden A, Deneer J, Luttik R and Smidt R, 2004. Dutch Environmental Indicator for Plant Protection Products. Description of Input Data and Calculation Methods. RIVM Report 716601009/2004. RIVM, Bilthoven, The Netherlands.

Vernetti and Freed, 1962: 2,4-D Volatility studies. (still to receive full paper – Not assessed in this response)

Weigle J, Denisen E and Sherwood C, 1970. 2,4-D as an Air Pollutant: Effects on Market Quality of Several Horticultural Crops. *HortScience*, Vol 5(4), pp 213-214.

Other literature cited:

Bamesberger W and Adams D, 1965. Collection Technique for Aerosol and Gaseous Herbicides. *Journal of Agriculture and Food Chemistry*. Vol 13.

Fletcher J, Pfleeger T, Ratsch H and Hayes R, 1996. Potential Impact of Low Levels of Chlorsulfuron and Other Herbicides on Growth and Yield of Nontarget Plants. *Environmental Toxicology and Chemistry*, Vol 15 (7), pp 1189-1196

Grover R and Kerr L, 1981. Evaluation of Polyurethane Foam as a Trapping Medium for Herbicide Vapour in Air Monitoring and Worker Inhalation Studies. *Journal of Environmental Science and Halth* B16 (1) pp 59-66.

Grover R, Shewchuk S, Cessna A, Smith A and Hunter J, 1985. Fate of 2,4-D *Iso*-octyl Ester after Application to a Wheat Field. *Journal of Environmental Quality* Vol 14 (2) pp 203-210.

Kunda S, Pal A and Dikshit A, 2005. UV Induced Degradation of Herbicide 2,4-D: Kinetics, Mechanism and Effect of Various Conditions on the Degradation. *Separation and Purification Technology* Vol 44, (2), 15 July 2005, Pages 121-129.

Maybank J, Yoshida K and Grover R, 1978. Spray Drift from Agricultural Pesticide Applications. *Journal of the Air Pollution Control Association*, Vol 28 (10) pp 1009-1014.

OECD, 1993. Environment Monograph No. 61. The Rate of Photochemical Transformation of Gaseous Organic Compounds in Air Under Tropospheric Conditions. OCDE/GD(92)172. Paris, 1993.

Robinson E and Fox L (1978). 2,4-D Herbicides in Central Washington. *Journal of the Air Pollution Control Association*, Vol 28 (10) pp 1015-1020.

Taylor A, 1978. Post application Volatilisation of Pesticides Under Field Conditions. *Journal of the Air Pollution Control Association*, Vol 28 (9) pp 922-927.

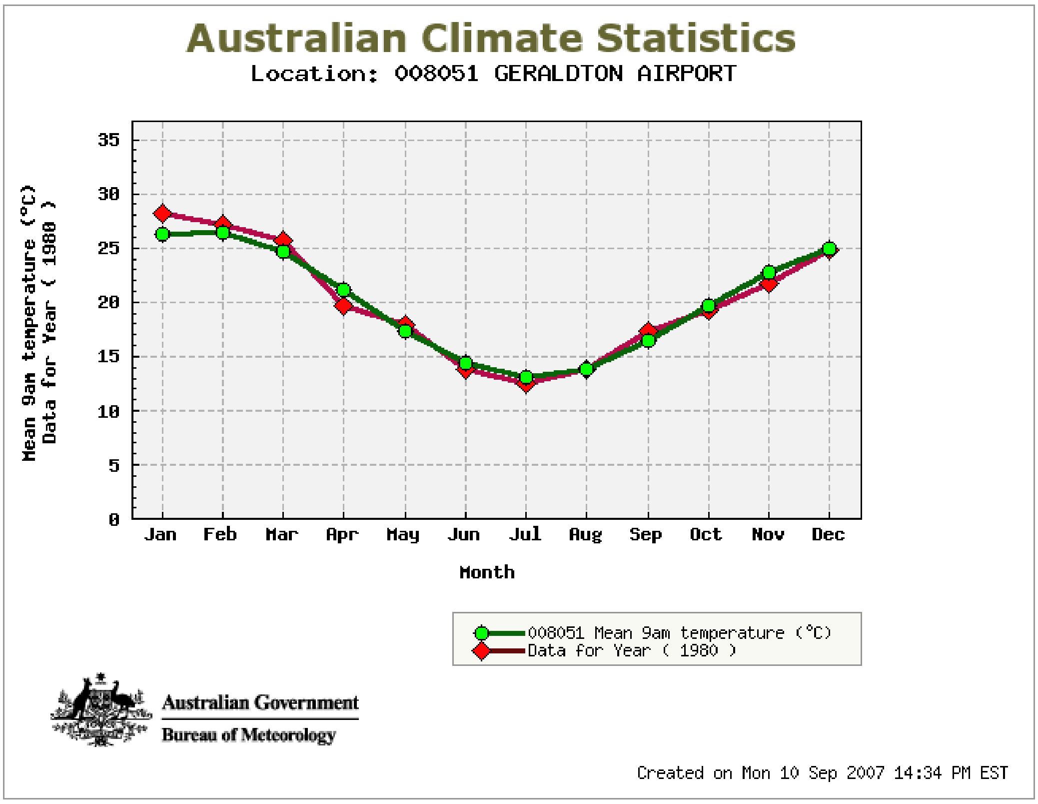
The Bureau of Meteorology offers the following synopsis of Geraldton's winter temperature and wind patterns:[1]

Winters are mild with the July average maximum temperature being the lowest of any month at just under 20°C. August minima are the lowest on average at just over 10°C near the coast and decreasing to about 9°C at the airport. Due to the position of the sub-tropical ridge during winter, winds with an onshore component are common and along with increased cloudiness help to moderate temperatures.

The wind climatology at Geraldton is strongly dominated by the effects of the land-sea interface where offshore land breezes are common in the morning, whilst afternoon sea breezes are common in the warmer months. Winter tends to be the period of most variability in winds due to the latitude and mobility of the sub-tropical ridge, and a weak land-sea temperature contrast. It also tends to be the season with the lightest winds, however cold fronts can occasionally bring strong winds and gales to the area. During the remainder of the year, the sub-tropical ridge is generally south of Geraldton and thus winds with an easterly component prevail overnight and in the morning, however afternoon sea breezes are regularly experienced, most commonly from the south to southwest sector.

In the Gilbey study, the 1980 portion of the study saw the samplers run for 21 weeks starting June 10. Data were reported until the end of week 15 (or within the second half of August). The following climate data have been obtained from the Bureau of Meteorology (http://www.bom.gov.au/climate/averages/tables/cw_008051.shtml).

Mean 9 am Temperature (and 1980 mean 9 am temperature):

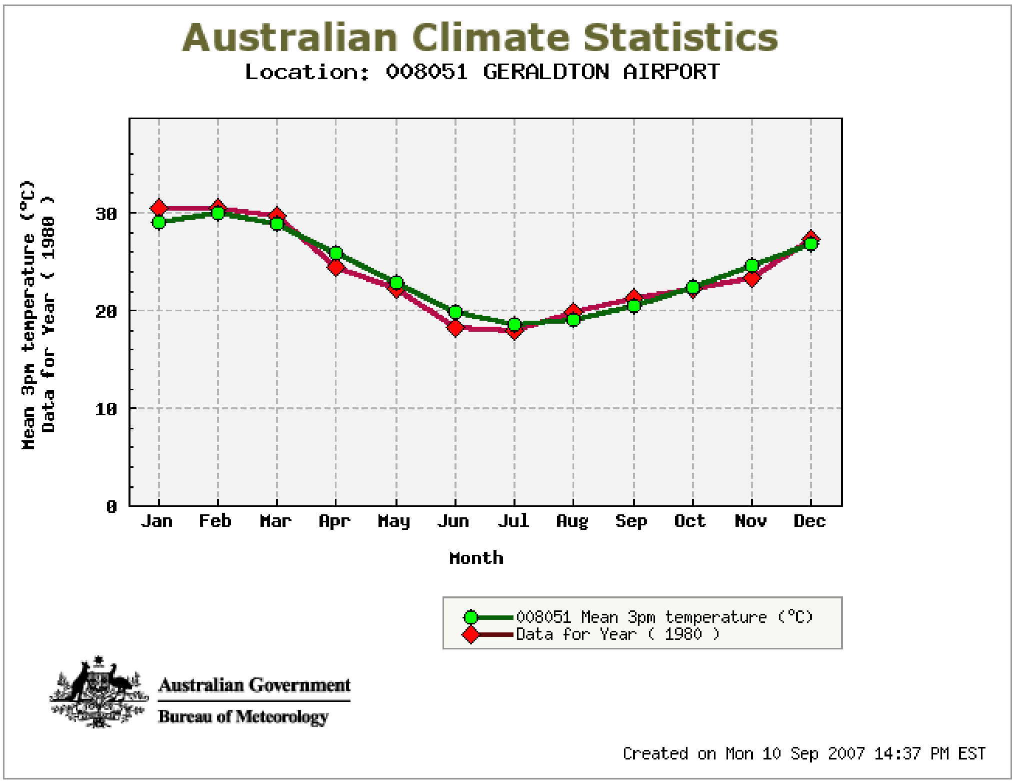


---

[1] http://www.bom.gov.au/weather/wa/geraldton/climate.shtml

In June, July and August, the mean 9 am temperatures were 13.8, 12.5 and 13.8°C respectively, and very similar to the long term averages shown in the above graph.

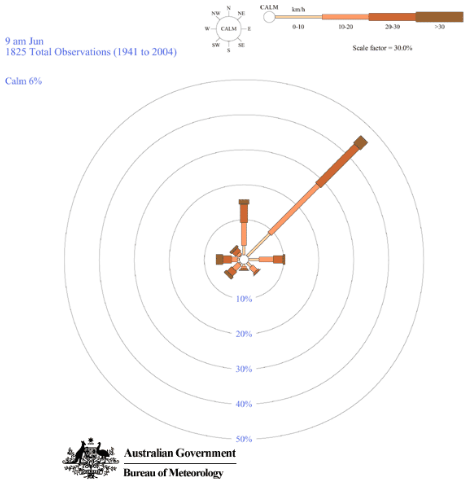
Mean 3 pm Temperature (and 1980 mean 3 pm temperature)



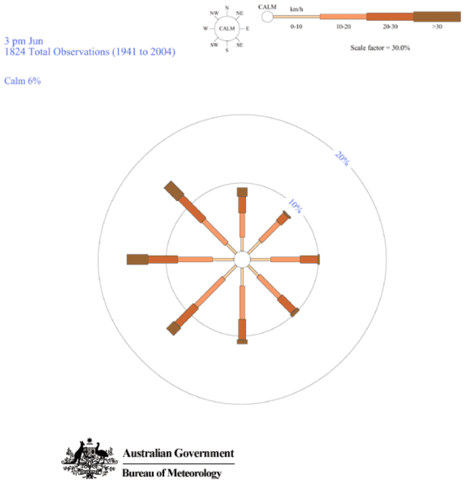
In June, July and August, the mean 3 pm temperatures were 18.3, 17.9 and 19.9°C respectively, and very similar to the long term averages shown in the above graph.

Mean wind direction data for 1980 are not available. However, long term mean wind directions and speeds (1941 to 2004) are available and the wind roses for 9 am and 3 pm at Geraldton airport for June, July and August are shown below.

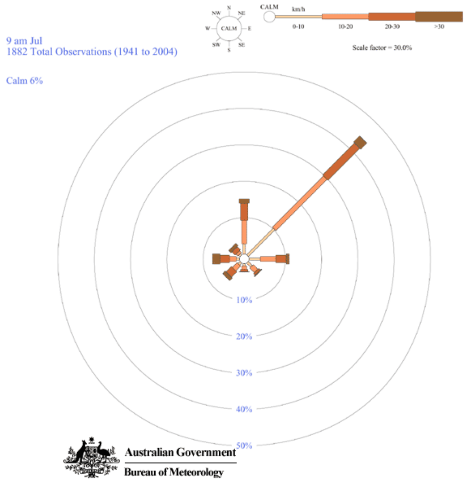
Morning winds (9 am June)



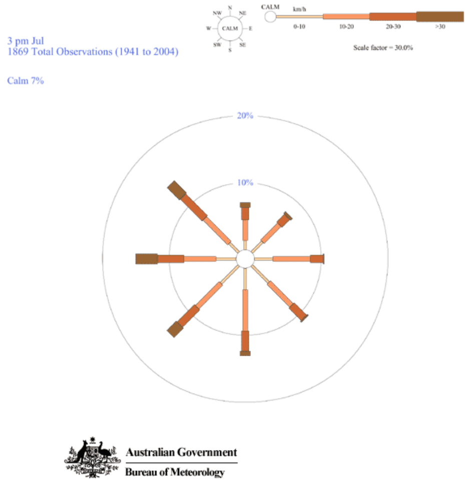
Afternoon winds (3 pm June)



Morning winds (9 am, July)

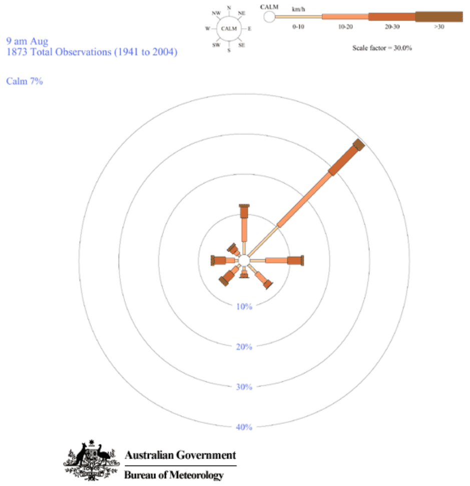


Afternoon winds (3 pm, July)

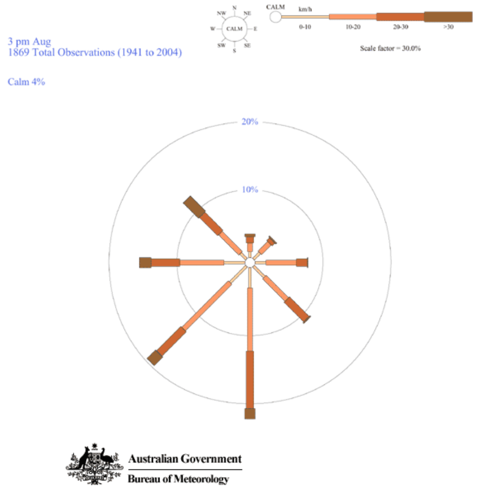


August (~ 4 weeks)

Morning winds (9 am, August)



Afternoon winds (3 pm, August)



The wind data and temperature data can be combined together in a general fashion. Earlier in the day during the period of sampling, the dominant wind direction was from the north-east. This would lead to movement of HVE in towards the Geraldton sampling area. However, at 9 am, the mean temperatures were quite low (<14^{o}C) and the airport, and therefore, probably colder further inland. This would limit the amount of HVE in the air column due to a negative influence on volatilisation. By 3 pm, the main wind direction (although variable) was from a westerly to southerly direction, moving HVE away from the Geraldton sampling area. Mean temperatures at this time in 1980 were higher (18-20^{o}C). This means the amount of vapour in the air column is expected to be higher due to increased volatilisation than at 9 am in the morning.

ATTACHMENT 6 – REFINED RISK ASSESSMENT - NOT RELEVAMNTY TO THE hve WORK – WILL NEED TO UPDATE THIS REPORT AND PREPARE FOR PUBLICATION - NOT PART OF THE PART 1 ASSESSMENT

Attachment 5

DSEWPaC’s assessment of a 2,4-D HVE AIR MONITORING STUDY - SEPTEMBER 2008

Introduction

Following the issuing of a permit to allow use of 2,4-D HVE in Western Australia in early 2008, the "Permit Support Group" (PSG) undertook one preliminary and two larger scale trials designed to measure the atmospheric dispersion of 2,4-D HVE vapour from a treated paddock (Hay, 2008). The trials were conducted in Western Australia during March and April, 2008. In the larger scale trials (70 ha), air was monitored for 2,4-D HVE vapour at the centre and perimeter of paddocks treated with 2,4-D ethyl ester, and at 200, 500 and 2,000 m from the perimeter of the treated paddocks, according to a protocol approved by the APVMA.

The Permit Support Group (via Nufarm) has now provided a report titled "2,4-D HVE Monitoring Study September, 2008" for assessment. DEWHA has been requested to undertake a full assessment of this report and provide advice to the APVMA regarding the acceptability of the study findings in relation to the ongoing review of 2,4-D High Volatile Esters.

The APVMA has also recently received a preliminary request for a permit to allow use of 2,4-D HVE in Western Australia during the upcoming summer season. DEWHA is requested to provide advice to the APVMA regarding the suitability of such a permit request in relation to the second part of the trial protocol "Regional Monitoring of 2,4-D HVE". This advice will assist the APVMA in determining whether or not to issue a permit to allow further HVE monitoring to take place.

Test Protocol

The final version of the protocol used for the test design, titled “2,4-D High-Volatile Ester Atmospheric Monitoring Draft Protocols Version 2” dated January 2008 followed comments from the 2,4-D Permit Support Group (PSG) to the APVMA on the first and subsequent draft protocols prepared by the APVMA for consideration.

The test protocol included monitoring on a regional level to attempt to quantify potential 2,4-D HVE concentrations in air within the region of application during the application season. However, this monitoring requirement was waived by the APVMA in March 2008 due to very limited supply of 2,4-D HVE into Western Australia and limited sales for 2,4-D HVE in the 2007/2008 summer season. Consequently, this report will only focus on the local monitoring undertaken to address the potential for 2,4-D HVE to move off target through the atmosphere from the field of application.

Samplers

For air sampling, SKC cat. 226-58 OSHA Versatile Sampler (OVS) Tubes, containing an initial aerosol particle filter (quartz) and two XAD-2 resin sorbent layers were used. The primary layer contained 270 mg XAD-2 resin. The secondary layer contains 140 mg XAD-2 resin. External batteries were connected to the pumps to maintain a 1 L/min flow rate over

24 h (total sample of 1440 L air over 24 hours). Unmodified pumps were able to maintain airflow for 8 h.

The flow rate was measured at the beginning and end of each sample collection period using a DryCal flow meter.

Storage stability

A trial was undertaken to ensure sample integrity was maintained when storing samples in the laboratory prior to analysis. Results showed that there was no significant change in 2,4-D ester recovery when spiked tubes were stored in a freezer up to 14 days prior to extraction.

Validation of analytical method

Validation of the analytical method was undertaken based upon the quality control and evaluation guidelines outlined in the NIOSH 5602 method. Validation spikes were prepared at six different concentration levels with a minimum of three XAD-2 tubes being spiked at each concentration level and recoveries calculated for each spiked tube. 10 blank XAD-2 tubes were also analysed.

For analysis, XAD-2 tubes were split and analysed in two portions, the front section comprising the filter and front sorbent section and the back section comprising the smaller sorbent section and middle polyurethane foam plug. 3 mL of 5% v/v diethyl ether/hexane was added to each sample section, sonicated for 1 h and the extract allowed to stand at room temperature for a minimum of 15 minutes. Analysis of the front section was conducted by GC-MS (SIM). Analysis of the back section was conducted only if sample results for the corresponding front section were high. Reported sample results were not corrected for extraction (desorption) efficiency.

Tubes were tested for 2,4-D ethyl ester, 2,4-D isobutyl ester and 2,4-D *n*-butyl ester. The results of this validation for 2,4-D ethyl ester are summarised as follows:

Table A1.1: Summary of Results from Experiment Validating Analytical Procedure

Spike level	Number of tubes	Recovery (%)		Mean
		Minimum	Maximum	
Blank	10	<0.015	<0.015	<0.015
0.0076-0.011 µg/sorbent tube	3	78	97	85.7
0.015-0.022 µg/sorbent tube	10	66	91	77.2
0.022-0.045 µg/sorbent tube	4	72	74	72.7
0.15-0.23 µg/sorbent tube	3	81	91	87.3
0.30-0.45 µg/sorbent tube	10	71	98	82.2
1.5-2.3 µg/sorbent tube	3	75	87	82

These results indicate an extraction efficiency of around 73 to 86% for 2,4-D ethyl ester. The report provides further quality control information.

Tube validation

The report provides an overview of an experiment performed to validate the sampling tubes where three tubes were spiked with 2,4-D ethyl ester or 2,4-D butyl ester (three replicate tubes, but spike levels not provided). The tubes were connected to a pump for 24 hours. In all three tubes, there was no “breakthrough”, that is, no chemical was detected in the second layer. Recoveries in the first layer ranged from 87-106% for 2,4-D ethyl ester and 87-108% for 2,4-D butyl ester.

Conclusion on sampling and extraction method used

DEWHA is satisfied that the sampling tubes, storage stability, and analytical methods used in the study were adequate.

Validation (Preliminary) Trial

The preliminary trial was conducted to validate the equipment and procedures planned for the larger scale trials. The location and weather details are adequately characterised for this part of the experiment. The test field was approximately 48 ha with 5 samplers, one in the "centre" of the plot, and others on, or approaching, each corner of the field. The application rate was 560 g ae/ha. Spraying was performed between 7-8:30 am and pumps were activated between 10:30 and 12:00 that day. It can therefore be reasonably assumed that detections found during the first day were not the result of spray drift.

From available weather records, the paddock likely experienced a 38-40^{o}C day on the day of spraying with a NW wind by afternoon. Night time temperature would have dipped to 18-19^{o}C. During the night and by early morning the wind moved through W to a SW direction. The first sampling period experienced a very hot initial day with a westerly wind direction, but had a cool change overnight. No rain was recorded. The day following application probably experienced a maximum temperature of 26-27^{o}C with a prevailing SW wind maintained all day. Overnight temperature probably dropped to 18-19^{o}C and by morning the wind had moved through S back to a SE wind.

In analysing sample tubes, one laboratory blank was analysed with every batch of samples submitted for analysis. No 2,4-D ethyl ester, 2,4-D *iso*-butyl ester or 2,4-D *n*-butyl ester was detected above the limit of detection (0.015 µ/L) for any laboratory blank.

Laboratory controls were used to determine retention efficiency and extraction efficiency. Results for laboratory controls were obtained by spiking two unexposed XAD-2 tubes with a known amount of 2,4-D ethyl, *iso*-butyl and *n*-butyl ester. One tube was stored in a freezer for 1 hour whilst the other had air drawn through at 1 L/minute for 1 hour. Both tubes were then extracted in the same manner as the samples. Two tubes were spiked with every batch of samples analysed. Retention efficiency was calculated to establish any loss or gain of the analyte related to the flow of air through the XAD-2 tube, and for 2,4-D ethyl ester, ranged from 97-105% indicating no loss related to flow of air. Field spike recoveries ranged from 84-109% for 2,4-D ethyl ester.

The extraction efficiency calculated to establish any loss or gain of analyte due to the extraction and analysis method ranged from 74-76% for 2,4-D ethyl ester. This is in good agreement with extraction efficiencies determined during validation of the analytical method described above.

Results

The only HVE detected was 2,4-D Ethyl ester. During the first 24 hours of sampling (from 2 to 26 hours after treatment), the tube in the "centre" of the plot returned a time weighted average (TWA) concentration of 0.542 µg/m^3. It is not clear in the report whether this has been corrected for extraction efficiency. If not, this indicates an actual level of 0.72 µg/m^3 if an extraction efficiency of 75% is assumed. The two samples at the downwind side of the field returned higher levels of 0.744 and 0.621 µg/m^3 (equivalent to actual levels of 0.99 and 0.83 µg/m^3 if the reported levels are corrected). This compared with much lower 2,4-D ethyl ester found in the upwind samplers 0.018-0.051 µg/m^3 (0.024 – 0.068 µg/m^3 corrected).

These are 24 hour average results. If it is taken that the majority of volatilisation would occur during daytime hours, peak exposure levels in the field of application could be 2 to 3 times higher than the 24 h averages.

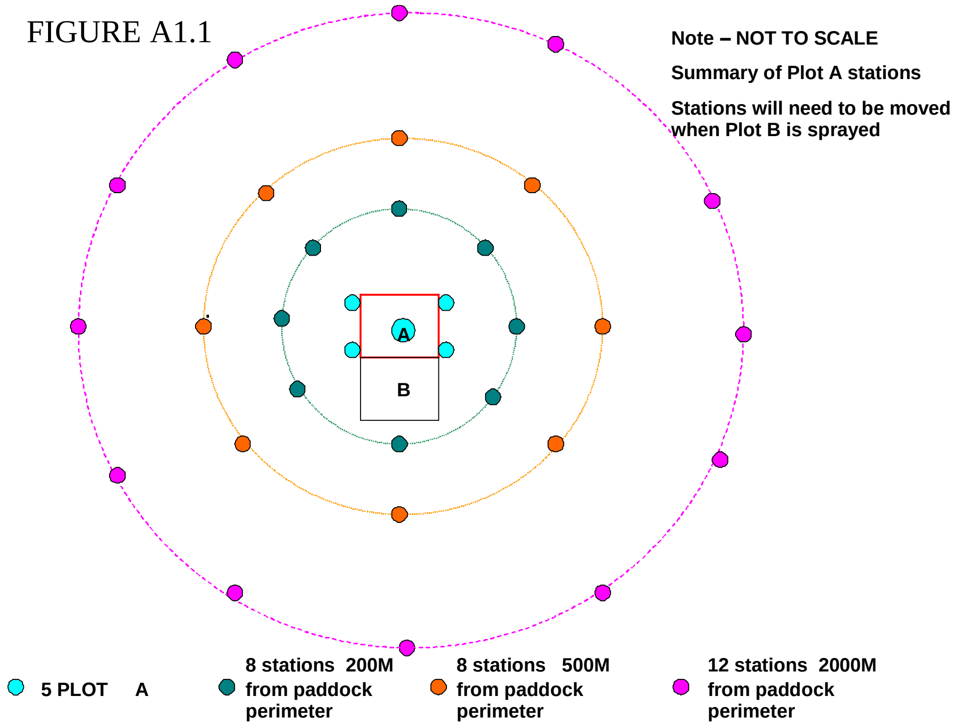
Samples taken during the next 24 hours (26 – 50 hours after treatment) showed much lower levels. In the “centre” of the plot, the 24 h average concentration was reduced to 0.045 µg/m^3 (0.06 µg/m^3 corrected). Those samplers on the upwind part of the field showed no detections of 2,4-D ethyl ester, while those at the downwind side showed again, much lower levels than the first day with 24 h average concentrations of 0.041-0.078 µg/m^3 (0.055-0.10 µg/m^3 corrected).

Definitive Trials

The location and characteristics of the test site are well characterised and the test plot sizes were 70 ha for each part. It appears there were no significant physical barriers between the plots and the perimeter samplers at 2000 m from the plot centres, and the report notes that in most cases, the 2000 m monitoring stations were visible from the plots.

The study design for the local monitoring was based on placing samplers (height of 1.7 m) at regular intervals on the 200 m, 500 m and 2000 m circumferences – an annular design. This was to better sample the whole area because of the unpredictability of vapour movement.

FIGURE A1.1



Sampling regime

The original draft protocol called for 5 x 3 day sampling periods with samplers to be run for 12 hours on each of the days. On the basis of existing evidence that most of the vapour movement occurs within the first 48 hours after application coupled with the limited availability of suitable samplers the 2,4-D PSG proposed instead that the sampling be concentrated in the first 3 days, that is 3 x 1 day with samplers to be run for 2 x 12 hours per day if possible to cover the night time as well. A final sample would be taken at 8 days based on the points raised in the following paragraph. This would then give 5 separate "day" points which will enable a decay curve to be generated to compare to published studies referred to above. This approach was considered acceptable.

Unfortunately, sampling was only able to be performed in 24 h segments. Given that vapour movement is most likely to occur during daytime hours, this means that TWA_{24} values determined in this experiment are likely to underestimate peak exposure concentrations, and it is not possible to determine the likely extent of time such peak concentrations exist for. This is considered further below.

In earlier drafts of the protocol, DEWHA had suggested as a criterion for the test plots that ground cover from target weeds be at least 30%. For unknown reasons, this was not included in the final protocol of January 2008, and the test plots used in this study had much less ground cover. Plot A is stated as having 1-2% cover. However, a significant rain event 8 days prior to application on Plot B meant there was much greater cover on this plot, but the actual level is not estimated.

DEWHA has received conflicting information as to the most likely conditions when spraying would occur. At the presentation provided by Nufarm (30 October 2008), the company and its representatives suggested the conditions found during Part A (that is, dry with very little ground cover) would be the normal conditions encountered during spraying. However, some users (farmers) suggested they are more likely to spray in conditions like Part B where some rain had caused an increase in weed pressure.

Baseline monitoring

In line with the protocol, baseline monitoring was performed prior to the first application. However, the baseline monitoring program was reduced to three days (instead of five) because of high winds forecast at the end of the planned baseline monitoring period, which had the potential to significantly delay spraying the trial block if the full monitoring program was completed. No sample tubes contained 2,4-D HVE in excess of the MDL (0.015 µg/sorbent). No rainfall was recorded during the baseline measurement period.

During the period of the baseline monitoring study, maximum daytime temperatures ranged from about 26 to 30^{o}C.

Plot A trial

At the time of spraying Plot A (22 March 2008), a strong east to south easterly prevailing wind was present (noted as continuing through the trial). Very light rain was recorded between 8.30 and 10.00 on the day of application. No other rain was recorded during Trial A.

Nufarm Estercide 800 (Batch 43739), an emulsifiable concentrate formulation of 2,4-D ethyl ester, was applied at 700 mL/ha (560 g 2,4-D ae/ha, spray volume 50 L/ha) using an AIRMIX 03 nozzle at 3-4 bar pressure. Ground speed averaged 25 km/h. Application was between 07.00 and 08.00 am. Pumps in the test plot were activated between 11:00 am and 2:30 pm (up to 7 hours after application) with similar timing for pump activation outside the plot area.

Based on information presented graphically, the maximum daytime temperature on the day of application approached 30^{o}C, with a maximum temperature the following day around 25^{o}C. Night time temperatures fell to around 13^{o}C on the first night and 8^{o}C during the second night.

Two samplers were positioned in the centre of the plot. The TWA$_{24}$ concentrations in these samplers were 0.219 and 0.229 µg/m^3, or a mean of 0.224 µg/m^3 (0.30 µg/m^3 corrected assuming an extraction efficiency of 75%). The edge of field sample positioned in the downwind edge of the treated plot had a TWA$_{24}$ concentration of 0.202 µg/m^3 (0.27 µg/m^3 corrected). The other edge of field samplers showed no detection of 2,4-D HVE. In this trial, movement off the plot was very minimal. The only sampler in the first 24 h to detect any 2,4-D HVE was sampler number 6 (200 m, downwind) with a 24 h average concentration of 0.029 µg/m^3 (0.039 µg/m^3 corrected). The other sampler in this general wind direction (number 13) showed 0.016 µg 2,4-D HVE in the sorbent, but this sampler was stopped and an actual TWA$_{24}$ could not be derived.

On the day following treatment, 2,4-D HVE was only detected in the field of application. The samplers at the centre of the plot both showed TWA$_{24}$ concentrations of 0.011 µg/m^3 (0.015 µg/m^3 corrected).

Plot B trial

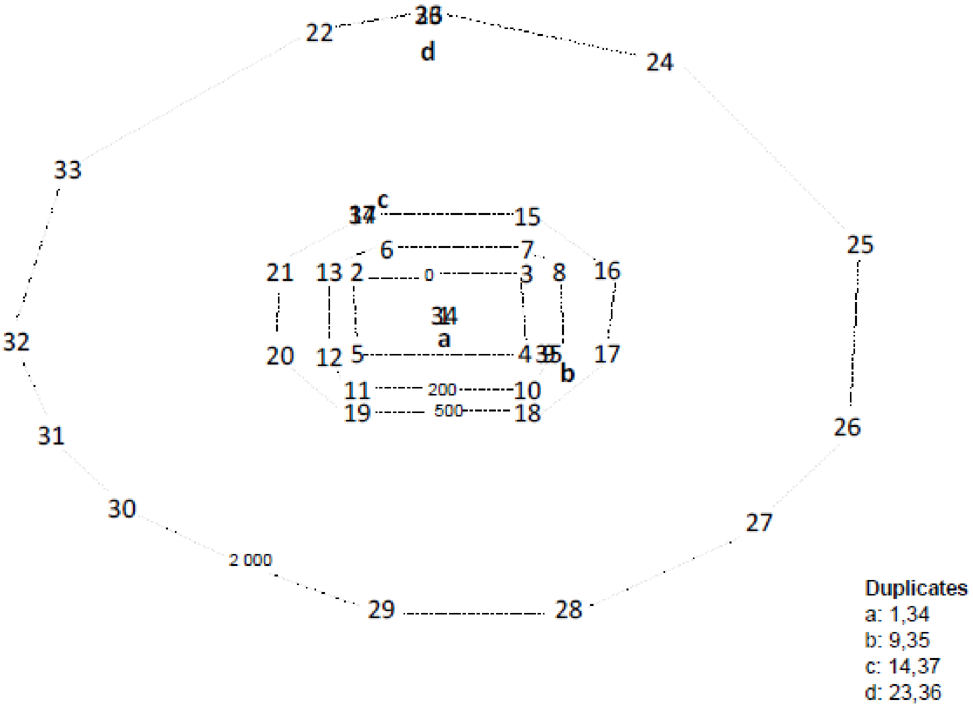
Application to Plot B occurred on 8 April 2008 in the same manner as that described above for Plot A. A significant rainfall event (total 23 mm) occurred at the trial site on 31 March, 2008, eight days before Trial B commenced. New weed emergence was observed as a result of this rainfall. Minor rainfall was observed on 5 April (0.4 mm), 10 April (0.4 mm) and 16 April (1.6 mm).

Based on graphical representation, the maximum day temperature on the day of application was around 24^{o}C. On the first and second days following application, the maximum temperatures were around 29^{o}C and 24^{o}C respectively. Minimum temperatures seemed to be between 12-15^{o}C. Application took place between 7:00 am and 8:00 am. Pumps in the treated field were activated between 11:00 am and 2:00 pm, again, several hours after application. This eliminates the prospect of sampler contamination through spray drift.

Information on wind strength and direction is not easy to interpret from the report. A diagram of wind speed and direction through the trial period is provided, but this does not identify when wind blew from a particular direction, or at what speed.

The following figure shows the sampler positions in relation to the treated plot:

FIGURE A1.2:



<u>0-24 h after application:</u>

Movement of 2,4-D HVE in this second trial was much more pronounced than that in the first trial. In-field concentrations during the first 24 hours were 0.46 µg/m^3 (0.61 µg/m^3 corrected) in the centre of the plot. During this time, the prevailing wind appeared to have come from the south east (moving to north east) as the highest edge of field concentrations came from sampler 2 (0.6 µg/m^3, or 0.80 µg/m^3 corrected), with 0.11 µg/m^3 (0.15 µg/m^3 corrected) in sampler 5 (south west corner of the plot). From the eastern side of the plot, 0.011 µg/m^3 (0.015 µg/m^3 corrected) was found in Sampler 3.

Outside the field of application, at 200 m, sampler 6 (north west of the field) showed a TWA$_{24}$ concentration of 0.14 µg/m^3 (0.19 µg/m^3 corrected), while samplers 11 and 12 (south west of the field) showed TWA$_{24}$ concentrations of 0.01 and 0.04 µg/m^3 (0.013 and 0.053 µg/m^3 corrected) respectively.

Three samplers at 500 m (numbers 20, 21 and 37, west to north west of the plot) showed TWA$_{24}$ concentrations of 0.04, 0.17 and 0.07 µg/m^3 (0.053, 0.23 and 0.0.093 µg/m^3 corrected) respectively.

One sampler (number 33, west north west) at 2000 m from the test plot showed a TWA$_{24}$ concentration of 0.01 µg/m^3 (0.013 µg/m^3 corrected).

<u>24-48 h after application</u>:

During the second day, the TWA$_{24}$ concentration in the centre of the plot was 0.437 µg/m^3 (sampler 1, 0.58 µg/m^3 corrected). The maximum edge of field concentration was found in sampler 3 (north east) with a TWA$_{24}$ concentration of 0.352 µg/m^3 (0.47 µg/m^3 corrected) indicating the wind was mainly from the south west during the period of volatilisation. A TWA$_{24}$ concentration of 0.066 µg/m^3 (0.088 µg/m^3 corrected) was found in sampler 2 (north west corner).

Outside the plot, several detections were found. At 200 m, the highest concentrations were found in samplers 7, 8 and 9 (north east, to eastern side of the plot), again suggesting the main direction of the wind during the time of volatilisation was from the south west to west. TWA$_{24}$ concentrations in samplers 7, 8 and 9 were 0.198, 0.141 and 0.343 µg/m^3 respectively (corrected values of 0.26, 0.19 and 0.46 µg/m^3 respectively). Sampler 35 was a duplicate of sampler 9, and this confirmed the measurement for sampler 9 with a TWA$_{24}$ of 0.314 µg/m^3 (0.42 µg/m^3 corrected). Much smaller levels were found in sampler 6 (north north west) and 13 (west north west) of 0.053 and 0.045 µg/m^3 respectively (0.07 and 0.06 µg/m^3 respectively). The fact that 2,4-D HVE was found in these samplers indicates some variation in the wind direction through the period of volatilisation. A reasonable amount of 2,4-D HVE was found in sampler 10 (east south east), but this sampler was stopped so average concentrations could not be confirmed. No substance was detected in samplers 11 and 12 (south west corner).

At 500 m, of the 8 sampling stations, 2,4-D HVE was not detected in two – stations 19 and 20 found in the south western part of the monitoring area. This is consistent with the 200 m sampling stations. Levels, where detected out at 500 m, were lower than those at 200 m and ranged from 0.014 µg/m^3 (0.019 µg/m^3 corrected) in sampler 14 (confirmed in the duplicate sampler number 37 at a corrected concentration of 0.022 µg/m^3), west north west of the plot, to 0.118 µg/m^3 (0.16 µg/m^3 corrected) in sampler 18 (east south east of the plot). Other TWA$_{24}$ corrected concentrations found out at 500 m were 0.11 µg/m^3 (sampler 15), 0.08 µg/m^3 (sampler 16), 0.14 µg/m^3 (sampler 17) and 0.03 µg/m^3 (sampler 21).

Out at 2000 m, detections were found samplers 25, 26 and 27, again all indicating movement from the plot to the easterly (south easterly) direction of the treated area. These samplers were in the opposite direction to detections made at 0-24 h. TWA$_{24}$ concentrations found in samplers 25 and 27 were 0.016 and 0.034 µg/m^3 respectively (0.02 and 0.045 µg/m^3 corrected respectively). In sampler 26, 0.015 µg sorbent was found, but the sampler had stopped and actual average concentrations could not be calculated.

There is no information on the samples taken at 4 days after application, except in the executive summary of the full report, it is stated that “2,4-D HVE was not detected at greater than the level of detection in the 4 DAT samples.”

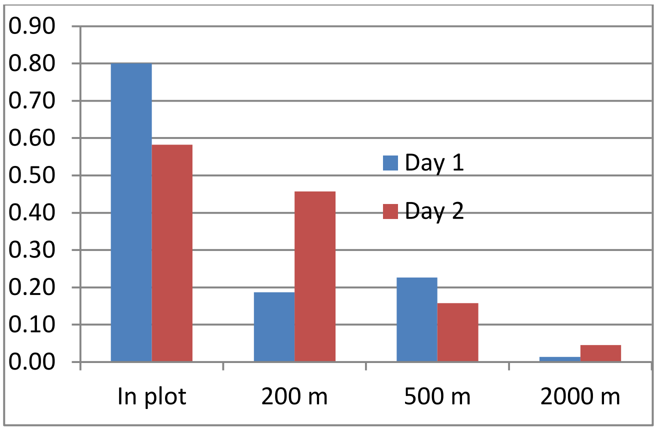
This second trial highlights some of the concerns DEWHA has expressed over volatilisation of the high volatile esters. If it is assumed that the maximum vapour concentrations found at all distances are reflective of wind direction, then a comparison of those samplers with the highest concentrations found during 0-24 h and 24-48 h show how exposure may be prolonged, that is, not an acute exposure situation as with spray drift, and levels can be higher later in the exposure period. The following table and figure illustrate this where maximum 24 h average samples (corrected for extraction efficiency) at 0, 200, 500 and 2000 m are shown for the 0-24 h and 24-48 h sampling periods:

Table A1.2: Maximum measured concentrations on 1 and 2 days following application (TWA$_{24}$ µg/m^3) at 0, 200, 500 and 2000m from the

Figure A1.3: Comparison of maximum measured concentrations on 1 and 2 days following application (TWA$_{24}$ µg/m^3) at 0, 200, 500 and 2000 m from the test plot.

test plot.

	Day 1	Day 2
In plot	0.80	0.58
200 m	0.19	0.46
500 m	0.23	0.16
2000 m	0.01	0.05



These figures show higher levels found at 200 m and 2000 m during the 24-48 h sampling time than at the 0-24 h sampling. As described above, the samplers with the highest concentrations during the second day were in a different direction (wind predominantly south easterly on day one and south westerly on day two) than those with highest levels on the first day, demonstrating that the exposure can occur over a much wider area than during application alone (from spray drift), where the downwind area at the time of application is known and can be protected.

These results also bring into question the assertion made in the PSG report that there will be rapid atmospheric dispersion given the findings of similar atmospheric concentrations (as 24 h averages) over a 48 h period, and underlines the importance of the regional trial to better understand total levels in air based on regional use and wind patterns.

Discussion of Results

DEWHA agrees the study has been generally well conducted. The variability involved with field trials always leads to greater uncertainty in results, and difficulties in interpreting them. The main criticism is that the sampling methods did not allow for a separation of the collection of samples from 24 hours to 12 hour periods (as required by the protocol). This would have helped tremendously in assessing the variability in levels due to volatilisation between night and day time conditions, and was one of the main factors restricting DEWHA's undertaking of a robust risk assessment based on this trial (see Attachment 2).

However, there are some very clear conclusions that can be drawn from this study. Firstly, it is clear that the potential for off target movement of 2,4-D HVE exists from the point of application, and that this is the result of vapour movement, not droplet drift. In the drier conditions experienced in the first trial, this movement was very limited and vapour concentrations found both in the field of application and outside (only at 200 m in one sampler on the first day) were low by comparison of the second trial.

The impact of increased moisture was very apparent (and in agreement with the literature). While ground cover was not characterised in the preliminary trial, the humidity at the time of application was very high (~80%) indicating a lot of moisture in the air. In the second plot trial of the definitive test, there was apparently a greater amount of green ground cover, and the soil moisture was likely to be much higher than from the first plot trial due to a large rain event 8 days prior to application. In both the preliminary trial, and the second plot trial, in-field air concentrations were much higher than in the first plot trial where conditions were dry.

Due to the limited sampling within the field of application, it is difficult to conclude whether levels in the air may accumulate as wind moves over sprayed areas, but in this regard, it is noted that downwind, edge of field concentrations were higher than in the centre of the plots in both the preliminary trial and the Plot B definitive trial (see Table A1.2 and Figure A1.3). This indicates a degree of enrichment in the air column.

In their interpretation of the levels observed, the PSG refers to rapid dispersion in the atmosphere. In doing this, PSG quotes Atkinson (2000) in noting the troposphere extends from the earth's surface to the tropopause at 10-18 km, and vertical mixing in the troposphere is fairly rapid, with a time scale of ~10 to 30 days. Atkinson, however, makes the following distinction not reported in Hay (2008). He notes that mixing is fairly rapid in the "free troposphere", and that the lowest kilometre or so of the troposphere contains the planetary boundary layer, and in this layer that vertical mixing of chemicals into the "free" troposphere could be inhibited through inversion layers. Therefore, it seems incorrect to assume a rapid and complete vertical mixing of volatilised chemical up into the atmosphere at all times.

Hay also determines a value for an atmospheric dispersion ratio (5,530) based on the saturated vapour concentration of 2,4-D ethyl ester compared with the observed values. While we don't dispute the calculations of saturated vapour concentration, we are uncertain of the relevance. DEWHA does not dispute that, over time, concentrations of 2,4-D in the atmosphere will fall due to degradation or dispersion. However, it is apparent from the monitoring study that localised exposures (within 2 km of the treated plot) can occur for at least 48 hours. It is also apparent from other monitoring information considered outside this current assessment, that 2,4-D can be detected in the air up to at least several kilometres from areas of application. Even though detected levels are low, they do not support a conclusion of rapid dispersion in the atmosphere.

The Plot B trial also demonstrates that, where conditions are more favourable for volatilisation, exposure can occur to a wide area. During the first day following application, low levels were found out to 2000 m in one sampler north west of the test plot. During the second day, wind directions favoured movement in the opposite direction, and samplers 2000 m out (three samplers) in the east to south east of the test plot contained lower levels of 2,4-D HVE.

It is interesting that during the second day, levels found outside the treated area were more widespread (found in more samplers) than those during the first day, and levels were comparable. Also interesting in the 2 days after application samples from the Plot B trial is that levels at 500 m were around the same as those at 2000 m. This further supports an argument for vapour movement, and reaffirms the difficulty in being able to predict and control off target movement of volatile substances following application.

One of the main questions needing an answer relating to the use of 2,4-D HVE is the likely gas phase exposure concentration. In this regard, the current trial can go some way towards answering this, but only on a local level. However, the use of TWA_{24} concentrations is not considered representative as exposure is most likely to occur during the day time hours. Maximum in-field concentrations based on the preliminary trial and Plot B definitive trial are in the order of 0.8-1 µg/m^3 over a 24 h period. If the majority of this exposure occurred during a 12 hour period, these in-field levels would be more like 1.6 to 2 µg/m^3, and if the exposure mainly occurred during the hotter 8 hours of the day, then they would increase further to 2.4 to 3 µg/m^3.

Outside the field of application, it is apparent that levels fall relatively quickly, but can still be found significant distances from the treated area. Based on the data obtained from the Plot B trial, the maximum measured concentrations out at 200, 500 and 2000 m represent (roughly) around 80%, 25% and 10% of maximum in-field rates at day 2. This compares with around 25%, 30% and 2% of maximum in-field rates at 200, 500 and 2000 m respectively at day 1.

These figures again demonstrate the variability of likely exposure outside the field of application. However, they do show it can happen. Levels found outside the area of local application could theoretically be in the order of 0.6 to 2.4 µg/m^3 (200 m); 0.6-0.9 µg/m^3 (500 m) and 0.05-0.3 µg/m^3 (2000 m) if it is assumed that the majority of volatilisation occurs over the warmer 8 hours of the day. Further work would be needed to confirm this.

The other implication of this local monitoring study is that areas surrounding the treated field(s) may be exposed for 1 to 2 days following application, but based on this study, the potential for extended exposure from *localised* application is low given 4 day samples did not detect 2,4-D HVE.

Conclusions:

The report “2,4-D-HVE Air Monitoring Study. September 2008” addresses the local monitoring as required in the APVMA permit issued for 2,4-D HVE use during 2007-08.

In terms of exposure conditions in the area considered local to a treatment area, the following can be concluded:

- Where favourable conditions exist, off target movement through volatilisation will occur;
- The movement through the vapour phase changes direction with wind changes, thereby potentially exposing a larger area;
- Highest levels of local exposure may be expected to occur during the first two days following a single application;
- Based on an application rate of 560 g ae/ha, maximum in-field air concentrations could approach 3 µg/m^3 (based on 8 hours exposure), with levels up to 0.3 µg/m^3 (8 hours exposure) predicted at 2 km off-site.

The report provided a risk assessment and this has been reviewed in Attachment 2. The risk assessment was not part of the monitoring requirements, and the data needed to adequately perform the hazard assessment component of a risk assessment are still outstanding.

The regional monitoring proposed as part of the 2007/08 permit could not be conducted due to limited sales of 2,4-D HVE. This component is still considered essential as it will help identify general atmospheric levels of 2,4-D HVE under normal use conditions. However, the relevance of such data becomes diminished if volumes of use are not at “normal” levels.

References:

Atkinson R, 2000. "Atmospheric Oxidation." In Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences, by R. S. Boethling and D. Mackay. CRC Press.

Hay P, 2008. 2,4-D HVE Air Monitoring Study, September 2008. 2,4-D Permit Support Group.

ATTACHMENT : ASSESSMENT OF RISK ASSESSMENT COMPONENT OF “2,4-D HVE AIR MONITORING STUDY, SEPTEMBER 2008.

While not part of the requirement of the monitoring study, the PSG have provided a risk assessment for vapour phase toxicity of 2,4-D HVE to terrestrial plants. In undertaking this assessment they have used the methodology outlined in the Preliminary Review Findings document (APVMA, 2006). Exposure endpoints were based on the monitoring results (TWA_{24} concentrations). Effects data were based on reviewed literature considering vapour phase toxicity of 2,4-D butyl ester to tomato plants. The effects data were converted from vapour concentrations to a value for “total available herbicide”, and this total amount of herbicide was then distributed into the 24 h volume of air collected during the field monitoring study (1.44 m^3) to give a TWA_{24} EC25 or EC05 value. DEWHA has significant concerns with the validity of this approach and this is discussed below.

In the PSG risk assessment, in discussing the duration of exposure, the PSG notes that:

> The first step of a risk assessment is to determine the relevant duration of exposure. The present study shows that the concentration of 2,4-D HVE in air decreases rapidly following exposure. This observation is consistent with the known effects of rapid atmospheric dispersion, hydrolysis of 2,4-D HVE on plants and soil to the 2,4-D acid form and atmospheric photodegradation.

DEWHA has previously argued that 2,4-D HVE may persist in the atmosphere with calculated half lives of 1.7-2.0 days for 2,4-D butyl ester and 2,4-D ethyl ester. This view has been accepted by industry in previous discussions. Further, DEWHA has argued above against the view that 2,4-D HVE will undergo rapid atmospheric dispersion. Finally, while we accept hydrolysis is a removal route for these substances in the environment, again, we don’t accept this is necessarily a rapid process, and the findings above of similar or higher levels of 2,4-D ethyl ester during the 24-48 h monitoring period compared to the 0-24 h period in Trial B shows this process will not always rapidly remove 2,4-D HVE from the environment.

The first part of the PSG risk assessment is a discussion on the assumptions in our preliminary report about vapour deposition. In that report, we had taken the assumption in our discussion on volatility that crop interception is 50%; and 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. The PSG has provided argument that these are false assumptions. In response, we accept that. In fact, the report states prior to the assumptions that they have no scientific basis, and were provided as an illustrative exercise only for a comparison between the different ester forms. This component does not have any further bearing on the risk assessment prepared by the PSG and is therefore, not considered further in this response.

Use of the “total herbicide available” concept

It appears that the basis for the PSG risk assessment is the concept of “total herbicide available”. The PSG report (Hay, 2008) attributes the introduction of this concept to Breeze (1990). In his report, Hay states:

> “The concept of “total herbicide available” was introduced by Breeze 1990. Breeze used ^{14}C-2,4-D butyl to show that <4% of total herbicide available (i.e. product of vapour concentration, flow rate and duration of exposure) was taken up by plants. The data shows uptake is linearly related to total herbicide available and that herbicide uptake can be predicted from total herbicide available.”

While Breeze does make the point that total amounts of herbicide taken up by the plants were <4% of the total herbicide *vapour* available, he does not then discuss results in this context, rather, he explicitly state that "relationships between external *vapour concentration* and plant uptake were linear in all cases". DEWHA has plotted total herbicide in the plant (µg/plant) against both the external vapour concentration (µg/m^3) as described in the Breeze report, and against total available herbicide calculated by DEWHA and the PSG, as described in the PSG risk assessment. There is little difference in the two outcomes, and shows there is as much justification for predicting plant uptake based on vapour concentration as opposed to total herbicide available.

Figure 1: 2,4-D Butyl Residues in Plants (ug) vs Atmospheric Concentration (µg/m^3)

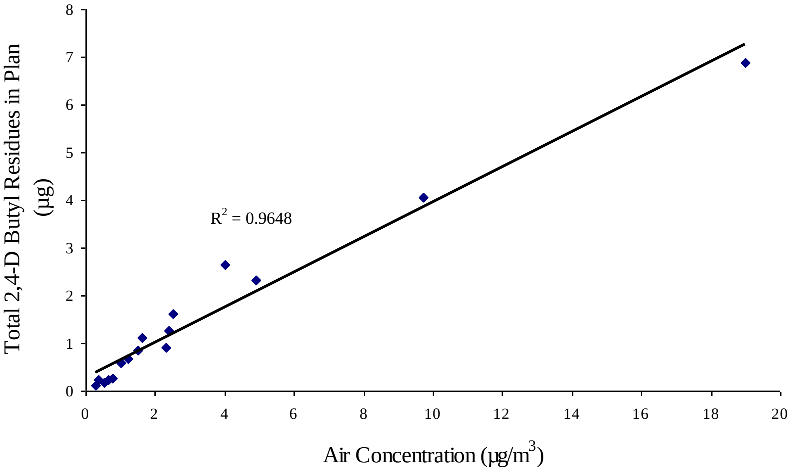
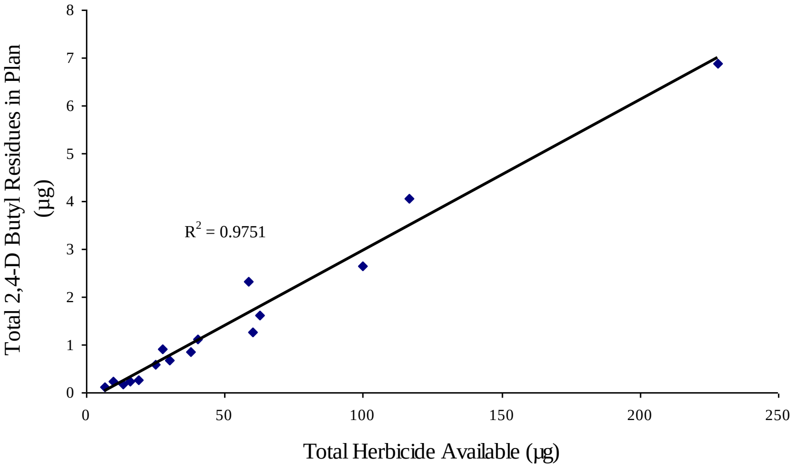


Figure 2: 2,4-D Butyl Residues in Plants (ug) vs Total Herbicide Available (µg)



DEWHA considers the use of "total available herbicide" as a basis for the risk assessment to be fundamentally flawed. It is raised in the paper by Breeze (1988) as being a better method to compare results from his paired experiments where he considered effects to tomato plants exposed to 2,4-D butyl ester for either 6 or 24 hours, and at a low and a high concentration range for each exposure period. In discussing the use of "total available herbicide", Breeze notes that in this set of experiments, better agreement between the experiments carried out at the two concentration ranges was obtained by expressing the herbicide vapour as the total amount to which the plants were exposed (total available herbicide) instead of concentration in air alone. However, as observed by the author, measurement of effects in this term rather than as concentration alone, reduced discrepancies between the pairs of experiments. Breeze also notes that greater similarity between the pairs of experiments due to expression of response in terms of total amount of herbicide, rather than in terms of vapour concentration alone, suggesting that a large fraction of the vapour is taken up by the plant. He concludes that these findings confirm the need for air-flow systems to observe effects of vapour on plants and indicate the experimental inadequacies of static systems. In fact, in his discussion of the results, Breeze compares the concentrations used in the study to those reported for analyses of air and in this context, does not consider using "total available herbicide". As pointed out by Breeze and West (1987), high air flow rates (hence a higher amount of "total available herbicide") are desirable in test systems when using low vapour concentrations as depletion due both to uptake by the plants and absorption by the test system is minimized.

DEWHA supports these conclusions, but notes they relate to an experimental procedure and fails to see how they suggest that field concentrations found during monitoring need to be related back to a value of total available herbicide rather than using the vapour concentration. In fact, it is our view that vapour concentrations found in the field cannot be reported in terms of total available herbicide. In order to do this, there needs to be information on continuous air exchange and concentration levels in the air during the monitoring period, and this is not possible. The air samplers extract a pre-set air volume, and this is **independent** of air flow around the samplers and within the test plots.

To enable a risk assessment, exposure and effects need to be compared in the same units. While it is possible to establish total available herbicide in an ecotoxicity test, it is not possible to derive total available herbicide from the field monitoring data. The PSG risk assessment attempts to do this by converting effects data to levels based on monitoring sampling methods (1 L/min over 24 hours). We believe this approach is incorrect. The sampling rate is fixed and samples 1 L/minute **independently and irrespectively** of the flow rate of surrounding air. The total available herbicide will be dependent on this surrounding air. It is therefore not possible to extrapolate an effect concentration that is re-calculated based on total available herbicide in the toxicity test system to a level found in a regulated field sampler.

Based on this, DEWHA does not believe effects data in terms of total available herbicide can be compared to monitoring data. However, as shown above by the Breeze (1990) data, plant uptake is related to *vapour concentration*, and this is the comparison that should be concentrated on for risk assessment purposes.

Vapour phase effects data

The PSG present three studies where they calculate EC25 and EC05 values from vapour phase exposure of 2,4-D butyl ester to tomato plants. The most comprehensive experiments in this set are reported by Breeze (1988). In addition, Breeze and West (1987) report a study with tomato plants and 2,4-D butyl ester where a vapour phase dose/response can be derived. DEWHA will only consider these two papers further.

In Breeze and West (1987), tomato plants (8 weeks old) were exposed to vapour concentrations of 5 to 50 ng/L (µg/m^3) for 5 h. For each concentration, four plants were used. The air flow rate >100 L/minute. After 5 h exposure, the vapour airstream was shut off and the plants given herbicide free air at around 150 L/min for a further 24 h. The chambers were then opened and the plants returned to the glasshouse. Forty seven days after the exposure period, when the plants of the controls and the lowest treatment had begun to flower and set fruit, the plants were harvested and assessed on a plant dry weight basis. In the control group, after 47 days, mean dry weight was 35 g per plant. This compared with 28.8, 19.1, 18.1 and 12.0 g/plant at measured exposure concentrations of 5, 14, 31 and 50 ng/L respectively.

In determining an EC50 for these results, the PSG fitted log-transformed data in terms of total available herbicide and arrived at an EC50 of 465 µg total 2,4-D butyl ester. The PSG then translates this to a TWA_{24} as follows:

1) convert total available 2,4-D butyl ester to 2,4-D acid equivalent = 370 µg total 2,4-D ae;
2) Assuming a collection flow rate of 1 L/min over 24 hours (1.44 m^3 air), the PSG then converts the total available herbicide to a TWA_{24} concentration of 258 µg/m^3.

As explained above, DEWHA believes this approach is flawed. The collection flow rate is fixed and does not bear any resemblance to actual air flow conditions in the field of exposure. It is sampling a pre-determined and fixed volume of air from the test plot regardless of the total air that may flow through the plot during the sampling period. Therefore, this direct conversion is not defensible.

DEWHA has re-analysed the toxicity results using TOXCALC v5.0. Based on Fisher's Exact Test, the reduction in dry weight (>17% at the lowest test concentration) was considered statistically significantly different from the control, and the NOEC was therefore <5 µg/m^3. In terms of 2,4-D butyl ester, the 5 h EC50 was calculated by probit analysis to be 24.8 µg/m^3, the 5 h EC25 as 6.9 µg/m^3 and the EC05 as 1.1 µg/m^3. In terms of acid equivalent, these values are 19.9, 5.5 and 0.88 µg/m^3 respectively.

In the Breeze (1988) experiments, tomato plants (5 to 7 weeks old) were exposed to a range of concentrations of 2,4-D butyl vapour from 0.12 to 2.4 µg/m^3 for either 6 hours (2 experiments) or 24 h (2 experiments). Six weeks after exposure, shoot dry weights of plants were measured. In this set of experiments, better agreement between the experiments carried out at the two concentration ranges was obtained by expressing the herbicide vapour as the total amount to which the plants were exposed (total available herbicide) instead of concentration alone as this reduced discrepancies between the pairs of experiments.

The broad experimental parameters for Breeze (1988) were reported as follows:

Table A2.1: Experimental Parameters outlined in Breeze (1988)

Experiment number	1	2	3	4
No. plants	10	8	8	10
Exposure duration (h)	6	24	6	24
Vapour concentrations µg/m^3	0.67 1.2 1.9 2.4	0.46 0.7 1.2 1.5	0.12 0.24 0.47 0.82	0.13 0.25 0.51 0.88
Exposure airflow (L/min)	115	125	205	190

With less than an order of magnitude between the lowest and highest test concentrations the range of exposure concentrations results do need to be interpreted with some caution. While there are no set test guidelines for vapour phase plant testing, it is common practice in other ecotoxicity tests to include test concentrations as a geometric series, often based on log units, where there could be several orders of magnitude between lowest and highest test concentrations.

The following results were found in terms of mean plant dry weight (g), based on vapour concentration and corresponding total herbicide available:

Table A2.2: Results Obtained by Breeze (1988)

Experiment	Concentration µg/m^3	Total available µg	Dry weight	% Control
1	0.67	27.74	6.03	82.83
	1.2	49.68	6.02	82.69
	1.9	78.66	5.13	70.47
	2.4	99.38	4.48	61.54
2	0.46	82.80	6.69	82.49
	0.7	140.40	6.25	77.07
	1.2	216.00	5.41	66.71
	1.5	270.00	4.15	51.17
3	0.12	8.86	7.35	80.95
	0.24	17.71	6.70	73.79
	0.47	34.69	6.45	71.04
	0.82	60.52	6.13	67.51
4	0.13	35.57	3.87	72.07
	0.25	68.40	3.94	73.37
	0.51	139.54	3.31	61.64
	0.88	240.77	3.32	61.82

In no experiment was any concentration sufficient to result in more than 50% reduction in plant weights compared to the control. The closest was inhibition of around 49% in experiment 2 after 24 h exposure to 1.5 µg/m^3 (total available 270 µg 2,4-D butyl ester). In all experiments, at the lowest rate tested, around 20% inhibition was observed at both 6 and 24 h exposure. Given this relatively narrow range of effects (between 20 and 50% inhibition) and the relatively small range of tested concentrations, predictions of effects concentrations can become more uncertain.

While reduction of dry weight was above 50% of control values in all results, it is worth noting that in the 24 h exposure tests, dead plants were found in experiment 2 (25%) and 4 (10%) at the highest test concentrations.

DEWHA has calculated EC25 values using TOXCALC v 5.0 using maximum likelihood-probit analysis. These values are compared to the PSG calculated EC25 values based on fitting of data to linear or quadratic equations in terms of total available herbicide, and converting to a TWA_{24} concentration as described above. The results are presented as follows:

Table A2.3: Comparison of PSG and TOXCALC calculated EC25 Values

Experiment	PSG EC25 (TWA_{24} µg 2,4-D ae/m^3)	EC25 (probit analysis) µg ae/m^3
1	35.1	1.19 (6 h)
2	84.3	0.62 (24 h)
3	9.8	0.18 (6 h)
4	19.6	0.20 (24 h)

There are obviously large differences between the PSG calculated results and those using TOXCALC. However, these are effects data and at this stage, must be considered independent of exposure levels in a risk assessment context. To consider a validation exercise, it is worth having a further look at the results obtained in Table 3 above, and the results reported by the PSG and TOXCALC above. In experiment 2, at the maximum exposure level of 1.5 µg butyl ester/m^3 (1.2 µg ae/m^3) over 24 hours (that is, essentially a TWA_{24}), exposed plants exhibited a decrease in plant fresh weight of around 49%, that is, approaching an empirical EC50. The PSG has calculated a TWA_{24} EC25 of 84.3 µg/m^3, which is a concentration around 70 times the empirical value from the experiment. Conversely, the EC50 calculated by TOXCALC for this experiment was 1.26 µg ae/m^3, which is in very good agreement with the reported results.

Similarly, in experiment 4 (also 24 h) at the end of the exposure period, the exposed plants had reduced plant weight compared to control plants of around 38% (approaching an empirical EC40) at 0.88 µg/m^3 (~0.70 µg ae/m^3). Yet, the PSG predicts a TWA_{24} EC25 of 19.6 µg ae/m^3, almost 30 times higher than the empirical EC40. Conversely, TOXCALC predicts a 24 h EC40 of 0.60 µg ae/m^3, again, in relatively good agreement with the reported results.

Use of a NOEC

All the available data here are for 1 plant only, the tomato. It is explained in the risk assessment methodology in APVMA (2006) that where further refinement is required, a representative NOEC will be determined based on the range of data, and a Q-value of 1 or less will be considered acceptable. In the preliminary assessment, NOEC data from standard exposure by spraying of plants or soil from over 100 different test results were available, covering more than 10 species of crop plants. This allows a distribution approach to be taken and is very different to the situation here with limited vapour phase exposure studies. It is inappropriate to use a NOEC based on a single plant as a refinement of the risk assessment.

In any event, for the same reasons discussed above relating to EC25 data, DEWHA disagrees with the PSG NOEC calculations. The following table provides the PSG calculated

NOECs (based on the EC05) for the 4 experiments described in Breeze (1988), and that in Breeze and West (1987). In addition, those predicted by TOXCALC are given for comparison:

Table A2.4: Comparison of PSG and TOXCALC calculated EC05 Values

Experiment	PSG EC05 (TWA$_{24}$ µg 2,4-D ae/m^3)	EC05 (probit analysis) µg ae/m^3
1 (Breeze, 1988)	5.3	0.33 (6 h)
2 (Breeze, 1988)	14.8	0.22 (24 h)
3 (Breeze, 1988)	0.83	0.0016 (6 h)
4 (Breeze, 1988)	1.3	0.015 (24 h)
Breeze and West, 1987	9.1	0.88 (5 h)

The very sensitive levels predicted by TOXCALC in experiments 3 and 4 are considered unreliable, although with results only available for a single species, they could be used in a risk assessment to add certainty to the level of protection. Because there are only a few data points, and similar levels of effects were found over the narrow range of tested concentrations, the effect in experiments 3 and 4 is to make the dose/response curve very steep. The effects found at the tested concentrations ranged from 20 to 40% inhibition over the tested concentrations. By making the dose/response curve steep in this area has the result of elongating the tails at either end of the sensitivity distribution. This is demonstrated in the following two figures. Figure 3 shows the distribution from experiment 2 (24 h) where a wider range of concentrations were tested and a wider range of effects observed (19.5% inhibition at the lowest concentration to almost 50% at the highest), compared to Figure 4 from experiment 4 (24 h) where a narrower range of concentrations were tested and effects ranged from inhibition of around 28% at the lowest concentration to around 38% at the highest.

Figure 3

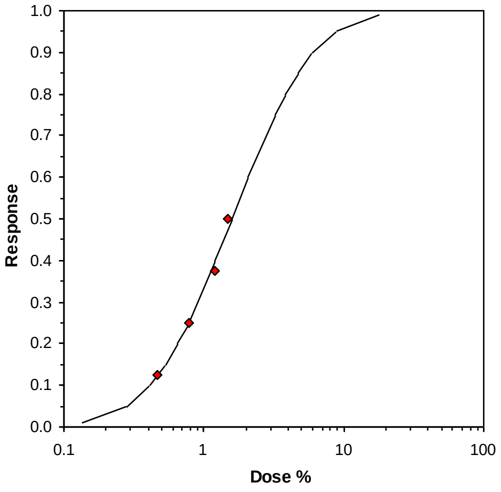
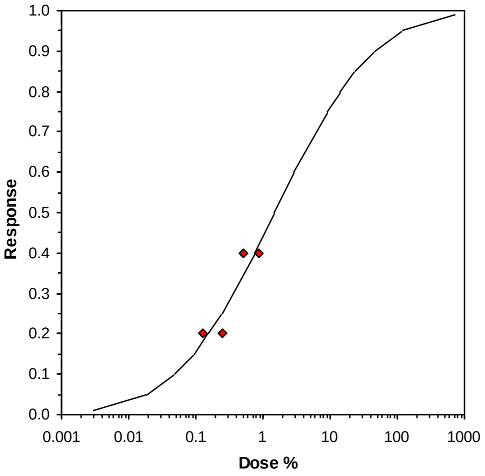


Figure 4



Breeze notes that there was a greater effect on the plants in experiments 3 and 4 for similar periods of exposure and concentrations of vapour. One possible reason he submits is that the air flow rates during exposure were greater in these experiments than in experiments 1 and 2 thereby not only exposing plants to a greater amount of herbicide but also limiting the opportunity for boundary layer formation.

While there is no way of actually determining the total herbicide available in the air column based on the monitoring data, it would appear more appropriate to use the 24 h concentration found from Experiment 2 as the data appear to fit the dose/response curve better over the range of results, and consequently, the problem of elongating the tail end of the distribution does not occur. Therefore, DEWHA considers a TWA_{24} EC05 of 0.22 µg/m^3 an appropriate surrogate for tomato plants for a 24 h exposure experiment.

In later work undertaken on determining the plant end-point for use in the risk assessment of 2,4-D acid/salts and LVE, DEWHA agreed to use the EC10 as an indication of the NOEC due to the high level of variability that can occur in plant toxicity tests. It is difficult to extend such a position yet in this case as there is only one species with results, and without a suitable data set, the EC05 should remain as representative of the NOEC for this exercise.

Risk Assessment

EC25 data, Acceptable risk quotient of 0.1 or less

The results from the monitoring trial based on two separate applications of 560 g ae/ha to 70 ha plots have been discussed above. DEWHA had presented these results in terms of both TWA_{24} concentrations (based on the samplers running for 24 h periods), and condensing these values into a smaller time period (12 and 8 h) based on the assumption that the volatilization will occur during the higher temperatures found during the day with very little movement during the night.

The highest levels of 2,4-D HVE found in a 24 h sampling period **outside** the field of application occurred 200 m away from the edge of the field during the second 24 h period (exposure must therefore have been through volatilization movement and not droplet drift) at a level of 0.343 µg ae/m^3. However, they appeared to be uncorrected for extraction efficiency, which was around 75%. Therefore, the actual TWA_{24} was estimated to be around 0.46 µg ae/m^3. Based on the TWA_{24} EC25 of 0.62 (experiment 2, Breeze, 1988), the Q-value is therefore calculated to be 0.74, indicative of an unacceptable risk.

At 500 m off-field, maximum TWA_{24} exposure concentrations were 0.23 and 0.16 µg/m^3 (corrected) in the second trial on 0-24 and 24-48 h sampling respectively. These exposure concentrations correspond to Q-values of 0.37 and 0.25 respectively, both indicative of a potential risk.

During the second 24 h period of the second trial, a TWA_{24} of 0.045 µg ae/m^3 (corrected) was recorded in a sampler 2000 m from the edge of the field. This results in a Q-value of 0.07, indicating an acceptable risk at 2000 m based on local exposure.

DEWHA believes this level of risk assessment is preliminary due to the lack of reliable ecotoxicity data to plants exposed through the gas phase. However, these preliminary results in themseLVE suggest a potential risk from off target movement resulting from vapour movement of 2,4-D HVE exists.

NOEC data, Acceptable risk quotient of 1.0 or less

It is certainly not appropriate to refine this risk assessment based on current data. The PSG refined their risk assessment by considering a tomato NOEC and a risk quotient of 1 or less being considered acceptable. DEWHA does not support the PSG generated NOEC.

Based on a NOEC (using the TOXCALC generated EC05 from the 2nd experiment in Breeze, 1988) of 0.22 µg ae/m^3, and based on the 200, 500 and 2000 m maximum TWA_{24} exposure values from the monitoring trial (corrected and defined above), Q values of 2.1, 1.0 and 0.2 respectively, again, only indicating an acceptable risk at 2000 m from the field of application.

Risk assessment based on other available endpoints

As noted in the discussion below Table A2.4 the 24 h EC05 calculated from experiment 4 is possibly unreliable due to the very narrow concentration range at which (significant) effects occurred, thereby elongating the tails of the sensitivity distribution. However, it is also noted that there is only 1 test species, and consequently, the use of the calculated NOEC (0.015 µg ae/m^3) could be justified to increase confidence in the risk assessment outcome. Using this 24 h EC05 value, Q values of 31 (200 m), 15.3 (500 m), and 3.0 (2000 m) are all indicative of an unacceptable risk out to at least 2 km from the field of application.

Risk assessment based on higher levels during daylight hours

In assessing the field monitoring data above, DEWHA hypothesised that the majority of volatilisation resulting in detections would occur during the daytime hours, and distributed the mean 24 h values over a 12 or 8 hour period. EC25 values generated by TOXCALC for the Breeze (1988) experiments with 6 h exposures were 1.19 and 0.18 µg/m^3 for experiments 1 and 3 respectively (Table A2.3), and in both experiments, around 20% effects were found at the lowest test concentrations of 0.67 µg/m^3 (experiment 1) and 0.12 µg/m^3 (experiment 3). DEWHA had predicted 8 h exposure concentrations could theoretically be 0.6-2.4 µg/m^3 at 200 m, 0.6-0.9 µg/m^3 at 500 m and 0.05-0.3 µg/m^3 at 2000 m. The following table demonstrates the range of Q-values based on the 6 h exposure experiments from Breeze (1988) with these 8 h predicted exposure concentrations:

Table A2.5: Risk Quotients Using Predicted 8 h Exposure Concentrations

Distance	Experiment (Breeze, 1988)	8 h exposure Min	8 h exposure Max	6 h EC25	Q Min	Q Max
200 m	1	0.6	2.4	1.19	0.50	2.02
	3	0.6	2.4	0.18	3.33	13.3
500 m	1	0.6	0.9	1.19	0.50	0.76
	3	0.6	0.9	0.18	3.33	5.00
2000 m	1	0.05	0.3	1.19	0.04	0.25
	3	0.05	0.3	0.18	0.28	1.67

These values show a potential to unacceptable risk in all scenarios except at 2000 m if the EC25 from experiment 1 is used.

As a further comment, if standard risk assessment methodology is to be applied, an additional assessment factor would be added to these EC25 values as there is such a small data set encompassing only one species. In that event, the Q values would be increased proportionately with the assessment factor. Further, the exposure estimates would be proportionately increased to allow for maximum label use rates, which are higher than the 560 g ae/ha applied in the HVE monitoring trial. Therefore, Q-values would again increase.

Conclusion from the preliminary risk assessment

The above preliminary risk assessment, undertaken in a number of different ways with different end points, all point to a potentially unacceptable risk even from this local monitoring trial. It could therefore reasonably be expected that the proposed regional trial would only exacerbate this situation, due to the expected much higher levels in situations of significant regional use, and would only serve to confirm the conclusion of an unacceptable risk.

The main deficiencies in the present assessment are the use of end points for vapour phase toxicity based on a single species (although with a spread of results for a relatively sensitive plant), and the need to extrapolate levels from 24 hour time weighted averages to those for shorter periods that might be expected more accurately reflect those during daylight hours when volatility will be highest.

The department considers that on the available evidence, the current risks from the use of 2,4-D HVE cannot be mitigated and it is likely that any regional trials, undertaken in accordance with the agreed protocols, will provide additional data confirming this view.

References:

APVMA, 2006. The reconsideration of approvals of the active constituent 2,4-D, registration of products containing 2,4-D and their associated labels. Preliminary Review Findings (Environment) Part 1: 2,4-D Esters. Volume 2: Technical Report. Australian Pesticides and Veterinary Medicines Authority.

Breeze V and West C, 1987. Long- and Short-term Effects of Vapour on the Herbicide 2,4-D butyl on the Growth of Tomato Plants. *Weed Research*, 1987, Vol 27 pp 13-21.

Breeze V, 1988. Effects of Low Concentrations of Vapour of the Phenoxyalkanoic Herbicide 2,4-D-Butyl on Growth of Tomato Plants. *Pesticide Science*, 1988 Vol 22 pp 251-261

Breeze V, 1990. Uptake by Tomato Plants of the Herbicide ^{14}C-2,4-D-Butyl in the Vapour Phase. *Pesticide Science*, 1990 Vol 29 pp 9-18

Hay P, 2008. 2,4-D HVE Air Monitoring Study, September 2008. 2,4-D Permit Support Group.

ATTACHMENT : ISSUES FOR FURTHER TESTING (IF FURTHER WORK IS TO BE DONE)

If further work is to be done, DEWHA considers the below to be essential to provide meaningful results in support a more robust risk assessment.

1. The regional monitoring will only be relevant in “normal” use seasons, in order to allow a better understanding of the likely atmospheric levels that could be encountered. It is imperative that this trial only be carried out under these conditions.

2. Daytime exposure concentrations will be much higher than the TWA_{24} concentrations and this should also be addressed in any further regional monitoring program. We note that based on the latest protocol the sampling periods for the regional monitoring stations are unresolved, even though it was indicated in October 2007 that 12 hourly daily sampling would be collected. Any sampling must be able to differentiate between daytime and night-time levels.

Alternatively, this could be done separately through combined use of samplers with a different sampling period, but occurring within the same field of application. For example, within a field where application occurs, three sampling stations could be erected, one sampling 0-6 h through the warmest time of the day, one sampling 0-12 h through the warmest part of the day, and one providing a 24 h sample. These can then be directly compared with each other, and also used in a comparative way with the results obtained in the HVE monitoring trial described above, to predict local levels outside the field of application. This would also provide valuable results to compare with detected levels found in the wider regional monitoring program. Such a sampling regime should be undertaken in several different fields (maybe from 5 to ten) as the current study has demonstrated the potential variability in results.

While this will add an additional requirement to the regional monitoring protocol, it is considered necessary, and we note again that 12 h sampling periods were part of the final January 2008 protocol agreed by industry. These were not done in the current study.

3. The preliminary risk assessment carried out by DEWHA above demonstrates the need for vapour phase exposure toxicity testing to a range of species given the variability found even with one species. This is considered essential but testing should informed by the above data on peak levels and differences in these during daylight hours and night time.

Limited evidence from Breeze (1988), indicates that, where exposure concentrations are similar, the level of effects will be similar whether exposure lasts for a few hours (6) or longer (24). For example, Experiment 1 and 2, 6 and 24 h EC25 = 1.19 $\mu g/m^3$ and 0.62 $\mu g/m^3$ respectively, and in experiment 3 and 4, 6 and 24 h EC25 of 0.18 and 0.2 $\mu g/m^3$ respectively. What cannot be ascertained is whether exposure for a shorter period at higher levels will lead to different effects than if that level of chemical is spread over a longer period of time. For example, would exposure to 1 $\mu g/m^3$ over 24 hours result in the same level of effects as 3 $\mu g/m^3$ exposed over 8 hours? This is an issue that must be addressed with generation of reliable ecotoxicity data.

APPENDIX 1: TOXCALC Results for Vapour Phase Ecotoxicity Tests

Experiment 1, Breeze (1988)

Conc-%	Mean	N-Mean	Resp	Not Resp	Total	N	Fisher's Exact P	1-Tailed Critical
B-Control	0.9615	1.0000	0.28	7	7.28	1		
0.67	0.8242	0.8571	1.28	6	7.28	1	0.5000	0.0500
1.2	0.8242	0.8571	1.28	6	7.28	1	0.5000	0.0500
1.9	0.6868	0.7143	2.28	5	7.28	1	0.2308	0.0500
2.4	0.5495	0.5714	3.28	4	7.28	1	0.0962	0.0500

Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	TU
Fisher's Exact Test	2.4	>2.4		41.666667
Treatments vs B-Control				

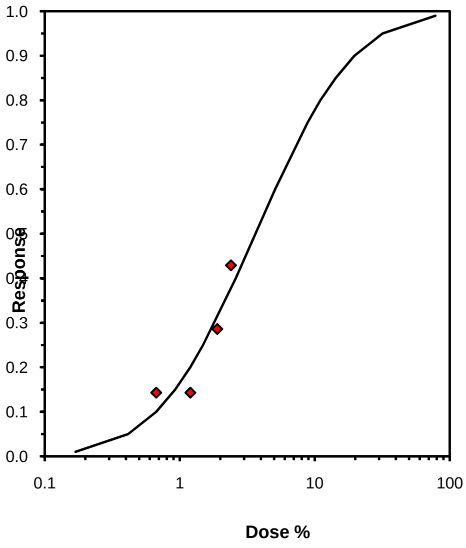
Conc-%	1
B-Control	1.0000
0.67	0.8283
1.2	0.8269
1.9	0.7047
2.4	0.6154

			Transform: Arcsin Square Root					Number	Total
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	N	Resp	Number
B-Control	1.0000	1.0000	1.3844	1.3844	1.3844	0.000	1	0	7
0.67	0.8283	0.8283	1.1435	1.1435	1.1435	0.000	1	1	7
1.2	0.8269	0.8269	1.1417	1.1417	1.1417	0.000	1	1	7
1.9	0.7047	0.7047	0.9963	0.9963	0.9963	0.000	1	2	7
2.4	0.6154	0.6154	0.9018	0.9018	0.9018	0.000	1	3	7

Auxiliary Tests	Statistic	Critical	Skew	Kurt
Normality of the data set cannot be confirmed				
Equality of variance cannot be confirmed				

					Maximum Likelihood-Probit						
Parameter	Value	SE	95% Fiducial Limits		Control	Chi-Sq	Critical	P-value	Mu	Sigma	Iter
Slope	1.7453893	1.5783487	-1.348174	4.8389527	0.0384615	0.3210639	5.9914765	0.85	0.5605206	0.5729381	3
Intercept	4.0216734	0.4686533	3.1031128	4.940234							
TSCR	0.0415959	0.0751425	-0.105683	0.1888753							

Point	Probits	%	95% Fiducial Limits
EC01	2.674	0.1689146	
EC05	3.355	0.41507	
EC10	3.718	0.6703026	
EC15	3.964	0.9262078	
EC20	4.158	1.197633	
EC25	4.326	1.4930684	
EC40	4.747	2.6023661	
EC50	5.000	3.6351354	
EC60	5.253	5.0777676	
EC75	5.674	8.8503704	
EC80	5.842	11.033606	
EC85	6.036	14.267004	
EC90	6.282	19.713793	
EC95	6.645	31.836096	
EC99	7.326	78.230135	



Experiment 2, Breeze (1988)

Conc-%	1
B-Control	1.0000
0.46	0.8249
0.78	0.7707
1.2	0.6671
1.5	0.5117

Conc-%	Mean	N-Mean	Resp	Not Resp	Total	N	Fisher's Exact P	1-Tailed Critical
B-Control	0.9864	1.0000	0.11	8	8.11	1		
0.46	0.8631	0.8750	1.11	7	8.11	1	0.5000	0.0500
0.78	0.7398	0.7500	2.11	6	8.11	1	0.2333	0.0500
1.2	0.6165	0.6250	3.11	5	8.11	1	0.1000	0.0500
*1.5	0.4932	0.5000	4.11	4	8.11	1	0.0385	0.0500

Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	TU
Fisher's Exact Test	1.2	1.5	1.3416408	83.333333
Treatments vs B-Control				

Conc-%	1
B-Control	1.0000
0.46	0.8249
0.78	0.7707
1.2	0.6671
1.5	0.5117

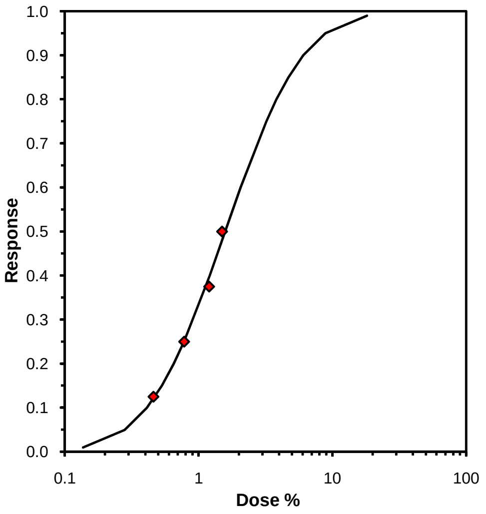
			Transform: Arcsin Square Root					Number	Total
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	N	Resp	Number
B-Control	1.0000	1.0000	1.3943	1.3943	1.3943	0.000	1	0	8
0.46	0.8249	0.8249	1.1391	1.1391	1.1391	0.000	1	1	8
0.78	0.7707	0.7707	1.0714	1.0714	1.0714	0.000	1	2	8
1.2	0.6671	0.6671	0.9558	0.9558	0.9558	0.000	1	3	8
1.5	0.5117	0.5117	0.7971	0.7971	0.7971	0.000	1	4	8

Auxiliary Tests	Statistic	Critical	Skew	Kurt
Normality of the data set cannot be confirmed				
Equality of variance cannot be confirmed				

Maximum Likelihood-Probit

Parameter	Value	SE	95% Fiducial Limits		Control	Chi-Sq	Critical	P-value	Mu	Sigma	Iter
Slope	2.1937807	1.3730713	-0.497439	4.8850004	0.0135635	0.0293122	5.9914765	0.99	0.1977986	0.4558341	3
Intercept	4.5660734	0.2600999	4.0562776	5.0758691							
TSCR	0.0137408	0.041116	-0.066847	0.0943281							

Point	Probits	%	95% Fiducial Limits
EC01	2.674	0.137205	
EC05	3.355	0.2805551	
EC10	3.718	0.4107936	
EC15	3.964	0.5313209	
EC20	4.158	0.6518669	
EC25	4.326	0.7768607	
EC40	4.747	1.2086883	
EC50	5.000	1.5768797	
EC60	5.253	2.0572299	
EC75	5.674	3.2007663	
EC80	5.842	3.8145052	
EC85	6.036	4.6799396	
EC90	6.282	6.0530375	
EC95	6.645	8.8629611	
EC99	7.326	18.122886	



Experiment 3, Breeze (1988)

Conc-%	1
B-Control	1.0000
0.12	0.8095
0.24	0.7379
0.47	0.7104
0.82	0.6751

Conc-%	Mean	N-Mean	Resp	Not Resp	Total	N	Fisher's Exact P	1-Tailed Critical
B-Control	0.9912	1.0000	0.08	9	9.08	1		
0.12	0.7709	0.7778	2.08	7	9.08	1	0.2353	0.0500
0.24	0.7709	0.7778	2.08	7	9.08	1	0.2353	0.0500
0.47	0.6608	0.6667	3.08	6	9.08	1	0.1029	0.0500
0.82	0.6608	0.6667	3.08	6	9.08	1	0.1029	0.0500

Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	TU
Fisher's Exact Test	0.82	>0.82		121.95122
Treatments vs B-Control				

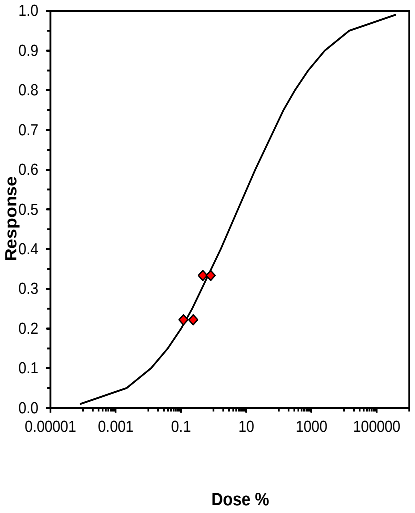
Conc-%	1
B-Control	1.0000
0.12	0.8095
0.24	0.7379
0.47	0.7104
0.82	0.6751

			Transform: Arcsin Square Root						
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	N	Number Resp	Total Number
B-Control	1.0000	1.0000	1.4041	1.4041	1.4041	0.000	1	0	9
0.12	0.8095	0.8095	1.1191	1.1191	1.1191	0.000	1	2	9
0.24	0.7379	0.7379	1.0333	1.0333	1.0333	0.000	1	2	9
0.47	0.7104	0.7104	1.0025	1.0025	1.0025	0.000	1	3	9
0.82	0.6751	0.6751	0.9643	0.9643	0.9643	0.000	1	3	9

Auxiliary Tests	Statistic	Critical	Skew	Kurt
Normality of the data set cannot be confirmed				
Equality of variance cannot be confirmed				

					Maximum Likelihood-Probit						
Parameter	Value	SE	95% Fiducial Limits		Control	Chi-Sq	Critical	P-value	Mu	Sigma	Iter
Slope	0.4820308	0.7303535	-0.949462	1.9135237	0.0088106	0.1016352	5.9914765	0.95	0.7482275	2.074556	3
Intercept	4.6393313	0.4143794	3.8271476	5.451515							
TSCR	0.0088181	0.031163	-0.052261	0.0698976							

Point	Probits	%	95% Fiducial Limits
EC01	2.674	8.358E-05	
EC05	3.355	0.0021671	
EC10	3.718	0.0122907	
EC15	3.964	0.0396359	
EC20	4.158	0.1005164	
EC25	4.326	0.223337	
EC40	4.747	1.6697242	
EC50	5.000	5.600509	
EC60	5.253	18.784964	
EC75	5.674	140.44111	
EC80	5.842	312.04552	
EC85	6.036	791.34672	
EC90	6.282	2551.9827	
EC95	6.645	14473.324	
EC99	7.326	375290.23	



Experiment 4 , Breeze (1988)

Conc-%	1
B-Control	1.0000
0.13	0.7207
0.25	0.7337
0.51	0.6164
0.88	0.6182

Conc-%	Mean	N-Mean	Resp	Not Resp	Total	N	Fisher's Exact P	1-Tailed Critical
B-Control	0.9311	1.0000	0.37	5	5.37	1		
0.13	0.7449	0.8000	1.37	4	5.37	1	0.5000	0.0500
0.25	0.7449	0.8000	1.37	4	5.37	1	0.5000	0.0500
0.51	0.5587	0.6000	2.37	3	5.37	1	0.2222	0.0500
0.88	0.5587	0.6000	2.37	3	5.37	1	0.2222	0.0500

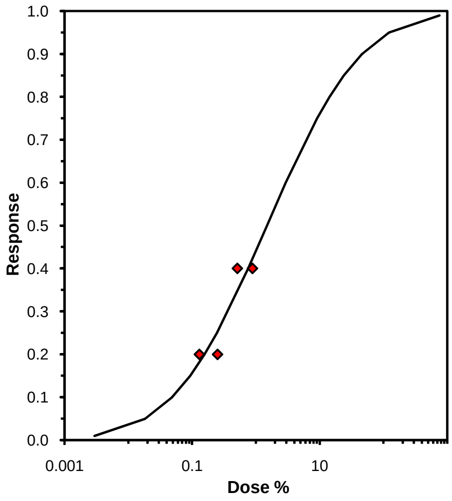
Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	TU
Fisher's Exact Test	0.88	>0.88		113.63636
Treatments vs B-Control				

			Transform: Arcsin Square Root					Number	Total
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	N	Resp	Number
B-Control	1.0000	1.0000	1.3533	1.3533	1.3533	0.000	1	0	5
0.13	0.7207	0.7207	1.0139	1.0139	1.0139	0.000	1	1	5
0.25	0.7337	0.7337	1.0286	1.0286	1.0286	0.000	1	1	5
0.51	0.6164	0.6164	0.9029	0.9029	0.9029	0.000	1	2	5
0.88	0.6182	0.6182	0.9048	0.9048	0.9048	0.000	1	2	5

Auxiliary Tests	Statistic	Critical	Skew	Kurt
Normality of the data set cannot be confirmed				
Equality of variance cannot be confirmed				

			Maximum Likelihood-Probit								
Parameter	Value	SE	95% Fiducial Limits		Control	Chi-Sq	Critical	P-value	Mu	Sigma	Iter
Slope	0.8603347	1.0894704	-1.275027	2.9956968	0.0689013	0.1392989	5.9914765	0.93	0.1736737	1.1623383	3
Intercept	4.8505825	0.6023618	3.6699534	6.0312116							
TSCR	0.069074	0.1133358	-0.153064	0.2912122							

Point	Probits	%	95% Fiducial Limits
EC01	2.674	0.002949	
EC05	3.355	0.0182725	
EC10	3.718	0.0483145	
EC15	3.964	0.0931081	
EC20	4.158	0.1568285	
EC25	4.326	0.2452948	
EC40	4.747	0.7571791	
EC50	5.000	1.4916732	
EC60	5.253	2.9386562	
EC75	5.674	9.0710789	
EC80	5.842	14.188037	
EC85	6.036	23.897915	
EC90	6.282	46.05428	
EC95	6.645	121.7727	
EC99	7.326	754.53148	



Breeze and West (1987)

B-Control
5.000
14.000
31.000
50.000

Conc-%	1
B-Control	1.0000
5	0.8229
14	0.5457
31	0.5171
50	0.3429

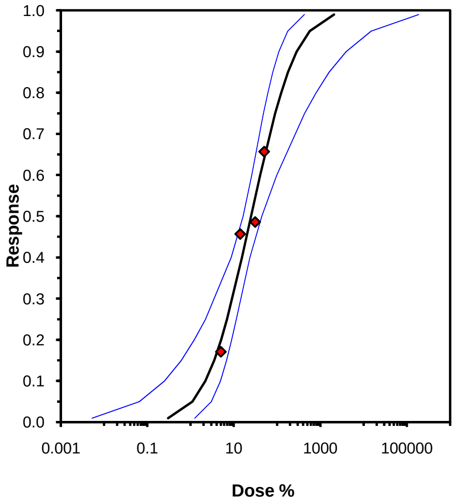
Conc-%	Mean	N-Mean	Resp	Not Resp	Total	N	Fisher's Exact P	1-Tailed Critical	Number Resp	Total Number
B-Control	1.0000	1.0000	0	35	35	1			0	35
*5	0.8286	0.8286	6	29	35	1	0.0124	0.0500	6	35
*14	0.5429	0.5429	16	19	35	1	0.0000	0.0500	16	35
*31	0.5143	0.5143	17	18	35	1	0.0000	0.0500	17	35
*50	0.3429	0.3429	23	12	35	1	0.0000	0.0500	23	35

Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	TU
Fisher's Exact Test	<5	5		
Treatments vs B-Control				

Maximum Likelihood-Probit

Parameter	Value	SE	95% Fiducial Limits		Control	Chi-Sq	Critical	P-value	Mu	Sigma	Iter
Slope	1.2144828	0.303388	0.6198423	1.8091233	0	1.5713908	5.9914765	0.46	1.3955333	0.8233958	3
Intercept	3.3051488	0.4064022	2.5086004	4.1016973							
TSCR											

Point	Probits	%	95% Fiducial Limits	
EC01	2.674	0.3020148	0.0053292	1.2372544
EC05	3.355	1.0994304	0.0658176	2.998786
EC10	3.718	2.1893195	0.249327	4.8467971
EC15	3.964	3.4844837	0.6079704	6.7496973
EC20	4.158	5.0413392	1.2247546	8.8530709
EC25	4.326	6.9208791	2.2104974	11.289405
EC40	4.747	15.379009	8.7092885	23.410022
EC50	5.000	24.861841	16.350576	44.118261
EC60	5.253	40.191873	26.032209	98.040941
EC75	5.674	89.311065	48.632756	428.75865
EC80	5.842	122.60852	61.192392	784.26439
EC85	6.036	177.38962	79.534016	1594.3491
EC90	6.282	282.33017	110.03711	3913.2643
EC95	6.645	562.21016	176.94004	14900.099
EC99	7.326	2046.6263	427.09787	184778.5



Attachment 6

DSEWPaC's assessment of the 2,4-D HVE REGIONAL MONITORING STUDY. FEBRUARY-MARCH 2009

Introduction

DEWHA initially requested regional monitoring be undertaken in the 2007-08 summer period. At that time, we stressed any monitoring should be tied to accurate records of use (both application rates and volumes). It was our desire at that stage to include sampling stations (minimum of 4) within the regional area of application, with samplers collecting both weekly and 12 h daily samples. This was considered important to try and correlate peak exposure concentrations with weekly samples as are often found in the literature.

The 2007-08 permit period did not address the regional requirements because sales volumes were too low during this summer to undertake any meaningful monitoring on this scale. Consequently, this was re-addressed under the 2008-09 permit.

DEWHA received the draft protocol for regional monitoring late in the season (6 February 2009), and while we were satisfied with the technical aspects of this protocol relating to issues such as personnel, sampling technology method, sample handling, chemical analyses and data analyses, we expressed concerns about the usefulness of the data that may be generated. Particularly, the regional study could only be of value if a "normal use" season was anticipated. We were assured that the region chosen would represent normal use for that region.

At that time, DEWHA also reinforced the need for a supplementary study that was originally part of our request for the 2007-08 monitoring requirements, but not able to be undertaken. This study was to generate data to allow us to compare 24 h samples with smaller exposure periods (8 h and 12 h), and would allow better guidance on future plant toxicity testing.

A revised protocol was received from Nufarm later in February 2009 and it was noted one of the two proposed regions no longer met requirements and a second region was being investigated. DEWHA considered that it was getting late in the season, and expressed concern that we would not obtain the necessary data from a single region. We suggested, given the lateness of the season, it may be more appropriate for Nufarm to focus on the supplementary study and provide us with the additional data we require for a local exposure assessment.

Nonetheless, Nufarm continued with the regional monitoring based on a single region, and in tandem, undertook the required supplementary study.

Study Design

The initial protocol proposed monitoring two zones on the south coast of Western Australia. One zone was centred on an axis from Salmon Gums Research Station in the north to Esperance in the south. The second zone proposed was south to the coast from a line between Newdegate to Lake King. The use of these zones for monitoring was conditional on anticipated 2,4-D HVE use. Use of 2,4-D HVE in the zone during the monitoring period should be consistent with usage in a “normal” season prior to the suspension of 2,4-D HVE.

The conditions for 2,4-D HVE use were considered to be met in the Esperance - Salmon Gums region and air sampling stations were established. However, due to very limited anticipated use of 2,4-D HVE in the Newdegate – Lake King region, monitoring was not considered appropriate.

The locations for the sampling stations in the Esperance - Salmon Ponds region are shown in Table 1.

Table 1: Sampling Locations for Regional Air Monitoring Study

Property	Coordinates	Notes
Salmon Gums Station	121.6633^{o} E 33.0374^{o} S	weekly & 12 h/day sampling Nufarm portable weather station
Mount Ridley Station	121.9413^{o}E 33.264^{o}S	weekly & 12 h/day sampling Nufarm portable weather station
Esperance Research Station Farm	121.7834^{o}E 33.6054^{o}S	weekly sampling only Ag Dept weather station approx 1 km from site

Sampling pumps were orientated in the direction of the expected prevailing winds, with the opening 1.55 m above ground level. At the beginning of each week, each pump was calibrated to the nominal flow.

Sampling continued for a calendar month from 24 February 2009. At the Mount Ridley site, for the 12 h samples, pumps were generally turned on between 7:00 and 8:00 am. The average sample collection period was 10.8 hours. At the Salmon Gums site, the pumps were generally switched on between 7:00 and 8:00 am. The average sample collection period was 11.7 hours.

Analysis

The limits of detection in terms of concentration of 2,4-D HVE in air at the nominal air sampling rates and collection periods were determined to be 0.0006 µg/m^3 for 12 h samples and 0.00033 µg/m^3 for weekly (168 h) samples. The results of sorbent tube analysis, including quality control samples, were provided in appendices to the main report, and are considered further below.

When analysing sample tubes for 2,4-D esters, 3 mL of 5% diethyl ether/hexane was added to the front section, sonicated for 1 hour and the extract maintained at room temperature for 15 minutes. Analysis was conducted by GC-MS. Analysis of the back section was conducted only if sample results for the corresponding front section were high (the definition of “high” residues was not provided). It is noted that reported sample results were not corrected for extraction efficiency.

Findings:

Hay (2009a) reports that no 2,4-D HVE was detected in weekly samples. However, the data presented in Hay (2009b) indicates detections in the weekly samples at Mt. Ridley and Salmon Gums. The samples at the Esperance Downs Research Station were only collected weekly. Over the period 24 February 2009 to 17 March 2009, no 2,4-D HVE was found in any of these weekly samples. However, 2,4-D HVE was found in both weekly and 12 h samples from the Mt Ridley and Salmon Gums sampling stations, and in all cases, was present as 2,4-D Ethyl Ester.

Quality control/Extraction efficiency

Field blanks and spikes as well as laboratory blanks and controls were prepared and analysed as part of the study. Results for field spikes were obtained by spiking sample tubes that had been taken into the field with a known amount of 2,4-D HVE and extracting in the same manner as the samples. The field spikes analysed with the Mount Ridley sample tubes showed recovery of 64% while the field spikes analysed with the Salmon Gums sample tubes showed recovery of 70%.

Results of 12 h sample

The following tables show the findings for the Mount Ridley and Salmon Gums 12 h sample tubes. All discussion of concentrations found during this trial are in terms of concentrations corrected for recovery. Bolded values indicate those where levels are reported in the raw data (Hay, 2009b), but not in the main report (Hay, 2009a).

Table 2: Mount Ridley, 12 h samples.

Date	Pump	Total flow (m^3) (Hay, 2009a)	µg/sorbent (Hay, 2009b)	µg/m^3	Corrected for recovery
24-02-2009	4	2.41	0.089	0.0369	0.0577
25-02-2009	4	2.89	0.019	0.0066	0.0103
26-02-2009	4	2.18	0.004	0.0018	0.0029
27-02-2009	4	2.18	0.008	0.0037	0.0057
28-02-2009	4	2.41	<LOD	-	-
01-03-2009	4	2.17	<LOD	-	-
02-03-2009	4	2.1	<LOD	-	-
03-03-2009	4	1.95	0.004	0.0021	0.0032
04-03-2009	4	2.32	<LOD	-	-
05-03-2009	4	2.49	nd		
06-03-2009	4	2.25	0.005	0.0022	0.0035
07-03-2009	4	1.93	0.005	0.0026	0.0040
08-03-2009	4	2.42	<LOD	-	-
09-03-2009	4	2.26	0.006	0.0027	0.0041
10-03-2009	4	1.86	<LOD	-	-
11-03-2009	4	2.16	<LOD	-	-
12-03-2009	4	2.53	<LOD	-	-
13-03-2009	4	2.37	<LOD	-	-
14-03-2009	4	2.36	<LOD	-	-
15-03-2009	4	2.27	<LOD	-	-
16-03-2009	4	2.22	<LOD	-	-
17-03-2009	4	2.04	<LOD	-	-
18-03-2009	4	2.41	<LOD	-	-
19-03-2009	4	2.24	<LOD	-	-
20-03-2009	4	2.31	0.005	0.0022	0.0034
21-03-2009	4	2.31	<LOD	-	-
22-03-2009	4	2.27	<LOD	-	-
23-03-2009	4	2.32	**0.002**	0.0009	0.0013

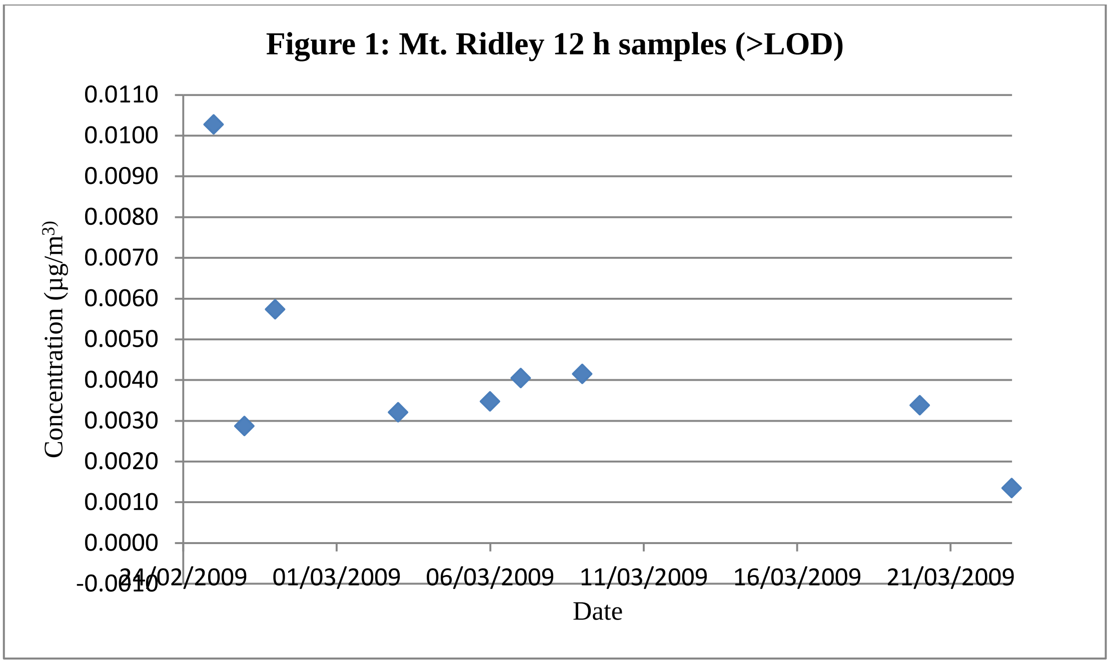
Table 3: Salmon Gums, 12 h samples

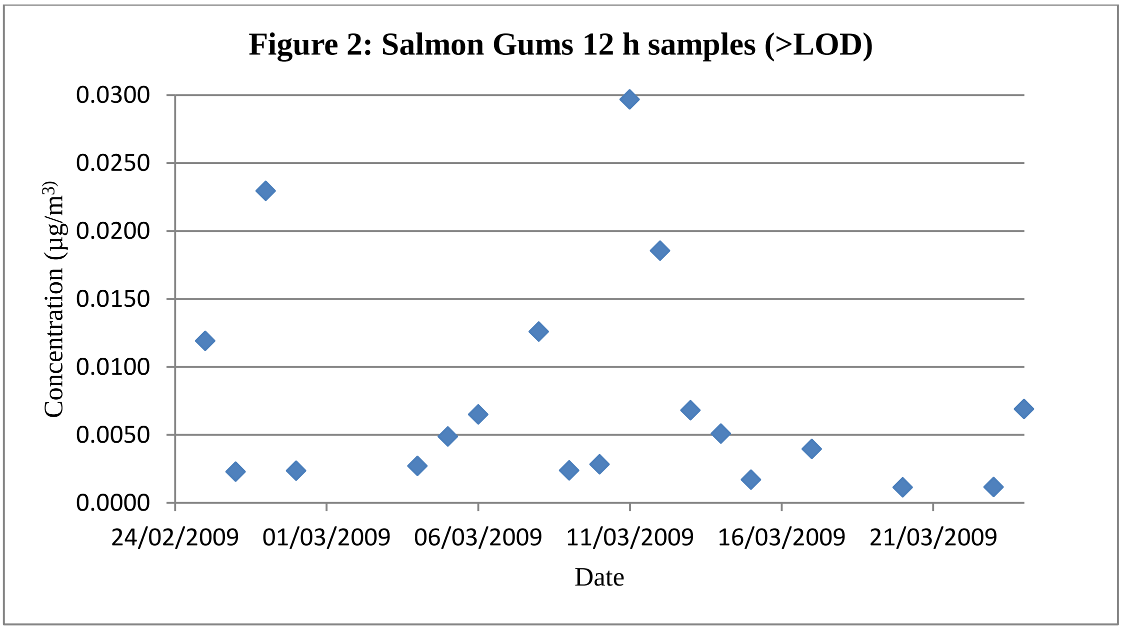
Date	Pump	Total flow (m^3) (Hay, 2009a)	µg/sorbent (Hay, 2009b)	µg/m^3	Corrected for recovery
25-02-2009	8	2.28	0.019	0.0083	0.0119
26-02-2009	8	2.49	0.004	0.0016	0.0023
27-02-2009	8	2.18	0.035	0.0161	0.0229
28-02-2009	8	2.43	0.004	0.0016	0.0024
01-03-2009	8	2.42	<LOD	-	-
02-03-2009	8	2.33	<LOD	-	-
03-03-2009	8	2.42	<LOD	-	-
04-03-2009	8	2.64	0.005	0.0019	0.0027
05-03-2009	8	2.64	0.009	0.0034	0.0049
06-03-2009	8	2.64	0.012	0.0045	0.0065
08-03-2009	8	2.61	**0.023**	0.0088	0.0126
09-03-2009	8	2.39	0.004	0.0017	0.0024
10-03-2009	8	2.52	0.005	0.0020	0.0028
11-03-2009	8	2.36	0.049	0.0208	0.0297
12-03-2009	8	2.31	0.03	0.0130	0.0186
13-03-2009	8	3.15	0.015	0.0048	0.0068
14-03-2009	8	2.52	0.009	0.0036	0.0051
15-03-2009	8	2.52	0.003	0.0012	0.0017
16-03-2009	8	2.31	<LOD	-	-
17-03-2009	8	2.52	**0.007**	0.0028	0.0040
18-03-2009	8	2.78	<LOD	-	-
19-03-2009	8	2.31	<LOD	-	-
20-03-2009	8	2.49	**0.002**	0.0008	0.0011
21-03-2009	8	2.42	<LOD	-	-
22-03-2009	8	2.36	<LOD	-	-
23-02-2009	8	2.45	0.002	0.0008	0.0012
24-02-2009	**8**	**2.48**	**0.012**	0.0048	0.0069

Discussion of 12 h Samples

The highest level detected was 0.058 µg/m^3, and this was found at the Mt. Ridley site on 24 February 2009. However, spray records indicate the paddock to the north east of this was sprayed the day before, and winds were moving into the sampler over the period of sampling. Therefore, this reading is considered more indicative of a local exposure situation than regional, and will not be considered in further discussion.

Discounting this value, Fig 1 and Fig 2 below show the detections found in 12 h samples from Mt. Ridley and Salmon Gums respectively:





2,4-D EE was detected more frequently and at higher concentrations at the Salmon Gums site compared to the Mt. Ridley site. The following table summarises these detections:

Table 4: Summary of detections of 2,4-D EE during the Regional Monitoring Trial

	Salmon Gums	Mt. Ridley
Number of 12 h samples	27	27
Detections >LOD	19	9
Percent of samples >LOD	70.4	33.3
Where detected		
Maximum (µg/m^3)	0.03	0.01
Minimum (µg/m^3)	0.0011	0.0013

Interpretation of 12 h samples

It is useful to consider the spatial scale of the regional trial. The GPS coordinates of the sampling stations as per Hay (2009a) are shown above in Table 1.

Using these coordinates, the distance between the three stations has been estimated from Vincenty's Formulae, Inverse Method, as provided on the Geoscience Australia web-site. The following matrix provides approximate distances between the sampling points:

	Salmon Gums	Mt. Ridley
Esperance Downs Research Station	64 km	40.5 km
Salmon Gums		36 km

While these distances give an idea of the spatial scale of the monitoring trial, it is also important to have an idea of the actual use of HVE over the trial period including locations of application and volumes of use. To this end, spray records provide an important mechanism to better interpret the data. Unfortunately, the spray records provided in the report are sparse with records provided for only 4 growers during the monitoring period, with a total of 1302 Ha treated, and application dates ranging from 25 February 2009 to 26 March 2009. In addition, spray records were provided for another grower where around 350 ha were treated, but this occurred on 11 January 2009, so was well outside the monitoring sampling period. Records were also provided for the treatment of paddock R1 (366 ha) on 23 February, but this paddock was the one located NE of the Mount Ridley sampling station, so the values obtained at this station on 24 February are considered more representative of local exposure and have not been taken into account any further in this regional assessment.

For the spray records provided within the sampling period, some 656 ha were treated in Gibson, which is slightly north west of the Esperance Downs Research Station, over the period 23-26 March 2009. No other spray records are available for this period, and sampling ceased on 24 March, so much of the spraying activity at this farm would not have been captured in the sampling anyway. At Salmon Gums, on 24 March, around 0.007 µg/m^3, which is the only sample that could coincide with spraying at this block. If this spraying (undertaken on 23 March) was the cause of the Salmon Gums detection on 24 March, then the vapour had to have travelled over 60 km, but without a better characterisation of spray operations in the region during the sampling time, it is not possible to make any firm conclusions.

GPS coordinates were only provided from one grower, who treated 72 ha on 27 February 2009, and a further 68 ha on 4 March 2009. These paddocks are slightly south east of the Esperance Downs Research Station based on GPS measurements, and based on wind direction data provided, the winds would seldom have been moving towards either the Salmon Gums or Mt. Ridley sampling stations. For the days immediately following these spraying operations, no 2,4-D EE was found at the Mt. Ridley sampling point (some 52 km away from the spray site). At the Salmon Gums station, on 28 February and 5 March 2009, 12 h samples showed concentrations of 0.0024 and 0.0049 µg/m^3. This station is around 88 km from the spray sites, and it is highly unlikely the detections were the result of these particular spray operations. Again, without better characterisation of spray operations in the region during the sampling time, it is not possible to make any firm conclusions.

The only other spray records available for the monitoring period include spraying of 200 ha on 25 February, and spraying on 306 ha over the period 7-9 March 2009. However, the actual location is not clear so no meaningful analysis of these operations can be undertaken.

Wind data

Wind data (direction and speed) over the sampling period were provided. DEWHA has constructed wind roses for the Salmon Gums and Mount Ridley sites to better understand the wind patterns during the study. Wind roses were constructed using WRPlot View software, v 5.9, Lakes Environmental (http://www.weblakes.com/).

Figure 3: Salmon Gums Wind Rose, 10 March to 24 March, 2009

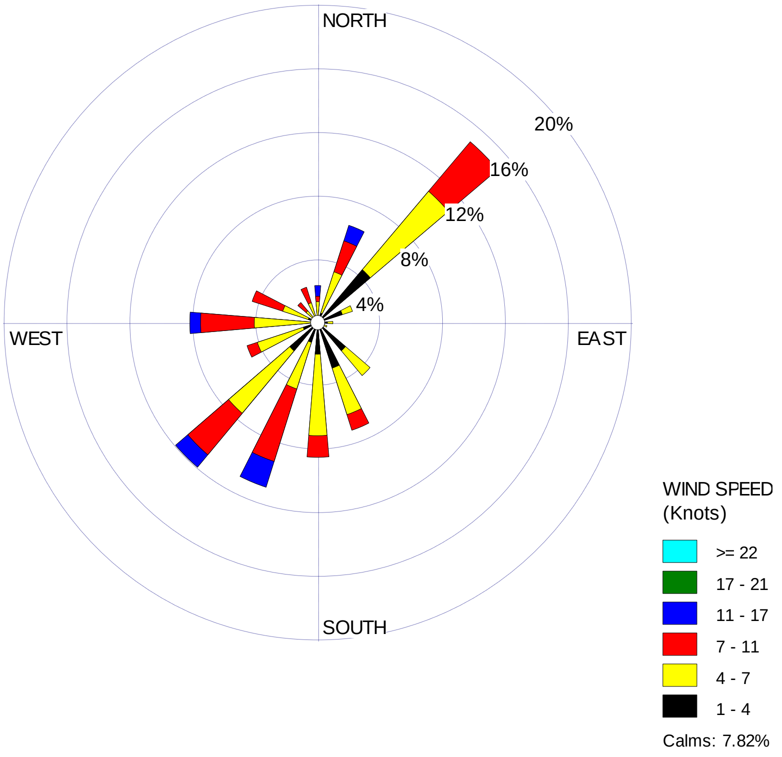
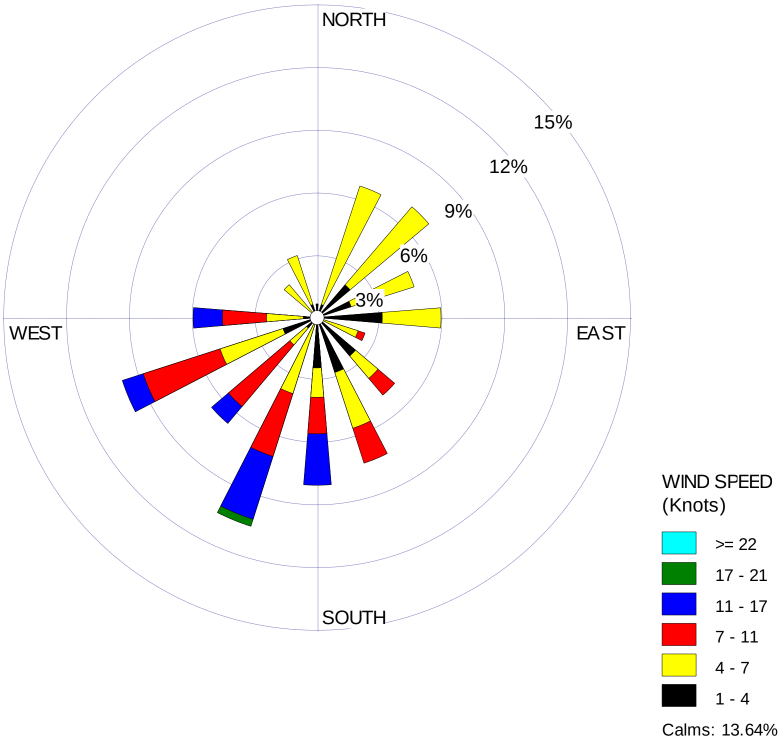


Figure 4: Mount Ridley Wind Rose, 12 March to 24 March 2009



Both wind roses indicate the main movement of wind from either the north east or south west quadrants. At Mount Ridley, wind was generally stronger, and more dominant from the south west than at Salmon Gums. As a general conclusion however, application occurring south east of the sampling stations would have a much lower likelihood of contributing to detections at the sampling stations.

To undertake any more meaningful analysis on the impacts of the wind data, much better spray application records during the sampling time frame are required.

Results of Weekly Samples

A combination of weekly and 12 h samples was considered necessary to try and relate literature reported values, that are often in terms of a weekly time weighted average concentration, with likely shorter term, or peak concentrations.

Table 5: Weekly Monitoring Results from Mount Ridley and Salmon Gums Sampling Stations

Mount Ridley, weekly samples

Date	Pump	Total flow (m^3) (Hay, 2009a)	µg/sorbent (Hay, 2009b)	µg/m^3	Corrected for recovery
24-02-2009	3	3.07	**0.01**	0.0033	0.0051
03-03-2009	3	2.98	**0.005**	0.0017	0.0026
03-03-2009	3	2.98	**0.005**	0.0017	0.0026
03-03-2009	3	2.98	**0.01**	0.0034	0.0052
03-03-2009	3	2.98	<LOD	-	-
10-03-2009	3	3.05	<LOD	-	-
10-03-2009	3	3.05	<LOD	-	-
17-03-2009	3	3.1	<LOD	-	-

Salmon Gums, weekly samples

24-02-2009	9	3.06	**0.033**	0.0108	0.0154
24-02-2009	9	3.06	**0.004**	0.0013	0.0019
24-02-2009	9	3.06	**0.011**	0.0036	0.0051
24-02-2009	9	3.06	<LOD	-	-
03-03-2009	9	3.15	**0.01**	0.0032	0.0045
10-03-2009	9	2.91	**0.13**	0.0447	0.0638
17-03-2009*	9	3	<LOD	-	-
24-03-2009	9	2.96	**0.006**	0.0020	0.0029

*reported in Hay (2009a), but no reference to sample analysis for this date in Hay (2009b).

For the Mount Ridley samples, it can be seen from Table 2 and Figure 1, that the most 12 h detections, and the higher levels found during the 12 h samples, occurred earlier in the sampling period (25 February to 11 March 2009). This is reflected somewhat in the weekly samples with the only weekly samples being able to quantify 2,4-D EE levels at the end of week 24 February and 3 March 2009. The other two weekly samples from Mt Ridley did not contain 2,4-D EE above the limit of detection.

By contrast, the 12 h Salmon Gums data indicate much more variable detections throughout the sampling period, and generally at levels higher than those found at Mt. Ridley (Table 3, Figure 2). Again, this seemed to be reflected in the weekly samples. From the raw data (Hay, 2009b), mean weekly concentrations were found for every sampling point, although there was not any reference to a weekly sample taken at 17 March 2009. Weekly concentrations ranged from 0.0019 to 0.0638 µg/m^3. The highest weekly concentration was found in the sample ending 10 March 2009, and this coincides with 12 h samples throughout this week showing consistent detections every day from 4 March to 10 March. During this week, the mean 12 h concentration was 0.0053 µg/m^3, so it is unclear why the weekly sample would some 12 times higher than this.

For the week 11-17 March 2009, the mean 12 h concentration was 0.0116 µg/m^3. However, there is no weekly sample in the raw data to compare this to. Hay (2009a) reports this weekly sample as being <LOD. However, this reference reports all weekly samples as <LOD, which is not supported by the raw data supplied, so it is difficult to draw any further conclusions.

Conclusions from Regional Monitoring Study

- The regional monitoring study was conducted for a single region situated between Esperance, Salmon Gums and Mount Ridley in Western Australia with three sampling stations within the region. Weekly samples from the southernmost part of the region, Esperance Downs Research Station, did not detect any 2,4-D HVE;
- Detections of 2,4 D ethyl ester (both 12 hourly and weekly) were found at the other two sites;
- 2,4-D ethyl ester was the only HVE found in samplers, and in the 12 h samples, was detected in Salmon Gums more frequently (70.4% of samples compared to 33% at Mt. Ridley), and at higher concentrations (0.001-0.03 µg/m^3 compared to 0.001-0.01 µg/m^3 at Mt. Ridley);
- Available wind data indicate wind moving predominantly from the south west in the test region;
- Prior to undertaking the regional scale trial, concern was expressed that results would only be meaningful if the trial were conducted under normal use. The report makes no comment on “normal use” in terms of areas sprayed during the trial period compared with historic use, or the total amounts of 2,4-D HVE used compared with historic amounts;
- Spray records are inadequate to properly interpret the sampled data with respect to areas of application or volumes of use, making it difficult to add any further context to the detected levels.

SUPPLEMENTARY STUDY

The supplementary study (Hay 2009c) was undertaken to determine variability in exposure concentrations with different lengths of sampling times (8, 12 and 24 h). An understanding of this will allow better direction in designing exposure periods and concentrations for non-target plant toxicity testing through the vapour phase.

This study was conducted at Salmon Gums, with the test paddock situated about 250 m south of the Regional Study air sampling station and weather station. In this study a 83 ha paddock was sprayed with 2,4-D ethyl ester. Test stations in the application area and on the boundaries collected air 8, 12, 24, 32, 36 and 48 h post application.

The paddock had about 50% ground cover, consisting of mature (40-60 cm height) fleabane (*Conyza spp*.) with an understory cover of wireweed and melons. The spraying operation was conducted between 06:30 and 08:30 on 11 March 2009 by the property using a 28 m boom fitted with Hardi 025 flat fan nozzles at 50 cm intervals. The boom was set at 1 m above ground level to clear the 50 – 60 cm tall mature fleabane. Spray drift was minimised by use of an air shroud on the spray boom. Ground speed was 25 km/h.

Sampling commenced on day 1 between 9:30 am and 10:00 am. Sampling stations consisted of 8, 12 and 24 h samplers in the centre of the plot, at the NW corner of the plot and the SE corner of the plot. In the SW corner, a 12 and 24 h sampler was located. The original protocol anticipated 8, 12 and 24 h sample stations on the NE corner and an 8 h sampler on the SW corner. However, these could not be established because 11 of the pumps available could not be calibrated to a stable initial flow.

This is unfortunate as the prevailing wind during most of the supplementary study was moving strongest from the south westerly direction, and mostly from a general southerly direction, thereby resulting in possibly the most exposure to this particular corner.

The following two diagrams show the wind rose for the test plot over the 48 hours following application.

Figure 3: Wind rose showing the wind direction and speed from 6:00 am until 1:00 pm on the day of spraying (11 March 2009)

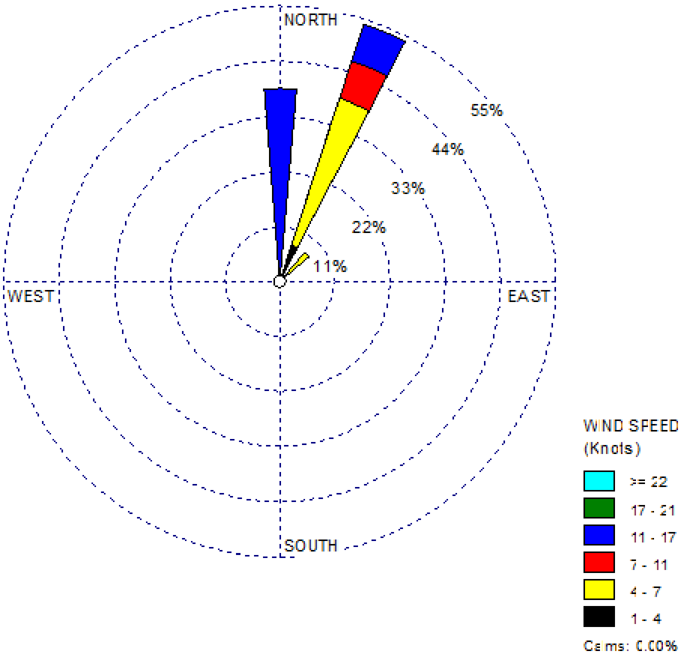
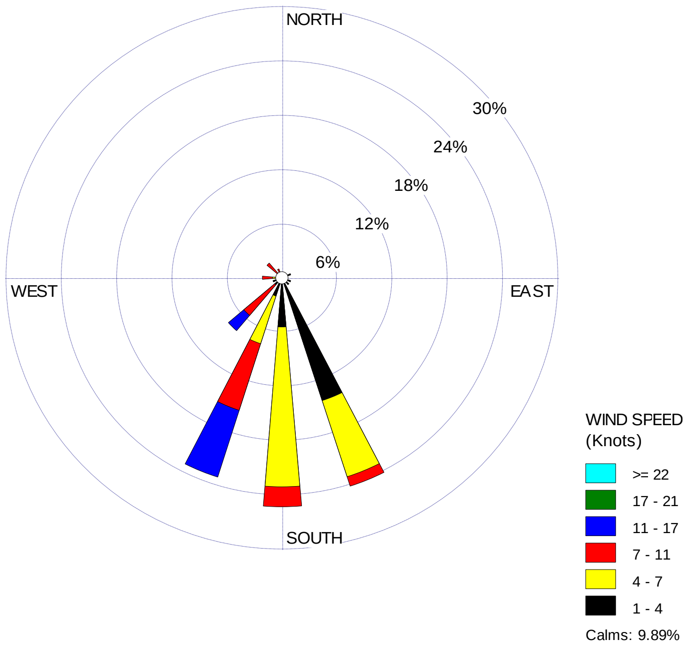


Figure 4: Wind rose shows the wind direction and speed from 1:00 pm on the day of spraying (11 March 2009) until 10:30 am on 13 March 2009 (48 h after sampling started):



What these two diagrams illustrate is that for the first few hours following application, the south west corner would be most exposed through downwind vapour movement, and from then on, the northern boundary and NE corner would be most exposed with winds generally from the south and south west for the remainder of the test period.

Table 6: Samples from the Centre of the Test Plot

Day	Pump	Total flow (m^3)	µg/sorbent	µg/m^3
1	8 h	1.62	1.5	0.93
1	12 h	2.4	2.5	1.04
1	24 h	2.15	1.7	0.79
2	8 h	1.4	0.044	0.03
2	12 h	2.31	0.062	0.03
2	24 h	1.01	0.097	0.096[1]

1) While this is nominally a 24 h sample, the information provided in the report suggests sampling was only undertaken for 11.1 hours, with the pump turned on at 10:55 am and turned off at 10:03 pm. Therefore, this is actually a 12 h concentration. It is unclear why it is around three times higher than the other 12 h sample taken in the centre of the plot on the same day, particularly noting the similarity in that 12 h sample and the 8 h sample. In any event, this concentration cannot be considered a 24 h concentration for comparison purposes.

The Day 1 results from the centre of the plot suggest that the rate of volatilisation remained relatively constant at the test site during both day time and night time hours. During the trial period, soil dried out decreasing from around 25 centibars to around 55 centibars. Soil temperature remained in a range of between around 20°C and 32°C. The day time temperature during Day 1 increased to almost 35°C, but after that, the range for both night and day temperatures was in the range of around 13°C to 23°C.

Table 7: Samples from the NW corner of the test plot

Day	Pump	Total flow (m^3)	µg/sorbent	µg/m^3
1	8 h	1.64	0.049	0.03
1	12 h	2.38	0.2	0.084
1	24 h	2.07	1.6	0.77
2	8 h	1.59	0.089	0.056
2	12 h	2.50	0.24	0.096
2	24 h	2.16	0.19	0.088

The values from the NW corner provide for some interesting interpretation. Given the test field dimensions, for the samplers at this corner to be exposed, the wind needed to blow anywhere from east around to south, with the maximum exposure where the wind was coming from the south east. On day 1, the wind did not come from an easterly to a southerly direction until after 11:00 pm on 11 March, and was predominantly from a south to south easterly direction until 4:30 am on the morning of 13 March 2009. This means, from Day 1, the 24 h samplers would have the most exposure, and this was reflected in the significantly higher concentrations within this sampler from Day 1 compared to the concentrations in the 8 and the 12 h samplers, and during day 2 (pumps turned on at around 9:30 am), exposure would have been fairly constant for around 19 hours, which is supported by the fairly consistent levels found in all three time period samplers.

Table 8: Samples from the SE corner of the test plot

Day	Pump	Total flow (m^3)	µg/sorbent	µg/m^3
1	8 h	1.65	1.7	1.03
1	12 h	2.45	0.98	0.40
1	24 h	2.15	0.64	0.30
2	8 h	-	-	-
2	12 h	2.45	0.016	0.0065
2	24 h	2.25	0.012	0.0053

Wind data indicates the wind never really blew across the plot towards the south east corner. This suggests detected levels were solely due to lift off in the immediate vicinity of the sampler, and not from contaminated air coming from other areas of the plot. It is unclear why at day 1 the 8 h concentration is so much higher than the 12 h concentration. However, the similarity in levels from the 12 and 24 h samples from both days 1 and 2 lends support to the view that volatilisation occurs at a relatively constant rate for both day and night in the test climate.

Table 9: Samples from the SW corner of the test plot

Day	Pump	Total flow (m^3)	µg/sorbent	µg/m^3
1	12 h	2.42[1]	0.40	0.165
1	24 h	2.10[1]	0.064[2]	0.030
2	12 h	2.42	0.011	0.0045
2	24 h	2.10	0.007	0.0033

1) Values not provided in report. Day 2 total flow volumes used as an indicator
2) Consisted of 2,4-D ethyl ester, 2,4-D isobutyl ester and 2,4-D 1-butyl ester

The south west corner samples also provide for some interesting interpretation. The day 1 results were not discussed or reported at all in the report, however, the raw data do contain some information. The flow rates have been assumed the same as Day 2 to estimate air concentrations. For maximum exposure to this corner, the wind would need to blow from a north easterly direction. This occurred at the time of application and the wind continued in this approximate direction (N, NNE and NE) until the 12:30 measurements, which may have resulted in about 3 hours exposure through wind if the pumps were turned on around 9:30 am (not actually reported for this corner on Day 1). This means, for the 12 h sample, the wind was blowing across the plot to the sampler for around 25% of the sampling time, while for the 24 h sample, it was only blowing across the plot to the sampler for around 12% of the time. Therefore, it would be expected that the 12 h sample would contain a higher concentration that the 24 h sample, and this did appear to be the case. However, from around 1:00 pm on the day of application, the wind was almost always blowing away from this corner. The day 2 samples show the 12 and 24 h concentrations to be relatively close, again indicating volatilisation occurs at a relatively constant rate for both day and night in the test climate.

Losses from volatilisation following application

The report addressed the potential loss to air following application as a result of volatilisation using the data generated in this supplementary study, and applying backwards Lagrangian stochastic modelling (bLs) within the WindTrax v 2.0 model. The emission (flux) rate varied from a maximum of 4.86 g/ha/h (12 h, Day 1) to 0.07 g/ha/h (8 h Day 2). The emission rate (flux) of 2,4-D HVE (as 2,4-D ethyl ester) reduced 20 times from Day 1 to Day 2. Applying the test data to the model, it was demonstrated that during the first 24 h post-application, the cumulative loss through volatilisation was 14.5% (range of 4.86-23.45%) of the applied amount, and most of the loss occurred during the first 24 h following application.

DEWHA accepts these calculations, although it would have been interesting to know how the results may have differed if the NE corner was sampled, as apart from the centre plot samplers, this would likely have had the highest detections.

Conclusions for the Supplementary Study

The supplementary study was designed to allow a comparison between sampling periods of different time frames, namely, 8 h, 12 h or 24 h samples. Where direct comparisons were able to be made, the data showed that the concentrations observed over a daytime sampling period (8 to 12 hours), were not remarkably different to those found over a 24 hour continuous sampling period. This further suggests, in the area tested, the rates of volatilisation were not substantially different between day and night time in the test climate.

These findings allow increased confidence in using a 24 h exposure concentration in vapour phase ecotoxicity testing.

The use of modelling incorporating the data obtained through this supplementary study indicate cumulative volatilisation of around 15% of the applied amount, with the majority of this being lost in the first 24 hours following application.

References

Hay P, 2009a. 2,4-D HVE Regional Monitoring Study. February – March, 2009. Esperance – Salmon Gums, WA. Volume 1 Report. Nufarm, July 2009.

Hay P, 2009b. Regional Monitoring Study. Esperance – Salmon Gums, WA. Volume 2 Report. Nufarm, July 2009.

Hay P, 2009c. Post-Application Volatilisation of 2,4-D HVE Measured at Different Time Scales from a Large Area Source. Salmon Gums, WA, March 2009. Nufarm.

Attachment 7

Revised 2,4-D HVE Air Monitoring Study report

A report, **2,4-D HVE Air Monitoring Study,** prepared by the 2,4-D Permit Support Group, was provided to DSEWPaC by the APVMA in early 2013.

Examination of the report identified it as essentially the same report **2,4-D HVE Air Monitoring Study** assessed by DSEWPaC in December 2008 (see Attachment 7). The present report contains, however, a revised risk assessment section which has now been examined by DSEWPaC.

The original report concluded that a preliminary risk assessment had determined an EC25 for 2,4-D butyl ester on 5 to 7 week old tomato plants of 9.8 µg acid equivalents/m^3 as a time weighted average over 24 hours. This was based on observations of weight reduction in tomato plants.

Using the highest 2,4-D acid equivalent determined in the associated trials (0.343 µg/m^3) and the risk quotient was 0.343/9.8 or 0.035. As this value is less than 0.1, risk to plants was considered as acceptable for a preliminary risk assessment. Also provided in Appendix 3 of the originally submitted report was a risk assessment based on an estimated NOEL of 0.83 µg 2,4-D acid equivalent/m^3 on a 24 hour time weighted average. In this case the risk quotient was 0.343/0.83 or 0.41.

The report submitted in 2013 also provided a risk assessment based on a no observed effect concentration or NOEL derived from the EC05 value determined from the study on the tomato plants. Based on the three different studies considered in the reports, the following NOEL values were identified:

NOEL as total herbicide available µg 2,4-D a.e./24 h	NOEL as TWA_{24} µg 2,4-D a.e./m^3/24 h
10.3	9.1
8	5.5
6.5, 5.1, 1.2, 1.6	4.5, 3.5, 0.8,1.1

The lowest reliable acute NOEL for 2,4-D HVE determined from the studies reviewed was set at 1.20 µg 2,4-D a.e., expressed as total herbicide available for 24 hour exposure, or as a TWA_{24}, 0.8 µg 2,4-D a.e./m^3.

Noting the highest value detected in the three trials was 0.29 µg 2,4-D a.e/m^3/24 h, a risk quotient of 0.29/0.8 or 0.36 was determined in the revised report with the conclusion that, as the value was less than 1, risk was acceptable (note that in the revised risk assessment provided in the report, the risk quotient is given on page 60 as

Q value = 0.5/0.8 = 0.36

This is an error and the expression should read: Q value = 0.29/0.8 = 0.36 (the reported risk quotient). The 0.36 value is considered by DSEWPaC as equivalent to the 0.41 value provided in the original report.

DSEWPaC concludes that apart from the use of a NOEL endpoint and some variation in reported data values, the revised study has not varied from the original version’s conclusion, that risk to plants was acceptable.

Unfortunately, the revised report has not taken account of DSEWPaC’s advice of in its letter of 11 December 2008 (see Attachment 7 (DSEWPaC’s assessment of a 2,4-D HVE AIR MONITORING STUDY - SEPTEMBER 2008 (CR284-1)) to the Annex) to the APVMA that:

> *The monitoring study was required to obtain more reliable data on likely vapour concentrations in local and regional use situations. The monitoring results obtained were for the local situation only, based on application to 70 ha fields. It was never a requirement that a risk assessment be conducted as this stage because the available plant toxicity data from gas phase exposure are inadequate for undertaking a risk*

> *assessment. Nonetheless, the Permit Support Group (PSG) has performed both a preliminary and refined risk assessment, and our assessment of this is also detailed in Attachment 2 [Provided as attachment 5 to the Annex to the 2006 PRF].*
>
> *In summary, their approach of relating available toxicity data in terms of “total available herbicide” back to monitored levels in the same terms is incorrect and cannot be used to assess risk. The toxicity data as referred to by the PSG has been reviewed and risk assessment end-points (EC25 and EC05) calculated using TOXCALC v5.0 software. There are very large discrepancies between our calculated values and those derived by the PSG.*
>
> *Our preliminary risk assessment, undertaken in a number of different ways with different end points, all indicate a potentially unacceptable risk from the local monitoring trial. It is anticipated that the proposed regional trial would only exacerbate this situation, due to the expected much higher levels in situations of significant regional use, and would serve only to confirm the conclusion of an unacceptable risk.*
>
> *The main deficiencies in the present assessment are the use of end points for vapour phase toxicity based on a single species (although with a spread of results for a relatively sensitive plant), and the need to extrapolate levels from 24 hour time weighted averages to those for shorter periods that might be expected more accurately reflect those during daylight hours when volatility will be highest.*
>
> *On the available evidence, the risks of the use of 2,4-D HVE are unacceptable and the risks cannot be mitigated. The conduct of regional trials is unlikely to provide evidence that would allow mitigation of the risks.*

Consequently, the revised 2,4-D HVE Air Monitoring Study has not resulted in any need to change the conclusions given in the 2006 Preliminary Review Findings, i.e. the 2,4-D HVE pose unacceptable environmental risk.