# Dossier According to Directive 91/414/EEC

# Plant Protection Product

# Requiem® EC (QRD 452)

## Terpenoid blend (α-terpinene, ρ-cymene, d-limonene) QRD 460

Product for insect pest control developed from plant extracts of *Chenopodium ambrosioides* near *ambrosioides*

## Document MIII, Section 5

## ENVIRONMENTAL FATE AND BEHAVIOUR

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# 9 FATE AND BEHAVIOUR IN THE ENVIRONMENT

AgraQuest Inc. has submitted this application for approval of the new active substance QRD 460 and its product, QRD 452 respectively, for registration in the EU. It is an insecticide for use on tomatoes and peppers in glasshouses and cucurbits in glasshouses and field at a maximum application rate of 1.523 kg a.s./ha up to 3 times with a 7 day interval between treatments.

**Table 6-1: EU Critical GAP for QRD 452 use on Tomatoes and Peppers and Cucurbits**

| Region | Outdoor/ Protected | Max. No. of Applications | Application Interval (days) | Max. Application | | Minimum PHI (days) |
|---|---|---|---|---|---|---|
| | | | | Rate (kg as/ha) | Water (L/ha) | |
| N EU | Protected | 3 | 7 | 0.381 – 1.523 | 400 - 1000 | 0 |
| S EU | Protected | 3 | 7 | 0.381 – 1.523 | 400 - 1000 | 0 |
| S EU | Outdoor | 3 | 7 | 0.762 – 1.523 | 400 - 1000 | 0 |

This section of the Dossier is addressed using primarily information already presented in the Annex II Section 5 and is summarised, accordingly.

It is the purpose of this Section to characterize the likely degradation pathways of the active substance, QRD 460, in QRD 452 as well as the degradation rates and extent of degradation in three environmental compartments, namely, soil, water and air. This characterization is based on the use of predictive modelling considering particularly the fugacity of the terpenes individually and research reports from the open literature. In addition to a literature-based and predictive characterization of the environmental fate of the active substance, recent experimental results characterizing degradation of the QRD 460 components in soil and natural water matrices are included.

Due to the use of predictive modelling that requires parameters from Section 1 Physical chemical properties, where appropriate, each terpene has been addressed individually. However QRD 460 was used for the two studies on the degradation in soil and in natural waters.

Reference is closely made to [redacted] (2011) and its respective appendices and references and to the FOCUS Air guidelines, Pesticides in Air – Considerations for Exposure Assessment SANCO /10553/2006 Rev 2 June 2008 and the US-EPA's EPI Suite™ model which is also discussed in the FOCUS guideline.

The physical-chemical properties of the three terpenes in QRD 460, α-terpinene, p-cymene, and d-limonene, indicate high vapor pressures and high Henry's Law Constants (see Section 1). This means that the dominant environmental sink for these compounds is likely to be the atmosphere. Monoterpenes, as a class, are released from vegetation in large amounts to the air (Fehsenfeld *et al.* 1992 and Guenther *et al.* 1995) which supports the assumption that volatilization is the most important environmental dissipation pathway for these compounds. Once in the air, research publications and predictive modeling indicate they are degraded rapidly based on interactions with hydroxyl radicals, ozone and nitrate radicals, the latter at night. To confirm this position, the fugacity of the three terpene components of QRD 452 were considered in Annex II Section 5 which should be referred to.

In one soil study on the degradation of QRD 460, the three test items α-terpinene, p-cymene and d-limonene disappear rapidly from the soil by evaporation. The $DT_{50}$ of all three test items was calculated to be <24 hours. The $DT_{90}$ which was actually also the $DT_{100}$ was <48 hours. This study confirms the assumptions made based on the physical chemical properties of QRD 460 and the fugacity models conclusions that the fate of QRD 460 in soil is of limited relevance as it volatilises rapidly into the air compartment. ([redacted], 2010).

In one water study, degradation of QRD 460 in natural filtered waters, the three test items α-terpinene, , p-cymene, and d-limonene, rapidly volatilized from the natural water test systems with $DT_{50}$s of 4.1, 11.2, and 3.0 hours and $DT_{90}$s of 13.7, 37.4, and 10.0 hours, respectively. This means that a $DT_{100}$ could be proposed for QRD 460 of <48 hours. The trapping solutions showed the presence of the test substances but no degradates. Degradates in the water were also not detected. Thus, rapid escape (fugacity via volatility) appears to be the predominant pathway for all three terpenes in natural water. ([redacted], 2011).

On this basis, the fate in air is the main parameter to be considered here in the Annex III Section 5 and soil and water compartments are not considered further.

To aid evaluation of the dossier, the code designations are described so that it is clear which test substance was used for each study. All substances listed are considered substantially equivalent.

**Code Designations**
The various AgraQuest code designations that relate to the active substance, products and the submitted documents are as follows:

QRD 406 = *Chenopodium ambrosioides* near *ambrosioides* plant extract technical grade active ingredient (tgai) – consisting of the three terpenes as the active component plus plant derived impurities. Three terpenes comprise approximately 68% of QRD 406.

QRD 400 = formulated EC product with 25% plant extract (QRD 406) active ingredient, 75% other formulants (Also known as FACIN 25EC in some reports and registered in the USA as Requiem® 25EC and Metronome™.) The three terpenes in QRD 400 comprise approximately 17%.

QRD 420 = blended tgai using the three terpenes in the same concentrations as found in QRD 406 with plant derived impurities replaced with canola oil. The three terpenes comprise approximately 67% of QRD 420.

QRD 416 = formulated EC product with 25% blended (QRD 420) a.i., 75% other formulants (same formulants in the same concentrations as QRD 400). The three terpenes comprise approximately 16.75 % of QRD 416.

QRD 452 = QRD 416 – due to a code designation error, the product was re-coded as QRD 452. There are a few studies that reference QRD 416, but the composition is identical to QRD 452. (Also known and registered in the USA as Requiem® EC and Metronome™ EC). The concentration of the three terpenes in QRD 416 and QRD 452 is 16.75%.

QRD 460 = Blended tgai without canola oil. This contains only the three terpenes. The proportions of the three terpenes are essentially the same as the plant extract tgai minus plant derived impurities. So, less QRD 460 is required in Requiem® EC (QRD 452), 16.75% instead of 25%. The percentage of each terpene in QRD 452 and QRD 400 are the same.

## IIIA 9.1 Rate of degradation in soil

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.1.1 Aerobic degradation of the preparation in soil

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.1.2 Anaerobic degradation of the preparation in soil

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

## IIIA 9.2 Field studies

### IIIA 9.2.1 Soil dissipation testing on a range of representative soils

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.2.2 Soil residue testing

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.2.3 Soil accumulation testing

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.2.4 Aquatic (sediment) field dissipation

This is not an EC data requirement.

### IIIA 9.2.5 Forestry field dissipation

This is not an EC data requirement.

## IIIA 9.3 Mobility of the plant protection product in soil

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.3.1 Column leaching

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.3.2 Lysimeter studies

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.3.3 Field leaching studies

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.3.4 Volatility – laboratory study

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

### IIIA 9.3.5 Volatility – field study

Degradation in soil is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further detail is presented in Annex II Section 5.

## IIIA 9.4 Predicted environmental concentrations in soil ($PEC_S$) for the active substance at the highest rate of application proposed and relating to the maximum number and highest rates of application proposed, for each relevant soil tested

Not relevant for QRD 452 as it has been demonstrated that the active substance, QRD 460, does not accumulate in soil and volatilises rapidly into air. The $DT_{50}$ for each terpene component was less than 24 hours, while the $DT_{90}$ (actually the $DT_{100}$) was <48 hours. Calculating the PEC in soil is not likely to be relevant, therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.4.1 Initial $PEC_S$ value

Not relevant for QRD 452 as it has been demonstrated that the active substance, QRD 460, does not accumulate in soil and volatilises rapidly into air. The $DT_{50}$ for each terpene component was less than 24 hours, while the $DT_{90}$ (actually the $DT_{100}$) was <48 hours. Calculating the PEC in soil is not likely to be relevant, therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.4.2 Short-term $PEC_S$ values – 24 hours, 2 days and 4 days after last application

Not relevant for QRD 452 as it has been demonstrated that the active substance, QRD 460, does not accumulate in soil and volatilises rapidly into air. The $DT_{50}$ for each terpene component was less than 24 hours, while the $DT_{90}$ (actually the $DT_{100}$) was <48 hours. Calculating the PEC in soil is not likely to be relevant, therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.4.3 Long-term $PEC_S$ values - 7, 28, 50 and 100 days after last application

Not relevant for QRD 452 as it has been demonstrated that the active substance, QRD 460, does not accumulate in soil and volatilises rapidly into air. The $DT_{50}$ for each terpene component was less than 24 hours, while the $DT_{90}$ (actually the $DT_{100}$) was <48 hours. Calculating the PEC in soil is not likely to be relevant, therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

## IIIA 9.5 Predicted environmental concentrations in soil ($PEC_S$) for relevant metabolites, degradation and reaction products, at the highest rate of application proposed and relating to the maximum number and highest rates of application proposed, for each relevant soil tested

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in soil, and furthermore, no metabolites, degradation, or reaction products in soil have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.5.1 Initial $PEC_S$ value

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in soil, and furthermore, no metabolites, degradation, or reaction products in soil have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.5.2 Short-term $PEC_S$ values – 24 hours, 2 days and 4 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in soil, and furthermore, no metabolites, degradation, or reaction products in soil have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.5.3 Long-term PECs values - 7, 28, 50 and 100 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in soil, and furthermore, no metabolites, degradation, or reaction products in soil have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

## IIIA 9.6 Predicted environmental concentrations in ground water ($PEC_{gw}$) at the highest rate of application proposed and relating to the maximum number and highest rates of application proposed

Degradation in water is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5. A water degradation study performed on the active substance QRD 460 constituents gave a $DT_{100}$ of <48 hours which confirms this position.

### IIIA 9.6.1 Active substance $PEC_{gw}$ value

Degradation in water is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.6.2 Relevant metabolites, degradation and reaction products $PEC_{gw}$ values

Degradation in water is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.6.3 Additional field testing

No additional field testing is necessary because degradation in water is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.6.4 Information on impact on water treatment procedures

No impact on water treatment procedures is to be expected because degradation in water is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

## IIIA 9.7 Predicted environmental concentrations in surface water ($PEC_{SW}$) for the active substance at the highest rate of application proposed and relating to the maximum number and highest rates of application proposed, relevant to lakes, ponds, rivers, canals, streams, irrigation/drainage canals and drains

Degradation in water is considered of minor relevance to the breakdown of QRD 452 in the environment as it is only a minor compartment, air being the major one. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5. A water degradation study performed on the active substance QRD 460 constituents gave a $DT_{100}$ of <48 hours which confirms this position.

### IIIA 9.7.1 Initial $PEC_{SW}$ value for static water bodies

Not relevant for QRD 452 as it volatilises rapidly into air and does not accumulate in water. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.7.2 Initial $PEC_{SW}$ value for slow moving water bodies

Not relevant for QRD 452 as it volatilises rapidly into air and does not accumulate in water. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.7.3 Short-term $PEC_{SW}$ values for static water bodies - 24 hours, 2 days and 4 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air and does not accumulate in water. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.7.4 Short-term $PEC_{SW}$ values for slow moving water bodies - 24 hours, 2 days and 4 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air and does not accumulate in water. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.7.5 Long-term $PEC_{SW}$ values for static water bodies - 7, 14, 21, 28, 42 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air and does not accumulate in water. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.7.6 Long-term $PEC_{SW}$ values for slow moving water bodies - 7, 14, 21, 28, 42 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air and does not accumulate in water. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

## IIIA 9.8 Predicted environmental concentrations in surface water ($PEC_{SW}$) for relevant metabolites, degradation and reaction products at the highest rate of application proposed and relating to the maximum number and highest rates of application proposed, relevant to lakes, ponds, rivers, canals, streams, irrigation/drainage canals and drains

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in water, and furthermore, no metabolites, degradation, or reaction products in water have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.8.1 Initial $PEC_{SW}$ value for static water bodies

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in water, and furthermore, no metabolites, degradation, or reaction products in water have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

### IIIA 9.8.2 Initial $PEC_{SW}$ value for slow moving water bodies

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in water, and furthermore, no metabolites, degradation, or reaction products in water have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5..

### IIIA 9.8.3 Short-term $PEC_{SW}$ values for static water bodies - 24 hours, 2 days and 4 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in water, and furthermore, no metabolites, degradation, or reaction products in water have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

## IIIA 9.8.4 Short-term PECsw values for slow moving water bodies - 24 hours, 2 days and 4 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in water, and furthermore, no metabolites, degradation, or reaction products in water have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

## IIIA 9.8.5 Long-term PECsw values for static water bodies - 7, 14, 21, 28, 42 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in water, and furthermore, no metabolites, degradation, or reaction products in water have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

## IIIA 9.8.6 Long-term PECsw values for slow moving water bodies - 7, 14, 21, 28, 42 days after last application

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in water, and furthermore, no metabolites, degradation, or reaction products in water have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5.

## IIIA 9.8.7 Additional field testing

Not relevant for QRD 452 as it volatilises rapidly into air, does not accumulate in water, and furthermore, no metabolites, degradation, or reaction products in water have been identified. Therefore no further information is provided here. Further explanation is presented in Annex II Section 5

# IIIA 9.9 Fate and behaviour in air

The summary below has been adapted directly from Annex II Section 5 Environmental Fate and Behaviour.

**Rate of Atmospheric Degradation.**

The three terpenes in terpenoid blend (α-terpinene, ρ-cymene and d-limonene,) QRD 460, which comprises16.75% of the plant protection product QRD 452, are degraded quickly in air. Rates of degradation were estimated using the AOPWIN (Atmospheric Oxidation Program for Microsoft Windows program in EPI Suite™ 4.0. The program estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals. It also estimates the rate constant for the gas-phase reaction between ozone and olefinic/acetylenic compounds. Finally, it also estimates the rate constant for gas-phase reactions between nitrate radicals and organic chemicals that occur at night. The rate constants estimated are then used to calculate atmospheric half lives for organic compounds based on average atmospheric concentrations of the hydroxyl radicals, ozone and nitrate radicals ([redacted], 2011).

The estimation methods used in AOPWIN are based on the structure-activity relationship methods developed by Atkinson and co-workers with some updates by EPA contractors. AOPWIN only requires chemical structures to make the estimations. Atkinson's work and the work of his colleagues for estimating half lives of organic chemicals in the atmosphere has been reviewed in Section 3.3 of the Focus Working Group on Pesticides in Air Report (SANCO/10553/2006 Rev 2, Pesticides in Air: Considerations for Exposure Assessment, Report prepared by the FOCUS Working Group on Pesticides in Air, June 2008.).

Table 9.9-1 (below) summarizes the estimated atmospheric half lives of the three monoterpenes in the terpenoid blend QRD 460 and the plant protection product QRD 452.

**Table 9.9-1. Estimated half lives of the monoterpenes in air based on the AOPWIN in EPI Suite™ 4.0.**

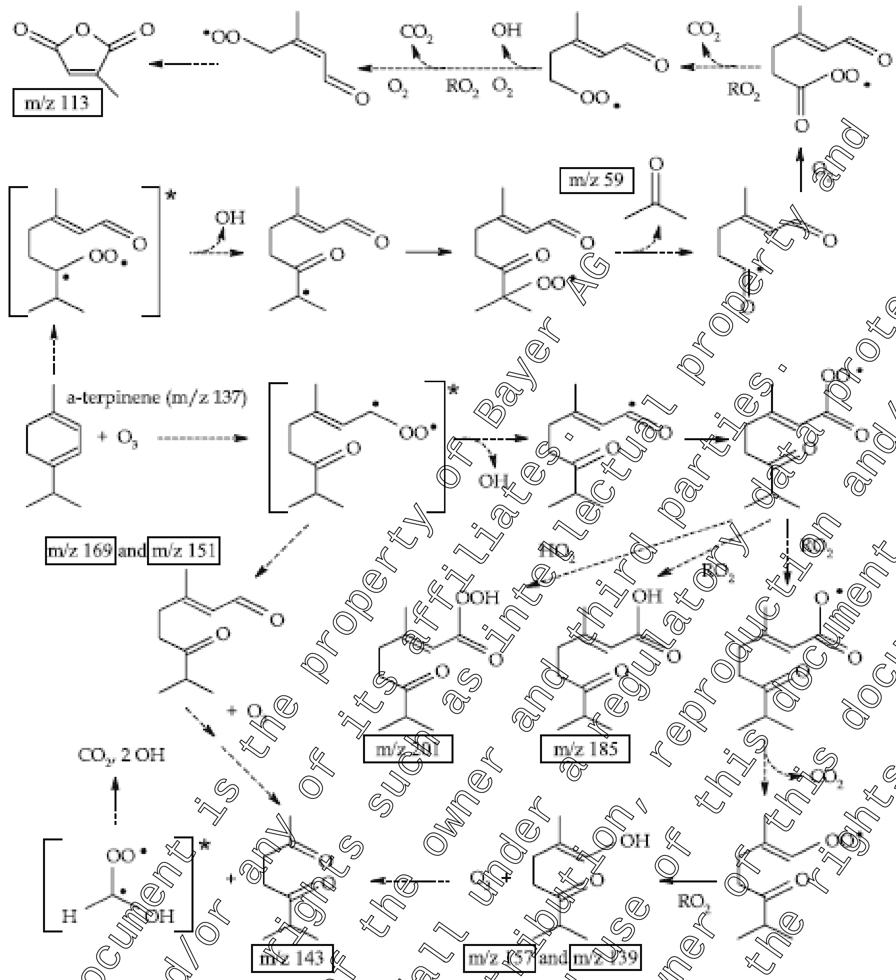
| Compound | Half Life in Air | Reactant |
|---|---|---|
| | | |
| α-terpinene | 29.1 minutes<br>1.7 minutes<br>"may be important" | hydroxyl radicals<br>ozone<br>nitrate radicals |
| p-cymene | 15 hours | hydroxyl radicals |
| d-limonene | 53 minutes<br>37.3 minutes<br>0.9 – 9 minutes | hydroxyl radicals<br>ozone<br>nitrate radicals |

It is appropriate to consider the fate of each terpene individually and so information from a literature search has been summarised as follows.

**Route of Atmospheric Degradation of α-Terpinene**

Identity and quantification of gas-phase products from the ozonolysis of α-terpinene was reported by [redacted] *et al.*, (2006). This monoterpene was rapidly oxidized (within 30 minutes) with the formation of numerous gas-phase products whose structures were deduced by mass spectrometry. Lower molecular weight products included formaldehyde (4 % molar yield), acetaldehyde (1 % molar yield), formic acid (10% molar yield), acetone (6 % molar yield), acetic acid (10% molar yield) and unidentified products (31 %). Based on the structural assignments derived from mass spectrometry, a partial mechanism for the ozonolysis of α-terpinene was proposed and is presented in Figure 9.9-2 below.

**Figure 9.9-2. Partial mechanism for the ozonolysis of α-terpinene ([redacted] et al, 2006)**




The authors noted that the highest yield of a single product, other than the low molecular weight products, accounted for no more than 6 % and that dominant first-generation products were not detected. Thus, certain observed product ions were likely second generation entities. Thus, α-terpinene is readily degraded by ozone in the air to form numerous gas-phase products.

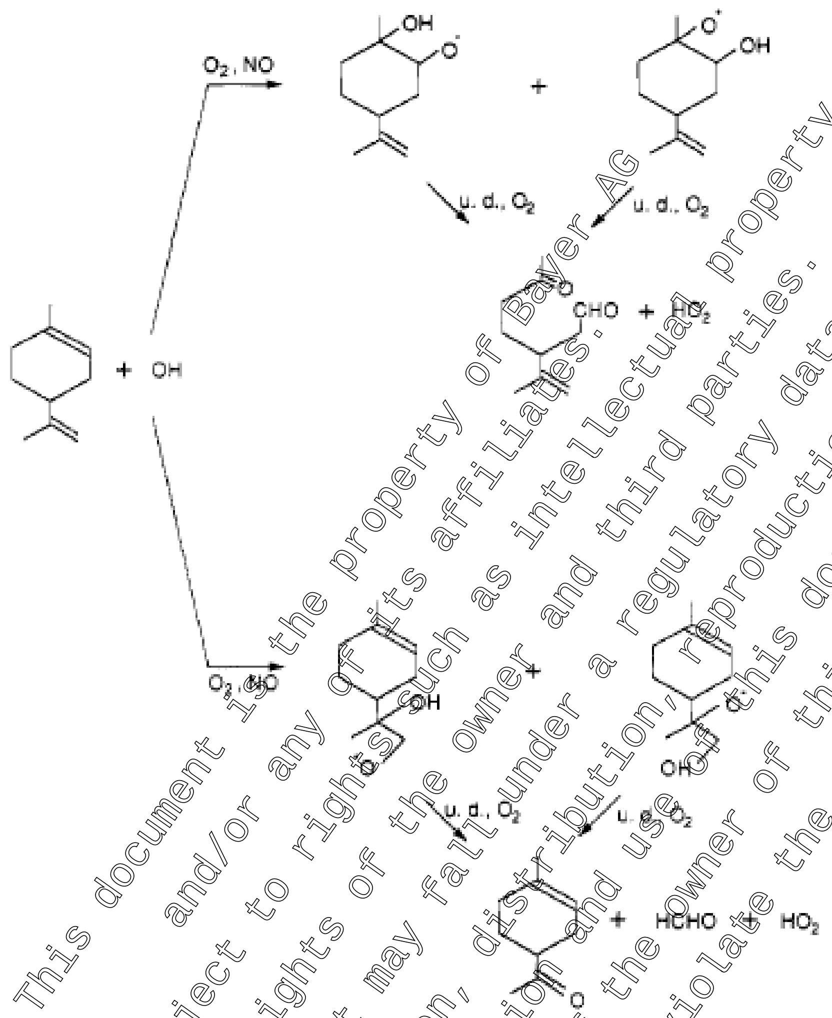
**Route of Atmospheric Degradation of p-Cymene**

Literature discussing the nature of the degradation of p-cymene in air was not available. Thus, for p-cymene, there are just the estimates for the rate of degradation in air. However all three terpenes have a lot in common and it is highly likely that their breakdown in air is similar and certainly rapid.

**Route of Atmospheric Degradation of d-Limonene**

[redacted] *et al*., (1992) studied the atmospheric oxidation of d-limonene and characterized the reaction products. They are depicted in Figure 9.9-3:

**Figure 9.9-3. Reaction products of the d-limonene-hydroxyl radical reaction taken from Figure 2 of [redacted] *et al.,* (1992). The abbreviation u.d. refers to unimolecular decomposition.**

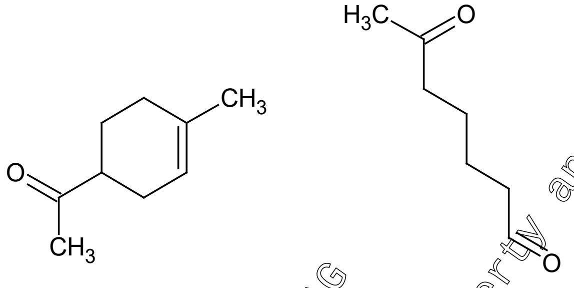





As shown, OH radicals add across either of the two unsaturated carbon-carbon bonds to ultimately form carbonyl degradates.

[redacted] *et al.*, (1994) also identified 4-acetyl-1-methylcyclohexene and a keto-aldehyde (Figure 9.9-4 below) by GC-FID using an authentic reference standard and by GC-MS and GC-FTIR, respectively, thus confirming the identifications for two of the hydroxyl radical-generated carbonyl degradates reported by [redacted] *et al.*, (1992).

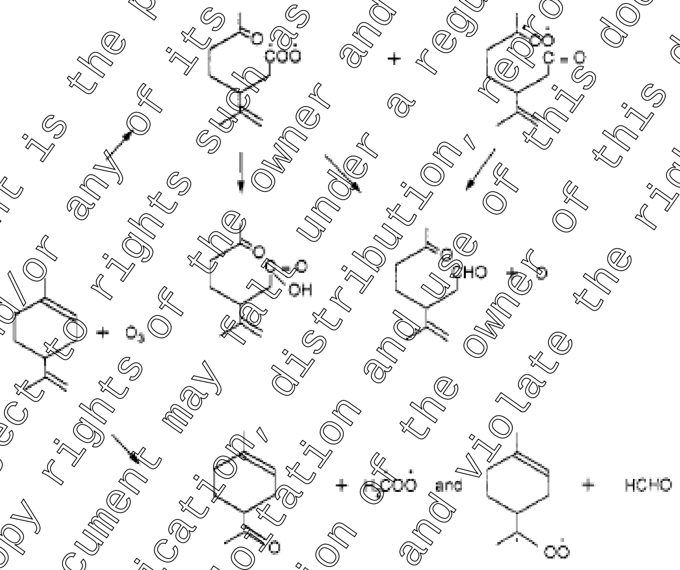
**Figure 9.9-4. Two identified products of the OH radical reaction with limonene ([redacted] et al., 1994) .**




4-acetyl-1-methylcyclohexene keto-aldehyde

The same carbonyl compounds form (along with formic and $C_8$ and $C_9$ carboxylic acids) by reaction of d-limonene with ozone (see Figure 9.9-5 below).

**Figure 9.9-5. Simplified mechanism for the interaction of d-limonene with ozone in air taken from Figure 3 of [redacted] *et al.*, (1992) .**



Importantly, the researchers also noted that the first-generation products were as reactive towards OH radicals and ozone as the parent compound. They go on to mention that the second-generation carbonyl products are not expected to accumulate in the atmosphere but rather undergo rapid oxidation to yield carbon monoxide and free radicals. An example illustrating the further degradation of 4-acetyl-1-methylcyclohexene, formed from the reaction of either hydroxyl radicals or ozone with limonene, is provided in Figure 9.9-6 below. In this case, smaller carbonyl compounds, namely, formaldehyde, glyoxal and 3-oxobutanal, were formed.

**Figure 9.9-6. Reactions of 4-acetyl-1-methylcyclohexene with hydroxyl radicals ([redacted] *et al*., 1992).**


It is also reported that reactions with oxides of nitrogen produce lower molecular products including formaldehyde, acetaldehyde, formic acid, acetone and peroxyacetylnitrate (International Programme on Chemical Safety, Concise International Chemical Assessment Document No. 5, Limonene, World Health Organization, 1998 (http://www.inchem.org/documents/cicads/cicads/cicad05.htm)).

Thus, reactions of d-limonene with hydroxyl radicals, ozone and nitrate radicals lead to a series of carbonyl compounds that are further converted to very small molecular weight entities.

## Conclusions

In conclusion, terpenoid blend (α-terpinene, p-cymene and d-limonene) QRD 460, being highly volatile, is likely to degrade rapidly in air and to form smaller, naturally occurring molecules in the air. This matches the anecdotal evidence from naturally occurring terpenes such as d-limonene in oranges where the citrus fragrance dissipates rapidly after breaking the orange skin or slicing the fruit. It also matches anecdotal evidence from the use of d-limonene where it is used as a fragrance and the scent disappears after a few minutes.

There is no evidence that any of the constituents of QRD 460 and QRD 452 persist in air. The models suggest that they all break down rapidly via hydroxyl radicals, ozone and nitrate radicals in a matter of minutes or hours and due to the nature of their chemistry as terpenes, it is commonly accepted that they and their break down components will present no significant risk to the atmospheric environment. Anecdotal evidence from natural foodstuffs containing these terpenes and from their use as fragrances in household items supports this position.

## Risk assessment in Air

Following the principles of the dossier guidelines and the Focus Working Group on Pesticides in Air Report (SANCO/10553/2006 Rev 2, Pesticides in Air: Considerations for Exposure Assessment, Report prepared by the FOCUS Working Group on Pesticides in Air, June 2008.), it is usual to estimate the likely predicted environmental concentration (PEC) of QRD 460 in its product QRD 452. This PEC calculation is usually performed to allow a comparison between the PEC and exposure scenarios in other parts of the dossier. As neither soil or water compartments are viewed as relevant for risk assessment, the following calculation, overleaf, has been performed on the basis that the concentration in Glasshouse air is most likely the worst case as it is a technically contained air compartment area (as opposed to the "open air" field).

## Calculation of the PEC of the Active Substances in QRD 452 in Glasshouse Air

EU Directive 91/414 requires the calculation of a Predicted Environmental Concentration (PEC) in air although does not provide detailed guidance on how this should be carried out (SANCO/10553/2006 Rev 2 [1]). For QRD 452, a product containing the three terpenes, α-terpinene, ρ-cymene and d-limonene, the $PEC_{air}$ relevant to a glasshouse application is presented here. The calculation was accomplished as follows:

**Assumptions**

- ✓ The maximum application rate of QRD 452 in the greenhouse is 1.523 kg (critical GAP) active substances/ha (10 L product/ha).
- ✓ Area of a typical EU glasshouse is 256 $M^2$ with a total volume of 901 $M^3$ (SANCO/10553/2006 Rev 2 )
- ✓ All three active substances are volatilized into the glasshouse air immediately after spraying. Previous residue decline studies with tomatoes, mustard greens and primrose at application rates greater than the currently proposed label rates have indicated that the terpenes volatilize within minutes to one hour after spray application (Metabolism and Residues Section 4[1]). Thus, the assumption of immediate and complete volatilization after spraying represents a reasonable, albeit a worst case, scenario.
- ✓ A glasshouse ventilation rate of 33%/hour (SANCO/10553/2006 Rev 2 [1])

Thus, 1523 g active substances x 0.0256* = 39 g active substances sprayed
39 g active substances/901 $M^3$ = 0.043 g/$M^3$ = 43 mg/1000 L = 0.043 mg/L = $PEC_{greenhouse\ \mathbf{air}}$.

*Area of greenhouse (256 $M^2$)/area of a hectare (10,000 $M^2$) = 0.0256 (i.e., 2.56% of a hectare).

It should be noted that all evidence from modelling, the literature and anecdotal evidence suggests that none of the terpene constituents of QRD 460 and QRD 452 persist in the air and are rapidly broken down. This means that the PEC air as calculated has limited value as it is a worst case and any exposure is very short lived.



[1] These studies are also submitted and fully evaluated in Section 4 of the QRD 460 dossier (Points IIA 6.3.1/01, IIA 6.3.3/01 and IIA 6.3.4/01)

### IIIA 9.9.1 Spray droplet size spectrum – laboratory studies

This is not an EC data requirement.

### IIIA 9.9.2 Drift – field evaluation

This is not an EC data requirement.

## IIIA 9.10 Other/special studies

### IIIA 9.10.1 Other/special studies – laboratory studies

No other/special studies have been carried out.

### IIIA 9.10.2 Other/special studies – field studies

No other/special studies have been carried out.