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This study presents a number of stepping stones towards answering the question if the current product-by-product and active substance-by-active substance evaluation provides sufficient protection in the context of the authorisation of plant protection products (PPPs) in the Netherlands. This report is based on a literature review and an evaluation of tank mixture applications in a spraying schedule for strawberries. The topic of tank mixtures has been identified by Ctgb (the Board for the Authorisation of Plant Protection Products and Biocides in The Netherlands) as an important knowledge gap. We have quantified the environmental risk for an intensively cultivated crop with sequential applications of products and mixtures of products based on a realistic application schedule and spray drift on surface water in a ditch, the corresponding exposure profiles and the effects based on the Regulatory Acceptable Concentrations of the used active substances. This study shows that the actual strawberry crop scenario is not protective for invertebrates and fish in surface water. Therefore, for the risk assessment of PPPs it needs to be considered that PPPs are part of a crop protection programme and thus should be evaluated in this context.

Keywords: multistress, tank mixture, plant protection product, environmental risk, spray drift, aquatic, exposure, pesticide



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Photo cover: Jan van de Zande (Spraying in strawberry crop)

# Contents

# Preface

This report is the product of *Project BO-20-002-031* commissioned by the Ministry of Economic Affairs. It presents a number of stepping stones towards answering the question if the current product-by-product and active substance-by-active substance evaluation provides sufficient protection in the context of the authorisation of PPPs in the Netherlands.

This report is based on a literature review performed by the authors in 2015 and an evaluation of tank mixture applications in a spraying schedule for strawberries that was performed in 2016.

The topic of tank mixtures has been identified by Ctgb (the Board for the Authorisation of Plant Protection Products and Biocides in The Netherlands) as an important knowledge gap. We have quantified the environmental risk for an intensively cultivated crop with parallel and sequential applications of products based on a realistic application schedule and spray drift on surface water in a ditch, the corresponding multiyear exposure profiles and the effects based on the Regulatory Acceptable Concentrations of the used active substances.

The authors would like to thank John Deneer for his contributions to Chapter 3 and colleagues of the Environmental Risk Assessment team of Wageningen Environmental Research for their valuable comments.

# Summary

This study has focused on plant protection products (PPPs), for which we define multistress as the frequent, repeated and simultaneous application of PPPs in time and space. This report summarizes the first stepping stones towards answering the question whether the product-by-product and active substance-by-active substance evaluations provide sufficient protection in the context of the authorisation of PPPs in the Netherlands.

This report is based on a literature review and a quantitative evaluation of tank mixture applications in a spraying schedule for strawberries. The topic of tank mixtures has been identified by Ctgb (the Board for the Authorisation of Plant Protection Products and Biocides in The Netherlands) as an important knowledge gap. The current practice of risk assessment for authorisation of PPPs in The Netherlands includes an evaluation of product mixtures (products with two or more active substances) only when these are included on the label. This risk assessment also evaluates multiple applications of one product if stated on the label, but does not evaluates multiple applications of tank mixtures of multiple products in crops during the season.

This report shows that adjuvants and formulations have an effect on spray droplet sizes and therefore on spray drift potential. These effects can both increase and decrease spray drift, depending on nozzle type, adjuvants and product formulations.

Our literature review shows that exposure to mixtures of PPPs is slightly influenced by interactions between PPPs, due to competition for sorption. Based on the current literature, no judgement can be given on the effect of the simultaneous presence of multiple PPPs on the degradation rates of the individual compounds.

The literature summarized in this report shows that synergistic effects occur relatively rarely, and can be traced back to combinations of specific compounds.

Using an intensive crop with many multiple and simultaneous applications (i.e. strawberries) we have calculated the spray drift values on surface water in a ditch and the exposure profiles over a 100–day period using the Dutch evaluation ditch. The effects were predicted based on the PEC and RAC values calculated for the most sensitive standard test organisms and the concentration addition approach. The effects were calculated for two scenario's: the Dutch authorisation scenario and the tank mixture scenario. The Dutch authorisation scenario is the current approach in the authorisation procedure of the Ctgb for single PPPs. In the tank mixture scenario the drift has been adjusted to one drift class lower than the highest drift reduction (DRT) class for each mixture. This lowering of one DRT class is an assumption we have made based on a literature research which shows that for tank mixtures spray drift might either increase or decrease compared to the spray drift of the single products. This increase or decrease can be ascribed to the effects of formulations and additives on spray drift potential.

The strawberry application schedule has shown that the actual strawberry crop scenario is not protective for invertebrates and fish. Repeated applications are the main cause for exceeding the authorisation standards. For fish, all single compounds meet the criteria for authorisation on the market, however the sum of the compounds as applied in the strawberry crop protection schedule, does not when based on toxicity data for fish.

It can be concluded that the actual strawberry crop scenario is not protective for invertebrates and fish. For the risk assessment of PPPs, it needs to be considered that PPPs are part of a crop protection programme and thus should be evaluated in this context.

# Samenvatting voor het beleid

In de Nederlandse landbouw kunnen gewasbeschermingsmiddelen frequent en tegelijkertijd toegepast worden. Ook worden veel gewasbeschermingsmiddelen herhaald in de tijd - soms wekelijks - gebruikt en gemengd in tankmengsels uit efficiëntie overwegingen. Omdat de toelating per middel geregeld is, blijft het onduidelijk of en in welke mate realistische blootstellingsscenario's gebaseerd op intensieve teelten in Nederland, voldoende bescherming bieden aan water- en landorganismen en of onder deze scenario's de hersteloptie kan worden toegepast. In deze context is de belangrijkste vraag of de product per product benadering voldoende bescherming biedt.

In de huidige risicobeoordeling ten behoeve van de toelating van gewasbeschermingsmiddelen op de Nederlandse markt worden de volgende mengsels en herhaalde toepassingen beschouwd:
- Een product met één actieve stof en herhaalde toepassingen van één product wanneer het op het label is opgenomen;
- Een product met meerdere actieve stoffen en herhaalde toepassing hiervan wanneer dit op het label is opgenomen;
- Tankmengsels (meerdere producten) en herhaalde toepassing hiervan wanneer het op het label is opgenomen.

De huidige risicobeoordeling ten behoeve van de toelating beschouwt niet:
- herhaalde toepassingen van een actieve stof door toepassing van meerdere producten met dezelfde actieve stof. Voor deze omissie zoekt Ctgb momenteel naar een oplossing;
- herhaalde toepassingen van een product met meerdere actieve stoffen wanneer dit niet op het label is opgenomen;
- tankmengsels (meerdere producten) en herhaalde toepassing hiervan wanneer dit niet op het label is opgenomen.

Deze niet-beschouwde toepassingen zijn wel algemeen agrarisch gebruik.

De vraag is of en wanneer herhaalde toepassingen en tankmengsels dienen te worden meegenomen in de risicobeoordeling t.b.v. de toelating van deze stoffen en zo ja, welke methodiek kan worden toegepast om deze herhaalde toepassingen en mengsels in de risicobeoordeling te beoordelen.

Het College voor de Toelating van Gewasbeschermingsmiddelen (Ctgb) heeft de blootstelling aan drift en risico's van tankmengsels voor het milieu als een belangrijke omissie in onze kennis gedefinieerd. Dit project richt zich dan ook op deze tankmengels. De herhaalde toepassing van meerdere actieve stoffen is daar een inherent onderdeel van. Naast een literatuuronderzoek naar blootstelling en effecten bij toepassing van tankmengsels, is in dit project een teeltscenario van aardbeien doorgerekend met intensief gebruik van gewasbeschermingsmiddelen. De bevindingen uit het literatuuronderzoek en de resultaten van de berekeningen aan het aardbeiscenario worden beschreven in dit rapport.

Het literatuuronderzoek heeft laten zien dat drift van een verspoten mengsel verhoogd of verlaagd kan worden wanneer mengsels met formuleringen en hulpstoffen worden beschouwd. Literatuuronderzoek heeft ook aangetoond dat de blootstelling nauwelijks wordt beïnvloed door interactie tussen gewasbeschermingsmiddelen bij competitie om sorptie-plaatsen. Geen uitspraak kan gedaan worden over de invloed van de aanwezigheid van meerdere stoffen op afbraaksnelheden.

Synergie in effecten (i.e. dat de effecten van een mengsel van stoffen groter is dan die van de afzonderlijke stoffen) komt maar zeer beperkt voor en kan herleid worden tot specifieke stofgroep-combinaties. In mengsels kan daarom worden uitgegaan van concentratie additie. Concentratie additie is dan ook toegepast bij de berekeningen van de drift van tankmengsels in de teelt van aardbeien, de blootstelling in oppervlaktewater als gevolg van deze drift en de effecten van deze tankmengsels op waterorganismen in de tijd.

Voor het doorrekenen van het teeltscenario voor aardbeien, is uitgegaan van een realistisch spuitschema voor aardbeien dat door aardbeitelers in de praktijk wordt toegepast. Het spuitschema van tankmengsels en herhaalde toedieningen van stoffen omvat driftwaarden en driftreductieklassen omgerekend naar een belasting van het oppervlaktewater. Met TOXSWA, het model voor gedrag van gewasbeschermingsmiddelen in oppervlaktewater, zijn de blootstellingsconcentraties in het oppervlaktewater berekend. Deze "Predicted Environmental Concentrations" (PEC) zijn vergeleken met de "Regulatory Acceptable Concentrations" zoals gehanteerd door het Ctgb bij de toelating van de afzonderlijke middelen.

Omdat het literatuuronderzoek naar drift van mengsels heeft aangegeven dat dit door grote onzekerheden omringd is, en de drift van mengsels zowel hoger als lager kan uitvallen, zijn voor de berekeningen van de drift twee scenario's gehanteerd. Het eerste scenario is het scenario gehanteerd bij de toelating voor gewasbeschermingsmiddelen in Nederland. Hierin is de maatgevende driftreductieklasse voor het mengsel gehanteerd, dat is de hoogste driftreductieklasse. Het tweede scenario is het tankmengselscenario, waarin een driftreductieklasse voor het gehele mengsel is gehanteerd die één klasse lager ligt dan de maatgevende driftreductieklasse. Deze aanpassing is gedaan als gevolg van verwachte formuleringseffecten op de driftgevoeligheid.

Het huidige aardbei-toedieningsschema is niet beschermend voor ongewervelde dieren en vissen in het oppervlaktewater. De effecten konden vooral worden toegeschreven aan de herhaalde toepassing van enkele insecticiden die de giftigheid het meest bepaalden.

# 1 Introduction

## 1.1 Background of the report

The aim of project *Project BO-20-002-031* – 'Investigating multi-stress in surface water' is to answer the following research question:

Is the current product-by-product and active substance-by-active substance evaluation providing sufficient protection in the context of the authorisation of PPPs in the Netherlands?

In normal agricultural practice, PPPs are frequently used, and they are used simultaneously on one crop and simultaneously in adjacent parcels of arable land in the same area. Since the authorisation of PPPs is currently based on a product-by-compound approach, it is unclear if and to what extent this approach in the Netherlands provide sufficient protection to aquatic organisms in ditches adjacent to arable land and at the higher landscape level, especially in the case of intensively sprayed crops. This last question is also relevant in the light of the application of the recovery option: what are the consequences of frequent exposures to different PPPs in space and time for the acceptance of recovery in the effect assessment by regulators ? The present project was a multidisciplinary project involving Wageningen Environmental Research (Alterra), Wageningen Plant Research and Ctgb (the Board for the Authorisation of Plant Protection Products and Biocides in The Netherlands), a collaboration providing knowledge from the fields of application technology, exposure, fate, effects and risk assessment.

The first step we identified was to consider the impact of mixtures of PPPs on the individual steps in the risk assessment, resulting in a number of stepping stones towards answering the main question whether the current evaluation is sufficiently protective. The present report presents the current state of knowledge based on a literature review and includes calculations of spray drift, exposure and effects of PPP tank mixtures in a spraying schedule for strawberries.

The main questions to be answered were:

- Is there a need to consider the effects of plant protection products and mixtures on spray drift in the exposure assessment and if so, how should this be effectuated?
- Is there a need to consider the effects of mixtures in the exposure assessment other than spray drift and if so, how and when should this be effectuated?
- Is there a need to consider multistress in the effect assessment and if so, how and when should this be effectuated?

This project has restricted itself to considering PPP mixtures only. Mixtures of PPPs with nutrients or with other organic chemicals are not included in our review. In addition, we focus on the water compartment and do not consider the soil or sediment compartments.

In 2015 a meeting was held with Ctgb in order to define multistress and to develop a common understanding of the consequences of multistress for PPP risk assessment. The current practice involves Ctgb evaluating product mixtures (products with two or more active substances) only when these are included on the label. Ctgb also evaluates multiple applications of one product if stated on the label, but does not evaluate multiple applications of tank mixtures or multiple products in crops during the season.

Ctgb uses the 'Concentration Addition' (CA) method by summing Toxicity Exposure Ratio (TER) values to account for the use of more than one product at the same time and for tank mixtures as included on the label. It follows a simple approach to the CA method. The approach proposed in the Aquatic Guidance document (EFSA, 2013) is not (or not yet) being followed (EFSA, 2013, page 148 and follow-up text in paragraph 10.3.3. Calculated mixture toxicity).

## 1.2 Structure of the report

Chapter 2 discusses the effects of formulations and adjuvants on spray drift and emission. Chapter 3 presents an overview of exposure assessment methodologies for PPP mixtures in the risk assessment. Chapter 4 presents and discusses methods for addressing PPP mixtures in the effect assessment. Chapter 5 describes an evaluation of realistic tank mixture applications in a spraying schedule for strawberries used by strawberry growers. Chapter 6 discusses the mixture concepts as well as the results of our evaluation of the tank mixture calculations for a strawberry crop. Chapter 7 presents an outlook for further research and testing the findings with spraying schedules for other crops.

# 2 The effects of formulations and adjuvants on spray drift and emission

## 2.1 Introduction

When applying plant protection products (PPPs), the spray drift to surface water, non-target terrestrial plants and arthropods, and bystanders and residents can be reduced by means of improved spraying techniques. As such, application techniques to reduce spray drift contribute to a safer use of PPPs. Such application techniques are being evaluated (TCT, 2016) based on laboratory and field measurements of spray drift (ISO22866). The spraying liquid used during these measurements is usually tap water, with a standardised additive added. The effect of PPPs and/or adjuvants in the tank mix can influence the classification of spray drift reducing techniques (DRTs). Adjuvants can have a positive additional effect on spray drift reduction but can also increase spray drift. The effect of adjuvants on spray drift also depends on the nozzle type used. Measurements of drop sizes and spray quality in the laboratory and spray drift modelling (IDEFICS; Holterman et al., 1997) as well as field measurements of spray drift, show that spray drift is influenced not only by the nozzle type but also by the formulation of the PPP and adjuvants. The relations between the different factors (application technique, adjuvants, formulation) and spray drift are discussed below.

## 2.2 Effects on drop size and spray drift potential

Earlier research (Ruiter et al., 2003a; 2003b) has found that the addition of an additive ('A') to the spray solution changed the spray quality. The spray volume of drops with sizes smaller than 100 µm ($V_{100}$), corresponding to the vulnerable fraction for spray drift, was changed compared to that for tap water alone, depending on the type of nozzle (Fig. 1). Whereas $V_{100}$ for the additive A remained the same for a standard flat fan nozzle (XR11002), it decreased slightly when spraying with a pre-orifice nozzle (DG11002) and also increased with a venturi type flat fan nozzle (ID12002). The effect of a tank mixture of Shirlan on $V_{100}$ was more or less the same for these nozzle types and for tap water plus additive A. However, when the additive was added to a tank mixture of Shirlan (fluazinam), the spray produced by a standard flat fan nozzle increased the $V_{100}$, and the spray became more drift-prone. This was also the case with a pre-orifice nozzle and the venturi flat fan nozzle type. The combination of Shirlan and additive A changed the spray qualities of the nozzle types in a different way from what happened when the additive and the product were administered in separate sprays.

Holterman et al. (1998) measured the effects of five different additives on spray quality (Southcombe et al., 1997), on the volume fraction of drops smaller than 100 µm, and on drop speed and top angle, and used these data in the IDEFICS spray drift model (Holterman et al., 1997) to estimate spray quality changes and consequent changes in spray drift potential due to the addition of adjuvants. Spray qualities were measured for three nozzle types (Fig. 2): a flat fan nozzle (XR11004), an anvil nozzle type (TT11004) and a venturi flat fan nozzle type (TD11003).

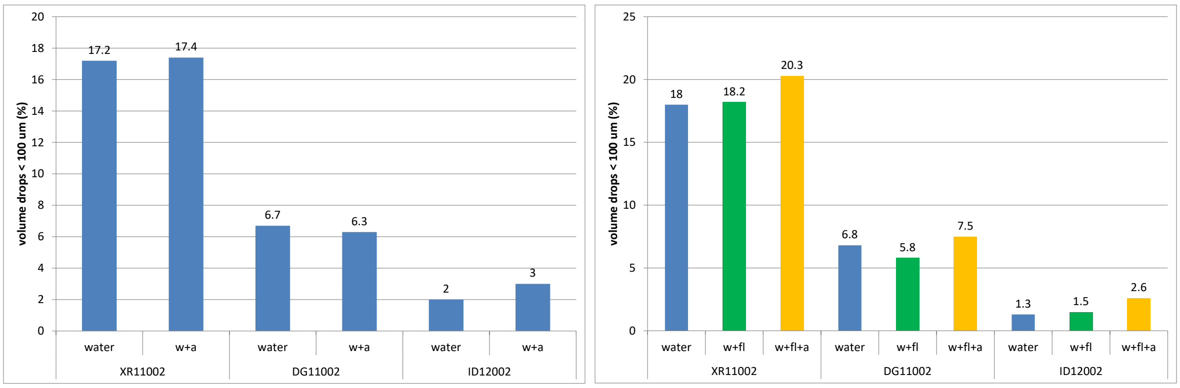


***Figure 1*** *Effect of additive A (left) and Shirlan (fl) in combination with additive A (fl+A; right) on the volume fraction of drops smaller than 100µm (after De Ruiter et al., 2003a).*

Additive #1 resulted in a finer drop size spectrum for all three nozzle types, and $V_{100}$ increased at different rates depending on the nozzle type. Additives #2 and #4 showed little effect on drop sizes, whereas additives #3 and #5 resulted in coarser spray qualities and a reduced volume of drops smaller than 100 µm in the spray fan.

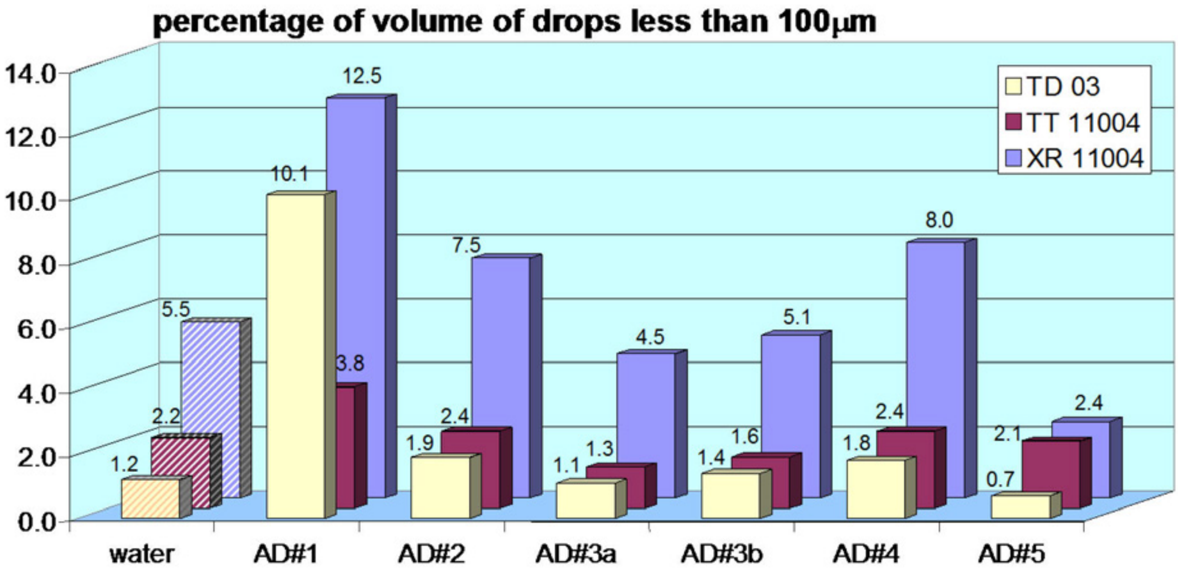


***Figure 2*** *Effects of nozzle type and 5 additives on volume fraction of drops smaller than 100 µm in the spray fan (after Holterman et al., 1998).*

These changes in spray qualities with different spray nozzles and additives result in changes in the spray drift deposition on surface water (Fig. 3). When the spray quality changes towards a finer spray (additive 1), i.e. a higher $V_{100}$, the spray drift deposition on water surface also increases. Similarly, coarsening the spray quality (as with additives 3 and 5) results in a decrease in spray drift deposition on the water surface. A change in tank mixture from tap water to one with an additive or a formulated product can change spray drift deposition (Table 1) and can cause an increase in spray drift deposition of 26% to 225% for additive 1. Additive 3 decreases spray drift deposition on surface water by 14% to 29% for the nozzle types XR11004 and TT11004, respectively, but increases spray drift deposition by 55% for the nozzle type TD11004. Additive 5 decreases spray drift deposition by 37% to 45% for the nozzle types TD11003 and XR11004, respectively, but has no effect on spray drift deposition for the TT11004 nozzle type. Hence, the effects of changes in tank mixtures on spray drift are very hard to predict.

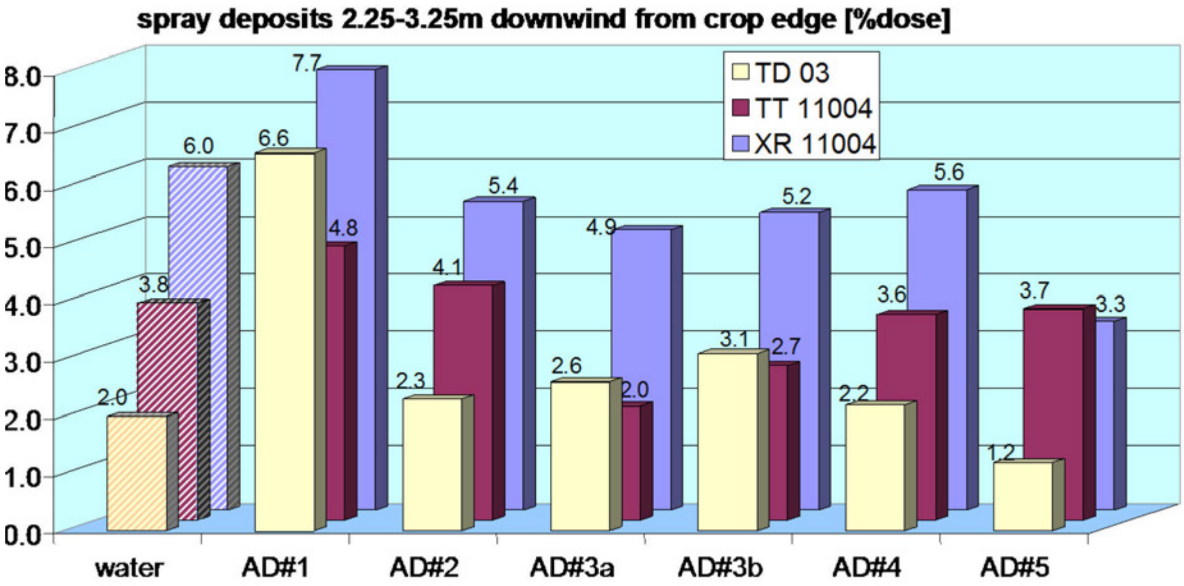


***Figure 3*** *Effects of nozzle type and 5 additives on spray drift (% of applied spray volume) at water surface distance for a standard ditch (2.25-3.25 m from crop edge) (after Holterman et al., 1998).*

***Table 1*** *Effect of change in spray quality with different additives and nozzle types on spray drift deposition at water surface distance.*

| Additive | XR11004 | TT11004 | TD11003 |
|---|---|---|---|
| AD#1 | +28% | +26% | +225% |
| AD#2 | - | - | - |
| AD#3 | -14% | -29% | +55% |
| AD#4 | - | - | - |
| AD#5 | -45% | - | -37% |

## 2.3 Literature review

A quick-scan review of the literature (CAB abstracts) using the key words ‘nozzle’, ‘formulation’ and ‘spray drift’, resulted in 14 references, whereas the key words ‘nozzle’, ‘formulation’ and ‘drop size’ resulted in 39 references, 8 of which appeared in both searches. This resulted in a total of 45 references. The abstracts of the papers were used to prepare an overview of combinations of nozzles and PPPs or additives that had been investigated for effects on drop sizes, spray quality and spray drift. Results are summarised in Tables 2 and 3 for drop sizes and spray drift, respectively.

***Table 2*** *Effect of plant protection products (PPPs) and additives on drop sizes for different nozzle types.*

| PPP | additive | Used Nozzle types | Measuring method | reference | PPP | additive |
|---|---|---|---|---|---|---|
| herbicide | 12 drift reduction agents | 1 nozzle; n.s. | | | Sympatec | Elsik et al., 2010 |
| Water | 12 drift reduction agents | 1 nozzle; n.s. | | | Sympatec | Elsik et al., 2010 |
| | polymer | 1 nozzle at different pressures; n.s. | | | PDA<br>Laser diffraction | Williams et al., 2008 |
| Phenmedipham EC, SC | 4 adjuvants | Hollow cone | Flat fan | venturi | Malvern | Stainier et al., 2006 |
| Phenmedipham EC, SC | 4 adjuvants | | Flat fan | | Malvern | Stainier et al., 2005 |
| | Water soluble surfactants | | Flat fan | venturi | PDA | Ellis et al., 2000 |
| | emulsions | | Flat fan | venturi | PDA | Ellis et al., 2002 |
| water | 7 adjuvants | | FF/110/9.8/3.0 | | Sympatec | Ellis & Bradley, 2002 |
| water | 2 anti-drift adjuvants; n.s. | Nozzle types; n.s. | | | n.s. | Marucco et al., 2012a |
| Imidacloprid formulations OD SC, WG, SL | agral | Flat fan<br>XR11003VS<br>03F110 | Pre-orifice<br>DG11003VS | Venturi<br>AI11003VS | Oxford visisizer | Hilz & Vermeer, 2012 |
| Formulations PPP, water,<br>EC, EW, WG, SC | Vegetable oil, fatty acid ester, mineral oil, white oil | Flat fan<br>XR11003 | | | Malvern | Hilz et al., 2012 |
| water | 3 adjuvants | XR8003 | | | Malvern | Oliveira & Antunassi, 2012 |
| water | 5 adjuvants | | anvil<br>TT11002 | Venturi anvil<br>TTI11002 | Malvern | Cunha et al., 2010 |
| 2 Glyphosate formulations<br>Diflufenzopyr+ dicamba | 5 adjuvants | XR11003<br>XR11004<br>XR11005 | Anvil<br>TT11004<br>TT11005 | AI11003<br>AI11004 | Malvern | Klein et al., 2008 |
| Quinclorac<br>2,4-D<br>2 formulations | | 3 nozzle types n.s. | | | Laser n.s. | Sciumbatto et al., 2005 |
| water | 8 adjuvants | | Twin-fluid<br>n.s. | 3 venturi nozzles n.s. | PMS | Butler Ellis & Tuck, 2000 |
| Glyphosate 2 formulations | Non-ionic surfactant | Flat fan n.s. | Pre-orifice n.s. | Anvil n.s. | n.s. | Mueller & Womac, 1997 |
| Water<br>Blank EC | 6 adjuvants<br>2 concentrations | FF110/0.8/3.0 | | | PMS | Butler Ellis & Tuck, 1997 |
| water | Vegetable oil<br>EC | Flat fan n.s. | Drift reducing n.s. | | malvern | Barnett & Matthews, 1992 |
| water | 3 Oil-water mixtures | Fan nozzle n.s. | | | Laser n.s. | Bouse et al., 1989a |
| Herbicide n.s. | Surfactants, polymers, n.s. | Hollow cone n.s. | | | Laser n.s. | Bouse et al., 1989b |

n.s. = not specified

From Tables 2 and 3 it can be concluded that research into drop size and spray drift has only shown the effects of single products or single additives relative to water as a spray solution. No experiments have been published measuring the effects of tank mixtures of PPPs or of PPPs and additives. Generally speaking, the effects of additives and PPPs on spray quality and spray drift were different for the different nozzle types, making it difficult to generalise the results into a common advice, although it can be stated that the change in terms of drift reduction classes might amount to one class more or one class less drift reduction.

***Table 3*** *Effect of Plant Protection Products (PPPs) and additives on spray drift for different nozzle types.*

| PPP | additive | Used Nozzle types | method | reference | PPP | additive |
|---|---|---|---|---|---|---|
| Phenmedipham EC, SC | 4 adjuvants | Hollow cone | Flat fan | venturi | Wind tunnel | Stainier et al., 2006 |
| Phenmedipham EC, SC | 4 adjuvants | | Flat fan | | Wind tunnel | Stainier et al., 2005 |
| | Water soluble surfactants | | Flat fan | venturi | Wind tunnel | Ellis & Tuck, 1997 |
| | emulsions | | Flat fan | venturi | Wind tunnel | Ellis &Tuck, 2000 |
| formulation | | Nozzle type, size, top angle, orientation, pressure | | | field | Maybank et al., 1979 |
| Chemical types; n.s. | Thickening adjuvants | Nozzle types, size; n.s. | | | field | Yates et al., 1981 |
| water | 2 anti-drift adjuvants; n.s. | Nozzle types; n.s. | | | testbench | Marucco et al., 2012 |
| Imidacloprid formulations OD SC, WG, SL | agral | Flat fan XR11003VS 03F110 | Pre-orifice DG11003VS | Venturi AI11003VS | Two wheel plot sprayer | Hilz & Vermeer, 2012 |
| glyphosate | 7 adjuvants | XR110015 | | AIXR110015 TTI110015 | field | Martini et al., 2015 |
| water | 3 adjuvants | XR8003 | | | field | Oliveira & Antunassi, 2012 |
| water | 7 adjuvants | HC/0.71/3.0 | FF/110/9.8/3.0 | Pre-orifice FRD110/0.8/3.0 Venturi AJ11002VS | Wind tunnel | Ellis & Bradley, 2002 |

n.s. = not specified

## 2.4 Conclusions

General conclusions of the experiments summarised in section 2.3 and in the literature are as follows:

- Adjuvants and formulated PPPs can either increase or decrease spray drift.
- Effects are different for different nozzle types.
- For sprays containing adjuvants (or agrochemicals), nozzles can be classified in terms of drift reduction as differing by one class or more from those containing only tap water.
- There is a need to quantify the effects of tank mixtures (agrochemicals; agrochemical plus adjuvant) on spray drift reduction and groups of spray nozzles for classification into spray drift reduction classes.
- There is a need to integrate the effects on spray drift reduction of application technologies and tank mixtures.

# 3 Overview of aquatic exposure assessment methodologies

## 3.1 Introduction

The environmental risk of using a particular active substance is assessed at EU level, whereas the risk related to products is assessed at Member State level.

The exposure assessment methodology currently used in the EU was developed by the FOCUS Surface Water Modelling Working Group (FOCUS, 2001). The assessment procedure follows a tiered approach and consists of four steps, starting with a simplified worst-case situation in the first step, and more realism being added at each subsequent step. If no acceptable environmental risk is found in a lower step (=tier), a higher step may be applied. The dissolved concentration in the edge-of-field water body of concern is used as the predicted environmental concentration (PEC). The risk assessment uses the annual peak concentration, the time-weighted averaged concentration or the entire calculated concentration profile over time to assess either the acute or the chronic risk (EFSA, 2013).

Step 3 is the most realistic of the four steps, and consists of ten realistic worst-case scenarios for which PECs must be calculated. The ten scenarios are realistic worst-case combinations of soil, climate and slope for the water body types of 'ditch', 'stream' and 'pond'. The entry routes being considered are drainage, spray drift and run-off/erosion. This step requires the use of mechanistic models including PRZM (run-off/erosion entries), MACRO (drainage entries), Spray Drift Calculator (spray drift entries) and TOXSWA (fate in surface water), which are combined in the software package FOCUS-SWASH (e.g. Van den Berg et al., 2015).

The exposure assessment methodology used in the Netherlands to assess the risk associated with the use of product formulations considers a single edge-of-field ditch, with a constant summer and winter flow velocity, which receives input from spray drift only. The TOXSWA model is used to calculate the dissolved water concentration (PEC). The Dutch exposure assessment methodology is currently being revised and adapted to the latest scientific insights. Drainage will be included as an entry route (Tiktak et al,2012) and a distinction will be made between spray drift deposition from upward, sideways and downward spraying.

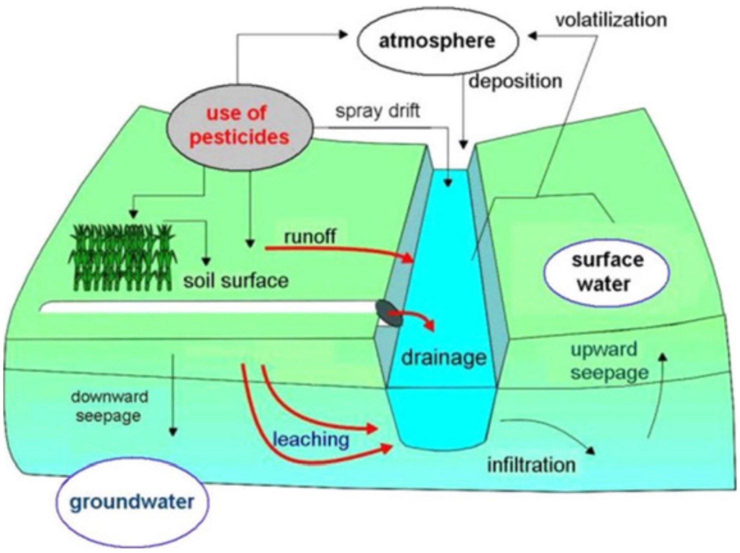


***Figure 4*** *Conceptual model showing a ditch receiving spray drift deposition, runoff and drainage from a field after application of a PPP (After Adriaanse et al., 1996).*

## 3.2 Realistic application practices

Application of a single product containing one active substance is probably still the most common way of using PPPs. However, it is increasingly common practice to apply combinations of active substances in a single product, or to apply several different products against a pest simultaneously, or to apply different active substances to combat several pests occurring at the same time. This gives rise to combinations/mixtures of active substances being emitted to the environment, and being present in surface waters simultaneously.

The prevalent assessment practice in Europe (and in the Netherlands) is to assess the risk of the single active substance within a formulation, although product mixtures are assessed as well (at a national level). Risks related to product mixtures are assessed using exposure models to calculate the PEC of each active substance separately, using the active substance characteristics. Hence, no interaction is assumed between the chemicals in the formulation, nor are changes in the behaviour and environmental fate of the individual chemicals assumed due to product mixtures.

Soil and water concentrations depend strongly on the entry routes being considered (spray drift, run-off) and on environmental characteristics such as water course size, catchment size, flow velocity and sediment characteristics. Spray drift deposition may be affected by the product formulation (see Chapter 2). But application rate and frequency of application are also important, as are PPP properties such as solubility, saturated vapour pressure, transformation half-life and sorption coefficient. There is no indication that other input parameters, including PPP characteristics, that are used in the model calculations are altered by the interaction of chemicals applied as part of a product mixture. Transformation in water and in sediment, and sorption to sediment organic matter are the main processes affecting fate and exposure in water. Therefore we focussed on mixture effects for these two processes.

## 3.3 Effects on transformation

Normal applications for agronomic purposes have no prolonged effect on bioactivity in soil. According to Dzantor & Felsot (1991), both selective stimulation and inhibition of different groups of microorganisms in the soil might occur at high concentrations of PPP mixtures. Such effects on transformation rates seem, however, unlikely at concentrations expected in soil during normal agricultural use.

The presence of a second compound may have implications for degradation rates of compounds in general. Studies on degradation of PPPs in water and in sediments have been rare, and none of those reports the degradation in the presence of other organic compounds, i.e. competitive degradation. Hence it is impossible to assess the effect of the simultaneous presence of multiple PPPs on the degradation rates of the individual compounds.

## 3.4 Effects on sorption

Sorption of organic compounds to sediments is a well-known and much studied phenomenon. However, whether and to what extent the sorption of a compound may be influenced by the presence of one or more other compounds has been much less investigated. Only a few papers were found during a Scopus search on this subject.

The sorption of dimethoate to sediment was found to decrease in the presence of promethryn and malathion (Cheng et al., 2014), whereas Wang et al. (2012) found increased sorption of dimethoate in the presence of promethryn and metalaxyl. Both papers also reported the effect of zinc and cadmium on the sorption of dimethoate. Cheng et al. (2014) reported increased sorption due to zinc, but decreased sorption due to cadmium, whereas Wang et al. (2012) reported decreased sorption in the presence of either metal.

Xu et al. (2015) reported increased sorption of the antibiotic sulfadiazine in two soils in the presence of copper (II); a slight effect was seen at pH below 5, but a larger effect at higher pH. Similarly, Yan et al. (2013) reported increased sorption of the antibiotic chloramphenicol in four different sediments in the presence of Cu (II).

Gao et al. (1998) investigated sorption of several PPPs in sediment of a pond located in Southern Germany. They found that the sorption of the relatively weakly sorbing atrazine was slightly reduced (< 4%) in the presence (1 – 5 mg/L) of the more strongly sorbing bifenox; the sorption of the latter was less affected by the presence of atrazine (1 – 5 mg/L).

Sudhakar and Dikshit (2010) studied the sorption of endosulfan from water to treated wood charcoal and found that the presence of atrazine and monocrotophos resulted in decreased sorption of endosulfan, possibly due to competition for available adsorption sites.

Shu et al. (2013) demonstrated that the sorption of 1,2,4-trichlorobenzene in 3 soils/sediments from South China was decreased by the presence of 1,2,4,5-tetrachlorobenzene, the extent of competition depending on the rigidity of the sediment's natural organic matter matrix, with more reduced and condensed matrixes resulting in a more pronounced competitive effect (Shu et al., 2013).

Surfactants have also been reported to affect the sorption of organic compounds by sediments. The cationic surfactant benzalkonium chloride and the cationic herbicide paraquat were found to mutually affect their respective adsorption isotherms to monmorillonite (Ilari et al., 2014), which is most likely due to competition between sorption sites on the mineral.

Tao et al. (2006) reported the sorption of atrazine by surface sediments collected at four different sites near Beijing, China. Anionic and cationic surfactants in concentrations of 0 – 20 mg/L reduced the sorption of atrazine, whereas neutral non-ionic surfactant decreased sorption even at concentrations below 1 mg/L.

Overall, the findings seem to indicate that for mixtures of organic compounds, it is not uncommon that the presence of a second compound reduces the sorption of the first. In view of the limited number of studies found, however, it is impossible to apply this conclusion to a broad range of combinations of PPPs. Moreover, it seems not to apply to combinations of PPPs and metals, as sorption of the organic compound in the studies we found was actually increased by the presence of the metal.

## 3.5 Conclusions

There have been very few studies on the degradation of PPPs in sediments: the literature provides no reports on degradation in the presence of other organic compounds, i.e. competitive degradation. It is therefore currently not possible to evaluate the effect of the simultaneous presence of multiple PPPs on the degradation rates of the individual compounds.

Overall, the findings seem to indicate that for mixtures of organic compounds, it is not uncommon that the presence of a second compound (slightly) reduces the sorption of the first compound. Only a limited number of studies were found and this represents a gap in our knowledge.

# 4 Effects of mixtures of plant protection products: how to address them in the risk assessment?

## 4.1 Introduction

Over the last decade, a number of studies have been published that provide an overview of effects of the toxicity of PPP mixtures (Verbruggen and Van de Brink, 2010; Deneer, 2000). These reports, summarizing a series of studies, showed that in binary and multiple mixtures of PPPs, concentration addition was most often observed in the case of products with the same mode of action. In the case of products with different modes of action, independent action (response addition) was usually observed. In some cases, a response was noticed that was in between these two concepts. Concentration addition provides a precautious but not overprotective approach to the predictive hazard assessment of PPP mixtures under realistic exposure scenarios (Junghans et al, 2006), irrespective of the similarity or dissimilarity of their mechanisms of action. Synergistic or antagonistic effects were seldom observed (Verbruggen and Van de Brink, 2010; Deneer, 2000). These observations confirmed earlier conclusions on mixture toxicity.

To study the possibilities for implementation of concepts of mixture toxicity in the risk assessment of PPPs, a working group led by RIVM carried out a multistress project (Luttik et al., in prep.). In the framework described by Luttik et al. (in prep.), the multiple stresses caused by parallel and sequential applications of PPPs was examined by 3 different methods: the so-called Toxic Unit method, in which the contributions of the individual substances are summed and the maximum concentration over time is calculated; the MS-PAF method, which calculates the potentially affected fraction of aquatic organisms, taking into account differences in sensitivities of the organisms to the various substances; and the MASTEP population model, which calculates the time required to recover from the exposure to the various substances. In all studies the multiple stresses used realistic application scenarios during the growing season of a potato tuber and an orchard crop over time.

Luttik et al. found that the Toxic Unit approach and the MS-PAF approach yielded higher risks for the multiple applications than those calculated by the current authorisation method for the individual products. However, these two methods used worst-case assumptions. The MASTEP method, using *Asellus aquaticus* as the indicator species, did not yield longer recovery times for the multiple applications in comparison to those calculated for the individual PPP applications, but cumulative effects were found in the orchard case. Nevertheless, their study suggested that the current assessment procedure appeared protective enough for species with poor dispersal capacity, synchronised reproduction and high offspring. Whether this assessment procedure was sufficiently protective for other species was not clear. In all three approaches, a few substances dominated the calculated overall toxicity.

This chapter tries to answer the question when synergy might play a role in studying the effects of PPP mixtures and when effects can be explained by concentration addition or independent action.

## 4.2 Antagony, synergy and additivity

Cedergreen (2014) published a review of the occurrence of antagony, additivity and synergy in PPP mixtures, using the database published by Belden et al. (2007) and the review by Cedergreen et al. (2008). Synergy is here defined as mixtures with at least a two-fold difference between observed and predicted effect concentrations using concentration addition (CA) as a reference model and including both lethal and sublethal endpoints. The database assembled by Belden et al. (2007) provided data on 207 mixtures, 194 of which were binary, and another 13 consisted of more than two PPPs (multiple

PPPs included). In addition, 84 papers were reviewed for synergy where the values of the model deviation ratio (MDR) were >2. The MDR is the ratio of predicted versus observed effect concentrations. This resulted in a database of synergistic interactions including 73 cases of synergy, derived from Belden et al. (2007) and the data search compiled from 36 studies. These studies tested the effect of combinations of 54 PPPs on 27 different species. Sixty-nine of the mixture combinations were binary mixtures, while the remaining four mixtures consisted of combinations of three or five organophosphate insecticides or eight chloroacetamide into groups with common modes of action according to Tomlin (2011).

According to Cedergreen (2014), five groups of PPPs in particular were overrepresented in the synergistic mixtures. These were (see Fig. 5):

- organophosphate and carbamate insecticides (cholinesterase inhibitors),
- azole fungicides (ergosterol biosynthesis inhibitors),
- triazine herbicides (photosystem II inhibitors)
- pyrethroid insecticides (interfering with sodium channels in nerve cells)

Grouping the cholinesterase inhibitors together and looking at which of the binary combinations of the above PPP groups displayed synergy in autotrophic organisms (plants and algae) and heterotrophic organisms (microorganisms and animals) revealed no cases of synergy within the autotrophic organisms (Fig. 6B). In the group of heterotrophic organisms, 69 of the 73 synergistic mixtures (95%) contained either cholinesterase inhibitors (organophosphates or carbamates) or azole fungicides (Fig. 6C). The remaining four mixtures were the abovementioned mixture of 8 herbicide safeners, a mixture of a pyrethroid and an organochloride insecticide, a pyrethroid insecticide and a piperidine fungicide and a photosystem II inhibitor (PSII). Of the 69 binary mixtures, 76% contained a cholinesterase inhibitor and another 24% an azole fungicide (Fig. 6C). The triazines only occurred in synergistic mixtures together with either chlorpyriphos, diazinon, malathion, methidathion or methyl-parathion, which belong to the phosphorothioate and phosphorodithioates class of organophosphates, or with trichlorfon, a phosphate class organophosphate. Pyrethroids, on the other hand, only occurred in synergistic mixtures together with azole fungicides.

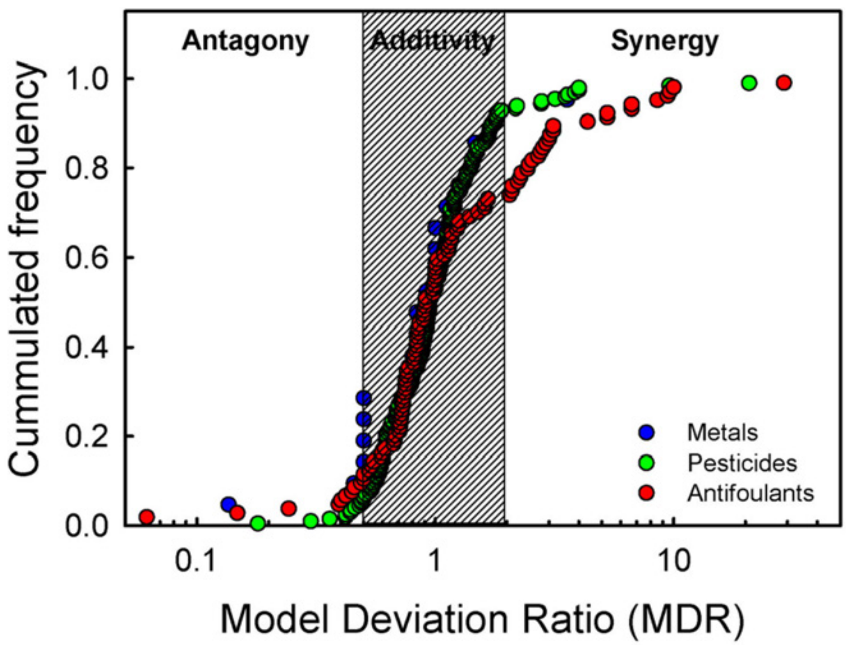


***Figure 5*** *Cumulated frequency of model deviation ratios (MDRs) of binary mixtures of PPPs (n = 195), metals (n = 20), and antifoulants (n = 103). The hatched interval, where 0.5 < MDR < 2, defines the mixtures that deviate less than two-fold from concentration addition (CA) predictions. Mixtures having MDR values < 0.5 are termed antagonistic, while mixtures with MDR values > 2 are synergistic. doi:10.1371/journal.pone.0096580.g002 Source: Cedergreen, 2014.*

An evaluation to ascertain which types of the PPPs from the review by Belden et al. (2007) were dominant in the antagonistic mixtures and which ones conformed to CA showed that cholinesterase inhibitors and azole fungicides made up 29% of the antagonistic mixtures and 48% of the mixtures conforming to CA (Figures 6B and C), which is considerably less than the 95% of the synergistic mixtures (Cedergreen, 2014). Hence, though these modes of action were present in all types of mixtures, they were clearly overrepresented in the mixtures displaying synergistic interactions. The triazines occurred in 1% of the antagonistic mixtures, 22% of the concentration-additive mixtures and 12% of the synergistic mixtures. Hence, triazines did not seem to occur particularly frequently in the synergistic mixtures, and when they did, it was only in mixtures with the abovementioned organophosphates. The 19 triazine mixtures with an MDR of 1 were dominated by auxin transport inhibitors and branched-chain and aromatic amino acid synthesis inhibitors, while the 19 triazine mixtures with MDR values between 1 and 2 were dominated by organophosphates, PSII inhibitors and cell division inhibiting herbicides. All 22 additive mixtures including pyrethroids were mixtures with organophosphates, carbamates or other pyrethroids.

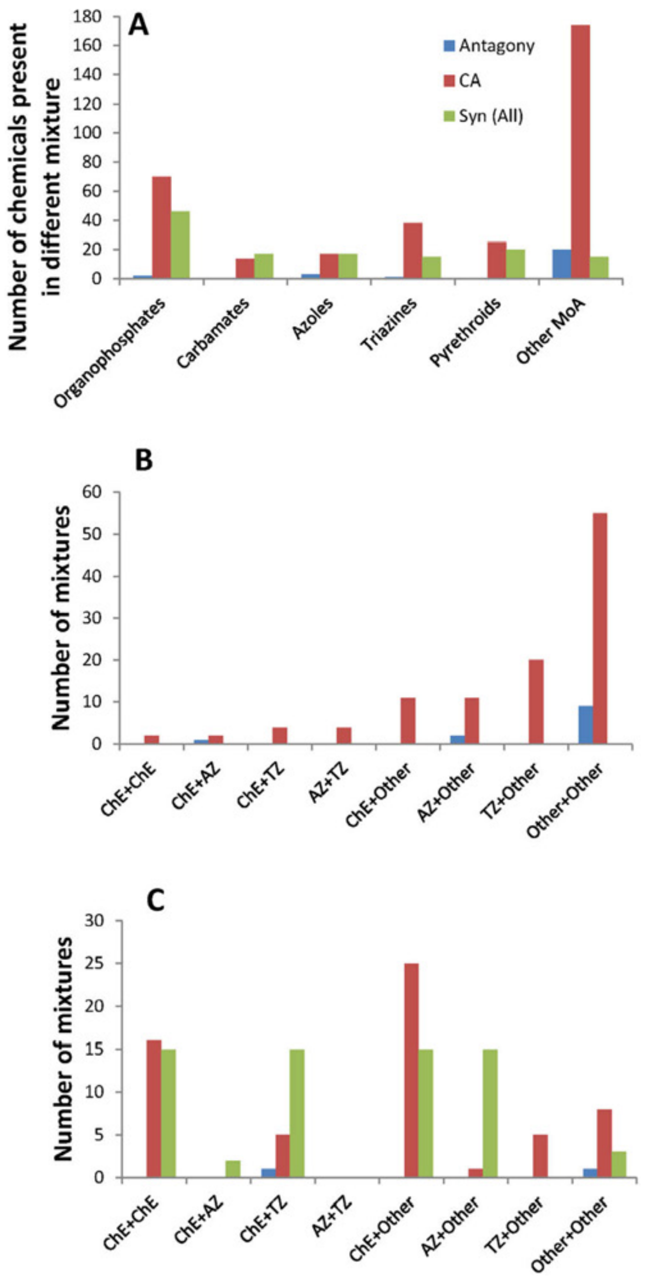


***Figure 6*** *Frequency of PPP antagony, additivity and synergy. Source: Cedergreen, 2014.*

## 4.3 Other studies

Other studies reviewing a range of papers from the open literature also came to the same conclusion (Verbruggen and van de Brink, 2010), i.e. that synergism has seldom been observed in laboratory studies with simultaneous exposure to binary mixtures. In almost all cases the results could be explained by independent actions (response addition) or concentration addition, or the results were somewhere in between (Verbruggen and Van de Brink, 2010). In mesocosm studies performed with mixtures of compounds, increased indirect effects are often observed due to food web interactions. These effects are rather complex and concepts such as response addition and concentration addition are difficult to assess. However, synergistic effects were observed neither in mesocosm studies nor in most laboratory studies with compounds that affect the same biological groups. Exceptional cases where synergism was sometimes observed were the combinations of an organophosphorus ester or a carbamate together with either another organophosphorus ester or a synthetic pyrethroid. However, the deviations from additivity were small even in these cases (Verbruggen and van de Brink, 2010).

Deneer (2000) showed that CA is a useful concept to describe the joint effect of PPPs on aquatic organisms. He based his conclusions on literature data from 1972 to 1998. For more than 90% of 202 mixtures in 26 studies, CA was found to predict effect concentrations correctly within a factor of two. The CA approach was also confirmed by the experimental results for mixtures of compounds with dissimilar modes of action. Deviations from CA did occur, but were mostly limited. The combinations most frequently leading to deviations from CA were those of either an organophosphorus ester or a carbamate with either another organophosphorus ester or a synthetic pyrethroid (Deneer, 2000).

## 4.4 Conclusions

The chemical groups causing synergy can be well defined for the synergistic interactions between PPPs, with cholinesterase inhibitors and azole fungicides being present in 95% of the described synergistic cases.

The results showed that synergy occurred in 7% of the 194 binary PPP mixtures included in the data compilation on frequency. The difference between observed and predicted effect concentrations was rarely more than 10-fold. For PPPs, synergistic mixtures included cholinesterase inhibitors or azole fungicides in 95% of the 69 cases described. Both groups of PPPs are known to interfere with the metabolic degradation of other xenobiotics. We conclude that true synergistic interactions between chemicals are rare and often occur at high concentrations. Addressing the cumulative rather than synergistic effect of co-occurring chemicals, using standard models such as CA, can therefore be regarded as the most important step in the risk assessment of chemical cocktails.

The observation that synergism is seldom observed has been confirmed by other studies.

# 5 Evaluation of tank mixture applications in a spraying schedule for strawberries

## 5.1 Introduction

After PPPs have been authorised by Ctgb for use in a crop (Ctgb, 2016) the products are only allowed to be used if the product label is adhered to. In practice, the product is used by growers in combination with other products in order to cover an entire crop season, and prevent diseases, pests and weed pressure as much as possible. PPPs are therefore used within a schedule of applications of similar products or different products in order to guarantee crop protection. Table 4 presents an example of a crop protection schedule for a strawberry crop.

Insecticides and fungicides are more frequently applied in specific periods in the crop growth cycle. As the frequency of applications can be very high in some intensively sprayed crops like potatoes, flower bulbs, strawberries and orchards, tank mixtures are composed to save time and minimise the number of field applications. In some applications, mixtures of up to 5 PPPs are applied in a crop like strawberries (see Table 4; Michielsen et al., 2012).

It is not only mixtures of insecticides and fungicides which are applied but also mixtures of herbicides, insecticides and fungicides. Table 4 also shows that in some periods a PPP is sprayed every 3-5 days, depending on disease pressure (e.g. Nimrod) or pest pressure (e.g. deltamethrin in different products such as Decis, Imex, WOPRO, DeltaM, Delta25) and this can add up to 10 times within a period of just 30 days.

Whereas the authorisation of PPPs is based on single products in single applications or in a sequence following the suggested label recommendation, it is obvious that the PPPs are applied differently in practice. The use of Individual PPPs can in practice still be in accordance with the label restrictions, but in combination with other PPPs in a tank mixture, the ecotoxicological effects can differ from those of single products. Also an active substance may be used more times and with a shorter application interval than indicated on the label, because different products based on that active substance are used (e.g. the use of deltamethrin in strawberries). Due to formulation interactions and related changes in spray quality and droplet size of the applied spray, effects on spray drift can be expected as well, indicating that the spray drift based exposure data used nowadays in the authorisation procedure may need to be adjusted too.

## 5.2 Methodology

### 5.2.1 Use of plant protection products in strawberry, mandatory drift reducing technologies and spray drift values

In the approach for this chapter we have calculated the drift values, the exposure concentrations resulting from this drift and the effects based on two scenario's:

1. The first scenario is the **Dutch authorisation scenario** which is the current approach in the authorisation procedure of the Ctgb for single PPPs. Appendix Table 1 presents the allowed dose (L/ha), the active substance concentration in the product, the mandatory class of drift reducing technology (DRT) and its accompanying spray drift value as used in the Dutch authorisation procedure for those authorised PPPs (Ctgb, 2016) that are used in strawberry growing based on the example application schedule (Table 4).
2. The second scenario is the **tank mixture scenario**, in which the drift class (DRT class) is applied at one drift class lower than the highest drift class. Based on the uncertainties surrounding changes in spray drift risk due to formulation aspects of tank mixtures, we present this adjusted spray drift value which is one DRT class lower (see Chapter 2; Appendix Table 1). This lowering of

one DRT class is an assumption we have made, as Chapter 2 clearly shows that for tank mixtures spray drift might either increase or decrease compared to the spray drift of the single products. This increase or decrease can be ascribed to the effects of formulations and additives on spray drift potential.

The minimally required mandatory DRT classes for the strawberry application schedule (Table 4) have been determined for the single products in the Dutch authorisation procedure, and are presented in Appendix Table 2. The highest DRT for an application date is also given in Appendix Table 2, as well as the corresponding spray drift value as currently used in the Dutch authorisation procedure. These drift values have been used in the Dutch authorisation scenario. In view of the uncertainties surrounding the effect of the formulation of an applied product and the combined effects of multiple products in a tank mixture, we have assumed that the DRT class is lowered by one step in the tank mixture scenario. Thus, a mandatory DRT of 75% for e.g. phenmedipham is reduced to 50% when used in combination with other products in the same tank mixture in the tank mixture scenario. The corresponding spray drift values for these adjusted DRT classes for the different application dates in the strawberry spraying schedule are also presented. In the example of phenmedipham and iprodion, the spray drift value of 0.5% spray drift deposition on surface water for a DRT75 as used in the Dutch authorisation procedure has been changed to a value of 1.0% for a DRT50 application technique in the tank mixture scenario.

Applied doses (L/ha) of PPPs in a field of strawberries (growing period 16/4-1/8-2012) are presented in Table 4. They were obtained from the Ctgb website (http://www.ctgb.nl/en/pesticides-database) and from a realistic spraying schedule as applied by strawberry growers in The Netherlands within the project Innovaties[2] (Michielsen et al., 2012).

The adjusted mandatory drift reducing technology class required for individual products used in a strawberry spraying schedule, their minimally required DRT for the tank mix and its corresponding spray drift value (%) and adjusted spray drift value (%) based on uncertainty regarding tank mixtures (assumption: one DRT class lower) are presented in Appendix Table 2. The restrictions for use of the different PPPs other than the drift reduction classes in a strawberry spraying schedule according to WGGA’s (Ctgb, 18/11/2016) are presented in Appendix Table 3.

***Table 4*** *Example of doses (l/ha) of PPPs applied in a field of strawberries (growing period 16 April – 1 August 2012) (from: Michielsen et al., 2012).*

| Product | Active substance | 19-4-2012 | 30-4-2012 | 7-5-2012 | 14-5-2012 | 19-5-2012 | 23-5-2012 | 25-5-2012 | 28-5-2012 | 30-5-2012 | 2-6-2012 | 6-6-2012 | 9-6-2012 | 14-6-2012 | 18-6-2012 | 21-6-2012 | 24-6-2012 | 30-6-2012 | 9-7-2012 | total [l/ha] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | daynr | 1 | 12 | 19 | 26 | 31 | 35 | 37 | 40 | 42 | 45 | 49 | 52 | 57 | 61 | 64 | 67 | 73 | 82 | |
| Paraat | dimethomorph | 2.0 | | | | | | | | | | | | | | | | | | 2.0 |
| Kontact320 | fenmedifam | | 1.0 | 1.0 | 1.0 | | | | | | | | | | | | | | | 3.0 |
| Dual Gold 960EC | metalochloor | | 0.4 | 0.4 | 0.4 | | | | | | | | | | | | | | | 1.2 |
| Several[1] | thiacloprid | | | | | 0.2 | 0.2 | | | | 0.2 | | | 0.2 | | | | | | 0.8 |
| Several[2] | deltamethrin | | | | | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | | | | | 2.0 |
| Nimrod vloeibaar | bupirimaat | | | | | 1.0 | | | | 1.0 | 1.0 | | 1.0 | 1.0 | 1.0 | | | | | 6.0 |
| Rovral aquaflo | iprodion | | | | | | 2.0 | | | | | | | | | | | | | 2.0 |
| Frupica SC | mepanipyrum | | | | | | | 1.0 | | | 1.0 | | | | 1.0 | | | | | 3.0 |
| Signum | boscalid+pyrasclostrobine | | | | | | | | | 1.0 | | | | 1.8 | | | | | | 2.8 |
| Vertimec | abamectine | | | | | | | | | 0.5 | | | 0.5 | | 0.5 | | | | | 1.5 |
| Targa | quizalafop-ethyl | | | | | | | | | | 0.7 | | | | | | | | | 0.7 |
| Switch | cyprodinil+fludioxonil | | | | | | | | | | | | 1.0 | | | 1.0 | | | | 2.0 |
| Teldor spuitkorrels | fenhexamide | | | | | | | | | | | | | | | | 1.4 | 1.4 | 1.2 | 4.0 |
| | | | | | | | | | | | | | | | | | | | | 34.4 |

[1]) Thiacloprid products are Calypso en Dadian

[2]) Deltamethrin products used are: Decis, Imex, WOPRO, DeltaM, Delta25

## 5.2.2 Strawberry crop protection schedule

The strawberry crop protection schedule is visualized in Figure 7. This figure shows the time schedule of the applications in the strawberry crop PPP-application schedule starting at 18 April, with the first application of a PPP at 19 April, and the DRT-(Drift Reducing Technology) class applied. The example schedule is based on a realistic scheme as applied by a Dutch grower (Michielsen et al., 2012). The sector has confirmed that this schedule can be considered as a crop protection schedule commonly applied by Dutch strawberry growers.

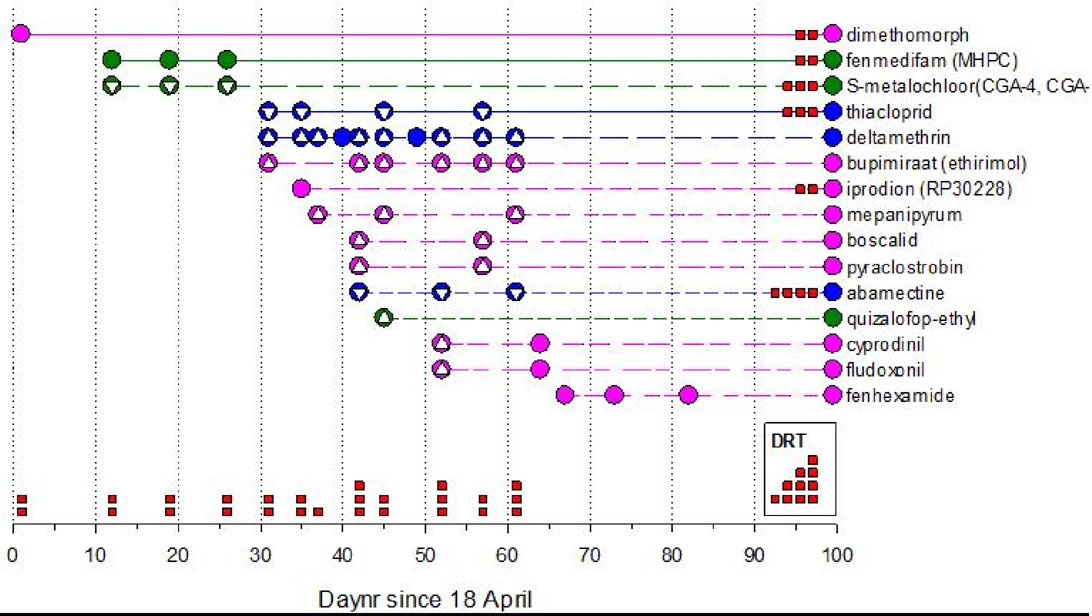


***Figure 7*** *Example application schedule of 13 PPPs (two mixtures) in strawberries in the Netherlands including a first application on 19th of April and a last application on 9th of July. The 15 active substances and their metabolites indicated between brackets are shown on the right hand side of the figure. Fungicides are indicated by pink circles, herbicides by green circles, and insecticides by blue circles. The red squares indicate the Drift Reduction Technology (DRT) class required for individual products (along vertical axis) and applied for the tank mix (along horizontal axis). DRT classes 50, 75, 90 and 95% are visualized by one to four squares, respectively. White triangles in the circles indicate that the DRT-class used in calculation for the tank mix differed from the DRT-class of the individual products; upward white triangles indicate a higher DRT-class, while downward white triangles indicate a lower DRT-class.*

## 5.2.3 Calculating exposure concentrations

Exposure concentrations were calculated using the methodology used in the Dutch authorisation scenario. Concentrations were calculated in a ditch, the so-called Dutch standard scenario ditch (Beltman and Adriaanse, 1999a), using the TOXSWA model (Adriaanse, 1996; Ter Horst et al., 2016), version 1.2 (Beltman and Adriaanse, 1999b). The standard scenario used is the spring and summer scenario for the Netherlands. The ditch has a depth of 30 cm and the section where the PPP is applied has a length of 300 m. The flow velocity is 10 m/d. Spray drift entries of PPP are simulated.

**Spray drift loading to surface water**

The 'drift' loading of the substance to the water surface was calculated using:

$$\boldsymbol{L} = \frac{\boldsymbol{D}}{\mathbf{100}}\,\frac{\mathbf{1}}{\mathbf{10000}}\,\boldsymbol{R}_{\mathbf{s}} \qquad (1)$$

where:

| | | |
|---|---|---|
| $L$ | = | drift loading of substance (g/m$^2$) |
| $D$ | = | drift percentage (%) |
| 100 | = | factor for converting from % to fraction (-) |
| 1/10000 | = | factor for converting from g/ha to g/m$^2$ (-) |
| $R_s$ | = | rate of application of substance, which can be the parent (Rp) of a metabolite (Rm) (g a.i./ha) |

The rate of application of the parent was calculated by:

$$R_{\mathrm{p}} = R_{\mathrm{p,f}} C_{\mathrm{as}} \qquad (2)$$

where:

| | | |
|---|---|---|
| $R_p$ | = | rate of application of parent (g a.i./ha) |
| $R_{p,f}$ | = | rate of application of formulated product (L/ha) [Appendix Table 1] |
| $C_{as}$ | = | concentration of active substance in formulated product (g/L) [Appendix Table 1] |

**Metabolites**

Only those metabolites were selected for calculations for which a RAC was derived in the evaluation report. For metabolites for which no RAC was given in the evaluation report, concentrations were not calculated.

In the Dutch registration the metabolites are simulated as 'mimicked spray drift' (see Beltman et al., 2016), This methodology is explained below.

The rate of application of the metabolite is calculated using the maximum observed percentage of metabolite in the water–sediment study, corrected for molar mass.

$$\boldsymbol{R}_{\mathbf{m}} = \boldsymbol{R}_{\mathbf{p}}\,\frac{\boldsymbol{F}}{\mathbf{100}}\,\frac{\boldsymbol{M}_{\mathbf{m}}}{\boldsymbol{M}_{\mathbf{p}}} \qquad (3)$$

where:

| | | |
|---|---|---|
| $R_m$ | = | metabolite rate of application (g a.i./ha) |
| 100 | = | factor for converting % to fraction (-) |
| $F$ | = | maximum observed percentage of metabolite formed (%) |
| $M_m$ | = | molecular mass of metabolite (g/mol) |
| $M_p$ | = | molecular mass of parent substance (g/mol) |

The 'drift' percentages are listed in Appendix Tables 1 and 2.

**Substance properties**

Substance properties were obtained from the Ctgb evaluation reports (Appendix Tables 4 and 5). Data for the substance quizalofop-ethyl were not present, therefore its data were taken from the Footprint database (http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm). Some of the data were not available, or were corrected as follows:

- When the Freundlich exponent *N* for sorption was not available, a default value of 0.9 was used. For Arrhenius enthalpy for transformation in water and in sediment, default values for activation energies used in the Dutch authorisation were used.
- The calculations with RP30228 (a metabolite of iprodion) the default value for the Freundlich exponent of 0.9 was used, instead of the value of 1.7 from the evaluation report, because 1.7 was

- considered unrealistic. For transformation in water there was no value given in the evaluation report, therefore a conservative value of 1000 d was used for DegT50 in water.
- When for the metabolite the molar mass, vapour pressure or solubility was not available in the evaluation report, the value of the parent was used.

**Calculations**
The spring scenario was applied with 15 active substances and 5 metabolites from the spray application schedule (Fig. 7). Two scenarios were evaluated, i.e. the 'Dutch authorisation scenario' (Table 4) and the 'tank mixture´ scenario (Appendix Table 2).

- Exposure calculations were performed for the period 18 April (one day before the first application of a PPP, Day 1) to 27 July (18 days after the last application of a PPP, Day 100).
- The application schedule used is given in Table 4. Spray drift values were taken as presented in Appendix Tables 1, 2 and 3).

### 5.2.4 Effects and PEC/RAC ratio

Toxicity data and RAC values used for the authorisation of the products in The Netherlands have been made available by Ctgb (Appendix 1 Table 6). For assessing the mixtures and their effects, the method of concentration addition has been applied. This method is also in use by Ctgb in their authorisation process, whereby PEC/RAC ratios are calculated and the valued summed up to account for any mixture effects.

- PEC/RAC values have been calculated for each of the substances, using RAC values for acute exposure of primary producers, invertebrates and fish.
- The sums of PEC/RAC values of the substances are presented in the figures as well. The figures also indicate the line for which the PEC/RAC ratio is 1.

## 5.3 Results and discussion

The results of the calculations are presented in Figures 8 – 15 and are discussed below. The line types in Figure 7 correspond to the line types in Figures 8 to 15 indicating the different active substances. Metabolites are indicated by grey curves.

The strawberry spraying schedule includes 9 fungicides, 3 herbicides and 3 insecticides. 5 metabolites are formed which potentially contribute to toxicity. Deltamethrin is applied with the highest frequency, i.e. 10 times. For tank mixtures spray drift rates of individual substances might become lower or higher than indicated on the label of the products based on these substances, due to the assumption made in this report that the spray drift for mixtures is one DRT class lower than the highest DRT class of the tank mixture application. This lowering of the DRT by one step has been performed in view of the uncertainties surrounding the effect of the formulation of an applied product and the combined effects of multiple products in a tank mixture (See chapter 2). For compounds that are categorized in a high DRT class in the Dutch authorisation scenario (corresponding to a relatively low drift rate), this might result in a lower DRT class (corresponding to a relatively higher drift rate) in the tank mixture scenario. In the strawberry application schedule this is the case with a number of insecticides (S-metolachlor, thiacloprid, deltamethrin, and abamectine, i.e. mainly insecticides). On the other hand, this lowering of the DRT by one step can result in a higher DRT class (corresponding to a lower drift rate) for compounds which are categorized in a low DRT class in the Dutch authorisation procedure (e.g. PPPs categorized in a drift class of 50% and for which the drift class of the tank mixture is increased to 75%).

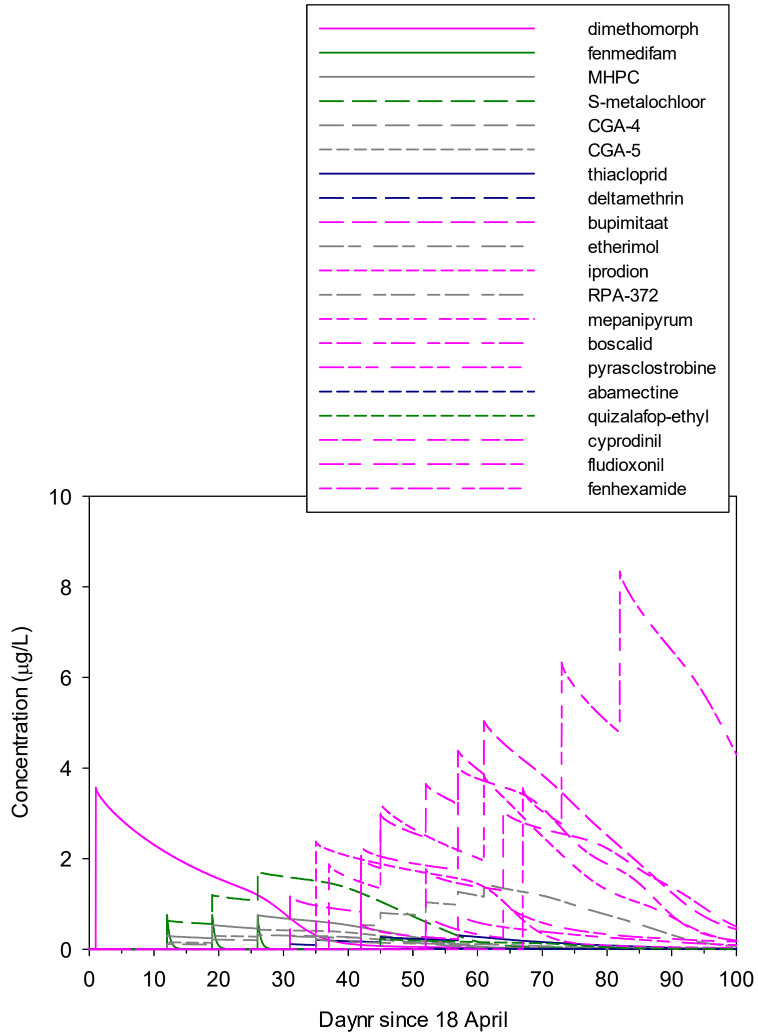


***Figure 8*** *Exposure of 13 PPPs (15 active substances and 5 metabolites) calculated with spray drift percentages used in the authorization for the Dutch standard ditch scenario.*

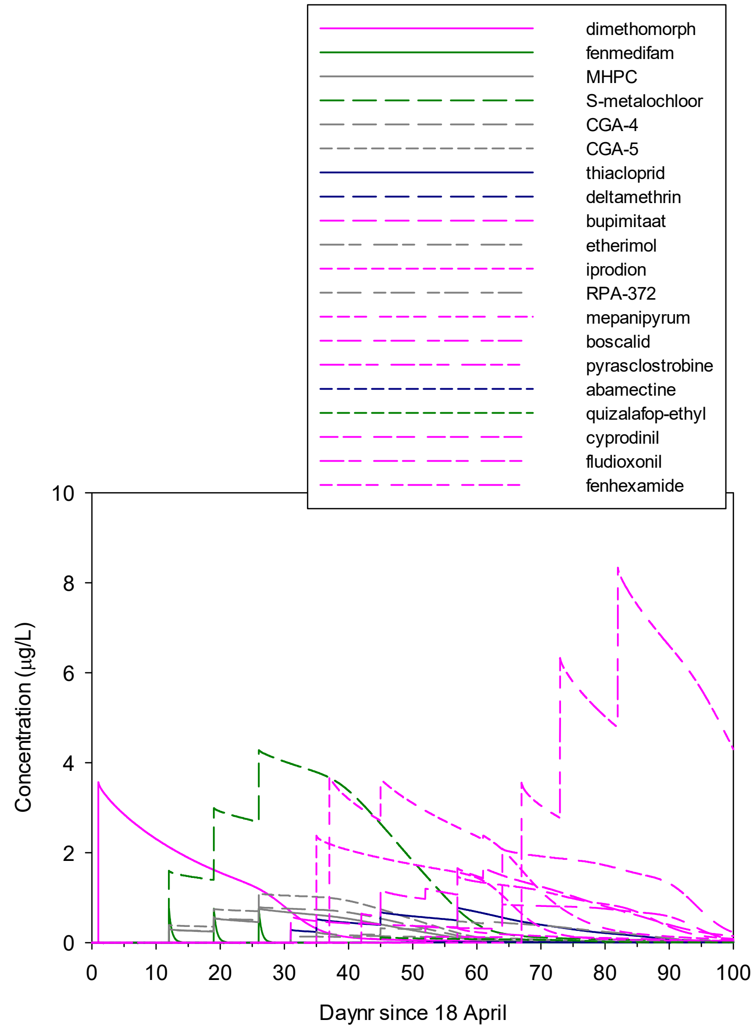


***Figure 9*** *Exposure of 13 PPPs (15 active substances and 5 metabolites) calculated with spray drift percentages used for* ***tank mixes*** *in the authorization for the Dutch standard ditch scenario.*

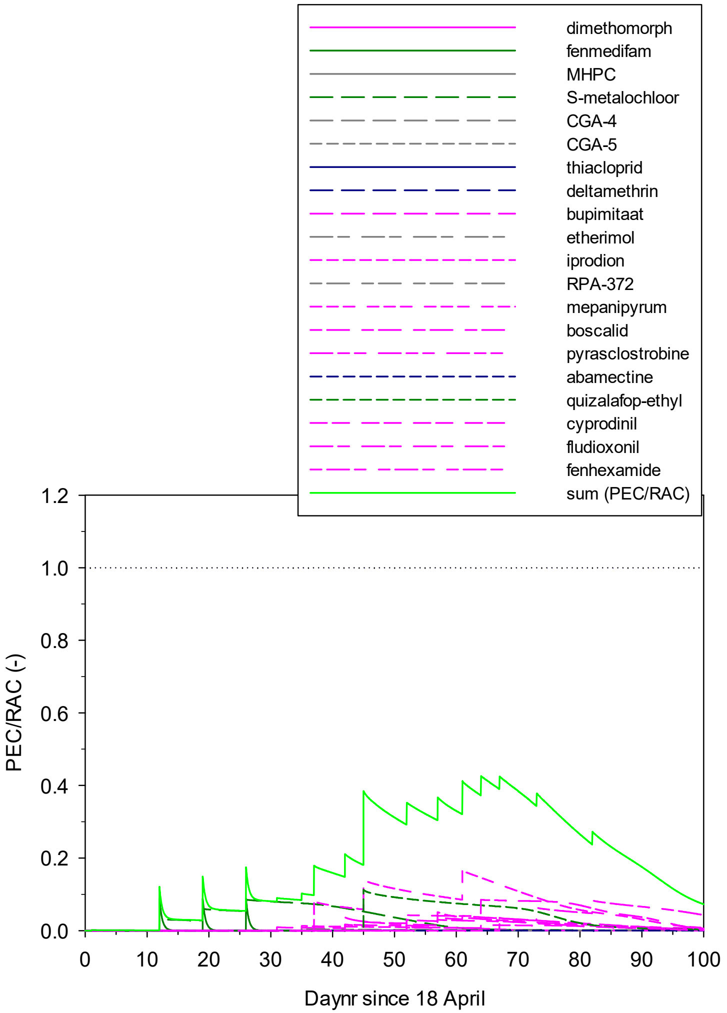


***Figure 10*** *PEC/RAC of 15 active substances and 5 metabolites. Exposure concentrations were calculated with spray drift percentages used in the Dutch authorization. RACs of acute effects of* ***primary producers*** *were used. The bright green curve indicates the sum of all PEC/RAC values.*

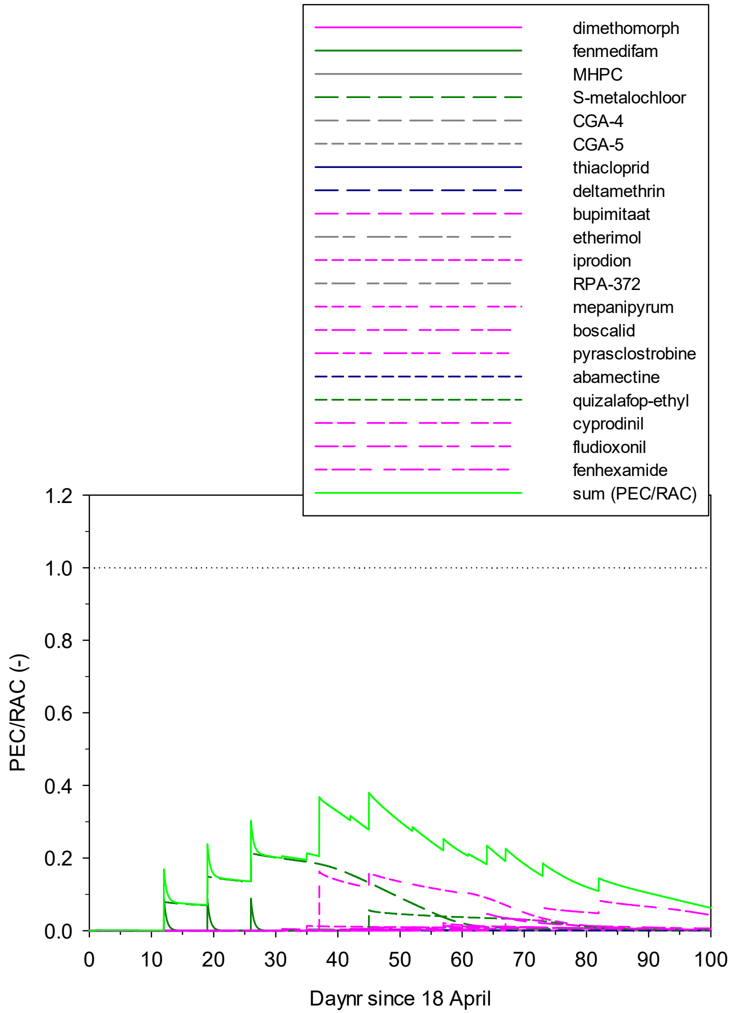


***Figure 11*** *PEC/RAC of 15 active substances and 5 metabolites. Exposure concentrations were calculated with spray drift percentages used for* ***tank mixes*** *in the Dutch authorization. RACs of acute effects of* ***primary producers*** *were used. The bright green curve indicates the sum of all PEC/RAC values.*

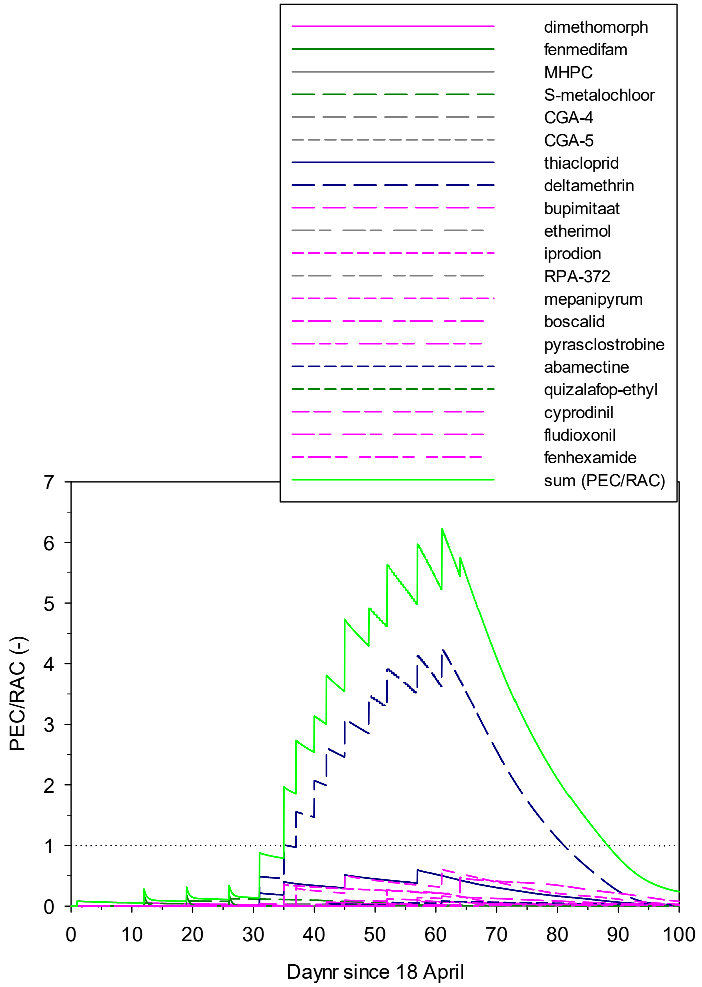


***Figure 12*** *PEC/RAC of 15 active substances and 5 metabolites. Exposure concentrations were calculated with spray drift percentages used in the Dutch authorization. RACs of acute effects of* ***invertebrates*** *were used. The bright green curve indicates the sum of all PEC/RAC values.*

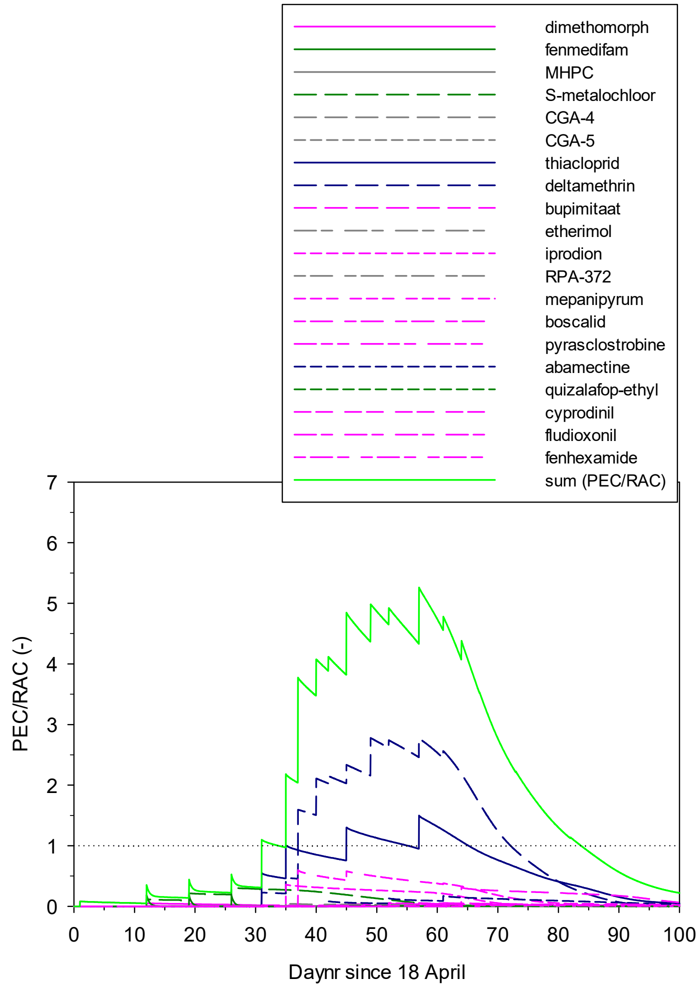


***Figure 13*** *PEC/RAC of 15 active substances and 5 metabolites. Exposure concentrations were calculated with spray drift percentages used for* ***tank mixes*** *in the Dutch authorization. RACs of acute effects of* ***invertebrates*** *were used. The bright green curve indicates the sum of all PEC/RAC values.*

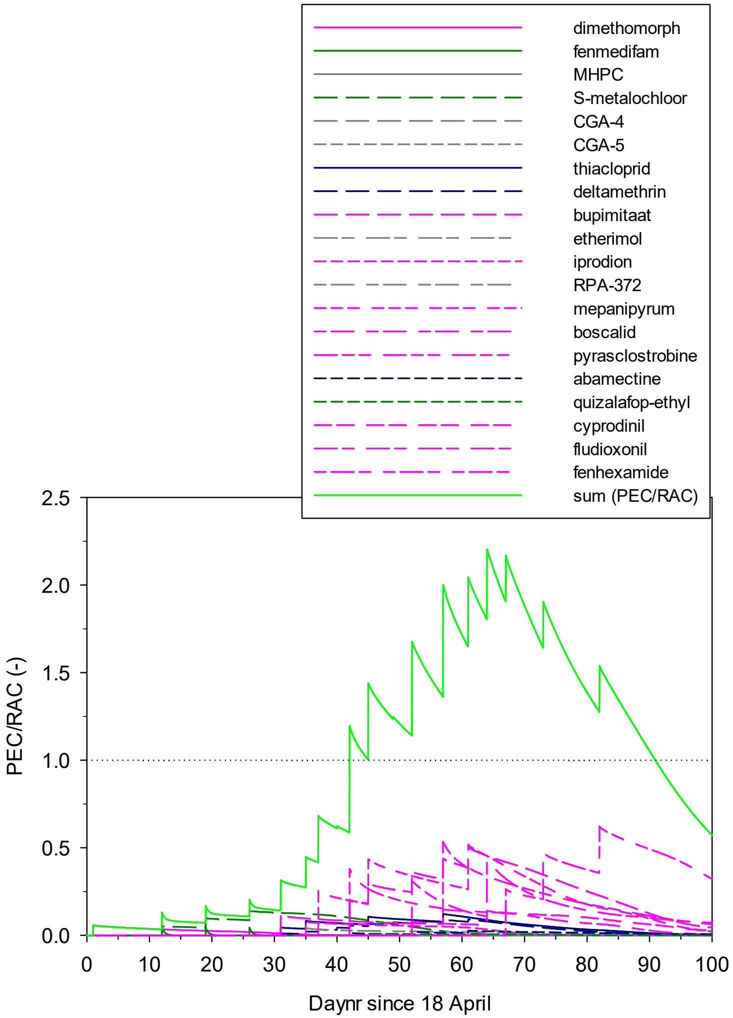


***Figure 14*** *PEC/RAC of 15 active substances and 5 metabolites. Exposure concentrations were calculated with spray drift percentages used in the Dutch authorization. RACs of acute effects of **fish** were used. The bright green curve indicates the sum of all PEC/RAC values.*

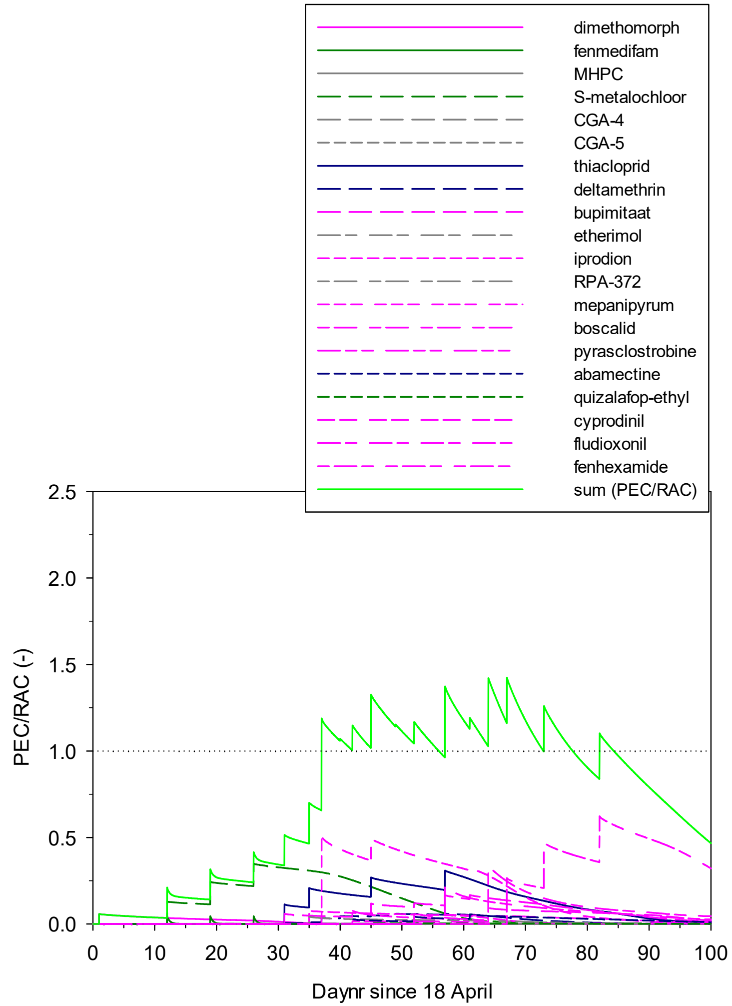


***Figure 15*** *PEC/RAC of 15 active substances and 5 metabolites. Exposure concentrations were calculated with spray drift percentages used for **tank mixes** in the Dutch authorization. RACs of acute effects of **fish** were used. The bright green curve indicates the sum of all PEC/RAC values.*

Figures 8 and 9 show the concentrations calculated for the 15 active substances and 5 metabolites based on spray drift as calculated in the Dutch authorisation scenario and in the tank mixture scenario, respectively.

In Figure 8, the concentrations of fungicides are highest, where the highest concentration is that of fenhexamide, the substance applied at the end of the crop application schedule. The insecticide and metabolite concentrations are lowest. In Figure 9, the concentrations of some of the fungicides in the tank mixture are lower than calculated according to the Dutch authorisation scenario, due to lower spray drift percentages (higher DRT classes of one of the products in the tank mixture). Some of the herbicide and insecticide concentrations are higher due to higher spray drift percentages in the tank mixture scenario (lower DRT classes because of assumed tank mixture effects).

Figure 8 further shows the stacking of PPP in case of multiple application of one active substance. For example this was the case for fenhexamide, which was applied three times.

Figures 10 and 11 show the PEC/RAC values based on primary producers for 15 active substances and 5 metabolites and their sum, as calculated in the scenario and in the tank mix scenario. Figure 10 shows that PEC/RAC values of all substances are lower than 1, as is the PEC/RAC sum. Figure 11 shows that for all substances PEC/RAC values are also lower than 1, as is the PEC/RAC sum. Thus, in both scenarios PEC/RAC values and their sum do not exceed 1.

Figures 12 and 13 show the PEC/RAC values based on invertebrates for 15 active substances and 5 metabolites and their sum, as calculated in the Dutch authorisation scenario and in the tank mixture scenario.

Figure 12 shows that PEC/RAC values of 19 substances are lower than 1. The PEC/RAC of deltamethrin exceeds one. For deltamethrin the time interval between applications is short (only 3 days), leading to accumulation of the substance in the water layer. The PEC/RAC sum also exceeds 1, and this sum is mainly determined by the same compound (deltamethrin). The PEC/RAC sum exceeds 1 by a factor of 6.

Figure 13 reveals that PEC/RAC values of 18 substances are lower than 1. The PEC/RAC values of deltamethrin and thiacloprid exceed one. In the tank mix scenario the spray drift percentage for thiacloprid is higher than the one in the Dutch authorisation scenario, due to a lower DRT class (lower drift reduction class) for thiacloprid in the tank mixture (lowering of 90% to 75%). The PEC/RAC sum also exceeds 1 by a factor of 5.

Figures 14 and 15 show the PEC/RAC values for 15 active substances and 5 metabolites and their sum, based on drift in the Dutch authorisation scenario and in the tank mixture scenario. Figure 14 shows that for all 20 substances PEC/RAC values are below 1. The PEC/RAC sum exceeds 1, but this cannot be attributed to specific substances. Figure 15 shows that for all 20 substances PEC/RAC values are below 1. The PEC/RAC sum exceeds 1, but this can not be attributed to specific substances. The PEC/RAC sum is lower than this value calculated in the Dutch authorisation scenario.

## 5.4 Conclusion

The results for primary producers show that the sum of the PEC/RAC values remain below the critical value of one in both scenarios, i.e. when considering drift percentages as used in the Dutch authorisation scenario as well as when considering drift percentages as used for tank mixes. Hence, the risk of the strawberry crop scenario for primary producers is acceptable based on both scenarios.

The results for invertebrates show a different picture in comparison with the results for primary producers. Especially some of the insecticides applied have a PEC/RAC value above one, i.e. deltamethrin exceeds the critical value of one in both scenario's. The PEC/RAC value exceeds the critical value of one by a factor of four in the Dutch authorisation scenario and by a factor of three in the tank mixture scenario. Thiacloprid, another insecticide, does not exceed the critical value of one in the Dutch authorisation scenario, but does exceed the critical value of one in the tank mixture scenario. This is caused by lowering of the spray drift reduction class in the tank mixture calculations (from 90% to 75%).

For fish the sum of the PEC/RAC values exceeds 1 in both scenarios.

# 6 General discussion

This report has focused on PPPs, for which we define multistress as the frequent, repeated and simultaneous application of PPPs in time and space. This report summarizes the first stepping stones towards answering the question whether the product-by-product and/or active substance-by-active substance valuations provide sufficient protection in the context of the market authorisation of PPPs in the Netherlands.

Mixtures of chemicals with a similar mode of action are usually described by a model referred to as concentration addition (CA) (Deneer, 2000). Mechanisms in mixtures of chemicals with a dissimilar mode of action are referred to as independent action, and in this case different responses caused by different modes of action add up to a total response in the community (Verbruggen and Van de Brink, 2010). Synergism means that the effects of a mixture exceed that expected from the individual compounds (Howard and Webster, 2009). Cedergreen (2014) has quantified this definition by defining synergistic effects as mixtures with at least a two-fold difference between observed and predicted effect concentrations. Antagonism means that the combined effects are less than the ones expected (Howard and Webster 2009). Additivity (non-interaction) means that the combined effects equal the expectations (Howard and Webster 2009).

Multistress and mixture effects considered in the current risk assessment for the authorisation of PPPs on the market as applied by Ctgb are:

- One product including one active substance and repeated applications of one product if included on the label;
- One product including several active substances and repeated applications of this product if included on the label;
- Tank mixtures (several products) and repeated applications of this mixture if included on the label.

However, current practice includes many multiple and simultaneous applications of different products in one season (e.g. in strawberries) (Michielsen et al, 2012).

This report shows that adjuvants and formulations have an effect on spray droplet sizes and therefore on spray drift potential. These effects can both increase and decrease spray drift, depending on nozzle type, adjuvants and product formulations.

Our literature review shows that exposure to mixtures of PPPs is slightly influenced by interactions between PPPs, due to competition for sorption. Based on the current literature, no judgement can be given on the effect of the simultaneous presence of multiple PPPs on the degradation rates of the individual compounds.

The literature summarized in this report shows that synergistic effects occur relatively rarely, and can be traced back to combinations of specific compounds. We concluded that in general concentration addition is a suitable approach to assess the risk of PPP mixtures. This approach was applied in the calculation of potential risk due to PPP use as part of a spraying schedule for strawberry. PEC/RAC quotients were summed and it was evaluated if the sum was below one and thus predicting a safe use.

Based on the results in the literature, calculations were performed to assess the risk for an intensive crop with many multiple and simultaneous applications (i.e. strawberries). We have calculated the spray drift values on surface water in a ditch and the exposure profiles over a 100–day period using the Dutch exposure scenario for surface water. The effects were predicted based on the PEC and RAC values calculated for the most sensitive standard test organisms and the concentration addition approach. The risk was assessed for PPPs in a spraying schedule for strawberries. Two scenarios were applied: one scenario follows the procedure of the authorisation of PPPs performed by Ctgb and calculates the potential effects of PPP used in strawberries on sensitive organisms in a ditch (Dutch authorisation scenario). This scenario takes into account repeated application of PPPs, but not the application of mixtures. The other scenario involves the application of the PPPs in tank mixtures (tank mixture scenario) used in strawberries. The latter approach predicts the effects on sensitive organisms in the ditch for repeated applications and spraying of PPPs in tank mixtures. For tank mixtures the drift percentages differ for some PPP in the mixture from those applied in the Dutch authorization scenario.

In the calculations it is assumed that mixture effects in the tank lead to more spray drift. For the calculations the highest drift reduction class (DRT) has been taken as the representative class. Calculations for the tank mixtures are based on the DRT class which is one class below this representative class. This scenario can be considered as a protective scenario.

For both scenarios the addition approach was used.

The calculation show that a realistic application scheme with multiple and simultaneous application on strawberries leads to:

i. acceptable risk for primary producers based on both scenarios.
ii. the critical value of one for the sum of PEC/RAC values being exceeded in the case of invertebrates and fish in both scenarios.

Specifically, the calculations show that Deltamethrin exceeds the critical value of one in both scenario's. The authorisation document of this active substance prescribes a maximum of three applications per product with an interval between the applications of 14 days. As the active substance is included in several different authorised products, the frequency of application in strawberries is much higher (10 times) and also the application interval much shorter (3 days) in the case of this crop scenario for strawberries. This causes extra stress for sensitive organisms as the time period between applications becomes shorter than the life cycle and might be too short to enable recovery. Actually this is shown in Figures 12 and 13 where the concentrations of deltamethrin and therefore also the effects on invertebrates build up over time. This higher use of deltamethrin in this crop scenario is an effect of the product-by-product approach and not an active substance-by-active substance approach (see chapter 6 General Discussion).

For fish, it was found that the sum of the PEC/RAC values does exceed the value of one when based on toxicity data for fish, however, all individual compounds meet the criteria for authorisation on the market in the crop scenario for strawberries. Based on these findings, the currently used product-by-product approach might not be protective for invertebrates and fish. This can be ascribed to the repeated applications of particularly a number of insecticides. It is recommended to assess the risk of PPPs as part of a crop protection programme and thus to evaluate the risk in this context.

It is important to realize that the exposure calculations have been performed with the summer scenario as it is currently applied in the Dutch authorization procedure. This authorisation scenario comprises a 300 m long ditch with a constant flow velocity of 10 m/d in which a series of applications with small intervals give rise to stacking concentrations and a high potential of a sum of PEC/RAC values larger than one. Based on recent analysis of flow velocities in the Rivierenland area in the Netherlands, the flow velocities as used in the current authorization procedure may be considered as low. E.g. in summer the median flow velocity in the Rivierenland area is estimated to be 77 m/d (Wipfler et al., in prep). In view of this, the calculated risks in this study are conservative, i.e. in reality the stacking of concentrations will probably occur less frequently as assumed in the calculations.

# 7 Outlook

In this report we have quantified the environmental risk for an intensively cultivated crop with parallel and sequential applications of products based on a realistic application schedule and spray drift on surface water in a ditch, the corresponding exposure profiles and the effects based on the Regulatory Acceptable Concentrations of the used active substances. However, this crop is only one out of a range of intensively cultivated crops in The Netherlands and in other European countries. As the rationale behind this report relates to a gap in our knowledge about tank mixtures, there is still a need for calculations of other intensively cultivated crops and crop-based application scenarios in a holistic way, i.e. including spray drift, exposure and effects. Additional calculations can be used to confirm the recommendations from this report, i.e. to regulate active substances instead of products. Scientifically, confirmation of results of research is necessary.

Also, the exposure calculations have been performed with the summer scenario as it is currently applied in the Dutch authorization procedure. This authorisation scenario comprises a 300 m long ditch with a constant flow velocity of 10 m/d in which a series of applications with small intervals give rise to stacking concentrations and a high potential of a sum of PEC/RAC values larger than one. Based on recent analysis of flow velocities in the Rivierenland area in the Netherlands, the flow velocities as used in the current authorization procedure may be considered as low. E.g. in summer the median flow velocity in the Rivierenland area is estimated to be 77 m/d (Wipfler et al., in prep). In view of this, the calculated risks in this study are conservative, i.e. in reality the stacking of concentrations will probably occur less frequently as assumed in the calculations.

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# Appendices

***Table 1*** *Doses (L/ha) and active substance concentrations of PPPs used in strawberries and their spray drift value (%), as used in the Dutch authorisation scenario, and suggested spray drift value (%) when used as in a tank mixture scenario. The active active substance are similar to those in Table 4.*

| | Product | Active substance | concentration ai | dose | DRT[1]) | width Cfbz[2]) | Used drift % Dutch authorisation | adapted drift % 1 DRT class lower Dutch authorisation |
|---|---|---|---|---|---|---|---|---|
| 1 | Paraat | dimethomorph | 50% | 3 kg/ha | DRT75 | none | 0.5 | 1.0 |
| 2 | (Agrichem fenmedifam)/Kontakt 320 SC | fenmedifam *) | 320 G/L | 3 L/ha | DRT75 | none | 0.5 | 1.0 |
| 3 | Dual Gold 960EC | metalochloor | 960 G/L | 0,7 l/ha | DRT90 | none | 0.2 | 0.5 |
| 4 | Calypso and Dadian | thiacloprid | 480 g/L | 0,25 l/ha | DRT90 water; DRT50 NTA | none | 0.2 | 0.5 |
| 5 | Deltamethrin products[3] | deltamethrin | 25 g/L | 0,2 l/ha | none | none | 1.0 | 2.0 |
| 6 | Nimrod vloeibaar | bupirimaat | 250 G/L | 1 l/ha | none | none | 1.0 | 2.0 |
| 7 | Rovral aquaflo | iprodion | 500 G/L | 2 l/ha | DRT75 | none | 0.5 | 1.0 |
| 8 | Frupica SC | mepanipyrum | 440 G/L | 0,9 l/ha | none | none | 1.0 | 2.0 |
| 9 | Signum | boscalid+pyrasclostrobine | 26,7%+ 6,7% | 1,8 kg/ha | none | none | 1.0 | 2.0 |
| 10 | Vertimec | abamectine | 18 G/L | 0,5 l/ha | DRT95 | none | 0.1 | 0.2 |
| 11 | Targa | quizalafop-ethyl | 50 G/L | 1 l/ha | none | none | 1.0 | 2.0 |
| 12 | Switch | cyprodinil+fludioxonil | 37,5% + 25% | 1 kg/ha | none | none | 1.0 | 2.0 |
| 13 | Teldor spuitkorrels | fenhexamide | 50% | 1,5 kg/ha | none | none | 1.0 | 2.0 |

[1]) Drift Reducing Technology class; none = DRT50

[2]) crop free buffer zone; none = 1.50 m; Following LOTV/AB

*) Agrichem fenmedifam not registered anymore; instead Kontakt 320 SCis taken

[3]) Deltamethrin products used are: Decis EC, Imex, WOPRO, DeltaM, Delta25

***Table 2*** *Mandatory drift reducing technology class required for individual products used in a strawberry spraying schedule, their minimally required DRT for the tank mix and its corresponding spray drift value (%) and adapted spray drift value (%) based on uncertainty regarding tank mixtures (assumption: one DRT class lower).*

| | **Product-DRT required** | | | | **Spraying schedule strawberry** | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Product** | **Active substance** | **19-4-2012** | **30-4-2012** | **7-5-2012** | **14-5-2012** | **19-5-2012** | **23-5-2012** | **25-5-2012** | **28-5-2012** | **30-5-2012** | **2-6-2012** | **6-6-2012** | **9-6-2012** | **14-6-2012** | **18-6-2012** | **21-6-2012** | **24-6-2012** | **30-6-2012** | **9-7-2012** |
| | **daynr** | **1** | **12** | **19** | **26** | **31** | **35** | **37** | **40** | **42** | **45** | **49** | **52** | **57** | **61** | **64** | **67** | **73** | **82** |
| Paraat | dimethomorph | 75 | | | | | | | | | | | | | | | | | |
| Agrichem fenmedifam | fenmedifam | | 75 | 75 | 75 | | | | | | | | | | | | | | |
| Dual Gold 960EC | metalochloor | | 90 | 90 | 90 | | | | | | | | | | | | | | |
| Several[1] | thiacloprid | | | | | 90 | 90 | | | | 90 | | | 90 | | | | | |
| Several[2] | deltamethrin | | | | | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | | | | |
| Nimrod vloeibaar | bupirimaat | | | | | 50 | 50 | | | 50 | 50 | | 50 | 50 | 50 | | | | |
| Rovral aquaflo | iprodion | | | | | | 75 | | | | | | | | | | | | |
| Frupica SC | mepanipyrum | | | | | | | 50 | | | 50 | | | | 50 | | | | |
| Signum | boscalid+pyrasclostrobine | | | | | | | | | 50 | | | | 50 | | | | | |
| Vertimec | abamectine | | | | | | | | | 95 | | | 95 | | 95 | | | | |
| Targa | quizalafop-ethyl | | | | | | | | | | 50 | | | | | | | | |
| Switch | cyprodinil+fludioxonil | | | | | | | | | | | | 50 | | | 50 | | | |
| Teldor spuitkorrels | fenhexamide | | | | | | | | | | | | | | | | 50 | 50 | 50 |
| DRT | | | | | | | | | | | | | | | | | | | |
| determining DRT | | 75 | 90 | 90 | 90 | 90 | 90 | 50 | 50 | 95 | 90 | 50 | 95 | 90 | 95 | 50 | 50 | 50 | 50 |
| DRT tank mix *) | | 75 | 75 | 75 | 75 | 75 | 75 | 0 | 50 | 90 | 75 | 50 | 90 | 75 | 90 | 50 | 50 | 50 | 50 |
| Spray drift | | | | | | | | | | | | | | | | | | | |
| spray drift Dutch authorisation [%] | | 0.5 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 1.0 | 1.0 | 0.1 | 0.2 | 1.0 | 0.1 | 0.2 | 0.1 | 1.0 | 1.0 | 1.0 | 1.0 |
| spray drift tank mixture [%] *) | | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 2.0 | 1.0 | 0.2 | 0.5 | 1.0 | 0.2 | 0.5 | 0.2 | 1.0 | 1.0 | 1.0 | 1.0 |

[1]) Thiacloprid products used are: Calypso and Dadian

[2]) Deltamethrin products used are: Decis EC, Imex, WOPRO, DeltaM, Delta25

*) one DRT class lower

***Table 3*** *Restrictions for use of different PPPs in a strawberry spraying schedule according to WGGA's (Ctgb, 18/11/2016).*

| Product and authorisation nr. | Type of application | Working area | Dose (product) perapplication | Maximum nr. of applications per crop growth cycle | Maximum liter product per ha per crop growth cycle | Minimum interval between applications in days | Safety period in days |
|---|---|---|---|---|---|---|---|
| Paraat 11432 N | Immediate after planting a full field application ; irrigate after treatment | Fungal diseases | 3 kg/ha | 1 | 3 kg/ha | - | 35 |
| Kontakt 320 SC, 12899 N | After emergence or after planting | Annual broadleaf weeds | 3 L/ha | 1x per 12 months | 3 L/ha per 12 months | - | |
| Dual Gold 960 EC, 12096 N | after planting | Annual weeds | 0,7 L/ha | 2 | 1,4 l/ha | 7 | 28 |
| Calypso, 12452 N | Crop treatment | Aphids<br>White fly | 0,025% (25 ml/ 100l water) | 0,25 l/ha | 2 per 12 months | 0,5 l per 12 months | 7 |
| Nimrod Vloeibaar,<br>6834 N | Apply with first detection of disease<br>Repeat after renewed detection of disease | Mildew | 1 L/ha | 3 strawberry<br>6 other crops | 3 L/ha strawberry<br>6 L/ha other crops | Other crops;<br>2 blocks of maximum 3 applications per block | - |
| Rovral Aquaflo 8928 N | Apply immediate after planting; followed by second application after 4 weeks | Rhizoctonia | 2 L/ha | 2 | 4 L/ha | 4 weeks | 2 |
| Rovral Aquaflo 8928 N | Apply from first flowering onward (opening of first flowers) with following applications every 10-14 days. | Grey mould | 1,5 L/ha | 4 | 6 L/ha | 10-14 days | 2 |
| Frupica SC 12229 N | First treatment from moment of stem elongation of flowers | Fruit rot | 0,9 L/ha | 2 | - | 7 days | 3 |
| Signum, 12630 N | First treatment from moment of stem elongation of flowers | Fruit rot | 1,8 kg/ha | 2 | | 7 | 1 |
| Vertimec Gold, 13087 N | Crop treatment | Spider mite<br>Thrips | 0,5 l/ha | 1 | 0,5 l/ha | - | 3 |
| Abamectine HF-G, 13207 N | Crop treatment | Spider mite<br>Thrips | 0,5 l/ha | 3 | 1,5 l/ha | 7 | 3 |
| Targa Prestige, 11155 N | On crop | Cereal emergence | 1 l/ha[2] | 1 | - | - | 21 |
| Switch, 12819 N | From start of flowering | Botryotinia fuckeliana and Colletotrichum acutatum | 1 kg/ha | 3 | - | 10-14 days | 3 |
| Teldor 12130 N | From start of flowering | Grey mould | 1,5 kg/ha | - | - | 7-10 days | 1 |

***Table 4*** *Substance properties of active substances of PPPs and their metabolites in a spray schedule for strawberries.*

| Name | Molar mass | Vapour pressure | Temperature vapour pressure | Solubility | Temperature solubility | Freundlich exponent sorption | Kom | DT50-sediment | DT50-water | Fraction metabolite formed | Use |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | g/mol | Pa | °C | mg/L | °C | - | L/kg | d | d | - | |
| dimethomorph | 387.9 | 9.60E-07 | 25 | 49.2 | 20 | 0.86 | 236.5 | 1000 | 8.7 | - | fung |
| fenmedifam | 300.3 | 7.00E-10 | 25 | 1.8 | 20 | - | 522/352 | 1000 | 0.14 | - | herb |
| MHPC | 167.2 | 7.00E-10 | 25 | 1.8 | 20 | - | 129 | 1000 | 21 | 0.7 | metab |
| S-metalochloor | 283.8 | 3.70E-07 | 25 | 480 | 20 | - | 131 | 1000 | 48.5 | - | herb |
| CGA 41507 | 283.8 | 3.70E-07 | 25 | 480 | 20 | - | 131 | 1000 | 1000 | 0.178 | herb |
| CGA 51202 | 329.2 | 3.70E-07 | 25 | 480 | 20 | - | 131 | 1000 | 1000 | 0.212 | herb |
| thiacloprid | 252.73 | 3.00E-10 | 20 | 184 | 20 | 0.88 | 357 | 1000 | 19 | - | insec |
| deltamethrin | 505.2 | 1.24E-08 | 25 | 0.0002 | 25 | - | 1000000 | 1000 | 65 | - | insec |
| bupirimate | 316.42 | 1.31E-04 | 25 | 13.06 | 20 | - | 1092 | 1000 | 42.5 | - | fung |
| ethiridimol | 209.29 | 2.67E-04 | 25 | 233 | 25 | - | 233 | 1000 | 1000 | 0.37 | metab |
| iprodione | 330.2 | 5.00E-07 | 25 | 12.2 | 25 | 0.92 | 221 | 1000 | 30 | - | fung |
| RP30228 | 330.2 | 5.00E-07 | 25 | 12.2 | 25 | 1.7* | 3814 | 1000 | 1000 | 0.1 | metab |
| mepanipyrim | 223.3 | 2.32E-05 | 25 | 3.1 | 20 | 0.83 | 514 | 1000 | 14.5 | - | fung |
| boscalid | 343.21 | 7.20E-07 | 20 | 4.6 | 20 | 0.868 | 447 | 1000 | 90 | - | fung |
| pyraclostrobin | 387.82 | 2.60E-08 | 20 | 19000 | 20 | 0.95 | 5473 | 1000 | 13.8 | - | fung |
| avermectin | 873.1 | 3.70E-06 | 25 | 1.21 | 20 | - | 3316 | 1000 | 89 | - | insec |
| quizalafop-ethyl | 372.8 | 4.00E-05 | 25 | 0.31 | 20 | - | 540 | 1000 | 39 | - | herb |
| cyprodinil | 225.3 | 4.70E-04 | 25 | 16 | 25 | - | 1004 | 1000 | 142 | - | fung |
| fludoxinil | 248.2 | 3.90E-07 | 25 | 1.8 | 25 | - | 85647 | 1000 | 787.5 | - | fung |
| fenhexamide | 302.2 | 4.00E-07 | 20 | 24 | 20 | - | 516 | 1000 | 17 | - | fung |

*Table 5* *Dosages and spray drift masses as applied in the Dutch authorisation scenario for a field of strawberries (m = metabolite).*

| Product | active substance | Content a.i. | Dosage product | Content a.i. in product (g/L) | Dosage a.i. (g/ha) | Spray drift (%) | Loading on ditch (g/m$^2$) |
|---|---|---|---|---|---|---|---|
| Paraat | dimethomorph | 50% | 3 kg | | 1500 | 0.5 | 0.00075 |
| Kontakt 320 SC | fenmedifam | 320 G/L | 1 | 320 | 320 | 0.5 | 0.00016 |
| | MHPC (m) | - | - | | 124.8 | 0.5 | 0.0000624 |
| Dual Gold 960 EC | S-metalochloor | 960 G/L | 0.7 | 960 | 672 | 0.2 | 0.0001344 |
| | CGA 41507 (m) | - | - | | 119.6 | 0.2 | 0.0000239 |
| | CGA 51202 (m) | - | - | | 165.3 | 0.2 | 0.0000331 |
| Several products[1] | thiacloprid | 480 g/L | 0.25 | 480 | 120 | 0.2 | 0.000024 |
| Several products[2] | deltamethrin | 25 g/L | 0.2 | 25 | 5 | 1 | 0.000005 |
| Nimrod vloeibaar | bupirimaat | 250 G/L | 1 | 250 | 250 | 1 | 0.00025 |
| | ethiridimol (m) | - | - | | 61.3 | 1 | 0.00006125 |
| Rovral aquaflo | iprodion | 500 G/L | 2 | 500 | 1000 | 0.5 | 0.0005 |
| | RP30228 (m) | - | - | - | 100 | 0.5 | 0.00005 |
| Frubpica SC | mepanipyrum | 440 G/L | 0.9 | 440 | 396.0 | 1 | 0.000396 |
| Signum | boscalid | 26,7% | 1.8 kg | | 480.6 | 1 | 0.0004806 |
| | pyrasclostrobine | 6,7% | 1.8 kg | | 120.6 | 1 | 0.0001206 |
| Vertimec | abamectine | 18 G/L | 0.5 | 18 | 9.0 | 0.1 | 0.0000009 |
| Targa | quizalafop-ethyl | 50 G/L | 1 | 50 | 50.0 | 1 | 0.00005 |
| Switch | cyprodinil | 37,5% | 1 kg | | 375 | 1 | 0.000375 |
| | fludioxonil | 25% | 1 kg | | 250 | 1 | 0.00025 |
| Teldor spray pellets | fenhexamide | 50% | 1.5 kg | | 750 | 1 | 0.00075 |

[1]) Thiacloprid products used are: Calypso and Dadian

[2]) Deltamethrin products used are: Decis EC, Imex, WOPRO, DeltaM, Delta25

***Table 6*** *RAC values for active substances and metabolites as included in the spraying schedule for strawberries.*

| | Deltamethrin (µg as/L) | Thiacloprid (µg as/L) | Bupirimaat (µg as/L) | Iprodion (µg as/L) |
|---|---|---|---|---|
| Fish: | | | | |
| RAC acute | 0.15 (field study) | 2.52 | 10 | 31 |
| RAC chronic | 0.15 (field study) | 2.4 | 30 | 26 |
| Invertebrates: | | | | |
| RAC acute | 0.0032 (mesocosm) | 0.52 (mesocosm) | 31 | 6.6 |
| RAC chronic | 0.0032 (mesocosm) | 0.52 (mesocosm) | 56 | 17 |
| Primary prod: | | | | |
| RAC | 178 | 447 | 123 | 180 |
| | | | | |
| Metabolites | Br2CA (µg a.i./L) | M02 en M30 (µg as/L) | Ethirimol (µg as/L) | RP30228 (µg as/L) |
| Fish: | Assessed in field study of fish | Factor >100 less toxic than a.i. | | |
| RAC acute | | | 608 | 5.5 |
| RAC chronic | | | 4140 | - |
| Invertebrates: | Assessed in mesocosm study | Factor >100 less toxic than a.i. | | |
| RAC acute | | | 500 | >5 |
| RAC chronic | | | 730 | 10 |
| Primary prod: | Assessed in mesocosm study | Factor >100 less toxic | | |
| RAC | | than a.i. | 2400 | >50 |

| | mepanipyrim (µg as/L) | boscalid (µg as/L) | pyraclostrobin | abamectin (µg as/L) | cyprodinil (µg as/L) | fludioxonil |
|---|---|---|---|---|---|---|
| Fish: | | | | | | |
| RAC acute | >7.4 | 27 | 1.45 (SSD) | 0.31 (SSD) | 21.7 | 2.3 |
| RAC chronic | 2.9 | 12.5 | 0.8 (mesoc) | 0.22 (SSD) | 8.3 | 3.9 |
| Invertebrates: | | | | | | |
| RAC acute | 6.3 | 53.3 | 0.16 | 0.1 (mesoc) | 4.3 (mesoc) | 16.4 (mesoc) |
| RAC chronic | 3.1 | 131.0 | 1.1 | 0.1 (mesoc) | 4.33 (mesoc) | 16.4 (mesoc) |
| Primary prod: | | | | | | |
| RAC | 23 | 134 | 15.2 | >159 | 211 | 16.4 (mesoc) |
| | | | | | | |
| Metabolites | - | - | | | - | |
| Fish:<br>RAC acute<br>RAC chronic | - | - | Factor >100 less toxic than a.i. | Metabolites covered by RA a.i. | - | Factor >100 less toxic than a.s. |
| Invertebrates:<br>RAC acute<br>RAC chronic | - | - | Factor >100 less toxic than a.i. | Metabolites covered by RA a.i. | - | Factor >100 less toxic than a.i. |
| Primary prod:<br>RAC | - | - | Factor >100 less toxic than a.i. | Metabolites covered by RA a.i. | - | Factor >100 less toxic than a.i. |

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