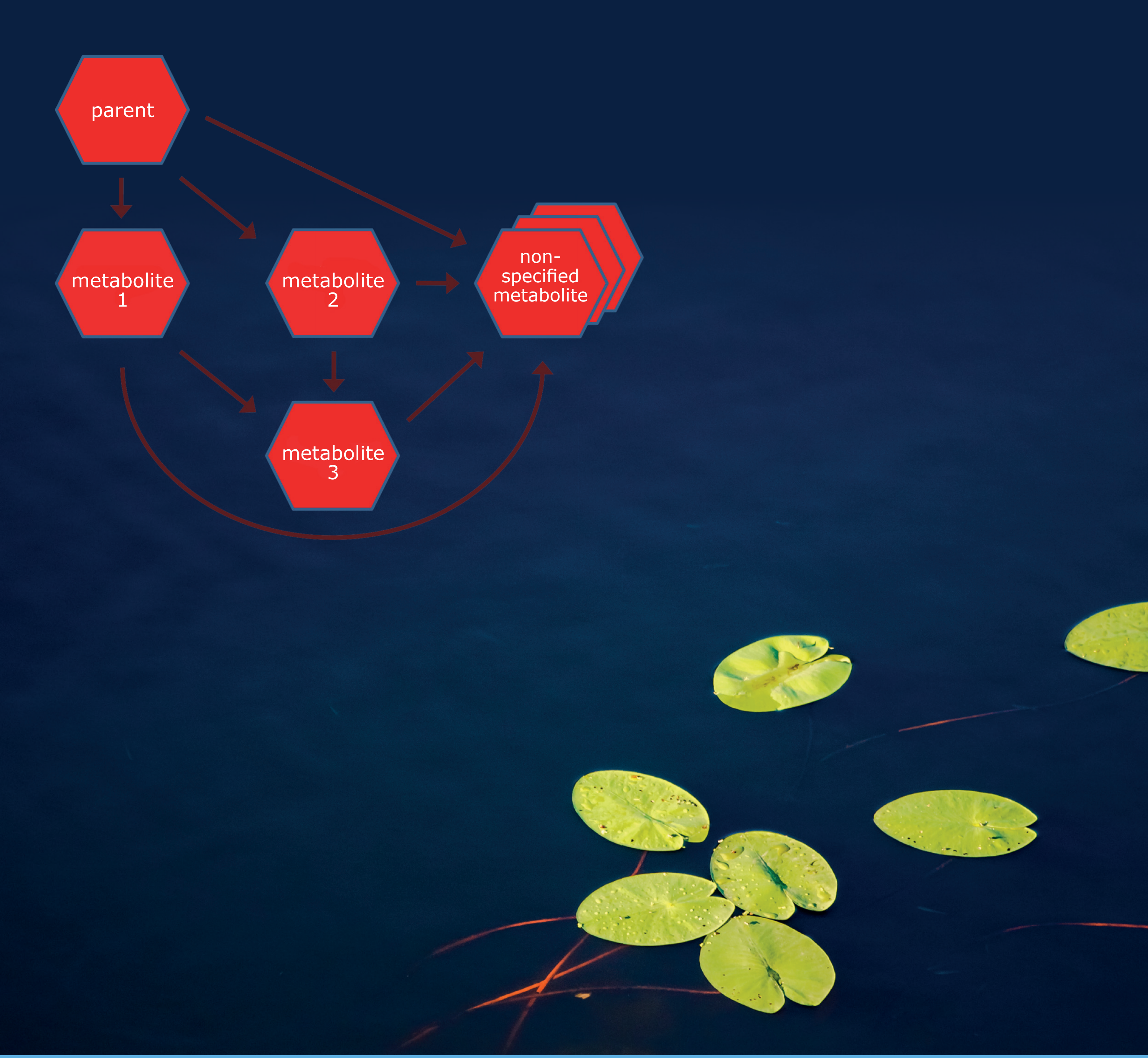

Metabolite formation in water and in sediment in the TOXSWA model

Theory and procedure for the upstream catchment of FOCUS streams

P.I. Adriaanse, W.H.J. Beltman and F. Van den Berg

ALTERRA
WAGENINGEN UR

Metabolite formation in water and in sediment in the TOXSWA model

Theory and procedure for the upstream catchment of FOCUS streams

P.I. Adriaanse, W.H.J. Beltman and F. Van den Berg

This research was funded by the Dutch Ministry of Economic Affairs
(project numbers BO-20-002-002 and WOT-04-008-024).

Alterra Wageningen UR
Wageningen, November 2014

Alterra report 2587
ISSN 1566-7197

WOt-technical report 15

Adriaanse, P.I., W.H.J. Beltman and F. Van den Berg, 2014. *Metabolite formation in water and in sediment in the TOXSWA model; Theory and procedure for the upstream catchment of FOCUS streams.* Wageningen, Alterra Wageningen UR (University & Research centre), Alterra report 2587. 52 pp.; 11 fig.; 8 tab.; 10 ref.

Het TOXSWA model is uitgebreid met de beschrijving van vorming en omzetting van metabolieten in water en sediment. Op EU niveau wordt TOXSWA gebruikt in de aquatische risico beoordelingsmethodiek van bestrijdingsmiddelen om blootstellingsconcentraties te berekenen in de diverse water typen van de zogenaamde EU-FOCUS oppervlaktewater scenario's. Voor de scenario's met FOCUS riviertjes is er een bovenstrooms stroomgebied van 100 ha waarvan 20 ha met bestrijdingsmiddel is behandeld. Bij deze scenario's willen we rekening houden met metabolieten die in het stroomgebied zijn gevormd. Daarom is een procedure ontwikkeld om de metaboliet concentraties en fluxen te corrigeren voor de FOCUS riviertjes, gevoed door het gedeeltelijk behandelde stroomgebied. De correctiefactoren van de procedure kunnen op twee manieren worden bepaald: (i) een simpele manier, waarbij de correctiefactor een functie is van de omzettingssnelheid van de moederstof en (ii) een meer gedetailleerde manier waarbij de correctiefactor een functie is van de omzettingssnelheid van zowel de moederstof als van de metaboliet, alsmede van de verblijftijd van de moederstof in het bovenstroomse stroomgebied.

The TOXSWA model now includes formation and transformation of metabolites in water and in sediment. TOXSWA is used in the aquatic risk assessment procedure of pesticides at EU level to calculate exposure concentrations in the so-called EU-FOCUS surface water scenarios. For some of these scenarios the water bodies (i.e. FOCUS streams) are fed by an upstream catchment of 100 ha of which 20 ha is treated with pesticides. For these scenarios we want to account for the formation of metabolites in the upstream catchment. Therefore we designed a procedure to correct the metabolite concentrations and fluxes for the FOCUS streams, fed by the partly treated upstream catchment. The correction factors of the procedure can be estimated by two methods: (i) a simple method with the correction factor being a function of the parent degradation rate only and (ii) a more detailed method with correction factor being a function of both the parent degradation rate and the metabolite degradation rate as well as the residence time of the parent in the upstream catchment.

Keywords: pesticide metabolites, TOXSWA model, FOCUS streams, EU aquatic risk assessment

The pdf file is free of charge and can be downloaded via the website www.wageningenUR.nl/en/alterra (scroll down to Publications - Alterra reports). Alterra does not deliver printed versions of the Alterra reports.

This report is also available as **WOt-technical report 15**: Adriaanse, P.I., W.H.J. Beltman, F. Van den Berg (2014). *Metabolite formation in water and in sediment of the TOXSWA model. Theory and procedure for the upstream catchment of FOCUS streams.* Wageningen, The Statutory Research Tasks Unit for Nature and the Environment, Wageningen UR. ISSN 2352-2739

© 2014 Alterra (an institute under the auspices of the Stichting Dienst Landbouwkundig Onderzoek), P.O. Box 47, 6700 AA Wageningen, The Netherlands, T +31 (0)317 48 07 00, E info.alterra@wur.nl, www.wageningenUR.nl/en/alterra. Alterra is part of Wageningen UR (University & Research centre).

- Acquisition, duplication and transmission of this publication is permitted with clear acknowledgement of the source.
- Acquisition, duplication and transmission is not permitted for commercial purposes and/or monetary gain.
- Acquisition, duplication and transmission is not permitted of any parts of this publication for which the copyrights clearly rest with other parties and/or are reserved.

Alterra assumes no liability for any losses resulting from the use of the research results or recommendations in this report.

Photo cover: Grisha Bruev

Contents

Preface

This report documents the simulation of metabolites in the FOCUS_TOXSWA model, version 4.4.2. Chapter 2 (Formation of metabolites in water and in sediment) has been described earlier as an internal document in 2005, when the software of the TOXSWA model (FOCUS version 1.1.1) was re-designed to become more object-oriented and metabolite formation was to be included. Chapters 3, 4 and 5 were developed from January 2013 to February 2014, when the release of FOCUS_TOXSWA 4.4.2 was prepared.

The Statutory Research Tasks Unit for Nature & the Environment (WOT N&M) financed the research described in Chapter 2 (project WOT-04-008-024), while the Chapters 3, 4 and 5 of this report were financed by the BO-Agro Research programme BO-20-002 "Beoordelingsmethodieken Toelating Gewasbeschermingsmiddelen" (project BO-20-002-002). Both research programmes are supported by the Dutch Ministry of Economic Affairs.

The procedure for estimating the formation of metabolites in the upstream catchment of the FOCUS streams described in Chapter 3 was designed by Alterra (W. Beltman and P. Adriaanse). Factors are introduced that correct the metabolite concentration in FOCUS streams for metabolite formation in their upstream catchment. The calculation of the correction factors was discussed and improved (Chapter 4) during a series of teleconferences between members of a sub working group of the FOCUS Version Control Group (http://focus.jrc.ec.europa.eu/), which was chaired by an EFSA representative. Therefore the authors thank D. Patterson (Syngenta, UK), N. MacKay (Du Pont, UK), R. Jones (Bayer, USA), M. Klein (Fraunhofer Institute, Germany) and C. Lythgo (EFSA, Italy) for their contributions. However, the Alterra authors are responsible for the contents of this Alterra report.

The report was seen and approved by Anja van Gemerden (contact of Dutch Ministry of Economic Affairs) and by Jennie van der Kolk (contact of WOT N&M, theme Agri-Environment. Finally, the report was reviewed by M.M.S ter Horst (researcher Alterra Wageningen UR).

Pauline Adriaanse, Wim Beltman & Erik van den Berg

Summary

The TOXSWA model simulates the behaviour of pesticides that enter small surface waters by e.g. spray drift deposition and runoff or drainage water. The model has now been extended to include the formation and transformation of metabolites, formed from the parent in the water layer or in the sediment. A flexible reaction scheme, presented in matrix form, indicates which metabolites can be formed and shows their precursor compounds (parent or other metabolite).

The TOXSWA model (FOCUS versions) is part of the aquatic risk assessment procedure for pesticide registration at EU level. Exposure concentrations for aquatic organisms living in streams, ditches or ponds in the so-called EU-FOCUS surface water scenarios are calculated. Ditches and streams in these scenarios are fed by an upstream catchment that is partly treated with pesticides. Now that the new FOCUS_TOXSWA 4.4.2 model includes metabolite formation in the simulated water bodies it is logical to also account for metabolites that are formed from parent compounds while travelling in the catchments towards their downstream FOCUS water bodies. As the FOCUS ditch and pond scenarios do not have upstream catchments treated with pesticides, this is only relevant for the FOCUS streams, where 20 ha of the 100-ha catchment is treated.

Therefore, a procedure was designed that corrects the metabolite concentration in FOCUS streams for additional metabolite mass coming out of the upstream catchment. For a spray drift-entered parent compound the metabolite concentration in the stream is increased to maximally 0.2 times the parent concentration (as is done for the parent, representing the situation that the parent from the catchment is present in the FOCUS stream at the time of the spray drift deposition from the treated adjacent 1 ha field). For a runoff or drainage entered parent compound an additional metabolite mass flux enters the stream from upstream, its maximum size equals the parent mass flux from the upstream catchment. Depending on e.g. the transformation rate of the parent, the maximum metabolite concentration of flux is lowered to a more realistic, but still conservative value by introducing correction factors: for rapidly transforming parents the metabolite concentration or flux is higher, (resulting in a correction factor close to 1) than for slowly transforming ones (resulting in a correction factor clearly lower than 1).

Two methods to estimate these correction factors $CF_{m,up}$ are presented: (i) a simple one, where the factor is only a function of the transformation rate of the parent and (ii) a more detailed one, where the factor is a function of the transformation rates of both the parent and the metabolite, as well as of a conservative estimate for the residence time in the upstream catchment of each stream scenario. Both methods are based upon the two possible, extreme layouts of the upstream catchment (a square shape with 10*10 1-ha fields or a long, rectangular shape with 2* 50 1-ha fields). The transformation rates of the parent and the metabolite are corrected for the average scenario temperature.

Example simulations are presented, demonstrating the formation of metabolites in water or in sediment. Other examples present the metabolite concentration in FOCUS streams and the effect of the two different values of the correction factors.

1 Introduction

In the framework of EU Directive 91/414 (EU, 1991) and its successor, Regulation 1107/2009 (EC, 2009), information is needed on the fate and behaviour of the active ingredient as well as of relevant metabolites in surface waters. The TOXSWA model (Adriaanse *et al*, 2013) simulates the behaviour of pesticides in water and in sediment; it is used to calculate exposure concentrations in the registration procedure at EU level: in step 3 of the tiered procedure of the aquatic risk assessment concentrations are calculated in a ditch, stream and pond of the so-called EU-FOCUS surface water scenarios (Adriaanse, 1996; FOCUS, 2001; Beltman *et al*, 2006). At present the current version of the TOXSWA model, FOCUS_TOXSWA_3.3.1, can only simulate metabolites that enter the water via drainage or runoff by treating the metabolite in the same way as a parent compound. So, the TOXSWA model is not able to simulate formation and transformation of metabolites in the water layer and in the sediment. Therefore, there was a need to improve the TOXSWA model to simulate formation and transformation of relevant metabolites of the parent compound in the water layer and in the sediment.

As FOCUS water bodies of the EU-FOCUS scenarios are fed by an upstream catchment that may be partly treated with pesticides it is logical to also account for metabolites that are formed from parent compounds in the catchment water bodies while travelling towards their downstream FOCUS water bodies. As the FOCUS ditch and pond scenarios do not have upstream catchments treated with pesticides, this is only relevant for the FOCUS streams, where 20 ha of the 100-ha catchment is treated. Therefore, there was also a need to design a procedure to correct the metabolite concentration in FOCUS streams by accounting for the metabolite formation in the upstream catchment water bodies.

So, this report describes the two improvements in the calculation of the metabolite concentration in the EU-FOCUS surface water scenarios:

1. The simulation of formation and transformation of metabolites in water and in sediment by the TOXSWA model and
2. A procedure, correcting the metabolite concentration in FOCUS streams for additional metabolite mass formed in the upstream catchment, implemented in the SWASH shell of the EU-FOCUS surface water scenarios.

After the introduction (chapter 1), chapter 2 presents the mathematical equations for the formation and transformation of metabolites and it is explained how the mass conservation equations are set up for the metabolites in the TOXSWA model. In chapter 3 a procedure is designed to correct for metabolite formation in the upstream catchment of FOCUS streams and a first, simple estimation of the needed correction factors is made. In chapter 4 an improved method to estimate the correction factors is presented; this is based not only on the degradation rate of the parent, but also on the degradation rate of the metabolite and the hydraulic residence time in the catchment. In addition, it is demonstrated that the two correction factors, one for spray drift entries and one for drainage/runoff entries, can be merged into one single variable, $CF_{m,up}$. In chapter 5 simulation examples are given that present the metabolite concentrations in a FOCUS stream for the two estimation methods for the correction factor. Chapter 6 presents a discussion and conclusions.

2 Formation of metabolites in water and in sediment

The TOXSWA model (Adriaanse, 1996; Beltman *et al*, 2006) is used to simulate exposure concentrations as part of the aquatic risk assessment procedure at EU level (http://focus.jrc.ec.europa.eu/). In step 3 of the FOCUS surface water scenarios concentrations are calculated in a ditch, stream and pond. The current version of the TOXSWA model, FOCUS_TOXSWA_3.3.1, is not able to simulate formation and transformation of metabolites in the water layer and in the sediment.

MACRO and PRZM models are used to calculate the entry of active ingredient via drainage and runoff. Both models are able to simulate the fate of the parent compound as well as the fate of one or more metabolites, formed in the soil. The fate and behaviour of a metabolite entering the water via drainage or runoff can be simulated by TOXSWA by treating the metabolite in the same way as a parent compound. For such a simulation, there is, by definition, no spray drift deposition on the water.

So, there is a need to improve the TOXSWA model (Adriaanse *et al*, 2013) to simulate formation and transformation of relevant metabolites of the parent compound in the water layer and in the sediment.

2.1 Description of processes in the TOXSWA model

In FOCUS_TOXSWA versions 1.1.1, 2.2.1 and 3.3.1 the following processes are considered for the water layer:
- Transport by advection and dispersion
- Transformation (only parent compound)
- Exchange with the atmosphere
- Exchange with the sediment

For the sediment the following processes are considered:
- Transport by advection, dispersion and diffusion
- Transformation (only parent compound)

The pesticide mass conservation equation for the water layer is described by (Adriaanse, 1996, eq. 3.6):

$$\frac{\partial\left(c^{*}A\right)}{\partial t}=-\frac{\partial\left(AJ\right)}{\partial x}-k\,(c^{*}A)+J_{wa}\cdot O_{x}-J_{wb}\cdot P_{x} \qquad (1)$$

where:

c^* = mass concentration in the water layer (including sorbed to suspended solids and sorbed to macrophytes) (M L^{-3})[1]
t = time (T)
A = cross sectional area of flow (L^2)
J = areic mass flux by advection and dispersion in the water layer (M L^{-2} T^{-1})
x = distance in direction of flow (L)
J_{wa} = areic mass flux across the water-air interface (M L^{-2} T^{-1})
O_x = width of water surface at location x (L)
k = rate coefficient for transformation in the water layer (T^{-1})
J_{wb} = areic mass flux across the water-sediment interface (M L^{-2} T^{-1})
P_x = wetted perimeter at location x (L)

The second term of the right-hand part of the equation is the term describing transformation.

The numerical solution of the mass conservation equation for the water layer can be described by:

$$AA\, c^{j+1} = BB\, c^{i} + d \tag{2}$$

where:

c = mass concentration in the water layer(M L^{-3}) and
j and *j+1* indicate the time steps *j* and *j+1*.

AA and BB are so-called tridiagonal matrices and *d* stands for a separate vector composed of constants. The elements of AA describe the concentration in the water layer of compartment *i*-1 (LOD), *i* (LDD) and *i*+1 (LBD). The term describing transformation figures only in the LDD element. The elements of BB describe the concentration in the water layer of compartment *i*-1 (ROD), *i* (RDD) en *i*+1 (RBD). The term describing transformation figures only in the RDD element.

In the TOXSWA model computations can be done using an explicit or an implicit numerical solution scheme. For the explicit scheme Θ equals 1 while for the implicit scheme Θ equals 0.

The term describing transformation in the LDD element, LDD_t, reads:

$$LDD_t = \frac{c^*}{c} \cdot k \cdot A_i^{j+1/2} \cdot (1-\Theta) \cdot \Delta t \tag{3a}$$

The term describing transformation in the RDD element, RDD_t, reads:

$$RDD_t = -\frac{c^*}{c} \cdot k \cdot A_i^{j+1/2} \cdot \Theta \cdot \Delta t \tag{3b}$$

The pesticide mass conservation equation for the sediment is described by (Adriaanse, 1996, eq. 3.12):

$$P\frac{\partial c_b^*}{\partial t} = -\frac{\partial \left(PJ_{lb}\right)}{\partial z} - k_b c_b^* P \tag{4}$$

---

[1] The dimension of the symbol introduced is given between the pair of brackets. L stands for length, T for time, M for mass, N for mole and θ for temperature (Schurer and Rigg, 1980).

where:

P = wetted perimeter (L)

c_b^* = mass concentration in the sediment (M L^{-3})

z = depth in sediment (L)

J_{lb} = areic mass flux by advection, dispersion and diffusion in the liquid phase of the sediment (M L^{-2} T^{-1})

k_b = rate coefficient for transformation in the sediment (T^{-1})

In analogy to the water layer, the numerical solution of the mass conservation equation for the sediment can be described by:

$$FF\ c_{lb}^{j+1} = GG\ c_{lb}^{j} + fg \tag{5}$$

where:

c_{lb} = mass concentration in the liquid phase of the sediment (M L^{-3}) and

= j and $j+1$ indicate the time steps j and $j+1$.

FF and GG are tridiagonal matrices and *fg* stands for a separate vector composed of constants (all zero, except for its last element). The elements of FF describe the concentration c_{lb} in the sediment of compartment i-1 (LOD), i (LDD) and i+1 (LBD). The term describing transformation figures only in the LDD element. The elements of GG describe the concentration in the sediment of compartment i-1 (ROD), i (RDD) en i+1 (RBD). The term describing transformation figures only in the RDD element.

The term describing transformation in the LDD element, LDD_t, reads:

$$LDD_t = \frac{c_b^*}{c_{lb}} \cdot k_b \cdot (1-\Theta)\ \Delta t \tag{6a}$$

The term describing transformation in the RDD element, RDD_t, reads:

$$RDD_t = -\frac{c_b^*}{c_{lb}} \cdot k_b \cdot (\Theta)\ \Delta t \tag{6b}$$

In the FOCUS_TOXSWA model the parameter Θ has been set to 1, so computations are made with the explicit numerical solution scheme, described in Annex 1.

2.2 General description of formation and transformation of metabolites

FOCUS_TOXSWA_4.4.2 has a flexible reaction scheme for formation and transformation of metabolites, comparable to the one in FOCUS_PEARL_2.2.2 (Leistra *et al.*, 2001).

An example of a reaction scheme is presented in Figure 1:

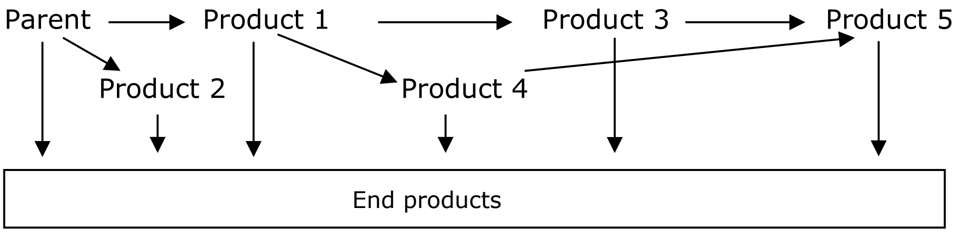

Figure 1. *Example reaction scheme of parent decomposed into various metabolites.*

The reaction scheme can be represented in a general way in a matrix, as shown in Table 1. The matrix indicates that a compound is usually transformed into various products. Furthermore, a product may be formed from one or more precursor compounds.

Table 1

Example of a matrix which represents the reactions between the compounds included in the reaction scheme of a pesticide. 0 = no reaction. χ = molar fraction of a compound transformed into a specific product. From Leistra et al. (2001).

Scenario	Parent	Product 1	Product 2	Product 3	Product 4	Product 5
Parent	0	$\chi_{p,1}$	$\chi_{p,2}$	0	0	0
Product 1	0	0	0	$\chi_{1,3}$	$\chi_{1,4}$	0
Product 2	0	0	0	0	0	0
Product 3	0	0	0	0	0	$\chi_{3,5}$
Product 4	0	0	0	0	0	$\chi_{4,5}$
Product 5	0	0	0	0	0	0

Transformation of the parent pesticide is described by the following first-order rate equation:

$$R_{t,p} = k_p c_p^* \tag{7}$$

where:

c_p^* = mass concentration of parent pesticide (M L^{-3})

k_p = rate coefficient for transformation of the parent pesticide (T^{-1})

$R_{t,p}$ = rate of transformation of the parent pesticide (M L^{-3} T^{-1})

Similar rate equations are used for each transformation product.

The rate of formation of reaction products can be described by first-order kinetics. For product 1, formed from the parent compound:

$$R_{f,p,1} = \chi_{p,1} \frac{M_1}{M_p} \cdot R_{t,p} \tag{8}$$

where:

$R_{f,p,1}$ = rate of formation of product 1 from the parent compound (M L^{-3} T^{-1})

$\chi_{p,1}$ = molar fraction of parent transformed to product 1 (-)

M_1 = molar mass of product 1(M N^{-1})

M_p = molar mass of parent compound (M N^{-1})

For the transformation of product 1:

$$R_{t,1} = k_1 c_1^* \tag{9}$$

where:
c_1^* = mass concentration of product 1 (M L^{-3})
k_1 = rate coefficient for transformation of product 1 (T^{-1})
$R_{t,1}$ = rate of transformation of the product 1 (M L^{-3} T^{-1})

A similar equation holds for each of the reaction products of the reaction scheme.

2.3 Description of formation and transformation of metabolites in the TOXSWA model

The conservation equation for the parent compound in the water layer reads:

$$\frac{\partial(c_p^* A)}{\partial t} = -\frac{\partial(AJ_p)}{\partial x} - k_p(c_p^* A) + J_{wa,p}O_x - J_{wb,p}P_x \tag{10}$$

where
c^*_p = mass concentration of parent compound in the water layer
= (including sorbed to suspended solids and sorbed to macrophytes) (M L^{-3})

The conservation equation for product 1, formed from the parent compound, reads:

$$\frac{\partial(c_1^* A)}{\partial t} = -\frac{\partial(AJ_1)}{\partial x} - k_1(c_1 A) + \chi_{w,p,1}\frac{M_1}{M_p}\, k_p(c_1^* A) + J_{wa,1}O_x - J_{wb,1}P_x \tag{11}$$

where:
c^*_1 = mass concentration of product 1 in the water layer
= (including sorbed to suspended solids and and sorbed to macrophytes) (M L^{-3})
$\chi_{w,p,1}$ = molar fraction of parent transformed to product 1 in the water layer (-)

The conservation equation for the parent compound in the sediment reads:

$$P\frac{\partial c_{b,p}{}^*}{\partial t} = -\frac{\partial\left(PJ_{lb,p}\right)}{\partial z} - k_{b,p}c_{b,p}{}^* P \tag{12}$$

where:
$c_{b,p}{}^*$ = mass concentration of parent compound in sediment (M L^{-3})

The conservation equation for product 1, formed from the parent compound, reads:

$$P\frac{c_{b,1}^*}{\partial t} = -\frac{\partial(PJ_{lb,1})}{\partial z} - k_{b,1}c_{b,1}^* P + \chi_{b,p,1}\frac{M_1}{M_p}\, k_{b,p}\, c_{b,p}^* P \tag{13}$$

where:
$c_{b,1}{}^*$ = mass concentration of product 1 in sediment (M L^{-3})
$\chi_{b,p,1}$ = molar fraction of parent transformed to product 1 in the sediment (-)

For a fully implicit numerical solution scheme with Θ equal to 0, and for a numerical solution scheme with 0 < Θ < 1 the term for formation of product 1 in RV, $RV_{w,f}$, for the water layer reads:

$$\boldsymbol{RV_{w,f} = \chi_{w,p,1} \frac{M_1}{M_p} k_p c_1^{*j+1/2} A^{j+1/2} \Delta t} \tag{14}$$

The term for formation of product 1 in RV, $RV_{b,f}$, for the sediment reads:

$$RV_{b,f} = \chi_{b,p,1} \frac{M_1}{M_p} k_{b,p} c_{b,p}^{*j+1/2} P_k^{j+1/2} \frac{\Delta t}{P_k^j} \tag{15}$$

As P is constant with time, Eq. (15) can be simplified to:

$$\boldsymbol{RV_{b,f} = \chi_{b,p,1} \frac{M_1}{M_p} k_{b,p} c_{b,p}^{*j+1/2} \Delta t} \tag{16}$$

2.4 Example simulations

Pesticides can be transformed into metabolites in water and in sediment. Examples for both types of metabolite formation are presented below.

Simulations[2] are done for the FOCUS R1 pond, a water body with low water flow dynamics in order to focus on pesticide processes. The example substances used are:

(i) an insecticide and its metabolite I (formation fraction 0.7 in water), and
(ii) a fungicide and its metabolite F (formation fraction 0.7 in sediment).

The applications and main substance properties are given in Table 2. Runoff is calculated by FOCUS_PRZM 3.1.1, and water body concentrations are calculated by FOCUS_TOXSWA 4.4.2.

Table 2
Applications and main properties of substances.

Application and properties	Insecticide	Metabolite I	Fungicide	Metabolite F
applications	apples, 70 + 105 g		winter cereals, 1 x 750 g	
K_{OM} (L/kg)	100	10	1000	10
DegT50 soil at 20°C (d)	100	not relevant	50	not relevant
DegT50 water at 20°C (d)	5	100	10	100
DegT50 sediment at 20°C (d)	100	100	20	100

Figure 2 shows the concentrations in water of the insecticide and of its metabolite formed in water. The two spray drift events lead to two peak concentrations of the insecticide. Due to its short half-life (5 d) the concentration of the insecticide decreases rapidly, while the concentration of metabolite I increases rapidly. As the metabolite's half-life is relatively long (100 d) its concentration decreases slowly.

---

[2] Simulations also published in Appendices to Scientific Opinion of the EFSA Panel on Plant health, Plant protection products and their Residues (PPR). European Food Safety Authority, Guidance Document on tiered risk assessment for plant protection products for aquatic organisms in edge-of-field surface waters. The EFSA Journal (2013) issue, 11(7):3290 [181 pp]. http://www.efsa.europa.eu/efsajournal

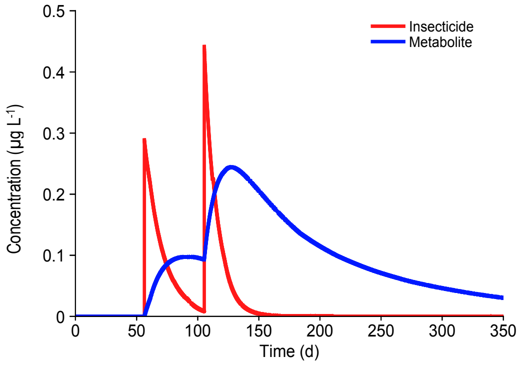

Figure 2 *Concentration in water of insecticide and of its metabolite formed in water. Days of application: 57 (26 April) and 106 (14 June).*

Figure 3a shows the concentrations in water of the fungicide and its metabolite F, formed in sediment. After the spray drift event at day 57 several runoff events lead to concentration peaks of the fungicide. The global maximum concentration at day 90 is due to runoff. The concentration of the fungicide decreases rapidly due to its short half-life (10 d). It also diffuses into the sediment, where its content increases (Figure 3b). Due to the short half-life in sediment (20 d) the fungicide is rapidly transformed into metabolite F and so, the content of metabolite F increases. Next the metabolite diffuses into the water layer, where it is visible from approximately day 70 onwards Figure 3a).

Figure 4a and 4b demonstrate well the various processes taking place: The fungicide mass enters the water layer by spray drift deposition (blue curve) and by several runoff events (green). It leaves the water layer mainly by transformation (purple) and in equivalent amounts by downstream outflow (red) and by diffusion into sediment (beige). The fungicide mass diffusing into sediment is transformed rapidly into metabolite F. Figure 4b shows the formation of metabolite F in the sediment (black curve). Nearly all formed metabolite mass diffuses into the water layer (navy blue curve).

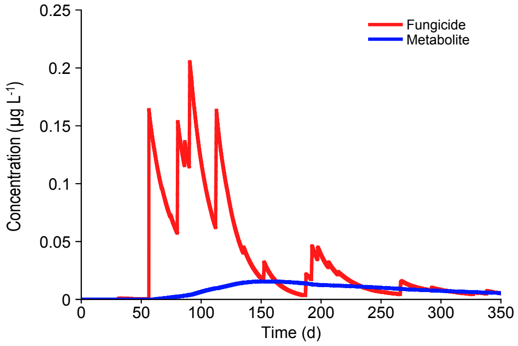

Figure 3a *Concentration in water of fungicide and of its metabolite. Day of application: 57 (26 April).*

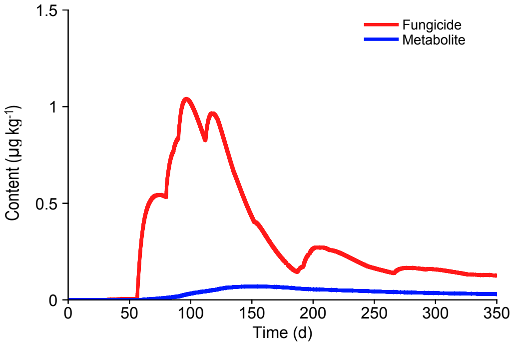

Figure 3b *Content in sediment of fungicide and of its metabolite formed in sediment.*

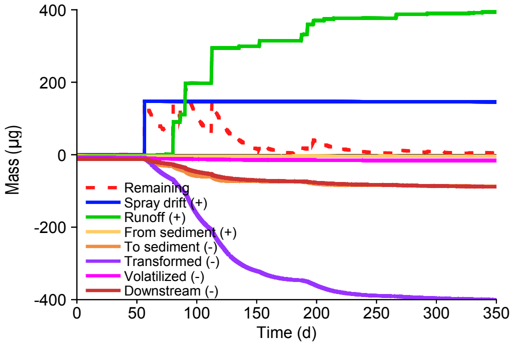

Figure 4a *Mass balance of fungicide in water layer.*

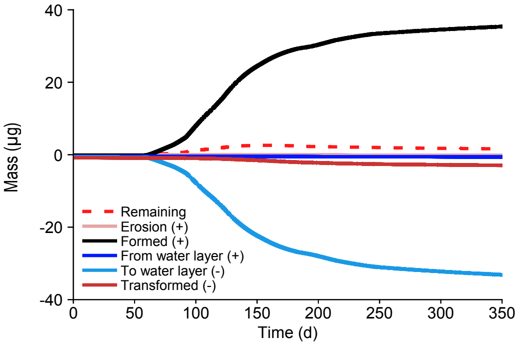

Figure 4b *Mass balance of metabolite F in sediment.*

3 Procedure to correct for metabolite formation in the upstream catchment of FOCUS streams

The FOCUS_TOXSWA_3.3.1 model, can only handle metabolites formed in soil that enter the water body via drainage or runoff/erosion.

The FOCUS_TOXSWA_4.4.2 model (FOCUS successor version after 3.3.1) can also handle the formation of metabolites in water and sediment. So, it handles a large number of metabolites in one run; these metabolites may be formed in soil and enter the water body via drainage or runoff+erosion or they may be formed in the water body, i.e. in water and/or in sediment. Metabolites formed in the water and in the sediment may be formed in so-called consecutive reactions, as well as in so-called simultaneous reactions. The user needs to set up the list of compounds to consider and to indicate in matrix form which compounds are connected by a reaction, as described in section 2.2. Additional input needed are the molar formation fractions and the physico-chemical properties of the metabolites. All present model output for the parent is also available for the metabolites, i.e. concentration as a function of time (i) in water (total and in dissolved phase), (ii) sorbed to suspended solids, and (iii) in sediment (in pore water or sorbed to sediment mass), mass present in different phases in water and sediment as a function of time and full mass balances for water and sediment as a function of time.

Consequence of this new feature in TOXSWA for the FOCUS scenario definition is that it seems logical to account for metabolites formed in the upstream catchment that enter the downstream water body via its upstream boundary. This is not needed for FOCUS ditches and ponds as these scenarios do not have upstream fields treated with pesticides. For FOCUS stream scenarios 20 ha of the 100-ha upstream catchment are treated with pesticides. Therefore, the FOCUS streams are the only FOCUS water bodies needing additional input of metabolites, originating from the upstream catchment.

3.1 Proposed procedure

Metabolites are thus formed in the upstream catchment water bodies and they may enter the FOCUS streams, located downstream. To account for these metabolites we make the following basic assumptions:

1. In agreement with the 'realistic worst case' situation to assess risks, as mentioned in EU Directive 91/414/EEC and its successor EU Regulation 1107/2009, we intend to make a conservative estimation of the metabolite concentration in the FOCUS stream.

However,

2. We only consider metabolites formed in the water layer of the catchment.
3. So, we do not consider metabolites formed in the sediment of the catchment.
4. We only consider metabolites that are formed directly from the parent, so we do not consider metabolites formed from other metabolites (that were formed in water or sediment). An exception are metabolites formed directly from the metabolites that were formed in the soil and that entered the water body via runoff or drainage. These metabolite fluxes are fed into TOXSWA by the p2t or m2t files created by PRZM (runoff) or MACRO (drainage) (and which the TOXSWA model treats in a way identical to parents from runoff or drainage).

For the layout of the 100-ha upstream catchment and related residence times in the catchment we consider two extremes:

(i) square catchment, i.e. 1000 * 1000 m with 1 ha plots, with an average travel distance to the outlet of approximately 750 m (Fig. 5) and

(ii) rectangular catchment, i.e. 200 * 5000 m with 1 ha plots, with an average travel distance to the outlet of approximately 2500 m (Fig. 5).

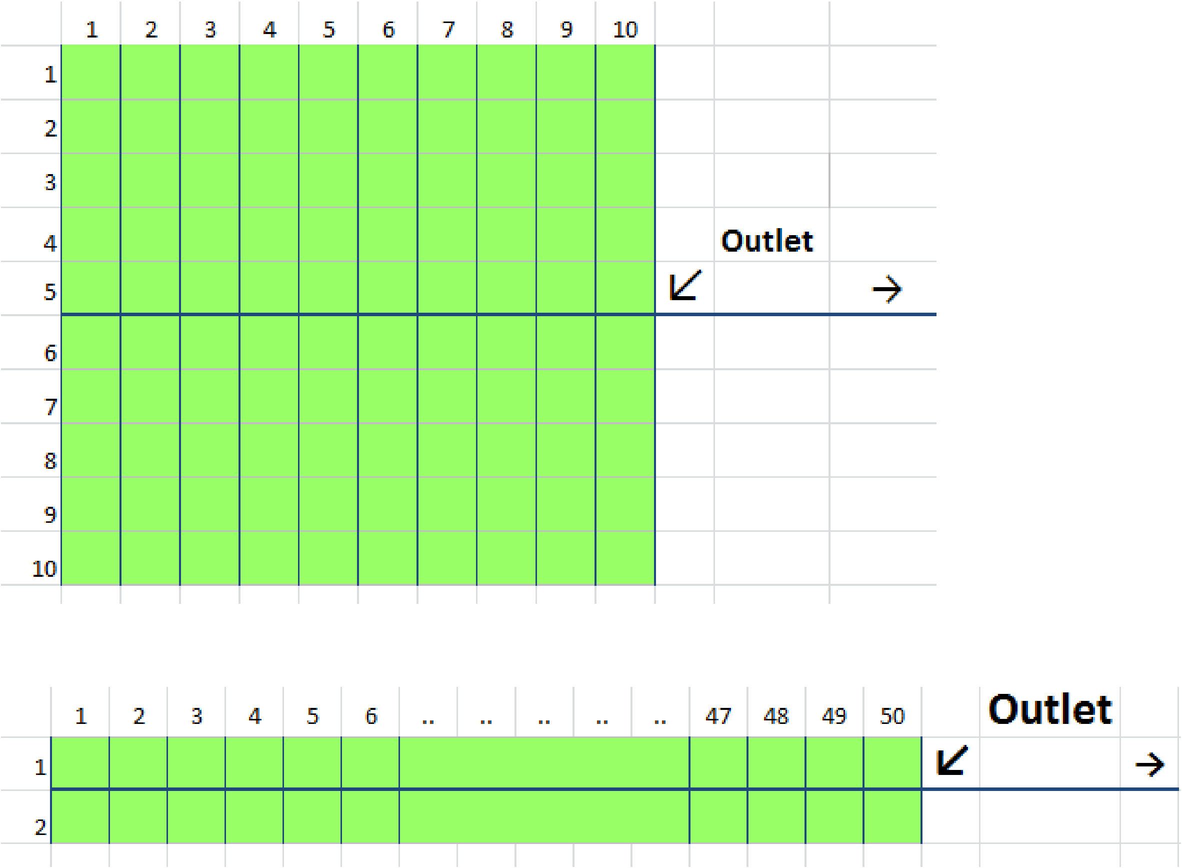

Figure 5 *Two possible extreme layouts of the 100-ha upstream catchment of the FOCUS stream. In the upper sketch 10 × 10 1-ha plots and in the lower sketch 2 × 50 1-ha plots are shown. The blue lines represent watercourses with water flowing towards the outlet. The FOCUS stream is located immediately downstream of the outlet.*

As in the two extreme layouts of the catchment the average travel distance is approximately 7.5 (square catchment) and 25 (rectangular catchment) times the length of the 100 m FOCUS stream, we assume that the residence time of a water droplet in the catchment to the upstream boundary of the FOCUS stream is approximately 7.5, respectively 25 times the residence time in the FOCUS stream. The residence time (d) is defined as stream volume (m^3) divided by the discharge in the stream ($m^3\ d^{-1}$).

Below we make a distinction between (i) the parent originating from spray drift deposition in the upstream catchment and its metabolites formed in the upstream catchment and (ii) the parent originating from runoff/drainage in the upstream catchment and its metabolites formed in the upstream catchment. We consider how the metabolite concentration in the FOCUS stream can be calculated for these two origins, looking at the parent concentration first. This results for standard FOCUS simulations in a metabolite concentration coming out of the catchment that consists of two components, spray drift and drainage/runoff each obtained with its own correction factor ($CF_{m,up,sd}$ and $CF_{m,up,rodr}$).

3.1.1 Spray drift deposition in the upstream catchment

Parent

In the upstream catchment spray drift from the 20 ha treated with the pesticide deposits on the water surface. Next, this water plus deposited pesticide mass travels to the 100 m FOCUS stream and its adjacent field. It arrives there at the moment this field is treated. This results in a concentration of the parent of 1.2 times the parent concentration caused by spray drift deposition from the adjacent field into the FOCUS stream (FOCUS (2001) assumption). So,

$$c_p^* = \left(1 + F_{up,tr}\right) c_{p\ by\ spray\ drift\ on\ stream}^* \tag{17}$$

where $c^*_{p,}$ is the total mass concentration of the parent (so including mass sorbed to suspended solids) (mg L^{-1}), $F_{up,tr}$ is the fraction of the area treated in the upstream catchment (-), i.e. 0.2, and $c^*_{p\ by\ spray\ drift\ on\ stream}$ is the total mass concentration of the parent in the stream water, entered by spray drift deposition from the adjacent field only (mg L^{-1}).

The TOXSWA model has operationalized this FOCUS assumption by multiplying the mass deposition of the adjacent 1 ha field onto the 100 m FOCUS stream with a factor of 1.2. As the travel time in the upstream catchment generally is longer than in the FOCUS stream, this procedure will not result in a conservative estimate of the metabolite formed in the water layer of upstream catchment. Therefore, in addition to this factor of 1.2 for the parent concentration in the 100 m FOCUS stream, we propose the correction procedure for the metabolite described below.

Metabolite

While the deposited parent mass travels from the upstream catchment to the FOCUS stream metabolites are formed. We propose to correct the metabolite concentration in the FOCUS stream for this phenomenon by adding the following concentration to the metabolite concentration in the FOCUS stream at the time of the spray drift deposition of the parent:

$$c_m^* = F_{up,tr} \cdot c^*_{p,by\ spray\ drift\ on\ stream} \cdot F_{p\to m} \cdot \frac{M_m}{M_p} \cdot CF_{m,up,sd} \tag{18}$$

where c^*_m is the total mass concentration of the metabolite in the stream water (mg L^{-1}), $F_{p\to m}$ is the formation fraction of the metabolite (mol mol^{-1}), M_p is the molar mass of the parent (g mol^{-1}), M_m is the molar mass of the metabolite (g mol^{-1}) and $CF_{m,up,sd}$ is the correction factor for metabolite formation in upstream catchment from parent mass entered by spray drift deposition from the 20 ha treated fields (-).

Estimation of correction factor (simple method)

For $CF_{m,up,sd}$ we propose the values tabulated in Table 3. Selecting a $CF_{m,up,sd}$ value of 0 implies that the metabolite concentration in the stream will not be corrected for metabolite formation in the upstream catchment from spray drift entries.

Table 3

Correction factor $CF_{m,up,sd}$ for metabolite formation in the upstream catchment from parent mass entered by spray drift deposition from the 20 ha treated fields, as a function of the $DegT_{50,p}$, i.e. the overall transformation half-life of the parent in water-sediment systems (d).

Intervals for $DegT50_p$ (d)	$CF_{m,up,sd}$ (-)
0-5 d	1
5-50 d	0.5
>50 d	0.1

Table 3 is based upon the following reasoning. Firstly, a $CF_{m,up,sd}$ factor of 1 implies that all parent mass has been transformed into metabolite mass, and this value is used for compounds that transform rapidly, i.e. with $DegT_{50,p}$ between 0 and 5 d. Secondly, most FOCUS streams (100 m length) have monthly residence times of approximately 0.1-0.3 d when there are no substantial runoff or drainage fluxes (Appendix F of FOCUS, 2001). This implies that the residence times in the upstream catchment are 0.75-2.25 d or 2.5-7.5 d for the two extreme catchment layouts (750 m and 2500 m length). So, if a parent has a $DegT_{50,p}$ between 5 and 50 d considerably less than 50% of the parent mass will be transformed in most cases and thus, using a 0.5 value for the $CF_{m,up,sd}$ factor in Eq.(18) to estimate c^*_m is on the conservative side. Finally, a $CF_{m,up,sd}$ factor of 0.1 is used for all compounds with $DegT_{50,p}$ greater than 50 d. So, by using the $DegT_{50,p}$ intervals and $CF_{m,up,sd}$ correction factors of Table 3 we intend to account in a conservative, but not over-conservative way, for metabolites formed from parent entered by spray drift from the 20 ha treated fields in the upstream catchment.

3.1.2 Runoff/drainage in the upstream catchment

Parent
Pesticide parent mass fluxes in runoff or drainage originating from the 20 ha treated fields in the upstream catchment enter the FOCUS stream.

Metabolite
While the parent mass travels from the upstream catchment to the FOCUS stream metabolites are formed. We propose to correct the metabolite concentration in the FOCUS stream for this phenomenon by adding the following mass flux (to be multiplied with the surface area of the 20 ha treated fields) across the upper boundary of the FOCUS stream at timings that run parallel to the parent mass fluxes.

$$J_m = J_{p,by\ runoff\ or\ drainage} \cdot F_{p\rightarrow m} \cdot \frac{M_m}{M_p} \cdot CF_{m,up,rodr} \qquad (19)$$

where J_m is the mass flux of the metabolite formed from the parent in the runoff/drainage water from the catchment (mg m^{-2} h^{-1}), $J_{p,by\ runoff\ or\ drainage}$ is the mass flux of the parent in runoff or drainage from the catchment (mg m^{-2} h^{-1}), and $CF_{m,up,rodr}$ is the correction factor for metabolites formation in the upstream catchment formed from parent mass in the runoff/drainage in the catchment (-).

Estimation method for correction factor (simple method)
For $CF_{m,up,rodr}$ we propose the values tabulated in Table 4. Selecting a $CF_{m,up,rodr}$ value of 0 implies that the metabolite concentration in the stream will not be corrected for metabolite formation in the upstream catchment from runoff or drainage entries.

Table 4
Correction factor $CF_{m,up,rodr}$ for metabolite formation in the upstream catchment from parent mass originating from runoff or drainage from the 20 ha treated fields, as a function of the $DegT_{50,p}$, i.e. the overall transformation half-life of the parent in water-sediment systems (d).

Intervals for $DegT50_p$ (d)	$CF_{m,up,rodr}$ (-)
0-1 d	1
1-10 d	0.5
>10 d	0.1

The $DegT_{50,p}$ intervals in Table 4 are narrower than those in Table 3, because during runoff and drainage events the residence time in the catchment is expected to be shorter than during spray drift events. The reason is that in case of runoff/drainage entries, the flow velocities within the upstream catchment increase sharply due to the additional drainage or runoff water from the 100-ha fields, thus the residence time in the catchment of the parent decreases compared to the residence time during spray drift entries and thus there is less time for metabolite formation. Firstly, a $CF_{m,up,rodr}$ factor of 1 implies that all parent mass has been transformed into metabolite mass, and this value is used for compounds that transform rapidly, i.e. with $DegT_{50,p}$ between 0 and 1 d. Secondly, the monthly residence times of most FOCUS streams are in the order of 0.01 d when there are substantial runoff or drainage fluxes (Appendix F of FOCUS, 2001). This implies that the residence times in the upstream catchment are 0.075 d or 0.25 d for the two extreme catchment layouts (due to the travel distances of 750 m and 2500 m in the catchment compared to the 100 m in the stream). So, if a parent has a

$DegT_{50,p}$ between 1 and 10 d considerably less than 50% of the parent mass will be transformed in most cases and thus using a 0.5 value for the $CF_{m,up,rodr}$ factor in Eq. (19) to estimate J_m is on the conservative side. Finally, a $CF_{m,up,rodr}$ factor of 0.1 is used for all compounds with $DegT_{50,p}$ greater than 10 d. So, by using the intervals and correction factor of Table 4 we intend to account in a conservative, but not over-conservative way, for metabolites formed from parent entered by runoff or drainage from the 20 ha treated fields of the upstream catchment.

As explained above, both correction factors, $CF_{m,up,sd}$ and $CF_{m,up,rodr}$, are used in standard FOCUS simulations. The reason is that in standard FOCUS simulations both spray drift and runoff/drainage occur and therefore the metabolite concentration coming out of the catchment, consists of these two components, each obtained with its own correction factor ($CF_{m,up,sd}$ and $CF_{m,up,rodr}$).

4 Improved estimation of correction factors

The procedure described in chapter 3 proposes correction factors for metabolite formation in the upstream catchment as a function of the half-lives for transformation of the parent. The $DegT_{50,p}$ intervals of Tables 3 and 4 of section 3.1 are based upon the logic that, in case of spray drift deposition there is more time for formation of metabolites in the upstream catchment, than in case of runoff/drainage entries, when the flow velocities within the upstream catchment increase sharply due to the additional drainage or runoff water from the 100-ha fields. However, the delimitation of the $DegT_{50,p}$ intervals is based upon a rough conservative estimate of the monthly residence time of the parent in the upstream catchment, considered for all scenarios together. Moreover, the exact value of the correction factors corresponds to a more or less arbitrary choice. Therefore, we here develop a more accurate procedure to quantify metabolite formation in the upstream catchment of FOCUS streams. This procedure is based upon (i) a conservative estimate of the residence time of the parent in the upstream catchment that is calculated for each scenario separately and (ii) a sound estimate of the metabolite mass formed during the estimated residence time. The result of this procedure is an improved estimate of the correction factors of the sections 3.1.1 and 3.1.2.

The procedure is described in detail below. First, a description for the formed metabolite mass as a function of time and degradation rates of the parent and of the metabolite is derived for water-only systems. Next, the time of occurrence of the maximum metabolite mass in such a system is calculated. For each scenario, this time of occurrence is compared to the residence time of the parent in the upstream catchment. If this residence time is greater than the time of occurrence of the maximum metabolite mass, the metabolite mass reaches its maximum and the maximum is calculated. If the residence time of the parent is shorter than the time of occurrence of the maximum metabolite mass, the metabolite mass produced during the residence time of the parent is calculated. Finally, mathematical descriptions for the two correction factors (section 3.1.1 and 3.1.2) are derived, one for metabolites formed from spray drift-deposited parent and one for metabolites formed from parent entered by drainage/runoff. This is done by comparing Eqns (18) and (19) to the analytical solution of the metabolite mass fraction for the water-only system. It is demonstrated that the two factors can be described by the same equation, so, the two factors merge into one single factor, $CF_{m,up}$.

The time of occurrence of maximum metabolite mass, t_{max}, as well as the correction factor $CF_{m,up}$ are a function of the degradation rates of the parent and of the metabolite, k_p and k_m. The degradation rates are a function of the water temperature and, as the FOCUS scenarios have different temperatures, this implies that the degradation rates need to be calculated for each scenario. This is done by applying the Arrhenius equation for the average scenario temperature. Thus, next to the residence time of the parent in the upstream catchment also the variables t_{max} and $CF_{m,up}$ are scenario-specific.

Finally, for each scenario the correction factor can be used in the Eqs. (18) and (19) of chapter 3, describing, respectively, the additional metabolite concentration in the 100-m FOCUS stream by spray drift entries and the metabolite mass flux by runoff/drainage entries of the parent entering the stream. These equations describe not only the size of the additional metabolite concentration or mass flux, but also their timings, because the additional metabolite concentration and mass flux are linked to the concentration and mass flux of the parent.

4.1 Formation of metabolite mass as a function of time in water-only systems

First, an analytical solution is derived for the formation of the metabolite in a stagnant water-only system, after a pulse application of the parent compound. This analytical solution describes the mass of the metabolite as a function of time and as a function of the formation fraction, the molar mass of the parent and of the metabolite and the transformation rates of the parent and of the metabolite. Next, this solution is used to calculate the time of occurrence of the maximum metabolite mass.

After a pulse application in a water-only system the parent mass can be described by:

$$m_p(t) = m_{p,0}\, e^{-k_p t} \tag{20}$$

The compound is assumed to degrade, but no volatilization or sorption (to e.g. suspended solids) occurs. The metabolite mass in this system can be described by:

$$\frac{dm_m(t)}{dt} = k_p F_{p\rightarrow m} \frac{M_m}{M_p} m_p(t) - k_m m_m(t) \tag{21}$$

Substituting Eq. (20) into Eq. (21) results in:

$$\frac{dm_m(t)}{dt} = k_p F_{p\rightarrow m} \frac{M_m}{M_p} m_{p,0} e^{-k_p t} - k_m m_m(t) \tag{22}$$

where

m_p = mass of parent (g)
$m_{p,0}$ = mass of parent at time of entry, $t = 0$ (g)
k_p = transformation rate coefficient of parent (d^{-1})
t = time since entry of parent (d)
m_m = mass of metabolite (g)
k_m = transformation rate coefficient of metabolite (d^{-1})
$F_{p->m}$ = formation fraction of metabolite on molar basis (mol mol^{-1})
M_p = molar mass of parent (g mol^{-1})
M_m = molar mass of metabolite (g mol^{-1})

The analytical solution of Eq. (22) for the metabolite mass as a function of time is (EFSA, 2012):

$$m_m(t) = \frac{k_p . F_{p\rightarrow m} \cdot \frac{M_m}{M_p} m_{p,0}}{k_p - k_m} \cdot \left[e^{-k_m t} - e^{-k_p t}\right] \qquad \text{(23)(EFSA, 2012, eq 11)}$$

Eq. (23) can be rewritten to give the metabolite mass as a fraction of the initial parent mass, f_m, as a function of time:

$$\frac{m_m(t)}{m_{p,0}} = f_m = \frac{k_p . F_{p\rightarrow m} \cdot \frac{M_m}{M_p}}{k_p - k_m} \cdot \left[e^{-k_m t} - e^{-k_p t}\right] \tag{24}$$

where

f_m = metabolite mass expressed as a fraction of the parent mass at time $t = 0$ (g g^{-1})

Figure 6 shows an example of the mass fraction of metabolite f_m as a function of time. The maximum metabolite mass can be calculated with Eq. (24) if the time when the maximum of the metabolite mass occurs, t_{max}, is known. We can calculate t_{max} by taking the derivative of Eq.(24) with respect to time, setting it to zero and next, solve the resulting equation (based on the mathematical rule that maximums and minimums of functions occur when the derivative of the function is zero).

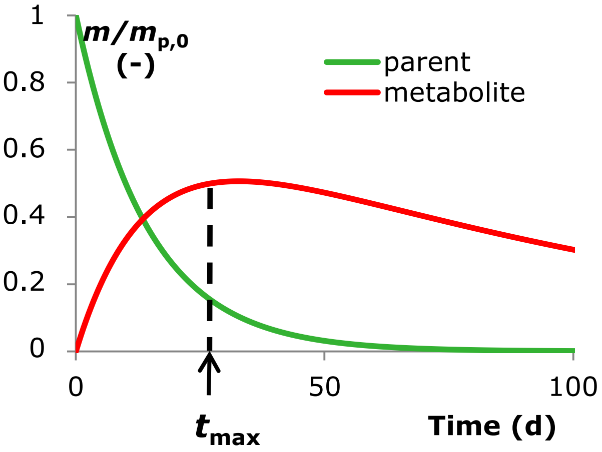

Figure 6 *Mass fraction of parent and metabolite as a function of time in a stagnant water-only system with only transformation.*

The derivative of Eq.(24) with respect to time is:

$$\frac{df_m}{dt} = \frac{k_p\, F_{p\rightarrow m}\, \frac{M_m}{M_p}}{k_p - k_m} \left[k_p\, e^{-k_p t} - \; k_m\, e^{-k_m t}\right] \tag{25}$$

The derivative (Eq. (25) is zero when the first and/or the second term is zero. For $k_p \neq 0$ (i.e. the parent is transformed), and $k_p \neq k_m$, the first term cannot become zero. Hence the second term has to be zero:

$$k_p\, e^{-k_p t} - \; k_m\, e^{-k_m t} = 0 \tag{26}$$

This equation can be reorganized into:

$$e^{-k_p t} - \frac{k_m}{k_p}\, e^{-k_m t} = 0 \tag{27}$$

Taking the natural logarithm of the terms gives:

$$\ln\left[\, e^{-k_p t}\right] - \ln\left[\frac{k_m}{k_p}\right] - \ln\left[e^{-k_m t}\right] = 0 \tag{28}$$

and this results in the solution for the time of the maximum, t_{max}:

$$t = t_{max} = \frac{\ln\left[\frac{k_m}{k_p}\right]}{k_m - k_p} \tag{29}$$

Note that t_{max} does not depend on the molar masses of the substances (M_p, M_m) nor the formation fraction of the metabolite ($F_{p\text{->}m}$).

Half-lifes, $DegT_{50}$ values are defined as:

$$DegT_{50,p} = \frac{ln2}{k_p} \tag{30a}$$

and

$$DegT_{50,m} = \frac{ln2}{k_m} \tag{30b}$$

where

$DegT_{50,\mathrm{p}}$ = transformation half-life of the parent (d) and

$DegT_{50,\mathrm{m}}$ = transformation half-life of the metabolite (d).

The results obtained above have been used to show the maximum metabolite mass fraction as a function of combinations of $DegT50_{\mathrm{p}}$ and $DegT50_{\mathrm{m}}$ for transformation in water. Figure 7a shows the time needed to obtain the maximum metabolite mass, t_{max}, calculated with Eq.(29). Figure 7b shows the maximum mass fraction of metabolite $f_m = m_{\mathrm{m}}/m_{\mathrm{p,0}}$ that will be reached, if the residence time is sufficiently long, i.e. t_{max} or longer. This maximum metabolite mass fraction has been calculated with Eq. (24) using the t_{max} value and assuming $F_{\mathrm{p->m}} = 1$ and $M_{\mathrm{m}}/M_{\mathrm{p}} = 0.7$.

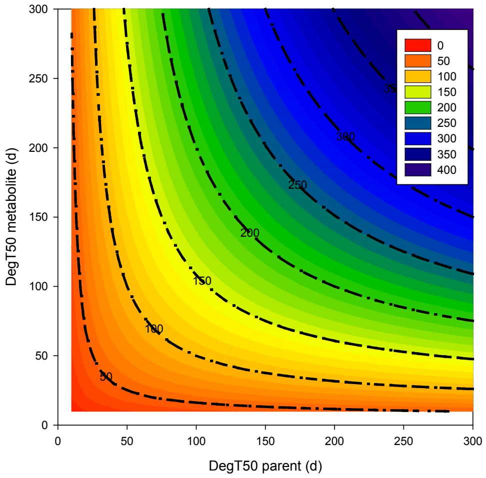

Figure 7a

Time of maximum metabolite mass, t_{max} (d), as a function of $DegT_{50,p}$ and $DegT_{50,m}$ for transformation in water.

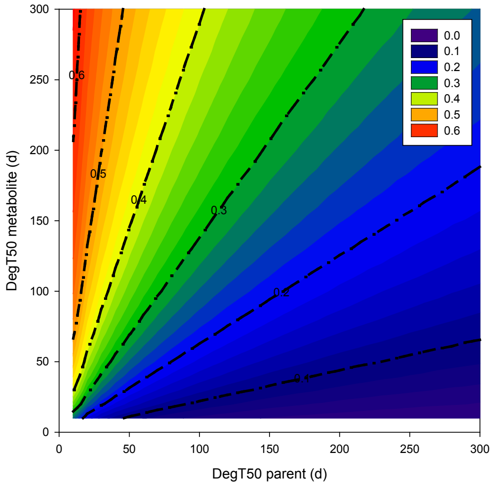

Figure 7b

Maximum mass fraction of metabolite, $f_m = m_m(t_{max})/m_{p,0}$ (-), as a function of $DegT_{50,p}$ and $DegT_{50,m}$ for transformation in water.

Figure 7a shows that the maximum metabolite mass occurs between 0 and approximately 430 days for combinations of $DegT50_{\mathrm{p}}$ and $DegT50_{\mathrm{m}}$ up to 300 d. E.g. the contour line indicated by '50' illustrates that times of maximum metabolite occurrence, t_{max}, shorter than 50 d happen for *DegT50* values (both parent and metabolite) shorter than approximately 30 d. Shorter times of maximum occurrence only happen for parents and metabolites with *DegT50* values clearly below 30 d. During runoff entries the residence time of the parent in the FOCUS streams are often short, often around 0.01 d. This implies that also in the upstream catchment the residence time of the parent is expected to be shorter than 1 d (based upon travel distances of 7.5 to 25 times more than the 100 m in the stream, see section 3.1). So, for most compounds the t_{max} will not be reached by the parent in the upstream catchment, so the maximum metabolite fraction will not be formed in the upstream catchment. E.g. for parents with $DegT_{50,p}$ above 40 d the t_{max} is approximately 30 d or higher, even when the $DegT_{50,m}$ of the metabolite is close to 0 d. This means that the t_{max} will never be reached by parents with $DegT_{50,p}$ above 40 d.

Figure 7b shows the maximum metabolite mass fraction in case the residence time of the parent is t_{max} or more. The maximum mass fraction is between 0 and 0.6 for combinations of $DegT_{50,\mathrm{p}}$ and $DegT_{50,\mathrm{m}}$ up to 300 d. E.g. the contour line indicated by '0.1' illustrates that metabolite mass fractions less than 0.1 occur for $DegT_{50,\mathrm{m}}$ of 50 d or less, combined with $DegT_{50,p}$ of approximately 250 d or less. This 0.1 maximum metabolite mass fraction is only reached if the residence time of the parent in the upstream catchment is equal or longer than the associated t_{max}.

4.2 Conservative estimates of the residence time of the parent in the upstream catchment

It is important to know whether the residence time of the parent in the catchment, τ_p, is shorter or longer than the t_{max}, the time of occurrence of the maximum metabolite mass fraction $f_m = m_m/m_{p,0}$: if the residence time of the parent in the catchment is longer, the maximum metabolite mass fraction will be reached and this value can be calculated by filling in t_{max} for t in Eq.(24). If the residence time of the parent is shorter than t_{max} a smaller fraction than the maximum metabolite mass fraction will be formed, this smaller fraction can be calculated by filling in the τ_p value for t in Eq. (24). As this residence time in the upstream catchment, τ_p, varies as a function of the incoming drainage and runoff water fluxes, the metabolite fraction would vary as well. Thus, the correction factors $CF_{m,up,sd}$ and $CF_{m,up,rodr}$ would need to vary as a function of time as well, during the simulations.

To keep the correction procedure as simple as possible we opted for correction factors, that are constant with time. For each scenario another constant correction factor is used. By selecting the highest value of all possible residence times, τ_p and using this highest value in Eq. (24) we obtain a conservative estimate of the metabolite mass fraction that could be formed in the catchment. Below we determined the longest residence times in the upstream catchment for each scenario, i.e. a conservative estimate of the residence time.

The residence time of the parent in the catchment heavily depends on whether runoff or drainage water from the fields enters the catchment watercourses. If runoff or drainage occurs discharges may increase considerably and residence times in the catchment may decrease considerably. Therefore we determined the conservative estimates of the residence time for days with and days without drainage or runoff entries separately, for each of the 8 stream scenarios (Figs 8 and 9):

First, we calculate the daily residence times, τ_p, in the 100-m FOCUS streams. To do so, the volume of the stream is divided by the daily average discharge in the 100-m stream. This daily average discharge is calculated from the discharge calculated by TOXSWA in the middle of the stream:

$$\tau_p = \frac{V}{\sum_{hn=1}^{hn=24} Q_{x=50m}} \qquad (31)$$

with

τ_p = residence time in 100-m FOCUS stream (d)

V = volume of 100-m FOCUS stream (m^3)

$Q_{\mathrm{x=50m}}$ = discharge at 50 m in the stream ($\mathrm{m}^3\ \mathrm{h}^{-1}$), (13th column in *.hyd file of TOXSWA)

hn = hour number during the considered day (-)

The volume of the rectangular 100-m FOCUS streams is calculated with

$$V = h \cdot b \cdot L \qquad (32)$$

with

h = average water depth during day (m), calculated from hourly water depths at end of hour (in *.hyd output file of TOXSWA)

b = bottom width of the stream (m) [1 m]

L = length of the stream (m), [100 m]

For each stream scenario the daily residence times are calculated. These are plotted to construct two cumulative frequency distributions of residence times in the 100-m FOCUS streams:

A: days that drainage or runoff occurs, conservative estimates of the residence time are obtained that characterise water flow in the catchment during drainage/runoff entries,

B: days that no drainage or runoff occurs, conservative estimates of the residence time are obtained that characterise water flow in the catchment when spray drift entries occur and no drainage/runoff.

The cumulative frequency distributions of residence times in the streams are shown in Figure 8 for the drainage scenarios D1, D2, D4 and D5, and in Figure 9 for the runoff scenarios R1, R2, R3 and R4.

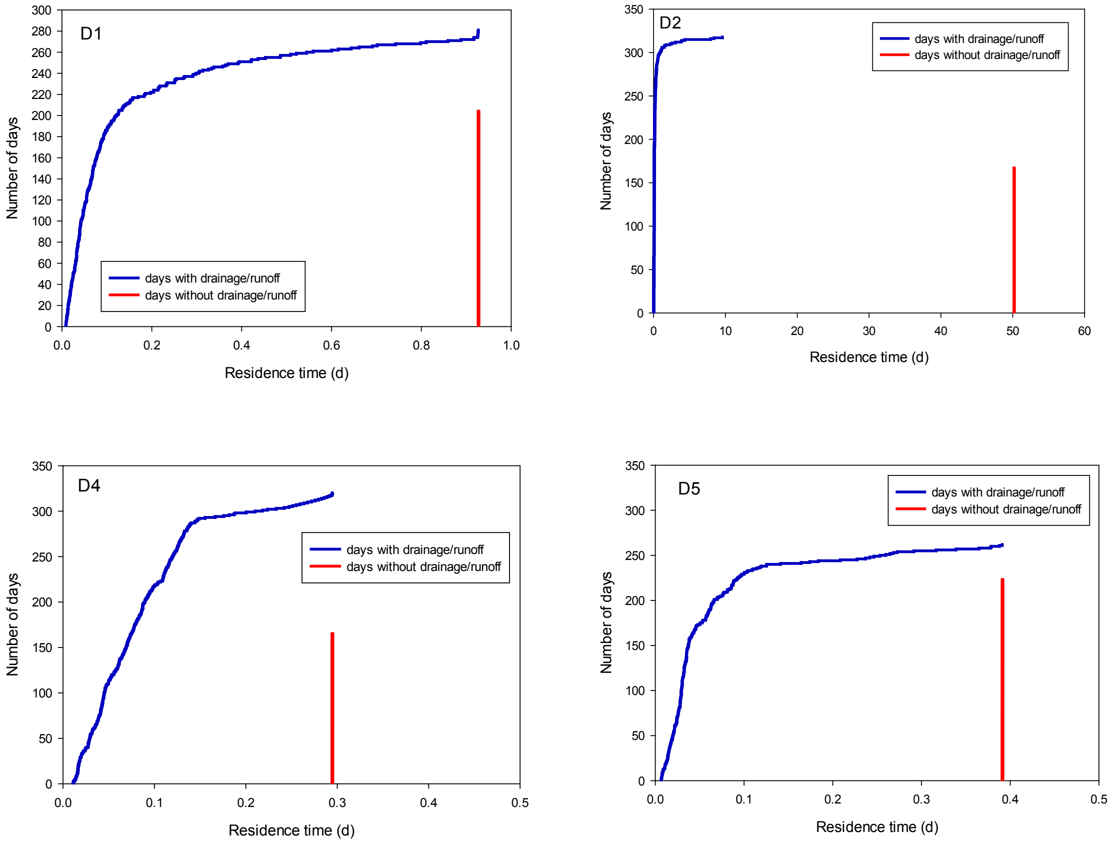

Figure 8 *Residence times of streams in the FOCUS drainage scenarios D1, D2, D4 and D5. Note that the scale of the horizontal axis differs considerably (D1: up to 1 day and D2 up to 60 days).*

The D1 scenario has 281 days with drainage and 204 days without drainage (16-months simulations, i.e. 485 d). The maximum daily residence time is 0.93 days for both cases; the smaller the drainage fluxes, the closer the situation with drainage approximates the situation without drainage, i.e. the residence time of 0.93 days. The residence times for days without drainage are the same during the whole simulation period, because at those days the residence time is solely determined by the base flow. The D2 scenario has 318 days with drainage and 167 days without drainage. The maximum daily residence time is 9.6 days for days with drainage, and 50.2 days for days without drainage. The D4 scenario has 320 days with drainage and 165 days without drainage. The maximum daily residence time is 0.29 days for both situations. The D5 scenario has 262 days with drainage and 223 days without drainage. The maximum daily residence time is 0.39 days for both situations.

The R1 scenario has 22 days with runoff and 343 days without runoff (12-months simulations). The maximum daily residence time is 0.21 days for both situations; the smaller the runoff fluxes, the closer the situation with runoff approximates the situation without runoff, i.e. the residence time of 0.21 days. Contrary to the drainage scenarios, the daily residence times for the days without runoff flux are not the same during the whole simulation period, because, apart from base flow, also a fraction of the downward infiltrating flux at 1 m is discharged into the stream. PRZM uses monthly averaged values for this flux, which explains the stepwise pattern of the curve. The graph also shows that this flux may be more important than the runoff flux: the daily residence time without runoff is then shorter than daily residence times with runoff. The R2 scenario has 72 days with runoff and 293 days without runoff. The maximum daily residence time is 0.10 days for days with runoff and 0.11 for days without runoff. The R3 scenario has 30 days with runoff and 335 days without runoff. The maximum daily residence time is 0.31 days for days with runoff and 0.38 for days without runoff. The R4 scenario has 21 days with runoff and 345 days without runoff. The maximum daily residence time is 0.21 days for both situations.

The longest daily residence time of all D and the R streams occurs in the D2 scenario and is 50 days. This long daily residence time can be explained by its extreme low value for the base flow, 0.0059 m^3 ha^{-1} d^{-1}, thus resulting in a long daily residence time.

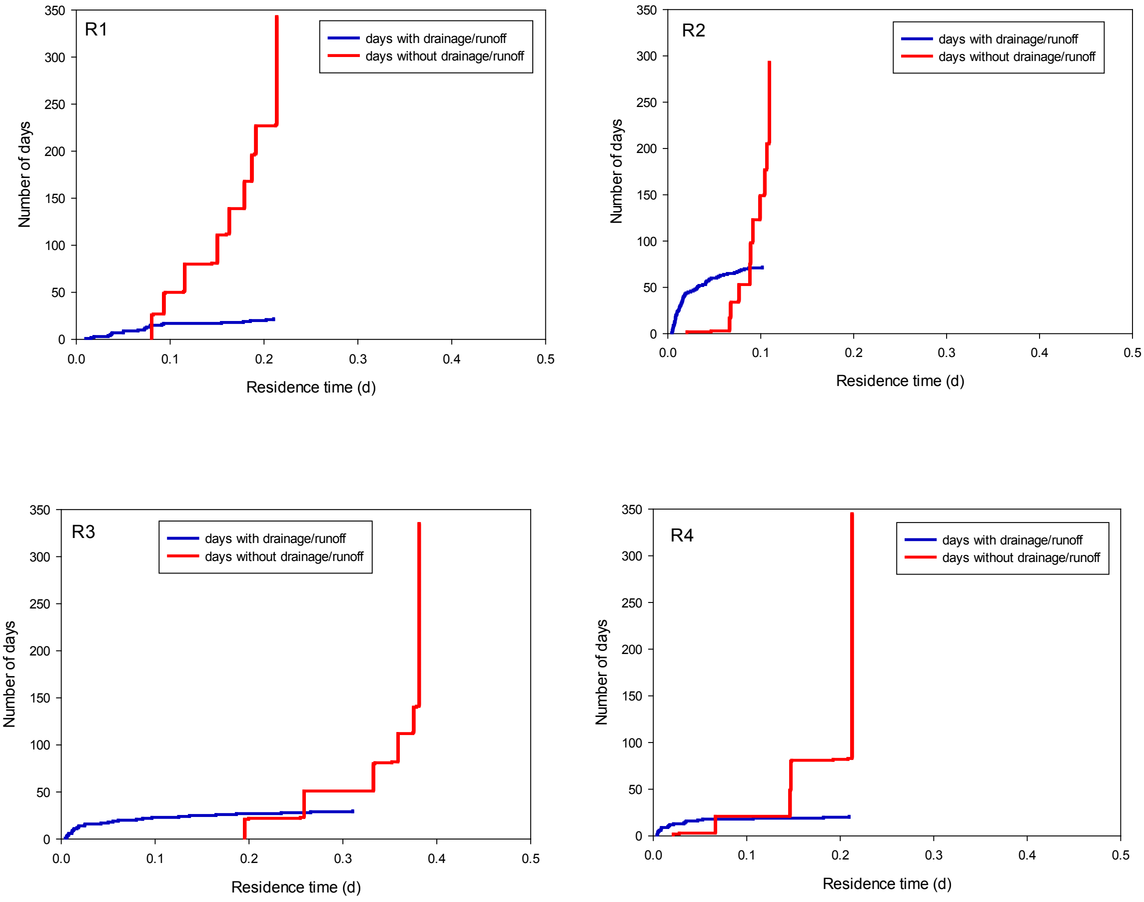

Figure 9 *Residence times of streams of the FOCUS runoff scenarios R1, R2, R3 and R4 with applications in autumn.*

To calculate the residence time of the parent in the upstream catchment two possible, extreme lay outs of the upstream catchment were presented in section 3.1. The average travel distances in those extreme catchments were approximately 7.5 and 25 times the length of the 100-m FOCUS streams and the assumption was that the residence time of a droplet in the upstream catchment would therefore be approximately 7.5, respectively 25 times the residence time in the FOCUS stream. Note that the value of 7.5 is the average of travel distances ranging from 1 to 15 times the 100 m of the

FOCUS stream and that the value of 25 is the average of travel distances ranging from 1 to 50 times the 100 m of the FOCUS stream.

Considering the fact that the catchment layout is a scenario-based parameter (that may incorporate some degree of conservativeness) we selected the value of 25 to define the conservative estimate of the residence time of the catchment:

$$t_{cons} = 25\,\tau_p \qquad (33)$$

with the conservative estimate of the residence time t_{cons} (d) representing the residence time of the parent in the upstream catchment of the FOCUS stream scenarios for all in real life possible layouts of the upstream catchment in a conservative way.

The longest daily residence time is found for D2, 50 days. The next longest daily resident time is found for the D1 scenario, 0.93 days. In all other scenarios the daily residence time is below 0.93 days.

The conservative estimates of the residence times in Table 5 are calculated with Eq. (33), using the maximal residence time for days without drainage or runoff. For D2 the calculation of the boundary value of the residence time is 1255 days. However this is not realistic, because such a long period between drainage events does not occur, so this long residence time will not materialise, i.e. it will not occur in the simulation. As can be seen from the drainage output file (MACRO output file for winter cereals (crop not irrigated)) the longest period without drainage in the D2 scenario is 90 days, from 27 May 1986 until 24 August 1986. Therefore the calculated value for the boundary value of the residence time of 1253 days has been replaced by 90 days.

Table 5

Maximal residence times for the FOCUS stream scenarios from all daily residence times calculated with Eq. (31), and conservative estimate of the residence time calculated with Eq. (33).

Scenario	**Maximal residence time days without drainage or runoff (d)**	**Maximal residence time days with drainage or runoff (d)**	**Conservative estimate of residence time, t_{cons} (d)**
D1	0.93	0.93	23
D2	9.6	50.2	90*
D4	0.29	0.29	7
D5	0.39	0.39	10
R1	0.21	0.21	5
R2	0.10	0.11	3
R3	0.31	0.38	10
R4	0.21	0.21	5

*see paragraph above Table 5 for how this value has been determined.

The cumulative frequency distributions of the runoff streams are based on the Autumn scenarios. Table 4.4.3-11 (FOCUS, 2001; p.105) shows that the range of minimum to maximum daily residence times per month of the Spring and of the Summer scenarios are equivalent to those of the Autumn scenarios. Hence, the daily residence times shown in Figure 9 for the Autumn runoff scenarios are also representative for Spring and Summer runoff scenarios.

Table 5 lists the conservative estimates of the residence times of the parent in the upstream catchment, t_{cons}, for all scenarios. They range from 3 days in the R2 scenario to 90 days in the D2 scenario. These conservative estimates of the residence times need to be used to calculate the corrections factors for metabolite formation in the upstream catchment of the FOCUS streams.

4.3 Parent and degradation rates at scenario temperature

As explained above, the correction factors are defined by comparing the time of occurrence of the maximum metabolite mass that can be formed from the parent (in water-only systems) to the conservative estimates of the residence time in the scenario. This implies that the correction factors need to be defined for each scenario. The scenarios cover Europe from North to South, so the water temperatures in the scenarios are different. Therefore, the transformation rate of the parent (and also of the metabolite) in the scenario water is different. Thus, there is a need to calculate scenario-specific transformation rates, based upon the average temperature in the water layer of the scenario. First, we determine the average temperature of the water layer in each scenario. Next, we describe how the transformation rates of the parent and the metabolite can be corrected to represent the transformation rate in the specific scenario.

Monthly average temperatures were determined as input for the calculation of exposure concentrations in water and in sediment with TOXSWA (FOCUS, 2001). To obtain an average value representing the scenario during the entire simulation period an average of 12 months is calculated. For the drainage scenarios the last 12 months of the 16 months scenario period have been used to calculate the scenario average. In this way the 12 most relevant months to evaluate a pesticide applied from Jan-Dec are considered and the months January to April are not over-represented. For the runoff scenarios, the 12 months of the scenario period have been used. As each of the runoff scenarios has an autumn, spring and summer version, being based on different years, all three average values are calculated, and then the average of the three values is determined. The average temperatures of the scenarios are shown in Table 6. The temperatures are also given in degrees Kelvin, because these values are needed for the correction of transformation rate coefficients for the temperature in Eq. (34).

The average temperature varies from 8.0 °C in D1 (Lanna in Sweden) to 14.9 °C in R2 (Porto in Portugal).

Table 6
Average temperatures of the water layer in the FOCUS stream scenarios are based on the monthly average temperatures used in the FOCUS surface water scenarios.

Scenario	Average temperature of 12 months (°C)	Average temperature of Autumn, Spring and Summer scenarios (°C)	Average temperature, T (K)
D1	8.0		281.1
D2	9.2		282.3
D4	8.2		281.4
D5	10.7		283.8
R1 Autumn	10.1		
R1 Spring	10.0	10.0	283.1
R1 Summer	9.7		
R2 Autumn	14.4		
R2 Spring	14.4	14.9	288.0
R2 Summer	15.9		
R3 Autumn	13.0		
R3 Spring	13.4	13.6	286.7
R3 Summer	14.3		
R4 Autumn	13.8		
R4 Spring	13.6	13.7	286.8
R4 Summer	13.7		

The transformation rates of the parent and the metabolite at their reference temperatures can be corrected to represent the transformation rates at the scenario temperatures by applying the Arrhenius equation:

$$k(T) = k(T_{ref})\, exp\left[\frac{E_A}{R\, T_{ref} T}(T - T_{ref})\right] \tag{34}$$

where:

T = average temperature of the water layer in the scenario (K)

T_{ref} = reference temperature, e.g. temperature at which the transformation rate has been measured (K)

k = transformation rate coefficient of the parent or of the metabolite in the water layer (d^{-1})

E_A = molar Arrhenius activation energy (= 65400 J mol^{-1} in FOCUS)

R = universal gas constant (≈ 8.3144 J mol^{-1} K^{-1})

So, these corrected transformation values k_p and k_m need to be used to calculate times of occurrence of maximum metabolite mass, t_{max}, by Eq. (29) of section 4.1, as well as to calculate the correction factors for metabolite formation in the upstream catchment for each scenario.

4.4 Correction factors for metabolite formation in the upstream catchment

Eq. (18) of section 3.1.1 defines c^*_m, the additional metabolite mass concentration in the stream (originating from spray drift deposited parent mass in the upstream catchment) as a function of $F_{up,tr}$, the fraction of the area treated in the upstream catchment (-) and $c^*_{p\ by\ spray\ drift\ on\ stream}$, the parent mass concentration in the stream by spray drift deposition from the adjacent field:

$$c^*_m = F_{up,tr} \cdot c^*_{p,by\ spray\ drift\ on\ stream} \cdot F_{p\rightarrow m} \cdot \frac{M_m}{M_p} \cdot CF_{m,up,sd} \tag{18}$$

while Eq. (19) of section 3.1.2 defines J_m, the metabolite mass flux entering the stream as a function of $J_{p,\ by\ runoff\ or\ drainage}$, the parent mass flux out of the catchment:

$$J_m = J_{p,by\ runoff\ or\ drainage} \cdot F_{p\rightarrow m} \cdot \frac{M_m}{M_p} \cdot CF_{m,up,rodr} \tag{19}$$

Eq. (24) of section 4.1 defines the metabolite mass fraction, $f_m = m_m(t)/m_{p,0}$, as a function of time, found with the aid of an analytical solution for the metabolite mass in a water-only system with only transformation:

$$\frac{m_m(t)}{m_{p,0}} = f_m = \frac{k_p \cdot F_{p\rightarrow m} \cdot \frac{M_m}{M_p}}{k_p - k_m} \cdot \left[e^{-k_m t} - e^{-k_p t}\right] \tag{24}$$

When we rewrite Eq. (18) in the form of 'c^*_m/c^*_p =' and Eq. (19) (in the form of 'J_m/J_p =' equivalent to Eq. (24), we see that the corrections factors $CF_{m,up,sd}$ and $CF_{m,up,rodr}$ are equal to:

$$CF_{m,up,sd} = \frac{k_p}{k_p - k_m} \cdot \left[e^{-k_m t} - e^{-k_p t}\right] \tag{35}$$

and

$$CF_{m,up,rodr} = \frac{k_p}{k_p - k_m} \cdot \left[e^{-k_m t} - e^{-k_p t}\right] \tag{36}$$

So, the equations describing the two correction factors as a function of time available for metabolite formation, have merged into one single equation, and thus the two factors can be identified by a single variable, $CF_{m,up}$, and so: $CF_{m,up,sd} = CF_{m,up,rodr} = CF_{m,up}$.

So, we can now calculate the correction factors $CF_{m,up}$ according to the improved procedure for each scenario. Table 7 gives an example for scenario D1. It presents the correction factors for metabolite formation in the upstream catchment calculated via the procedure proposed in the sections 3.1.1 and 3.1.2 and those calculated via the improved procedure, described above.

Table 7

Correction factors $CF_{m,up}$ for metabolite formation in the upstream catchment calculated via the procedure of sections 3.1.1. and 3.1.2 and via the improved procedure, for scenario D1, where the water temperature is 8°C and the conservative estimate of the residence time, t_{cons}, is 23 days.*

DegT50,p at 20°C (d)	**DegT50,m at 20°C (d)**	**DegT50,p at 8°C (d)**	**DegT50,m at 8°C (d)**	**t_{max} (d)**	**$CF_{m,up,sd}$ simple (-)**	**$CF_{m,up,rodr}$ simple (-)**	**$CF_{m,up}$ $t_{cons} > t_{max}$ (t_{max} reached) (-)**	**$CF_{m,up}$ $t_{cons} < t_{max}$ (t_{max} not reached) (-)**
0.1	0.1	0.31	0.31	0.5	1	1	0.37	
0.1	1	0.31	3.1	1.2	1	1	0.77	
0.1	5	0.31	15.7	1.8	1	1	0.92	
0.1	10	0.31	31.4	2.1	1	1	0.95	
0.1	50	0.31	157.2	2.8	1	1	0.99	
0.1	100	0.31	314.3	3.1	1	1	0.99	
1	0.1	3.1	0.31	1.2	1	1	0.08	
1	1	3.1	3.1	4.5	1	1	0.37	
1	5	3.1	15.7	9.1	1	1	0.67	
1	10	3.1	31.4	11.6	1	1	0.77	
1	50	3.1	157.2	18.1	1	1	0.92	
1	100	3.1	314.3	21.1	1	1	0.95	
5	0.1	15.7	0.31	1.8	1	0.5	0.02	
5	1	15.7	3.1	9.1	1	0.5	0.13	
5	5	15.7	15.7	22.7	1	0.5	0.37	
5	10	15.7	31.4	31.4	1	0.5		0.48
5	50	15.7	157.2	58.0	1	0.5		0.60
5	100	15.7	314.3	71.5	1	0.5		0.62
10	0.1	31.4	0.31	2.1	0.5	0.5	0.01	
10	1	31.4	3.1	11.6	0.5	0.5	0.08	
10	5	31.4	15.7	31.4	0.5	0.5		0.24
10	10	31.4	31.4	45.3	0.5	0.5		0.31
10	50	31.4	157.2	91.2	0.5	0.5		0.38
10	100	31.4	314.3	116.0	0.5	0.5		0.39
50	0.1	157.2	0.31	2.8	0.5	0.1	0.002	
50	1	157.2	3.1	18.1	0.5	0.1	0.02	
50	5	157.2	15.7	58.0	0.5	0.1	0.00	0.06
50	10	157.2	31.4	91.2	0.5	0.1	0.00	0.08
50	50	157.2	157.2	226.7	0.5	0.1	0.00	0.09
50	100	157.2	314.3	314.3	0.5	0.1	0.00	0.09
100	0.1	314.3	0.31	3.1	0.1	0.1	0.001	
100	1	314.3	3.1	21.1	0.1	0.1	0.01	
100	5	314.3	15.7	71.5	0.1	0.1		0.03
100	10	314.3	31.4	116.0	0.1	0.1		0.04
100	50	314.3	157.2	314.3	0.1	0.1		0.05
100	100	314.3	314.4	453.5	0.1	0.1		0.05

*Eq. (24) cannot be used when $DegT50_p = DegT50_m$. For these cases the $DegT50_m$ is slightly changed by adding 0.001 d to the $DegT50_m$ value.

Table 7 shows that for most $DegT_{50}$ combinations the correction factors calculated by the improved procedure are lower than the simple correction factors of sections 3.1.1. and 3.1.2 in the D1 scenario. Only two correction factors in the D1 scenario are higher (marked by values in grey-shaded areas).

Annex 2 gives a recipe describing step by step how the correction factors can be calculated for a specific set of scenario and half-lives of parent and metabolite according to the improved procedure of this chapter.

5 Example simulations using the two correction factor estimation methods for metabolite formation in the upstream catchment

Two example simulations were done to demonstrate the difference between the two estimation methods for the correction factors. In both simulations we used the compounds 6_sw and its metabolite 6m_sw as described in FOCUS (2001). However, in these examples metabolite 6m_sw is not the soil metabolite, as it is in FOCUS (2001), but it is formed in the water layer from the parent compound 6_sw. We also used other formation fractions: in our two example simulations the fraction of 6m_sw formed from 6_sw equals 1 on a molar basis (used for the PRZM model) and 0.77 on a mass basis (used for the MACRO model). For the remaining properties FOCUS (2001) applies, so the main properties for 6_sw and 6m_sw are: (i) transformation half-lives are 24 and 33 d in water at 20◦ C, (ii) coefficients describing linear sorption to soils, suspended solids and sediment (based on the organic carbon content) are 66 and 580 L kg^{-1} and (iii) molar masses are 255 and 197 g mol^{-1}. Compound 6_sw was applied at a rate of 1000 g ha^{-1} in winter cereals. Calculations are performed for the R1 stream and the D2 stream scenarios.

In these two example simulations we demonstrate the difference between the correction factors estimated with the aid of the two simple tables of chapter 3 and those estimated by the improved procedure of chapter 4. To be able to do so, we focus on the effect of the correction factor on only spray deposited mass (example with the R1 stream scenario) or on only drained mass (example with the D2 scenario) from the treated fields in the upstream catchment. Therefore we performed non-standard FOCUS runs. In the R1 stream run, we disabled the runoff (and erosion) mass entry route: no pesticide mass enters the water of the upstream catchment or the FOCUS stream by runoff (and erosion). So, mass enters only by spray drift deposition. In the D2 stream run we disabled the spray drift entry route: no pesticide mass enters the water of the upstream catchment or the FOCUS stream by spray drift. So, mass enters only by drainage in this second example run.

R1 stream with metabolite formed from parent entered by spray drift

As described above, this run for the R1 stream scenario is not a standard FOCUS run, because we disabled mass entrance by runoff (and erosion). A mass of 1.716 g m^{-2} was deposited by spray drift on the water surface area and, out of this mass, metabolite 6m_sw was formed in the water layer of the stream. Next to metabolite formation in the FOCUS stream itself, metabolites are formed in the water in the upstream catchment. First, we selected a value of $CF_{m,up,sd}$ of Table 3 of section 3.1.1 to account for this metabolite formation; as the $DT_{50,p}$ equals 24 d we select the recommended value of 0.5 for $CF_{m,up,sd}$. This value was applied in Eq. (18) of section 3.1.1 to calculate the contribution of metabolites formed in the upstream catchment to the metabolite concentration in the stream. Figure 10 presents the concentrations of 6_sw and 6m_sw in the target segment of the water layer, i.e. the last segment in the FOCUS stream from 95 to 100 m.

The total concentration of the metabolite 6m_sw is shown in Figure 10 by the blue line; in principle it is composed of two elements: (i) the additional metabolite mass originating from the catchment (calculated by $CF_{m,up,sd}=0.5$ in Eq. (18)) and (ii) the metabolite mass formed in the stream itself from the parent mass deposited by spray drift of the adjacent field. The second element is very small in this case as the residence time in stream is too short for significant formation given the $DT_{50,p}$ of 24 d (shorter than 0.21 d, see Table 5). Thus, the main contribution to the metabolite formation in the stream is by the additional contribution from the catchment. This implies that the value of the correction factor determines the metabolite concentration in the R1 stream to a great extent, and thus, we expect that the difference between the two methods of estimating the correction factors described in respectively chapter 3 and chapter 4 will be visible in Figure 10.

Next, we calculated the improved value for the correction factor as described in chapter 4 (and Annex 2). The time of the maximum fraction, t_{max}, is 104 days. This time is longer than the conservative estimate of the travel time in the catchment of the R1 scenario, t_{cons} of 5 d. Hence the correction factor is calculated using t_{cons} and its value is 0.127. This value is lower than the former value of the correction factor $CF_{m,up,sd}$ and thus it results in concentrations of metabolite 6m_sw that are lower than those calculated with $CF_{m,up,sd}$. Thus, as expected, the difference between the two methods estimating the correction factors, is indeed clearly visible in Figure 10.

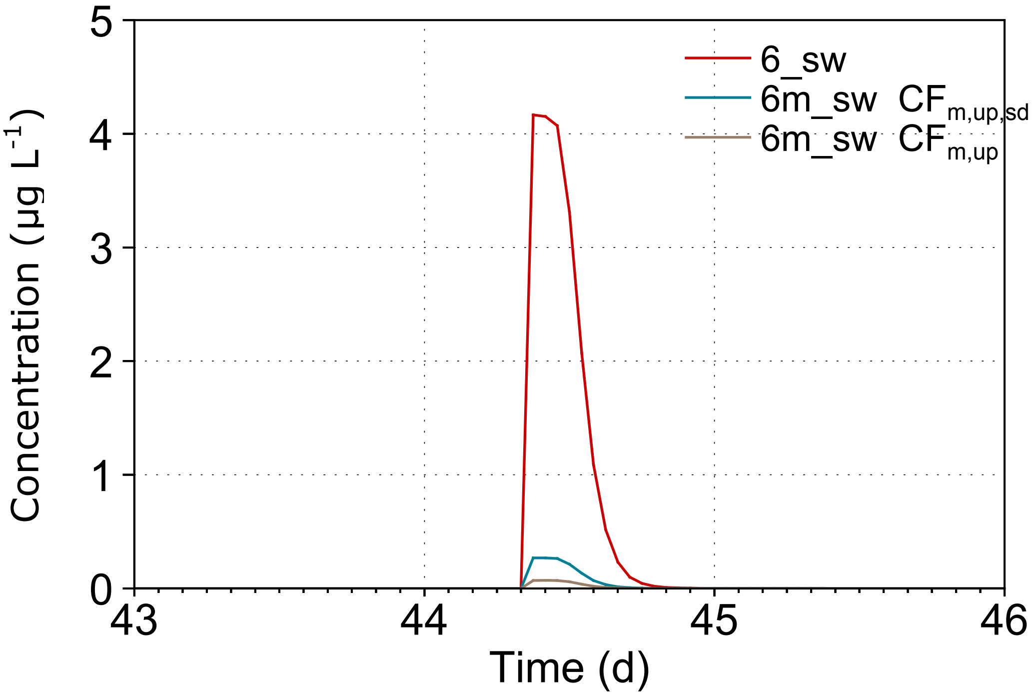

Figure 10 *Concentration of parent 6_sw and metabolite 6m_sw in the 95-100 m segment of a non-standard FOCUS R1 stream run after one application of 1000 g m^{-2} in winter cereals. The metabolite concentrations shown include the additional concentrations calculated by Eq. (18) using (i) a $CF_{m,up,sd}$ factor of 0.5 on the basis of Table 3, and (ii) a $CF_{m,up}$ factor of 0.127 calculated by using the method of chapter 4 (and Annex 2), to account for metabolite formation out of spray-deposited mass in the upstream catchment.*

D2 stream with metabolite formed from parent entered by runoff or drainage

A second example run was done for the D2 stream scenario. The parent compound 6_sw is applied on day 11. As the spray drift entries are disabled in this example run no mass was deposited on the water surface. After some time drainage starts and parent mass is drained into the water layer in the upstream catchment as well as in the water layer of the stream. In the water metabolite 6m_sw is formed. First, we selected a value of $CF_{m,up,rodr}$ of Table 4 of section 3.1.2 to account for metabolite formation in the water layer of the upstream catchment; as the $DT_{50,p}$ equals 24 d we select the recommended value of 0.1 for $CF_{m,up,rodr}$. Figure 11 presents the concentrations of 6_sw and 6m_sw in the target segment of the water layer, i.e. the last segment in the FOCUS stream from 95 to 100 m.

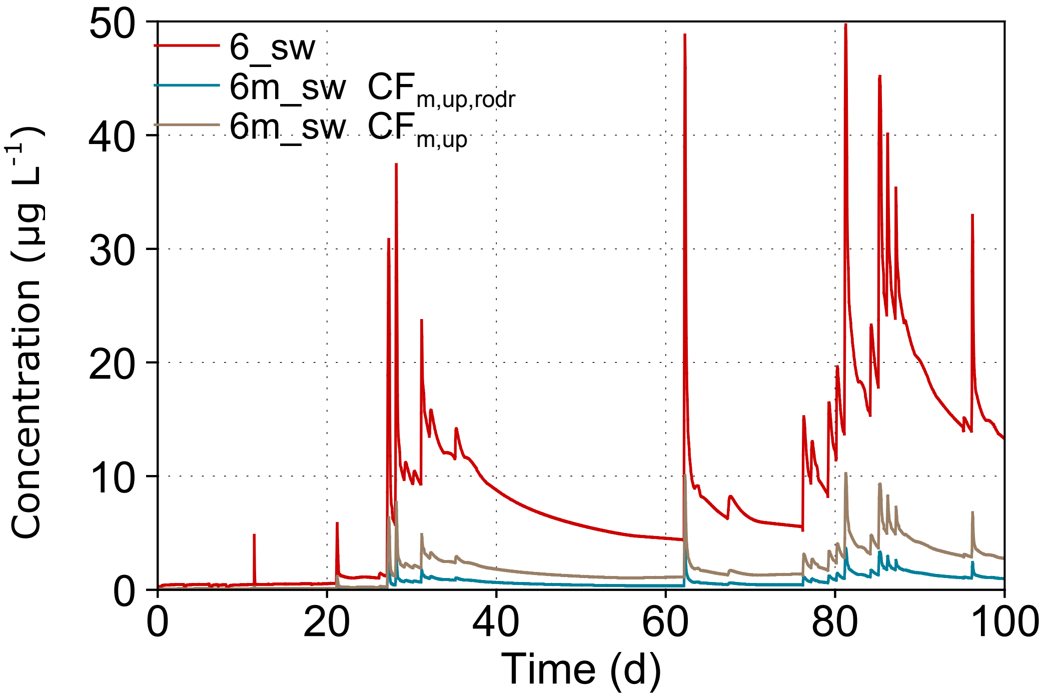

Figure 11 *Concentration of parent 6_sw and metabolite 6m_sw in the 95-100 m segment of a non-standard FOCUS D2 stream run after one application of 1000 g* m^{-2} *in winter cereals. The metabolite concentrations shown include the additional mass of the catchment as calculated by Eq. (19) using (i) a* $CF_{m,up,rodr}$ *factor of 0.1 on the basis of Table 4, and (ii) a* $CF_{m,up}$ *factor of 0.281 calculated by using the method of chapter 4 (and Annex 2), to account for metabolite formation out of drained mass in the upstream catchment.*

As spray drift is disabled, no mass is deposited on the water surface and there is no concentration peak of the parent or of the metabolite in the stream at day 11, immediately after application. (A low concentration of the parent compound is visible during this period in Figure 11 due to the application in the former year.) From around day 21 drainage events start to occur and the parent compound is drained into the upstream catchment water and into the 100-m FOCUS stream. Metabolite 6m_sw is formed in the water. The total metabolite concentration is Figure 11 again consists of two elements: (i) metabolite formed in the upstream catchment calculated with the aid of Eq. (19) of section 3.1.2 and (ii) metabolite formed within the FOCUS stream itself. As the simulated residence times in the D2 stream during the period 20-100 d are short (most days less than 1 d, see Appendix F of FOCUS (2010), compare also the monthly average residence times for January to April 1986, 0.65 up to 4.8 d, in Table 4.4.3-5 of FOCUS (2001)), compared to the half-life of 24 d for the parent, there is little time for metabolite formation within the 100-m FOCUS stream itself and therefore, we expect that the main contribution to the metabolite concentration in the stream is by Eq. (19). This implies that the value of the correction factor determines the metabolite concentration in the D2 stream to a great extent, and thus, we expect that the difference between the two estimations of the metabolite concentration will be visible in Figure 11.

Next, we calculated the improved value for the correction factor as described in chapter 4 (and Annex 2). The time of the maximum metabolite fraction, t_{max}, is 112 days. This time is longer than the conservative estimate of the travel time in the catchment of the D2 scenario, t_{cons} of 90 d. Hence the correction factor is calculated using t_{cons}. Its value is 0.281, i.e. a higher value than the one obtained by the simple method to estimate the correction factor. This higher value of $CF_{m,up}$ results in concentrations of metabolite 6m_sw that are higher than those calculated with the $CF_{m,up,rodr}$ of 0.1. Thus, as expected, the difference between the two methods estimating the correction factors, is clearly visible in Figure 11.

6 Discussion and conclusions

Below some aspects are discussed concerning the designed correction procedure and the estimation of the correction factors.

Mass balances
The metabolite mass from the upstream catchment is estimated in a conservative way and this implies that a conservative estimation of the metabolite concentration in the FOCUS stream is made. In addition, the incoming parent mass from the upstream catchment (0.20 * $c^*_{p\ by\ spray\ drift\ on\ stream}$ for spray drift deposition and $J_{p,by\ runoff\ or\ drainage}$ for runoff/drainage entries) is not reduced by the metabolite formation in the catchment. So, this incoming parent mass enters also the 100-m FOCUS stream, where metabolites are formed and this results in an overestimation of the metabolite formation in the FOCUS stream. Thus there is no conservation of mass (parent+metabolite) in the upstream catchment. This approach of not reducing the incoming parent mass from the catchment results in parent concentrations that do not differ from those calculated by the former FOCUS_TOXSWA_3.3.1, i.e. the version that does not simulate the formation of metabolites in water and in sediment.

Another reason for not observing mass conservation in the upstream catchment is the fact that the formation of sediment metabolites and metabolite formation from metabolites (by consecutive reactions) is neglected. However, once all mass has entered the FOCUS stream mass conservation in the FOCUS stream is maintained (Eqs. (1) and (4) of section 2.1.).

Primary water metabolites only
The correction method is applied to primary water metabolites only, i.e. metabolites formed in the water layer from the parent compound. So, metabolites formed from these primary water metabolites are not corrected and these types of metabolites can be present in FOCUS streams by formation from primary water metabolites within the FOCUS streams themselves. So, their concentrations may be underestimated.

Metabolites formed in catchment sediment
Metabolites formed in the sediment of catchment water bodies have not been taken into consideration in the correction of the metabolite concentration in FOCUS streams (section 3.1). Especially for compounds with high sorption coefficients (such as pyrethroids), relatively high transformation rates and for drainage or runoff events with relatively low flow velocities this simplification may lead to an underestimation of chronic metabolite concentrations in FOCUS streams. In reality in these cases one might expect some back-diffusion of metabolite mass out of catchment sediment into the catchment water, once the drainage or runoff event has finished. This back-diffusion might result in very low, but sustained concentration levels in catchment water flowing into the downstream FOCUS streams.

True degradation rates
The estimations of the correction factors for the metabolite concentration in FOCUS streams are based upon the use of true degradation rates in water of the parent and of the metabolite. By underestimating the parent degradation rate (e.g. by approximating it by the overall degradation rate of water-sediment systems for a compound with a high sorption coefficient and a slow degradation in sediment) the metabolite formation would be underestimated, so, the maximum metabolite fraction would be underestimated and so, the correction factor $CF_{m,up}$ would be underestimated. In addition the t_{max} would be too short.

Conservative estimates of the residence time in the upstream catchment
It is important to know whether the residence time of the parent in the catchment, τ_p, is shorter or longer than the t_{max}, the time of occurrence of the maximum metabolite mass fraction: if the residence

time of the parent in the catchment is longer, the maximum metabolite mass fraction will be formed, but if the residence time of the parent is shorter than t_{max} a smaller fraction than the maximum metabolite mass fraction will be formed. The residence time in the upstream catchment, $\tau_{p,}$ varies as a function of the incoming drainage and runoff water fluxes and thus, in principle the metabolite fraction would vary as well. In section 4.2 we wanted to keep the metabolite calculation as simple as possible, and therefore, we estimated the residence time of the parent, τ_p, in a conservative way and used this value in the correction procedure for the scenarios.

Another option would be to use residence times that occur at the time of entry of the parent and immediately thereafter. This would lead to a correction factor $CF_{m,up}$ that is a function of time during the simulations and to a more precise estimation of the metabolite mass that could be formed. However, this estimation would represent the single, simulation year of the FOCUS scenarios. Thus, it would not represent a robust percentile of probability of occurrence for the metabolite. The robustness of the probability of occurrence could be increased by considering the relevant time window (e.g. month) in a series of years (e.g. 20 years), and not in the single FOCUS simulation year. For the FOCUS runoff scenarios the FOCUS_PRZM model already produces 20 years of runoff entries and the FOCUS_TOXSWA model (version 4.4.2) is able to simulate such a 20-year time series.

Parent and metabolite having the same Arrhenius activation energy for transformation
For parent and metabolite compounds having the same Arrhenius activation energy for transformation, we can derive that, if the conservative estimate of the residence time is greater than or equal to the time of maximum metabolite mass occurrence, i.e. if $t_{cons} \geq t_{max}$, the value of the $CF_{m,up}$ factor does not depend on the temperature (see Annex 3). So, this implies that in these cases the value of the $CF_{m,up}$ factor is not scenario-specific. However, the t_{max} value does depend on the temperature in the scenario and thus, the condition $t_{cons} \geq t_{max}$ remains scenario-specific.

In conclusion, the FOCUS_TOXSWA _4.4.2 model is now able to simulate metabolite formation and transformation in water and in sediment. A flexible reaction scheme is used, that can be represented in a general way as a matrix. Metabolites may be formed in consecutive as well as simultaneous reactions.

In addition, a procedure has been designed to account for the formation of metabolites in the water layer of the upstream catchment of streams of the EU_FOCUS scenarios, thus increasing the metabolite concentration in FOCUS streams. Its intention is to do this in a conservative, but not over-conservative way. As the concentrations are used for risk assessment purposes, it is general practice to estimate concentrations on the conservative side, in order not to underestimate the risks.

For a spray drift-entered parent compound the metabolite concentration in the stream is increased to maximally 0.2 times the parent concentration. For a runoff-entered or drainage-entered parent compound an additional metabolite mass flux enters the stream from upstream, its maximum size equals the parent mass flux from the upstream catchment. The maximum values are lowered by correction factors $CF_{m,up}$ estimated by two methods: (i) a simple one, where the factor is only a function of the transformation rate of the parent and (ii) a more detailed and less conservative one, where the factor is a function of the transformation rates of both the parent and the metabolite, as well as of a conservative estimate for the residence time in the upstream catchment of each stream scenario. Both methods are based upon the two possible, extreme layouts of the upstream catchment (a square shape with 10*10 1-ha fields or a long, rectangular shape with 2* 50 1-ha fields). The transformation rates of the parent and the metabolite are corrected for the average scenario temperature. In this way a sound estimation of the total metabolite concentration in FOCUS streams was obtained.

References

Adriaanse, P.I. 1996. Fate of pesticides in field ditches: the TOXSWA simulation model. Report 90, Staring Centrum, Wageningen, the Netherlands.

Adriaanse, P.I., J.J.T.I. Boesten and S.J.H. Crum. 2013. Estimating degradation rates in outdoor stagnant water based on inverse modeling with TOXSWA: a case study with prosulfocarb. Pest Manag Sci 69, 6:755-767.

Beltman, W.H.J., M.M.S. Ter Horst, P.I. Adriaanse, A. De Jong. 2006. Manual of FOCUS_TOXSWA version 2.2.1. Alterra-rapport 586, Alterra, Wageningen, The Netherlands.

EC. 2009. Regulation (EC) No 1107/2009 of the European Parliament and the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. Official Journal of the European Union L 309:1-50.

EFSA. 2012. Scientific opinion on the science behind the guidance for scenario selection and scenario parameterisation for predicting environmental concentrations of plant protection products in soil. EFSA Journal 2012; 10(2):2562.

EU. 1991. Council directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market, Official Journal of the European Communities, L230, 1-32.

FOCUS. 2001. FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC. Report of the FOCUS Surface Water Scenarios Workgroup (P.I. Adriaanse, R. Allen, E. Capri, V. Gouy, J. Hollis, N. Jarvis, M. Klein, J. Linders, P. Lolos, W-M Maier, S. Maund, M.H. Russell, J-L Teixeira, S. Vizantinopoulos and D. Yon), EC. Document Reference SANCO/4802/2001-rev2.

Leistra, M., A.M.A. Van der Linden, J.J.T.I. Boesten, A. Tiktak and F. Van den Berg. 2001. PEARL model for pesticide behaviour and emissions in soil-plant systems. Descriptions of the processes in FOCUS PEARL v 1.1.1. Alterra-Rapport 013, RIVM report 711401009.

Schurer, K. en J.C. Rigg. 1980. Grootheden en eenheden in de landbouw en de biologie. Wageningen, Pudoc.

Walker, A.K., 1974. A simulation model for prediction of herbicide persistence. J. Environ. Qual. 3: 396-401.

Annex 1 Numerical solution of the differential equation according to the explicit solution scheme

In the FOCUS_TOXSWA model the parameter Θ has been set to 1, so computations are made with the explicit numerical solution scheme. By using the explicit scheme the solution of Eq. (1) is simplified, because the elements LOD and LBD equal zero. In addition the term describing transformation in the LDD element is left out. So, only the terms at the main right-hand diagonal are not equal to zero.

Using the explicit scheme the transformation term in the LDD element of the water layer is left out. The transformation term in the RDD element, RDD_t (see Eq. 3b), now reads:

$$RDD_t = -\frac{c^*}{c} \cdot k \cdot A_i^{j+1} \cdot \Delta t \qquad \text{[A1]}$$

Using the explicit scheme to solve the mass conservation equation for the sediment (Eq. 4) the transformation term in the LDD element is left out. The transformation term in the RDD element, RDD_t (see Eq. 6b), is simplified to:

$$RDD_t = -\frac{c_b^*}{c_{lb}} \cdot k_b \cdot \Delta t \qquad \text{[A2]}$$

Annex 2 Recipe to calculate the correction factor for formation of water metabolites in the upstream catchment of FOCUS streams

The TOXSWA_4.4.2 version now simulates metabolite formation in water and in sediment. Therefore, in the FOCUS scenarios we now account for metabolite formation in the upstream catchment. This is relevant for FOCUS streams only, as the ponds and ditches do not have upstream fields treated with pesticides. Metabolites formed in the sediment of the upstream catchment are assumed not to enter the 100-m FOCUS stream, so the procedure only corrects the metabolite concentration in the FOCUS stream for additional metabolite mass that is formed in the water layer of the upstream catchment.

To do so, a correction factor $CF_{m,up}$ is introduced, that accounts for water metabolites formed from both spray drift entries and lateral drainage or runoff entries in the upstream catchment. This factor needs to be set manually in the FOCUS_TOXSWA GUI (see the TOXSWA manual, Section 4.4.4). Default is the maximum value of 1. A case-specific, lower value for $CF_{m,up}$ can be calculated by following the steps described below.

This procedure is for temporary use, because a new release of the current FOCUS_SWASH_4.2 is planned, in which the calculation of the correction factor will be automated.

Note that:

a. The factor is only valid for primary metabolites formed in the water layer, i.e. metabolites formed directly from the parent,
b. The correction factor is metabolite-specific. As TOXSWA can handle one correction factor only, this means that, if more than one (primary) metabolite is formed, more TOXSWA simulations are needed, one for each metabolite,
c. The correction factor is scenario-specific, because its value is a function of the water temperature and of the residence time in the upstream catchment of the scenario.

So, for **each scenario** the steps are to calculate:
(1) the transformation rates of the parent (k_p) and of the metabolite (k_m) for the scenario temperature,
(2) the time of occurrence of the maximum metabolite mass (t_{max}) and
(3) the correction factor $CF_{m,up}$ using k_p, k_m and t_{max}.

The calculation steps are described in detail below.

1. Calculate the transformation rates of the parent, k_p, and of the metabolite, k_m, for the average water temperature of the scenario (Table b1) using the Arrhenius equation (with the molar Arrhenius activation energy E_A = 65400 J mol^{-1} in FOCUS calculations) by Eq. (B1):

$$k(T) = k(T_{ref})\, exp\left[\frac{65400}{8.3144 \cdot T_{ref}T}\left(T - T_{ref}\right)\right] \tag{B1}$$

T = average water temperature in the scenario (K)
T_{ref} = temperature at which the transformation rate was measured (K)
k = transformation rate coefficient (d^{-1}) for the parent or the metabolite in the water layer [$k = \ln(2)/DegT50$]

2. Calculate the time of occurrence of the maximum metabolite mass that may be formed in the upstream catchment, $t_{\max}$, by substituting the k_p and k_m values (obtained in step (1)) in Eq. (B2):

$$t_{max} = \frac{\ln\left[\frac{k_m}{k_p}\right]}{k_m - k_p} \qquad \text{(B2)}$$

$t_{\max}$ = time of occurrence of the maximum metabolite mass (d)
k_p = transformation rate coefficient of the parent at scenario temperature (d^{-1})
k_m = transformation rate coefficient of the metabolite at scenario temperature (d^{-1})

3. Calculate the correction factor $CF_{m,up}$ by substituting k_p, k_m and $t_{\max}$ values (obtained in steps (1) and (2)) in Eq. (B3):

$$CF_{m,up} = \frac{k_p}{k_p - k_m} \cdot \left[e^{-k_m t_{true}} - e^{-k_p t_{true}}\right] \qquad \text{(B3)}$$

t_{true} = true residence time of the parent in the upstream catchment (d)

The true residence time of the parent in the upstream catchment t_{true}, is approximated by a conservative estimate of the residence time, t_{cons}, which is specific for each scenario. If the conservative estimate of the residence time of the parent (i.e. t_{cons}) is shorter than the time needed to form the maximum metabolite mass in the upstream catchment the residence time t_{cons} need to be used in Eq. (B3), if it is longer, then use t_{max} in Eq. (B3). So,

if $t_{cons} > t_{max}$ use $t_{true} = t_{max}$

if $t_{cons} \leq t_{max}$ use $t_{true} = t_{cons}$ in Eq. (B3).

Table b1
Temperatures and conservative estimates of residence times of the FOCUS streams.

Scenario	**Average temperature T (°C)**	**Average temperature T (K)**	**Conservative estimate of residence time, t_{cons} (d)**
D1	8.0	281.1	23
D2	9.2	282.3	90
D4	8.2	281.4	7
D5	10.7	283.8	10
R1	10.0	283.1	5
R2	14.9	288.0	3
R3	13.6	286.7	10
R4	13.7	286.8	5

Annex 3 Derivation of simplified correction factor $CF_{m,up}$ for metabolite formation in the upstream catchment of FOCUS streams for transformation rates k_p and k_m determined at the same reference temperature and having the same Arrhenius activation energy

The general procedure for the calculation of the metabolite mass formed can be simplified if (i) the temperature at which the transformation rates k_p and k_m are given are equal, e.g. at the T_{ref} of 20 °C or at any other temperature, e.g. one of the scenario temperatures T_{scen} and, (ii) the Arrhenius activation energies for transformation of the parent and of the metabolite are equal. To do so, we introduce factors A, B and ω. Then, the correction factor $CF_{\mathrm{m,up}}$ can be calculated with the aid of the factor B (equal to the ratio of k_{p} and k_{m}) and the factor ω (equal to $t_{\mathrm{cons,scen}}/t_{\mathrm{max,scen}}$ or 1). The factor B does not depend on temperature, so it is not scenario-specific, provided that the conditions (i) and (ii) apply. Furthermore, it is shown that for all scenarios where $t_{\mathrm{cons,scen}} > t_{\mathrm{max,scen}}$, the factor $CF_{m,up}$ is the same and thus the maximum metabolite mass fraction is the same.

The analytical solution for the fraction of metabolite formed Eq. (24) can be written as:

$$\frac{m_m(t)}{m_{p,0}} = F_{p\rightarrow m}\,\frac{M_m}{M_p}\;CF_{m,up}\,(t) \qquad \text{(C1)}$$

where:

$$CF_{m,up}(t) = \frac{k_p}{k_p - k_m}\cdot\left[exp(-k_m t) - exp\left(-k_p t\right)\right] \qquad \text{(C2)}$$

the time of occurrence of the maximum metabolite fraction, $t_{\mathrm{max,scen}}$ is given by:

$$t_{max,scen} = \frac{\ln\left[\frac{k_{m,scen}}{k_{p,scen}}\right]}{k_{m,scen} - k_{p,scen}} \qquad \text{(C3)}$$

where the transformation rates k have been calculated for the temperature of the scenario T_{scen}, using the Arrhenius equation. So, the time of occurrence of the maximum metabolite mass fraction is scenario-specific, because each scenario has its own average temperature.

We simplify the $CF_{\mathrm{m,up}}$ and $t_{\mathrm{max,scen}}$ equations via introduction of the terms A and B, where

$$A = k_{m,scen} - k_{p,scen} \qquad \text{(C4)}$$

and

$$B = \frac{k_{m,scen}}{k_{p,scen}} = \frac{k_{m,Tref}}{k_{p,Tref}} \tag{C5}$$

B does not depend on temperature: If the two transformation rates determined at the same temperature T_{ref} are corrected for the same scenario temperature T_{scen} with the Arrhenius equation of Walker (1974) (see also Eq. (34)) , given below, the equation reduces to Eq. (C5) because in the division of the two transformation rates the temperature correction is cancelled.

$$B = \frac{k_{m,Tref}\, exp\left(\frac{E_A}{R\, T_{ref} T_{scen}}\left(T_{scen} - T_{ref}\right)\right)}{k_{p,Tref}\, exp\left(\frac{E_A}{R\, T_{ref} T_{scen}}\left(T_{scen} - T_{ref}\right)\right)} = \frac{k_{m,Tref}}{k_{p,Tref}} \qquad \text{(Arrhenius Eq.)}$$

Hence, Eq. (C5) is valid for any temperature. However, *A* remains dependent on the temperature.

Combining Eqs. (C4) and (C5), $k_{p,scen}$ and $k_{m,scen}$ can also be defined in terms of *A* and *B*:

$$k_{p,scen} = k_{m,scen} - A \tag{C6}$$

and

$$k_{m,scen} = B \cdot k_{p,scen} \tag{C7}$$

Substituting $k_{m,scen}$ from Eq. (C7) into (C6) results in:

$$k_{p,scen} = B \cdot k_{p,scen} - A \qquad \Leftrightarrow \tag{C8}$$

$$k_{p,scen}(1 - B) = -A \tag{C9}$$

So, $k_{p,scen}$ in terms of *A* and *B* is:

$$k_{p,scen} = \frac{-A}{1 - B} = \frac{A}{B - 1} \tag{C10}$$

Substituting $k_{p,scen}$ from Eq. (C6) into (C5) results in:

$$B = \frac{k_{m,scen}}{k_{m,scen} - A} \qquad \Leftrightarrow \tag{C11}$$

$$Bk_{m,scen} - BA = k_{m,scen} \qquad \Leftrightarrow \tag{C12}$$

$$k_{m,scen}(B - 1) = BA \tag{C13}$$

Hence $k_{m,scen}$ in terms of *A* and *B* is:

$$k_{m,scen} = \frac{BA}{(B - 1)} \tag{C14}$$

Replacing $k_{\mathrm{p,scen}}$ and $k_{\mathrm{m,scen}}$ in the $CF_{\mathrm{m,up}}$ equation (C2) results in a new equation, defined solely in terms of *A, B* and *t:*

$$CF_{m,up}(t) \ = \frac{1}{1-B} \cdot \left[exp\left(\frac{BA}{(1-B)}t\right) \ - exp\left(\frac{A}{1-B}t\right)\right] \tag{C15}$$

We want to reduce Eq. (C15) to an equation in terms of only *B*, hence to get rid of *A*. To do so, we introduce ω, which is defined as:

$$\omega = \frac{t_{scen}}{t_{max,scen}} \quad \text{and if} \quad t_{scen} > t_{max,scen}\text{: } \omega = 1 \tag{C16}$$

where t_{scen} is the residence time of the parent in the water-only system, i.e. the residence time in the upstream catchment of the scenario. Thus, ω is also a scenario-specific parameter.

Rearrangement of Eq. (C16) results in $t_{scen} = \omega \cdot t_{\mathrm{max,scen}}$, which is further rewritten in terms of *A* and *B* by substituting of *A* (via Eq. (C4)) and *B* (via Eq. (C5)) into Eq. (C3):

$$t_{scen} = \omega \cdot \ \frac{\ln[B]}{A} \tag{C17}$$

Note that t_{scen} in Eq. (C17) is scenario-specific, because the value of *A* depends on the scenario (see Eq. (C4)).

Substitution of t_{scen} from Eq. (C17) into Eq. (C15) results in:

$$CF_{m,up}(t_{scen}) \ = \frac{1}{1-B}\left[exp\left(\frac{BA}{(1-B)} \ \omega \ \frac{\ln[B]}{A}\right) \ - exp\left(\frac{A}{1-B} \ \omega \ \frac{\ln[B]}{A}\right)\right] \tag{C18}$$

The parameter *A* is cancelled out in Eq. (C18), giving:

$$CF_{m,up}(t_{scen}) \ = \frac{1}{1-B}\left[exp\left(\frac{B\ln[B]}{(1-B)}\omega\right) \ - exp\left(\frac{\ln[B]}{1-B}\omega\right)\right] \tag{C19}$$

Eq. (C19) can be rewritten to

$$CF_{m,up}(t_{scen}) \ \ = \frac{1}{1-B}\left[\left(exp(\ln[B])\right)^{\frac{B}{(1-B)}\omega} \ - \left(exp(\ln[B])\right)^{\frac{1}{(1-B)}\omega}\right] \tag{C20}$$

Then, the exponential functions in Eq. (C20) can be rewritten to

$$CF_{m,up}(t_{scen}) \ \ = \frac{1}{1-B}\left[B^{\frac{B}{(1-B)}\omega} \ - B^{\frac{1}{(1-B)}\omega}\right] \tag{C21}$$

Now ω can be set apart as exponent

$$CF_{m,up}(t_{scen}) \ \ = \frac{1}{1-B}\left[\left(B^{\frac{B}{(1-B)}}\right)^{\omega} \ - \left(B^{\frac{1}{(1-B)}}\right)^{\omega}\right] \tag{C22}$$

and, using the equivalency

$$B^{\frac{1}{(1-B)}} = B \cdot B^{\frac{B}{(1-B)}} \tag{C23}$$

(because: $B^1 \cdot B^{\frac{B}{(1-B)}} = B^{1+\frac{B}{(1-B)}} = B^{\frac{(1-B)}{(1-B)}+\frac{B}{(1-B)}} = B^{\frac{1}{(1-B)}}$)

to substitute the last term of the Eq. (C22), giving

$$CF_{m,up}(t_{scen}) \quad = \frac{1}{1-B}\left[\left(B^{\frac{B}{(1-B)}}\right)^{\omega} - B^{\omega}\left(B^{\frac{B}{(1-B)}}\right)^{\omega}\right] \tag{C24}$$

This equation can be rearranged to

$$CF_{m,up}(t_{scen}) \quad = \frac{1-B^{\omega}}{1-B}\left(B^{\frac{B}{(1-B)}}\right)^{\omega} \tag{C25}$$

and finally to

$$CF_{m,up}(t_{scen}) \quad = \frac{1-B^{\omega}}{1-B} \cdot B^{\frac{B\cdot\omega}{(1-B)}} \tag{C26}$$

Thus Eq. (C26) turns out to be equal to Eq. (C15), without term *A*.

We now distinguish two cases to calculate the correction factor $CF_{\mathrm{m,up}}$:

1. The conservative estimate of the residence time of the parent in the upstream catchment is shorter than the time of the maximum metabolite fraction, hence if

$$t_{cons,scen} \; < \; t_{max,scen} \qquad \text{then use} \qquad \omega = \frac{t_{cons,scen}}{t_{max,scen}} \tag{C27}$$

to calculate $CF_{\mathrm{m,up}}$ with:

$$CF_{m,up}\,(t_{cons,scen}) = \frac{1-B^{\omega}}{1-B} \cdot \left(B^{\frac{B}{(1-B)}}\right)^{\omega} \tag{C28}$$

For Eq. (C28) there is still dependency of $CF_{\mathrm{m,up}}$ on the temperature, via ω determined by $t_{\mathrm{max,scen}}$.

2. The conservative estimate of the residence time of the parent in the upstream catchment is longer than the time of the maximum metabolite fraction, hence if:

$$t_{cons,scen} \; > \; t_{max,scen} \qquad \text{then use } t_{scen} = t_{\mathrm{max,scen}}\text{, hence} \qquad \omega = 1 \tag{C29}$$

to calculate $CF_{\mathrm{m,up}}$ with:

$$CF_{m,up}(t_{max,scen}) \quad = B^{\frac{B}{(1-B)}} \tag{C30}$$

In this case for $\omega = 1$, Eq. (C26) reduces to the simple Eq. (C30).

Eq. (C30) is valid for any temperature because B does not depend on temperature as long as k_p and k_m are given at the same temperature and have the same Arrhenius activation energies for transformation (see explanation below Eq. (C5).

We use $\omega = 1$, to calculate the correction factor $CF_{m,up}(t_{\mathrm{max,scen}})$, because the maximum metabolite mass is formed at $t_{scen} = t_{\mathrm{max,scen}}$, so at $\omega = t_{\mathrm{max,scen}} / t_{\mathrm{max,scen}} = 1$. For the conservative estimate of the residence time in the catchment , $t_{\mathrm{cons,scen}}$, that exceeds $t_{\mathrm{max,scen}}$, less metabolite mass than the mass at $t_{\mathrm{max,scen}}$ is formed (see Figure 6 in section 4.1). So, we do not use a value ω greater than 1, resulting by simply filling in $t_{\mathrm{cons,scen}}$ and $t_{\mathrm{max,scen}}$ values in Eq. (C16): $\omega = t_{\mathrm{cons,scen}} / t_{\mathrm{max,scen}}$ for $t_{\mathrm{cons,scen}} \geq t_{\mathrm{max,scen}}$.

So, the conclusion is that in cases that $t_{\mathrm{max,scen}}$, the time of maximum metabolite occurrence for a scenario (for its own average scenario temperature), is shorter or equal to $t_{\mathrm{cons,scen}}$, the conservative estimate of the residence time of the parent in the upstream catchment, (i.e. $t_{\mathrm{cons,scen}} > t_{\mathrm{max,scen}}$), the correction factor $CF_{\mathrm{m,up}}$ can be calculated in a very simple way, by Eq. (C31):

$$CF_{m,up} = B^{\frac{B}{(1-B)}} \qquad \text{(C31)}$$

in which the factor B does not depend on temperature, and thus is not scenario-specific. Furthermore, for all scenarios where $t_{\mathrm{cons,scen}} > t_{\mathrm{max,scen}}$, the maximum fraction is the same.

Thus, the Eqs. (C28) and (C31)[3] can be used if the temperature at which the transformation rates k_p and k_m are given are equal, and the Arrhenius activation energies for transformation of the parent and of the metabolite are equal.

---

[3] Note that the equations derived cannot be used for $B = 1$, i.e. $k_{\mathrm{p,scen}} = k_{\mathrm{m,scen}}$, because this leads to divisions by zero. When $k_{\mathrm{p,scen}} = k_{\mathrm{m,scen}}$, we advise to change one of the k's with a tiny value (relative to k).

Alterra Wageningen UR
P.O. Box 47
6700 AA Wageningen
The Netherlands
T +31 (0)317 48 07 00
www.wageningenUR.nl/en/alterra

Alterra report 2587
ISSN 1566-7197

Alterra Wageningen UR is the research institute for our green living environment. We offer a combination of practical and scientific research in a multitude of disciplines related to the green world around us and the sustainable use of our living environment, such as flora and fauna, soil, water, the environment, geo-information and remote sensing, landscape and spatial planning, man and society.

The mission of Wageningen UR (University & Research centre) is ‘To explore the potential of nature to improve the quality of life’. Within Wageningen UR, nine specialised research institutes of the DLO Foundation have joined forces with Wageningen University to help answer the most important questions in the domain of healthy food and living environment. With approximately 30 locations, 6,000 members of staff and 9,000 students, Wageningen UR is one of the leading organisations in its domain worldwide. The integral approach to problems and the cooperation between the various disciplines are at the heart of the unique Wageningen Approach.

To explore
the potential
of nature to
improve the
quality of life

Alterra Wageningen UR
P.O. Box 47
6700 AB Wageningen
The Netherlands
T +31 (0) 317 48 07 00
www.wageningenUR.nl/en/alterra

Alterra Report 2587
ISSN 1566-7197

Alterra Wageningen UR is the research institute for our green living environment. We offer a combination of practical and scientific research in a multitude of disciplines related to the green world around us and the sustainable use of our living environment, such as flora and fauna, soil, water, the environment, geo-information and remote sensing, landscape and spatial planning, man and society.

The mission of Wageningen UR (University & Research centre) is ‘To explore the potential of nature to improve the quality of life’. Within Wageningen UR, nine specialised research institutes of the DLO Foundation have joined forces with Wageningen University to help answer the most important questions in the domain of healthy food and living environment. With approximately 30 locations, 6,000 members of staff and 9,000 students, Wageningen UR is one of the leading organisations in its domain worldwide. The integral approach to problems and the cooperation between the various disciplines are at the heart of the unique Wageningen Approach.