



Comparison of pesticide concentrations at drinking water abstraction points in The Netherlands simulated by DROPLET version 1.2 and 1.3.2 model suites

P.I. Adriaanse and W.H.J. Beltman

| WOt-technical report 100



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The 'WOt-technical reports' series presents the findings of research projects implemented for the Statutory Research Tasks Unit for Nature & the Environment by various centres of expertise.

WOt-technical report 100 presents the findings of a research project commissioned and funded by the Dutch Ministry of Agriculture, Nature and Food Quality.

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Statutory Research Tasks Unit for Nature & the Environment

Wageningen, December 2017

WOt-technical report 100

ISSN 2352-2739

DOI: 10.18174/434929

Abstract

Adriaanse, P.I. and W.H.J. Beltman (2017). *Comparison of pesticide concentrations at drinking water abstraction points in The Netherlands simulated by DROPLET version 1.2 and 1.3.2 model suites*. Wageningen, the Statutory Research Tasks Unit for Nature & the Environment (WOT Natuur & Milieu). WOT-technical report 100. 52 p.; 6 Figs; 12 Tabs; 5 Refs; 5 Annexes.

The user-friendly software tool DROPLET (acronym for **DR**inkwater uit **OP**pervlaktewater-**L**andbouwkundig gebruik **E**valuatie **T**ool) assists the Dutch Board for the Authorization of Plant Protection Products and Biocides (Ctgb) in evaluating whether pesticides may exceed the 0.1 µg/L standard in one of the Dutch surface water abstraction points for drinking water production. Based upon Good Agricultural Practice DROPLET uses the peak concentration in the FOCUS D3 ditch (with spray drift deposition according to Dutch numbers) as starting point for the final, expected concentration at the abstraction points situated in the larger waterbodies downstream. This report compares concentrations in the abstraction points calculated by the old model suite (FOCUS-SWASH 3.1, FOCUS-MACRO 4.4.2, FOCUS-TOXSWA 3.3.1 and DROPLET 1.2) with those calculated by the more recently released model suite (FOCUS-SWASH 5.3, including the substance database SPIN 3.3, FOCUS-MACRO 5.5.3, FOCUS-TOXSWA 4.4.3 and DROPLET 1.3.2). The concentrations in the drinking water abstraction points calculated by the new model suite may be up to a factor of approximately 2.5 higher than the ones calculated by the old model suite. This is practically entirely due to the increased pesticide mass in the drainage fluxes calculated by the new version of the MACRO model. The calculations by the TOXSWA and DROPLET models have not been changed. Because no measured water and mass fluxes for drainage are available for the D3 scenario, it is not possible to indicate whether the fluxes calculated by MACRO 4.4.2 or those by MACRO 5.5.3 reflect better reality. Thus no recommendation can be made on the model suite to be used in the Dutch exposure assessment for drinking water production from surface waters.

Key words: surface water abstraction for drinking water production, pesticides, registration, DROPLET model suite

Referaat

Adriaanse, P.I. & W.H.J. Beltman (2017). *Vergelijking van concentraties gewasbeschermingsmiddel in de drinkwaterinnamepunten van Nederland, zoals berekend door DROPLET versies 1.2 en 1.3.2 modellentrein*. (2017). WOT Natuur & Milieu. WOT-technical report 100. 52 blz.; 6 fig.; 12 tab.; 5 ref; 5 Bijlagen.

Het gebruikersvriendelijke instrument DROPLET (acroniem voor **DR**inkwater uit **OP**pervlaktewater-**L**and-bouwkundig gebruik **E**valuatie **T**ool) ondersteunt het Nederlandse College voor de toelating van gewas-beschermingsmiddelen en biociden (Ctgb) bij het evalueren of gewasbeschermingsmiddelen de drinkwater norm van 0.1 µg/L overschrijden in één van de negen innamepunten van oppervlaktewater voor drinkwater-bereiding. Uitgaande van Goed Landbouwkundig Gebruik gebruikt DROPLET de piekconcentratie in de FOCUS D3 sloot (met spuitdriftdepositie volgens Nederlandse cijfers) als startpunt voor de berekening van de uiteinde-lijke concentratie bij de drinkwater innamepunten die benedenstrooms in grotere wateren zijn gesitueerd. Dit rapport vergelijkt de concentraties in de innamepunten zoals berekend door de vorige modellentrein (FOCUS-SWASH 3.1, FOCUS-MACRO 4.4.2, FOCUS-TOXSWA 3.3.1 en DROPLET 1.2) met die van de meer recent uitgebrachte modellentrein (FOCUS-SWASH 5.3, inclusief de stoffendatabase SPIN 3.3, FOCUS-MACRO 5.5.3, FOCUS-TOXSWA 4.4.3 en DROPLET 1.3.2). De concentraties in de drinkwaterinname-punten, zoals berekend door de nieuwe modellentrein blijken tot een factor 2.5 hoger te kunnen zijn dan die berekend door de oude modellentrein. Dit wordt praktisch geheel veroorzaakt door de toegenomen massa bestrijdingsmiddel in de drainagefluxen berekend door de nieuwe versie van het MACRO model. De berekeningen in de modellen TOXSWA en DROPLET zijn niet gewijzigd. Daar er geen gemeten water- en stoffluxen voor drainage beschikbaar zijn in het D3 scenario, is het niet mogelijk om aan te geven of de fluxen berekend door MACRO 4.4.2 of die van MACRO 5.5.3 beter de realiteit weergeven en dus ook niet welke modellentrein wordt aanbevolen voor gebruik in de Nederlandse blootstellingsbepaling voor drinkwaterbereiding uit oppervlaktewater

Trefwoorden: extractie van oppervlaktewater voor productie van drinkwater, gewasbeschermingsmiddel, registratie, DROPLET modellentrein

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The WOT-technical reports series is published by the Statutory Research Tasks Unit for Nature & the Environment (WOT Natuur & Milieu), part of Wageningen University & Research. This document is available from the secretary's office, and can be downloaded from www.wur.nl/wotnatuurenmilieu

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Preface

The Netherlands is the only country of the EU that applies the so-called drinking water standard of EU Regulation 1107/2009 for drinking water production from surface water during the registration procedure for plant protection products. The assessment methodology that evaluates agricultural use of plant protection products for drinking water production from surface water was developed in 2008 (Adriaanse *et al.*, 2008) and an user-friendly software tool DROPLET (acronym for **DR**inkwater uit **OP**pervlaktewater-**L**andbouwkundig gebruik **E**valuatie **T**ool) was released in March 2010 (Van Leerdam *et al.*, 2010).

In May 2012 an update, version 1.1 was released and in April 2014 another update, version 1.2 was released. Both updates concerned software technical aspects only and did not involve any changes in the calculated concentrations in the surface water at the abstraction points.

On request of the main user of DROPLET, the Ctgb, the Dutch Board for the Authorization of Plant Protection Products and Biocides, the Ministry of Agriculture, Nature and Food Quality has commissioned an update of DROPLET. This updated version communicates with the newest released versions of the EU FOCUS models, i.e. FOCUS_SWASH 5.3 (including the substance database package SPIN) FOCUS-MACRO 5.5.3 and FOCUS-TOXSWA 4.4.3. At the same time the numbering of DROPLET version was changed in order to follow the FOCUS logic, implying that the three numbers represent the version of the model, user interface and databases, respectively. This resulted in the current version of DROPLET 1.3.2.

The authors would like to thank Dr Nicholas Jarvis, professor at the Department of Soil and Environment at the SLU, Swedish University of Agricultural Sciences in Uppsala, Sweden and developer of the MACRO model for pesticide behaviour in soils, for his help on explaining the differences between FOCUS-MACRO version 4.4.2 and version 5.5.3. They also thank Drs Anton Poot from the Dutch Ctgb for commenting on earlier versions of this report.

DROPLET and accompanying information can be found at the website www.pesticidemodels.eu, from where it can also be downloaded.

Paulien Adriaanse en Wim Beltman

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Summary

The user-friendly software tool DROPLET (acronym for **DR**inkwater uit **OP**pervlaktewater-**L**andbouwkundig gebruik **E**valuatie **T**ool) assists the Dutch Board for the Authorization of Plant Protection Products and Biocides (Ctgb) in evaluating whether pesticides may exceed the 0.1 µg/L standard in one of the Dutch surface water abstraction points for drinking water production. Based upon Good Agricultural Practice DROPLET uses the peak concentration in the FOCUS D3 ditch (with spray drift deposition according to Dutch numbers) as starting point for the final, expected concentrations at the abstraction points situated in the larger waterbodies downstream.

The Dutch Ministry of Agriculture, Nature and Food Quality has commissioned a new version of DROPLET that makes use of the most recently released versions of the FOCUS models, i.e. the FOCUS-MACRO 5.5.3 model calculating pesticide losses via drainage plus the FOCUS-TOXSWA 4.4.3 model calculating next the resulting concentration in the FOCUS D3 ditch. The update resulted in increased concentrations at the abstraction points. The unexpected increase in simulated concentrations at the drinking water abstraction points means that for the same substance and use pattern as before the risk assessment for drinking water from surface water may now indicate higher risks than before. So, the new release of DROPLET may have impact on decisions made in the registration procedure of the Netherlands.

To know the size and origin of the increase in concentrations we compared results of the old model suite (FOCUS-SWASH 3.1, FOCUS-MACRO 4.4.2, FOCUS-TOXSWA 3.3.1 and DROPLET 1.2) to those of the recently released model suite (FOCUS-SWASH 5.3, including the substance database SPIN 3.3, FOCUS-MACRO 5.5.3, FOCUS-TOXSWA 4.4.3 and DROPLET 1.3.2) in a systematic way, i.e. for a number of combinations of model versions as well as for a number of substances, that span a range of sorption coefficients, K_{oc} , and half-lives for degradation, $DegT_{50}$, in soil, water and sediment.

We found that the concentrations in the surface water abstraction points calculated by the entirely new model suite may be up to a factor of approximately 2.5 higher than the ones by the entirely old model suite. The increase is nearly entirely due to the increase in pesticide mass in the drainage fluxes of version 5.5.3 of the MACRO model with respect to those of the former version 4.4.2. The calculations by the TOXSWA and DROPLET models have not been changed. The reason for the changes in drainage fluxes lies in important changes in the numerical solution of the flow and transport equations and some underlying mathematical functions the MACRO model. The current increase in PECs is largest for compounds that are relatively mobile (K_{oc} around 100 L/kg or smaller) and/or persistent in soil ($DegT_{50,soil}$ 30 d or greater), e.g. the tracer, substance D, G and H. Because no measured water and mass fluxes for drainage are available for the D3 scenario, it is not possible to indicate which simulation results describe reality better, those by MACRO 4.4.2 or those by MACRO 5.5.3. Therefore it is not possible to indicate from a scientific point of view which model suite should be used to calculate the concentrations in the drinking water abstraction points. To be able to do so, a possible recommendation is to perform a field study for a mobile and persistent substance in which measured water and mass fluxes for drainage are compared to fluxes simulated by MACRO 4.4.2 and 5.5.3.

Samenvatting

Het gebruikersvriendelijke instrument DROPLET (acroniem voor **DR**inkwater uit **OP**pervlaktewater-**L**andbouwkundig gebruik **E**valuatie **T**ool) ondersteunt het Nederlandse College voor de toelating van gewasbeschermingsmiddelen en biociden (Ctgb) bij het evalueren of gewasbeschermingsmiddelen de drinkwater norm van 0.1 µg/L overschrijden in één van de negen innamepunten van oppervlaktewater voor drinkwaterbereiding. Uitgaande van Goed Landbouwkundig Gebruik gebruikt DROPLET de piekconcentratie in de FOCUS D3 sloot (met spuitdriftdepositie volgens Nederlandse cijfers) als startpunt voor de berekening van de uiteindelijke concentratie bij de drinkwater innamepunten die benedenstrooms in grotere wateren zijn gesitueerd.

Het ministerie van Landbouw, Natuur en Voedselkwaliteit (LNV) heeft opdracht gegeven om een nieuwe versie van DROPLET te maken, die gebruik maakt van de meest recent uitgebrachte versies van de FOCUS modellen, i.e. het FOCUS-MACRO 5.5.3 model dat de afvoer van bestrijdingsmiddel via drainage berekent plus het FOCUS-TOXSWA 4.4.3 model dat vervolgens de concentratie in de FOCUS D3 sloot berekent. Er bleek dat de update tot hogere concentraties bij de drinkwaterinnamepunten leidde. Deze onverwachte toename in berekende concentratie in het drinkwater innamepunt houdt in dat voor dezelfde stof met hetzelfde gebruikspatroon de risicobeoordeling voor drinkwater uit oppervlaktewater nu tot hogere risico's kan leiden dan met de vorige versie. Dus de nieuwe versie van DROPLET zou beslissingen in de registratieprocedure van Nederland kunnen wijzigen.

Om grootte en oorsprong van de toename in concentratie vast te stellen, zijn de resultaten vergeleken die zijn berekend met de vorige modellentrein (FOCUS-SWASH 3.1, FOCUS-MACRO 4.4.2, FOCUS-TOXSWA 3.3.1 en DROPLET 1.2) met die van de meer recent uitgebrachte modellentrein (FOCUS-SWASH 5.3, inclusief de stoffendatabase SPIN 3.3, FOCUS-MACRO 5.5.3, FOCUS-TOXSWA 4.4.3 en DROPLET 1.3.2). Dit is op een systematische manier gedaan, dat wil zeggen, zowel voor een aantal verschillende combinaties van de diverse modelversies als voor een aantal verschillende stoffen, die een range van sorptie coëfficiënten, K_{oc} , en halfwaardetijden, $DegT_{50}$, voor afbraak in bodem, water en sediment omvatten.

De concentraties in de drinkwater innamepunten berekend door de nieuwe modellentrein blijken tot een factor 2.5 hoger te kunnen zijn dan die door de oude modellentrein. De toename wordt praktisch geheel veroorzaakt door de toename in massa bestrijdingsmiddel in de drainage fluxen in MACRO versie 5.5.3 ten opzichte van die in versie 4.4.2. De berekeningen in de modellen TOXSWA en DROPLET zijn niet gewijzigd. De reden voor de gewijzigde drainage fluxen zijn belangrijke wijzigingen in de numerieke oplossing van de stromings- en transportvergelijkingen en in enkele onderliggende wiskundige vergelijkingen van het MACRO model; de parametrisatie van de modelinvoer voor het D3 scenario is slechts weinig gewijzigd. De huidige toename in concentratie is het grootst voor relatief mobiele stoffen, (K_{oc} van 100 L/kg of kleiner) en/of stoffen die persistent in grond zijn ($DegT_{50,soil}$ van 30 d of groter), bv. de tracer, stof D, G en H. Daar er geen gemeten water- en stoffluxen voor drainage in het D3 scenario beschikbaar zijn, is het niet mogelijk aan te geven welke berekende resultaten de werkelijkheid beter beschrijven, die door MACRO 4.4.2 of die door MACRO 5.5.3. Daardoor is het niet mogelijk om aan te geven welke modellentrein vanuit wetenschappelijk perspectief de voorkeur zou verdienen bij de berekeningen van de concentraties in de drinkwaterinnamepunten. Om dit wel te kunnen doen, is een mogelijke aanbeveling daarom om een veldtoets uit te voeren voor een mobiele en persistente stof, waar gemeten water- en stoffluxen in drainage worden vergeleken met gesimuleerde fluxen uit MACRO 4.4.2 en 5.5.3.

1 Introduction

On request of the Ctgb a new version of DROPLET 1.3.2 was made, that communicates with the newest released versions of the FOCUS models, i.e. FOCUS-SWASH 5.3 (including the substance database SPIN), FOCUS-MACRO 5.5.3 and FOCUS-TOXSWA 4.4.3. Fig 1 gives an overview of the sequence in which these tools and models are used to perform so-called Step 3 FOCUS Surface Water Scenarios simulations (Figure 1).

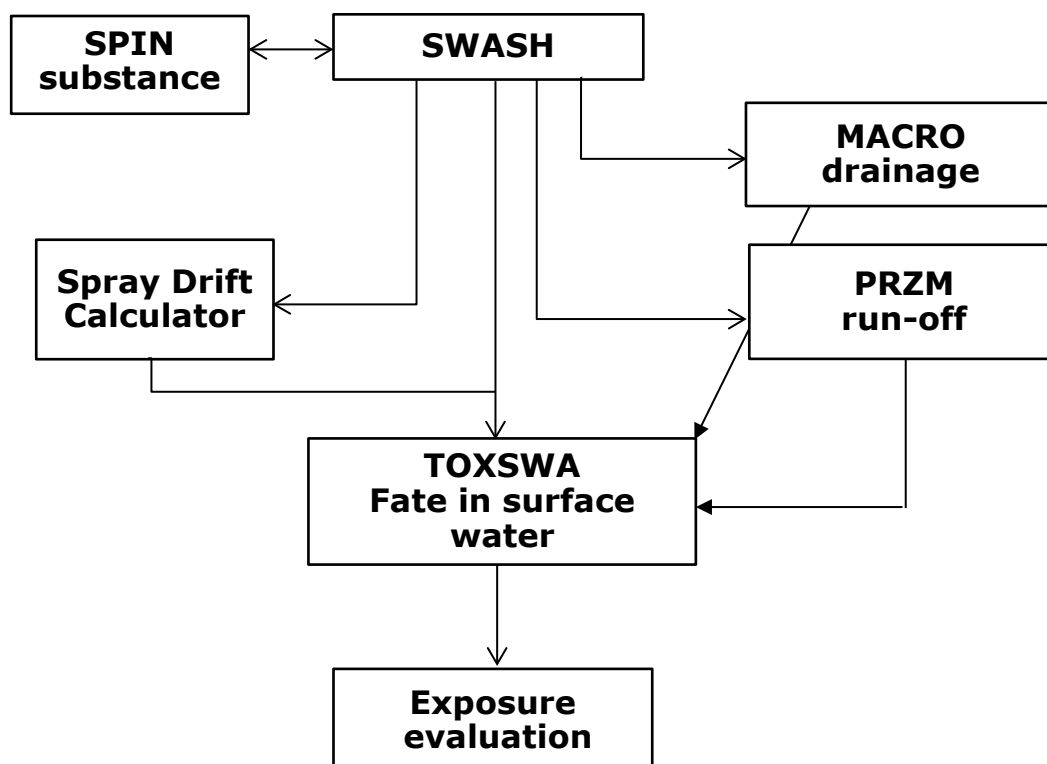


Figure 1. Sequence of tools and models used to calculate pesticide exposure in the proposed Step 3 EU FOCUS Surface Water Scenarios.

Some preliminary calculations performed with the updated version 1.3.2 of DROPLET (coupled to the newest released FOCUS models of SWASH, MACRO and TOXSWA) showed relatively large differences in the calculated PEC_{Tier1} at the drinking water abstraction points by DROPLET 1.2 (coupled to former releases of SWASH, MACRO and TOXSWA). This was an unexpected result, as some technical software issues were solved in the updated DROPLET version, but no changes were made in DROPLET concerning the calculation method of the PEC_{Tier1} values at the drinking water abstraction points. Also in the new FOCUS-TOXSWA version only minor changes were made in the PEC calculation of parent molecules and these were expected not to explain the observed differences. Therefore we looked into the MACRO model and found that there were considerable differences between the drainage fluxes in the m2t output files of the newest released MACRO version and the former one.

So, we decided to look into the differences in a more structured way. The m2t files are input in FOCUS_TOXSWA for the calculation of PEC_{max} in the FOCUS D3 ditch (with Dutch drift deposition, called NL D3 ditch from here onwards) and on its turn, the PEC_{max} in the NL D3 ditch are input in DROPLET for the calculation of the PEC_{Tier1} at the drinking water abstraction points in the Netherlands. We here compare m2t files of FOCUS-MACRO 4.4.2 to those of FOCUS-MACRO 5.5.3 and next also the resulting PEC_{max} in the NL D3 ditch of the two FOCUS-TOXSWA versions. Finally, we added the DROPLET calculations to obtain PEC_{Tier1} values.

The suite of models used for the PEC_Tier1 in the drinking water abstraction points by DROPLET 1.2 are listed below (called old suite) as well as the suite of newest released model versions used for DROPLET 1.3.2 runs (called new suite).

Old suite (DROPLET 1.2 model suite)

FOCUS-SWASH 3.1
FOCUS-MACRO 4.4.2
FOCUS-TOXSWA 3.3.1
DROPLET 1.2

New suite (DROPLET 1.3.2 model suite)

FOCUS-SWASH 5.3
SPIN 3.3
FOCUS-MACRO 5.5.3
FOCUS-TOXSWA 4.4.3
DROPLET 1.3.2

Note that the new suite now includes a SPIN substance database, because all substance input has been taken out of FOCUS-SWASH and entered in a new database called SPIN (acronym for Substance Plug IN, Van Kraalingen *et al.*, 2013), that serves not only the TOXSWA model, but also the greenhouse emission model GEM (Wipfler *et al.*, 2015) and the soil leaching model PEARL (Van den Berg *et al.*, 2015).

2 Method

In this chapter the procedures and setup of calculations for comparing the old with the new model suites are described. Simulations were done according to the standard FOCUS procedure for nine substances; a tracer, a pyrethroid and FOCUS example substances A, C, D, F, G, H and I. The only difference was that spray drift deposition onto the FOCUS D3 ditch was according to the Dutch drift table, used in the registration procedure for risks for drinking water abstraction (Table 1, based upon Appendix 4 of Van Leerdam *et al.*, 2010). Simulations were done for one application of 1 kg/ha in winter cereals in autumn with the standard application window offered in SWASH. For the tracer, the maximum number of eight applications was simulated as well (application window 27 Sep 1992-30 Apr 1993 and application interval of 21 d). The pyrethroid was run in TOXSWA for the standard sediment segmentation (i.e. not using the thinner segments).

In addition to differences in the source of the old and new model versions some parameter values have been changed, as can be seen by comparing the old and new version of SWASH. Table 2 presents an overview of the parameters that especially affect MACRO and TOXSWA.

The compound and management sections (6 and 7, resp.) of TOXSWA's txw input file is given in Appendix 1 for substance A. For the other substances the input is identical, only the Kom and DT50 values for degradation in soil, surface water and sediment differ, these are shown in Appendix 2. An overview of the input values for all nine substances, used in the calculations with the old as well as new MACRO and TOXSWA versions, is given in Appendix 3 (export of SPIN database).

Table 1. Spray drift on winter cereals: 1% (van Leerdam *et al.*, 2010; Appendix 4)

Applications	Dose per application (kg/ha)	Spray drift (%)
1	1	1
8	1	1

Table 2. Parameter values that differ between the old and new model suite.

	Old suite	New suite
TOXSWA and DROPLET Molar activation energy for the effect of temperature on transformation rate in water and in sediment	54 kJ/mol	65.4 kJ/mol
MACRO soil hydraulic functions	Brooks-Corey	Van Genuchten
MACRO Effect of temperature on transformation in soil	0.079	0.0948
MACRO and PRZM Exponent for the effect of moisture content on transformation rate in soil	0.7 (MACRO) 0.7 (PRZM)	0.49 (calibrated in MACRO) 0.7 (PRZM)

Below we first calculated the PEC_{max} in the NL D3 ditch water with the old and new model versions of MACRO and TOXSWA (Chapter 3, Tables 3 and 4) and determined for which simulations the differences were largest (Table 5). Secondly, to ascertain that the differences in the PEC_{max} were caused by differences between the old and new MACRO versions and not the old and new TOXSWA versions, we repeated the simulations by using m2t files of the old MACRO (vs 4.4.2) as input for the

new TOXSWA (vs 4.4.3) (Table 6) and compared their results to the results obtained with the old versions of MACRO and TOXSWA (Table 7).

Finally, we calculated the PEC_Tier1 at the drinking water abstraction points for the nine substances (Chapter 4). First we used the old and new model suites, as the obtained differences in PEC_Tier1 values are important for the Ctgb to estimate the regulatory impact of the DROPLET update. Next, we used the old and new version of DROPLET with identical input (the PEC_{max} in the NL-D3 ditch obtained by the old versions of MACRO and TOXSWA) to demonstrate that the update of the DROPLET model alone has no influence on the PEC_Tier1.

3 Comparison of simulation results by combinations of old and new versions of MACRO and TOXSWA

3.1 Overview of PEC_{max}, the maximum concentrations in the NL D3 ditch, for all simulations

The maximum concentrations, PEC_{max}, simulated for the NL D3 ditch by the old versions of the MACRO and PRZM model are presented in Table 3. The PEC_{max} ranges from 3.274 to 103.34 µg/L for the tracer (single application) and it is 279.04 µg/L for the tracer (eight applications).

A drift deposition of 1% of the applied 1 kg/ha on the D3 ditch (rectangular cross-section, water width of 1 m and water depth of 30 cm) corresponds to a deposition of 1 mg/m² and an increase in concentration of 3.33 µg/L, occurring at the time of application, i.e. 6 November 1992, at 9 am. This implies that the PEC_{max} of substances A, C, F, I and the pyrethroid that are close to 3.33 µg/L are caused by spray drift deposition (Table 3). No mass has been carried over from applications in the six years of the so-called warming-up period, as well for substance A and C because their half-life in soil is very short (3 d), so they degraded rapidly, as for substance F, I and the pyrethroid because their K_{oc} value is 1000 or 100 000 L/kg, resulting in negligible drainage mass fluxes after 1 year. The PEC_{max} of A, C, F and I are slightly lower than the 3.33 µg/L calculated above, 3.274 to 3.294 µg/L, because some mass has been sorbed instantaneously to the suspended solids. As expected the PEC_{max} of the pyrethroid is even lower, 3.038 µg/L, because of its high sorption capacity (K_{oc} of 100 000 L/kg).

Table 3. Maximum concentrations, timings and cause of peaks in NL D3 ditch water calculated by FOCUS-MACRO 4.4.2 and FOCUS-TOXSWA 3.3.1 (both part of the old model suite)

Substance	Timing applications (Date)	PEC _{max} (µg/L)	Timing PEC _{max} (Date)	Cause of peak
Tracer	06-Nov-1992-09h00	103.34	13-Sep-1992-08h00	drainage
Tracer 8 applns	26-Sep-1992-09h00 18-Oct-1992-09h00 14-Nov-1992-09h00 10-Dec-1992-09h00 31-Dec-1992-09h00 11-Feb-1993-09h00 16-Mar-1993-09h00 06-Apr-1993-09h00	279.04	14-Nov-1992-09h00	drift+drainage
A	06-Nov-1992-09h00	3.294	06-Nov-1992-09h00	drift
C	06-Nov-1992-09h00	3.274	06-Nov-1992-09h00	drift
D	06-Nov-1992-09h00	16.98	06-Nov-1992-09h00	drift+drainage
F	06-Nov-1992-09h00	3.274	06-Nov-1992-09h00	drift
G	06-Nov-1992-09h00	78.87	06-Nov-1992-09h00	drift+drainage
H	06-Nov-1992-09h00	23.94	06-Nov-1992-09h00	drift+drainage
I	06-Nov-1992-09h00	3.277	06-Nov-1992-09h00	drift
Pyrethroid	06-Nov-1992-09h00	3.038	06-Nov-1992-09h00	drift

Although substances D, G and H have their PEC_{max} also at 6 Nov 1992 9 am, their values are clearly higher than 3.33 $\mu\text{g/L}$, namely 16.98, 78.87 and 23.94 $\mu\text{g/L}$. So, their peak concentrations are caused not only by drift deposition, but by drift deposition falling on top of a sustained concentration level. The latter is caused by sustained drainage entries after applications of the six former warming-up years. Their combinations of $DT_{50,soil}$ and K_{oc} values (D: 30 d and 10 L/kg, G: 300 d and 10 L/kg and H: 300 d and 100 L/kg) are such that even a year later pesticide mass is still present in the drain flows, especially substance G with its relatively high $DT_{50,soil}$ and low K_{oc} value.

Finally the table presents two PEC_{max} values for the tracer occurring at other dates than the application date of 6 Nov 1992. As the tracer does not degrade nor sorb onto soil the PEC_{max} values are high, compared to those of the other substances. The PEC_{max} of 103.34 $\mu\text{g/L}$ at 13 Sept 1992 for the tracer (single application) is caused by a drainage entry. However, the PEC_{max} of 279.04 $\mu\text{g/L}$ at 14 Nov 1992 corresponds to the date of the third application of the tracer, applied in total eight times, implying that spray drift deposition as well as drainage entries cause this peak.

Table 4 presents the maximum concentrations, PEC_{max} , simulated for the NL D3 ditch by the new versions of the MACRO and PRZM model. The PEC_{max} ranges from 3.278 to 109.8 $\mu\text{g/L}$ for the tracer (single application) and it is 403.4 $\mu\text{g/L}$ for the tracer (eight applications). The reasoning for magnitude and cause for peak is analogue to the reasoning above for Table 3, except for the tracer applied 8 times. So, the PEC_{max} for substance A, C, F, I and the pyrethroid are caused by spray drift deposition only and for D, G and H by a spray drift deposition falling on top of sustained drainage entries. The dates of PEC_{max} for the tracer, both single and eight applications, indicate that in both cases drainage entries cause the peak concentrations, PEC_{max} and that these entries result from applications before the first application on 26 September 1992, i.e. they result from applications in the warming-up years. In Table 3 the peak of the tracer applied 8 times was caused by the third spray drift deposition event of the series starting 26 September 1992, falling on top of sustained drainage entries.

Table 4. Maximum concentrations, timings and cause of peaks in NL D3 ditch water calculated by FOCUS_MACRO 5.5.3 and FOCUS-TOXSWA 4.4.3 (both part of the new model suite)

Substance	Timing applications (Date)	PEC_{max} ($\mu\text{g/L}$)	Timing PEC_{max} (Date)	Cause of peak
Tracer	06-Nov-1992-09h00	109.8	15-Sep-1992-02h00	drainage
Tracer 8 applns	26-Sep-1992-09h00 18-Oct-1992-09h00 14-Nov-1992-09h00 10-Dec-1992-09h00 31-Dec-1992-09h00 11-Feb-1993-09h00 16-Mar-1993-09h00 06-Apr-1993-09h00	403.4	03-Jan-1992-01h00	drainage
A	06-Nov-1992-09h00	3.959	06-Nov-1992-09h00	(nearly only) drift
C	06-Nov-1992-09h00	3.278	06-Nov-1992-09h00	drift
D	06-Nov-1992-09h00	41.24	06-Nov-1992-09h00	drift+drainage
F	06-Nov-1992-09h00	3.278	06-Nov-1992-09h00	drift
G	06-Nov-1992-09h00	91.22	06-Nov-1992-09h00	drift+drainage
H	06-Nov-1992-09h00	30.85	06-Nov-1992-09h00	drift+drainage
I	06-Nov-1992-09h00	3.278	06-Nov-1992-09h00	drift
Pyrethroid	06-Nov-1992-09h00	3.043	06-Nov-1992-09h00	drift

Table 5 presents the comparison of the PEC_{max} values calculated by the old and the new versions of the MACRO and TOXSWA models. It shows an unexpected increase of the PEC_{max} values, especially for the PEC_{max} values above 3.33 µg/L that are mainly caused by drainage entries. Therefore, we expect that the output of the MACRO model has changed significantly going from version 4.4.2 to 5.5.3. The small differences of 0.1 to 0.2% in spray drift-caused PEC_{max} may be due to rounding off numbers in the TOXSWA model.

Table 5. Comparison of maximum concentrations in NL D3 ditch water calculated by the FOCUS models of MACRO and TOXSWA of the old and new model suites. Difference has been defined as 100* (PEC_{new} – PEC_{old}) / PEC_{old}

Substance	Old suite PEC max (µg/L)	New suite PEC max (µg/L)	Difference (%)
Tracer	103.34	109.8	6.3
Tracer 8 applns	279.04	403.4	44.6
A	3.294	3.959	20.2
C	3.274	3.278	0.1
D	16.98	41.24	142.9
F	3.274	3.278	0.1
G	78.87	91.22	15.7
H	23.94	30.85	28.8
I	3.277	3.278	0.0
Pyrethroid	3.038	3.043	0.2

To ascertain that the update of the TOXSWA model does not entail significant differences in PEC_{max} values, we also calculated the PEC_{max} values obtained by using the old version of MACRO and the new version of TOXSWA (Table 6) and compared these to the PEC_{max} of Table 3, obtained by the old versions of MACRO and TOXSWA (Table 7).

Table 6. Maximum concentrations, timings and cause of peaks in NL D3 ditch water calculated by MACRO 4.4.2 (version in old model suite) and FOCUS_TOXSWA 4.4.3 (version in new model suite)

Substance	Timing applications (Date)	PEC max (µg/L)	Timing PEC max (Date)	Cause of peak
Tracer	06-Nov-1992-09h00	103.3	13-Sep-1992-08h00	drainage
Tracer 8 applns	26-Sep-1992-09h00 18-Oct-1992-09h00 14-Nov-1992-09h00 10-Dec-1992-09h00 31-Dec-1992-09h00 11-Feb-1993-09h00 16-Mar-1993-09h00 06-Apr-1993-09h00	279.0	26-Sep-1992-09h00	drift+drainage
A	06-Nov-1992-09h00	3.295	06-Nov-1992-09h00	(nearly only) drift
C	06-Nov-1992-09h00	3.274	06-Nov-1992-09h00	drift
D	06-Nov-1992-09h00	17.01	06-Nov-1992-09h00	drift+drainage
F	06-Nov-1992-09h00	3.274	06-Nov-1992-09h00	drift
G	06-Nov-1992-09h00	78.89	06-Nov-1992-09h00	drift+drainage
H	06-Nov-1992-09h00	23.95	06-Nov-1992-09h00	drift+drainage
I	06-Nov-1992-09h00	3.277	06-Nov-1992-09h00	drift
Pyrethroid	06-Nov-1992-09h00	3.038	06-Nov-1992-09h00	drift

Table 7 shows that, except a few minor differences, the results of Table 6 are identical to those of Table 3, thus confirming that the differences are caused by the difference in drainage flux calculations by the old and new version of the MACRO model, 4.4.2 vs 5.5.3.

The minor differences of 0.03 to 0.21% in PEC_{max} in Table 7 are due to the difference in activation energy for transformation in the water (Table 2) and/or to rounding off numbers in the TOXSWA model.

Table 7. Comparison of maximum concentrations calculated by two versions of TOXSWA (old and new), but using the same m2t files (old) Difference has been defined as 100* ($PEC_{newTOXSWA+oldMACRO} - PEC_{old}$) / PEC_{old}

Substance	Old suite PEC_{max} ($\mu\text{g/L}$)	New TOXSWA coupled to old m2t file PEC_{max} ($\mu\text{g/L}$)	Difference (%)
Tracer	103.34	103.3	0.00
Tracer 8 applns	279.04	279.0	0.00
A	3.294	3.295	0.03
C	3.274	3.274	0.00
D	16.98	17.01	0.21
F	3.274	3.274	0.00
G	78.87	78.89	0.03
H	23.94	23.95	0.03
I	3.277	3.277	0.00
Pyrethroid	3.038	3.038	0.00

To get an impression of the importance of the change in Q10 value from 0.079 in the old version of MACRO to 0.0948 in the new version (see Table 2), we performed one simulation for substance D. Substance D has a $DegT_{50,soil}$ of 30 d and a K_{oc} value of 10 L/kg, so it is quite mobile. We redid a simulation for D with the entire old model suite, only changing the Q10 value into 0.0948. We obtained a PEC_{max} of 20.443 $\mu\text{g/L}$ instead of the 16.98 $\mu\text{g/L}$ of Table 3, so there is an increase in leaching of approximately 20% caused by the change in effect of temperature on degradation in soil.

As Table 7 convincingly demonstrates that the differences in the PEC_{max} of the NL D3 ditch water must originate from the differences between the old and new MACRO model versions, we next looked into detail to the water and mass fluxes of the old and new versions of the MACRO models and the resulting PEC as a function of time in the NL D3 ditches. We did so for the tracer with the single and eight applications and for substance D, G and H, i.e. substances with large differences in PEC_{max} .

3.2 Drainage water fluxes into NL D3 ditch

Figure 2 presents the drainage water flux for the 16 months' simulation period calculated by the old and new version of the MACRO model.

The water fluxes for the D3 ditch are identical for all substances. Highest water fluxes of ca. 0.09 $\text{mm}/(\text{m}^2 \text{ h})$ occur in January 1992 and the lowest of ca 0.01 (vs 4.4.2) and 0.02 (vs 5.5.3) $\text{mm}/(\text{m}^2 \text{ h})$ around day 250, i.e. in the beginning of September 1992. From November onwards the water fluxes rapidly increase again, up to ca 0.06 $\text{mm}/(\text{m}^2 \text{ h})$ and decrease after January 1993. An eye-catching difference between the water fluxes of the two versions is that the oscillations in fluxes in the old version do not figure anymore in the fluxes of the new version. Besides the disappearance of the oscillations, the water fluxes of the two MACRO versions only slightly differ.

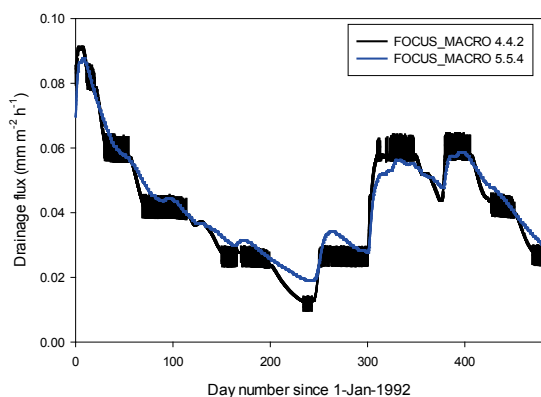


Figure 2
Drainage water flux for old and new MACRO (FOCUS_MACRO 4.4.2 and FOCUS_MACRO 5.5.3)

3.3 Simulations with tracer

Single application

The PEC_{max} for the tracer (single application) was 103.34 $\mu\text{g/L}$ for the old MACRO and TOXSWA versions and 109.8 $\mu\text{g/L}$ for the new versions, an increase of 6.3% (Table 5). Figure 3 presents the mass fluxes by drainage as well as the concentration in the NL D3 ditch water as a function of time for the 16 months' simulation period. Mass fluxes range from ca 0.027 down to 0.003 (MACRO vs 4.4.2) and 0.007 (MACRO vs 5.5.3) $\text{mg}/(\text{m}^2 \text{ h})$. So, they slightly differ (Figure 3 left).

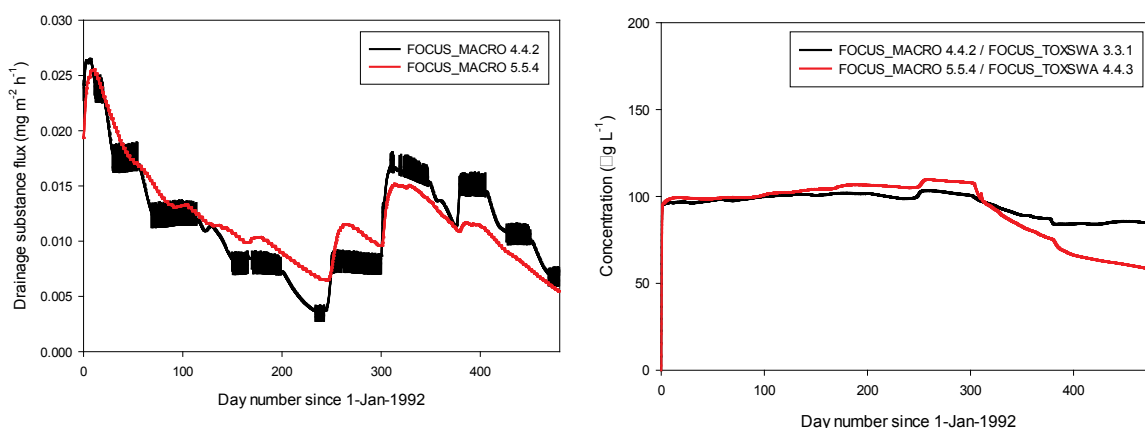


Figure 3 Drainage mass flux (left) and concentration in NL D3 ditch water (right) for the tracer (single application), calculated by the old and new model versions as indicated.

The concentrations in the ditch water differ slightly, but from approximately day 150-200 onwards differences increase. First the concentration by the new model versions increases more than the one by the old versions, the reason is that also the mass fluxes of the new versions increase more than the mass fluxes of the old versions. Later on, after day 300, the concentration of the new versions decreases faster than the concentration of the old versions, the reason is that the mass fluxes of the former decrease more than those of the latter (Figure 3 left). As well for the old as new MACRO fluxes Figure 3 shows that, surprisingly the maximum concentration occurs before the application of 6 Nov 1992, namely on 13, resp. 23 Sept 1992 (the right-hand graph: little peak after day 300 being lower than the plateau value before). This is confirmed by the values in Table 3 and 4, and is caused by drainage of mass applied during the six year warming-up period before 1st January 1992.

Eight applications

The PEC_{max} for the tracer (eight applications) was 279.04 $\mu\text{g/L}$ for the old MACRO and TOXSWA versions and 403.4 $\mu\text{g/L}$ for the new versions, an increase of 44.6% (Table 5). Figure 4 presents the mass fluxes by drainage as well as the concentration in the NL D3 ditch water for the 16 months' simulation period. The mass fluxes are about 4x higher than the fluxes from the single application. They considerably differ between the two MACRO versions and range from ca 0.05 down to 0.01 $\text{mg}/(\text{m}^2 \text{ h})$ (vs 4.4.2) and from 0.11 down to 0.02 $\text{mg}/(\text{m}^2 \text{ h})$ (vs 5.5.3).

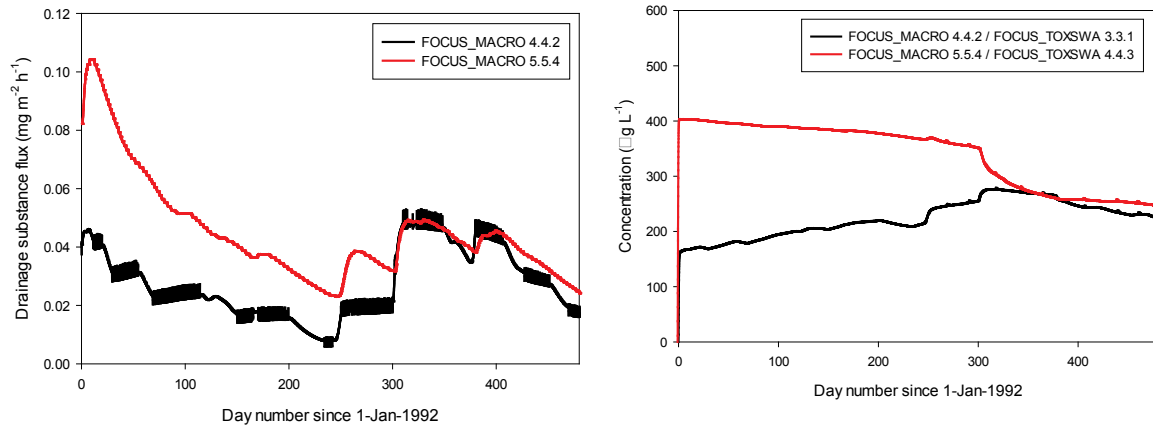


Figure 4 Drainage mass flux (left) and concentration in NL D3 ditch water (right) for the tracer (8 applications), calculated with old and new model versions as indicated.

The concentrations in the ditch water also considerably differ, especially from day 0 to approximately 300: initially, around day 0, the concentration by the new MACRO fluxes increases rapidly up to the value of 403.4 $\mu\text{g/L}$ due to the initial high mass flux of around 0.10 $\text{mg}/(\text{m}^2 \text{ h})$ of the new MACRO and thereafter the difference gradually lowers, but remains considerable. From day 300 onwards the difference is smaller. The PEC_{max} is at 14 Nov 1992 (day number 319) for the old model versions and at 10 January 1992 (day number 10) for the new versions (Tables 3 and 4) and in both cases by drainage entries. Although the PEC_{max} at 10 January 1992 is caused by drainage entries it may possibly be on an application day of one of the eight applications started in the autumn of the former year. We cannot confirm this as the selected application days of the warming-up period are no output of the models.

3.4 Simulations with substance D

The PEC_{max} for the substance D was 16.98 $\mu\text{g/L}$ for the old MACRO and TOXSWA versions and 41.24 $\mu\text{g/L}$ for the new versions, an increase of 142.9% (Table 5). This is the largest relative difference of all nine substances.

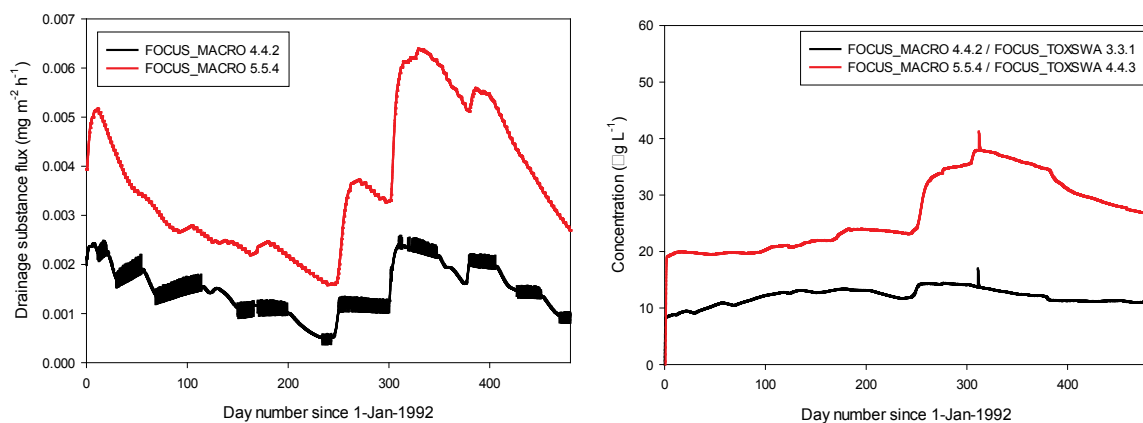


Figure 5 Drainage mass flux (left) and concentration in NL D3 ditch water (right) for substance D ($K_{oc} = 10 \text{ L/kg}$, $DT_{50,soil} = 30 \text{ d}$ and $DT_{50,water} = 10 \text{ d}$), calculated by the old and new model versions as indicated..

The mass fluxes by drainage of the new MACRO version are approximately 2x higher than those of the old MACRO version for substance D (Figure 5 left), they range from nearly 0.007 down to 0.002 mg/(m² h) and 0.003 down to 0.0005 mg/(m² h).

As the water fluxes did not change significantly between the two versions, the concentrations in the ditch water are also approximately a factor 2 higher for the new MACRO version (Figure 5 right). In both cases the spray drift deposition comes on top of drainage entries and causes the PEC_{max} (Tables 3 and 4).

3.5 Simulations with substance G

The PEC_{max} for the substance G was 78.87 µg/L for the old MACRO and TOXSWA versions and 91.22 µg/L for the new versions, an increase of 15.7% (Table 5). Figure 6 presents the mass fluxes by drainage as well as the concentration in the NL D3 ditch water for the 16 months' simulation period. The mass fluxes only slightly differ between the two MACRO versions: they range from ca 0.017 down to 0.002 mg/(m² h) (vs 4.4.2) and from 0.018 down to 0.005 mg/(m² h) (vs 5.5.3).

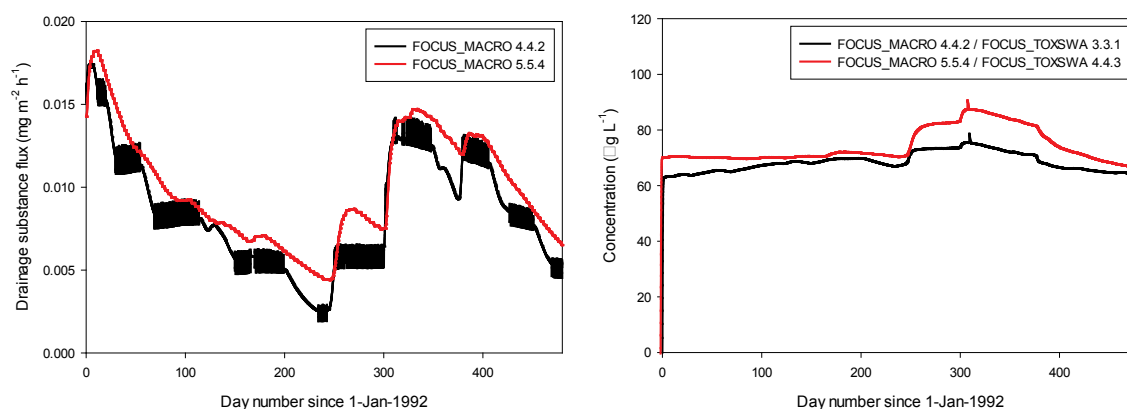


Figure 6 Drainage mass flux (left) and concentration in NL D3 ditch water (right) for substance G ($K_{oc} = 10$ L/kg, $DT_{50,soil} = 300$ d and $DT_{50,water} = 100$ d), calculated by the old and new model versions as indicated.

As the mass fluxes only slightly differ between the MACRO versions, the resulting concentrations in the ditch water also do not differ much (Figure 6 right). The figure clearly shows that the PEC_{max} values are caused by a spray drift deposition on top of sustained drainage entries.

3.6 Simulations with substance H

The PEC_{max} for the substance H was 23.94 µg/L for the old MACRO and TOXSWA versions and 30.85 µg/L for the new versions, an increase of 28.8% (Table 5).

The mass fluxes by drainage by the new MACRO are clearly higher than those of the old MACRO version for substance H (Figure 7 left), they range from approximately 0.007 down to 0.002 mg/(m² h) and 0.005 to 0.0005 mg/(m² h).

As the water fluxes do not differ significantly between the two MACRO versions the concentrations in the ditch water are also clearly higher for the simulations with new MACRO version (Figure 7 right). The figure clearly shows that the PEC_{max} values are caused by a spray drift deposition on top of sustained drainage entries.

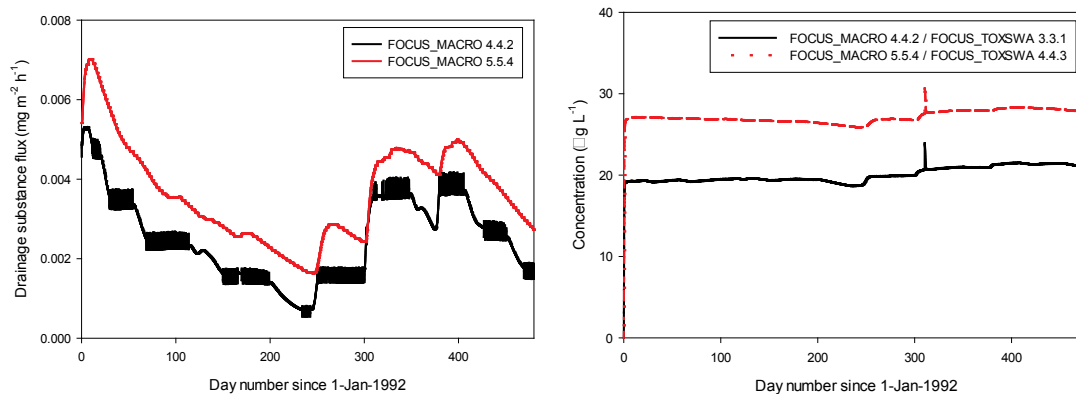


Figure 7 Drainage mass flux (left) and concentration in NL D3 ditch water (right) for substance H ($K_{oc} = 100$ L/kg, $DT_{50,soil} = 300$ d and $DT_{50,water} = 100$ d), calculated by the old and new model versions as indicated.

3.7 Changes between MACRO model versions 4.4.2 and 5.5.3

Below we list the main changes between the MACRO model versions 4 and versions 5 (Pers. comm. N. Jarvis, 24 November and 13 December 2017). The overview did not allow us to relate the details of the changes in mass fluxes of the tracer, substance D, G or H for the D3 ditch scenario to the distinct, individual changes in the model.

During the release procedure of FOCUS-MACRO version 5 it had already been identified that Predicted Environmental Concentrations in the FOCUS surface water bodies had increased significantly with the transition from version 4.4.2 to version 5.5.3 for some scenarios, especially those heavily influenced by macropore transport. For the most critical scenario for registration, D2, a study had been performed to identify options for re-alignment to the results of version 4.4.2 (Beulke, 2014). Finally, FOCUS-MACRO version 5.5.3 had been released by FOCUS Version Control after calibration of the results of D2 to match those of version 4.4.2 as well as possible (<http://eussoils.jrc.ec.europa.eu/projects/focus-dg-sante>). The results of the D3 scenario were not considered in 2013-2014, as this scenario, the only one without macropore transport, generally is not critical in the exposure assessment at EU level.

In general, it can be stated that for the D3 ditch the changes in the MACRO model had more influence on the substances that leach most, i.e. that have a relatively low K_{oc} (e.g. substance D and G and H with their K_{oc} values of 10, 10 and 100 L/kg respectively) and do not disappear very rapidly (such as e.g. substance A, B and C with their $DegT_{50,soil}$ of 3 d).

The main changes in the model itself were:

- a. New implicit numerical solutions to flow and transport equations
- b. Much improved discretization in the soil profile (200 instead of 20 segments, so much thinner soil segments)
- c. Change from Brooks-Corey to Van Genuchten soil hydraulic functions
- d. New function for water content effects on degradation.

The main changes in the parameterization were (see also Table 2 in Chapter 2):

- a. Parameter controlling temperature effect on degradation (0.079 to 0.0948)
- b. Parameter controlling water content effect on degradation (0.7 to 0.49), in order to try to maintain 'back-compatibility' with the previous function
- c. Mixing depth reduced, to try to minimize effects of changed discretization (to maintain 'back-compatibility'). Note that this item will probably not have any effect at the D3 scenario.

4 Comparison of PEC_Tier1, the maximum concentration at the drinking water abstraction points, by the old and new model suites

Below we first present the PEC_Tier1, i.e. the PEC in the drinking water abstraction points, calculated by the old and new model suite. The difference between the old and new PEC_Tier1 is what the Ct_g will be confronted with after their update of DROPLET to DROPLET version 1.3.2. As demonstrated before this difference is mainly due to the difference in calculated drainage entries between the old MACRO (vs 4.4.2) and the new MACRO (vs 5.5.3) and thus not due to the DROPLET update. We will confirm this by presenting PEC_Tier1 results in which only the DROPLET version had been changed (Appendix 5).

We first calculated the PEC_Tier1¹ by the old and the new model suite, using the PEC_{max} in the NL D3 ditch of respectively Table 3 and Table 4. Tables 8 to 12 present the PEC_Tier1 for the nine substances and tracer with eight applications for the nine abstraction points. Appendix 4 presents the input and output files for substance A used for DROPLET 1.2.

Table 8 Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for the tracer (1 and 8 applications) calculated by the old and new model suite.

Abstraction point	Tracer (1 appln)			Tracer (8 applns)		
	old	new	difference (%)	old	new	difference(%)
De Punt	4.359	4.632	6.26	11.769	17.018	44.60
Andijk	0.383	0.407	6.27	1.035	1.497	44.64
Nieuwegein	2.430	2.582	6.26	6.560	9.486	44.60
Heel	5.498	5.843	6.28	14.846	21.468	44.60
A'dam-Rijnkanaal	1.961	2.084	6.27	5.296	7.657	44.58
Brakel	2.100	2.232	6.29	5.672	8.201	44.59
Petrusplaat	2.063	2.193	6.30	5.571	8.055	44.59
Twentekanaal	0.677	0.719	6.20	1.827	2.642	44.61
Scheelhoek	2.724	2.895	6.28	7.355	10.635	44.60
Bommelerwaard	0.987	1.049	6.28	2.666	3.855	44.60

Table 9 Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for substance A and C calculated by the old and new model suite

Abstraction point	Substance A			Substance C		
	old	new	difference (%)	old	new	difference (%)
De Punt	0.001	0.002	100.00	0.001	0.002	100.00
Andijk	0.000	0.000	0.00	0.000	0.000	0.00
Nieuwegein	0.001	0.001	0.00	0.001	0.001	0.00
Heel	0.002	0.003	50.00	0.002	0.002	0.00
A'dam-Rijnkanaal	0.001	0.001	0.00	0.001	0.001	0.00
Brakel	0.001	0.001	0.00	0.001	0.001	0.00
Petrusplaat	0.001	0.001	0.00	0.001	0.001	0.00
Twentekanaal	0.000	0.000	0.00	0.000	0.000	0.00
Scheelhoek	0.001	0.001	0.00	0.001	0.001	0.00
Bommelerwaard	0.005	0.006	20.00	0.005	0.005	0.00

¹ For all calculations of Tables 8-12 drainage was attributed as main cause in the DROPLET UI, tab 'Wizard: Enter Peak (3/4)' for the PEC_{max} in case drift+drainage were mentioned in Table 3 or 4. Note that this does not correspond to the current guidance given in 7.3.1 of Van Leerdam *et al*, 2010. The calculation of the PEC_Tier1 was further straightforward.

Table 10. Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for substance D and F calculated by the old and new model suite

Abstraction point	Substance D			Substance F		
	old	new	difference (%)	old	new	difference (%)
De Punt	0.541	1.344	148.43	0.017	0.018	5.88
Andijk	0.048	0.118	145.83	0.002	0.002	0.00
Nieuwegein	0.302	0.749	148.01	0.010	0.010	0.00
Heel	0.683	1.695	148.17	0.022	0.022	0.00
A'dam-Rijnkanaal	0.243	0.605	148.97	0.008	0.008	0.00
Brakel	0.261	0.648	148.28	0.008	0.009	12.50
Petrusplaat	0.256	0.636	148.44	0.008	0.008	0.00
Twentekanaal	0.084	0.209	148.81	0.003	0.003	0.00
Scheelhoek	0.338	0.840	148.52	0.011	0.011	0.00
Bommelerwaard	0.162	0.394	143.21	0.005	0.005	0.00

Table 11 Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for substance G and H calculated by the old and new model suite

Abstraction point	Substance G			Substance H		
	old	new	difference (%)	old	new	difference (%)
De Punt	3.243	3.759	15.91	0.984	1.271	29.17
Andijk	0.285	0.331	16.14	0.087	0.112	28.74
Nieuwegein	1.808	2.095	15.87	0.549	0.709	29.14
Heel	4.091	4.742	15.91	1.242	1.604	29.15
A'dam-Rijnkanaal	1.459	1.691	15.90	0.443	0.572	29.12
Brakel	1.563	1.811	15.87	0.474	0.613	29.32
Petrusplaat	1.535	1.779	15.90	0.466	0.602	29.18
Twentekanaal	0.503	0.584	16.10	0.153	0.197	28.76
Scheelhoek	2.027	2.349	15.89	0.615	0.794	29.11
Bommelerwaard	0.754	0.872	15.65	0.229	0.295	28.82

Table 12 Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for substance I and the pyrethroid calculated by the old and new model suite

Abstraction point	Substance I			Pyrethroid		
	old	new	difference (%)	old*	new	difference (%)
De Punt	0.022	0.023	4.55	<0.021	<0.021	0.00
Andijk	0.002	0.002	0.00	<0.002	<0.002	0.00
Nieuwegein	0.013	0.013	0.00	<0.012	<0.012	0.00
Heel	0.028	0.028	0.00	<0.027	<0.027	0.00
A'dam-Rijnkanaal	0.010	0.010	0.00	<0.010	<0.010	0.00
Brakel	0.011	0.011	0.00	<0.010	<0.010	0.00
Petrusplaat	0.011	0.011	0.00	<0.010	<0.010	0.00
Twentekanaal	0.003	0.003	0.00	<0.003	<0.003	0.00
Scheelhoek	0.014	0.014	0.00	<0.013	<0.013	0.00
Bommelerwaard	0.005	0.005	0.00	<0.005	<0.005	0.00

* For this project the current Tier1 calculation method does not result in realistic PEC-Tier1 values. Therefore they have been replaced by "< calculated value µg/L". The Tier1 calculation method does not account for sorption of mass entered by spray drift deposition. For the current substance with a Kom greater than 10000 L/kg this artefact results in unrealistically high values of the calculated PEC-Tier1. Based upon calculations reported in Appendix 9 of the DROPLET user manual (Van Leerdam *et al.*, 2010), we suggest to divide the calculated values by a factor of 5.

Considering the columns with the percentage difference in PEC_Tier1 of Tables 8 to 12 we see that for each of the substances the difference is virtually identical for each of the nine abstraction points. The reason is that the PEC_Tier1 in all extraction points have the same new value of PEC_{max} in the D3 ditch with NL drift deposition as input and are a linear function of this PEC_{max}. Excluding very low PEC_Tier1 values (below around 0.01-0.02 µg/L) the percentages difference range from approximately 6 to 150% for the substances considered and they are always positive, so there is an increase in concentration. So, for the example calculations shown the PEC_Tier1 is maximally a *factor of approximately 2.5 higher* in the updated model suite.

The percentage for the Bommelerwaard often is slightly different from the percentage for the nine abstraction points. Its results are presented separately from the nine abstraction points for drinking water production. The reason is that the Bommelerwaard is a subarea of the Brakel intake area, adjacent to the abstraction point of Brakel. As the quality of the abstracted water at Brakel is strongly influenced by water pumped from the Bommelerwaard polder, the concentration at the abstraction point Brakel has been calculated on the basis of agriculture in the Bommelerwaard only. The authors of *Adriaanse et al (2008)* suggest to compare the result of the Bommelerwaard calculation to the general PEC_Tier1 for Brakel, select the highest and thus assess the risks for drinking water production at Brakel in a conservative way. The Bommelerwaard has intensive agriculture including glasshouses and pesticides have been detected in its surface waters in the past (*Adriaanse et al, 2008*).

In Appendix 5 we compared the PEC_Tier1 of the old model suite to the PEC_Tier1 of the old MACRO/TOXSWA plus new DROPLET 1.3.2, i.e. the PEC_Tier1 calculated by FOCUS-SWASH 3.1, FOCUS-MACRO 4.4.2, FOCUS-TOXSWA 3.3.1 and DROPLET 1.2 was compared to the PEC_Tier1 calculated by FOCUS-SWASH 3.1, FOCUS-MACRO 4.4.2, FOCUS-TOXSWA 3.3.1, coupled to FOCUS-SWASH 5.3, SPIN 2.2 and DROPLET 1.3.2. This was done for the nine compounds and the nine abstraction points for drinking water production, plus the Bommelerwaard.

As expected, the comparison indicates that the upgrade of DROPLET 1.2 to 1.3.2 does not influence the calculation of the PEC_Tier1. All PEC_Tier1 values of the old model suite are identical to the PEC_Tier1 values of the old MACRO/TOXSWA plus new DROPLET 1.3.2.

(Note that before running DROPLET 1.3.2 the molar activation energy for the effect of temperature on the transformation rate in water and in sediment had been set equal to 54 kJ/mol, i.e. the value in the old versions of SWASH and TOXSWA (FOCUS_SWASH 3.1 and FOCUS_TOXSWA 3.3.1) in order to be able to compare DROPLET 1.2 to DROPLET 1.3.2 for exactly the same substance input parameters.).

5 Conclusions and recommendations

The release of an updated DROPLET version that is coupled to the most recent releases of the FOCUS-MACRO and FOCUS-TOXSWA models, versions 5.5.3 and 4.4.3 respectively, results in PEC_Tier1 values at the drinking water abstraction points that are maximally a *factor of approximately 2.5 higher* than PEC_Tier1 from the former suite of models. So, for the same compound and use pattern as before the risk assessment now may indicate *higher risks than before*. This implies that the new release of DROPLET may have impact on decisions made in the registration procedure of the Netherlands.

The difference in PECs at the drinking water abstraction points is practically entirely due to the increased drainage fluxes simulated by the new FOCUS-MACRO model. It has been demonstrated that the new FOCUS-TOXSWA and DROPLET models do not result in increased PEC values at the drinking water abstraction points.

The important changes made in the model concepts of the FOCUS_MACRO model version 5.5.3, especially the improved discretisation of the soil profile, account for the increased drainage fluxes in the D3 scenario. It is unclear whether these increased fluxes reflect better reality or not, because no comparison to fluxes of a field study has been performed with MACRO for the D3 scenario.

The change in PECs is largest at the drinking water abstraction points for compounds that are relatively mobile (K_{oc} around 100 L/kg or smaller) and/or persistent in soil ($DegT_{50,soil}$ 30 d or greater), e.g. the tracer, substance D, G and H.

As it is unclear which version of MACRO results in drainage fluxes reflecting best reality for the D3 scenario, we recommend to (i) perform a field study for validation, comparing simulated drainage water and pesticide mass fluxes to measured fluxes for the D3 scenario, or (ii) perform such a study at a location with similar characteristics, i.e. no macropore transport, but only transport through the soil matrix, or (iii) compare simulation results of MACRO version 4.4.2 and version 5.5.3 to existing measurements in soil at the D3 scenario location, Vredepeel.

Because there are no measured water and mass fluxes for drainage available for the D3 scenario, it is not possible to indicate whether the results of MACRO 4.4.2 or those of MACRO 5.5.3 reflect better reality. So, it is not possible to make any recommendation on the preferred model suite for use in the exposure assessment procedure at EU level and in The Netherlands: DROPLET 1.2 model suite containing the MACRO 4.4.2 version or DROPLET 1.3.2 model suite containing the MACRO 5.5.3 version.

The update of the DROPLET 1.2 model suite to DROPLET 1.3.2 model suite led to a surprising increase in peak concentration in the D3 ditch of a factor up to 2.5. This may influence the evaluation of the drinking water standard in the Dutch registration procedure, performed by the Ctgb. Therefore we suggest for future updates of FOCUS models to make a systematic comparison between results of the former and future model version for a range of compounds and all scenarios in order to avoid such surprises.

References

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List of used abbreviations

Variable	Description
m2t output file	output file from the MACRO model that is input to the TOXSWA model, containing hourly drainage water and mass fluxes
PEC _{max}	Maximum Predicted Environmental Concentration in water of the FOCUS D3 ditch receiving spray drift deposition according to Dutch deposition numbers
PEC_Tier1	Predicted Environmental Concentration at the surface water abstraction points for drinking water production

Justification

Since the release of version DROPLET 1.2 in 2014, new versions of the other models in the DROPLET model suite, i.e. FOCUS-MACRO and FOCUS-TOXSWA, have been released to assess the exposure concentrations of plant protection products at the EU level. Therefore, an updated version of DROPLET was needed using these new versions. This report presents the results of the comparison of the pesticide concentrations at surface water abstraction points for the production of drinking water in The Netherlands calculated by DROPLET 1.2 to those calculated by the DROPLET 1.3.2 model suite.

The report was written by Paulien Adriaanse and Wim Beltman from Wageningen Environmental Research (WENR). Nick Jarvis from the Swedish University of Agricultural Sciences was consulted on the FOCUS-MACRO model and Anton Poot of the Ctgb commented on drafts of the report. The project was supervised by Jennie van der Kolk (contact of WOT N&M, theme Agri-environment) and seen and approved by Miranda Meijsters (Ministry of Agriculture, Nature and Food Quality).

Annex 1 Compound and application management

Compound and application management sections of the txw file for substance A (FOCUS_TOXSWA 4.4.3)

```
*-----
*
* Section 6: Compound section
*-----
*
A                    SubstanceName        ! Name of parent substance

table compounds                    ! List of substances
A
end_table

* Substance properties for each substance given in table compounds
* Substance code is extension of parameter name
*----- Parent: A -----

300.                MolMas_A (g.mol-1) ! Molar mass of parent substance [10.0 - 10000]

1.                  DT50WatRef_A (d)    ! Half-life transformation in water [0.1 - 100000]
20.                TemRefTraWat_A (C) ! Temperature at which half-life was measured [5.0 - 30]
65.4               MolEntTraWat_A (kJ.mol-1) ! Molar activation enthalpy of transformation in water [0.0 - 200]
3.                  DT50SedRef_A (d)    ! Half-life transformation in sediment [0.1 - 100000]
20.                TemRefTraSed_A (C) ! Temperature at which half-life was measured [5.0 - 30]
65.4               MolEntTraSed_A (kJ.mol-1) ! Molar activation enthalpy of transformation in sediment [0.0 - 200]

5.80046403712297 KomSed_A (L.kg-1) ! Coefficient of equilibrium sorption in sediment [0.0 - 10000000]
1.                  ConLiqRefSed_A (mg.L-1) ! Reference concentration in liquid phase in sediment [0.001 - 100]
1.                  ExpFreSed_A (-)    ! Freundlich exponent in sediment [0.1 - 2]
5.80046403712297 KomSusSol_A (L.kg-1) ! Coefficient of equilibrium sorption suspended solids [0.0 - 10000000]
1.                  ConLiqRefSusSol_A (mg.L-1) ! Reference concentration in liquid phase suspended solids [0.001 - 100]
1.                  ExpFreSusSol_A (-) ! Freundlich exponent suspended solids [0.1 - 2]

0.                  CofSorMph_A (L.kg-1) ! Coefficient for linear sorption on macrophytes [0.0 - 20000]

1.E-7               PreVapRef_A (Pa) ! Saturated vapour pressure [0.0 - 200000]
20.                TemRefVap_A (C) ! Temperature of reference at which the saturated vapour pressure was measured [0.0 - 40]
95.                MolEntVap_A (kJ.mol-1) ! Molar enthalpy of the vaporization process [-200 - 200]

1.                  SlbWatRef_A (mg.L-1) ! Water solubility [0.001 - 1000000]
20.                TemRefSlb_A (C) ! Temperature of reference at which the water solubility was measured [0.0 - 40]
27.                MolEntSlb_A (kJ.mol-1) ! Molar enthalpy of the dissolution [-200 - 200]
4.3E-5              CofDifWatRef_A (m2.d-1) ! Reference diffusion coefficient in water [0.0 - 200]
```

```

*-----
*
* Section 7: Management section
*-----
*
* Loading options (OptLoa):
* DriftOnly = spray drift only entry route
* PEARL      = drainage calculated by PEARL
* MACRO      = drainage calculated by MACRO
* PRZM       = runoff and erosion calculated by PRZM
* GEM        = point source calculated by GEM

MACRO          OptLoa          ! Loading options (DriftOnly, PEARL, MACRO, PRZM, GEM)

FOCUS_EXAMPLE ApplicationScheme ! Name of the application scheme

* Table loadings
* Column 1: Date of application, relevant if OptLoa = DriftOnly, otherwise the date is a dummy values
* Column 2: Type of loading (-)
* Column 3: Drift deposition (mg.m-2) []
* Column 4: Start of stretch of watercourse loaded by all loading types (m) []
* Column 5: End of stretch of watercourse loaded by all loading types (m)[]

table Loadings
01-Jan-1970  drift    1.        0.        100.
end_table

* If: OptLoa = MACRO or OptLoa = PRZM
* Table with path+name of lateral entries files

table Soil substance files
C:\SwashProjects\project_A\MACRO\cereals_winter\macro00021_p.m2t
end_table

```


Annex 2 Properties of substances used in example runs

Test compounds A, C, D, F, G, H and I taken from FOCUS (2001) and the tracer and pyrethroid were added by the authors.

	Example Compound:									tracer	pyrethroid
	A	B	C	D	E	F	G	H	I		
Molar mass (g/mol)	300 for all compounds										
Vapour pressure (Pa @ 20°C)	1.0 x 10 ⁻⁷ for all compounds										
Water solubility (mg/L @ 20°C)	1.0 for all compounds										
Log Kow	0.2	2.1	4.1	0.2	2.1	4.1	0.2	2.1	4.1	-	-
Application rate (kg/ha)	1										
Soil half-life (days)	3	3	3	30	30	30	300	300	300	1000	1000
Koc (cm³ g⁻¹)	10	100	1000	10	100	1000	10	100	1000	0	100 000
Freundlich 1/n	1										
Surface water half-life (days)	1	1	1	10	10	10	100	100	100	1000	1000
Sediment half-life (days)	3	3	3	30	30	30	300	300	300	1000	1000
Total system half-life (days)	1	1	2	10	12	22	102	126	219	-	-

Annex 3 Properties of example substances in the old and new model suite

The substance properties of the nine example substances are used in the old and new model runs, taken from the SPIN database

Table A3-1 specifies the substance properties used in the calculations by the new model suite. For calculations by the old suite two parameter values differ:

- 1 the exponent for effect of moisture content on transformation in soil, ExpLiqTraCal (MACRO), and
- 2 the molar enthalpy of transformation; in soil ExpTemTra (MACRO) and in water and in sediment; MolEntTraWat and MolEntTraSed (TOXSWA).

See Table 2 in the main text for the values used in the old suite.

Table A3-1 Substance properties in SPIN database used for calculations with the new model suite

SubstanceCode	Name	MolMass (g mol ⁻¹)	PreVapRef (Pa)	TemRefVap (°C)	MolEntVap (kJ mol ⁻¹)	SibWatRef (mg L ⁻¹)	TemRefSib (°C)	MolEntSib (kJ mol ⁻¹)	KomEqL (L kg ⁻¹)	ExpFre (-)	ExpFreSed (-)	ExpFreSus (-)	KsonMph (L kg ⁻¹)	KomSed (L kg ⁻¹)	KomSus (L kg ⁻¹)	ConLiqRefSed (mg L ⁻¹)	ConLiqRefSus (mg L ⁻¹)	DTS0Ref (d)	DTS0SedRef (d)	DTS0WatRef (d)	TemRefTra (°C)	TemRefTraSed (°C)	TemRefTraWat (°C)	OptCntLiqTraRef (-)	ExpLiqTra (-)	FacUpt (-)	FacWasCp (m ⁻¹)	DTS0DspCp (d)	CofDirAirRef (m ² d ⁻¹)	CofDirWatRef (m ² d ⁻¹)	MolEntTraSed (kJ mol ⁻¹)	MolEntTraWat (kJ mol ⁻¹)	ExpTemTra (K ⁻¹)	PfTra (log(cm))	CntLiqTraMea (%)	OptCntLiqTraMea (-)	ExpLiqTraCal (-)
A	DROPLET A	300	1.00E-07	20	95	1	20	27	5.800464	1	1	1	0	5.800464	5.800464	1	1	3	3	1	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49
C	DROPLET C	300	1.00E-07	20	95	1	20	27	580.0464	1	1	1	0	580.0464	580.0464	1	1	3	3	1	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49
D	DROPLET D	300	1.00E-07	20	95	1	20	27	5.800464	1	1	1	0	5.800464	5.800464	1	1	30	30	10	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49
F	DROPLET F	300	1.00E-07	20	95	1	20	27	580.0464	1	1	1	0	580.0464	580.0464	1	1	30	30	10	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49
G	DROPLET G	300	1.00E-07	20	95	1	20	27	5.800464	1	1	1	0	5.800464	5.800464	1	1	300	300	100	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49
H	DROPLET H	300	1.00E-07	20	95	1	20	27	58.00464	1	1	1	0	58.00464	58.00464	1	1	300	300	100	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49
I	DROPLET I	300	1.00E-07	20	95	1	20	27	580.0464	1	1	1	0	580.0464	580.0464	1	1	300	300	100	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49
Pyrt	DROPLET Pyreth	300	1.00E-07	20	95	1	20	27	58004.64	1	1	1	0	58004.64	58004.64	1	1	1000	1000	1000	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49
Tracr	DROPLET Tracer	300	1.00E-07	20	95	1	20	27	0	1	1	1	0	0	0	1	1	1000	1000	1000	20	20	20	Yes	0.7	0.5	50	10	0.4	4.30E-05	65.4	65.4	0.0948	2	100	1	0.49

Table A3-2 Description of substance properties given in Table 3-1, with their units

Name	Units	Description
CntLiqTraMea	%	Moisture content (%) at which half-life is measured for transformation in soil
CntLiqTraRef	kg kg-1	Liquid content in incubation experiment for transformation in soil
CofDifAirRef	m ² d-1	Reference diffusion coefficient in air
CofDifWatRef	m ² d-1	Reference diffusion coefficient in water
ConLiqRef	mg L-1	Reference concentration in liquid phase - soil
ConLiqRefSed	mg L-1	Reference concentration in liquid phase - sediment
ConLiqRefSus	mg L-1	Reference concentration in liquid phase - suspended solids
DT50Ref	d	Half-life in soil
DT50SedRef	d	Half-life in sediment
DT50TraCrp	d	Half-life due to transformation at crop
DT50WatRef	d	Half-life in water
ExpFre	-	Freundlich sorption exponent in soil
ExpFreSed	-	Freundlich sorption exponent in sediment
ExpFreSus	-	Freundlich sorption exponent in suspended solids
ExpLiqTra	-	Exponent for the effect of liquid for transformation in soil
ExpLiqTraCal	-	Calibrated value of the exponent for the effect of liquid for transformation in soil
ExpTemTra	K-1	Effect of temperature fro transformation in soil
FacUpt	-	Coefficient for uptake by plant (TSCF)
FacWasCrp	m-1	Wash-off factor
KomEqL	L kg-1	Coefficient for equilibrium sorption on organic matter in soil
KomSed	L kg-1	Coefficient for sorption in sediment
KomSus	L kg-1	Coefficient for sorption in suspended solids
KsorEqL	L kg-1	Freundlich coefficient for equilibrium sorption
KsorMph	L kg-1	Coefficient for linear sorption on macrophytes
MolEntSlb	kJ mol-1	Molar enthalpy of dissolution in water
MolEntTra	kJ mol-1	Molar activation energy for transformation in soil
MolEntTraSed	kJ mol-1	Molar activation energy for transformation in sediment
MolEntTraWat	kJ mol-1	Molar activation energy for transformation in water
MolEntVap	kJ mol-1	Molar enthalpy of vaporisation
MolMass	g mol-1	Molar mass
PfTra	log(cm)	pF at which DT50 in soil is measured (1,2)
PreVapRef	Pa	Saturated vapour pressure
SlbWatRef	mg L-1	Solubility in water
TemRefDif	°C	Reference temperature for diffusion in water
TemRefSlb	°C	Temperature at which solubility in water is measured
TemRefTra	°C	Temperature at which half-life in soil is measured
TemRefTraAir	°C	Temperature at which half-life in air is measured
TemRefTraSed	°C	Temperature at which half-life in sediment is measured
TemRefTraWat	°C	Temperature at which half-life in water is measured
TemRefVap	°C	Temperature at which saturated vapour pressure is measured

Annex 4 Input files and output file for substance A of DROPLET 1.2.

CompoundProperties.inp file

```
* Summary of used pesticide property data
*
* Project name       : Asw
* Created at        : 10/31/2017 2:30:47 PM
* Version DROPLET GUI : 1.2
*
* DT50-w & T_w     = half-life time in water [d] and temperature [K]
* Solub & T_sol    = Solubility [mg/L] & temperature at which this is determined [K]
* M_mass           = Molar mass of pesticide [g]
* Psat & T_vap     = Saturated vapour pressure [Pa] & temperature at which this is determined [K]
* KOM              = "General" or "detailed sediment" organic matter-water partitioning coefficient [L/kg]
* E_arrh           = molar Arrhenius activation energy for transformation rate
*
* pesticide         DT50-w   T_w     Solub   T_sol   M_mass   Psat    T_vap   Kom     E_arrh
*                   [d]      [K]    [mg/L]  [K]    [g/mol]  [Pa]    [K]    [L/kg]  [J/mol]
Dummy_compound_A_sw 1.0     293.0  1.0E+000 293.0   300.00  1.0E-007 293.0   5.80    54000.0
```

CropPEC.inp file

```
* Relevant crops and PEC values for Dummy compound A_sw compound, market share and additional dilution
factors
*
* Project name       : Asw
* Created at        : 10/31/2017 2:30:47 PM
* Version DROPLET GUI : 1.2
*
* This file contains crop & PEC data and the market share for the substance used in the DROPLET project
* and it contains additional dilution factors for abstraction points
* PEC_FOCUS_NL,D3 = Global maximum concentration [ug/L] for step 3 FOCUS D3 run (TOXSWA output)
* PEC_code         = Code indicating main contributor to global maximum concentration; (SPRAY DRIFT = 1;
DRAINAGE = 2)
* fmarket          = market share of the pesticide [-]; DEFAULT = 0.4
* codeID           = GeoPEARL code for crop groupings; values must correspond with codes in CropArea.inp
file;
*
*                 NB: >> GeoPEARL crops groupings may not be used more than once in a simulation <<
* GP_crop          = name of GeoPEARL crop grouping
* D3_FOCUS_crop    = name of the crop grouping in the FOCUS SW D3 scenario that corresponds with used
GeoPEARL crop groupings
*
1 total number of crops with different GeoPEARL crop grouping codeIDs
1 total number of crops in FOCUS-SW D3 project
1 total number of applications for all FOCUS-SW D3 crops
*
*|--FOCUS D3 crop--| |--Number of applications--| |--application rate (kg/ha)--| |--application date--|
Cereals_winter      1                      1.000                      6-Nov-1992
*
```

```

*|-----D3-----| |-----GeoPEARL-crops-----| |-----FOCUS-SW D3-crops-----|
* PEC_FOCUS_NL,D3 date peak PEC_code codeID GP_crop FOCUS-SW D3-crop used in calculation
* [ug/L] [dd-mm-yyyy] [-] [-]
* 3.294 06-nov-1992 1 014 cereals Cereals_winter YES
*
* In case two or more FOCUS-SW D3-crop are connected to the same GeoPEARL crop grouping, only the FOCUS-
SW D3-crop with the highest PEC_FOCUS_NL,D3
* will be used for the calculation of the PEC_Tier I at the abstraction points.
* In case of NO the PEC_FOCUS_NL,D3 of this FOCUS-SW D3-crop is lower than the PEC_FOCUS_NL,D3 of the
crop connected to the same
* GeoPEARL crop grouping and therefore there this FOCUS-SW D3-crop will NOT be used for the calculation
of the PEC_Tier I at the abstraction points.
*
* ID abstraction point 1 2 3 4 5 6 7 8 9 6b
*Name abstraction point (KIWA) DE_PUNT ANDIJK N'GEIN HEEL A'DAM BRAKEL PETRUS TWENTE SCHEELH BOMMELERW
* Additional pesticide dilution factor
* 1.00 0.17 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00
*
* fmarket [-] per GP_crop and abstraction point
014 cereals 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40

```

Summary.out file

```

*
* project name : Asw
* Calculated PEC abstraction in Tier I for Dummy_compound_A_sw
* summary file generated on : 31/10/2017 at 14:30
*
* executable name: DROPLET_CalcPEC
* model version: 1.2
* model date: 03 February 2014
* compiler name: Intel Visual Fortran XE 12.1.4.325
* Working directory: C:\PesticideModels\DROPLET\data\PEC
*
*
* **** MAIN INPUT DATA ****
*
* Relevant physical chemical properties for DROPLET tool of substance: Dummy_compound_A_sw
* Molar mass = 300.0 g/mol
* DT50-w = 1.0 days at 293.0 K
* Psat = .10E-06 Pa at 293.0 K
* Solub = .10E+01 mg/L at 293.0 K
* E_arrh = .54E+05 J/mol
*
*
* FOCUS D3 crop Number of applications application rate (kg/ha) application date
* -----
* Cereals_winter 1 1.000 6-Nov-1992
* -----
*
*
* GeoPEARL crop FOCUS D3 crop Date PEC_FOCUS_NL,D3 Main
* PEC_FOCUS_NL,D3 (ug/L) entry route
* -----
* cereals Cereals_winter 06-nov-1992 3.294 spray drift
* -----

```



```

*
* In case two or more FOCUS-SW D3-crops are connected to the same GeoPEARL crop grouping, only the
FOCUS-SW D3-crop
* with the highest PEC_FOCUS_NL,D3 will be used for the calculation of the PEC_Tier I at the abstraction
points.
*
* **** DATA FOR CALCULATION OF PEC_TIER1 ****
*
* PEC_Tier1 = SUM_all_crops((PEC_FOCUS_NL,D3 * f_corrFOCUSscen) * f_use_int) * f_timing * f_dissipation *
f_add_dil
*
* f_use_int = RCA * f_market * f_relevant_contributing_area
*
* f_corrFOCUSscen:          3 for peaks caused by drainage, 1 for peaks caused by spray drift
* f_relevant_contributing_area: 1 for drainage, 0.5 for spray drift
* f_timing:                 0.5
* f_dissipation:            0.058988
* f_dissipation Bommelerwaard: 1.00
* Assumed surface water temp.: 288.0 K
*
* Abstraction point  FOCUS          f_use_int  RCA          f_market  f_add_dil
*                   D3 crop        (-)        (-)          (-)        (-)
* -----
* DE PUNT           Cereals_winter    0.014099    0.070497    0.40       1.00
* ANDIJK            Cereals_winter    0.007295    0.036473    0.40       0.17
* NIEUWEGEIN       Cereals_winter    0.007859    0.039296    0.40       1.00
* HEEL              Cereals_winter    0.017786    0.088929    0.40       1.00
* A'DAM-RIJNKANAAL Cereals_winter    0.006344    0.031720    0.40       1.00
* BRAKEL            Cereals_winter    0.006794    0.033972    0.40       1.00
* PETRUSPLAAT      Cereals_winter    0.006674    0.033369    0.40       1.00
* TWENTEKANAAL     Cereals_winter    0.002189    0.010945    0.40       1.00
* SCHEELHOEK       Cereals_winter    0.008811    0.044057    0.40       1.00
*
* BOMMELERWAARD    Cereals_winter    0.003185    0.015926    0.40       1.00
* -----
* (Bommelerwaard is a subarea of Brakel)
*
*
* **** OUTPUT ****
*
*
*                   PEC_Tier1 [µg/L]
* DE PUNT           0.001
* ANDIJK            0.000
* NIEUWEGEIN       0.001
* HEEL              0.002
* A'DAM-RIJNKANAAL 0.001
* BRAKEL            0.001
* PETRUSPLAAT      0.001
* TWENTEKANAAL     0.000
* SCHEELHOEK       0.001
* BOMMELERWAARD    0.005

```


Annex 5 Comparison of simulation results

Comparison of simulation results by the entire old suite of models to results by the old MACRO and TOXSWA versions coupled to the new DROPLET 1.3.2 version.

Tables B5-1 to B5-5 compare the PEC_Tier1 calculated by FOCUS-SWASH 3.1, FOCUS-MACRO 4.4.2, FOCUS-TOXSWA 3.3.1 and DROPLET 1.2 (the entire old suite of models) to the PEC_Tier1 calculated by FOCUS-SWASH 3.1, FOCUS-MACRO 4.4.2, FOCUS-TOXSWA 3.3.1, coupled to FOCUS-SWASH 5.3, SPIN 2.2 and DROPLET 1.3.2 (old suite for PEC_{max} in NL D3 ditch coupled to new DROPLET 1.3.2) for the nine compounds and the nine abstraction points for drinking water production, plus the Bommelerwaard. Note that before running DROPLET 1.3.2 the molar activation energy for the effect of temperature on the transformation rate in water and in sediment had been set equal to 54 kJ/mol, i.e. the value in the old versions of SWASH and TOXSWA (FOCUS_SWASH 3.1 and FOCUS_TOXSWA 3.3.1) in order to be able to compare DROPLET 1.2 to DROPLET 1.3.2 for exactly the same substance input parameters.

They demonstrate that for all compounds and abstraction points the PEC_Tier1 values obtained by DROPLET 1.2 corresponds exactly to the PEC_Tier1 values obtained by DROPLET 1.3.2. This result is as expected, because no changes were implemented in the calculation module CalcPEC of DROPLET.

Table B5-1. Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for the tracer (1 and 8 applications) calculated by the old model suite and old MACRO/TOXSWA plus new DROPLET 1.3.2

Abstraction point	Tracer (1 appln)			Tracer (8 applns)		
	old	old/new	difference %	old	old/new	difference %
De Punt	4.359	4.359	0.00	11.769	11.769	0.00
Andijk	0.383	0.383	0.00	1.035	1.035	0.00
Nieuwegein	2.430	2.430	0.00	6.560	6.560	0.00
Heel	5.498	5.498	0.00	14.846	14.846	0.00
A'dam-Rijnkanaal	1.961	1.961	0.00	5.296	5.296	0.00
Brakel	2.100	2.100	0.00	5.672	5.672	0.00
Petrusplaat	2.063	2.063	0.00	5.571	5.571	0.00
Twentekanaal	0.677	0.677	0.00	1.827	1.827	0.00
Scheelhoek	2.724	2.724	0.00	7.355	7.355	0.00
Bommelerwaard	0.987	0.987	0.00	2.666	2.666	0.00

Table B5-2. Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for substance A and C calculated by the old model suite and old MACRO/TOXSWA plus new DROPLET 1.3.2

Abstraction point	Substance A			Substance C		
	old	old/new	difference %	old	old/new	difference %
De Punt	0.001	0.001	0.00	0.001	0.001	0.00
Andijk	0.000	0.000	0.00	0.000	0.000	0.00
Nieuwegein	0.001	0.001	0.00	0.001	0.001	0.00
Heel	0.002	0.002	0.00	0.002	0.002	0.00
A'dam-Rijnkanaal	0.001	0.001	0.00	0.001	0.001	0.00
Brakel	0.001	0.001	0.00	0.001	0.001	0.00
Petrusplaat	0.001	0.001	0.00	0.001	0.001	0.00
Twentekanaal	0.000	0.000	0.00	0.000	0.000	0.00
Scheelhoek	0.001	0.001	0.00	0.001	0.001	0.00
Bommelerwaard	0.005	0.005	0.00	0.005	0.005	0.00

Table B5-3. Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for substance D and F calculated by the old model suite and old MACRO/TOXSWA plus new DROPLET 1.3.2

Abstraction point	Substance D			Substance F		
	old	old/new	difference %	old	old/new	difference %
De Punt	0.541	0.541	0.00	0.017	0.017	0.00
Andijk	0.048	0.048	0.00	0.002	0.002	0.00
Nieuwegein	0.302	0.302	0.00	0.010	0.010	0.00
Heel	0.683	0.683	0.00	0.022	0.022	0.00
A'dam-Rijnkanaal	0.243	0.243	0.00	0.008	0.008	0.00
Brakel	0.261	0.261	0.00	0.008	0.008	0.00
Petrusplaat	0.256	0.256	0.00	0.008	0.008	0.00
Twentekanaal	0.084	0.084	0.00	0.003	0.003	0.00
Scheelhoek	0.338	0.338	0.00	0.011	0.011	0.00
Bommelerwaard	0.162	0.162	0.00	0.005	0.005	0.00

Table B5-4. Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for substance G and H calculated by the old model suite and old MACRO/TOXSWA plus new DROPLET 1.3.2

Abstraction point	Substance G			Substance H		
	old	old/new	difference %	old	old/new	difference %
De Punt	3.243	3.243	0.00	0.984	0.984	0.00
Andijk	0.285	0.285	0.00	0.087	0.087	0.00
Nieuwegein	1.808	1.808	0.00	0.549	0.549	0.00
Heel	4.091	4.091	0.00	1.242	1.242	0.00
A'dam-Rijnkanaal	1.459	1.459	0.00	0.443	0.443	0.00
Brakel	1.563	1.563	0.00	0.474	0.474	0.00
Petrusplaat	1.535	1.535	0.00	0.466	0.466	0.00
Twentekanaal	0.503	0.503	0.00	0.153	0.153	0.00
Scheelhoek	2.027	2.027	0.00	0.615	0.615	0.00
Bommelerwaard	0.754	0.754	0.00	0.229	0.229	0.00

Table B5-5. Concentrations at drinking water abstraction points (PEC_Tier1) in µg/L for substance I and the pyrethroid calculated by the old model suite and old MACRO/TOXSWA plus new DROPLET 1.3.2

Abstraction point	Substance I			Pyrethroid		
	Old	old/new	difference %	old*	old/new*	difference %
De Punt	0.022	0.022	0.00	<0.021	<0.021	0.00
Andijk	0.002	0.002	0.00	<0.002	<0.002	0.00
Nieuwegein	0.013	0.013	0.00	<0.012	<0.012	0.00
Heel	0.028	0.028	0.00	<0.027	<0.027	0.00
A'dam-Rijnkanaal	0.010	0.010	0.00	<0.010	<0.010	0.00
Brakel	0.011	0.011	0.00	<0.010	<0.010	0.00
Petrusplaat	0.011	0.011	0.00	<0.010	<0.010	0.00
Twentekanaal	0.003	0.003	0.00	<0.003	<0.003	0.00
Scheelhoek	0.014	0.014	0.00	<0.013	<0.013	0.00
Bommelerwaard	0.005	0.005	0.00	<0.005	<0.005	0.00

* For this project the current Tier1 calculation method does not result in realistic PEC-Tier1 values. Therefore they have been replaced by "< calculated value µg/L". The Tier1 calculation method does not account for sorption of mass entered by spray drift deposition. For the current substance with a K_{om} greater than 10000 L/kg this artefact results in unrealistically high values of the calculated PEC-Tier1. Based upon calculations reported in Appendix 9 of the DROPLET user manual (Van Leerdam *et al.*, 2010), we suggest to divide the calculated values by a factor of 5.

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