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Implementation report

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The TOXSWA model has been extended with the functionality to simulate photolysis in water. TOXSWA simulates the fate of substances in water bodies to calculate exposure concentrations for aquatic organisms or sediment-dwelling organisms as part of the risk assessment of plant protection products (PPP). Photolysis is modelled as a first-order process, where transformation occurs in the water phase only. The transformation rate is considered to be linearly proportional to global radiation. Studies in outdoor surface water systems can in principle be used to derive the PPP transformation rates due to photolysis.

Keywords: photolysis, surface water, pesticide, TOXSWA model

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Preface

Since 1999 TOXSWA v1.2 has been applied in the Dutch registration procedure for plant protection products to calculated exposure concentrations for an edge-of-field ditch with constant flow rates. Since 2003 FOCUS_TOXSWA (versions 1.1.1, 2.2.1 and 3.3.1) has been applied in the EU registration procedure to calculate exposure concentrations in ponds, ditches and streams with transient flow conditions. FOCUS_TOXSWA v.4.4.3 calculates also exposure concentrations for metabolites formed in water and in sediment. This version was released in 2015. The TOXSWA kernel (=v. 3.3) used in FOCUS_TOXSWA v.4.4.3 is now extended with the option to simulate transformation by photolysis. This report describes the implemented concept of photolysis in water in the new TOXSWA kernel version 3.4.

Summary

The TOXSWA model has been extended with the functionality to simulate photolysis in water. TOXSWA simulates the fate of substances in water bodies to calculate exposure concentrations for aquatic or sediment-dwelling organisms as part of the risk assessment of plant protection products (PPP). Transformation of a PPP is one of the main processes determining the exposure concentration. Especially for water bodies with stagnant water or low flow velocities, repeated applications in combination with slow transformation may lead to accumulation of PPP in water and sediment. This may lead to high risks for the aquatic or sediment-dwelling organisms. By enabling the separate simulation of transformation due to light, i.e. photolysis, TOXSWA allows for the simulation of PPP fate in water bodies with a higher level of reality.

In the new TOXSWA (kernel version 3.4), the user may select the (already existing) option to simulate transformation as a lumped process, occurring in all phases of the water layer (i.e. water phase and adsorbed to suspended solids and aquatic macrophytes) or as a separate or a combination of the separate transformation processes: photolysis, hydrolysis or biotic transformation. Transformation in the water layer due to these processes is now considered to occur in the water phase only. In this report only photolysis is described.

Photolysis is modelled as a first-order process, where the transformation rate is considered to be linearly proportional to global radiation. Studies in outdoor surface water systems with algae and/or macrophytes can in principle be used to derive the PPP transformation rates due to photolysis.

Tests with the new functionality of TOXSWA confirmed that the concept of photolysis is implemented correctly and that the numerical solutions are robust.

Samenvatting

Het TOXSWA model is uitgebreid met de mogelijkheid om fotolyse in water te simuleren. TOXSWA simuleert het gedrag van stoffen in oppervlaktewater om blootstellingsconcentraties te berekenen voor organismen die in water of sediment leven, als onderdeel van de aquatische risicobeoordeling van gewasbeschermingsmiddelen (GBM). De blootstellingsconcentratie wordt voor een belangrijk deel bepaald door omzetting in water en sediment. In langzaam stromend water kan bij herhaalde toedieningen een langzame afbraak ervoor zorgen dat GBM accumuleren, waardoor er hoge concentraties kunnen ontstaan en daarmee hoge acute en chronische toxiciteitsrisico's. De optie tot het berekenen van omzetting onder invloed van licht, d.w.z. fotolyse, maakt het mogelijk om het gedrag van GBM in waterlopen realistischer te simuleren.

In de nieuwe TOXSWA (broncode versie 3.4), kan de gebruiker de (bestaande) optie selecteren voor het simuleren van 'overall' omzetting als gevolg van zowel hydrolyse, fotolyse als biologische omzetting. Deze omzetting wordt verondersteld plaats te vinden in alle fasen in de waterlaag (d.w.z. opgelost en geadsorbeerd aan zwevend materiaal en waterplanten). Daarnaast kan de gebruiker nu de afzonderlijke omzettingsprocessen of een combinatie van twee of drie afzonderlijke processen kiezen: fotolyse, hydrolyse of biologische omzetting. Deze afzonderlijke processen worden verondersteld alleen in de opgeloste fase op te treden. In dit rapport wordt alleen de fotolyse behandeld.

Fotolyse wordt beschreven als een eerste orde proces waarbij de omzettingssnelheid lineair evenredig is met de globale straling. Studies in watersystemen in de open lucht met algen en macrofyten kunnen in principe worden gebruikt om de omzettingssnelheid van GBM af te leiden als gevolg van fotolyse.

De testen uitgevoerd met het nieuwe fotolyse concept in TOXSWA bevestigen dat het concept goed geïmplementeerd is en dat de numerieke oplossingen robuust zijn.

1 Introduction

The TOXSWA model simulates the fate of substances in water bodies to calculate exposure concentrations for aquatic organisms or sediment-dwelling organisms as part of the risk assessment of plant protection products (PPP). TOXSWA simulates the fate processes: convective and dispersive transport in water and sediment, diffusive transport in sediment, transformation, volatilization and sorption to suspended solids, macrophytes and sediment.

TOXSWA version 3.3 is the kernel of FOCUS_TOXSWA 4.4.3. (which includes also a user interface and a database). This report concerns the new version 3.4 and further updates. Hence, where in this report TOXSWA is mentioned, this refers to kernel 3.4, unless indicated otherwise.

Calculated exposure concentrations are a function of transformation processes. Especially for water bodies with stagnant water or low water velocities, repeated applications in combination with slow transformation may lead to accumulation of PPP, so, to higher concentrations leading to higher acute and chronic risks for aquatic organisms (Westein *et al.*, 1998). In the TOXSWA model (kernel versions up to 3.3), transformation in water is simulated as a lumped first-order transformation process, assuming one transformation rate for the total mass in the water layer. Transformation in water, however, may be split in at least three separate processes; hydrolysis, photolysis and biotic transformation (Deneer *et al.*, 2010). Simulation of these processes separately and in more detail is expected to improve the performance of TOXSWA as it accounts better for external environmental conditions related to specific PPP properties. Deneer *et al.* (2010) provided suggestions for how these individual processes could be implemented in TOXSWA.

Following the suggestions by among others Deneer *et al.* (2010) to specify the transformation process in more detail, three transformation processes have been implemented into TOXSWA by redefining the lumped transformation term in the conservation equation of the water layer. The option to simulate transformation via lumped transformation remains available.

The concepts used and the consequences for the implementation in TOXSWA are to be reported for each process separately. This report describes the photolysis transformation process only. Hydrolysis and biotic transformation will be reported later.

Chapter 2 describes the concepts and implementation of the concepts in TOXSWA. In Chapter 3 the input and output relevant for the implementation of photolysis is described, and an example simulation is given. Tests to check whether the concepts have been implemented correctly in the source code and whether the model can handle the range of input values are described in Chapter 4. In Chapter 5 some conclusions and recommendations are given.

2 Implementation of photolysis in TOXSWA

2.1 The TOXSWA model

The TOXSWA model describes the behaviour of substances in a water body at the edge-of-field scale, i.e. a ditch, pond or stream adjacent to a single, treated field (Adriaanse, 1996; Adriaanse *et al.*, 2014). TOXSWA calculates concentrations of parent substances and their metabolites. The modelled system consists of two types of subsystem: the water layer containing suspended solids and macrophytes and the sediment layer; the properties of the sediment layer. i.e. porosity, organic matter content and bulk density, may vary with depth. In the water layer concentrations may vary in the horizontal direction, whereas in the sediment concentrations may vary in the horizontal and the vertical direction.

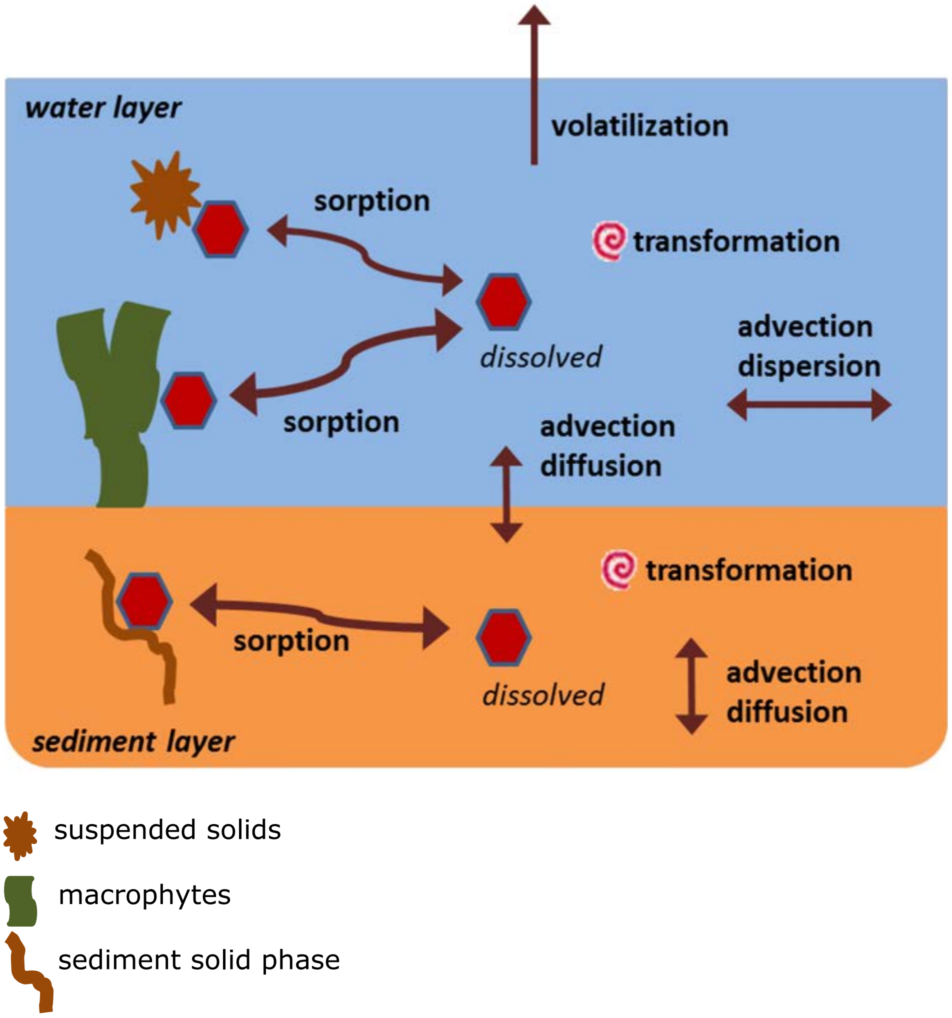

Figure 1 *Processes in TOXSWA.*

TOXSWA considers four processes for the parent substance and its metabolites: (i) transport, (ii) transformation, (iii) sorption and (iv) volatilization (see Figure 1). In the water layer substances are transported by advection and dispersion, in the water phase (dissolved) or while being sorbed to suspended solids. In the sediment substances are transported by advection, dispersion and by diffusion. Exchanges across the water-sediment interface is facilitated by advection (upward or downward seepage) and by diffusion. Transformation is simulated in the water layer as well as in the sediment layer. The transformation rate covers the combined effects of hydrolysis, photolysis and biodegradation. The transformation rates are assumed to be temperature dependent, using the Arrhenius equation. Sorption to suspended solids and to sediment is described by the Freundlich isotherm. Sorption to macrophytes is described by a linear sorption isotherm.

The model solves two mass conservation equations to simulate the substance fate; one for the water layer and one for the sediment.

2.2 Concepts of photolysis (background)

Photolysis is a complex process. The rate of transformation depends on the wavelength of the light reaching a molecule in the water layer and the absorption spectrum of the molecule. Diurnal and seasonal changes in the composition of daylight has a direct bearing on the rate of photolysis. Usually a distinction is being made between direct photolysis and indirect photolysis. Direct photolysis refers to the absorption of light by the molecule followed by the reaction of the excited molecule. Indirect photolysis refers to the absorption of light by an intermediate molecule, becoming a transient molecule, which transfers its energy to the reacting molecule. In natural water bodies, for many substances the rate of indirect photolysis is larger than the rate of direct photolysis (Deneer *et al.*, 2010). Indirect photolysis is associated with the absorption of light by molecules in dissolved and suspended matter, e.g. humic acids either dissolved or in colloïdial structures, functioning as the transient molecule. As the type of transient molecule in relation to the type of substance has a direct bearing on the reaction rate, differences in dissolved and suspended matter between various natural water bodies lead to a broad range of reaction rates across natural water bodies. The rate of photolysis is to a negligible extent influenced by temperature.

It is generally assumed that light in the UVB range (280-320 nm) is the most relevant part of the light with respect to generating photolysis. Measurements in Dutch surface waters by De Lange *et al.* (1999) showed that UVB does penetrate only shallowly into the water layer: 7-46 cm below the water surface the UVB intensity is observed to be reduced with 99%, inferring that the amount of light available for photolysis in the water layer is lower as compared to the water surface. The penetration depth is influenced by concentrations of humic substances and organic and inorganic particulate matter in the water body.

Both the complexity of the processes and the variability across water bodies hamper translation into workable concepts and derivation of realistic transformation rates. On the other hand, from outdoor studies it is known that direct and indirect photolysisn may play a considerable role. In view of this Boesten *et al.* (2014) consider it defensible to assume that the rate coefficient for photolysis is proportional to global radiation. Boesten *et al.* (2014) provide suggestions how to use photolytic transformation rates of outdoor studies by back calculation observed rates to a reference global radiation. In this way photolysis rates obtained from different outdoor experiments are standardised and can be compared. They further proposed to use (OECD) laboratory photolysis studies to assess the probability of transformation due to photolysis, the identification of photo metabolites and the estimation of their fractions. The approach suggested by Boesten *et al.* (2014) is implemented into TOXSWA.

2.3 Implementation into the TOXSWA model

The mass conservation equation for the water layer solved by TOXSWA version 3.3 and lower is (see Adriaanse, 1996):

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

with

c^* = mass concentration of substance in the water layer (M.L^{-3})

A = cross sectional area of flow (L^2)

J = aeric mass flux of substance in water layer by advection and dispersion (M.L^{-2}.T^{-1})

k^* = transformation rate coefficient for substance in the water layer (i.e. in water phase, sorbed to suspended solids and sorbed to macrophytes) (T^{-1})

J_{wa} = aeric mass flux of substance across the water-air interface (M.L^{-2}.T^{-1}) [the flux is negative in upward direction]

J_{wb} = aeric mass flux of substance across the water-sediment interface (M.L^{-2}.T^{-1})

O_{x} = width of water surface at location x (L)

P_{x} = wetted perimeter at location x (L)

x = distance in direction of flow (L)

where sorption to suspended solids is described with a Freundlich sorption isotherm, hence

$$X_{ss} = m_{om,ss} K_{F,om,ss}\, c_{e,ss} \left(\frac{c}{c_{e,ss}}\right)^{n_{ss}} \tag{2}$$

with

X_{ss} = content of substance sorbed to suspended solids (M^{-1} M^{-1})

$m_{\mathrm{om,ss}}$ = mass fraction of organic matter in suspended solids (M^{-1} M^{-1})

$K_{\mathrm{F,om,ss}}$ = slope of the Freundlich sorption isotherm, based on organic matter (L^3 M^{-1})

$c_{e,\mathrm{ss}}$ = concentration c (in the water phase) at which $K_{\mathrm{F,ss}}$ has been estimated (M L^{-3})

n_{ss} = Freundlich exponent for sorption to suspended solids (1)

and the total concentration in the water layer is given by:

$$c^* = c + \frac{DW\, P_{z=0}}{A} X_{mp} + ssX_{ss} \tag{3}$$

with

DW = dry weight of macrophytes per area of sediment (M L^{-2})

$P_{\mathrm{z=0}}$ = wetted perimeter at z = 0 (L)

X_{mp} = content of substance sorbed to macrophytes (M M^{-1})

ss = mass concentration of suspended solids in the water layer (M L^{-3})

c = mass concentration of substance in the water phase (M L^{-3})

To account for the three separate transformation processes, i.e. hydrolysis, photolysis and biotic transformation, the transformation term of Eq. (1) is rewritten as:

$$k^*(c^*A) = k(cA) \tag{4}$$

with

$$k = k_h + k_{ph} + k_b \tag{5}$$

and

k = transformation rate coefficient for substance in the water phase (T^{-1})

k_{h} = overall rate coefficient for hydrolysis of substance (T^{-1})

k_{ph} = rate coefficient for photolysis of substance (T^{-1})

k_{b} = rate coefficient for biotic transformation of substance in the water phase (T^{-1})

Note that, transformation is now considered to occur in the water phase only. This, in contrast to the lumped transformation process that presumes transformation to occur in the water phase as well as in the sorbed phase. PPP transformation is commonly attributed to the water phase, e.g. for soils (Haws *et al.*, 2006; Alexander, 2000; Scow and Alexander, 1992), which is now applied for hydrolysis, photolysis and biotic transformation in surface water. PPP sorbed to suspended solids and macrophytes are considered to be not available for transformation.

Following Boesten *et al.* (2014) and Deneer *et al.* (2010), photolysis may be approximated as a first order process, which can be written as:

$$\frac{dc}{dt} = -k_{ph}c \qquad (6)$$

where k_{ph} is derived from the outdoor study. Following Boesten et al (2014) k_{ph} is considered to be linearly proportional to daily global radiation:

$$k_{ph} = k_{ph,ref}\ \frac{G}{G_{ref}} \qquad (7)$$

with:

k_{ph} = rate coefficient for photolysis (d^{-1})
$k_{\mathrm{ph,ref}}$ = rate coefficient for photolysis at the reference global radiation (d^{-1})
G = daily global radiation (kJ m^{-2})
G_{ref} = reference daily global radiation (kJ m^{-2})

The reference rate constant, $k_{\mathrm{ph,ref}}$, is assumed to be temperature independent and should be derived from outdoor studies. The reference value for global radiation is an arbitrary value needed to standardise photolysis rates obtained from different outdoor studies. For further guidance we refer to Boesten *et al.*, 2014).

The global radiation (G) varies over the day; G is zero in the night and maximal at noon (when there are no clouds). G should preferable be based on real conditions expected for the simulated situation.

2.4 Change in transformation concept between TOXSWA kernel versions 3.3 and 3.4

The change in concept of a lumped transformation, presuming transformation to occur in the water phase as well as in the sorbed phase, to transformation occurring in the water phase only is elaborated in this section.

Using the lumped transformation rate corresponds to using an overall transformation rate determined in a system that may include suspended solids and macrophytes. When using the new concept of transformation in the water phase only, also the derivation of the transformation rate from the study should consider transformation in the water phase only.

To be able to derive the transformation rate in the water phase k from k^* determined from the study, c^* in Eq. (4) is replaced using Eqs (2) and (3):

$$k^*\left(c + \frac{DW\ P_{z=0}}{A}X_{mp} \ + ss\ \ A\ \ m_{om,ss}K_{F,om,ss}\ c_{e,ss}\ \left(\frac{c}{c_{e,ss}}\right)^{n_{ss}}\right)A = k(cA) \qquad (8)$$

A simple calculation example is given. A transformation study is done using a flask with one liter of surface water containing 50 mg suspended solids with an organic matter content of 50%. There are no macrophytes in the flask. The lumped *DegT50*, i.e. *DegT50**, determined from the total concentrations c^* in the study is 10 d, hence $k^* = 0.069\ \mathrm{d}^{-1}$.

In the example there are no macrophytes present in the flask and we assume a linear sorption coefficient (n_{ss} = 1). Then Eq. (8) can be rewritten for the example case into:

$$\frac{k^*}{k} = \frac{1}{1 + ss\, m_{om,ss} K_{F,om,ss}} \tag{9}$$

Note that *DegT50*/*DegT50** = *k**/*k.* For a substance with a high sorption coefficient, e.g. $K_{F,om,ss}$ = 10 000 L/kg, the ratio *DegT50*/*DegT50** for the example transformation study is 0.8, resulting in a shorter *DegT50* of 8 days.

Calculations with the lumped transformation concept in TOXSWA and the lumped *DegT50** for the example lab study will give the same concentrations as using the transformation in the water phase only concept with the *DegT50*-dissolved. The lumped transformation concept ignores that substance sorbed to suspended solids may not be available for transformation, but it does correspond to the experimental practice of measuring the decrease in the water of the flask, without filtering the suspended solids out of the water before the measurements.

3 Input, output and example calculation

3.1 Introduction

TOXSWA requires minimally two input files: (1) the txw file, with parameter values for the scenario, the substance and the entries of the substance, and (2) a meteo file with a time series of temperature or weather data. Additional input files are needed when drainage or runoff entries occur (Beltman *et al.*, 2014). TOXSWA reports a summary of the results in the summary output file.

New parameters needed to simulate photolysis are the rate coefficient for photolysis at reference global radiation ($k_{ph,ref}$), the reference daily global radiation (G_{ref}) and the global radiation (G). In this chapter the required input to use the photolysis option and to simulate photolysis are discussed as well as additional output as compared to earlier TOXSWA versions.

3.2 Selection of photolysis

Four main options for transformation in water can be used: lumped transformation, hydrolysis, photolysis and biotic transformation. Also combinations of options can be selected. However, selection of the lumped transformation option excludes the use of the other transformation processes (see Table 1). The user can select the options via the parameter `OptTra_xxxxx` in the txw input file of TOXSWA, where `xxxxx` refers to the substance code. The option for lumped transformation was the only option available in previous versions of TOXSWA.

Table 1
Options for simulation of transformation by TOXSWA (presented in the two columns).

Transformation process	Lumped	Separate processes
Lumped transformation	yes	blocked
Hydrolysis	blocked	yes/no
Photolysis	blocked	yes/no
Biotic transformation	blocked	yes/no

The option `OptTra_XXXXX` is given in the txw input file (Section 6, Compound section), for each substance that is simulated (see Figure 2).

```
*-----------------------------------------------------------------------------------
* Section 6: Compound section
*-----------------------------------------------------------------------------------

Pho    OptTra_EXSW2 (-)           ! Option transformation (Lumped, Hdr, Pho, Bio, HdrPho,
                                  ! HdrBio, PhoBio, HdrPhoBio)
```

Figure 2 *Excerpt from Compound section of the txw file.*

In Table 2 it is shown which processes are simulated for the various options.

Table 2
Activated processes in the simulation as a function of the selected option for transformation in txw input file.

Option	Lumped	Hydrolysis	Photolysis	Biotic transformation
Lumped	+			
Hdr		+		
Pho			+	
Bio				+
HdrPho		+	+	
HdrBio		+		+
PhoBio			+	+
HdrPhoBio		+	+	+

To simulate only photolysis of the substance EXSW2, set OptTra_EXSW2 to `Pho`, or to `HdrPho` or `PhoBio` to combine photolysis with either hydrolysis or biotic transformation, or to `HdrPhoBio` when all three transformation processes must be simulated.

To allow for the simulation of photolysis, meteorological data should be provided on an hourly basis and the option for meteo data should be set to 'hourly' (see Section 3.3).

3.3 Input and output

In this section all changes in the txw file, in the meteo file, and in the summary output file are discussed.

The txw file consists of 9 sections, of which the sections 6 'Compound' and 5 'Meteo' need to be adapted to simulate photolysis.

Txw file, Compound section
After selection of the photolysis options via `OptTra_XXXXX`, the photolysis half-life, *$DegT50_{ph,ref}$* and the value of the reference global radiation, G_{ref}, need to be provided in the Compound section, i.e. `DT50WatLiqPhoRef_xxxxx` and `RadGloRef` (see Figure 3).

```
*-----------------------------------------------------------------------------
* Section 6: Compound section
*-----------------------------------------------------------------------------

Pho    OptTra_EXSW2 (-)     ! Option transformation (Lumped, Hdr, Pho, Bio, HdrPho,
                            ! HdrBio, PhoBio, HdrPhoBio)

10.      DT50WatLiqPhoRef_EXSW2 (d) ! Half-life photolysis in water at reference
                                    ! daily global radiation [0.1 – 100000]
10000.0  RadGloRef (kJ.m-2)         ! Reference daily global radiation [1000 – 50000]
```

Figure 3 *Excerpt from Compound section of the txw file.*

TOXSWA converts the half-life for photolysis at reference global radiation *($DegT50_{ph,ref}$)* to the first-order rate coefficient for photolysis at the reference global radiation($k_{ph,ref}$) via

$$k_{ph,ref} = \frac{\ln(2)}{DegT50_{ph,ref}} \tag{10}$$

Txw file, Meteo section

In the Meteo section data on the meteo station need to be entered. The name of the meteo file (`MeteoStation`) and the type of input data (`OptMetInp`) must be given in the file (see Figure 4).

```
*-------------------------------------------------------------------------------
* Section 5: Meteo section
*-------------------------------------------------------------------------------
DeBilt       MeteoStation       ! Name of the *.met or *meth file with meteo data
Hourly       OptMetInp          ! Option for hourly or monthly input data (Hourly,
                                ! Monthly)
```

Figure 4 *Excerpt from Meteo section of the txw file.*

Meteo file

There are two types of meteo files that can be used by TOXSWA, of which one is needed for a simulation. The two types are:

- the monthly meteo file, providing the monthly temperature of the waterbody, used with FOCUS surface water scenarios. The file name of this type of file has extension 'met'.
- the hourly meteo file, providing hourly meteo data, including global radiation. The file name of this type of file has extension 'meth'.

TOXSWA needs the hourly meteo file to simulate photolysis. The global radiation (*G*) over the whole simulation period should be provided on an hourly basis. The global radiation varies over the day, i.e. it is zero during the night and maximal at noon (when there are no clouds).

An example of the hourly meteo file for TOXSWA is given in Figure 5. The global radiation *G* (`RAD`) is read from such a file. In TOXSWA the values of the reference daily global radiation (G_{ref}) and of the global radiation (*G*) are converted into S.I. units (i.e. per second), and used as such in the quotient G/G_{ref} with Eq. (7).

The description of the headers of the columns in the 'meth' file is given below.

MSTAT = name of weather station
YYYY = year
MM = month
DD = day
HH = time (in hours)
RAD = global radiation per hour (in kJ/m^2)

```
*  MSTAT  YYYY  MM  DD  HH    RAD
*                            kJ.m-2
*************************************
'DeBilt'  1986   6   1   1      0
'DeBilt'  1986   6   1   2      0
'DeBilt'  1986   6   1   3      0
'DeBilt'  1986   6   1   4     20
'DeBilt'  1986   6   1   5    130
'DeBilt'  1986   6   1   6    270
'DeBilt'  1986   6   1   7    580
'DeBilt'  1986   6   1   8    470
'DeBilt'  1986   6   1   9    400
'DeBilt'  1986   6   1  10    490
'DeBilt'  1986   6   1  11    540
'DeBilt'  1986   6   1  12    390
'DeBilt'  1986   6   1  13    290
'DeBilt'  1986   6   1  14    150
'DeBilt'  1986   6   1  15    220
'DeBilt'  1986   6   1  16    140
'DeBilt'  1986   6   1  17     70
'DeBilt'  1986   6   1  18     60
'DeBilt'  1986   6   1  19     20
'DeBilt'  1986   6   1  20      0
'DeBilt'  1986   6   1  21      0
'DeBilt'  1986   6   1  22      0
'DeBilt'  1986   6   1  23      0
'DeBilt'  1986   6   1  24      0
```

Figure 5 *Example of hourly meteo file *.meth file, used for simulation of photolysis.*

Summary file
In the summary output file (runID.sum) the input value used for the half-life for photolysis at reference global radiation ($DegT50_{ph,ref}$) and the reference global radiation (`RefGloRad`) are echoed.

```
* --------------------------------------------------------------------------------
* TOXSWA REPORT: Substance properties and substance loadings
*
* Summary for the following substances
*
* Substance  1:  EXSW_2

* Half-life in water, photolysis (d):      10.00 at reference daily global
                                                 radiation (kJ.m-2) : 10000
```

Figure 6 *Excerpt from substance properties and loadings section of the summary output file.*

3.4 Suggestions for derivation of input parameters

In this section some suggestions for deriving the input parameters needed to simulate photolysis are given.

Reference $DegT50_{ph,ref}$ *for photolysis* `DT50WatLiqPhoRef`
The $DegT50_{ph,ref}$ for photolysis at reference daily global radiation can be derived from outdoor studies. One or more studies may be used to derive the mean of the $DegT50_{ph,ref}$ values. To scale all studies to the same reference daily global radiation, a simple procedure would be to (i) determine the period in which the main degradation has taken place (e.g. 40 days), (ii) calculate the average daily global radiation during this period (e.g. G_{study} = 18 000 kJ m^{-2}), and (iii) calculate $DegT50_{ph,ref}$ by $DegT50_{study} * (G_{study}/G_{ref})$, where G_{ref} = 10 000 kJ m^{-2}). However, we recommend to develop a more refined method to normalize photolysis to the reference daily global radiation. Such a procedure may take

example of existing procedures for normalization of *DegT50* values in soil from field dissipation studies in which the measurements are scaled in time by normalising the temperature. A similar approach may be used for deriving the photolysis rate from an outdoor study, through scaling the measurements in time on basis of the cumulative global radiation.

Reference daily global radiation `RadGloRef`
Daily global radiation varies in the Netherlands typically from 200 J cm^{-2} in winter to 2 000 J cm^{-2} in summer (Velds, 1992) (= 2 000 – 20 000 kJ m^{-2}). Therefore Boesten *et al.* (2014) propose to use a G_{ref} of 1 000 J cm^{-2} (= 10 000 kJ m^{-2}) as reference daily global radiation. This reference value of the daily global radiation is an arbitrary value needed to standardise *DegT50* values obtained from different outdoor experiments, so if different *DegT50* values have to be averaged, they have to be calculated back first to the same reference *G* value (G_{ref}).

3.5 Example calculation

In this section an example of a TOXSWA simulation with transformation by photolysis is given. We simulated a water only system with a length of 360 m, a rectangular cross section with a width of 1 m and a water depth of 0.5 m. The constant flow velocity was 20 m d^{-1}. The water layer of the ditch was divided into sixty segments of 6 m for the numerical solution of the mass conservation equation. The time step used in the model simulations was 600 s. The substance is non-volatile and the photolysis $DegT50_{ph,ref}$ was 5.2 days at the reference daily global radiation. The reference daily global radiation G_{ref} was 10 000 kJ/m^2. Sorption to suspended solids was not included ($K_{om,ss}$ = 0 L kg^{-1}), and there was no diffusion to sediment. A $t = 0$ a spray drift deposition of 5.5 mg/m^2 entered the water layer in the segment between $x = 60$ and $x = 66$ m. The total mass that entered the water layer was 0.033 g. Hourly global radiation values (*G)* measured by meteo station De Bilt from 1 to 4 June 1986 were used (see Annex 1).

In this simulation only transformation in the water phase due to photolysis is considered. Other processes that may decrease the concentration are not considered, i.e. no volatilization, sorption to suspended solids or macrophytes and no transport to sediment.

The effect of variable global radiation *G* on the total mass of the substance in the system is shown in Figure 7. The figure shows the total mass in the water layer of the ditch and the global radiation as a function of time. The red curve showing the mass is flat in periods that the global radiation is zero, i.e. the substance is not degraded. In periods with high values of radiation (at the middle of the day) the decrease in mass due to transformation by photolysis is strongest.

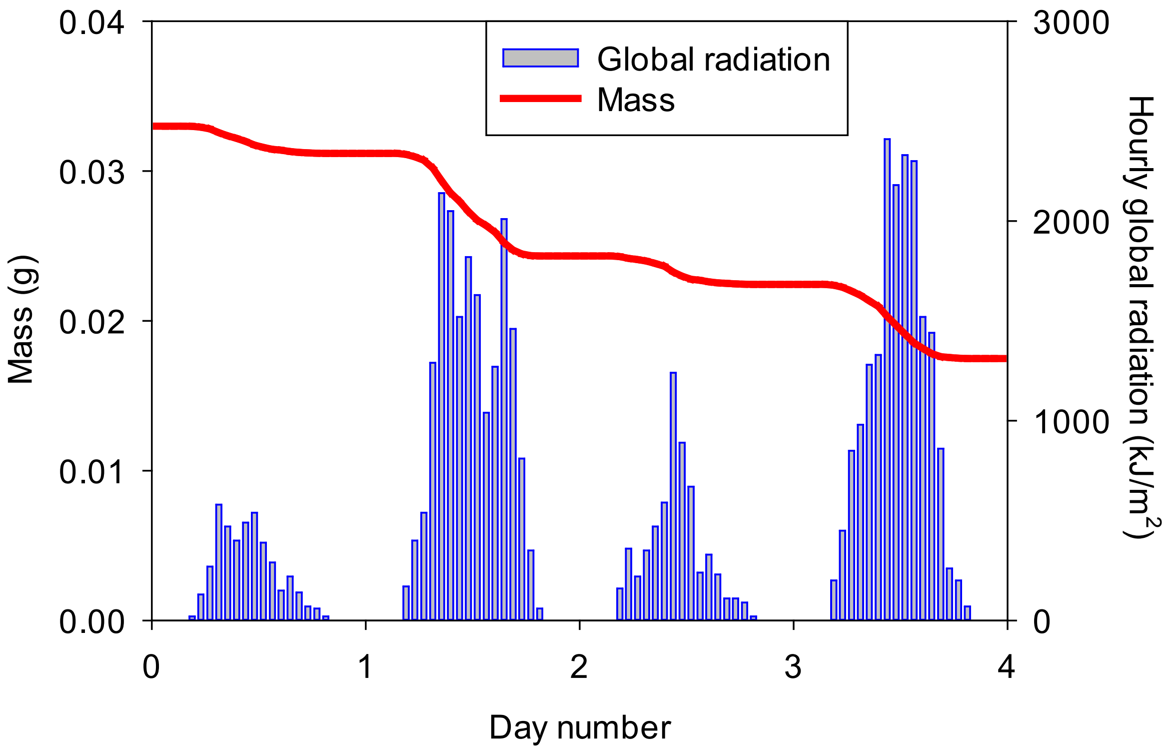

Figure 7 *Substance mass in the watercourse (left-hand axis) and hourly global radiation (right-hand axis) up to four days after entry of the substance (meteo 1 to 4 June 1986). Photolysis half-life* $DegT50_{ph,ref}$ = *5.2 days at reference daily global radiation* G_{ref} *= 10 000 kJ* m^{-2}.

4 Verification of photolysis concept in the TOXSWA model

4.1 Introduction

To verify the implementation of the photolysis concepts TOXSWA simulation results were compared to analytical solutions. Also, the robustness of TOXSWA was tested for a broad range of photolysis-related input parameter values. In total three tests were performed:

Test 1: Implementation of transformation in the water phase only by testing TOXSWA against an analytical solution of the convection-dispersion equation assuming transformation of the substance in the water phase only. The analytical solution was derived analogous to the solution in Adriaanse (1996, section 7.3.3). The derivation is described in Annex 3.

Test 2: Implementation of photolysis driven by global radiation by testing TOXSWA against an analytical solution for mass decrease in an ideally mixed reservoir due to transformation only.

Test 3: The robustness of the model was tested for the minimum and maximum values of substance parameters and watercourse parameters that directly affect the rate of photolysis in water.

The system parameters, loading parameters and substance parameters used for the tests are those of the example described in section 3.5.

4.2 Criteria for tests against analytical solution

For test 1, two criteria were used to evaluate whether the test result was satisfactory. The test result is the correspondence between the target concentration calculated with TOXSWA and the concentration calculated with the analytical solution: (i) visual, from the graph, and (ii) numerical, by comparing the Root Mean Squared Error of differences between the concentrations calculated by TOXSWA and those calculated by the analytical solution of photolysis of the test to the corresponding RMSE value of a reference case.

The reference case was a simulation for the 360 m water-only system of section 3.5 using the lumped transformation option. In this reference case the concentrations simulated by TOXSWA were compared against the concentrations of the analytical solution provided in Adriaanse (1996). The reference case is described in Annex 4.

The Root Mean Squared Error (RMSE) was calculated at four different times: t = 0.5, 1, 2 and 4 days:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(c_{A,i} - c_{T,i}\right)^2} \qquad (11)$$

where $c_{A,i}$ is the concentration calculated by the analytical solution at distance (i+1/2)*Δx, $c_{T,i}$ is the concentration calculated by TOXSWA at the same distance and n is the number of distances (60).

The RMSE calculated for the test was compared to the RMSE of the reference case. When the RMSE of the test did not increase compared to the RMSE value of the reference case, the test was judged to be acceptable.

4.3 Test 1: Simulation of transformation in the water phase only

4.3.1 Set up of the test

The aim of the test is to verify that the concept of transformation in the water phase only is implemented correctly in TOXSWA.

Test 1 consisted of two sub-tests:

a. The substance is fully present in the water phase, $K_{F,om,ss}$ is set to 0; hence all mass can be transformed.
b. The substance is partly present in the water phase, $K_{F,om,ss}$ is set to 200 000 L kg^{-1}; the other part of substance mass is adsorbed to suspended solids, hence only mass dissolved can be transformed.

Table 3 shows the most important parameter values used in the tests. In Annex 5 other parameters used for the TOXSWA model and for the analytical solution are given.

Table 3

Overview of parameter values used in Test 1.

Test	$DegT50_{ph,ref}$ (d)	G (kJ m^{-2} per day)	$K_{F,om,ss}$ (L kg^{-1})
1a	5.2	12 500	0
1b	5.2	12 500	200 000

In Test 1b part of the substance mass is adsorbed to suspended solids. The concentration of suspended solids was set to 100 mg L^{-1} with an organic matter content of 10% to obtain about 50% of the substance adsorbed.

In the test the global radiation, G, was set to 12 500 kJ m^{-2} per day and remained constant for the entire simulation period, hence 521 kJ m^{-2} per hour (set in the *.meth file).

4.3.2 Results and discussion

a. Substance fully present in water phase

Figure 8 shows the concentration in water as a function of the distance in the ditch for the first 250 m at t = 0, 0.5, 1, 2 and 4 days. The dissipation of the substance is due to photolysis.

Visual inspection of Figure 8 shows that the correspondence in concentration profiles calculated by TOXSWA and the analytical solution is satisfactory. Table 4 gives the RMSE values of the difference in concentration in water calculated by TOXSWA and the analytical solution after 0.5, 1, 2 and 4 days. The RMSE values are in the same order of magnitude as those of the reference test. Both the visual correspondence of concentration profiles and the RMSE values met our requirements, thus pointing towards a correct implementation of the concept of transformation in the water phase in TOXSWA.

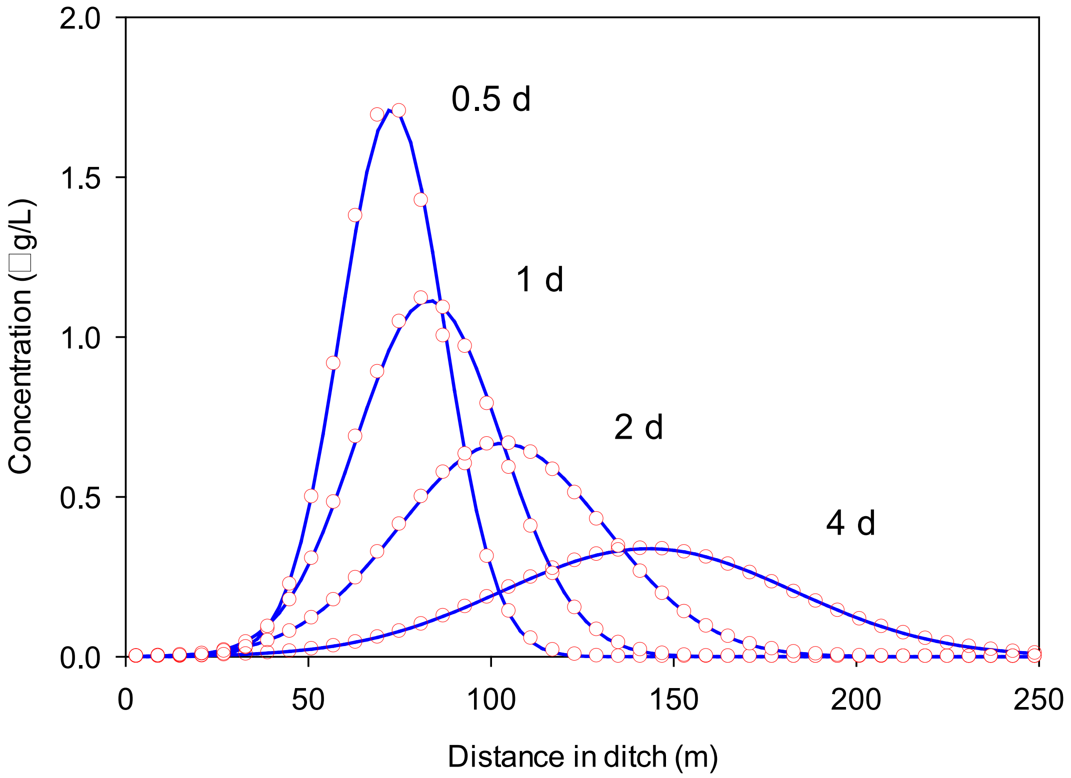

Figure 8 *Comparison of concentration in water byTOXSWA (markers) with the concentration by the analytical solution for transformation in the water phase only (lines) of the watercourse after 0.5, 1, 2 and 4 days. Photolysis DegT50$_{ph,ref}$ is 5.2 days at reference daily global radiation of 10 000 kJ m^{-2}. Global radiation is constant in time: 12 500 kJ m^{-2} per day period.*

Table 4

Root Mean Squared Error of the difference in concentration in water calculated by TOXSWA and an analytical solution for transformation in the water phase only of the watercourse after 0.5, 1, 2 and 4 days. Photolysis half-live used: 5.2 days at reference daily global radiation of 10 000 kJ/m^2. Global radiation is constant in time: 12 500 kJ/m^2 per day period. The RMSE of the reference case is given in the last column.

Time (d)	RMSE (μg/L)	RMSE reference case (μg/L)
0.5	0.0124	0.0126
1	0.0059	0.0062
2	0.0027	0.0029
4	0.0010	0.0012

b. Substance partly present in water phase

Figure 9 shows the concentration in water (i.e. dissolved in water) as a function of the distance in the ditch for the first 250 m at *t* = 0, 0.5, 1, 2 and 4 days. In the whole simulation period about half of the substance mass is adsorbed to suspended solids. This is the reason why the maximum concentration in the ditch at *t* = 0.5 d is at least a factor 2 lower compared to test a. (Note the difference in scale of the y-axis of Figures 8 and 9). The relative decrease of the concentration in time is lower when the substance is partly adsorbed. This can be seen from the peak heights at *t* = 0.5 d and *t* = 4 d. In the test a the ratio of peak concentrations at *t* = 0.5 d / *t* = 4 d is approximately 7. In test b this ratio is approximately 3. The substance mass adsorbed is not available for transformation. Desorption replenishes the transformed mass, dissolved in the water phase.

Visual inspection of Figure 9 shows that correspondence in concentration profiles calculated by TOXSWA and the analytical solution is satisfactory. Table 5 gives the RMSE values of the difference in concentration in water calculated by TOXSWA and an analytical solution for transformation in the water phaseonly after 0.5, 1, 2 and 4 days. The RMSE values are lower than those of the reference test. Due to sorption to suspended solids the concentration dissolved in water is lower, thus lowering the value of the RMSE. It may be concluded that both the visual correspondence of the concentration profiles and the RMSE values met our requirements, thus pointing towards a correct implementation of the photolysis concept in TOXSWA.

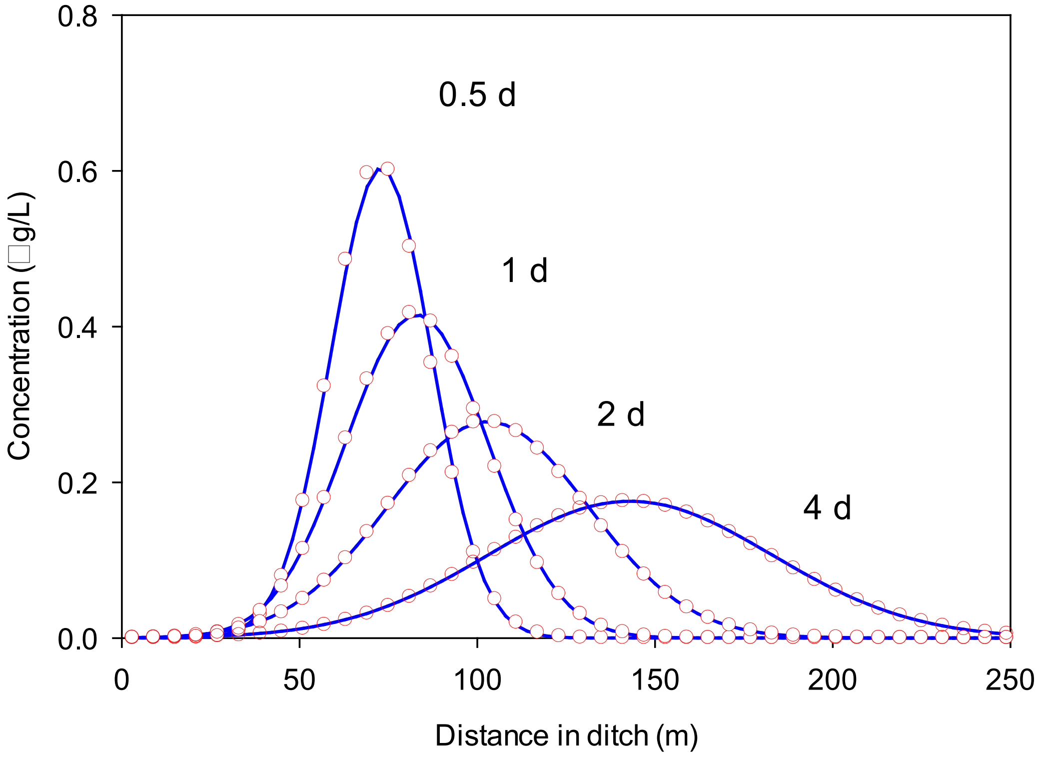

Figure 9 *Comparison of concentration in water of TOXSWA (markers) with an analytical solution for transformation in the water phase only (lines) of the watercourse after 0.5, 1, 2 and 4 days. Photolysis DegT50$_{ph,ref}$ = 5.2 days at reference daily global radiation of 10 000 kJ m^{-2}, K$_{F,om,ss}$ = 200 000 L/kg. Global radiation is constant in time: 12 500 kJ m^{-2} per day period.*

Table 5

Root Mean Squared Error of the difference in concentration in water calculated by TOXSWA and an analytical solution for transformation in the water phase of the watercourse after 0.5, 1, 2 and 4 days. Photolysis half-live used: 5.2 days at reference daily global radiation of 10 000 kJ m^{-2}. K$_{om,ss}$ = 200 000 L/kg. Global radiation is constant in time: 12 500 kJ m^{-2} per day period. The RMSE of the reference case is given in the last column.

Time (d)	**RMSE (µg/L)**	**RMSE reference case (µg/L)**
0.5	0.0044	0.0126
1	0.0023	0.0062
2	0.0012	0.0029
4	0.0006	0.0012

4.4 Test 2: Linear relation between photolysis rate and global radiation

4.4.1 Set up of the test

The aim of the test is to verify whether the linear relationship between the photolysis rate and global radiation is implemented correctly.

For this test we used the results of the example described in section 3.5. In this simulation only transformation in the water phase due to photolysis is considered. Other processes that may decrease the concentration are not considered, i.e. there is no volatilization, sorption to suspended solids or macrophytes and transport to sediment.

To test the linear relationship between photolysis and global radiation the decrease in mass taken from the output of the TOXSWA simulation is compared to an analytical solution for decrease in mass in an ideally mixed reservoir due to transformation only.

The analytical solution for the decrease in mass as a function of the global radiation is derived in Annex 6, which resulted in:

$$\frac{\Delta M}{M} = exp\left[-\frac{G}{G_{ref}} k_{ph,ref} \Delta t\right] - 1 \tag{12}$$

where M is the mass in the water layer in grams.

TOXSWA gives the total mass dissolved in the water layer (M) at the end of each hour in the *.out file. The decrease in mass M is calculated via:

$$\left(\frac{\Delta M}{M}\right)_{t_1} = \frac{(M_{t_2} - M_{t_1})}{M_{t_1}} \tag{13}$$

where M_{t1} and M_{t2} are the mass dissolved at $t = t_1$ and t_2, respectively (e.g. 11:00 and 12:00).

The $DegT50_{ph,ref}$ was 5.2 d, and the reference daily global radiation, G_{ref}, was set to 10 000 kJ m^{-2}. In the test G varied over time (between 0 and 2 410 kJ m^{-2} per hour period).

4.4.2 Results and discussion

Figure 10 shows the relationship between the decrease in mass and the global radiation from the analytical solution, Eq. (12), and decrease of mass from TOXSWA, Eq. (13).

The relative decrease calculated with TOXSWA corresponds well with Eq. (12).The decrease calculated by TOXSWA becomes increasingly, slightly higher than calculated with Eq. (12) (visible in Figure 10 in the upper range). The difference has a numerical background. A decrease of the time step from 600 s to 60 s, reduces the differences because non-linear processes are approximated better using smaller time steps (not shown here). The linear relationship between transformation by photolysis and global radiation shown supports the correct implementation of the photolysis concept in TOXSWA.

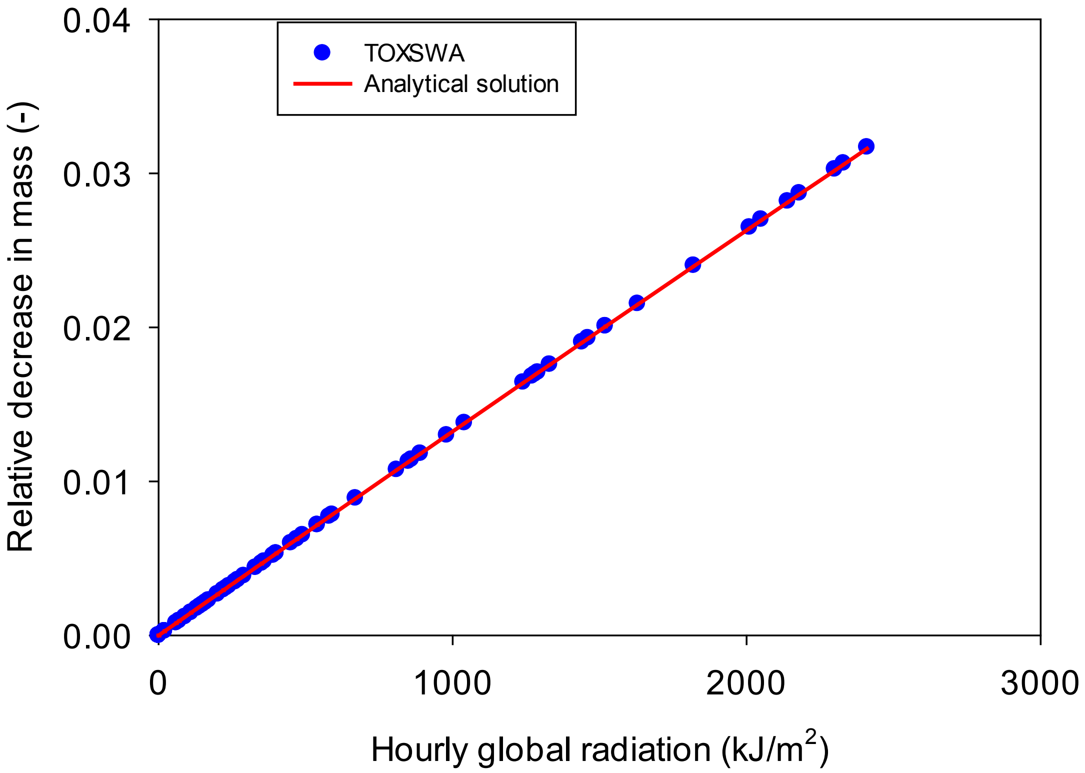

Figure 10 *Relative decrease in mass per hour as a function of the global radiation per hour calculated by TOXSWA (markers) and by the analytical solution (line).*

4.5 Test 3: Robustness of TOXSWA kernel version 3.4

4.5.1 Set up of the test

The aim of the test is to check if the TOXSWA model is numerically robust for the implemented concepts. For the robustness test, we used the scenario and substance properties of the test case as described in section 3.5. The parameters that affect the photolysis rate directly were tested. We varied the properties $DegT50_{\mathrm{ph,ref}}$, G_{ref} and G (constant in time during simulation), because they determine the rate of transformation. We varied the concentration of suspended solids and the sorption coefficient for sorption to suspended solids ($K_{\mathrm{F,om,ss}}$), because they determine the availability of the substance for transformation. For the test combinations the minimum and maximum values of the parameters were used, because in this way the whole domain of options is covered.

Table 6

Combinations of parameter values used for the robustness test: $DegT50_{ph,ref}$, G, G_{ref}, concentration of suspended solids and sorption coefficient for suspended solids $K_{F,om,ss}$. The test values correspond to the minimum and maximum input values allowed by TOXSWA.

Test nr	**$DegT50_{ph,ref}$ (d)**	**G (kJ/m^2 per day)**	**G_{ref} (kJ/m^2)**	**G/ G_{ref}**	**Conc. susp. sol. (g/m^3)**	**$K_{F,om,ss}$ (L/kg)**	**Sorption**
1	0.1	1 000	1 000	1	0	0	no sorption
2	$1 \cdot 10^5$	1 000	1 000	1	0	0	no sorption
3	0.1	50 000	1 000	50	0	0	no sorption
4	$1 \cdot 10^5$	50 000	1 000	50	0	0	no sorption
5	0.1	1 000	50 000	0.02	0	0	no sorption
6	$1 \cdot 10^5$	1 000	50 000	0.02	0	0	no sorption
7	0.1	1 000	1 000	1	$1 \cdot 10^5$	$1 \cdot 10^7$	sorption
8	$1 \cdot 10^5$	1 000	1 000	1	$1 \cdot 10^5$	$1 \cdot 10^7$	sorption
9	0.1	50 000	1 000	50	$1 \cdot 10^5$	$1 \cdot 10^7$	sorption
10	$1 \cdot 10^5$	50 000	1 000	50	$1 \cdot 10^5$	$1 \cdot 10^7$	sorption
11	0.1	1 000	50 000	0.02	$1 \cdot 10^5$	$1 \cdot 10^7$	sorption
12	$1 \cdot 10^5$	1 000	50 000	0.02	$1 \cdot 10^5$	$1 \cdot 10^7$	sorption

Simulations with TOXSWA were done for the twelve cases specified in Table 6. It was tested whether TOXSWA runned without giving warnings, e.g. no substance mass balance errors above 0.1%.

In Table 6 also the ratio G/G_{ref} is given. From Eq. (7) it can be seen that this ratio affects the photolysis rate to a great extent. Hence the cases 1, 2, 7 and 8 do not represent a minimum or a maximum for photolysis. Nevertheless, the cases are included to cover all input values. Furthermore, in reality the value of global radiation may be zero during simulations (e.g. at night). Hence the cases 5. 6, 11 and 12 do not represent a real minimum for photolysis.

4.5.2 Results

TOXSWA finalized the runs without giving warnings or substance mass balance errors for all twelve cases.

4.6 Conclusions

The conclusions of the tests with TOXSWA kernel version 3.4 described in the sections 4.3 to 4.5 are:

- The concept of transformation in the water phase only is implemented correctly in TOXSWA.
- The linear relationship between photolysis and global radiation is implemented correctly in TOXSWA.
- The calculation of photolysis with the TOXSWA model is robust.

5 Conclusions and recommendations

The TOXSWA model has been extended with the functionality to simulate photolysis. Photolysis is modelled as a first-order process and is assumed to occur in the water phase only. So, mass sorbed onto e.g. suspended solids is assumed not to degrade. The photolysis is described as a linear function of global radiation.

Calculations with the lumped transformation concept in TOXSWA and the lumped *DegT50** for the example lab study will give the same concentrations as using the transformation in the water phase only concept with the *DegT50*-dissolved. The lumped transformation concept ignores that substance sorbed to suspended solids may not be available for transformation, but it does correspond to the experimental practice of measuring the decrease in the water of the flask, without filtering the suspended solids out of the water before the measurements.

Tests with TOXSWA confirmed that the concepts of transformation in the water phase only and the linear relationship between photolysis and global radiation are implemented correctly. Also shown was that the calculation of photolysis with the TOXSWA model is robust. Outdoor studies may be used to derive the mean of the *DegT50* values for photolysis. To scale the *DegT50* values of all studies to the same reference daily global radiation, a simple procedure is given in section 3.4. However, we recommend to develop a more refined method to normalize photolysis to the reference daily global radiation. Such a procedure may take example of existing procedures for normalization of *DegT50* values in soil from field dissipation studies.

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Annex 1 Meteo file with time-dependent values of the global radiation

The hourly meteo file used in the example described in section 3.5 is given in Figures A1a and A1b.

```
*  MSTAT  YYYY  MM  DD  HH    RAD
*                           kJ.m-2
***********************************
'DeBilt'  1986   6   1   1      0
'DeBilt'  1986   6   1   2      0
'DeBilt'  1986   6   1   3      0
'DeBilt'  1986   6   1   4     20
'DeBilt'  1986   6   1   5    130
'DeBilt'  1986   6   1   6    270
'DeBilt'  1986   6   1   7    580
'DeBilt'  1986   6   1   8    470
'DeBilt'  1986   6   1   9    400
'DeBilt'  1986   6   1  10    490
'DeBilt'  1986   6   1  11    540
'DeBilt'  1986   6   1  12    390
'DeBilt'  1986   6   1  13    290
'DeBilt'  1986   6   1  14    150
'DeBilt'  1986   6   1  15    220
'DeBilt'  1986   6   1  16    140
'DeBilt'  1986   6   1  17     70
'DeBilt'  1986   6   1  18     60
'DeBilt'  1986   6   1  19     20
'DeBilt'  1986   6   1  20      0
'DeBilt'  1986   6   1  21      0
'DeBilt'  1986   6   1  22      0
'DeBilt'  1986   6   1  23      0
'DeBilt'  1986   6   1  24      0
'DeBilt'  1986   6   2   1      0
'DeBilt'  1986   6   2   2      0
'DeBilt'  1986   6   2   3      0
'DeBilt'  1986   6   2   4    170
'DeBilt'  1986   6   2   5    400
'DeBilt'  1986   6   2   6    540
'DeBilt'  1986   6   2   7   1290
'DeBilt'  1986   6   2   8   2140
'DeBilt'  1986   6   2   9   2050
'DeBilt'  1986   6   2  10   1520
'DeBilt'  1986   6   2  11   1820
'DeBilt'  1986   6   2  12   1630
'DeBilt'  1986   6   2  13   1040
'DeBilt'  1986   6   2  14   1270
'DeBilt'  1986   6   2  15   2010
'DeBilt'  1986   6   2  16   1460
'DeBilt'  1986   6   2  17    810
'DeBilt'  1986   6   2  18    350
'DeBilt'  1986   6   2  19     60
'DeBilt'  1986   6   2  20      0
'DeBilt'  1986   6   2  21      0
'DeBilt'  1986   6   2  22      0
'DeBilt'  1986   6   2  23      0
'DeBilt'  1986   6   2  24      0
```

Figure A1a *Hourly meteo file, the *.meth file for TOXSWA, used in the example simulation of Section 3.5 (first part).*

```
*  MSTAT  YYYY  MM   DD  HH     RAD
*                            kJ.m-2
***********************************
'DeBilt'  1986   6   3    1       0
'DeBilt'  1986   6   3    2       0
'DeBilt'  1986   6   3    3       0
'DeBilt'  1986   6   3    4     160
'DeBilt'  1986   6   3    5     360
'DeBilt'  1986   6   3    6     220
'DeBilt'  1986   6   3    7     350
'DeBilt'  1986   6   3    8     470
'DeBilt'  1986   6   3    9     590
'DeBilt'  1986   6   3   10    1240
'DeBilt'  1986   6   3   11     890
'DeBilt'  1986   6   3   12     670
'DeBilt'  1986   6   3   13     240
'DeBilt'  1986   6   3   14     330
'DeBilt'  1986   6   3   15     230
'DeBilt'  1986   6   3   16     110
'DeBilt'  1986   6   3   17     110
'DeBilt'  1986   6   3   18      90
'DeBilt'  1986   6   3   19      20
'DeBilt'  1986   6   3   20       0
'DeBilt'  1986   6   3   21       0
'DeBilt'  1986   6   3   22       0
'DeBilt'  1986   6   3   23       0
'DeBilt'  1986   6   3   24       0
'DeBilt'  1986   6   4    1       0
'DeBilt'  1986   6   4    2       0
'DeBilt'  1986   6   4    3       0
'DeBilt'  1986   6   4    4     200
'DeBilt'  1986   6   4    5     450
'DeBilt'  1986   6   4    6     850
'DeBilt'  1986   6   4    7     980
'DeBilt'  1986   6   4    8    1280
'DeBilt'  1986   6   4    9    1330
'DeBilt'  1986   6   4   10    2410
'DeBilt'  1986   6   4   11    2180
'DeBilt'  1986   6   4   12    2330
'DeBilt'  1986   6   4   13    2300
'DeBilt'  1986   6   4   14    1520
'DeBilt'  1986   6   4   15    1440
'DeBilt'  1986   6   4   16     860
'DeBilt'  1986   6   4   17     260
'DeBilt'  1986   6   4   18     200
'DeBilt'  1986   6   4   19      70
'DeBilt'  1986   6   4   20       0
'DeBilt'  1986   6   4   21       0
'DeBilt'  1986   6   4   22       0
'DeBilt'  1986   6   4   23       0
'DeBilt'  1986   6   4   24       0
```

Figure A1b *Hourly meteo file, the *.meth file for TOXSWA, used in the example simulation of Section 3.5 (second part).*

Annex 2 TOXSWA input file

This annex shows an example of a TOXSWA input file (Figures A2a – A2f). The input file shown is used in Test 1 described in section 4.3.

```
*-------------------------------------------------------------------------------
* INPUT FILE for TOXSWA
*-------------------------------------------------------------------------------
*
* Contact address:
* -----------------
* Wim Beltman
* Alterra
* PO BOX 47
* 6700 AA Wageningen
* The Netherlands
* e-mail: wim.beltman@wur.nl
*
* (c) Alterra
*

*-------------------------------------------------------------------------------
* Section 1: Control section
*-------------------------------------------------------------------------------

01-Jan-1975 TimStart  ! Starting time of simulation [01-Jan-1900|31-Dec-9999]
05-Jan-1975 TimEnd    ! End time of simulation [01-Jan-1900|31-Dec-9999]

* Version of calling program (CallingProgram):
* NL          = in DRAINBOW for Dutch authorization
* FOCUS       = in FOCUS_TOXSWA for EU authorization
* CHINA       = in TOPrice for Chinese authorization
* GEM         = in GEM-GUI for Dutch greenhouse authorization
FOCUS       CallingProgram


* Version numbers (CallingProgramVersion) (x,y,z):
* x = version number of the model
* y = version number of the GUI
* z = version number of the database
1.1.1       CallingProgramVersion
Hourly      OptInp     ! Options are 'Hourly' and 'Daily'

* Hydrology simulation option (OptHyd):
* Only      = Runs only hydrology
* OnLine    = Runs hydrology and substance
* OffLine   = Assumption the hydrology has been run,runID.hyd file must be present
* Automatic = TOXSWA checks if the hydrology file (runID.hyd) exists. Then the
*             hydrology simulation is skipped
OnLine     OptHyd


* Temperature simulation option (OptTem):
* Only      = Runs only temperature
* OnLine    = Runs temperature and substance
* OffLine   = Assumption the temperature has been run, runID.tem file must be
*             present
* Automatic = TOXSWA checks if the temperature file (runID.tem) exists. Then the
*             temperature simulation is skipped
OnLine     OptTem


Liss               OptVol   ! Option for volatilization [Liss, Jacobs]

* Time step substance simulation options (OptTimStp):
* Input = User defined
* Calc  = Calculated by TOXSWA
Calc        OptTimStp
```

Figure A2a *TOXSWA input file used in Test 1 described in section 4.3 (first part).*

```
* If: OptTimStp =  Calc
600         MaxTimStpWat (s) ! Maximum calculation time step in water layer
[0.001|3600]
600         MaxTimStpSed (s) ! Maximum calculation time step in sediment layer
                             ! [0.001|3600]

* If: CallingProgram = NL or GEM
900          TimStpHyd (s) ! Calculation time step for hydrology [0.001|3600.0]

Yes          OptScreen    ! Option to show output on screen [Yes, No]
*-------------------------------------------------------------------------------
*  Section 2: Waterbody
*-------------------------------------------------------------------------------

Analyt     Location     ! Name of the location
Analyt     WaterbodyID  ! ID of the water body

* Table WaterBody
* Len           = Length (m) [0.05|-]
* NumSeg        = Number of segments (-)[1|-]
* WidWatSys     = Width of the bottom of water system (m) [0.05|100]
* SloSidWatSys  = Side slope  of the water system (-)[0|10]
* DepWatDefPer  = Water depth defining perimeter for exchange between water layer
*                 and sediment (m) [0|lowest water depth]

Table WaterBody
Len   NumSeg   WidWatSys   SloSidWatSys DepWatDefPer
(m)    (-)       (m)            (-)          (m)
360    60        1.0          1.0E-5         0.1
EndTable

0.0        ConSus (g.m-3)       ! Concentration of suspended solids
                                ! [0.0|100000.0]
1.0        CntOmSusSol (kg.kg-1) ! Mass ratio of organic matter in suspended solids
                                ! [0.0|1.0]
0.0        AmaMphWatLay (g.m-2) ! Dry weight of macrophyte biomass per m2 bottom
                                ! [0.0|1000.0]

*-------------------------------------------------------------------------------
* Section 3: Hydrology: general
*-------------------------------------------------------------------------------

Pond        OptWaterSystemType ! Option for selecting the water system type
                               ! [Pond, WaterCourse]
Constant    OptFloWat          ! Option for water flow [Constant, Variable]


* if: OptWaterSystemType = WaterCourse
Input       OptDis             ! Option for selecting dispersion method
                               ! [Fischer, Input]

* if: OptWaterSystemType = WaterCourse and OptDis = Input
200         CofDisPhsInp (m2.d-1) ! Dispersion coefficient  [0.0|1000000.0]


*-------------------------------------------------------------------------------
* Section 3a: Constant water flow
*-------------------------------------------------------------------------------

* if:  OptFloWat  = Constant
0.5        DepWat (m)           ! Water depth [0.001|10.0]
20.0       VelWatFlwBas (m.d-1) ! Flow velocity [-100000.0|100000.0]
*-------------------------------------------------------------------------------
```

Figure A2b *TOXSWA input file used in Test 1 described in section 4.3 (second part).*

```
* Section 4: Sediment section
*-------------------------------------------------------------------------------

FOCUS      SedimentTypeID ! Name of sediment type

* Table SedimentProfile
* ThiHor = thickness of horizon [0.0001|-]
* NumLay = number of layers in horizon [1|500]
table SedimentProfile
ThiHor NumLay
(m)
0.004    4
0.006    3
0.01     2
0.03     3
0.02     1
0.03     1
end_table

Input      OptSedProperties ! Option sediment properties [Input, Calc]
0.05               ThiTopLaySed (m)

* table specifying SedimentProperties for each horizon:
* Nr        = number horizon [1|500]
* Rho       =  bulk density [10|3000]
* CntOm     = organic matter mass content [0.0|1.0]
* ThetaSat  = saturated water content [0.001|0.999]
* CofDifRel = relative diffusion coefficient [0.0|1.0]
table  horizon SedimentProperties
Nr     Rho        CntOm     ThetaSat   CofDifRel  (volgorde gewijzigd)
       (kg.m-3)   (kg.kg-1)  (m3.m-3)   (-)
1      800.0      0.09       0.68       0.560
2      800.0      0.09       0.68       0.560
3      800.0      0.09       0.68       0.560
4      800.0      0.09       0.68       0.560
5      800.0      0.09       0.68       0.560
6      800.0      0.09       0.68       0.560
end_table

0.      FlwWatSpg (m3.m-2.d-1) ! Rate of percolation through the sediment
                               ! [0.0|0.01]

* if: FlwWatSpg not zero
* table DispersionLength for each horizon
* Nr           = Horizon number [1|500]
* LenDisSedLiq = Dispersion length of solute in liquid phase (m) [0.01|1.0]
table  horizon DispersionLength
Nr     LenDisSedLiq
       (m)
1      0.015
2      0.015
3      0.015
4      0.015
5      0.015
6      0.015
end_table

*-------------------------------------------------------------------------------
* Section 5: Weather section
*-------------------------------------------------------------------------------

0        MeteoStation    ! Name of the *.met or *.meth file with meteo data
Hourly  OptMetInp          ! Option for hourly or daily input data (Hourly, Monthly)

* if: OptMetInp = Hourly
52.00    LocLat (Degrees)   ! Latitude of meteostation
-4.00    LocLong (Degrees)  ! Longitude of meteostation
1.0      TimZone (-)        ! Time zone
20.00    FacWatTur1 (W.m-2) ! Turbidity factor a1
20.00    FacWatTur2 (W.m-2) ! Turbidity factor a2
-0.75    FacCldB1 (-)       ! Cloud contribution factor b1
3.4      FacCldB2 (-)       ! Cloud contribution factor b2
70.00    FacCldC1 (W.m-2)   ! Cloud contribution factor c1
0.00     FacCldC2 (W.m-2)   ! Cloud contribution factor c2
1.50     MetLvlRef (m)      ! Reference level meteo measurements
10.00    MetLvlObs (m)      ! Height of meteo measurements
```

Figure A2c *TOXSWA input file used in Test 1 described in section 4.3 (third part).*

```
*-------------------------------------------------------------------------------
* Section 6: Temperature section
*-------------------------------------------------------------------------------

5.       TemWatIni (C)      ! Initial temperature in water layer
10.      AvgTemGrw (C)      ! Average temperature in groundwater

*-------------------------------------------------------------------------------
* Section 7: Substance section
*-------------------------------------------------------------------------------

AO1             SubstanceName
table compounds
AO1
end_table

table FraPrtDauWat (mol.mol-1)
end_table

table FraPrtDauSed (mol.mol-1)
end_table

*--------------- Parent: AO1 ---------------
300.       MolMas_AO1 (g.mol-1)        ! Molar mass [10.0|10000.0]
Pho        OptTra_AO1                  ! Options: Lumped Hdr Pho Bio HdrPho HdrBio
                                       ! PhoBio HdrPhoBio

5.2        DT50LiqPhoRef_AO1 (d)       ! Half-life photolysis in water at reference
                                       ! daily global radiation [0.1|100000.0]
10000.0    RadGloRef (kJ.m-2)          ! Reference daily global radiation [1000|50000]

1000000    DT50SedRef_AO1  (d)         ! Half-life transformation in sediment
                                       ! [0.1|100000.0]
20.        TemRefTraSed_AO1  (C)       ! Temperature at which half-life was
                                       ! measured [5.0|30.0]
0.         MolEntTraSed_AO1 (kJ.mol-1) ! Molar activation enthalpy of
                                       ! transformation in sedment [0.0|200.00]

35.        KomSed_AO1  (L.kg-1)        ! Coefficient of  equilibrium sorption in
                                       ! sediment [0.0|10000000.0]
1.         ConLiqRefSed_AO1  (mg.L-1)  ! Reference concentration in liquid phase in
                                       ! sediment [0.001|100.0]
1.         ExpFreSed_AO1  (-)          ! Freundlich exponent  in sediment [0.1|1.5]
0.         KomSusSol_AO1  (L.kg-1)     ! Coefficient of  equilibrium sorption
                                       ! suspended solids [0.0|10000000.0]
1.         ConLiqRefSusSol_AO1 (mg.L-1) ! Reference concentration in liquid phase
                                       ! suspended solids [0.001|100.0]
1.         ExpFreSusSol_AO1  (-)       ! Freundlich exponent suspended solids
                                       ! [0.1|1.5]
0.         CofSorMph_AO1  (L.kg-1)     ! Coefficient for linear sorption on
                                       ! macrophytes [0.0|10000000.0]

0.0001     PreVapRef_AO1  (Pa)         ! Saturated vapour pressure of substance
                                       ! [0.0 |200000.0]
20.        TemRefVap_AO1  (C)          ! Temperature of reference at which the
                                       ! saturated vapour pressure was measured
                                       ! [0.0|40.0]
95.        MolEntVap_AO1  (kJ.mol-1)   ! Molar enthalpy of the vaporization process
                                       ! [-200|200]
90.        SlbWatRef_AO1  (mg.L-1)     ! Water solubility of substance
                                       ! [0.001|1000000.0]
20.        TemRefSlb_AO1  (C)          ! Temperature of reference at which the
                                       ! water solubility was  measured [0.0|40]
27.        MolEntSlb_AO1  (kJ.mol-1)   ! Molar enthalpy of the dissolution
                                       ! [-200.0|200.0]
0.         CofDifWatRef_AO1  (m2.d-1)  ! Reference diffusion coefficient in water
                                       ! [0.0|200.0E-5]
20.        TemRefDif_AO1 (C)           ! Reference temperature for diffusion
0.43       CofDifAirRef_AO1 (m2.d-1)   ! Reference diffusion coefficient in air
                                       ! [0.0|200.0E-5]
```

Figure A2d *TOXSWA input file used in Test 1 described in section 4.3 (fourth part).*

```
*-------------------------------------------------------------------------------
* Section 8: 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
DriftOnly      OptLoa

AO1   ApplicationScheme ! Name of the applicaton 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) [0.|-]
* Column 4: Start of stretch of watercourse loaded by all loading types (m)
*           [0.0|10000.0]
* Column 5: End of stretch of watercourse loaded by all loading types (m)
*           [0.0|10000.0]
table Loadings
01-Jan-1975-0000 Drift 5.5   60.  66.0
end_table

* if: CallingProgram = FOCUS
No         OptUpsInp             ! Switch for upstream catchment treated (Yes, No)

0.0        ConAir (kg.m-3)       ! Concentration of the substance in air [0.0|-]
0.         ConSysWatIni (g.m-3)  ! Initial total concentration in water layer
                                 ! [0.0|-]

* if: FlwWatSpg not zero
0.0        ConWatSpg (g.m-3)     ! Concentration in incoming seepage water [0.0|-]

table interpolate CntSysSedIni (mg.kg-1)
end_table

*-------------------------------------------------------------------------------
* Section 9: Output control
*-------------------------------------------------------------------------------

No        OptDelOutFiles   ! Swith for removing *.out files after run (Yes, No)
DaysFromSta DateFormat     ! Date format (DaysFromSta, DaysFrom1900, Years)
e14.6     RealFormat       ! Number format of the reals
No        PrintCumulatives ! Specify whether fluxes should be cumulated over
                           ! the entire simulation period (Yes , No)

* Option to set output time step (OptDelTimPrn):
* (Hour, Day, Decade, Month, Year, Automatic, Other)
* Automatic = length of simulation period
* Other     = user defined
Hour         OptDelTimPrn


FOCUS     OptReport ! Options for report type (DutchRegistration, FOCUS)
Yes       ExposureReport   ! Exposure report (Yes, No)
No        PercentileReport ! Percentile report (Yes, No)

0.05       ThiLayTgt (m)   ! Thickness of target layer of sediment
                           ! [0.00001|1.0]

table HorizontalProfiles
05-Jan-1975-0000
end_table

All        OptOutputDistances ! Switch output distances [None, All, table]
* Table output distances (OutputDistances):
* Column 1: Distance [0.0|-]
table OutputDistances (m)
end_table
```

Figure A2e *TOXSWA input file used in test described in section 4.3 (fifth part).*

```
* Table output depths (OutputDepths):
* Column 1: Depth [0.0|-]
table OutputDepths (m)
end_table


* Print to *.out file:
No       print_DepWat          ! Water depth [Yes, No]
No       print_QBou            ! Discharge [Yes, No]
No       print_VelWatFlw       ! Flow velocity [Yes, No]
No       print_VvrLiqDra       ! Drain flow [Yes, No]
No       print_VvrLiqRnf       ! Runoff (+ infiltration) flow [Yes, No]
No       print_FlmDra          ! Drain substance flux [Yes, No]
No       print_FlmRnf          ! Runoff substance flux [Yes, No]
No       print_FlmErs          ! Erosion substance flux [Yes, No]
No       print_ConLiqWatLay    ! Concentration in water,hour average [Yes, No]
Yes      print_ConLiqWatLayCur ! Concentration in water, at end hour [Yes, No]
No       print_CntSorMph       ! Content sorbed to macrophytes [Yes, No]
No       print_CntSorSusSol    ! Content sorbed suspended solids [Yes, No]
No       print_ConSysWatLay    ! Total concentration in water [Yes, No]
No       print_ConLiqSed       ! Concentration in pore water sediment [Yes, No]
No       print_CntSorSed       ! Content sorbed to sediment [Yes, No]
No       print_ConSysSed       ! Total content in sediment [Yes, No]
No       print_CntSedTgt       ! Total content in target layer sediment [Yes, No]
No       print_ConLiqSedTgt    ! Concentation in pore water in target layer
                               ! sediment [Yes, No]
No       print_CntSorSedTgt    ! Content sorbed in target layer sediment [Yes, No]
No       print_VolErrWatLay    ! Volume error in waterbody [Yes, No]
No       print_AmaWatLay       ! Mass in water layer [Yes, No]
No       print_AmaLiqWatLay    ! Mass in liquid phase in water layer [Yes, No]
No       print_AmaSorSusSol    ! Mass sorbed to suspended solids in water layer
                               ! [Yes, No]
No       print_AmaSorMph       ! Mass sorbed to macrophytes in water layer
                               ! [Yes, No]
No       print_AmaSed          ! Mass in sediment layer [Yes, No]
No       print_AmaLiqSed       ! Mass in liquid phase in sediment layer [Yes, No]
No       print_AmaSorSed       ! Mass sorbed in sediment layer [Yes, No]
No       print_AmaDrfWatLay    ! Mass entered water layer by spray drift [Yes, No]
No       print_AmaAtmDepWatLay ! Mass entered water layer by atmospheric
                               ! depositon [Yes, No]
No       print_AmaDraWatLay    ! Mass entered water layer by drainage [Yes, No]
No       print_AmaRnoWatLay    ! Mass entered water layer by runoff [Yes, No]
No       print_AmaSedInWatLay  ! Mass penetrated into sediment from water layer
                               ! [Yes, No]
No       print_AmaSedOutWatLay ! Mass transfered from sediment into water layer
                               ! [Yes, No]
No       print_AmaDwnWatLay    ! Mass flowed across downstream boundary out of
                               ! water layer [Yes, No]
No       print_AmaUpsWatLay    ! Mass flowed across upstream boundary into water
                               ! layer [Yes, No]
No       print_AmaTraWatLay    ! Mass transformed in water layer [Yes, No]
No       print_AmaForWatLay    ! Mass formed in water layer [Yes, No]
No       print_AmaVolWatLay    ! Mass volatilised in water layer [Yes, No]
No       print_AmaErrWatLay    ! Mass error in water layer [Yes, No]
No       print_AmaTraSed       ! Mass transformed in sediment layer [Yes, No]
No       print_AmaForSed       ! Mass formed in sediment layer [Yes, No]
No       print_AmaWatLayInSed  ! Mass transfered into water layer from sediment
                               ! layer  [Yes, No]
No       print_AmaWatLayOutSed ! Mass transfered from water layer into sediment
                               ! layer [Yes, No]
No       print_AmaDwnSed       ! Mass leaving sediment layer across lower boundary
                               ! [Yes, No]
No       print_AmaErsSed       ! Mass entering sediment layer by erosion [Yes, No]
No       print_AmaErrSed       ! Mass error in sediment layer [Yes, No]
No       print_ConLiqWatNLAvg  ! Concentration in water, average in evaluation
                               ! stretch [Yes, No]

*-------------------------------------------------------------------------------
* End of TOXSWA input file
*-------------------------------------------------------------------------------
```

Figure A2f *TOXSWA input file used in Test 1 described in section 4.3 (final part).*

Annex 3 Analytical solution of the convection-dispersion equation for substance in water, transformed only in the water phase

The derivation of the analytical solution was done analogously to Adriaanse (1996), but now for transformation in the water phase only. Photolysis is assumed to occur in the water phase only, so therefore, this analytical solution applies to photolysis, considered in this report.

The conservation equation for the water layer (see Eqs (1) and (4)) is:

$$\frac{\partial(c^*A)}{\partial t} = -\frac{\partial(A\,J)}{\partial x} - k(c\,A) + J_{wa}O_x - J_{wb}P_x \tag{A1}$$

For the analytical solution sorption to suspended solids is assumed to be a linear process, hence

$$X_{ss} = K_{L,ss}c \tag{A2}$$

with

X_{ss} = content of substance sorbed to suspended solids (M^{-1} M^{-1})

$K_{L,ss}$ = slope of linear sorption isotherm of suspended solids[1] (L^3 M^{-1})

The total concentration in water is given by (Eqs (4.1) and (4.4) in Adriaanse (1996) and Eq. (A2):

$$c^* = \left(1 + \frac{DW\ P_{z=0}}{A}K_{mp} + ssK_{L,ss}\right)c \tag{A3}$$

with

c^* = mass concentration of substance in the water layer ($M\ L^{-3}$)

DW = dry weight of macrophytes per area of sediment ($M\ L^{-2}$)

$P_{z=0}$ = wetted perimeter at z = 0 (L)

A = cross sectional area of flow (L^2)

K_{mp} = distribution coefficient for substance between macrophytes and water (L^3 M^{-1})

ss = mass concentration of suspended solids in the water layer ($M\ L^{-3}$)

The following substitutions based on Adriaanse (Eqs. (4.6), (4.11), and (4.14)) are used:

$$J = u\left(1 + ssK_{L,ss}\right)c - E_x\frac{\partial\left(1 + ssK_{L,ss}\right)c}{\partial x} \tag{A4}$$

with

u = flow velocity of water ($L\ T^{-1}$)

E_x = dispersion coefficient in direction of flow (L^2 T^{-1})

---

[1] Where $K_{L,ss} = m_{om,ss}\,K_{om,ss}$ (see Eq. (2) in section 2.3)

$$J_{wa} = -k_{t,l}\left(c - \frac{c_a}{K_H}\right) \tag{A5}$$

with

$k_{t,l}$ = overall transfer coefficient for the air-water interface, based on the liquid phase (L T^{-1})
c_a = mass concentration of substance in air (M L^{-3})
K_H = Henry coefficient (-)

$$J_{wb,adv} = \frac{l}{P_{z=0}} q\, c \tag{A6}$$

with

l = length of drained or infiltrated plot, perpendicular to the waterbody (L)
q = aeric volume flux, i.e. volume of drained or supplied water divided by the plot area (L T^{-1})

For a constant wetted area A, assuming exclusively convective downward seepage, mass concentration of substance in the air is zero, and using substitutions (A4) – (A6) the conservation equation (A1) can be rewritten to (see also Eq. (7.42) of Adriaanse):

$$\begin{aligned} R_{wl}\frac{\partial c}{\partial t} = {} & -u\frac{\partial c}{\partial x} + E_x\frac{\partial^2 c}{\partial x^2} - \frac{kc}{\left(1 + ssK_{L,ss}\right)} - \frac{k_{t,l}\, O_x}{A\left(1 + ssK_{L,ss}\right)} c \\ & - \frac{lq}{A\left(1 + ssK_{L,ss}\right)} c \end{aligned} \tag{A7}$$

in which R_{wl} (-) is a retardation factor is given by

$$R_{wl} = \frac{\left(1 + \frac{DW\, P_{z=0}}{A} K_{mp} + ssK_{L,ss}\right)}{1 + ssK_{L,ss}} \tag{A8}$$

Comparing (A7) to Eq. 7.42 of Adriaanse (1996) we see that k^* (noted as k in Adriaanse, 1996) has been replaced by $k/[R_{wl}\cdot(1 + ssK_{L,ss})]$. So, substituting this in Eq. 7.43 of Adriaanse et al, we obtain the following solution for Eq. (A7) for finite system with a pulse input on cross-sectional area of flow-averaged mass M (M L^{-2}) applied at t=0 is:

$$\begin{aligned} c = {} & \frac{M}{2R_{wl}\left(1 + ssK_{L,ss}\right)} \frac{1}{\sqrt{\pi E_x}\, \frac{t}{R_{wl}}} \\ & \cdot\ exp\left[-\left(\frac{k}{R_{wl}\left(1 + ssK_{L,ss}\right)} + \frac{k_{t,l}\, O_x}{AR_{wl}\left(1 + ssK_{L,ss}\right)} \right.\right. \\ & \left.\left. + \frac{lq}{AR_{wl}\left(1 + ssK_{L,ss}\right)}\right) t\right]\ \cdot\ exp\left[\frac{\left(x - u\frac{t}{R_{wl}}\right)^2}{4E_x\frac{t}{R_{wl}}}\right] \end{aligned} \tag{A9}$$

Note that the first exponential term in Eq. (A9), contains all dissipation processes. In test 1 and test 2 of this report there is no convective, downward transfer to sediment (q = 0) and no sorption to macrophytes (K_{mp}=0)

Annex 4 Reference case: test of TOXSWA against analytical solution for lumped transformation in water

For this reference case the input is almost identical to the input used for the example simulation described in section 3.5. Differences in input for the system of the reference case are:

- Using monthly input of meteorological data (water temperatures), set at 20 °C.
- Using a *DegT50** at the reference temperature of 20 °C for lumped transformation of 5.2 days.

The analytical solution was programmed in a FORTRAN program. The concentration in the water layer was calculated with TOXSWA and with the analytical solution. Figure A3 shows the calculated concentration in the water layer as a function of time. The graph shows a good agreement between the two models.

Table A1 gives the RMSE values of the difference in concentration in water in the water layer (in µg/L) calculated with TOXSWA and an analytical solution, applying lumped transformation. The RMSE decreases in time because the concentrations decrease in time.

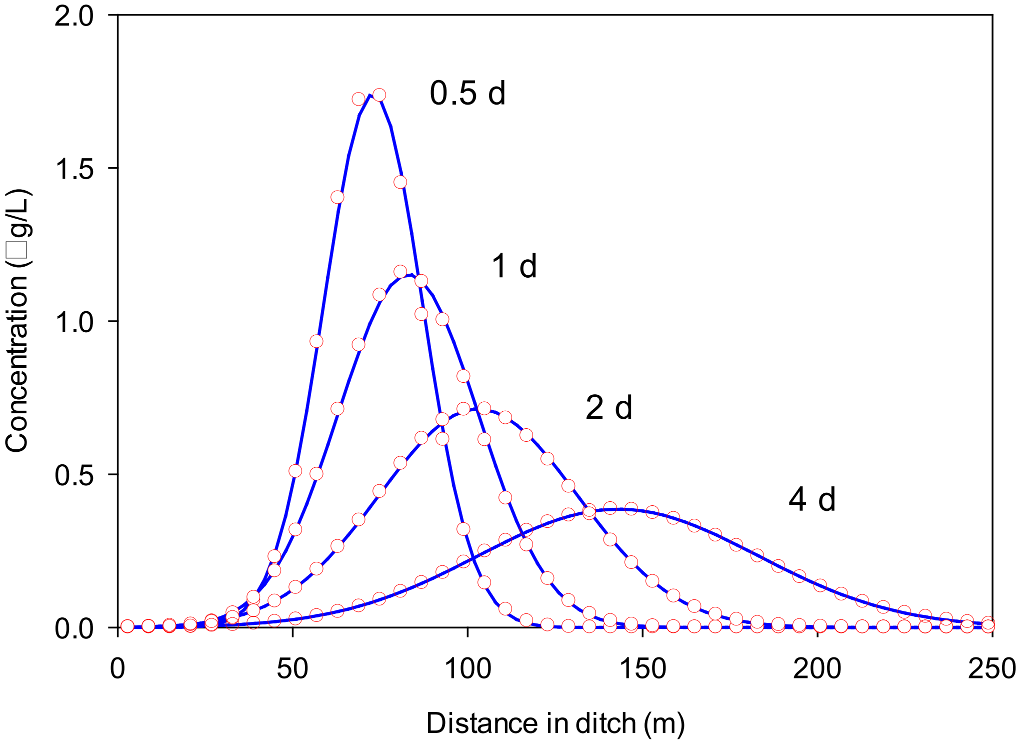

Figure A3 *Comparison of concentration in water layer, of TOXSWA (markers) with an analytical solution for lumped transformation (lines) after 0.5, 1, 2 and 4 days. Lumped transformation half-life at the reference temperature of 20 °C is 5.2 days.*

Table A1

Root Mean Squared Error of the difference in concentration in water calculated with TOXSWA and an analytical solution for lumped transformation in the water layer. Lumped transformation half-life at the reference temperature of 20 °C is 5.2 days.

Time (d)	RMSE (µg/L)
0.5	0.0126
1	0.0062
2	0.0029
4	0.0012

Annex 5 Scenario and substance properties used for testing TOXSWA against the analytical solution

In Table A2 the values of the scenario and substance properties as used for the test described in section 4.3 (i.e. transformation in the water phase only) are given for TOXSWA and for the FORTRAN program used to calculate the analytical solution.

The spray drift mass used for the TOXSWA simulation is recalculated to an initial mass for the analytical solution entering the cross sectional area of flow. For the TOXSWA simulation the deposition on the water surface is 5.5 mg/m^2. The entry in one segment of 6 m length and 1 m width of the water body is then 33 mg/m^2. This mass is introduced in the analytical solution as the mass deposited on the cross sectional area of flow at 63 m, hence 33 mg/m^2 on the cross sectional surface area of 0.5 m^2, this equals 66 mg/m^2.

Table A2

Values of scenario and substance properties used in test of TOXSWA against an analytical solution described in section 4.3.

Property	Input FORTRAN program analytical solution	TOXSWA
Flow velocity	VelWatFlw (m/d) = 20	VelWatFlwBas (m/d) =20
Seepage	FlwWatSpg (mm/d) = 0	FlwWatSpg (mm/d) = 0
Dispersion coefficient	CofDis (m^2/d) = 200	OptDis = Input, CofDisPhsInp = 200 m^2/d)
Water body dimensions		
water depth	DepWat (m) = 0.5	DepWat (m) = 0.5
width of the bottom	WidWatSys (m) = 1.0	WidWatSys (m) = 1.0
side slope	SloSidWatSys (-) = 0.00001	SloSidWatSys (-) = 0.00001
depth defining perimeter	DepWatDefPer (m) = 0.1	DepWatDefPer (m) = 0.1
length of the water body	no input	Len (m) = 360
number of segments	no input	NumSeg (-) = 60
		OptWaterSystemType: Watercourse
Loading on water body		
mass loading cross section	AmaLoa (g/m^2) = 0.066	no input
drift deposition	no input	01-Jan-1975-0000 Drift **5.5** 60. 66.0
location of mass loading	DisPul (m) = 63	01-Jan-1975-0000 Drift 5.5 **60. 66.0**
		OptLoa: DriftOnly
Width of field contributing drainage (not used)	WidFldDra (m) = 100 (dummy)	WidFldDra (m) = 100 (dummy)
SUBSTANCE		
Molar mass	no input	MolMas (g.mol^{-1}) = 300
Volatilisation	CofHenry (-) = 0	PreVapRef (Pa) = 0
Solubility	no input	SlbWatRef (mg/L) = 90 (not used)
Diffusion (to sediment)	not used	CofDifWatRef = 0

Property	Input FORTRAN program analytical solution	TOXSWA
Transformation		
half-life due to photolysis	$DT50_{ph,ref}$ (d) = 5.2	DT50WatLiqPhoRef (d) = 5.2
G: daily global radiation	G/G_{ref} =1.25	G: RAD (kJ/m^2) =12 500
G_{ref}: reference daily global radiation		G_{ref}: RadGloRef (kJ/m^2) = 10 000
		OptTra = Pho
Sorption to suspended solids		
Concentration suspended solids	ConSus (g/m^3) = 50/1·10^5	ConSus (g/m^3) = 50/1·10^5
Sorption coefficient	KomSusSol (L/kg) = 0/1·10^7	KomSusSol (L/kg) = 0/1·10^7
Mass ratio of organic matter in suspended solids	CntOmSusSol (kg/kg) = 0.1	CntOmSusSol (kg/kg) = 0.1
Reference concentration		ConLiqRefSusSol (mg/L) = 1
Freundlich exponent		ExpFreSusSol (-) = 1
Sorption to macrophytes		
Coefficient for linear sorption on macrophytes	CofSorMph (L/kg) = 0	CofSorMph (L/kg) = 0
Dry weight of macrophyte biomass per m^2 bottom	AmaMphWatLay (g/m^2) = 0	AmaMphWatLay (g/m^2) = 0

Annex 6 Analytical solution for decrease of mass as function of the global radiation

A system is considered with transformation in the water phase due to photolysis. No other processes are considered that may decrease the water concentration, i.e. there is no volatilization, no sorption to suspended solids or to macrophytes and no transport to the sediment. The decrease in mass in the water due to photolysis as a function of global radiation is then derived by combining Eqs. (6) and (7) giving:

$$\frac{\partial c}{\partial t} = -\frac{G}{G_{ref}} k_{ph,ref}\, c \qquad \text{(A10)}$$

The integral of this equation is:

$$c(t) = c_0 exp\left[-\frac{G}{G_{ref}} k_{ph,ref} t\right] \qquad \text{(A11)}$$

The difference in concentration between the concentration c_1 and c_2, i.e. Δc, at times t_1 and t_2 is given by:

$$\Delta c = c_2 - c_1 = c_1\, exp\left[-\frac{G}{G_{ref}} k_{ph,ref}(t_2 - t_1)\right] - c_1 \qquad \text{(A12)}$$

Rearranging the equation, and using $\Delta t = t_2 - t_1$, Eq (A12) becomes:

$$\frac{\Delta c}{c_1} = exp\left[-\frac{G}{G_{ref}} k_{ph,ref} \Delta t\right] - 1 \qquad \text{(A13)}$$

A system is considered with a volume of the water layer, *V*, which is constant. Hence $\Delta c/c = V\Delta c/Vc = \Delta M/M$, so for the change of mass in the water layer follows:

$$\frac{\Delta M}{M} = exp\left[-\frac{G}{G_{ref}} k_{ph,ref} \Delta t\right] - 1 \qquad \text{(A14)}$$

The relationship shown in Eq. (A14) is used for comparison in the test described in section 4.4.

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