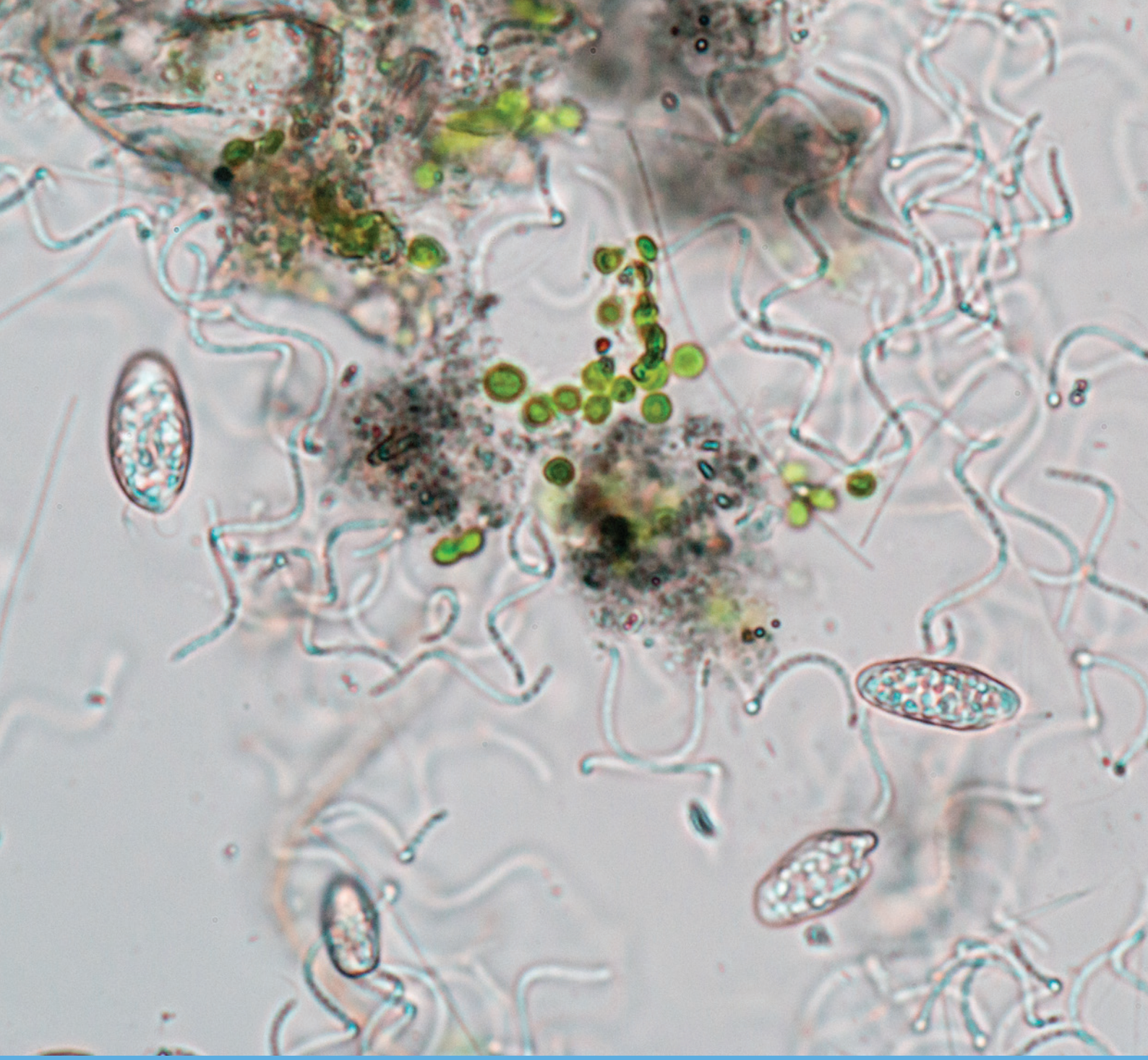

Hydrolysis and biotic transformation in water in the pesticide model TOXSWA

Implementation report

M.M.S. ter Horst, W.H.J. Beltman, P.I. Adriaanse and H.M. Mulder

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This research was funded by the Dutch Ministry of Economic Affairs (project number BO-20-002-002).

Wageningen Environmental Research
Wageningen, December 2017

Report 2848
ISSN 1566-7197

WAGENINGEN
UNIVERSITY & RESEARCH

Ter Horst, M.M.S., Beltman, W.H.J., Adriaanse, P.I., Mulder, H.M., 2017. *Hydrolysis and biotic transformation in water in the pesticide model TOXSWA; Implementation report.* Wageningen, Wageningen Environmental Research, Report 2848. 56 pp.; 18 fig.; 7 tab.; 27 ref.

The TOXSWA model has been extended with the functionality to simulate hydrolysis and biotic transformation in water. TOXSWA simulates the fate of pesticides in water bodies to calculate exposure concentrations for aquatic organisms or sediment-dwelling organisms as part of the aquatic risk assessment of pesticides. Hydrolysis and biotic transformation are modelled as first-order processes, occurring in the water phase only. The hydrolysis transformation rates are considered to be dependent on both pH and temperature. The biotic transformation rate is considered to be temperature-dependent only.

Keywords: hydrolysis, biotic transformation, surface water, pesticide, TOXSWA model

Wageningen Environmental Research Report 2848 | ISSN 1566-7197

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Contents

Preface

Since 1999 TOXSWA v1.2 has been applied in the Dutch registration procedure for plant protection products to calculate exposure concentrations for an edge-of-field ditch with constant flow rates. Since 2003 FOCUS_TOXSWA (versions 1.1.1, 2.2.1, 3.3.1 and 4.4.3) 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 (TOXSWA kernel v. 3.3) calculates also exposure concentrations for metabolites formed in water and in sediment. This version was released in 2015. The TOXSWA kernel is the subject of continuous improvement and the version currently developed (v. 3.4) is now extended with the option to simulate transformation by hydrolysis and biotic transformation in the water layer. This report describes the implemented concepts of hydrolysis and biotic transformation in the TOXSWA kernel version 3.4.

Summary

The TOXSWA model has been extended with the functionality to simulate hydrolysis and biotic transformation 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 aquatic risk assessment of pesticides. Pesticide transformation is an important process determining the exposure concentration. Especially for water bodies with stagnant water or low flow velocities, slow transformation in combination with repeated applications may lead to accumulation of pesticides in water and sediment. This may lead to high risks for the aquatic or sediment-dwelling organisms. Hydrolysis, *i.e.* transformation due to a chemical reaction with water and biotic transformation *i.e.* transformation due to the presence of organisms (for instance microbes) are modelled as first-order processes. The hydrolysis transformation rates are considered to be dependent of both pH and temperature. The biotic transformation rate is considered to be temperature-dependent only.

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), as a single transformation process or a combination of the single transformation processes: photolysis (Beltman *et al.*, 2015), hydrolysis or biotic transformation. Transformation by these processes is considered to occur in the water phase of the water layer only, so, not including pesticide mass sorbed onto suspended solids or onto macrophytes. This shift in concept implies that similar decline of mass in the water layer results in a different transformation rate for the overall transformation and the sum of the transformation rates of the three separate processes. These different concepts correspond to the determination of transformation rates in laboratory experiments.

Tests with the new functionality of TOXSWA confirmed that the concepts of hydrolysis and biotic transformation are implemented correctly and that the numerical solutions are robust. Furthermore, it was verified that the simulation of combined transformation processes is implemented correctly in TOXSWA.

Now that TOXSWA is able to simulate the different transformation processes as a function of environmental parameters, the simulated concentration profiles better reflect the variability in time and space in surface water. In this way TOXSWA provides a more robust picture of the environmental exposure concentrations used in the aquatic risk assessment of pesticides in the Netherlands and the European Union.

Samenvatting

Het TOXSWA model is uitgebreid en kan nu de afbraakprocessen hydrolyse en biotische omzetting simuleren. TOXSWA simuleert het gedrag van gewasbeschermingsmiddelen in klein oppervlaktewater en berekent hier blootstellingsconcentraties voor water- en sedimentorganismen, die in de aquatische toelatingsprocedure in Nederland en de EU worden gebruikt. Afbraak van gewasbeschermingsmiddel is een belangrijk proces voor de blootstellingsconcentratieberekening. Vooral in stilstaand oppervlaktewater of water met lage stroomsnelheden kan de combinatie van langzame afbraak en herhaald toepassen leiden tot accumulatie van het middel in water en/of sediment en mogelijk hoge risico's voor de organismen.
Hydrolyse, i.e. afbraak door een chemische reactie met water, en biotische omzetting, i.e. afbraak door organismen, zoals bv. bacteriën, zijn gemodelleerd als een eerste orde afbraakproces, d.w.z. de afbraak is recht evenredig met de concentratie van het middel in het water. Hydrolysesnelheden zijn een functie van zowel de temperatuur als de pH van het water, terwijl de biotische omzetting alleen afhangt van de temperatuur.

In deze nieuwe versie van TOXSWA, kernversie 3.4, kan de gebruiker nu kiezen uit de opties om afbraak als een overall proces te simuleren, of als een enkel proces of als combinatie van de enkele processen fotolyse (Beltman *et al.*, 2015), hydrolyse en biotische omzetting. De laatstgenoemde processen zijn gemodelleerd als functie van de concentratie in alleen de waterfase, terwijl de overall afbraak een functie is van de totale concentratie in de waterlaag, d.w.z. inclusief massa geadsorbeerd aan zwevende stof en waterplanten. Dit verschil in concept heeft tot gevolg dat een gelijke afname van massa in het waterlaag systeem overeenkomt met een verschillende afbraaksnelheid voor de overall afbraak en de som van de afbraaksnelheden van de drie afzonderlijke processen. Deze verschillende concepten sluiten aan bij de bepaling van de afbraaksnelheden in laboratoriumexperimenten.

Testen met de nieuwe functionaliteiten in TOXSWA wezen uit dat de implementatie van de concepten van hydrolyse en biotische omzetting in het model correct is en dat de numerieke oplossingen robuust zijn. De implementatie van de gecombineerde omzettingsprocessen is ook correct uitgevoerd.

Nu TOXSWA de verschillende afbraakprocessen als functie van omgevingsvariabelen kan simuleren, geven de gesimuleerde concentratieprofielen een beter beeld van de variabiliteit in tijd en plaats in het oppervlaktewater. Op deze wijze geeft TOXSWA een robuuster beeld van de blootstellingsconcentraties in het milieu voor gebruik in de aquatische risicobeoordeling van gewasbeschermingsmiddelen in Nederland en op EU niveau.

1 Introduction

The TOXSWA model simulates the behaviour of pesticides in water bodies to calculate exposure concentrations for aquatic organisms or sediment-dwelling organisms as part of the aquatic risk assessment of pesticides. TOXSWA simulates the processes of 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.

Transformation processes affect exposure concentrations in surface water and in sediment. Especially for water bodies with stagnant water or low flow velocities, slow transformation in combination with repeated applications may lead to accumulation of pesticides. As a result pesticide concentrations in water as well as in sediment may be higher leading to increased 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 into more detail is expected to improve the performance of TOXSWA as it accounts better for external environmental conditions related to specific pesticide properties. Deneer *et al.* (2010) provided suggestions for how these individual processes could be implemented in TOXSWA.

Therefore, the three transformation processes of hydrolysis, photolysis and biotic transformation have been implemented into TOXSWA. The lumped transformation term in the conservation equation of the water layer has been redefined. The option to simulate transformation in the water layer via lumped transformation remains available. In the sediment transformation continues to be described by a lumped transformation rate over the total sediment concentration only.

The concepts used have been reported for each process separately in Deneer *et al.* (2010) and for photolysis more in detail in Beltman *et al.* (2015). This report only treats the hydrolysis and biotic transformation processes. The photolysis transformation process has been implemented in the TOXSWA model as described by Beltman *et al.* (2015).

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

2 Implementation of hydrolysis and biotic transformation 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; Ter Horst *et al.*, 2016; Adriaanse *et al.*, 2017). 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; the properties of the sediment, *i.e.* porosity, organic matter content and bulk density, may vary with depth. In the water layer concentrations vary in the horizontal direction, whereas in the sediment concentrations vary in the horizontal and the vertical direction.

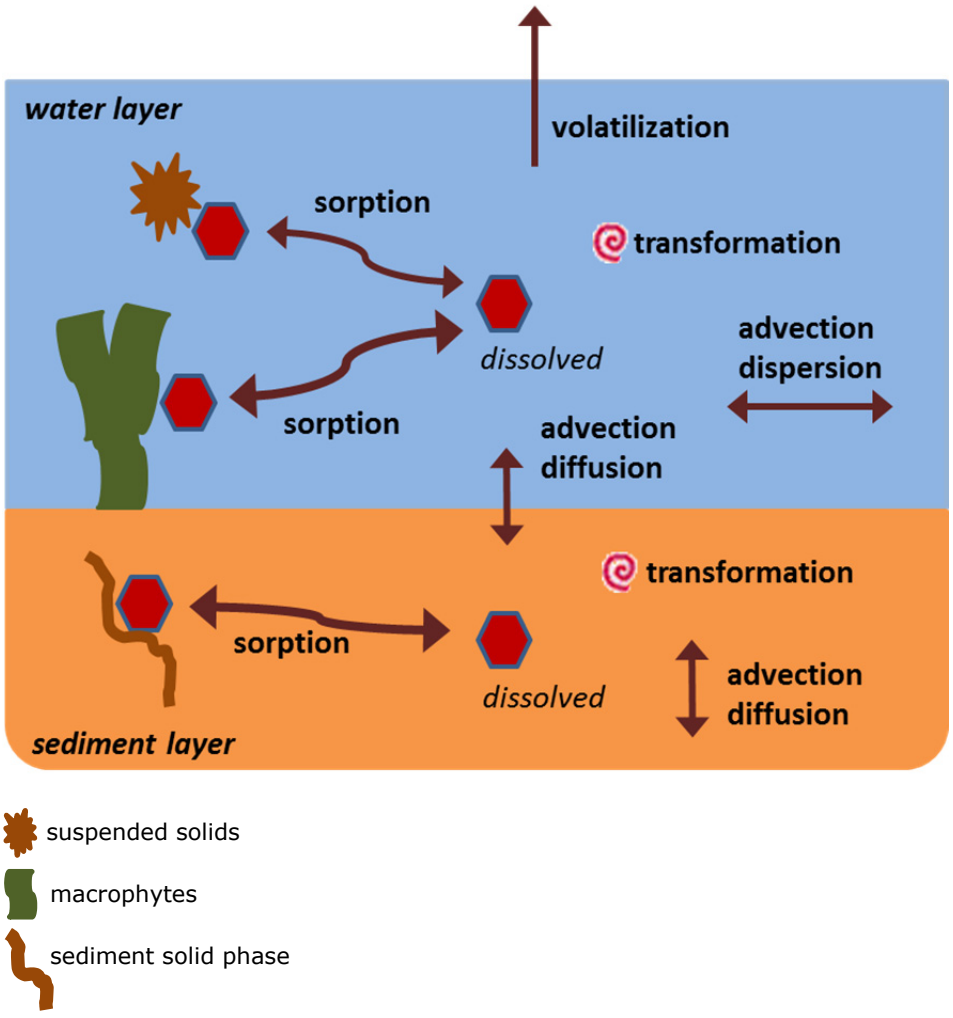

Figure 1 *Processes in TOXSWA.*

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, both dissolved in the water phase 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 are facilitated by advection (upward or

downward seepage) and by diffusion. Transformation is simulated in the water layer as well as in the sediment. Up to version 3.3 included, 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 pesticide behaviour; one for the water layer and one for the sediment.

2.2 Hydrolysis

Hydrolysis occurs when a compound reacts chemically with water and (new) reaction products are formed. The most common hydrolysis reaction of pesticides in the aquatic environment is the replacement of a functional group by an –OH (hydroxide ion) originating from a water molecule, but also additional reactions occur.

Hydrolysis basically depends on pH and temperature. However, in the aquatic environment components like metal ions and dissolved organic matter may also influence the hydrolysis rate (Katagi, 2002). Hydrolysis of pesticides in water mostly follows (pseudo) first-order kinetics, implying that the rate of disappearance of a pesticide is proportional to its aqueous concentration (first-order reactions have a constant half-life/rate coefficient). If pH and temperature remain constant the hydrolysis half-life is independent of pesticide concentration. The pH-dependency of the first-order hydrolysis rate is the result of three separate reactions, *i.e.* the base-catalysed, neutral and acid-catalysed reactions, which occur simultaneously (Schwartzenbach *et al.*, 2003):

$$k_h = k_a [H_3O^+] + k_b [OH^-] + k_n \quad (1)$$

with:

k_h = overall rate coefficient for hydrolysis of substance (d^{-1})
k_a = rate coefficient for acid-catalysed hydrolysis (d^{-1})
k_b = rate coefficient for base-catalysed hydrolysis (d^{-1})
k_n = rate coefficient for neutral hydrolysis (d^{-1})
$[H_3O^+]$ = aqueous concentrations of H_3O^+ (mol L^{-1})
$[OH^-]$ = aqueous concentrations of OH^- (mol L^{-1})

The overall hydrolysis rate coefficient, k_h, is usually measured at three values of pH (*i.e.* in this report $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$; see section 2.5.3). From these data numerical values for k_a, k_b and k_n can be established (see section 2.5.3 for more details). k_a, k_b and k_n are compound-specific properties and therefore do not depend on the ambient pH.

2.3 Biotic transformation

The presence of organisms, be it fungi, micro-organisms, plants or vertebrates may result in a considerable increase in the rate of transformation of pesticides in the water layer and/or sediment (Deneer *et al.*, 2010). The reason is that they contain enzymes (catalytic proteins) that can induce transformation reactions. Micro-organisms are ubiquitously distributed in the natural environment and will therefore usually have larger contributions to biotransformation of pesticides than plants or animals.

Biotic transformation is often modelled as a pseudo first-order process. Biotic transformation depends on temperature, pH and composition of the microbial community. Deneer *et al.* (2010) performed a literature review on the influence of temperature, pH, and composition of the microbial community on biotic transformation, shortly summarized in the remainder of this section.

Temperature affects the rate of biotic transformation and for many situations with temperature changes of only a few degrees Celsius an Arrhenius-type relationship will be sufficiently accurate to estimate the changed biotic transformation rates. Changes in pH (particularly diurnal variation over three pH units) may have a significant effect on enzymatic activity and thus on biotic transformation rates. To predict the effect of pH on enzymatic activity, the intracellular pH of the organism needs to be known. This type of information is not available in pesticide registration dossiers. Furthermore, the effect on intracellular pH upon a decrease or increase of extracellular pH might be very different for different species. Given the complexity of the problem and the lack of information in pesticide registration dossiers the effect of pH on biotic transformation is not taken into account in TOXSWA.

The composition of the microbial community affects the rate of biotic transformation. Consequently, even for a given substance large variations can be expected between transformation rates under different conditions and locations. These effects are however difficult to predict without detailed (experimental) evidence concerning the microbial community present in the sample. Therefore the biotic transformation rate in the TOXSWA model is given by:

$$k_{bio} = f_{t,bio}\, k_{bio,ref} \qquad (2)$$

with:

$f_{t,bio}$ = factor for the effect of temperature on the rate coefficient of biotic transformation (-)

$k_{bio,ref}$ = rate coefficient for biotic transformation of pesticide in the water layer at reference conditions (d^{-1})

In the TOXSWA model the transformation rate coefficient is set at zero for temperatures below 0 °C (273.15 K).

2.4 Calculation of pH of the system

For the calculation of hydrolysis the acidity (characterized by pH) needs to be modelled. The pH of surface water fluctuates during the year and within the day. The pH of water is strongly influenced by the presence of macrophytes and algae. Under light conditions they consume carbon dioxide and produce oxygen in the photosynthesis process. Consequently, the concentration of carbon dioxide in water decreases during the day and increases again during the night. Carbon dioxide affects the calcium-carbonate equilibrium in water; at low carbon dioxide concentration the pH increases, and at high carbon dioxide concentration the pH decreases. With the daily cycle of light, the pH of water follows a sinus function. To model the pH of water during the day the following sinus function is used (Deneer *et al.*, 2010):

$$pH = pH_m + pH_a \sin\left[\frac{(12 + t_h)}{24} 2\pi\right] \qquad (3)$$

with:

pH = daily pH in the water layer (-)

pH_m = monthly mean pH in the water layer (-)

pH_a = amplitude of the monthly mean pH in the water layer (-)

t_h = number of hours after midnight, (h)

The factor 12 (h) is put into the equation to shift the modules of the curve in order to obtain the lowest pH at 6 a.m.

2.5 Implementation into the TOXSWA model

2.5.1 Conservation equation water layer

The mass conservation equation for the water layer, solved by TOXSWA version 3.4 is (see Adriaanse, 1996):

$$\frac{\partial(c_w^* A)}{\partial t} = -\frac{\partial(A\,J_w)}{\partial x} - k^*(c_w^* A) + J_a W - J_s P_0 \qquad (4)$$

with

c_w^* = mass concentration of substance in the water layer (*i.e.* total of dissolved in water phase, sorbed to suspended solids and sorbed to macrophytes) (kg.m^{-3})
A = cross-sectional area of flow (m^2)
J_w = aeric mass flux of substance in water layer by advection and dispersion (kg.m^{-2}.d^{-1})
k^* = transformation rate coefficient for substance in the water layer (*i.e.* in water phase, sorbed to suspended solids and sorbed to macrophytes) (d^{-1})
J_a = aeric mass flux of substance across the water-air interface (kg.m^{-2}.d^{-1}) [the flux is negative in upward direction]
J_s = aeric mass flux of substance across the water-sediment interface (kg.m^{-2}.d^{-1})
W = width of water surface (m)
P_0 = length of the wetted perimeter at depth z=0, via which exchange between water and sediment occurs (m)
x = distance in direction of flow (m)
t = time (d)

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

$$X_{ss} = m_{om,ss} K_{F,om,ss}\, c_{ss,r} \left(\frac{c_w}{c_{ss,r}}\right)^{N_{ss}} \qquad (5)$$

with

X_{ss} = content of substance sorbed to suspended solids (kg^{-1} kg^{-1})
$m_{om,ss}$ = mass fraction of organic matter in suspended solids (kg^{-1} kg^{-1})
$K_{F,om,ss}$ = Freundlich coefficient of equilibrium sorption on organic matter in suspended solids (m^3 kg^{-1})
$c_{ss,r}$ = reference concentration in the liquid phase for sorption to suspended solids (kg m^{-3})
N_{ss} = Freundlich exponent for sorption to suspended solids (1)

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

$$c_w^* = c_w + \frac{DW\,P_0}{A} X_{mp} + ssX_{ss} \qquad (6)$$

with

DW = dry mass of macrophytes per area of sediment (kg m^{-2})
X_{mp} = content of substance sorbed to macrophytes (kg kg^{-1})
ss = mass concentration of suspended solids in the water layer (kg m^{-3})
c_w = mass concentration of substance dissolved in the water phase (kg m^{-3})

To account for the three separate transformation processes, *i.e.* hydrolysis, photolysis and biotic transformation, the transformation term of Eq. (4) is rewritten as:

$$k^*(c_w^* A) = k(c_w A) \quad (7)$$

with

$$k = k_h + k_{ph} + k_b \quad (8)$$

and

k = transformation rate coefficient for substance in the water phase (d^{-1})
k_h = rate coefficient for hydrolysis of substance (d^{-1})
k_{ph} = rate coefficient for photolysis of substance (d^{-1})
k_b = rate coefficient for biotic transformation of substance in the water phase (d^{-1})

Note that, the consequence of Eq. (7) and (8) is that transformation is considered to occur in the water phase only. This is in contrast to the lumped transformation process that presumes transformation to occur in the water phase as well as in the sorbed phase. Note, that in TOXSWA 3.4 the lumped concept as used in TOXSWA versions 3.3 and lower has been maintained. So, from TOXSWA 3.4 onwards hydrolysis, photolysis and biotic transformation are assumed to occur in the water phase only. Pesticides sorbed to suspended solids and macrophytes are considered to be not available for transformation. The consequence of this change in concept in the TOXSWA model is that the lumped transformation rate for the water layer, k^*, and the sum of the individual transformation by photolysis, hydrolysis and biotransformation, k, cannot be easily compared, as they refer to different pesticide masses, so, they are not identical, *i.e.* $k^* \neq k$.

The explanation of Beltman *et al.* (2015) on the change in the transformation concept of lumped transformation, presuming transformation to occur in the water phase as well in the sorbed phase (TOXSWA kernel version 3.3) to transformation occurring in the water phase only (TOXSWA kernel version 3.4), is repeated in Annex 1.

2.5.2 Hydrolysis concept

Following Deneer *et al.* (2010), hydrolysis is approximated as a first-order process, which can be written as:

$$\frac{dc_w}{dt} = -k_h c_w \quad (9)$$

k_h in Eq. (9) is the overall hydrolysis rate at the ambient temperature in the water layer. This overall hydrolysis rate at the ambient temperature in the water layer, k_h is calculated according two steps.

First Eq. (1) is used to calculate the overall hydrolysis rate at reference temperature using values k_a, k_b and k_n at the same reference temperature:

$$k_{h,ref} = k_{a,ref}\,[H_3O^+] + k_{b,ref}\,[OH^-] + k_{n,ref} \quad (10)$$

with:

$k_{x,ref}$ = rate coefficient for hydrolysis, ($k_{a,ref}$, $k_{b,ref}$ or $k_{n,ref}$) at reference temperature (d^{-1})

We also need the values of the concentration of H_3O^+ and OH^- ions to be able to calculate the overall hydrolysis rate at reference temperature $k_{h,ref}$ of Eq.(10).

The relationship between the concentration of H_3O^+ and OH^- is given by the equation:

$$K_w = [H_3O^+] \cdot [OH^-] \quad (11)$$

with
K_w = the ionization constant of water (-)

Due to the temperature dependency of the concentration of H_3O^+ and OH^- ions in neutral water (where the concentrations of H_3O^+ and OH^- are by definition equal), the numeric value of K_w is also temperature dependent; its value is approximated by:

$$pK_w = -1 \ log(K_w) = \left(\frac{6014}{T_w}\right) + 23.65 \ log(T_w) - 64.70 \quad (12)$$

with
T_w = temperature in the water layer (K)

and where:

$$K_w = 10^{(-pK_w)} \quad (13)$$

The aqueous concentration $[H_3O^+]$ is calculated from the pH of the system as:

$$[H_3O^+] = 10^{-pH} \quad (14)$$

As $log\ [OH^-] = pH - pK_w$, the aqueous concentration $[OH^-]$ associated with a given pH and temperature is calculated with:

$$log[OH^-] = pH - \frac{6014}{T_w} - 23.65 log(T_w) + 64.70 \quad (15)$$

So, we have now obtained both the $[H_3O^+]$ and the $[OH^-]$ concentrations at the same pH and temperature. These values are needed to be able to calculate the overall hydrolysis rate at reference $k_{h,ref}$ of Eq. (10).

In a second step TOXSWA corrects the overall hydrolysis rate constant at reference temperature, $k_{h,ref}$ into a rate constant at the ambient temperature in the water layer as follows:

$$k_h = f_{T,h} \ k_{h,ref} \quad (16)$$

with:
k_h = overall rate coefficient for hydrolysis, k_h at ambient water temperature (d^{-1})
$f_{T,h}$ = factor for the effect of temperature on the rate coefficient of hydrolysis, k_h (-)
$k_{h,ref}$ = overall rate coefficient for hydrolysis at reference temperature (d^{-1})

The factor for the effect of temperature on the rate coefficient of transformation, $f_{T,H}$, is calculated with the Arrhenius equation:

$$f_{T,h} = exp\left[\frac{-\Delta H_{T,h}}{R}\left(\frac{1}{T_w} - \frac{1}{T_{ref,h}}\right)\right] \quad (17)$$

with:

$\Delta H_{T,h}$ = molar activation enthalpy of hydrolysis in water (J mol^{-1})

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

$T_{ref,h}$ = reference temperature for hydrolysis in water (K)

In the TOXSWA model, the hydrolysis rate in frozen water is set at zero, *i.e.* for $T < 273.15$ K, $f_{T,h} = 0$.

2.5.3 Calculation of substance-specific hydrolysis rate constants, $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ at reference temperature from three hydrolysis rate constants, $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ determined in experiments

TOXSWA can calculate the overall hydrolysis rate k_h at the ambient water temperature from two types of input:

1. the acid-catalysed, neutral and base-catalysed hydrolysis rates at the reference temperature, $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ and
2. three hydrolysis rates measured in three experiments with different pH and temperature, $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$

The first option is explained in the previous section (*i.e.* the values are known), so we limit ourselves here to the description of the second option: calculate the overall hydrolysis rate k_h at the ambient water temperature from three hydrolysis rates measured in three experiments with different pH and temperature, $k_{1,m}$, $k_{2,m}$ and $k_{3,m.}$

The method for these calculations is taken from Annex B and D in Deneer *et al.* (2010) and repeated in this report for completeness. The method is based upon a method given in an US EPA guideline (US EPA, 1998), but adapted such that it is applicable for the EU common practice of reporting hydrolysis rates at pH 5, 7 and 9, instead of the pH values 3, 7 and 11 used by the US EPA.

Based on Eq. (1) the US EPA have published a test guideline on the analysis of hydrolysis as function of pH (US EPA, 1998). The overall rate constant k_h is the sum of the acid-catalysed, neutral and base-catalysed hydrolysis rates, k_a, k_b and $k_{n.}$ These are substance properties, thus independent of the system. Values of k_a, k_b and k_n are calculated from measurements in three systems, each with a different pH, resulting in three unknown variables in three equations. Once the values of k_a, k_b and k_n are known, the hydrolysis rate at any given pH can be calculated. Due to some approximations in the derivation of the equations, EPA's recommendation is to establish hydrolysis rates at pH values of 3, 7, and 11. The text given in the EPA guideline (US EPA, 1998) suggests that the equations can be used whenever the lowest pH is ≤3 and pH intervals of ≥2 are used. Using rate constants measured at more closely spaced values of pH is expected to result in larger uncertainties of the estimates for k_a, k_b and k_n and thus less reliable predictions of k_h at interpolated or extrapolated values of pH.

Unfortunately, in the EU it is common practice to report values for hydrolysis rates at pH values 5, 7 and 9, *i.e.* a much narrower range than assumed in the EPA equations. The approximations employed by the EPA equations are likely to result in slightly inaccurate estimates for hydrolysis rates when using experimental values established over such a narrow pH interval (some examples are given in Section 2.2 in Deneer *et al.*, 2010). Moreover, the EPA equations do not readily allow for situations where experimental data are used that do not closely adhere to the description given by Eq. (1) (an example of such data is shown in Section 2.2 in Deneer *et al.*, 2010). For this reason it was decided to derive a more generic solution of Eq. (1), removing the constraints on the pH interval for the determination of experimental values for the hydrolysis rates, and allowing for experimental error in the values used for the estimation. These generic equations are specified in Annex D in Deneer *et al.* (2010) (including some example calculations) and for completeness they are repeated in this report.

So, the method for calculating rate coefficients k_a, k_b and k_n from measured hydrolysis rate coefficients $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ is given below.

The three hydrolysis studies might be performed at different temperatures. Therefore in a **first step** the hydrolysis rates need to be set to the same reference temperature. The effect of temperature on the coefficients $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ is modelled with:

$$k_{y,ref} = f_{T,h,m}\, k_{y,m} \tag{18}$$

with:

$k_{y,ref}$ = rate coefficient for hydrolysis, ($k_{1,ref}$, $k_{2,ref}$ or $k_{3,ref}$) at reference temperature (d^{-1})

$k_{y,m}$ = rate coefficient for hydrolysis, $k_{1,m}$, $k_{2,m}$ or $k_{3,m}$ determined from measurements at other temperature than the reference temperature (d^{-1})

$f_{T,h,m}$ = factor for the effect of temperature on the rate coefficient of hydrolysis, $k_{y,ref}$, ($k_{1,ref}$, $k_{2,ref}$ or $k_{3,ref}$) at reference temperature for measurements (-)

The hydrolysis rate of pesticide is dependent on the temperature. The factor for the effect of temperature on the rate coefficient of transformation, $f_{T,h,m}$, is calculated with the Arrhenius equation:

$$f_{T,h,m} = exp\left[\frac{-\Delta H_{T,h}}{R}\left(\frac{1}{T_{ref,m}} - \frac{1}{T_m}\right)\right] \tag{19}$$

with:

$T_{ref,m}$ = reference temperature for measured hydrolysis rates (K). In TOXSWA a fixed value of 293.15 K (20 °C) is used.

T_m = temperature at which hydrolysis rate was measured in the hydrolysis study (K)

So, we thus obtain the measured hydrolysis rates $k_{1,ref}$, $k_{2,ref}$ and $k_{3,ref}$ at the reference temperature.

Note that Eqs. (18) and (19) are largely similar to Eqs. (16) and (17), however rewritten for conversion from measured temperatures in the three experimental systems to reference temperature instead of conversion from reference temperature to measured temperatures.

In a **second step** rate coefficients for acid-catalysed, neutral and base-catalysed hydrolysis at the reference temperature ($k_{a,ref}$, $k_{b,ref}$ or $k_{n,ref}$) are calculated using the measured hydrolysis rates at reference temperature $k_{1,ref}$, $k_{2,ref}$ and $k_{3,ref}$ as well as the $K_{w,ref}$ at reference temperature. The method to do so is described below.

The approach assumes to have three values for the hydrolysis reaction rate $k_{h,ref}$ available, measured at three different pH values:

1. For pH = pH_1 we have the experimental outcome $k_{h,ref} = k_{1,ref}$
2. For pH = pH_2 we have the experimental outcome $k_{h,ref} = k_{2,ref}$
3. For pH = pH_3 we have the experimental outcome $k_{h,ref} = k_{3,ref}$

With
pH_1 << 7, acidic conditions
pH_2 = 7, neutral conditions
pH_3 >> 7, basic conditions

From these three measurement data we want to fit the coefficients $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ in the function of Eq. (20) that is obtained by substituting [H_3O^+] by 10^{-pH} and [OH-] by $10^{pH-pKw,ref}$ in Eq. (10):

$$k_{h,ref} = k_{a,ref}\ 10^{(-pH)} + k_{b,ref}\ 10^{(pH-pK_{w,ref})} + k_{n,ref} \tag{20}$$

Substituting Eq. (13) in Eq. (20) results in:

$$k_{h,ref} = k_{a,ref}\ 10^{(-pH)} + \overline{k_{b,ref}}\ 10^{(pH)} + k_{n,ref} \quad (21)$$

with the definition:

$$\overline{k_{b,ref}} = K_{w,ref} \cdot k_{b,ref} \quad (22)$$

$K_{w,ref}$ = the ionization constant of water at reference temperature (-)

It now suffices to estimate $k_{a,ref}$, $\overline{k_{b,ref}}$ and $k_{n,ref}$, after which $k_{b,ref}$ follows directly from:

$$k_{b,ref} = \frac{\overline{k_{b,ref}}}{K_{w,ref}} \quad (23)$$

Substituting each of the three measured rate coefficients $k_{1,ref}$, $k_{2,ref}$ and $k_{3,ref}$ in $k_{h,ref}$ and their corresponding pH values in Eq. (21) results in three equations with three unknown values, $k_{a,ref}$, $\overline{k_{b,ref}}$ and $k_{n,ref}$. This can be solved to give $k_{a,ref}$, $\overline{k_{b,ref}}$ and $k_{n,ref}$. Finally, $k_{b,ref}$ can be calculated using Eq. (23).

Calculation methods are provided for two types of cases i) the symmetric case and ii) the asymmetric case. These methods are described in Annex D in Deneer *et al.* (2010) and for completeness also given in Annex 2 of this report.

Summarizing, the complete procedure for calculating the overall hydrolysis rate at ambient temperature, k_h from measured hydrolysis rates $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ is as follows:

1. The measured hydrolysis rates $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ are converted from the temperature at which they were measured in the hydrolysis study to rates $k_{1,ref}$, $k_{2,ref}$ and $k_{3,ref}$ at the reference temperature of 20 °C (293.15 K) (Eqs. (18) and (19))
2. These values of $k_{1,ref}$, $k_{2,ref}$ and $k_{3,ref}$ are used to calculate the acid-catalysed, neutral and base-catalysed hydrolysis rates $k_{a,ref}$, $k_{n,ref}$ and $k_{b,ref}$ at the reference temperature of 20 °C (Annex 2).
3. The acid-catalysed, neutral and base-catalysed hydrolysis rates $k_{a,ref}$, $k_{n,ref}$ and $k_{b,ref}$ at the reference temperature of 20 °C are subsequently used to calculate the overall hydrolysis rate, $k_{h,ref}$ at the reference temperature of 20 °C (Eq. (21))
4. The overall hydrolysis rate at reference temperature, $k_{h,ref}$ is converted to the overall hydrolysis rate at ambient temperature, k_h (Eqs. (16) and (17))

Steps 1. and 2. are described in this section (2.5.3) and steps 3. and 4. are described in section 2.5.2.

2.5.4 Biotic transformation

Following Deneer *et al.* (2010), biotic transformation may be approximated as a first order process, which can be written as:

$$\frac{dc_w}{dt} = -k_{bio} c_w \quad (24)$$

with:

k_{bio} = rate coefficient for biotic transformation of pesticide in the water layer (d^{-1})

The effect of temperature on the biotic transformation rate is given by:

$$k_{bio} = f_{T,bio}\, k_{bio,ref} \qquad (2)$$

with:

$f_{T,bio}$ = factor for the effect of temperature on the rate coefficient of biotic transformation (-)

$k_{bio,ref}$ = rate coefficient for biotic transformation of pesticide measured in water at reference temperature (d^{-1})

So, the biotic transformation rate of pesticides is dependent on the temperature in the water. The factor for the effect of temperature on the rate coefficient of transformation, $f_{T,bio}$, is again calculated with the Arrhenius equation:

$$f_{T,bio} = exp\left[\frac{-\Delta H_{T,bio}}{R}\left(\frac{1}{T_w} - \frac{1}{T_{ref,bio}}\right)\right] \qquad (25)$$

with:

$\Delta H_{T,bio}$ = molar activation enthalpy of biotic transformation (J mol^{-1})

T_w = temperature in the water layer (K)

$T_{ref,bio}$ = reference temperature for biotic transformation in water (K)

In the TOXSWA model the transformation rate coefficient for biotic transformation is set at zero for temperatures below 0 °C (273.15 K).

Within EU pesticide registration procedures, data obtained from laboratory tests (*e.g.* OECD 308 or OECD 309) are often used to assess the degree to which biotic transformation reactions occur in outdoor surface water. Deneer *et al.* (2010) provide an overview of different type of laboratory tests that are potentially suitable for this purpose. From these tests, the OECD water-sediment transformation test (OECD 308), is the test that is most often used in pesticide regulatory practice to derive degradation half-lives from outdoor surface water. Disadvantages of the OECD 308 test have been discussed in various publications (Ter Horst and Koelmans, 2016; Shrestha *et al.*, 2016; Honti and Fenner, 2015; Adriaanse *et al.*, 2012; Adriaanse *et al.*, 2002). Main shortcomings with respect to the derivation of accurate compartment-specific degradation half-lives are due to the entanglement of several processes in combination with *e.g.* (an)aerobic conditions that affect concentration profiles (*i.e.* real degradation in contrast to dissipation, transport across the water-sediment interface by sorption and desorption, water volume – solid surface ratio). Consequently, several publications report that *e.g.* degradation of the same substance is significantly faster in (larger) outdoor systems (*e.g.* microcosms) than in the small vessels with a sediment:water ratio of about 1:3 or 1:4 that are used in the OECD water-sediment transformation tests (Adriaanse *et al.*, 2012; Bromilow *et al.*, 2006; Rönnefahrt *et al.*, 1997).

The different compartments in the OECD 308 test include different degradation regimes (i.e. hydrolysis, biotic transformation, Non-Extractable Residue (NER) formation). Besides, micro-organisms mainly reside at the water-sediment interface. The derivation of compartment-specific degradation half-lives is not straightforward (Ter Horst and Koelmans, 2016; Honti and Fenner, 2015), let alone the derivation of the separate degradation processes (*e.g.* hydrolysis, biotic transformation) in each compartment. Honti *et al.*, 2016 defined a biomass-corrected, generalized aerobic biotransformation parameter (k_{bio}; one overall biotransformation rate per unit of biofilm surface) and tested whether this parameter could be calibrated from data from different types of experiments (*i.e.* two variants of OECD 308 and two variants of OECD 309). Although this approach seems promising, it is questionable whether microbial activity in different water systems and in pore water of the sediment is globally universal (Vink, 1997).

3 Input, output and example calculations

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 sum output file.

New parameters needed to simulate hydrolysis are either the acid-catalysed, neutral and base-catalysed rate coefficients at reference temperature ($k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$) and the reference temperature, or the rate coefficients from experimental data and the three different values of pH at which the rate coefficients were measured ($k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ measured at respectively pH_1, pH_2, and pH_3), the temperatures at which these hydrolysis rates were measured and the molar activation enthalpy for hydrolysis.

The new parameters needed to simulate biotic transformation are the rate coefficient for biotic transformation in the water layer (k_{bio}), the temperature at which the biotic transformation was measured and the molar activation enthalpy for biotic transformation.

In this chapter the required input to use the options for hydrolysis and biotic transformation and to simulate these two processes are discussed as well as related output that is additional to the output of earlier TOXSWA versions.

3.2 Selection of hydrolysis and/or biotic transformation

Four main options for transformation in water can be used: lumped transformation, hydrolysis, photolysis and biotic transformation. Also combinations of options can be selected. Selection of the lumped transformation option excludes the use of the other transformation processes (see **Table 1**). Note, that the option for lumped transformation (transformation assumed over total mass; dissolved + sorbed in the water layer) was the only option available in previous versions of TOXSWA.

Table 1 *Options for simulation of transformation by TOXSWA[1] (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

Selection of hydrolysis, photolysis and/or biotic transformation is done via a two-stage process. First the user should indicate in the txw file that the lumped transformation process should not be selected. This is done by setting `OptTraWatLumped_xxxxx` to `No`, where `xxxxx` refers to the substance code. Next, the user can specify which of the other three transformation options (hydrolysis, photolysis and biotic

[1] Note that this setup differs from that reported in Beltman *et al.* (2016). The setup of this part of the input file has been changed.

transformation) should be used. *E.g.* to simulate only hydrolysis of the substance EXSW2, set `OptTraWatHdr_EXSW2` to `Yes` and the other two transformation processes to No. To simulate hydrolysis combined with photolysis set both `OptTraWatHdr_EXSW2` and `OptTraWatPho_EXSW2` to `Yes` and the remaining process to No, and to simulate all three transformation processes `OptTraWatHdr_EXSW2`, `OptTraWatPho_EXSW2` and `OptTraWatBio_EXSW2` must all three be set to `Yes`.

The options `OptTraWatLumped_xxxxx`, `OptTraWatHdr_xxxxx`, `OptTraWatPho_xxxxx` and `OptTraWatBio_xxxxx` are given in the txw input file (Section 7, Compound section), for each substance that is simulated (see **Figure 2**).

```
*-----------------------------------------------------------------------------------------
* Section 7b: Substance properties for parent 'EXSW2'
* (note extension of parameter name is substance code)
*-----------------------------------------------------------------------------------------


* Transformation in water

* Options are lumped or specified: hydrolysis, photolysis, biotic transformation.
* Using option lumped excludes use of the specified options.

Yes    OptTraWatLumped_ EXSW2      ! Option for lumped transformation in water [Yes, No]


    * If OptTraWatLumped is 'No' specify which options for transformation in water
    * phase(so, excluding sorbed to suspended solids or to macrophytes)
    No    OptTraWatHdr_ EXSW2      ! Option for hydrolysis in water [Yes, No]
    No    OptTraWatPho_ EXSW2      ! Option for photolysis in water [Yes, No]
    No    OptTraWatBio_ EXSW2      ! Option for biotic transformation in water [Yes, No]
```

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

3.3 Selection of acid-catalysed, neutral and base-catalysed hydrolysis rate coefficients or rate coefficients from experimental data

In TOXSWA the overall hydrolysis rate k_h is calculated from the three hydrolysis rate coefficients: $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ characterising respectively the acid-catalysed hydrolysis rate coefficient, the base-catalysed hydrolysis rate coefficient and the neutral hydrolysis rate coefficient at reference temperature. $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ are input into the TOXSWA model. However, often only rate coefficients from experimentals at three different values of pH are available in the dossier ($k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ measured at respectively pH_1, pH_2, and pH_3). TOXSWA offers the user the option to select between either i) input of $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ which are compound properties, *i.e.* do not depend on the pH of the experiment or scenario or ii) input of $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ measured at respectively pH_1, pH_2, and pH_3, which depend on the pH and the temperatures in the experiments.

The user can select the preferred option via the parameter `OptTraHdrInp_xxxxx` in the txw input file of TOXSWA, where `xxxxx` refers to the substance code. The two options to select from are `Input` or `Calc`. Selection of `OptTraHdrInp_xxxxx = Input` implies that the user needs to provide values for $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$. Selection of `OptTraHdrInp_xxxxx = Calc` implies that the user needs to provide values for $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ and the values for the pH (resp. pH_1, pH_2, and pH_3) and temperature (resp. $T_{1,m}$, $T_{2,m}$, and $T_{3,m}$) at which they are measured.

In case the user wishes to calculate the overall hydrolysis rate k_h using the rate coefficients from experimental data at three different values of pH and temperatures ($k_{1,m}$, $k_{2,m}$ and $k_{3,m}$) a value for the weighting factor γ (see Annex 2 for more details) needs to be provided by the user. The user can set

the value of the weighting factor γ via the parameter `GamHdr_xxxxx` in the txw input file of TOXSWA, where `xxxxx` refers to the substance code.

The value of γ is commonly set to 1 (*i.e.* assuming equal confidence in the three measured rate coefficients). However, the user may use another value if for instance one of the measured rate coefficients is considered less reliable than the other two measured rate coefficients. In situations of either acid-catalysed or base-catalysed hydrolysis, the rate coefficient may become relatively low (*e.g.* > 17 d^{-1}; half-life < 1h). Such high rate coefficients may be accompanied by increased experimental error resulting in a relatively large relative standard deviation. This may be a reason to adjust the parameter, γ, reflecting higher confidence in the experimental values of the rate coefficients with smaller relative standard deviations. Annex 2 provides some guidance on how to choose a value for the weighting factor γ.

3.4 Input and output

In this section all changes in the txw file and in the summary output file are discussed. The txw file consists of 10 sections, of which section 2 'Waterbody section' and section 7 'Substance' needs to be adapted to simulate hydrolysis. To simulate biotic transformation only the 'Substance' section of the txw file needs to be adapted.

3.4.1 Hydrolysis

Txw file, Waterbody section
A daily pH regime of the water layer is simulated in TOXSWA according Eq. (3). Inputs of the average daily pH of the water layer (pH_m) and it corresponding amplitude (pH_a) need to be provided to TOXSWA per month in the year. This is done via the table pH in the Waterbody section of the txw file (Figure 3). The information needs to be given as a table specifying for each month pH_m and pH_a. The month numbers are coupled directly to the corresponding months (*i.e.* month '1' corresponds to January, month '2' corresponds to February etc.). The pH table is specified for one year only and this input will be used for all years in the simulation. Examples of pH values measured in outdoor ditches (*i.e.* course of pH over time in a year) are given in section 5.3.2 of Deneer *et al.* (2010)

```
*-------------------------------------------------------------------------------
* Section 2: Waterbody
* Description
*-------------------------------------------------------------------------------

    * If OptTraWatHdr is "Yes"
    * pH table: yearly pH regime of the water layer
    * Month   Number of the month [1|12]
    * pH      Average pH [3|12]
    * Ampl    Amplitude of pH [0|9]
    table pH
    Month   pH      Ampl
    (-)    (-)      (-)
     1     8.2     0.3
     2     7.5    0.1
     3     8.1     0.6
     4     8.7     0.6
     5     9.7     0.4
     6     9.4     0.4
     7     8.7     0.9
     8     8.1     0.9
     9     7.6     0.6
    10     8.5     0.6
    11     8.2     0.4
    12     7.3     0.1
end_table
```

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

Txw file, Compound section
After selection of the hydrolysis options via `OptTraWatHdr_XXXXX`, the user can select the preferred option for hydrolysis rates input via the parameter `OptTraHdrInp_xxxxx` (Figure 4).

In case `OptTraHdrInp_xxxxx` is set to `Input` the user needs to provide values for the hydrolysis half-lives for acid-catalysed, neutral and base-catalysed hydrolysis $DegT50_{a,ref}$, $DegT50_{n,ref}$ and $DegT50_{b,ref}$ *i.e.* `DT50LiqAcidRef_xxxxx`, `DT50LiqNeuRef_xxxxx`, `DT50LiqBaseRef_xxxxx`, respectively (see Figure 4). Furthermore, the reference temperature for which these reference half-lives are valid needs to be specified, *i.e.* one value is used for all three reference hydrolysis half-lives (`TemRefTraHdrWat_xxxxx`).

In case `OptTraHdrInp_xxxxx` is set to `Calc` the user needs to provide values for the hydrolysis half-lives $DegT50_{1,m}$, $DegT50_{2,m}$ and $DegT50_{3,m}$ *i.e.* `DT50LiqHdr1_xxxxx`, `DT50LiqHdr2_xxxxx`, and `DT50LiqHdr3_xxxxx`. For each DegT50 ($DegT50_{1m}$, $DegT50_{2,m}$ and $DegT50_{3,m}$) values need to be provided for the pH and the temperature for which they are measured (resp. pH_1, pH_2, and pH_3 and resp. $T_{1,m}$, $T_{2,m}$, and $T_{3,m}$), *i.e.* `pHHdr1_xxxxx`, `pHHdr2_xxxxx`, `pHHdr3_xxxxx`, and `TemHdr1_xxxxx`, `TemHdr2_xxxxx`, `TemHdr3_xxxxx`.

Finally, for all options `OptTraHdrInp_xxxxx`, the value of the molar enthalpy of hydrolysis, $\Delta H_{T,h}$, needs to be provided in the Substance section *i.e.* `MolEntTraHdrWat_ xxxxx`. Deneer *et al.* (2010) recommends a value of 75 kJ mol^{-1} for this parameter.

TOXSWA converts the half-lives for acid-catalysed, neutral and base-catalysed hydrolysis at reference temperature (respectively $DegT50_{a,ref}$, $DegT50_{n,ref}$, $DegT50_{b,ref}$) to the corresponding first-order rate coefficients for hydrolysis (respectively $k_{a,ref}$, $k_{n,ref}$ and $k_{b,ref}$) at the reference temperature via:

$$k_{x,ref} = \frac{ln(2)}{DegT50_{x,ref}} \tag{26}$$

with:
$k_{x,ref}$ = rate coefficient for hydrolysis, either k_a, k_b or k_n at reference temperature (d^{-1})
$DegT50_{x,ref}$ = half-life for either acid-catalysed, neutral and base-catalysed hydrolysis, (respectively $DegT50_{a,ref}$, $DegT50_{n,ref}$, $DegT50_{b,ref}$) at reference temperature (d)

TOXSWA converts the hydrolysis half-lives from experimental data at three different values of pH (pH_1, pH_2, and pH_3) and temperature ($T_{1,m}$, $T_{2,m}$, and $T_{3,m}$), respectively $DegT50_{1,m}$, $DegT50_{2,m}$, $DegT50_{3,m}$ to the corresponding first-order rate coefficients for hydrolysis (respectively $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$) via:

$$k_{y,m} = \frac{ln(2)}{DegT50_{y,m}} \tag{27}$$

with:
$k_{y,m}$ = rate coefficient for hydrolysis, either $k_{1,m}$, $k_{2,m}$ or $k_{3,m}$ measured at pH_1, pH_2, and pH_3 and at temperature $T_{1,m}$, $T_{2,m}$, and $T_{3,m}$, respectively (d^{-1})
$DegT50_{y,m}$ = half-life for hydrolysis either $DegT50_{1,m}$, $DegT50_{2,m}$, or $DegT50_{3,m}$ measured at pH_1, pH_2, and pH_3 and at temperature $T_{1,m}$, $T_{2,m}$, and $T_{3,m}$, respectively (d)

```
*-----------------------------------------------------------------------------------------
* Section 7b: Substance properties for parent 'EXSW2'
* (note extension of parameter name is substance code)
*-----------------------------------------------------------------------------------------

* Transformation in water

* Options are lumped or specified: hydrolysis, photolysis, biotic transformation.
* Using option lumped excludes use of the specified options.

No    OptTraWatLumped_EXSW2      ! Option for lumped transformation in water [Yes, No]

    * If OptTraWatLumped is 'Yes' specify
    1000  DT50WatRef_EXSW2 (d)   ! Half-life transformation in water at reference
                                 ! temperature [0.1|1e5]
    20    TemRefTraWat_EXSW2 (C) ! Reference temperature for half-life measured in water
                                 ! [5|30]
    75    MolEntTraWat_EXSW2 (kJ.mol-1) ! Molar activation enthalpy of transformation in
                                        ! water [0|200]

    * If OptTraWatLumped is 'No' specify which options for transformation in water
    * phase(so, excluding sorbed to suspended solids or to macrophytes)
    Yes       OptTraWatHdr_EXSW2    ! Option for hydrolysis in water [Yes, No]
    No        OptTraWatPho_EXSW2    ! Option for photolysis in water [Yes, No]
    No        OptTraWatBio_EXSW2    ! Option for biotic transformation in water [Yes, No]

    * If OptTraWatHdr is 'Yes' then specify
    Input      OptTraHdrInp_EXSW2   ! Method to obtain hydrolysis rates [Input|Calc]

        * If OptTraHdrInp is 'Input' then specify hydrolysis DT50 input for acid-
        * catalysed, base-catalysed and neutral conditions at the reference temperature
        1.e-6   DT50LiqAcidRef_EXSW2 (d)  ! Half-life for acid-catalysed hydrolysis at
                                          ! reference temperature [1e-6|1e5]
        10.     DT50LiqNeuRef_EXSW2 (d)   ! Half-life for neutral hydrolysis at reference
                                          ! temperature [1e-6|1e5]
        30.     DT50LiqBaseRef_EXSW2 (d)  ! Half-life for base-catalysed hydrolysis at
                                          ! reference temperature [1e-6|1e5]
        20.     TemRefTraHdrWat_EXSW2 (C) ! Reference temperature for these three
                                          ! half-lives measured in water [5|30]

        * If OptTraHdrInp is 'Calc' then specify hydrolysis DT50 of three studies
        * differing in pH
        25    DT50LiqHdr1_EXSW2 (d)  ! Half-life from hydrolysis in study 1 [0.1|1e5]
        5     pHHdr1_EXSW2 (-)       ! pH at which half-life was measured in
                                     ! study 1 [0|14]
        20    TemHdr1_EXSW2 (C)      ! Temperature at which half-life was measured
                                     ! study 1 [5|80]
        43    DT50LiqHdr2_EXSW2 (d)  ! Half-life from hydrolysis in study 2 [0.1|1e5]
        7     pHHdr2_EXSW2 (-)       ! pH at which half-life was measured in
                                     ! study 2 [0|14]
        18    TemHdr2_EXSW2 (C)      ! Temperature at which half-life was measured
                                     ! in study 2 [5|80]
        2.1   DT50LiqHdr3_EXSW2 (d)  ! Half-life from hydrolysis study 3  [0.1|1e5]
        9     pHHdr3_EXSW2 (-)       ! pH at which half-life was measured in
                                     ! study 3 [0|14]
        25    TemHdr3_EXSW2 (C)      ! Temperature at which half-life was measured
                                     ! in study 3 [5|80]
        * If three half-lives increase with pH or decrease with pH (asymmetric cases)
        1     GamHdr_EXSW2 (-)       ! Weighting factor for calculation of hydrolysis
                                     ! rate constants [0|]

    75      MolEntTraHdrWat_EXSW2 (kJ.mol-1) ! Molar activation enthalpy of hydrolysis in
                                             ! water [0|200]
```

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

Summary file

Figure 5 shows an excerpt from the summary output file (runID.sum) in case the user provided values for the half-lives for acid-catalysed, neutral and base-catalysed hydrolysis at reference temperature (respectively $DegT50_{a,ref}$, $DegT50_{n,ref}$, $DegT50_{b,ref}$) to TOXSWA (`OptTraHdrInp_xxxxx` is set to `Input`). The user is informed of the hydrolysis option chosen and the values for acid-catalysed, neutral and base-catalysed hydrolysis half-lives (resp. $DegT50_{1,ref}$, $DegT50_{2,ref}$, $DegT50_{3,ref}$) and the value of the reference temperature used are reported.

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

* Transformation options, water phase(so, excluding sorbed to suspended solids or to
* macrophytes) :  # hydrolysis
* Hydrolysis half-lives input from user
* Half-life in water, acid-catalysed hydrolysis (d)     :  > 1000000
* Half-life in water, hydrolysis neutral conditions (d) :   68.0
* Half-life in water, base-catalysed hydrolysis (d)     :  0.220E-04
* Reference temperature for acid-catalysed, neutral and base-catalysed hydrolysis
* half-lives (C) : 25.0
```

Figure 5 *Excerpt from substance properties and loadings section of the summary output file; example of a TOXSWA run where* ***OptTraHdrInp_****xxxxx* *is set to* ***Input*** *(user needs to provide values for the half-lives for acid-catalysed, neutral and base-catalysed hydrolysis at reference temperature).*

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

* Transformation options, water phase (so, excluding sorbed to suspended solids or to
* macrophytes):  # hydrolysis
* Hydrolysis rates calculated by TOXSWA from half-life values of three hydrolysis
* studies
* Half-life in water, study 1 (d):   68.0     at pH:  5.00 measured at (C) : 25.0
* Half-life in water, study 2 (d):   25.5     at pH:  7.00 measured at (C) : 25.0
* Half-life in water, study 3 (d):   23.0     at pH:  8.00 measured at (C) : 25.0
* Half-life in water, acid-catalysed hydrolysis (d)     :  > 1000000
* Half-life in water, hydrolysis neutral conditions (d) :   68.0
* Half-life in water, base-catalysed hydrolysis (d)     :  0.219E-04
* Reference temperature for acid-catalysed, neutral and base-catalysed hydrolysis
* half-lives (C) : 20.0
```

Figure 6 *Excerpt from substance properties and loadings section of the summary output file example of a TOXSWA run where* ***OptTraHdrInp_****xxxxx* *is set to* ***Calc*** *(TOXSWA calculates the overall hydrolysis rate k_h using half-lives from experiments at three different values of pH and temperature).*

Figure 6 shows an excerpt from the summary output file (runID.sum) in case the user provided values of the hydrolysis half-lives from experiments at three different values of pH *(pH_1*, *pH_2*, and *pH_3*) and temperatures ($T_{1,m}$, $T_{2,m}$, and $T_{3,m}$), respectively, $DegT50_{1,m}$, $DegT50_{2,m}$, $DegT50_{3,m}$ to TOXSWA (`OptTraHdrInp_xxxxx` is set to `Calc`). The user is informed of the hydrolysis option chosen. The data provided to the model (*i.e.* the half-lives and corresponding pH and temperature from the experiments) are reported first. Next, the values for acid-catalysed, neutral and base-catalysed hydrolysis half-lives at reference temperature (resp. $DegT50_{1,ref}$, $DegT50_{2,ref}$, $DegT50_{3,ref}$) that are calculated by the model (this is the result of step 1 and step 2 in section 2.5.3) and the value of the corresponding reference temperature are reported.

3.4.2 Biotic transformation

Txw file, Substance section

After selection of the biotic transformation options via `OptTraWatBio _XXXXX`, the half-life for biotic transformation at reference temperature, $DegT50_{bio,ref}$, the reference temperature itself and the value of the molar enthalpy of transformation in the water layer, $\Delta H_{T,bio}$, need to be provided in the Substance section, *i.e.* `DT50LiqBioRef_xxxxx`, `TemRefTraBioWat_xxxxx` and `MolEntTraBioWat_xxxxx`, respectively (see Figure 7).

```
*-------------------------------------------------------------------------------------
* Section 7b: Substance properties for parent 'EXSW2'
* (note extension of parameter name is substance code)
*-------------------------------------------------------------------------------------

* Transformation in water

* Options are lumped or specified: hydrolysis, photolysis, biotic transformation.
* Using option lumped excludes use of the specified options.

No    OptTraWatLumped_EXSW2      ! Option for lumped transformation in water [Yes, No]

    * If OptTraWatLumped is 'No' specify which options for transformation in water
    * phase(so, excluding sorbed to suspended solids or to macrophytes)
    No       OptTraWatHdr_EXSW2   ! Option for hydrolysis in water [Yes, No]
    No       OptTraWatPho_EXSW2   ! Option for photolysis in water [Yes, No]
    Yes      OptTraWatBio_EXSW2   ! Option for biotic transformation in water [Yes, No]
    * If OptTraWatBio is 'Yes' then specify
    5.3       DT50LiqBioRef_EXSW2 (d)     ! Half-life for biotic transformation at
                                          ! reference temperature [0.1|1e5]
    20        TemRefTraBioWat_EXSW2 (C)   ! Reference temperature for  biotic
                                          ! transformation half-life [5|30]
    75        MolEntTraBioWat_EXSW2 (kJ.mol-1) ! Molar activation enthalpy of biotic
                                               ! transformation in water [0|200]
```

Figure 7 *Excerpt from Substance section of the txw file.*

TOXSWA converts the half-life of biotic transformation ($DegT50_{bio,ref}$) at the reference temperature to the first-order rate coefficient for biotic transformation ($k_{bio,ref}$) at the reference temperature via:

$$k_{bio,ref} = \frac{ln(2)}{DegT50_{bio,ref}} \tag{28}$$

with:

$k_{bio,ref}$ = rate coefficient for biotic transformation at reference temperature (d^{-1})
$DegT50_{bio,ref}$ = half-life for biotic transformation ($DegT50_{bio,ref}$) at reference temperature (d)

Subsequently, $k_{bio,ref}$ is converted to k_{bio} using equations (2) and (25).

Summary file

In the summary output file (runID.sum; Figure 8) the input value used for the half-life for biotic transformation at reference temperature ($DegT50_{bio,ref}$) is echoed.

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

* Transformation options, water phase (so, excluding sorbed to suspended solids or to
* macrophytes):      # biotic transformation
* Half-life in water, biotic transformation (d) :       5.30  at reference temperature
* (C) : 20.0
```

Figure 8 *Excerpt from substance properties and loadings section of the summary output file.*

3.5 Example calculation

In this section examples of TOXSWA simulations with transformation by i) hydrolysis and ii) biotic transformation are given. We simulated a stagnant water-sediment system (pond without inflow and outflow) with a length of 100 m, a rectangular cross section with a width of 10 m and a water depth of 0.32 m. The concentration of suspended solids in the water layer was set to 15 g m^{-3} and the mass ratio of organic matter in suspended solids was set to 0.1 kg kg^{-1}. Macrophytes were not simulated, *i.e.* the dry mass of macrophyte biomass was set to zero. Monthly average water temperatures were set to monthly average air temperatures taken from weather station De Bilt in the Netherlands. The water layer of the pond consisted of one segment (100 m) for the numerical solution of the mass conservation equation. Time steps used in the model simulations varied. The option to optimise the time step (`OptTimStp = Calc`) was used.

3.5.1 Hydrolysis

Substance properties of the example run are given in Annex 3. The hydrolysis rate of the substance shows a strong dependency on the pH. $DegT50_{a,ref}$ is 100 000 d, $DegT50_{n,ref}$ is 68 d and $DegT50_{b,ref}$ is $2.2 \cdot 10^{-5}$ d (all three at reference temperature of 20 °C), *i.e.* more substance is hydrolysed as the pH of the water layer increases. In this simulation only transformation in the water phase due to hydrolysis is considered. Other processes that may decrease the concentration are not considered, *i.e.* there is no volatilization, no sorption to suspended solids or macrophytes and no transport to sediment.

Two simulations, differing in date of the spray drift event (*i.e.* 1 May 1986 and 1 August 1986) were done. The simulation started at the day of the spray drift event and 30 days were simulated. Simulations were done using a spray drift deposition of 0.1 mg/m^2 (equivalent of 0.1% of 1 kg/ha) entering the water layer over the entire length of the pond (x = 0 to x = 100 m). Monthly average water temperatures were used as input and set at a constant value of 20 °C for the entire simulation period to exclude any effects of temperature differences on the hydrolysis rate. The daily pH regime of the water layer is simulated in TOXSWA according to Eq. (3). Inputs of the average monthly pH of the water layer (pH_m) and its corresponding amplitude (pH_a) are provided in **Table 2**.

The effect of pH on the hydrolysis rate is shown through the decline of the substance concentration in the water layer (Figure 9). The figure shows the concentration in the water layer as result of spray drift events on two different dates and the pH as a function of time.

Table 2 *Inputs of the average daily pH of the water layer per month (pH_m) and its corresponding amplitude per month (pH_a), taken from Deneer et al., 2010.*

Month	average daily pH of the water layer per month (pH_m)	amplitude of the average daily pH in the water layer per month (pH_a)
1	8.2	0.3
2	7.5	0.1
3	8.1	0.6
4	8.7	0.6
5	9.7	0.4
6	9.4	0.4
7	8.7	0.9
8	8.1	0.9
9	7.6	0.6
10	8.5	0.6
11	8.2	0.4
12	7.3	0.1

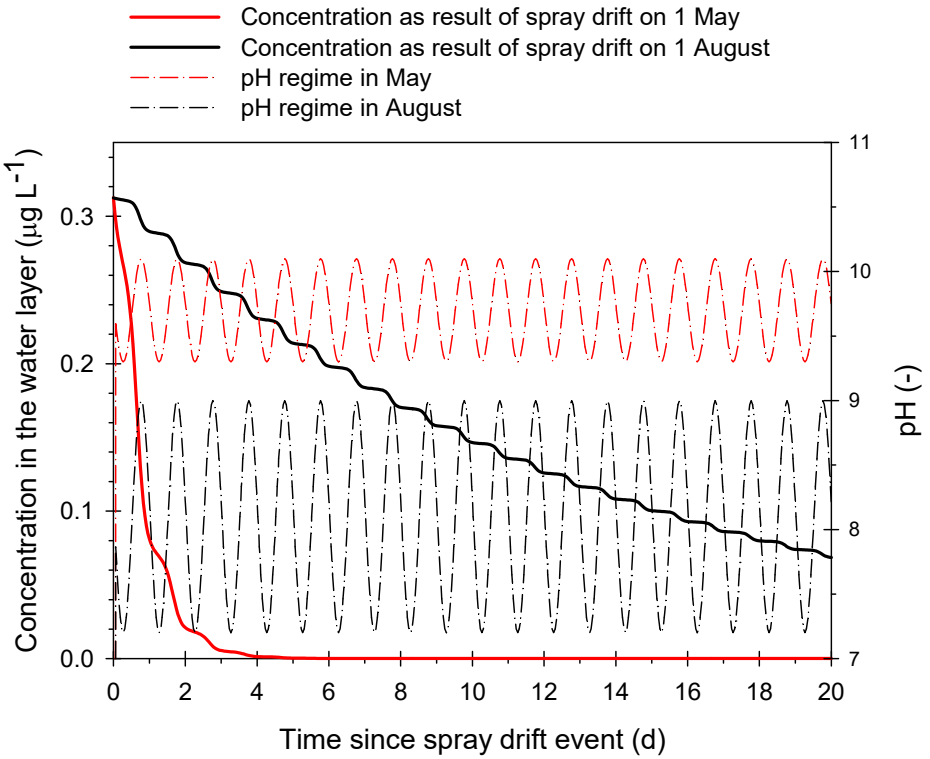

Figure 9 *Substance mass in the water layer as function of time since a spray drift event on i) 1 May (red solid line) and ii) 1 August (black solid line) and pH regimes in May (red dashed line) and August (black dashed line).*

Figure 9 shows that for the simulation with the spray drift event on May 1st the concentration decreases to almost zero within only four days. For the simulation with the spray drift event on August 1st, a much slower decline of the concentration is observed. This difference is attributed to the difference in pH of the water layer. Applying Eq. (1) using the $DegT50_{a,ref}$, $DegT50_{n,ref}$, $DegT50_{b,ref}$ values of our test substance results in effective DegT50 values for hydrolysis of about 56, 22, 3 and 0.3 d for respectively pH 7, 8, 9 and 10. Consequence of Eq. (1) is that at any pH value all three types of hydrolysis contribute to the total hydrolysis rate (k_h in Eq. (1)), *e.g.* under neutral conditions (pH = 7) the total hydrolysis half-life is not equal to the $DegT50_{n,ref}$ of 68 d, but it equals 56 d.

In May the average monthly pH is 9.7 with a daily sinusoidal pattern with a minimum pH of 9.3 and a maximum pH of 10.1. Effective DegT50 values for hydrolysis are between 0.3 – 3 days in this month, resulting in full disappearance of the substance in the water layer in about 4 days.

In August the average monthly pH is 8.1 with a daily sinusoidal pattern showing an increase of the pH from the minimum value of 7.2 at 6 am to a maximum pH of 9.0 around 6 pm. Effective DegT50 values for hydrolysis are between 3 – 51 days in this month, resulting in a decrease of the concentration to 0.7 µg L^{-1} after 20 days. The effect of the difference in pH within a single day on the concentration is clearly visible: a slow decline of the concentration during the night and a faster decline during the day.

The example simulation shows that for substances that are subject to hydrolysis the decrease of concentrations can differ strongly due to differences in the actual pH of the water layer, as a result of differences in the average daily pH per month that is input in the model. For the example substance used in this section (*i.e.* effective DegT50 values for hydrolysis of 56, 22, 3 and 0.3 d for respectively pH 7, 8, 9 and 10), in May, with average daily pH of 9.7 after 5 days the substance was entirely hydrolysed; in August, with average daily pH of 8.1, after 5 days only approximately 32% of the substance was hydrolysed.

3.5.2 Biotic transformation

Substance properties of the example runs are given in Annex 4. To illustrate the difference between biotransformation and the lumped approach two simulations were performed: 1) using biotransformation only (`OptTraWatBio = Yes`) and 2) using the lumped approach (`OptTraWatLumped = Yes`). For both simulations the half-life was set to the same value of 1 d.

The simulation started at 1 June 1986 and 14 subsequent days were simulated (Figure 10). At the start of the simulation a spray drift deposition of 0.1 mg/m^2 entered the water layer over the entire length of the pond (x = 0 to x = 100 m).

The difference between biotransformation and the lumped approach is shown by the declines of the substance concentration in the water layer (Figure 10). The figure shows the concentration of substance dissolved in the water layer as a function of time using 1) biotransformation and 2) lumped transformation.

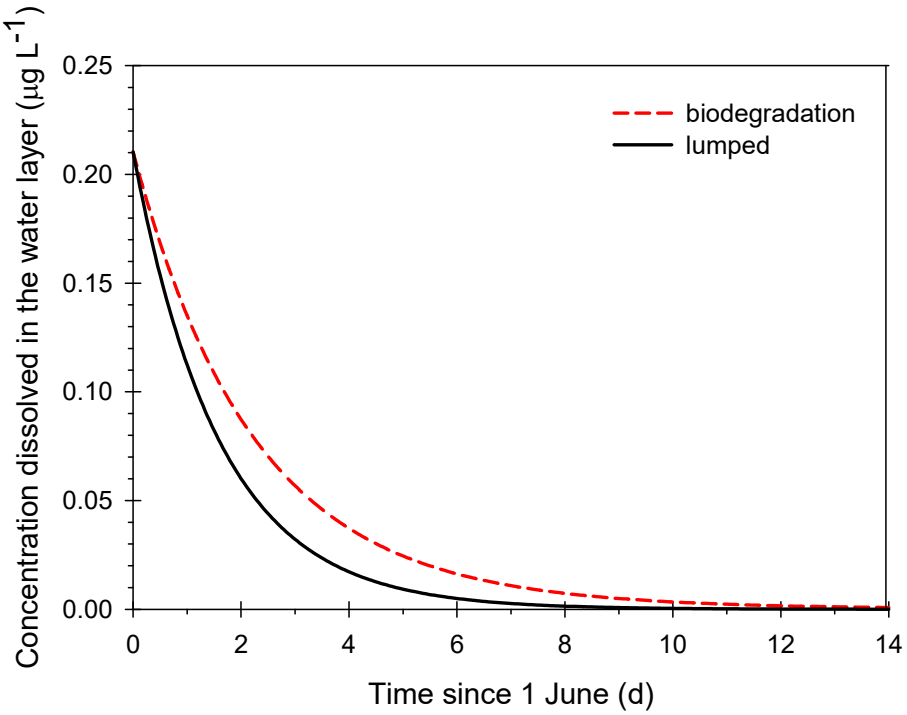

Figure 10 *Concentration dissolved in the watercourse as function of time since 1 June for a simulation using i) only biotic transformation (red dashed line) and ii) lumped transformation (black solid line).*

Biotic transformation occurs in the water phase only (*i.e.* the transformation rate is proportional to the concentration dissolved in water), whereas lumped transformation encompasses substance mass both in the water phase as well as in the sorbed phase (*i.e.* the transformation rate is proportional to the total concentration in water; note that for this example the total concentration in water around t = 0 d is about 0.3 µg/L whereas the concentration dissolved in water is about 0.2 µg/L around t = 0 d). This difference in concept (biotic transformation: k proportional to c_w versus lumped transformation: k^* proportional to c^*_w) is reflected in the decline pattern of the concentration in Figure 10.

4 Verification of the hydrolysis concept and the biotic transformation concept in TOXSWA

4.1 Introduction

To verify the implementation of the hydrolysis and biotic transformation concepts TOXSWA simulation results were compared to analytical solutions of the mass balance equation for the water layer. Also, the robustness of TOXSWA was tested for a broad range of hydrolysis-related and biotic transformation-related input parameter values. In total three tests were performed:

Test 1: A - Implementation of hydrolysis by testing TOXSWA against an analytical solution for concentration (dissolved) in water as a function of time in an ideally-mixed reservoir due to transformation by hydrolysis only.

Test 1: B - Implementation of biotic transformation by comparing the results of a TOXSWA run simulating biotic transformation of the substance in the water phase only with the results of a TOXSWA run simulating lumped transformation of the substance, *i.e.* in the water phase as well as in the sorbed phase.

Test 2: 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 hydrolysis and biotic transformation in water.

Test 3: The aim of test 3 was to establish whether combinations of transformation processes (*e.g.* a combination of biotic transformation and photolysis) are accurately simulated. Testing the simulation of all three transformation processes (photolysis, hydrolysis and biotic transformation) simultaneously was considered sufficient to fulfil the aim of test 3. Reasoning here is that when simulating all three processes simultaneously is done correctly, this will apply for simulating two of the three processes simultaneously as well.

All tests were done with diffusion set to zero.

4.2 Test 1A: Hydrolysis – test against an analytical solution

4.2.1 Set up of the test

The aim of the test is to verify that the concept of hydrolysis in the water phase is implemented correctly in TOXSWA. Concentrations (dissolved) in the water layer as a function of time resulting from a TOXSWA simulation considering hydrolysis as the only dissipation process in the system are compared with concentrations (dissolved) in the water layer as a function of time resulting from a calculation with an analytical solution.

The analytical solution used is:

$$c_{w,t} = c_{w,t-\Delta t} e^{[-k_h \Delta t]} \qquad (29)$$

with

$c_{w,t}$ = mass concentration of substance in the water phase, *i.e.* at time t (kg m^{-3})
t = time (-)
Δt = hourly time step (d)

Two calculations were performed: i) using effective DegT50 values for hydrolysis of about 56, 22, 3 and 0.3 d for respectively pH 7, 8, 9 and 10 at 20 °C, *i.e.* fast degradation around pH values 9-10 ($DegT50_{a,ref}$ is 100 000 d, $DegT50_{n,ref}$ is 68 d and $DegT50_{b,ref}$ is $2.2 \cdot 10^{-5}$ d; all three at reference temperature of 20 °C) and ii) using effective DegT50 values for hydrolysis of about 60, 57, 30, 10 d for respectively pH 7, 8, 9 and 10 at 20 °C, *i.e.* slower degradation around pH values 9-10 ($DegT50_{a,ref}$ is 100 000 d, $DegT50_{n,ref}$ is 60 d and $DegT50_{b,ref}$ is $8.22 \cdot 10^{-4}$ d; all three at reference temperature of 20 °C). The difference between i) and ii) in effective DegT50 values for hydrolysis is found in the pH range 9-10. For i) effective DegT50 values are between 0.3 – 3 days and for ii) effective DegT50 values are in this pH range between 10– 30 days.

The system simulated is the same as used for the example calculation of hydrolysis (Section 3.5.1). The run simulating a spray drift event on 1 May 1986 was used. Instead of the reference value of 20 °C the monthly average water temperatures in were set to the actual values of 13.3, 17.6, 18.5, 18.2, 13.2, 10.8, 6.7 and 4.7 °C for respectively the months May, June, July, August, September, October, November and December (thus testing the implementation of temperature dependency of hydrolysis as well). Input for simulating the daily pH regime is given in **Table 2**. As the pH is a very important factor determining the hydrolysis rate, we also compared the pH calculated by TOXSWA to the pH calculated by Eq. (3). The analytical solution of Eq. (29) was applied on an hourly basis because the pH changed also at the beginning of each hour.

4.2.2 Results

Calculation i) fast degradation (DegT50 0.3-3 d) around pH 9-10
At the end of the day the concentration calculated with TOXSWA is 0.2144 µg L^{-1} and the concentration calculated with the analytical solution of Eq. (29) at the same time is 0.2146 µg L^{-1}. After 50 days of simulation ($c_w \sim 10^{-9}$ µg L^{-1}) the relative difference between the concentration calculated by TOXSWA and the concentration calculated by the analytical solution is about 3.6%. The comparison of the concentrations as a function of time is shown in Figure 11 for May 1st. Figure 11 also shows the comparison of the pH as function of time calculated with i) TOXSWA and ii) manually according Eq. (3). As well the quantitative concentrations as the visual correspondence of the concentration profiles and the pH profiles indicate that the test is satisfactory.

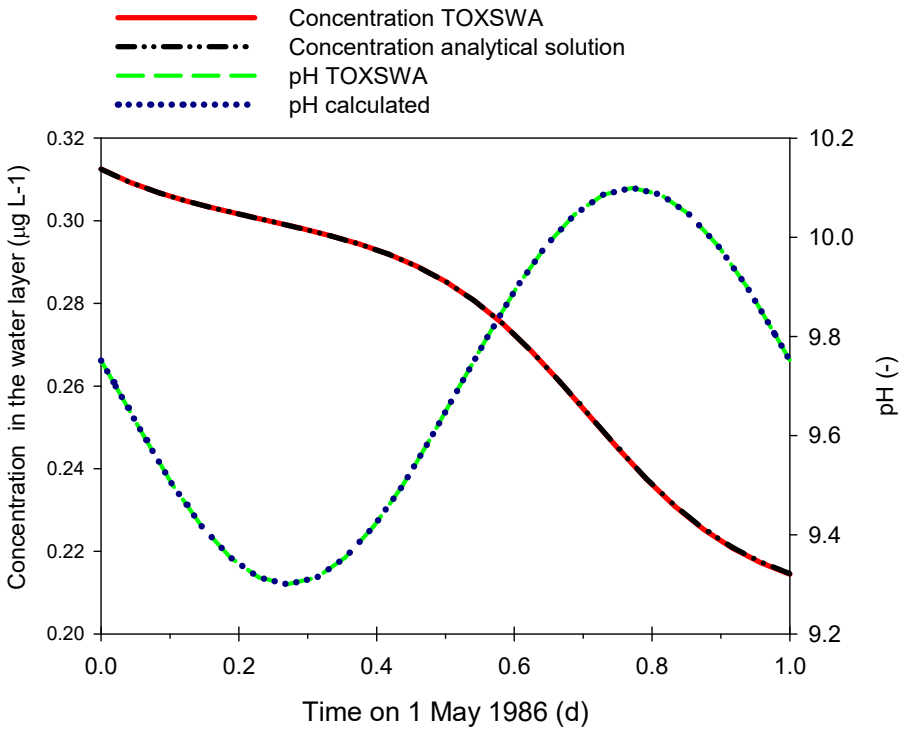

Figure 11 *Results of simulation i) fast degradation around higher pH values. Concentration dissolved in the water layer as a function of time on 1 May 1986 for a simulation with i) TOXSWA (red solid line) and ii) analytical solution (black dashed line) and pH regimes in the water layer as a function of time on 1 May 1986 calculated with i) TOXSWA (green dashed line) and ii) manually using Eq. (3) (blue dotted line).*

Calculation ii) slow degradation (DegT50 10-30 d) in the pH range 9 – 10

At the end of the simulation (31 December 1986) both the concentration calculated with TOXSWA and the concentration calculated with the analytical solution of Eq. (29) is 0.0294 µg L^{-1}. The comparison of the concentrations as a function of time is shown in Figure 12. As well the numerical as the visual correspondence of the concentration profiles is satisfactory. Figure 12 does not show the comparison of the pH as function of time calculated with TOXSWA and calculated manually according Eq. (3), because on the time scale used in Figure 12 the daily pH fluctuations cannot be visualized adequately. However, their correspondence was checked and proven to be satisfactory.

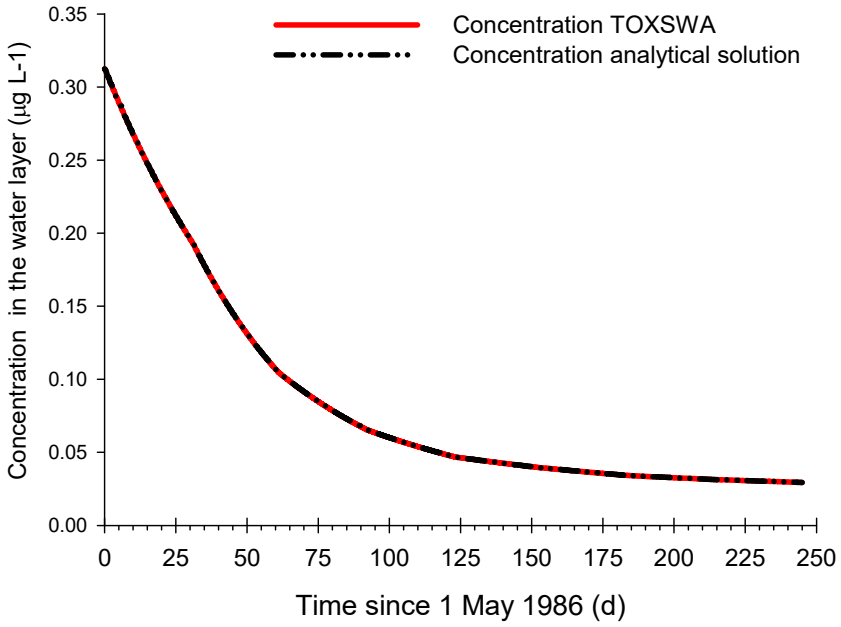

Figure 12 *Results of simulation ii) slow degradation in the pH range 7 – 10. Concentration dissolved in the water layer as a function of time since 1 May 1986 for a simulation with i) TOXSWA (red solid line) and ii) analytical solution (black dashed line).*

Given the results of both calculations, we conclude that the hydrolysis concept has been correctly implemented in the TOXSWA model.

4.3 Test 1B: Biotic transformation – test against lumped transformation

4.3.1 Set up of the test

The aim of the test is to verify that the concept of biotic transformation in the water phase only is implemented correctly in TOXSWA. This is done by comparing the results of a TOXSWA run simulating biotic transformation of the substance in the water phase only with the results of a TOXSWA run simulating lumped transformation of the substance in the water phase as well as in the sorbed phase.

For this test the case described in Annex 4 was taken, however, instead of a Freundlich coefficient of N_{ss}= 0.9, linear sorption was assumed (N_{ss} = 1.0). Two different TOXSWA runs were done: i) simulating biotic transformation (half-life is 1 d at 20°C) and ii) simulating lumped transformation (k^* = 1.208 d at 20°C).

The lumped transformation rate k^* was calculated such that the mass transformed is comparable to the mass transformed in the run simulating biotic transformation only (see Beltman *et al.*, 2015 for the elaboration):

$$\frac{k^*}{k_{bio}} = \frac{1}{1 + ss\, m_{om,ss}\, K_{om,ss}} \qquad (30)$$

Eq. (30) is only valid when macrophytes are not present and linear sorption is assumed.

4.3.2 Results

Figure 13 shows the concentration as function of time for the simulations with i) biotic transformation with a half-life of 1 d at 20°C and ii) lumped transformation k^* = 1.208 d at 20°C. The decline pattern for both simulations is identical.

The visual correspondence of the concentration profiles shown in Figure 13 demonstrates that test 1B has been satisfactory. This demonstrates that the biotic transformation process is implemented correctly in TOXSWA.

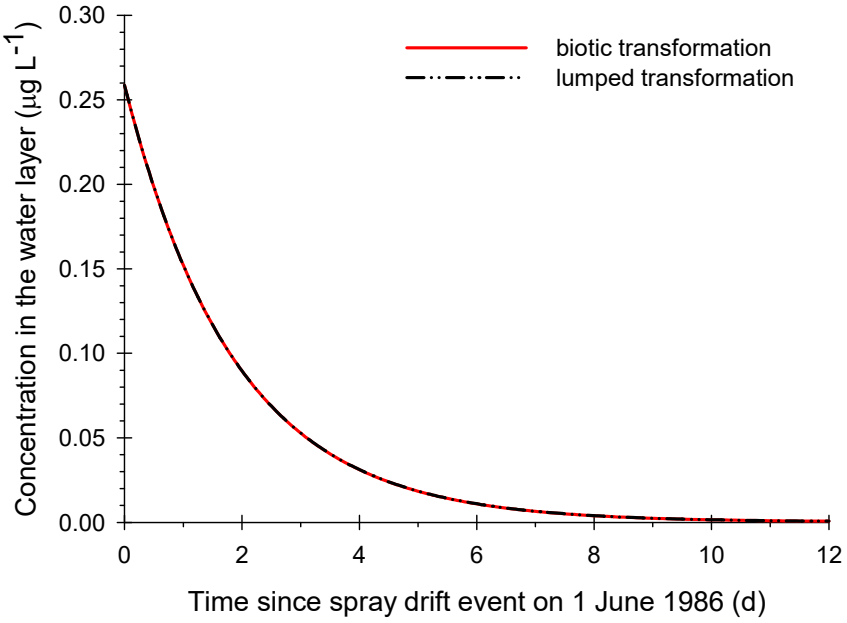

Figure 13 *Concentration dissolved in the water layer as a function of time since 1 June 1986 for a simulation using i) only biotic transformation (red solid line) and ii) lumped transformation (black dashed line). The lumped transformation rate k* is calculated such that the mass transformed is identical to the mass transformed in the run simulating biotic transformation.*

4.4 Test 2: Robustness for the implemented concepts of hydrolysis and biotic transformation

4.4.1 Set up of the test

The aim of the test is to check if the implemented kernel 3.4 of the TOXSWA model is numerically robust for the implemented concepts of hydrolysis and biotic transformation. The parameters that affect the hydrolysis and biotic transformation rate directly were tested using the values of the parameter outer ranges or combinations of parameters setting extreme conditions.

For hydrolysis we used the scenario and substance properties specified in Annex 3. For the first test (Test 2A) the properties pH_m and pH_a were varied as specified in **Table 3**. The simulation period was 1 May – 31 July 1986. Simulations were done using a spray drift deposition of 0.1 mg/m^2 on 1 May 1986 entering the water layer over the entire length of the pond (x = 0 to x = 100 m). Monthly average water temperatures of weather station De Bilt in the Netherlands were used as input (13.3, 17.6 and 18.5 °C for respectively May, June and July 1986).

Table 3 *Combinations of parameter values used for the robustness Test 2A: the average daily pH of the water layer per month (pH_m) and its corresponding amplitude (pH_a) per month.*

Test nr	Average daily pH of the water layer per month (pH_m)	Amplitude of the average daily pH in the water layer per month (pH_a)
1	3	0
2	12	0
3	7.5	4.5
4	7.5	0.01

Test 2A was repeated a second time using different values for the half-lives for acid-catalysed, neutral and base-catalysed hydrolysis at reference temperature ($DegT50_{a,ref}$ was 100 000 d, $DegT50_{n,ref}$ was 200 d and $DegT50_{b,ref}$ was $1.4 \cdot 10^{-3}$ d; all three at reference temperature of 20 °C). These new values result in effective DegT50 values for hydrolysis of about 198, 182, 66 and 19 d for respectively pH 7, 8, 9 and 10, *i.e.* compared to the half-lives for acid-catalysed, neutral and base-catalysed hydrolysis at reference temperature given in Annex 3, these values of $DegT50_{a,ref}$, $DegT50_{n,ref}$ *and* $DegT50_{b,ref}$ result in slower degradation in the relevant pH trajectory.

For the second test (Test 2B) of hydrolysis we use the test set up of Test 2A. However, we varied the properties $DegT50_{a,ref}$, $DegT50_{n,ref}$ and $DegT50_{b,ref}$ and the monthly water temperature (**Table 4**). The parameter values of pH_m and pH_a were fixed as specified in **Table 2**.

Table 4 *Combinations of parameter values used for the robustness test 2B: $DegT50_{a,ref}$, $DegT50_{n,ref}$ and $DegT50_{b,ref}$ and the monthly water temperature.*

Test nr	$DegT50_{a,ref}$ (20°C) (*d*)	$DegT50_{n,ref}$ (20°C) (*d*)	$DegT50_{b,ref}$ (20°C) (*d*)	Monthly water temperature (°C)
1	0.1	0.1	100000	De Bilt
2	100000	100000	0.1	De Bilt
3	0.1	100000	0.1	De Bilt
4	100000	0.1	100000	De Bilt
5	0.1	0.1	100000	0
6	100000	0.1	100000	35

The third test (Test 2C) concerned biotic transformation using the scenario and substance properties specified in Annex 4. The simulation period was 1 June – 31 August 1986. Simulations were done using a spray drift deposition of 0.1 mg/m^2 on 1 June 1986 entering the water layer over the entire length of the pond (x = 0 to x = 100 m). For Test 2C we disabled substance transport to and from the sediment (diffusion coefficient, D = 0 m^2 d^{-1}). Parameters varied are $DegT50_{bio,ref}$ and the monthly water temperature (**Table 5**).

Table 5 *Combinations of parameter values used for the robustness test 2C: $DegT50_{bio,ref}$ and the monthly water temperature.*

Test nr	$DegT50_{bio,ref}$ (20°C) (*d*)	Monthly water temperature (°C)
1	0.1	scenario
2	100000	scenario
3	0.1	0
4	0.1	35

4.4.2 Results

TOXSWA finalized all runs of Tests 2A, 2B and 2C without giving warnings or substance mass balance errors. Calculated pH patterns (Test 2A) and calculated decline patterns of the concentrations (Tests 2B and 2C were all judged to be plausible. Influence of the scenario temperature is conformable to expectations: low water temperatures (Test 2B-run 5, Test 2C-run 3) result in a slower decline of the concentration and high water temperatures (Test 2B-run 6, Test 2C-run 4) result in a faster decline of the concentration. As these tests concern only the robustness of the model (the test results are not shown).

4.5 Testing the implementation of combined transformation processes in TOXSWA

4.5.1 Set up of the test

The aim of this test (Test 3) is to check if the simulation of combined transformation processes is implemented correctly in TOXSWA.

For the test we use the scenario and substance properties specified in Annex 3. Simulations were done using a spray drift deposition of 0.1 mg/m^2 entering the water layer over the entire length of the pond (x = 0 to x = 100 m) at the start of the simulation. The pH is fixed to a constant value of 8 and the daily global radiation, G, is fixed to a constant value of 10 000 kJ m^{-2}. The water temperature was fixed to 293.15 K (20 °C) for the entire simulation period (*i.e.* no simulation of the water temperature as a function of the global radiation was done). The analytical solution was solved at an hourly basis and for TOXSWA a fixed time step of 600 s was used.

For this test hydrolysis, photolysis and biotic transformation were simulated simultaneously (OptTra = HdrPhoBio). Transformation parameters $DegT50_{ph,ref}$ (photolysis), $DegT50_{a,ref}$, $DegT50_{n,ref}$ and $DegT50_{b,ref}$ (hydrolysis) and $DegT50_{bio,ref}$ (biotic transformation) were selected such that the transformation rate of the separate processes are exactly the same.

Two calculations were performed: *i)*: $DegT50_{ph,ref}$ = 2 d, $DegT50_{a,ref}$ = 1000 d, $DegT50_{n,ref}$ = 2 d, $DegT50_{b,ref}$ = 0.01 d *and* $DegT50_{bio,ref}$ = 2 d and *ii)* $DegT50_{ph,ref}$ = 100 d, $DegT50_{a,ref}$ = 100 000 d, $DegT50_{n,ref}$ = 113 d, $DegT50_{b,ref}$ = 0.0006 d *and* $DegT50_{bio,ref}$ = 100 d.

For calculation *i*, the simulation period was one day; 1 May. For calculation *ii*, the simulation period was 245 days; 1 May – 31 December.

The following equation is used to calculate the rate coefficient for photolysis, k_{ph} (Beltman *et al.*, 2015):

$$k_{ph} = k_{ph,ref} \frac{G}{G_{ref}} \qquad (31)$$

with:

k_{ph} = rate coefficient for photolysis (d^{-1})
$k_{ph,ref}$ = 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})

Following Boesten *et al.* (2014) we used a value of 10 000 kJ m^{-2} for G_{ref} and for simplicity a value of 10 000 kJ m^{-2} for G, resulting in $k_{ph} = k_{ph,ref}$.

Furthermore, all processes that may decrease the concentration were disabled, *i.e.* volatilization, sorption to suspended solids or macrophytes and transport to the sediment were not simulated.

Concentrations (dissolved) in the water layer as a function of time resulting from a TOXSWA simulation considering all three transformation processes simultaneously were compared with concentrations (dissolved) in the water layer obtained by solving the analytical solution for t = 1, 2, 3 etc. hours:

$$c_{w(t)} = c_{w(t=0)} e^{[-kt]} \qquad (32)$$

with

$c_{w,t}$ = mass concentration of substance in the water phase, *i.e.* at hour, *t* (kg m^{-3})

$c_{w,t=0}$ = mass concentration of substance in the water phase, *i.e.* at hour, *t* = 0 (kg m^{-3})

The overall transformation rate, *k* is calculated according Eq. (8) and results in a value of 1.04 d^{-1} (k_h = k_{ph} = k_{bio} = 0.347 d^{-1}) for calculation *i* and in a value of 0.0208 d^{-1} for calculation *ii* (k_h = k_{ph} = k_{bio} = 0.0069 d^{-1}).

4.5.2 Results

Calculation i) fast degradation

The concentration calculated with TOXSWA is 0.1101 µg L^{-1} at the end of day on 1 May 1986 (*i.e.* the spray drift deposition enters the watercourse at 00:00 h at this day). At the same time, the concentration calculated with the analytical solution of Eq. (32) is 0.1105 µg L^{-1}. At this time the relative difference between the concentration calculated by TOXSWA and the concentration calculated by the analytical solution is about 0.4%. The difference increases to about 4% after 12 days of simulation (c_w ~ 10^{-6} µg L^{-1}). However, this difference will decrease if a smaller time step is used for the TOXSWA simulation (*i.e.* when using a time step of 60 s, the relative difference is about 0.45% after 12 days of simulation). The concentrations as function of time are shown in Figure 14. Visual inspection shows that the correspondence in concentration profiles calculated by TOXSWA and the analytical solution is satisfactory.

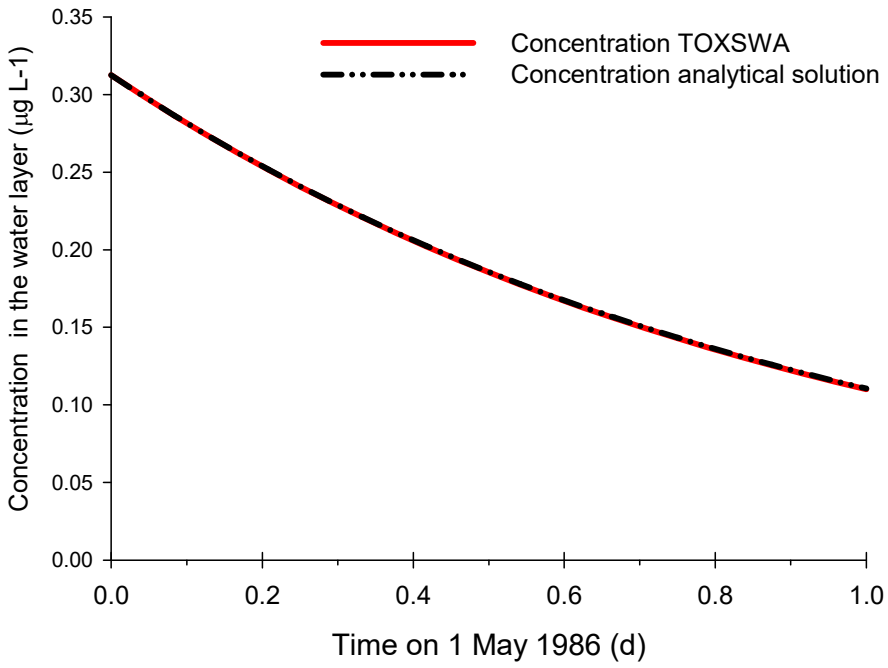

Figure 14 *Concentration dissolved in the water layer as a function of time on 1 May 1986 for a simulation with i) TOXSWA (red solid line) and ii) analytical solution (black dashed line), both simulating the three transformation processes of photolysis, hydrolysis and biotic transformation simultaneously using a transformation rate, k, of 1.04 d^{-1} (DegT50 is ca. 0.7 d).*

Calculation ii) slow degradation

The concentrations as function of time are shown in Figure 15. Visual inspection shows that the correspondence in concentration profiles calculated by TOXSWA and the analytical solution is satisfactory. The relative difference between the concentration calculated by TOXSWA and the concentration calculated by the analytical solution increases to 0.033% after 245 d (time step of 600 s). The system of calculation *ii* is less dynamic than that of calculation *i* because of the slower degradation (DegT50 ~ 0.7 d for *i* and DegT50 ~ 33 d for *ii*). Using the same time step of 600 s for *ii* therefore results in smaller relative differences between the concentration calculated by TOXSWA and the concentration calculated by the analytical solution.

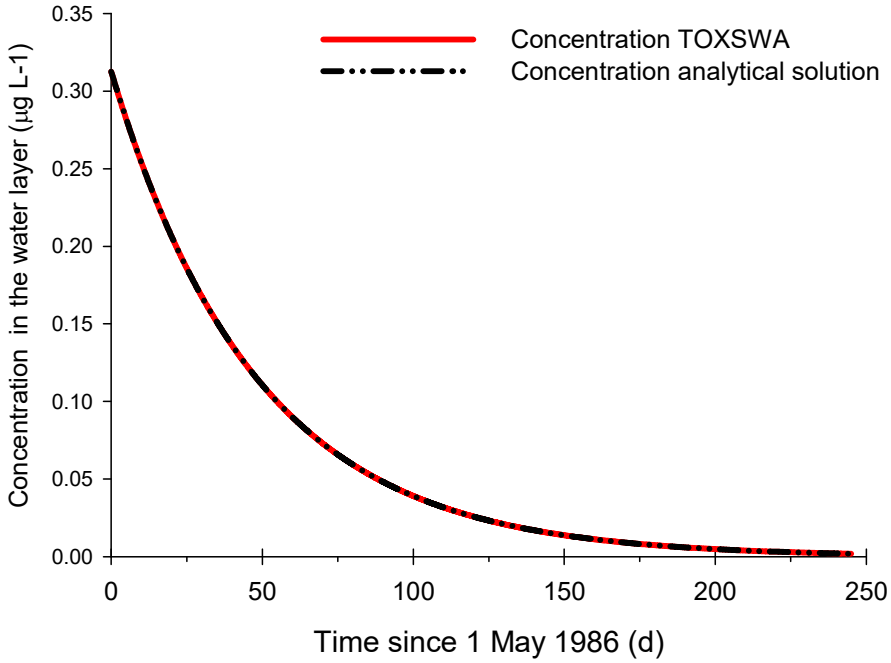

Figure 15 *Concentration dissolved in the water layer as a function of time since 1 May 1986 for a simulation with i) TOXSWA (red solid line) and ii) analytical solution (black dashed line), both simulating the three transformation processes of photolysis, hydrolysis and biotic transformation simultaneously using a transformation rate, k, of 0.0280 d^{-1} (DegT50 is ca. 33 d).*

4.6 Conclusions

The conclusions of the tests with TOXSWA kernel version 3.4 described in sections 4.2 – 4.5 are:

- The concept of hydrolysis including its dependency on the temperature and the pH in the water layer is implemented correctly in TOXSWA.
- The concept of biotic transformation in the water layer is implemented correctly in TOXSWA.
- The calculation of hydrolysis and biotic transformation with the TOXSWA model is robust.
- The simulation of combined transformation processes is implemented correctly in TOXSWA.

5 Conclusions and recommendations

5.1 Considerations for the use of transformation rates in a regulatory context

To use these newly implemented processes to calculate exposure concentrations in water for pesticide registration purposes, it is necessary to determine the rate constants (or half-lives) of the separate processes. To experimentally establish hydrolysis rate constants at three pH levels is rather straightforward and the values of these constants are reported in the dossiers for pesticide registration. Photolysis rate constants can be derived from experiments. However, converting an experimental rate constant obtained under specific conditions into a rate constant applicable to conditions assumed during a simulation may not be straightforward (Deneer *et al.*, 2010).

The largest difficulty lies however in the determination of the biotic transformation rate constant. A ready available test and/or method is not available at the moment. A new test to determine the biotic transformation rate constant or a method using data of existing tests reported in pesticide registration dossiers (*e.g.* OECD 308, OECD 309) to determine the biotic transformation rate constant needs to be developed. The latter was the focus of the work of Honti *et al.* (2016). They inherently assumed that microbial activity in different water systems and in pore water of the sediment is globally universal. This assumption is controversial (Vink, 1997).

Another option is to estimate degradation half-lives in water from outdoor experimental systems (*e.g.* cosms). When decline is measured in outdoor cosm systems, *e.g.* as higher-tier aquatic risk assessments, we recommend to well monitor environmental conditions relevant for transformation and mentioned in Jacobs *et al.* (2010) and Deneer *et al.* (2010) such as light intensity, water temperature, pH as function of time to be able to back calculate observed transformation rates to reference conditions. In this way we will be able to compare transformation rates between cosm types and/or locations and obtain insight into the variability of transformation over the Netherlands or in the EU. This variability in transformation will reflect the variability in microbial activity, the variability in hydrolysis due to pH conditions and the variability of the light conditions important for direct and indirect photolysis.

5.2 Conclusions

The TOXSWA model has been extended with the functionality to simulate hydrolysis and biotic transformation. Hydrolysis and biotic transformation are modelled as first-order processes, where transformation occurs in the water phase only. So, mass sorbed onto *e.g.* suspended solids is assumed not to degrade. Hydrolysis is described as a function of both the pH and the temperature in the water layer. Biotic transformation is considered to be temperature-dependent only.

TOXSWA offers two options for hydrolysis rate inputs: *i)* on the basis of measured hydrolysis rates at three different pH values and possibly different temperatures, TOXSWA calculates the rates for acid-catalysed hydrolysis, base-catalysed hydrolysis and neutral hydrolysis or *ii)* rates for acid-catalysed hydrolysis, base-catalysed hydrolysis and neutral hydrolysis at reference temperature are given as input to the model. For the first option the user needs to provide a value for the weighting factor, to indicate the degree of reliability of the three measured rate coefficients (i.e. a weighting factor of one indicates equal confidence in the three measured rate coefficients).

Example calculations simulating hydrolysis showed that the daily sinusoidal pattern of the pH is reflected in the concentration profile in the water layer. When simulating a larger time span (several months or more) larger differences in the average monthly pH of the water layer may lead to very

different decline patterns of the substance concentration in the water layer from month to month (*e.g.* one month the substance degrades slowly, another month degradation might be very fast). Whether this occurs depends on the degree of contribution of one or more of the three hydrolysis types (*i.e.* acid-catalysed hydrolysis, base-catalysed hydrolysis and neutral hydrolysis) to the total hydrolysis rate at a given pH and temperature of the water in the water body.

Tests with TOXSWA confirmed that the concepts of hydrolysis and biotic transformation are implemented correctly. It was also shown that the calculation of hydrolysis and biotic transformation with the TOXSWA model is robust. Furthermore, it was verified that the simulation of combined transformation processes is implemented correctly in TOXSWA.

By having implemented the processes of hydrolysis, biotic transformation and photolysis (Beltman *et al.*, 2015) TOXSWA is now able to account better for changes in overall transformation rate by *e.g.* changes in pH or light intensity. In this way simulated concentration profiles may reflect reality better.

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Annex 1 Change in transformation concept between TOXSWA kernel versions 3.3 and 3.4; taken from Beltman *et al.* (2015)

Using the lumped transformation rate corresponds to using an overall transformation rate determined in an experimental 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 experiment should consider transformation in the water phase only.

To be able to derive the transformation rate in the water phase k from k^*, c_w^* in Eq. (7) is replaced using Eq. (5) and (6):

$$k^*\left(c_w + \frac{DW\ P_0}{A}X_{mp} \ + \ ss \quad m_{om,ss}K_{F,om,ss}\ c_{e,ss}\left(\frac{c_w}{c_{e,ss}}\right)^{N_{ss}}\right)A = k(c_w A) \qquad (33)$$

A simple calculation example is given. A transformation study is done using a flask with one litre 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_w^* in the study is 10 d, hence $k^* = 0.069\ d^{-1}$.

In the example there are no macrophytes present in the flask and we assume a linear sorption coefficient ($N_{ss} = 1$). Then Eq. (33) can be rewritten for the example case into:

$$\frac{k^*}{k} = \frac{1}{1 + \ ss\ m_{om,ss}K_{F,om,ss}} \qquad (34)$$

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.

Annex 2 Generic equations to establish hydrolysis rate constants at any pH from experimental data on hydrolysis rates at three different values of pH

The full content of this Annex is taken from Annex D in Deneer *et al.*, 2010.

Three methods are available to determine the hydrolysis rate coefficients $k_{a,ref}$, $k_{n,ref}$ and $k_{b,ref}$ from three hydrolysis studies resulting in $k_{1,ref}$, $k_{2,ref}$ and $k_{3,ref}$ (after calculating $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ measured at three values of pH and temperature to $k_{1,ref}$, $k_{2,ref}$ and $k_{3,ref}$ at reference temperature):

1. symmetric cases, *i.e.* when $k_{1,ref} > k_{2,ref}$, $k_{3,ref} > k_{2,ref}$

2. asymmetric acid-catalysed hydrolysis, *i.e.* when $k_{1,ref} > k_{2,ref}$, $k_{2,ref} > k_{3,ref}$

3. asymmetric base-catalysed hydrolysis, *i.e.* when $k_{1,ref} < k_{2,ref}$, $k_{2,ref} < k_{3,ref}$

Each of the three methods is described below.

Note that from here onwards in this Annex, the measured rate coefficients at reference temperature are indicated as k_1, k_2 and k_3 (so without the subscript 'ref').

1. Symmetric case

We refer to this situation as the 'symmetric case', since the data suggest for $k_{h,ref}$, a parabolic behaviour with the minimum around $pH_2 = 7$ (Figure 16).

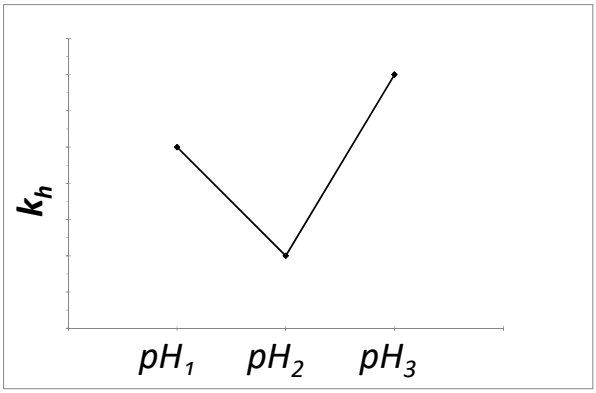

Figure 16 *Symmetric case.*

Eq. (21) is well suited to fit such data. Substituting the data we obtain the linear equations:

$$k_1 = k_{a,ref}\ 10^{(-pH_1)} + \overline{k_{b,ref}}\ 10^{(+pH_1)} + k_{n,ref}$$

$$k_2 = k_{a,ref}\ 10^{(-pH_2)} + \overline{k_{b,ref}}\ 10^{(+pH_2)} + k_{n,ref} \qquad (35)$$

$$k_3 = k_{a,ref}\ 10^{(-pH_3)} + \overline{k_{b,ref}}\ 10^{(+pH_3)} + k_{n,ref}$$

This system can be solved using standard methods, *e.g.* Cramer's rule. First we calculate the determinant of the following matrix:

$$Det = Determinant \begin{bmatrix} 10^{-pH_1} & 10^{+pH_1} & 1 \\ 10^{-pH_2} & 10^{+pH_2} & 1 \\ 10^{-pH_3} & 10^{+pH_3} & 1 \end{bmatrix} \quad (36)$$

Using the standard evaluation rules it holds that *Det* is given by the expression:

$$Det = 10^{(pH_2-pH_1)} - 10^{(pH_3-pH_1)} - 10^{(pH_1-pH_2)} + 10^{(pH_3-pH_2)} + 10^{(pH_1-pH_3)} - 10^{(pH_2-pH_3)} \quad (37)$$

The rate coefficients $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ are then given by equations (38), (39), and (40).

$$k_{a,ref} = \frac{1}{Det}\{k_1(10^{pH_2} - 10^{pH_3}) - k_2(10^{pH_1} - 10^{pH_3}) + k_3(10^{pH_1} - 10^{pH_2})\} \quad (38)$$

$$k_{b,ref} = \frac{1}{K_w}\frac{1}{Det}\{k_1(10^{-pH_3} - 10^{-pH_2}) - k_2(10^{-pH_3} - 10^{-pH_1}) + k_3(10^{-pH_2} - 10^{-pH_1})\} \quad (39)$$

$$k_{n,ref} = \frac{1}{Det}\{k_1(10^{(pH_3-pH_2)} - 10^{(pH_2-pH_3)}) - k_2(10^{(pH_3-pH_1)} - 10^{(pH_1-pH_3)}) + k_3(10^{(pH_2-pH_1)} - 10^{(pH_1-pH_2)})\} \quad (40)$$

2. Asymmetric acid catalysed hydrolysis

Often measured values of k_1, k_2 and k_3 (note that $k_{1,m}$, $k_{2,m}$ and $k_{3,m}$ measured at three values of pH and temperature are calculated to k_1, k_2 and k_3 at reference temperature) will not satisfy the conditions of the symmetric case (when $k_1 > k_2$, $k_3 > k_3$). In such cases negative values for $k_{a,ref}$, $k_{b,ref}$ or $k_{n,ref}$ are obtained, if one tries to fit the data with the function in Eq. (20). The reason for this unrealistic outcome is obvious: the function in Eq. (20) is not suited for fitting purposes for which it is applied. This concerns the asymmetric cases.

Let us focus first on the asymmetric case where $k_1 > k_2$, $k_2 > k_3$ (*i.e.* acid catalysed hydrolysis; Figure 17). The function $k_{n,ref}$ in Eq. (21) is a linear combination of three totally different functions: a decaying exponential 10^{-pH}, and a constant. The decaying exponential is nearly negligible in the range pH > 7. This implies that in the symmetric case the coefficient $k_{n,ref}$ is nearly completely determined by the value of k_2, the coefficient $k_{a,ref}$ is mainly determined by the value of k_1, and the coefficient $k_{b,ref}$ by the value of k_3. The algorithm outlined above for the symmetric case tens to take for $k_{n,ref}$ a value close to k_2. However, if $k_3 < k_2$, the constant in expression (21) is bigger than k_3, which has as a consequence that for $k_{b,ref}$ a negative value will be estimated in order to obtain a curve that passes through (pH_3, k_3). To avoid this, we should choose for $k_{n,ref}$ a value ≤ k_3. The constant contribution in Eq. (20) is then not big enough to represent the value k_2 at pH_2, but since the exponentials in Eq. (20) cannot compensate for this, it is not possible to fit asymmetric data with the function in Eq. (20). To overcome this problem, one has to accept that approximations have to be made. In the following a realistic approach for this fitting problem is proposed.

Consider the asymmetric case that $k_1 > k_2$, $k_2 > k_3$ (acid catalysed hydrolysis; Figure 17).

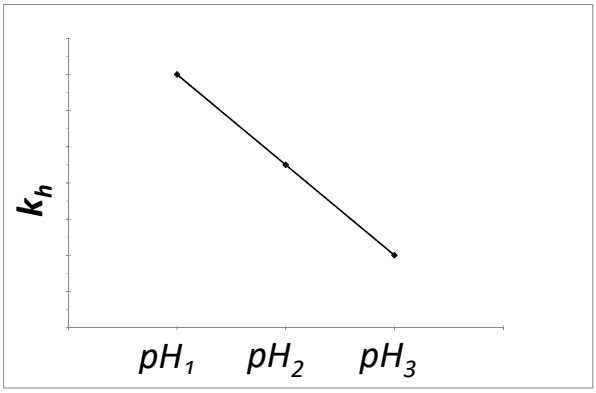

Figure 17 Asymmetric case of acid catalysed hydrolysis ($k_1 > k_2, k_2 > k_3$).

The increasing exponential in Eq. (21) does not contribute, so we set:

$$\overline{k_{b,ref}} = 0 \tag{41}$$

For the constant $k_{n,ref}$ we apply:

$$k_{n,ref} = k_3 \tag{42}$$

The decaying exponential and the corresponding coefficient $k_{a,ref}$ form the only remaining degree of freedom. It is impossible to fit the data points (pH_1, k_1) and (pH_2, k_2) simultaneously with a proper choice for $k_{a,ref}$. One should select one of these points and ignore the other, but we prefer an approach in which the user has the freedom to give weights to both data points.

The fitting function now reads as:

$$k_{h,ref}\left(k_{a,ref}\right) = k_{a,ref}\ 10^{(-pH)} + k_3 \tag{43}$$

This function should approach (pH_1, k_1) and (pH_2, k_2) in some optimal way. The errors are:

$$\varepsilon_1 = k_{a,ref}\ 10^{(-pH_1)} + k_3 - k_1 \tag{44}$$
$$\varepsilon_2 = k_{a,ref}\ 10^{(-pH_2)} + k_3 - k_2 \tag{45}$$

This can be combined in the error function:

$$H\left(k_{a,ref}\right) = \left(\frac{\varepsilon_1}{k_1}\right)^2 + \gamma \left(\frac{\varepsilon_2}{k_2}\right)^2 \tag{46}$$

The term ε_1/k_1 accounts for the relative error at pH_1, and the term ε_2/k_2 for the relative error at pH_2. The constant γ is introduced as a weighting factor: if $\gamma = 1$, both errors are equally important, but if $\gamma >> 1$, the error at pH_2 gets most emphasis.

In practice:
- if $\gamma = 0$, the curve will pass through (pH_1, k_1), but has a considerable error at pH_2;
- if $\gamma >> 1$ (say 10 000) the curve will more or less pass through (pH_2, k_2) with a considerable error at pH_1.

By minimising $H(k_{a,ref})$ with respect to $k_{a,ref}$, we obtain the following estimate for $k_{a,ref}$:

$$k_{a,ref} = \frac{(k_1 - k_3){k_2}^2\, 10^{-pH_1} + \gamma(k_2 - k_3){k_1}^2\, 10^{-pH_2}}{{k_2}^2\, 10^{-2\,pH_1} + \gamma {k_1}^2\, 10^{-2\,pH_2}} \tag{47}$$

3. Asymmetric base catalysed hydrolysis

Consider the asymmetric case that $k_1 < k_2, k_2 < k_3$ (base catalysed hydrolysis; Figure 18).

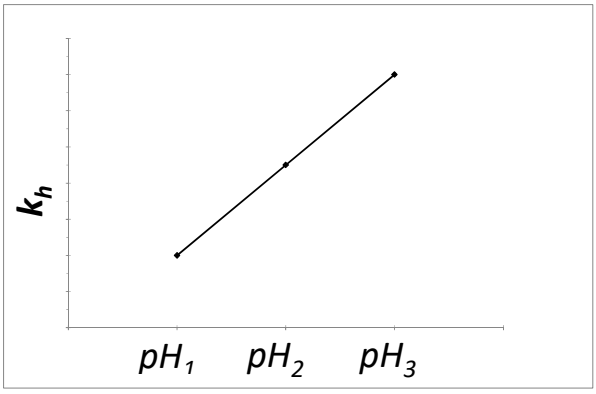

Figure 18 *Asymmetric case base catalysis ($k_1 < k_2, k_2 < k_3$).*

The fitting function now is:

$$k_h\left(\overline{k_{b,ref}}\right) = \overline{k_{b,ref}}\ 10^{(pH)} + k_{n,ref} \tag{48}$$

since the decaying exponential does not contribute and thus

$$k_{a,ref} = 0 \tag{49}$$

As above, we choose for the constant contribution

$$k_{n,ref} = k_1 \tag{50}$$

i.e., we force the fitting function to pass through (pH_1, k_1), the lowest data point.

The estimate for $\overline{k_{b.,ref}}$ is now given by:

$$\overline{k_{b,ref}} = \frac{(k_3 - k_1){k_2}^2\, 10^{pH_3} + \gamma(k_2 - k_1){k_3}^2\, 10^{pH_2}}{{k_2}^2\, 10^{2\,pH_3} + \gamma {k_3}^2\, 10^{2\,pH_2}} \tag{51}$$

For $\gamma = 0$, the fitting function passes through (pH_3, k_3) and for $\gamma >> 1$, say $\gamma = 10\,000$, the function passes more or less through (pH_2, k_2)

Weighting factor for asymmetric methods

In TOXSWA weighting factor, γ, used to calculate $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ from k_1, k_2 and k_3 measured at respectively pH_1, pH_2, and pH_3 is an input parameters. In case the user has reasons for using other values than 1 for γ, the user can calculate rate coefficients $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ using the equations given in this section. Subsequently, the user can use calculated rate coefficients $k_{a,ref}$, $k_{b,ref}$ and $k_{n,ref}$ as

input in TOXSWA. Deneer *et al.* (2010; p. 78) provides some guidance on the selection of values for the weighting factor, γ. For completeness this guidance is repeated below.

How to choose the weighting factor, γ?
In situations of either acid or base catalysed hydrolysis, the DT50 may become relatively small (*e.g.* < 1h). Such low DT50 values may be accompanied by increased experimental error resulting in a relatively large relative standard deviation. This may be reason to adjust the parameter γ given in the above equations, reflecting higher confidence in experimental values of DT50 with smaller relative standard deviations.

Consider the case of acid catalysed hydrolysis (the argument for base catalysed hydrolysis is very similar), where $k_1 > k_2$, $k_2 > k_3$. Suppose that the standard deviation in k_1 is SD1, and the standard deviation in k_2 is SD2. Relative standard deviations RSD1 and RSD2 are then given by SD1/k_1 and SD2/k_2 resp.

Because the error function *H* contains the squares of RSD1 and RSD2, the contribution of k_1 and k_2 can be weighted according to their relative standard deviations by choosing

$$\gamma = \left(\frac{RSD1}{RSD2}\right)^2 \qquad (52)$$

To give k_1 a larger weight, γ can be chosen smaller, and to give k_2 a larger weight γ can be chosen larger.

Annex 3 Scenario and substance properties used to illustrate the effect of pH on hydrolysis

In Table A1 the values of the scenario and substance properties as used for the example calculations in section 3.5.1 (*i.e.* illustrating the effect of pH on the hydrolysis rate) are given for TOXSWA. In this simulation only transformation in the water phase due to hydrolysis is considered. Other processes that may decrease the concentration are not considered, *i.e.* volatilization (saturated vapour pressure set to 0 Pa), sorption to suspended solids or macrophytes (ConSus = 0, CofSorMph = 0) and transport to sediment (CofDifWatRef = 0) have been set to zero. Input parameters in TOXSWA that are not relevant for the calculations are not specified in Table A1.

Table A1 *Values of scenario and substance properties used in the TOXSWA example calculation to illustrate the effect of pH on the hydrolysis rate.*

Property	TOXSWA
Flow velocity	VelWatFlwBas (m/d) =0
Seepage	FlwWatSpg (mm/d) = 0
Water body dimensions	
water depth	DepWat (m) = 0.32
width of the bottom	WidWatSys (m) = 10.0
side slope	SloSidWatSys (-) = 0.00001
depth defining perimeter	DepWatDefPer (m) = 0.1
length of the water body	Len (m) = 100
number of segments	NumSeg (-) = 1
	OptWaterSystemType: **Pond**
Sediment dimensions and properties[2]	
thickness of the sediment	ThiHor (m) = 0.06 (one horizon)
number of segments	NumLay (-) = 60
setup for rectangular sediment (see last section on p.27 in Beltman *et al.*, 2014)	SloSidWatSys (-) = 0 DepWatDefPer (m) = 0
dry bulk density	Rho ($kg.m^{-3}$) = 800
porosity	ThetaSat (-) = 0.6
relative diffusion coefficient (tortuosity)	CofDifRel (-) = 0.6
Loading on water body	
mass loading cross section	no input
drift deposition	01-May-1986 Drift **0.1** (mg/m^2)
location of mass loading	01-May-1986 Drift 0.1 **0.0 100.** (m)
	OptLoa: DriftOnly
SUBSTANCE	
Molar mass	MolMas ($g.mol^{-1}$) = 350.6
Volatilisation	PreVapRef (Pa) = 0.
Reference temperature for saturated vapour pressure	TemRefVap (C) = 20
Molar enthalpy of the vaporization process	MolEntVap (kJ/mol) = 95

[2] Note that sediment dimensions and properties are not relevant for the calculations because the diffusion coefficient (CofDifWatRef) is set to zero.

Property	TOXSWA
Solubility in water	SlbWatRef (mg/L) = 2
Reference temperature for water solubility	TemRefSlb (C) = 20
Molar enthalpy of dissolution	MolEntSlb (kJ/mol) = 27
Diffusion	
diffusion coefficient	CofDifWatRef = 0 ($m^2.d^{-1}$)
Reference temperature for diffusion	TemRefDif = 20 (C)
Transformation in water	
half-life by hydrolysis (acid-catalysed, neutral, base-catalysed, resp.)	DT50LiqAcidRef (d) = 100000. DT50LiqNeuRef (d) = 68. DT50LiqBaseRef (d) = 2.2 E-5
Temperature at which half-life in water was measured	TemRefTraHdrWat (C) = 20
Molar activation enthalpy of hydrolysis in water	MolEntTraHdrWat (kJ/mol) = 75.
	OptTraWatLumped = No OptTraWatHdr = Yes OptTraWatPho = No OptTraWatBio = No
Transformation in sediment[3]	
Half-life transformation in sediment	DT50SedRef (d) = 173.
Temperature at which half-life in sediment was measured	TemRefTraSed (C) = 20
Molar activation enthalpy of transformation in sediment	MolEntTraSed (kJ/mol) = 65.4
Sorption to sediment[2]	
Coefficient for equilibrium sorption in sediment	KomSed (L/kg) = 16400.
Reference concentration in liquid phase in sediment	ConLiqRefSed (mg/L) = 1.
Freundlich exponent in sediment	ExpFreSed (-) = 0.984
Sorption to suspended solids	
Concentration suspended solids	ConSus (g/m^3) = 0.
Coefficient for equilibrium sorption of suspended solids	KomSusSol (L/kg) = 16400.
Mass ratio of organic matter in suspended solids	CntOmSusSol (kg/kg) = 0.1
Reference concentration	ConLiqRefSusSol (mg/L) = 1.
Freundlich exponent	ExpFreSusSol (-) = 0.984
Sorption to macrophytes	
Coefficient for linear sorption on macrophytes	CofSorMph (L/kg) = 0
Dry mass of macrophyte biomass per m^2 bottom	AmaMphWatLay (g/m^2) = 0

[3] Note that substance properties relating to transformation and sorption processes in the sediment are not relevant for the calculations because the diffusion coefficient (CofDifWatRef) is set to zero.

Annex 4 Scenario and substance properties used to illustrate the difference of biodegradation and lumped degradation

In Table A2 the values of the scenario and substance properties as used for the example calculations in section 3.5.2 (*i.e.* illustrating difference between biotransformation and the lumped approach) are given for TOXSWA. Two simulations were done: 1) using biotransformation only (OptTraWatLumped = No and OptTraWatBio = Yes) and 2) using the lumped approach (OptTraWatLumped = Yes). For both simulations the half-life (DT50LiqBioRef and DT50WatRef) was set to the same value of 1 d.

Table A2 *Values of scenario and substance properties used in the TOXSWA example calculation to illustrate difference between biotransformation and the lumped approach.*

Property	TOXSWA
Flow velocity	VelWatFlwBas (m/d) =0
Seepage	FlwWatSpg (mm/d) = 0
Water body dimensions	
water depth	DepWat (m) = 0.32
width of the bottom	WidWatSys (m) = 10.0
side slope	SloSidWatSys (-) = 0.00001
depth defining perimeter	DepWatDefPer (m) = 0.1
length of the water body	Len (m) = 100
number of segments	NumSeg (-) = 1
	OptWaterSystemType: **Pond**
Sediment dimensions and properties	
thickness of the sediment	ThiHor (m) = 0.06 (one horizon)
number of segments	NumLay (-) = 60
setup for rectangular sediment (see last section on p.27 in Beltman *et al.*, 2014)	SloSidWatSys (-) = 0 DepWatDefPer (m) = 0
dry bulk density	Rho ($kg.m^{-3}$) = 800
porosity	ThetaSat (-) = 0.6
relative diffusion coefficient (tortuosity)	CofDifRel (-) = 0.6
Loading on water body	
mass loading cross section	no input
drift deposition	01-Jun-1986 Drift **0.1** (mg/m^2)
location of mass loading	01-Jun-1986 Drift 0.1 **0.0 100.** (m)
	OptLoa: DriftOnly
SUBSTANCE	
Molar mass	MolMas ($g.mol^{-1}$) = 449.9
Volatilisation	PreVapRef (Pa) = $2 \cdot 10^{-7}$
Reference temperature for saturated vapour pressure	TemRefVap (c) = 20
Molar enthalpy of the vaporization process	MolEntVap (kJ/mol) = 95
Solubility	SlbWatRef (mg/L) = 0.005
Reference temperature for water solubility	TemRefSlb (C) = 20
Molar enthalpy of the dissolution	MolEntSlb (kJ/mol) = 27

Property	TOXSWA
Diffusion	
diffusion coefficient	CofDifWatRef = 4.3E-5 ($m^2.d^{-1}$)
Reference temperature for diffusion	TemRefDif = 20 (C)
Transformation in water	
half-life by biodegradation	DT50LiqBioRef (d) = 1. If OptTraWatLumped = No and OptTraWatBio = Yes and OptTraWatPho = No and OptTraWatHyd = No
half-life in water (lumped)	DT50WatRef (d) = 1. If OptTraWatLumped = Yes
Temperature at which half-life in water was measured	TemRefTraWat (C) = 20
Molar activation enthalpy of hydrolysis in water	MolEntTraWat (kJ/mol) = 75.
Transformation in sediment	
Half-life transformation in sediment	DT50SedRef (d) = 1000.
Temperature at which half-life in sediment was measured	TemRefTraSed (C) = 20
Molar activation enthalpy of transformation in sediment	MolEntTraSed (kJ/mol) = 65.4
Sorption to sediment	
Coefficient of equilibrium sorption in sediment	KomSed (L/kg) = 138820.
Reference concentration in liquid phase in sediment	ConLiqRefSed (mg/L) = 1.
Freundlich exponent in sediment	ExpFreSed (-) = 0.9
Sorption to suspended solids	
Concentration suspended solids	ConSus (g/m^3) = 15
Coefficient of equilibrium sorption of suspended solids	KomSusSol (L/kg) = 138820.
Mass ratio of organic matter in suspended solids	CntOmSusSol (kg/kg) = 0.1
Reference concentration	ConLiqRefSusSol (mg/L) = 1.
Freundlich exponent	ExpFreSusSol (-) = 0.9
Sorption to macrophytes	
Coefficient for linear sorption on macrophytes	CofSorMph (L/kg) = 0
Dry weight of macrophyte biomass per m^2 bottom	AmaMphWatLay (g/m^2) = 0

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Wageningen Environmental Research
Report 2848
ISSN 1566-7197

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ISSN 1566-7197

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