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Abstract

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Keywords: TOXSWA, hydrolysis, photolysis, biotransformation

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# Contents

# Summary

This report aims to give a general description of transformation processes for future use in the TOXSWA model. Hydrolysis, photolysis and biotic transformation are described as distinct processes, employing separate rate constants. Additionally, a way to introduce into TOXSWA the daily variation of pH and temperature is proposed.

*Chapter 2 Hydrolysis*
Hydrolysis is described as the sum of acid catalysed, base catalysed and neutral hydrolysis rate constants. Estimation of these three hydrolysis rate constants from experimental hydrolysis rates at three pH levels, as described by the United States EPA Guideline, was adapted by removing the approximations in the EPA method and catering for experimental errors. The resulting method to estimate the three separate hydrolysis rates is demonstrated by analyzing hydrolysis data at variable pH for two compounds. It is suggested to account for the influence of temperature on hydrolysis by using an Arrhenius type of equation. If no compound specific value for the activation energy is available, the use of an estimated value of 75 kJ $mole^{-1}$ is suggested.

*Chapter 3 Photolysis*
Direct photolysis near the surface of clear water can be estimated from the wavelength distribution of incoming irradiation, combined with information on the absorption spectrum of the degrading compound and knowledge about quantum yields of the photolysis process. Examples of software programs enabling this calculation are given (GCSOLAR and ABIWAS). A drawback of these methods is that quantum yields are often unknown. However, assuming a quantum yield of 1 gives an estimated maximum rate of photolysis, whereas assuming a quantum yield of 0.032 may give a more realistic estimate of direct photolysis in water. The results of some example calculations for two compounds using GCSOLAR are given.

Indirect photolysis occurs when light is adsorbed by a molecule which subsequently transfers its energy to the acceptor molecule, causing the latter to react. For many compounds the rate of indirect, sensitized photolysis is much larger than the rate of direct photolysis. As the type of transient molecule may vary between compounds as well as between locations (each having different dissolved organic matter material) no simple 'rules of thumb' are available and therefore indirect photolysis is at the present time not incorporated in TOXSWA.

*Chapter 4 Biotic transformations*
Transformation reactions, although thermodynamically feasible, often proceed slowly due to kinetic limitations. In natural waters, microorganisms are ubiquitously present, and the enzymes they contain can greatly increase the rate of transformation of organic compounds. Usually the rate of transformation is limited by either the growth of the amount of microorganisms (Monod, 1942) or by the rate of the enzymatic conversions within the microorganism (Michaelis and Menten, 1913). Both types of descriptions result in kinetics which are first-order with regard to the concentration of the compound and first-order with regard to cell abundance.

Increase in temperature generally results in an increase in reaction rate. However, microorganisms may adapt to slow, e.g. seasonal, changes in temperature. From the few studies cited in this report, rate increases resulting from small (1 - 2 °C) temperature increases near 20 °C corresponded to a median energy of activation of 65 kJ $mole^{-1}$, which is very close to the value recommended by EFSA (65.4 kJ $mole^{-1}$) for use in the modelling of transformation rates in soils (EFSA, 2007). However, even for a given substance large variations may exist between transformation rates under different conditions. Thus, attempting to correct the biodegradation rate for a change in temperature may introduce relatively large uncertainties.

In view of the limited information available, one may choose to limit corrections for variations in pH and temperature to systems for which experimental data with regard to such variations are available. However, other considerations, e.g. the aim to strive for conservative estimates of exposure concentrations, may indicate the need to apply corrections despite limited information.

*Chapter 5 Temperature and pH in surface water*
Depending on the substance, both temperature and pH may affect transformation rates. The current versions of TOXSWA use average monthly temperatures for the adjustment of a transformation rate encompassing both abiotic and biotic transformation reactions. The effect of pH on transformation reactions is not taken into account.

However, reaction rate constants are related to temperature in an exponential fashion, due to the nature of the Arrhenius equation. Similarly, pH dependent hydrolysis is governed by an exponential type of relationship between hydrolysis rate and pH. The adjustment of transformation rates should therefore not only include monthly or seasonal changes in average temperature and pH, but should also reflect the daily variation and the occurrence of maximum values.

Estimates of monthly average water temperatures and their daily variations were obtained from data gathered in two experimental ditches, using 15 min recordings collected during 1991.
For each month, the daily average and the 90-th percentile of the difference between daily maximum and minimum values were determined.

*Chapter 6 Proposals for modelling of transformation processes in TOXSWA*
Chapter 6 specifies in more detail how the described processes can be incorporated into the TOXSWA software model. A resume is given of descriptions for hydrolysis as a function of pH and temperature, direct photolysis, as well as biotic degradation as a function of short term changes in temperature. Similarly, a proposal for the description of the daily course of the environmental parameters pH and temperature in surface water is given.

# 1 Introduction

Transformation is one of the four processes considered to simulate the fate of pesticides by the TOXSWA model (TOXic substances in Surface WAter). The other three processes are transport, sorption and volatilisation (Adriaanse, 1996; Adriaanse, 1997). TOXSWA simulates the fate of pesticides in ponds and in watercourses, including their sediments, to assess risks of pesticides to the aquatic ecosystem.

The first version of TOXSWA was released on 23 April 1996 (Beltman et al., 1996). TOXSWA 1.2 is applied in the Dutch pesticide registration procedure to calculate exposure concentrations for an edge of field ditch with constant flow rates (Beltman and Adriaanse, 1999a and 1999b). FOCUS_TOXSWA is applied in the EU pesticide registration procedure under Directive 91/414/EEC (Beltman et al., 2005) to calculate exposure concentrations in pond, ditch and stream scenarios (FOCUS, 2001; <focus.jrc.ec.europa.eu/sw/>) with transient flow conditions (Adriaanse and Beltman, 2009).

In stagnant waters or waters with low flow, transformation in the water layer is one of the most sensitive processes determining the exposure concentration (Westein et al., 1998). Transformation is modeled in TOXSWA as a lumped process, assuming one transformation rate for the total mass in the water layer. However at least three separate transformation processes can be considered for transformation in water: hydrolysis, photolysis and biotic transformation. Describing these underlying processes enables a better quantification of the overall transformation rate, and thus improves the description of the pesticide's behavior.

In this study knowledge about the transformation processes is reviewed and available data and parameter values are assessed. We focused our study on process descriptions and parameterisations' that are especially useful in a regulatory context, i.e. descriptions that are valid for a range of substances and environmental conditions and that use predominantly input data required in the standard registration procedure.

For the water layer only transformation of the dissolved substance is considered, disregarding the part of the substance adsorbed to solid phases like suspended solids and macrophytes. This is a major change of concept in TOXSWA, because in TOXSWA 1.2 and FOCUS_TOXSWA 3.3.1 transformation was considered to concern both dissolved and adsorbed phases (see Adriaanse, 1996). For hydrolysis and photolysis the assumption of transformation in the dissolved phase is evident. For biotic transformations some principles are adopted, commonly adhered to when dealing with biotic transformation in soil (Beltman et al., 2008; Alexander, 2000; Scow and Alexander, 1992).

This study concerns only the transformation processes in water, not those in sediment. For the sediment the description of processes remains as given by Adriaanse (1996), i.e. overall transformation expressed on the basis of total concentrations. In analogy with soil, it is assumed that in sediments the transformation is mainly biotic. Typical for sediments is that aerobic and anaerobic layers may co-exist, each typified with different rates of transformation. Future improvements may thus include the distinction between aerobic and anaerobic transformations in the sediment layer.

Transformation is considered as three separate processes: hydrolysis, photolysis and biotic transformation. These processes may be affected by the temperature and pH of the water body. Hydrolysis is described in Chapter 2, photolysis in Chapter 3 and biotic transformation in Chapter 4. The environmental variables temperature and pH are addressed in Chapter 5. In Chapter 6 we propose how the processes and environmental conditions can be modelled in TOXSWA, based on the results of the preceding chapters.

This study intends to provide the TOXWA modelers with up to date process descriptions. However, guidance on actual parameterisation of the process descriptions is beyond the scope of this study and will be dealt with at a later stage.

# 2 Hydrolysis

## 2.1 Influence of pH on hydrolysis

The results of a limited search for recently published papers on hydrolysis and photolysis are given in Annex A. This search was primarily conducted to provide a quick and general overview of recently published literature, especially to infer whether emphasis was mostly on experimental studies or mostly on more theoretical considerations.

A thorough discussion of hydrolysis of pesticides in the aquatic environment, mainly focusing on pathways and reaction products for various chemical classes of pesticides, is given by 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. If pH and temperature remain constant, the hydrolysis half-life is independent of pesticide concentration.

The effect of pH on hydrolysis can be understood by considering the contribution of acid catalysed hydrolysis, base catalysed hydrolysis and neutral hydrolysis separately (Schwarzenbach et al., 2003). The overall rate of hydrolysis ($k_h$) is given by:

$$k_h = k_a[H_3O^+] + k_b[OH^-] + k_n \qquad (2.1)$$

where $k_a$, $k_b$ and $k_n$ denote the rate constants for acid catalysed, base catalysed and neutral hydrolysis at a given temperature resp. ($k_n$ contains the molar concentration of water, which is approximately constant at constant temperature) and $[H_3O^+]$ and [OH] denote the aqueous concentrations of $H_3O^+$ and $OH^-$ ions resp.

The United States EPA have published a test guideline on the analysis of hydrolysis as a function of pH (US EPA, 1998), based on equation 1. The overall rate constant $k_h$ is measured at three values of pH and from these data numerical values for $k_a$, $k_b$ and $k_n$ can be established according to a set of equations. Once these values are known, the hydrolysis rate at any given pH can be calculated. Due to some approximations in the derivation of the equations, their recommendation is to establish hydrolysis rates at pH values of 3, 7 and 11. However, 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 less reliable predictions of $k_h$ at interpolated or extrapolated values of pH. The equations to analyse hydrolysis data and to provide estimates of hydrolysis rates for untested pH values are given in Annex B.

Unfortunately, in the EU it is common practice to report values for hydrolysis rates at pH values of 5, 7 and 9, i.e. a much narrower range than assumed in the EPA equations. The approximations employed in 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). 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. (2.1) (see Section 2.2 for an example of such data). For this reason it was decided to derive a more generic solution of Eq. (2.1), 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 were kindly provided by Dr J. Molenaar of Biometris, Plant Science Group of Wageningen UR (University & Research centre) and are given in Annex D.

## 2.2 Using the EPA equations and the generic solution to estimate hydrolysis rates

Whether a substance is prone to acid catalysed, base catalysed or neutral hydrolysis is very much dependent on its chemical structure. Many chemicals are not prone to hydrolysis at all, regardless of pH, whereas others are stable at neutral pH but hydrolysis increases rapidly as pH changes even if only by a few units. In general terms, substances prone to acid catalysed or both acid and base catalysed hydrolysis seem to be rare, whereas substances prone to base catalysed hydrolysis are more common. Some examples of chemicals whose hydrolysis rate is dependent upon pH are given in Table 2.2.1. Unless indicated otherwise values for hydrolysis half life (DT50) at different values of pH were taken from Tomlin (2003). For many substances only qualitative information was found, e.g. stating that 'the substance is stable in neutral and alkaline conditions, but unstable in acidic conditions' without providing any values for DT50 at all, or only providing a DT50 for the conditions under which hydrolysis occurs. Obviously, when examining the hydrolysis behavior of these substances, more detailed information would have to be gathered to enable analysis through algebraic equations.

***Table 2.2.1***

*Hydrolysis DT50 for some plant protection products at several values of pH.*

| Substance | Hydrolysis half life (DT50, days) at some values of pH | | | | | |
|---|---|---|---|---|---|---|
| | pH = 4 | pH = 5 | pH = 7 | pH = 8 | pH = 9 | pH = 10 |
| Dicloflop-methyl | | 363 | 32 | | 0.5 | |
| Carbendazim | | > 350 | > 350 | | 124 | |
| Chlorpyrifos | | | 100 | 8 | | |
| Carbaryl | | | 12 | | 0.1 | |
| Carbofuran | > 365 | | 121 | | 1.3 | |
| Carfentrazone-ethyl | | > 8.6 | 8.6 | | 0.15 | |
| Chlorpyrifos-methyl | 27 | | 21 | | 13 | |
| Cymoxanil | | 148 | 1.4 | | 0.02 | |
| Diazinon | 0.5[a] | | 185[a] | | 6[a] | |
| Dichlofluanid | > 15 | | > 0.75 | | < 0.01 | |
| Dicofol | | 85 | 3.5 | | 0.02 | |
| Ethoxysulfuron | | 65 | 259 | | 331 | |
| Fluazinam | | Stable | 42 | | 6 | |
| Lufenuron | | 160 | 70 | | 32 | |
| Metalaxyl | > 200[b] | | | | 115 | 12 |
| Metamitron | 410 | | 31 | | 10 | |
| Nicosulfuron | | 15 | Stable | | Stable | |
| Oxamyl | | > 31 | 8 | | 0.1 | |
| Rimsulfuron | | 4.6 | 7.2 | | 0.3 | |
| Simazine | 8.8[c] | 96 | | | | 3.7[c] |
| Tolylfluanid | 12 | | 1.2 | | 0.01 | |
| Triflusulfuron-methyl | | 3.7 | 32 | | 36 | |

[a] pH = 3.1, 7.4 and 10.4 resp.
[b] pH = 1, 9 and 10 resp.
[c] pH = 1, 5 and 13 resp.

In an attempt to demonstrate the use of the equations provided by the US EPA (1998) given in Annex B or, alternatively, the use of the more generic equations given in Annex D, the pH dependency of two substances was analysed using these equations. One substance was chosen which is prone to acid as well as base catalysed hydrolysis (diazinon), and another substance prone to base catalysed hydrolysis but not acid catalysed hydrolysis (tolylfluanid).

The analysis was carried out by estimating values for acid catalysed hydrolysis, base catalysed hydrolysis and neutral hydrolysis ($k_a$, $k_b$ and $k_n$ resp.) from the DT50 values given for three values of pH. These values were then used to generate values for DT50 over the entire range of pH 1 - 14. The analysis was carried out using a value of 1 for the parameter $\gamma$ used in the generic equations, assuming that errors in $k_a$, $k_n$ and $k_b$ were of similar magnitude.

**Diazinon**

The DT50 values given by Tomlin (2003) for diazinon (taken from Table 2.2.1) were determined at widely spaced values of pH (3.1, 7.4 and 10.4 resp.) and should thus provide a good basis for estimation of the 3 hydrolysis rate constants. The results of using EPA and generic equations are given in Table 2.2.2 and a graph of hydrolysis DT50 as a function of pH estimated from these rate constants is given in Figure 2.2.1.

***Table 2.2.2***

*Values for acid catalysed, base catalysed and neutral hydrolysis rates for diazinon estimated from EPA and generic equations.*

| | $k_a$ ($h^{-1}$) | $k_b$ ($h^{-1}$) | $k_n$ ($h^{-1}$) |
|---|---|---|---|
| EPA, Annex B | 72.53 | 26.93 | $1.54 * 10^{-4}$ |
| Generic, Annex D | 75.53 | 26.95 | $1.49 * 10^{-4}$ |

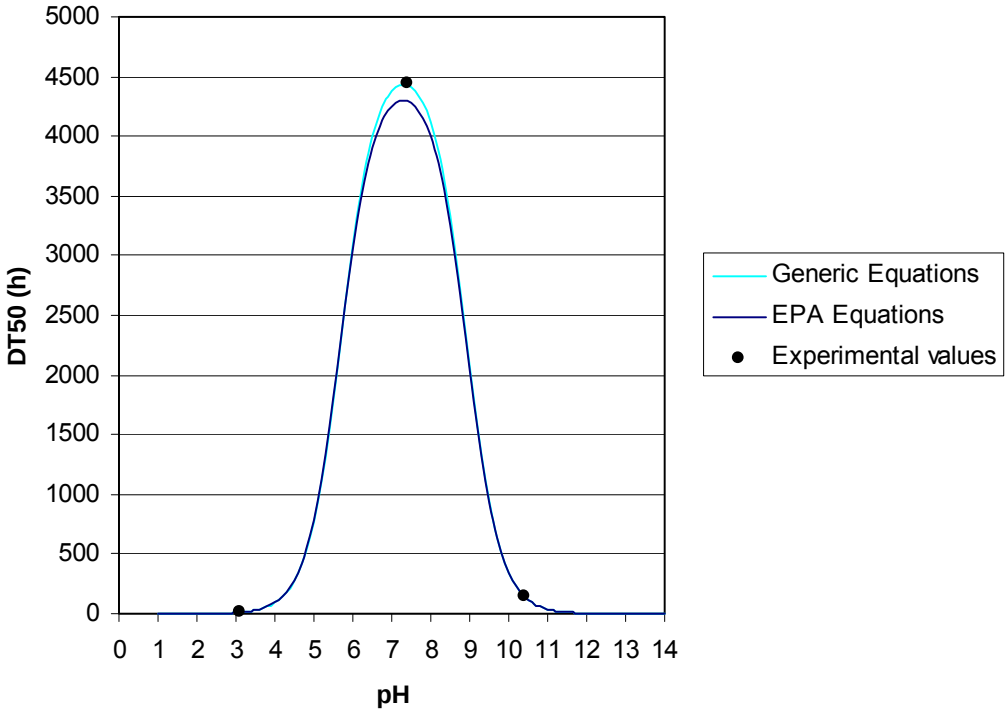


***Figure 2.2.1***

*Estimated hydrolysis half-life (DT50, hours) of diazinon using EPA and generic equations for estimation of ka, kb and kn.*

From Table 2.2.2 it is obvious that there are very slight differences in the calculated values for the rate constants calculated with either the EPA or the generic equations, which are most likely due to the approximations used in the derivation of the EPA equations.

Calculation of the DT50 at pH = 7.4 (which would ideally result in the value originally used as input at pH = 7.4 for the estimation of the constants) with the EPA based constants results in a DT50 of 4286 h (178.6 days), whereas using the constants derived with the generic equations results in a DT50 of 4440 h (185 days), which is exactly equal to the experimental value for DT50. The generic equations clearly provide a slightly better

solution in this situation, since they are the exact solution of the general equations whereas the EPA equations use some slight approximations. The influence of these approximations will become more apparent when using input data that were measured at less widely spaced values of pH.

### Tolylfluanid

The DT50 values given by Tomlin (2003) for tolylfluanid (taken from Table 2.2.1) were determined at less widely spaced values of pH (4, 7 and 9 resp.) and indicate that its hydrolysis is base catalysed but not acid catalysed. Remarkably, the hydrolysis rate decreases substantially when decreasing the pH from 7 to 4, which is not in line with the general equations linking hydrolysis rate to pH, but may in part be due to experimental errors.

The results of using EPA and generic equations are given in Table 2.2.3 and a graph of hydrolysis DT50 as a function of pH estimated from these rate constants is given in Figure 2.2.2.

***Table 2.2.3***

*Values for acid catalysed, base catalysed and neutral hydrolysis rates for tolylfluanid estimated from EPA and generic equations.*

| | $k_a$ ($h^{-1}$) | $k_b$ ($h^{-1}$) | $k_n$ ($h^{-1}$) |
|---|---|---|---|
| EPA, Annex B | 72.2 | 415672 | -0.00481 |
| Generic, Annex D | 0 | 357178 | 0.00241 |

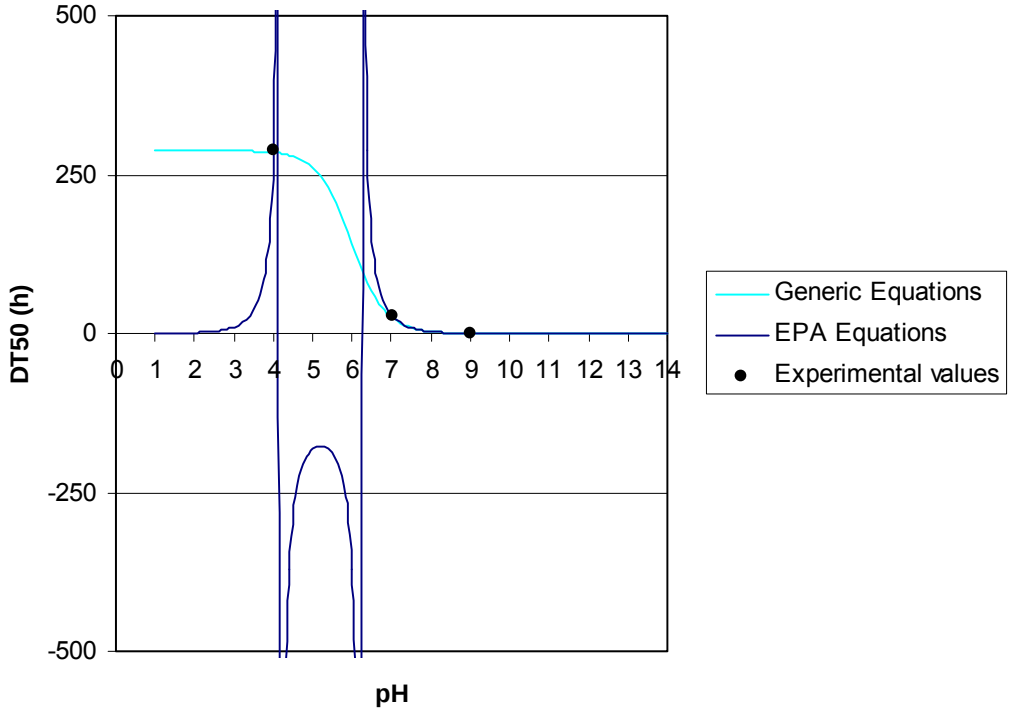


***Figure 2.2.2***

*Estimated hydrolysis half-life (DT50, hours) of tolylfluanid using EPA and generic equations for estimation of $k_a$, $k_b$ and $k_n$.*

Estimates provided by EPA and generic equations differ widely. Most disconcertingly, however, the EPA estimation method provides a less than zero value for the neutral rate constant, which clearly is not a plausible solution since rate constants less than zero do not have a physical meaning. Moreover, a non-zero value for the acid-catalysed rate constant is calculated, which results in invalid estimates of the overall rate over a large pH range (Figure 2.2.2) when using the EPA derived estimated rate constants.

Calculation of the DT50 at pH = 4 (which would ideally result in the value originally used as input at pH = 4 for the estimation of the constants) with the EPA based constants results in a DT50 of 284.1 h (11.8 days), whereas using the constants derived with the generic equations results in a DT50 of 285.1 h (11.9 days), both which are close to the experimental value for DT50 at pH = 4.

Similarly, calculation of the DT50 at pH = 9 (which would ideally result in the value originally used as input at pH = 9 for the estimation of the constants) with the EPA based constants results in a DT50 of 0.2424 h (0.0101 days), whereas using the constants derived with the generic equations results in a DT50 of 0.28 h (0.0117 days).

The EPA equations give a slightly better fit of the experimental value at pH = 4. However, from Figure 2.2.2 it is obvious that the rate constants derived using the EPA equations result in very low estimates of DT50 at pH < 4 and are unable to give a reliable estimate of DT50 when pH ranges from 4 to 7. In the input data used for the estimation, the DT50 substantially increases when pH is lowered from 7 to 4, which is not expected from Eq. (2.1) describing base catalysed hydrolysis. The use of input data with such unexpected behavior results in a negative estimate of $k_n$ when using the EPA equations to estimate $k_n$, $k_a$ and $k_b$. The EPA equations solve Eq. (2.1), but are not able to cope with experimental data that do not closely adhere to this equation.

The generic equations, given in Annex D, cater for experimental error and deviations from theory, which is further illustrated in Annex D. Therefore they provide a more reliable method for the estimation of rate constants when dealing with either acid or base catalysed hydrolysis.

In situations where both acid and base catalysed hydrolysis occur, the EPA and generic equations provide nearly equal estimates of the rate constants, although the EPA equations assume slight approximations which are only applicable when experimental rate constants determined at widely spaced values of pH are used. Therefore, the use of the generic equations in Annex D is preferred in all situations.

## 2.3 Influence of temperature on hydrolysis

When using the Arrhenius equation (Eq. 2.2) the influence of temperature on the reaction rate of hydrolysis should be considered for acid catalysed, base catalysed and neutral hydrolysis separately.

$$k = A * e^{-\frac{E_a}{RT}} \tag{2.2}$$

where A is denoted as the frequency factor (which accounts for the frequency of collisions between molecules and for the occurrence of an orientation favoring the reaction at the moment of collision), $E_a$ is the activation energy (kJ mole$^{-1}$), R is the gas constant (8.31 J K$^{-1}$ mole$^{-1}$), T is temperature (K). A more thorough discussion of the frequency factor and how it relates to transition state theory can be found in Atkins (1978), Moelwyn-Hughes (1966) or Schwarzenbach et al. (2003).

Numerical values for activation energies of $k_a$, $k_b$ and $k_n$ can be retrieved by establishing values for these hydrolysis rate constants at several different temperatures. However, this information will often not be available for the individual rate constants and an estimated average value for $E_a$ or $\Delta H$ of 50 - 100 kJ mole$^{-1}$ is often used to describe the influence of temperature on the overall hydrolysis rate constant $k_h$ at any given pH. Using an average value of 75 kJ mole$^{-1}$ for $E_a$, changes of temperature in water of 1 °C and 10 °C will result in changes in the rate constant of factors 0.10 and 2.5 resp. (Harris, 1990).

## 2.4 Hydrolysis in some surface water models

For the surface water models EXAMS (Burns et al., 1982; Burns, 1997), PestSurf (Styczen et al., 2004, 2004b) and PCPF-1 (Watanabe and Takagi, 2000) a short summary was made to which extent hydrolysis is included in the model and what data the user can or should provide to perform a calculation in which hydrolysis is accounted for.

In EXAMS hydrolysis is described as the sum of acid catalysed, neutral and base catalysed hydrolysis. Moreover, EXAMS enables the user to distinguish between several forms of a substance. Where appropriate, parameter values can be given for the neutral substance, three cationic forms and three anionic forms. Each of these separate parameter values can be given for aqueous (dissolved), sediment associated and suspended solids associated forms of the substance. Thus, EXAMS gives the user the possibility to enter 21 values for rate constants for hydrolysis (and 21 Arrhenius activation energies for each of these rate constants) for the 21 separate forms of a single substance. EXAMS uses monthly average temperatures, which can be specified by the user. Similarly, the pH of each compartment can be specified by the user, but is assumed constant during the calculations. The temperature and pH specified for each of the compartments are used to correct, amongst others, hydrolysis rate constants for temperature using an Arrhenius type equation. However, no diurnal variation of temperature or pH is assumed, nor can it be specified by the user. The rationale behind the use of environmental descriptors in preference to dynamic environmental state variables, as given by Burns (1997), is that using highly detailed time-series for environmental variables would introduce costs and labour requirements not in line with the intended use of EXAMS as an efficient screening tool for a large number of newly invented chemicals.

Similar to EXAMS, PestSurf describes hydrolysis as the sum of acid catalysed, neutral and base catalysed hydrolysis for which the user can enter three separate rate constants. Although water temperature series are part of the user provided input, no mention is made whether or how rate constants are adjusted for variations in temperature in the technical documentation (Styczen et al., 2004). The pH of the water body appears to be non-adjustable and is set at 7.5 (Styczen et al., 2004), although a value of 7.6 is mentioned as well (Styczen et al., 2004b), and is taken as constant during a model run. Diurnal variation of pH is not taken into account.

PCPF-1 does not distinguish between hydrolysis and biotic transformation reactions and the user has to provide a lumped rate constant for the sum of these processes. The user cannot specify pH or temperature of the aqueous phase, but has to account for pH or temperature by providing an appropriately corrected input value for the rate constant. Directions on how to derive a value for the rate constant are given in a separate paper (Takagi et al., 1998) in a Japanese magazine which is not readily available. The model does not allow for diurnal variations of temperature or pH.

## 2.5 Modelling hydrolysis in TOXSWA

In the previous paragraphs it has been established that the dependence of hydrolysis on pH can be modelled through the use of a set of relatively simple equations based on the contributions of acid catalysed, neutral and base catalysed hydrolysis (Eq. 2.1). Parameter values needed to perform calculations can be derived in a straightforward manner from data which is usually provided during registration of the pesticide (hydrolysis rates at three different values of pH) through the procedure outlined in Section 2.1 and Annex D.

The influence of temperature on hydrolysis can be accounted for by using an Arrhenius type equation (Eq. 2.2). If detailed information about the influence of temperature on hydrolysis rates is available an estimate of the activation energy can be derived from these data, otherwise an approximated value of 75 kJ $mole^{-1}$ can be used in the calculations.

# 3 Photolysis

## 3.1 Photolysis in water

A distinction between two types of photochemical conversion is usually made:
- direct photolysis, in which the reacting molecule absorbs light and the excited molecule reacts;
- indirect (or 'sensitised') photolysis, where light is absorbed by a molecule which then transfers its energy to the acceptor molecule, causing the latter to react.

According to Van den Berg et al. (1995) penetration of light will usually only occur in oxic systems, and hence most products formed will be in an oxidised state compared to the parent substance.

Photolysis is a very complex process, whose rate is very much dependent upon the wavelength of the light reaching a molecule in the water column in relation to the absorption spectrum of that molecule. Changes in the (wavelength) composition of light over a day, as well as changes over the course of seasons, have a direct bearing on the rate of photolysis. The rate of photolysis is to a negligible extent influenced by temperature.

The absorption of light by dissolved and suspended matter in a water body may give rise to indirect photolysis. Zepp (1992) has given a brief overview of transient reactants that may form when dissolved organic matter interacts with sunlight, giving rise to various reactions with xenobiotics. For many substances the rate of indirect, or sensitised, photolysis is much larger than the rate of direct photolysis. Miller and Hebert (1987) provide some data originally published by Zepp et al. (1978) which show that the photodecomposition of methoxychlor in several natural (river) waters is up to 40 times faster than its decomposition in distilled water. The type of transient reactant affecting the decomposition rate may be different between types of substances, and may also be different between locations because of differences between the dissolved organic material present at various locations. It seems unlikely therefore that a simple 'rule of thumb' can be used to account for differences in the rate of photolysis of pesticides caused by the presence of organic matter. For this reason indirect photolysis is not considered for incorporation into TOXSWA at this point.

As a first approximation direct photolysis can be described as a second-order process, in which both light intensity and the concentration of the substance determine the rate at which photolysis will occur:

$$\frac{dC}{dt} = k_p IC \tag{3.1}$$

where $k_p$ is the second-order photochemical reaction rate constant, I is the light intensity in water (E $L^{-1}$ $s^{-1}$), which is proportional to the light intensity at the surface of the water, and C is the concentration of the substance undergoing photolysis (mole $L^{-1}$).

For direct photolysis to occur, a molecule must first absorb a photon, upon which the molecule will transit from an electronic ground state to an excited state. The photon will only be absorbed if the energy of the photon corresponds to the energy difference between the ground state and one of the possible excited states of the molecule. For the wavelengths of concern (290 - 800 nm, lower wavelengths are cut off by the earth's atmosphere) the photon energies range from 150 kJ $mole^{-1}$ at 800 nm to slightly more than 400 kJ $mole^{-1}$ at 290 nm (OECD, 2007). Absorption of a photon is a necessary, but often not sufficient, prerequisite for

a molecule to undergo photolysis. Often the fraction of excited molecules actually undergoing photo-transformation (the quantum yield) is much less than 1 (usually < 0.1 and sometimes < 0.01) (Harris, 1982; Mill, 1999; OECD, 2007).

For an optically dilute solution (absorbance < 0.02 for λ ≥ 290 nm) of a chemical in pure water, the direct photolysis rate constant $k_d$ is given by equation 3.2 (OECD, 2007):

$$k_d = 2.3 \frac{L\varphi}{jD_{sys}} \sum_{\lambda} \varepsilon(\lambda) I_0(\lambda) \qquad (3.2)$$

where $k_d$ is the direct photolysis rate constant ($day^{-1}$), φ is the quantum yield (which is approximated to be independent of wavelength), ε(λ) is the molar absorption coefficient ($mole^{-1}$ $cm^{-1}$) at wavelength λ (nm), $I_0(\lambda)$ is the spectral photon irradiance on number basis ($cm^{-2}$ $day^{-1}$ $nm^{-1}$), L is the light pathlength (cm), $D_{sys}$ is the depth of the irradiated system (cm) which corresponds to the volume/incident area of the system, and j is a conversion factor (j = $6.02 \cdot 10^{20}$ L $cm^{-3}$ $mole^{-1}$). The summation of ε(λ)* $I_0(\lambda)$ should be performed over the entire range of relevant wavelengths, i.e. from 290 to 800 nm.

In near surface, clear natural water exposed to solar radiation the following equation is often used (OECD, 2007):

$$k_{d,solar} = \varphi \sum_{\lambda} \varepsilon(\lambda) L(\lambda) \qquad (3.3)$$

where $k_{d,solar}$ is the direct photolysis rate constant ($day^{-1}$), φ is the quantum yield (which is approximated to be independent of wavelength), ε(λ) is the molar absorption coefficient at wavelength λ ($mole^{-1}$ $cm^{-1}$) and L(λ) is the average daily solar spectral photon irradiation on amount basis (mmole $cm^{-2}$ $day^{-1}$ $\Delta nm^{-1}$) over wavelength interval Δλ (nm).

Assuming a quantum yield of 1, this enables the calculation of a maximum possible photolysis rate constant on the basis of the absorption spectrum of the substance and a suitable table of irradiation values. Since quantum yield is often < 0.1 (OECD, 2007), the actual photolysis rate constant will usually be smaller than the maximum possible value.

It has been pointed out that photolysis reactions are pseudo-first order if the photon irradiance remains constant over time, which is usually valid when using filtered xenon arc lamps in laboratory experiments. Although solar irradiance in the field varies cyclically over 24 h periods, the data obtained from studies conducted in natural sunlight seem in general to fit single pseudo-first order rate models reasonably well. It is assumed that for studies conducted for one to several weeks or for only a few hours mid-day, changes in the average pseudo-first order rate constant over time are relatively small and not systematic. It may, however, not be valid for studies lasting four hours to several days or studies lasting more than 30 days (OECD, 2007).

The fraction of excited molecules which undergo photolysis (i.e., the quantum yield) is in aqueous solutions often approximately independent of wavelength. This is due to the fact that, in aqueous solutions, molecules in higher excited electronic states usually undergo radiationless transition to their first excited state before any photoreaction occurs (OECD, 2000). Therefore, if photoreactions occur, they generally occur while the molecule is in its first (not higher) excited state, which renders the wavelength of the light primarily used to excite the molecule irrelevant. For this reason, the assumption used in the above equations, i.e. quantum yield φ is independent of wavelength, is generally a fair approximation (OECD, 2007). For situations where

experimentally determined quantum yields are available and found to be dependent on wavelength, a more general set of equations is provided by the OECD (2000). Some general information on the estimation of quantum yields is given by Harris (1982) and Mill (1999). Experimental procedures for establishing quantum yields are described by Zepp (1978) and an OECD guideline for such determinations is in preparation (OECD, 2007).

## 3.2 GCSOLAR: Photolysis modelled by Zepp and Cline

Zepp and Cline (1977) have described a general set of equations which make it possible to calculate direct photolysis rates for organic chemicals in water bodies of moderate depth (up to 0.5 meters). Basic processes are described using the equations given previously (Eq. (3.2), (3.3)). However, by including data on solar irradiation strength as a function of latitude, the four seasons and time of day and accounting for attenuation of light upon entry into a water body, they provide a means of quickly and easily calculating direct photolysis rates of substances under more or less realistic conditions occurring in the field. The equations and data were incorporated into a freely available (MS-DOS) computer program (GCSOLAR) which allows calculation of seasonal or diurnal changes in the photolysis rate of a substance. The user has to provide some basic data on the substance (ultraviolet/visible light absorption spectrum) and an estimate of the quantum yield of the photolysis reaction. When no experimental data on quantum yields is available, the authors suggest to use a value between 0 and 1 for photolysis in aquatic systems (Zepp and Cline, 1977).

The executable, source code and a user manual for the program GCSOLAR are available for download at www.epa.gov/ceampubl/swater/gcsolar/index.html

## 3.3 ABIWAS: Photolysis modelled by Frank and Klöpffer

Frank and Klöpffer (1989) have developed a model (and accompanying computer program) describing abiotic degradation of chemicals in natural waters. One of the processes considered in the program is direct photolysis. The derivation of rates of direct photolysis is very similar to Zepp and Cline (1977), but one of the principal differences was the use of a table of solar irradiation which was more suitable to Central European conditions (Frank and Klöpffer, 1989). The values for radiation have been published separately (Frank and Klöpffer, 1988). The computer program was later developed further; abiotic processes other than photolysis were removed from the calculations and the program in its present form only considers photolysis. Specific details about the program were not found in the literature, it is therefore not known whether e.g. the software accounts for diurnal changes in irradiation. The program can be obtained for a small fee from the Fraunhofer-Institut für Molekularbiologie und Angewandte Ökologie (IME), 57392 Schmallenberg in Germany (www.ime.fraunhofer.de).

## 3.4 Experimentally determined photolysis rate constants

The computer programs GCSOLAR and ABIWAS assume knowledge about the absorption spectrum of the substance under investigation. From either of these programs estimates of photolysis rates in water can be obtained. Since they incorporate knowledge about the seasonal differences in wavelengths of sunlight with user provided data about the absorption spectrum of the substance, using these estimation methods is preferred over the simpler method of using a 'generic' value for the photolysis rate constant derived in a laboratory photolysis study. Quantum efficiencies have to be determined experimentally or estimated by the user. As a first approximation a quantum yield of 1 can be used. This will in most cases result in over-estimation of photolysis rates, but can provide some idea about the maximum rate of disappearance that

can be achieved through photolysis. The use of a quantum yield in the range of 0.01 to 0.1 will often result in more realistic estimates of photolysis rates (OECD, 2007).

However, there may be situations where detailed knowledge of the photochemical behavior of the substance is not available and the absorption spectrum of the substance is unknown. If results from one or more photolysis studies from the field or laboratory are available the user is faced with the difficulty of using such a 'generic' value from a photolysis study for his simulation. If the irradiation strength and the wavelength composition of the light used during the experimental determination are known, photolysis rates for the conditions assumed to prevail during the simulation can be estimated using equations provided by the OECD (2007).

$$k_{d,solar} = \frac{j}{2.3}\frac{D_{cell}}{l}\frac{k_{d,xenon}\sum_{\lambda=290}^{\lambda=800}\varepsilon_\lambda L_\lambda}{\sum_{\lambda=290}^{\lambda=800}\varepsilon_\lambda I_{0\lambda}} \qquad (3.4)$$

where $k_{d,solar}$ is the average daily direct photolysis rate constant ($day^{-1}$) for the chemical in the near surface of clear natural water exposed to average daily solar spectral irradiance $L_\lambda$, $k_{d,xenon}$ is the direct photolysis rate constant ($day^{-1}$) for the test chemical in buffered pure water exposed to constant filtered xenon arc lamp irradiances $I_{0\lambda}$, $\varepsilon_\lambda$ denotes the molar absorption coefficient ($mole^{-1}$ $cm^{-1}$) at wavelength λ, $D_{cell}$ is the depth of the irradiation cell (cm), l denotes the pathlength (cm) in the cell exposed to filtered xenon light, $I_{0\lambda}$(xenon) denotes the photon irradiance on number basis ($cm^{-2}$ $day^{-1}$ $nm^{-1}$) of the filtered xenon arc lamp over a 1 nm interval (centered at wavelength λ), $L_\lambda$ is the 24 h average daily solar photon irradiance on amount basis (mmol $cm^{-2}$ $day^{-1}$ $\Delta nm^{-1}$ over wavelength interval Δλ and j is a conversion factor ($j = 6.02 \cdot 10^{20}$ L $cm^{-3}$ $mole^{-1}$).

Eq. (3.4) converts the photolysis rate constant observed when using a filtered xenon lamp into an equivalent rate constant which would be observed when irradiating the substance with average sun light, by taking into account the differences between the intensity of the irradiation at various wavelengths from 290 - 800 nm. The irradiation strength and wavelength composition applicable to the simulation conditions, i.e. average solar irradiation, can be taken from tables provided by the US EPA (1996) for 20, 30, 40 or 50° Northern Latitude (which are the values used in the GCSOLAR program) or from the tables published by Frank and Klöpffer (1989) (which are the values used in ABIWAS).

If the conditions used during the experimental determination are not known the user can do very little but assume that the reaction rate for photolysis established during the experiment will also apply to the conditions assumed during the simulation.

## 3.5 Comparison of GCSOLAR derived and experimentally determined photolysis reaction rates

The outcome of estimations with GCSOLAR is compared to experimentally determined photolysis rates for two compounds, 2,4-D and pyrimethanil. According to Tomlin (2003) the DT50 for photolysis of 2,4-D under simulated sunlight is 7.5 days, whereas no photolysis DT50 is given for pyrimethanil. The ultraviolet/visible light (UV/VIS) spectra of 2,4-D and pyrimethanil were taken from Feigenbrugel et al. (2006) and are shown in Figures 3.5.1 and 3.5.2 resp., and are also given in tabular form in Annex E. The values of molar absorption coefficients used in the calculations with GCSOLAR are also given in Annex E; for some wavelengths interpolated absorption coefficients or values of nearby wavelengths were used.

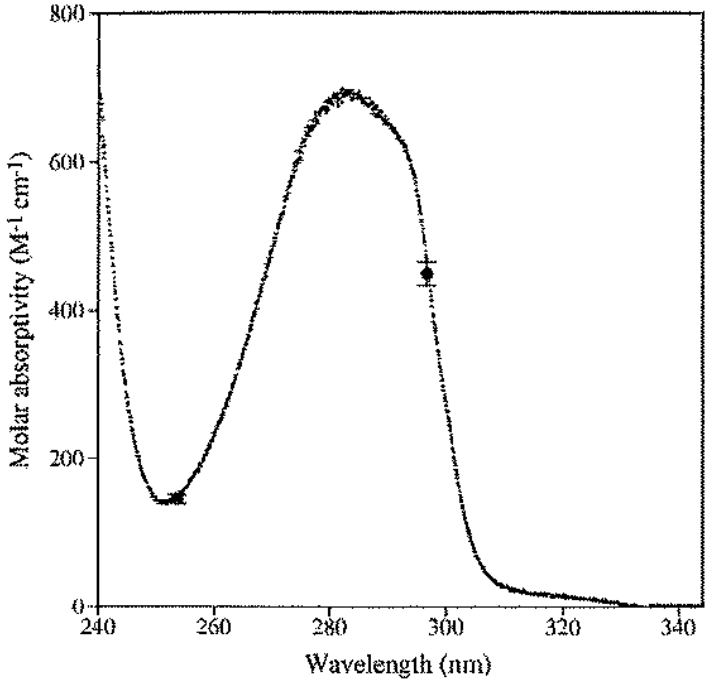


***Figure 3.5.1***

*Molar absorption coefficient ($M^1$ $cm^{-1}$) of 2,4-D measured between 240 and 344 nm at 298 ± 2 K; detailed tabular data are given in Annex E (reprinted with permission from Feigenbrugel et al., 2006).*

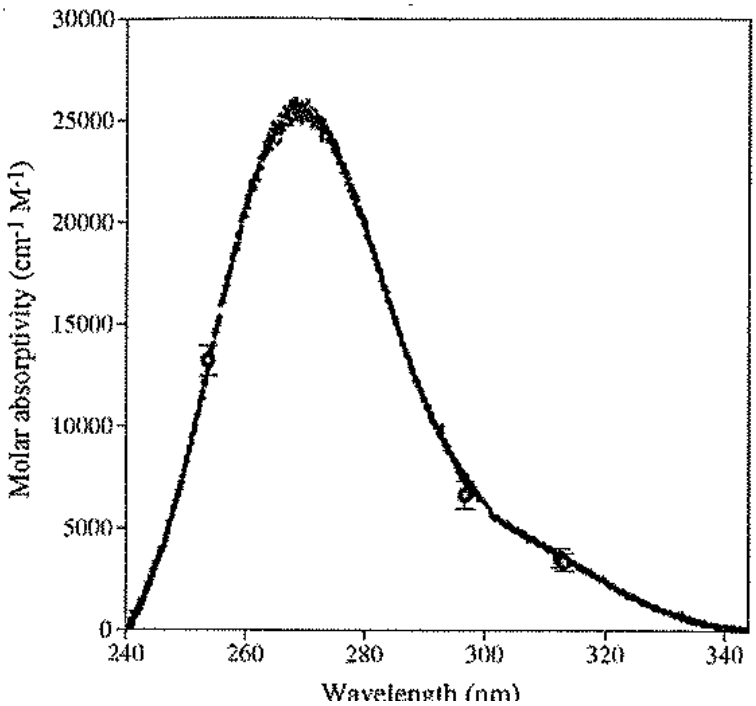


***Figure 3.5.2***

*Molar absorption coefficient ($M^1$ $cm^{-1}$) of pyrimethanil measured between 240 and 344 nm at 298 ± 2 K; detailed tabular data are given in Annex E (reprinted with permission from Feigenbrugel et al., 2006).*

For both substances the molar absorption coefficients at 295 - 330 nm were entered; wavelengths below 290 nm are not present in sunlight at the earth surface and the substances hardly absorb any radiations with wavelengths above 330 nm. Pyrimethanil shows much higher absorbance in this wavelength range, and its potential rate of photolysis is therefore much higher than for 2,4-D. Quantum yield was set at 0.032, i.e. the geometric mean of 0.001 and 0.01. Time of day calculations were performed using default ephemerical and ozone parameter values. Calculations were performed for spring and summer, for longitude of 4 degrees and for latitudes of 40, 50 and 60 degrees. Half lives (DT50) calculated by GCSOLAR are given in Tables 3.5.1 - 3.5.2 as the value at noon, average daylight values and average full day values for 40, 50 and 60 degrees latitude (Amsterdam is located at latitude of 52 degrees, longitude of 4 degrees). DT50 calculated for noon and average daylight conditions may be most useful for substances with very high photolysis rates, where 90% disappearance of the substance takes only a few hours. For more slowly degrading substances where 90% disappearance takes days or even longer, average full day values may be more representative.

***Table 3.5.1***

*Direct photolysis half-lives of 2,4-D in spring and summer at 40, 50 and 60 degrees latitude calculated by GCSOLAR.*

| Season | Latitude | Half-life DT50 (days) | | |
|---|---|---|---|---|
| | | Noon | Average daylight | Average full day |
| Spring | 40 | 3.2 | 6.6 | 11.9 |
| | 50 | 4.4 | 9.2 | 16.1 |
| | 60 | 6.5 | 14.0 | 23.0 |
| Summer | 40 | 2.5 | 5.2 | 8.6 |
| | 50 | 3.1 | 6.5 | 10.1 |
| | 60 | 4.0 | 9.0 | 12.3 |

Tomlin (2003) gives a DT50 under simulated sunlight for 2,4-D of 7.5 days. This is slightly shorter than the DT50 value calculated for summer at 50° latitude (10.1 days). These results are very sensitive to a correct choice of a value for the quantum yield, which was set at a value of 0.032, the geometric mean of 0.01 and 0.1. Changing the quantum yield from 0.032 to a higher value of e.g. 0.32 results in a corresponding change of the average full day DT50 of 2,4-D in summer at 50° latitude from 10.1 to 1.0 days, because of the linear relationship between rate constant and quantum yield.

***Table 3.5.2***

*Direct photolysis half-lives of pyrimethanil in spring and summer at 40, 50 and 60 degrees latitude calculated by GCSOLAR.*

| Season | Latitude | Half-life DT50 (days) | | |
|---|---|---|---|---|
| | | Noon | Average daylight | Average full day |
| Spring | 40 | 0.02 | 0.04 | 0.07 |
| | 50 | 0.03 | 0.05 | 0.09 |
| | 60 | 0.04 | 0.08 | 0.12 |
| Summer | 40 | 0.02 | 0.03 | 0.05 |
| | 50 | 0.02 | 0.04 | 0.06 |
| | 60 | 0.02 | 0.05 | 0.07 |

Tomlin (2003) does not specify a photolysis DT50 for pyrimethanil, which suggests that photolysis is very slow or absent. The EFSA concludes that direct photolysis does not contribute to the environmental degradation of pyrimethanil in water (www.efsa.europa.eu/cs/BlobServer/PRAPER_Conclusion/praper_concl_sr61_summary_pyrimethanil_en1.pdf?ssbinary=true). However, the FAO 2007 panel on pesticide residues in food (FAO, 2007) concluded that, even though pyrimethanil is stable to hydrolysis in water at pH 5, 7 and 9, it undergoes photolytic degradation in sterile buffer at pH 4 and 7 with estimated half lives of 1 and 80 days resp. Underlying detailed experimental data are given by the FAO at www.fao.org/ag/AGP/AGPP/Pesticid/JMPR/Download/2007_eva/Pyrimethanil.pdf
The discrepancy between both reports is probably due to the fact that EFSA considers the increased photolytic degradation at pH 4 to be caused by the presence of citric acid during the testing of pyrimethanil at pH 4; it is suggested that the citric acid may have acted as a photolytic sensitiser. There is no obligation for the applicant of the registration of a plant protection product to provide data on the photolysis at pH 4. Therefore the cause of the increased photolytic degradation at pH 4 was not further investigated.

The high UV absorbance of pyrimethanil provides information about the potential photolysis rates in aqueous phases, even if quantification is not possible because the quantum yield for photolysis is unknown (Feigenbrugel et al., 2006). However, the photolysis rates calculated for pyrimethanil, as given in Table 3.5.2, demonstrate that the lack of an experimentally determined quantum yield may result in a large difference between potential and actual photolysis rates.

These two examples demonstrate that in some situations the use of a method such as GCSOLAR may result in values relatively close, i.e. within a factor 2, to experimental data even when using default parameter values. On the other hand, there may also be substances for which very large discrepancies between estimated and actual photolysis rates will occur when sufficiently detailed data are not available.

## 3.6 Photolysis in some surface water models

For the surface water models EXAMS (Burns et al., 1982; Burns, 1997), PestSurf (Styczen et al., 2004, 2004b) and PCPF-1 (Watanabe and Takagi, 2000) a short summary was made to which extent photolysis is included in the model and what data the user can or should provide to perform a calculation in which hydrolysis is accounted for.

EXAMS offers several procedures for estimating photolysis rate constants. The user has to choose which of these procedures should be used, since they are mutually exclusive. Photolysis rates are either provided by the user or are calculated in the model from the absorption spectrum of the substance.

The first and simplest procedure is based on using an average reaction rate for photolysis, input by the user, which is derived e.g. from laboratory studies of photolysis of the substance. The user guide (Burns, 1997) suggests to use this simpler procedure only when the absorption spectrum of the substance in pure water is not available. If the ecosystem to be modelled is at a location different from the outdoor study where the photolysis rate constant was determined experimentally, a correction for displacement of the ecosystem is possible by providing separate latitude values for the ecosystem to be modelled and the location of the photochemical study. This procedure cannot be used to correct reaction rates that were obtained in laboratory photolysis studies using e.g. filtered xenon lights, since such studies usually employ much higher light intensities (up to 1000 fold higher) than commonly seen in studies conducted in sunlight.

If the absorption spectrum in the ultraviolet (> 280 nm) and visible part of the spectrum are available, a more complex procedure to calculate photolysis rate constants is preferred in EXAMS. This procedure is based on an assessment of the absorption spectrum of the substance, where the user has to provide molar extinction

coefficients for the substance and its ions at several different wavelengths and measured or estimated values of quantum yields. The calculations are based on the principles described by Zepp and Cline (1977). The user has to provide quantum yields, for which no estimation procedures are provided. Experimental procedures for establishing quantum yields are described by Zepp (1978). Spectral irradiation values used for the calculation of photolysis rates are average summer and winter mid-noon values as given by Zepp and Cline (1977) which were corrected for day length and a sinusoid averaging of the photoperiod (Burns et al., 1982). It is possible for the user to provide his own irradiation values. No diurnal or seasonal variation of irradiation is taken into account, apart from using different values for summer and winter.

EXAMS allows for the presence of competing light absorbers (chlorophylls, suspended sediments, dissolved organic carbon) by decreasing the light that is available for induction of photolysis reactions. The EXAMS user manual (Burns et al., 1982) provides spectral absorption coefficients of water, chlorophylls and pheophytins, (humic) dissolved organic matter and suspended sediments which are fully taken into account when the absorption coefficient of the substance under study is known. If only limited information on the absorption spectrum of the studied substance is available, i.e. when the user does not use the absorption spectrum but provides a reaction rate constant for photolysis, a slightly modified procedure is used. The user may provide either the range of wavelengths of greatest overlap of the absorption spectrum of the chemical with the solar spectrum or, if this information is not available, a single wavelength of maximum absorbance of the substance. If the maximum in the absorption spectrum is also not known, a wavelength of 300 nm is assumed by EXAMS. Based on the range or single wavelength thus established, the absorbance of light by competing species is calculated over this range or single wavelength, resulting in an appropriately corrected light intensity used for the calculation of photolysis rates.

In PestSurf the photolysis rate of organic substances is calculated on the basis of the absorption spectrum of the substance, which has to be provided by the user alongside estimates of quantum yields as input data. Values for light attenuation in water and loss of light at the water surface due to scattering are set at non-adjustable values suitable for the two different water bodies simulated in the program (Styczen et al., 2004). Contrary to EXAMS, the procedure does not allow for the presence of competing light absorbers (chlorophylls, suspended sediments, DOC). Radiation data used in the calculations are not provided by the user, but consist of radiation data measured at a location (Hornum) considered to be representative for Denmark (Styczen et al., 2004). The composition of total radiation was derived from data given by OECD (1995). Separate average values for the four seasons are used in the calculations, hence diurnal variation is not accounted for but seasonal variations are included.
PCPF-1 describes the rate of photolysis as the product of a user supplied rate constant and the average daily intensity of UV-B radiation in the 280 - 320 nm range. All other wavelengths are ignored, on the assumption that UV-B radiation will have the largest impact on photolysis. In a later version the description of photo-chemical degradation was modified to include the effect of higher wavelengths (Watanabe et al., 2006). Attenuation of light in the water body and loss of light due to scattering at the water surface are neglected, being only a small percentage of the total irradiation (Watanabe and Takagi, 2000). No clear indication is given on how to derive a value for the user-supplied photolysis rate constant, other than 'The value of the parameter $k_{PHOTO}$ is determined by laboratory measurements of pesticide dissipation under UV-B radiation' (Watanabe et al., 2006). Since the model was later adapted to include the contribution of higher wavelengths, it may be assumed that reaction rates determined under field or 'standard' laboratory conditions can be used to estimate photolysis rate constants. In PCPF-1 average solar irradiation can be specified by the user on a daily basis. Since a daily average value is used, diurnal variation is not accounted for but seasonal variations can be included in the calculations.

## 3.7 Modelling direct photolysis in TOXSWA

**Experimental rate constants**

Using photolysis rates derived from experimental systems, be it in the laboratory using filtered xenon lamps or in the field using solar radiation, is an efficient way of accounting for degradation of substances through photolysis. However, the main drawback of this approach is the difficulty to account for changes in the conditions under which photolysis occurs, e.g. changes in the wavelength composition of solar irradiance or the presence of competing light absorbers. Converting an experimental rate constant obtained under specific conditions into a rate constant applicable to conditions assumed during the simulation may be far from straightforward. Ultimately, if the conditions used during the experimental determination are not known the user will have to assume that the experimental rate will also apply to the conditions assumed during the simulation. This assumption will often result in incorrect estimates of the photolysis rate.

**Absorption spectrum**

Knowledge of the absorption spectrum from 290 - 800 nm enables the user to calculate the potential photolysis of the substance. However, for the calculation of actual photolysis rates information about the quantum yield is needed. In the most recent OECD draft guideline (OECD, 2007) the determination of quantum yields is optional. From an experimental point of view determining quantum yields is by no means a trivial undertaking, and therefore it seems likely that information on quantum yields will often not be available. Although knowledge of the substances absorption spectrum, combined with assumptions on spectral irradiance enables estimation of potential photolysis rates, insufficient knowledge of quantum yields may still result in rather poor approximations of the true rate constants. When no information on quantum yield is available, simulations could be performed for assumed values of the quantum yield. Since often quantum yields are in the range of 0.01 - 0.1, performing simulations with values for quantum yield of 0 (no photolysis), 1 (maximum direct photolysis) and 0.032 (the geometric mean of 0.01 and 0.1) may give sufficient information on the possible contribution of photolysis on the fate of the substance in the water system.

The spectrum based estimation method is based on a theoretical model of the processes resulting in photolysis and should therefore enable the user to adapt the method to the conditions of his choice more easily. However, when incorporating such adaptations care should be taken that they are applicable to the conditions assumed for the simulation, i.e. parameter values used during simulation of U.S. conditions may not be applicable to simulations of European conditions. As far as light conditions are concerned, it might seem preferable to enable the user to choose between the tables used in ABIWAS for Central European conditions, or the tables used in GCSOLAR as provided by the US EPA (1996) which enable the user to choose between 20 - 60° Northern Latitude. However, the effect of choosing an incorrect value of the quantum yield may outweigh the choice of a different irradiation table or latitude.

**Direct photolysis in TOXSWA**

Enabling the user to input a single (average) value for the photolysis rate constant to be used during the simulation is probably the most effective way of incorporating photolysis into TOXSWA. The rate constant employed is considered a temperature-independent first-order rate constant, implying that the loss of substance due to photolysis is described by a first-order differential equation:

$$\frac{dC_{subs\,tance}}{dt} = -k_{photo} C_{subs\,tance} \tag{3.5}$$

The derivation of this rate constant should preferably occur outside of the main simulation, which enables the user to adapt the rate constant to conditions assumed during the simulation. Based on available information the user may choose either to use an experimentally determined rate constant, which can be adapted if detailed information about experimental conditions is available, or to use an absorption spectrum with either experimentally determined quantum yields. If experimental values for quantum yield are not available, assumed values of 0, 1 and 0.032 (the geometric mean of 0.01 and 0.1) will provide information about the potential impact of photolysis on the fate of the substance under study.

# 4 Biotic transformations

## 4.1 Introduction

Many transformation reactions, although thermodynamically feasible, will proceed only slowly due to kinetic limitations. However, living organisms contain catalytic proteins (enzymes) which are used in the synthesis (anabolism) and degradation (catabolism) of substances like amino acids, sugars, fatty acids and many more. Such enzymes usually do not have perfect substrate specificity and will have the ability to bind and induce reactions in structurally similar substances. Moreover, most organisms seem to have an array of relatively non-specific enzymes for attacking unexpected or unwanted substances. Therefore, the presence of organisms, be it fungi, microorganisms, plants or vertebrates, may therefore result in a considerable increase in the rate of transformation or organic substances in sediment or water. Due to their ubiquitous presence, microorganisms will usually be more important than plants and animals in natural systems (Schwarzenbach et al., 2003).

The fact that organisms are genetically able to produce a given enzyme does not necessarily imply that the enzyme will always be present, i.e. the enzyme does not need to be constitutive. In response to a stimulus the production of appropriate enzymes can be turned on, or 'induced', sometimes resulting in a lag period between first exposure to the stimulus and the moment that enzymatic activity becomes apparent. Unfortunately, lag periods may be due to various other phenomena as well:

- enzymes already present are repressed (made ineffective) and some time must pass or some condition must change before they are altered into an active state;
- time may be required for organisms to multiply to significant numbers (growth);
- mutation to enable development of enzymes performing new or more efficient transformations;
- plasmid/DNA transfers may be required to develop new enzymatic tools;
- particular species or organisms must migrate to the location of interest, or cysts or spores must germinate.

The timescales of these phenomena may be very different and may depend on local environmental conditions; induction and derepression will usually occur within minutes, but population growth may take days. The complexity of various phenomena occurring simultaneously may make it difficult to predict the rate of transformation in a given environmental setting (Schwarzenbach et al., 2003).

The overall rate of biotransformation is usually limited by either of three processes:

- uptake of the substance by the microorganisms,
- growth of the amount/number of microorganisms, or
- the rate of the enzymatic conversion of the substance within the microorganism.

**Uptake**

For the most part, non-polar organic chemicals will move across the cell membrane by passive diffusion. Experimental determinations using non-polar organic substances have shown that passive transfer across membranes occurs on a timescale of hours or less, (Schwarzenbach et al., 2003). The biotic transformations of substances lasting days or more in the environment are therefore unlikely to be limited by their ability to enter microorganisms. Noteworthy exceptions are ionizable and/or highly charged organic substances like ethylene diamine tetraacetic acid (EDTA) which are thought to be persistent due to very slow uptake (Schwarzenbach, 2003).

In relation to biotic transformation reactions the current version of TOXSWA (Beltman et al., 2006) does not distinguish between the biotic transformation of sorbed and dissolved fractions of the substance. Assuming that neither bioavailability, which is considered through separate process descriptions, nor uptake by the microorganisms limit the rate of transformation, it can be expected that kinetics will either reflect the rate of growth of the microorganisms or the rate of enzyme processing within the microorganisms.

**Microbial growth**

Monod (1942) has developed a mathematical description for microbial growth, where the growth rate is related to the concentration of a substance (or substances) sustaining the microbes growth. Increasing the concentration of this substance will result in more growth, up to some point where the maximum growth rate is reached and some other factor(s) become limiting for the specific growth rate μ ($h^{-1}$):

$$\mu = \frac{\mu_{\max} * [i]}{K_{iM} + [i]} \tag{4.1}$$

where [i] denotes the concentration (mole $L^{-1}$) of the growth limiting chemical, $K_{iM}$ (mole $L^{-1}$) denotes the Monod constant, i.e. the concentration at which growth rate is half of the maximum growth rate ($\mu_{max}$). This equation can be extended to situations where more than one substance is growth limiting, but only the case for a single limiting substance of interest is described here.

In response to a new food source cell numbers of microorganisms will increase exponentially:

$$\frac{d[B]}{dt} = \mu * [B] \tag{4.2}$$

where [B] is cell abundance (cells $L^{-1}$), t denotes time ($h^{-1}$).

Degrading a certain amount of chemical will result in a proportional enhancement of microbial biomass:

$$\frac{d[B]/dt}{d[i]/dt} = Y \tag{4.3}$$

where Y is a proportionality factor (cells $mole^{-1}$), referred to as the yield of the biological process under consideration.

Relating the production rate of new cells to the disappearance rate of the chemical (substituting eq. 4.2 into 4.3):

$$\frac{d[i]}{dt} = -\frac{\mu * [B]}{Y} \tag{4.4}$$

or, when substituting eq. 4.1 into 4.4:

$$\frac{d[i]}{dt} = -\frac{\mu_{\max}}{(K_{iM} + i) * Y} * [B] * [i] \tag{4.5}$$

.

At low concentrations (where $i << K_{iM}$) this simplifies to

$$\frac{d[i]}{dt} = -k_{bio} * [B] * [i] \tag{4.6}$$

where $k_{bio}$ is the rate constant for biodegradation, equal to $\frac{\mu_{\max}}{K_{iM} * Y}$.

From Eq. (4.4) it is obvious that when the chemical is present in large amounts relative to microbial needs ([i] >> $K_{iM}$, and hence $\mu = \mu_{max}$ and therefore independent of the concentration of the chemical) the rate of removal becomes independent of the concentration of the chemical and is first-order in cell abundance [B]. At low chemical concentrations the rate of removal is first-order both in cell abundance and in the concentration of the chemical, Eq. (4.6).

Schwarzenbach et al. (2003) gives some examples for xenobiotics added to an environment containing some cells capable of living solely on the xenobiotic, from which a range for $k_{bio}$ is deduced of $10^{-16}$ - $10^{-13}$ mole cell$^{-1}$ h$^{-1}$).

In order to estimate the biotic breakdown rate of a substance on the basis of this range for $k_{bio}$, one needs to know the abundance of the subpopulation of microorganisms which is able to degrade the substance. Although for cultured systems in the laboratory this information may be available, it is not usually available for natural systems. Moreover, microbial growth as the limiting factor for biodegradation will usually apply to situations where high concentrations of the substrate are present, and may thus be less relevant for microbial transformation of pesticides at environmental concentrations.

**Enzyme limited reactions**

The use of a substance for sustaining growth of the microbial community implies that the substance should be present at relatively high concentrations and that the substance is degraded sufficiently easily by the organisms. If a substance is either present at low concentrations or is quite persistent, it will probably not be able to support growth of biomass and therefore Monod kinetics will not apply. Under such circumstances the transformation reactions will be limited by the speed at which the substance is transformed by enzymes within the organisms.

Michaelis and Menten (1913) have devised a scheme for enzyme-mediated reactions involving a simple sequence of stepwise reactions: binding of the substrate to the enzyme, transformation of the bound substrate to bound product, and release of the product from the enzyme. The mathematical description is usually referred to as Michaelis-Menten kinetics:

$$\frac{d[i]}{dt} = -\frac{k_E * [Enz]_{tot} * [i]}{K_{iMM} + [i]} \tag{4.7}$$

where $k_E$ is the rate constant for the enzyme catalysed transformation step (mole substance l mole$^{-1}$ enzyme h$^{-1}$), $[Enz]_{tot}$ denotes the total (free + substrate complexed) enzyme concentration (mole enzyme L$^{-1}$), [i] is the free substrate concentration (mole compd l L$^{-1}$) and $K_{iMM}$ is the half-saturation (Michaelis-Menten) constant, equal to the concentration of substance l when enzymatic rate is half of the maximum rate (mole compd l L$^{-1}$).

The rate of disappearance of the substance - d[i]/dt is usually referred to as the velocity of the reaction, denoted *v*. Equation 4.7 is usually given in its most common form:

$$v = \frac{V_{\max} * [i]}{K_{iMM} + [i]} \tag{4.8}$$

The maximum velocity is governed by both the intrinisic rate constant for the catalysed transformation reaction, $k_E$, and the concentration of catalyst $[Enz]_{tot}$.

At sufficiently high concentrations of the substance the rate of disappearance is constant and independent of substance concentration and dependent on cell abundance (which is accounted for in $V_{max}$). At lower concentrations the rate of disappearance is first-order in the concentration of the substance and first-order in cell abundance.

From a mathematical point of view the description of Michaelis-Menten and Monod kinetics are therefore very similar as far as dependence on the concentration of the substance and cell abundance are concerned. However, Monod type kinetics are only expected in situations where high concentrations of the substrate are present.

It may be tempting to use experimental values of $K_{iMM}$ and $V_{max}$ to other situations with different conditions, e.g. applying them to predict biotic transformations in water or sediment obtained at another location. $V_{max}$ can be normalised to cell counts or protein content, but due to differences in the composition of microbial populations the use of data obtained under different conditions may not necessarily result in good estimates of biotic transformation rates. As already pointed out when discussing Monod type kinetics, information on the abundance of the subpopulation of microorganisms able to degrade the substance is not usually available for natural systems.

## 4.2 Influence of temperature on biotic transformations

For most chemical reactions an increase of temperature results in an increase of its reaction rate. Generally, this also holds true for enzyme catalysed reactions and hence for most biotransformation reactions. Complications arise from the fact that many enzymes become inactive when heated above physiological temperatures due to changes in the three dimensional structure of the protein involved, a process usually

referred to as denaturation. For many enzymes this sets in at 40 - 50 °C and results in a sharp decrease of activity with increasing temperature. For this reason, analysis of rates as a function of temperature is for most enzymes limited to temperatures between 0 °C and 50 °C.

Leskovac (2004) treats some general cases of the influence of temperature on the rates of enzyme-catalysed monosubstrate reactions using transition state theory. Only in special cases will such reactions adhere exactly to an Arrhenius-type relationship (see Eq. (2.2) in Section 2.3), where a plot of ln (k/T) versus 1/T yields a straight line. However, for many situations with temperature changes of only a few degrees Celsius an Arrhenius type relationship will be sufficiently accurate to estimate reaction rates (Larson, 1980).

Only very little experimental information on the influence of temperature on enzyme-catalysed reactions involving the transformation of pesticides was found in the literature.

Worthingthon (1972) states that variations of 1 - 2 °C may introduce changes of 10 - 20% in reaction rates, which corresponds to an energy of activation of 65 - 68 kJ $mole^{-1}$, and that a 10 °C rise in temperature will increase the activity of most enzymes by 50 - 100%, corresponding to an energy of activation of 30 - 52 kJ $mole^{-1}$. Similarly, Guilbault (1976) remarks that a temperature increase of 10 °C will approximately double the reaction rate in many cases.

Larson (1980) demonstrates the effect of temperature on the biodegradation of nitrilotriacetate (NTA, a chelating agent) and linear alkylbenzene sulfonate (LAS, surface active detergents) in environmental water samples. This resulted in estimates of activation energies of 60.6 and 38.0 kJ $mole^{-1}$ for NTA and LAS resp., which according to Larson 'are in the range observed for many enzyme-catalysed reactions'. For the average activation energy of 50 kJ $mole^{-1}$ from this study, a temperature increase of 1 °C from 20 to 21 °C corresponds to an increase of the reaction rate constant with 7.2%, whereas a temperature increase of 10 °C from 20 to 30 °C corresponds to an increase of 97%.

Tros (1996) has determined the effect of temperature on the biotransformation rates of 3-chlorobenzoate and acetate by *Pseudomonas* sp. strain B13 during growth and in a recycling fermentor. The energies of activation were 61 and 56 kJ $mole^{-1}$ for 3-chlorobenzoate and acetate resp., over a temperature range from 20 °C to 30 °C.

For simulations in PestSurf, Styczen et al. (2004b) have analysed biodegradation data of eight pesticides. Although for most of these substances biodegradation rates could be estimated, only for two of these substances (ioxynil and fenpropimorph) the influence of temperature could be estimated. For ioxynil the reaction rate constant increased with 9.6% for a temperature increase of 1 °C, whereas for fenpropimorph the increase was 10.4% for each degree of temperature increase. This corresponds to activation energies of 66 and 71 kJ $mole^{-1}$ for ioxynil and fenpropimorph resp.

In a recent opinion on the effect of temperature on transformation rates of pesticides in soil, EFSA (2007) concluded that in soils the use of the Arrhenius equation is appropriate for temperatures between 0 and 30 °C, using a median value for the activation energy of 65.4 kJ $mole^{-1}$. They warn, however, that there are (chemical) group and substance specific differences in activation energies. The use of substance specific values for activation energy instead of the default is recommended only when at least four soils were tested at a minimum of three temperatures and all studies were in accordance with the requirements given in detail in the opinion (EFSA, 2007).

Although there seems to be agreement that an increase of temperature will usually result in an increase in reaction rate, Larson (1980) has pointed out that microorganisms may be able to adapt to a particular temperature when it is maintained over a longer period. A decrease of biodegradation upon a decrease in

temperature, as predicted from the use of the Arrhenius equation, may be balanced by increases in efficiency due to changes in the microbial population. With regard to long-term changes in temperature, Burns et al. (1982) make a similar remark, that 'because microbial communities frequently adapt their metabolic capacity to keep pace with slow (e.g. seasonal) changes in environmental temperatures, temperature responses measured in a laboratory setting do not always apply to environmental conditions'.

From the few studies cited, rate increases resulting from small (1 - 2 °C) temperature increases near 20 °C (6 values) corresponded to energies of activation in the range of 38 - 71 kJ $mole^{-1}$, corresponding to an increase of the biotransformation rate of 5 - 10% per degree Centigrade. The median value for the activation energy in water from these six studies is 65 kJ/mole, which is very close to the value recommended by EFSA (65.4 kJ $mole^{-1}$) for use in the modelling of transformation rates in soils (EFSA, 2007). Allowing for temperature increases of up to 10 °C, resulting in eleven studies, yields a median activation energy of 61 kJ $mole^{-1}$. However, the data concerning degradation in water are very limited and a more accurate estimate of the average activation energy for biotic degradation should be based on a more elaborate examination of available literature, which is outside the scope of this report.

One should be aware, however, that transformation rates and their activation energies will be dependent on both the exact nature of the substance and on the composition of the microbial population present. Hence, even for a given substance large variations may exist between transformation rates under different conditions.

When no information specific to the substance and the microbial population in the surface water under consideration is available, attempting to correct the biodegradation rate for a change in temperature will possibly introduce relatively large uncertainties, especially when basing such a correction on the scarce information presented here. Therefore it seems prudent to account for temperature changes only when detailed information is available from studies for the substance and surface water under consideration. This applies to corrections for short term (diurnal) temperature changes but also to the effect of seasonal changes in temperature.

## 4.3 Influence of pH on biotic transformations

Most reactions catalysed by enzymes have an optimum range of pH, where the rate will be maximal. Changes in pH may have a profound effect on the structure of an enzyme, resulting in orders of magnitude changes in the rate of an enzyme catalysed reaction. Since living cells may be exposed to changes of pH by up to three units over a 24 h period in eutrophic systems with photosynthetic communities or sewage oxidation ponds, regulation of cytoplasmic pH is of the utmost importance for their survival (Padan et al., 1981; Padan and Schuldner, 1986).

Booth (1985) has enumerated some of the mechanisms responsible for the stability of internal pH. The membrane of most bacteria is relatively impermeable to protons, complemented by a low permeability for cations in general, which means that for high proton concentration differentials the net proton influx will often be limited by the capacity for cation extrusion. Moreover, Booth (1985) points out that due to its composition, the cytoplasm usually has a high buffering capacity, of 50 - 100 nmol of $H_3O^+$ per pH unit per mg of cell protein (cells at an internal pH near 7). Thus the effect of protons that manage to enter the interior of the cell will be mitigated to some extent.

However, the mechanisms driving pH homeostasis can be very complex, and are often influenced by the availability of specific organic substances in the external medium. E.g. Belguendouz et al. (1997) have described the effect on intracellular pH upon a decrease of extracellular pH from 7 to 4 in *Leuconostoc*

*mesenteroides* and *Lactococcus lactis*. It was observed that in *L. mesenteroides* the effect was mitigated by the presence of citric acid in the medium, whereas *L. lactis* did not benefit from the presence of citric acid. Thomassin et al. (2006) found that the acid tolerance of *Bacillus cereus* was dependent on culture pH, growth rate and intracellular pH. Stingl et al. (2002) have described the influence of urease activity on the pH homeostasis in *Helicobacter pylori*, a species that is able to survive for hours under extremely acidic conditions (pH = 1). The pH regulation appears to be dependent on a reaction involving urease and yielding ammonium as a sink for hydrogen.

From the multitude of studies into the pH homeostasis in microorganisms it appears that although most species are capable of mitigating the external variation of pH through internal buffering and extrusion of cations, the extent to which they succeed may be very different between species and also very dependent on environmental conditions. Generally it appears likely that a slight change in the pH of the surrounding environment (i.e. aqueous phase) will cause the intracellular pH to change somewhat as well. As long as this intracellular change is slight, e.g. within 1 pH unit, the effect on enzymatic activity will often be slight enough to be considered negligible. However, the effect of more profound changes in pH, e.g. a diurnal variation over three pH units, may have a significant effect on enzymatic activity which is difficult to predict without detailed (experimental) evidence concerning the microbial population present in the sample.

## 4.4 Biotic transformations in some surface water models

For the surface water models EXAMS (Burns et al., 1982; Burns, 1997), PestSurf (Styczen et al., 2004, 2004b) and PCPF-1 (Watanabe and Takagi, 2000) a short summary was made to which extent biodegradation is included in the model and what data the user can or should provide to perform a calculation in which biotic transformations are accounted for.

EXAMS describes biotic degradation both in the aqueous layer and in the sediment, and separate rate constants for both compartments are supplied by the user. In each of the compartments degradation is described using a second-order equation:

$$\frac{d[S]}{dt} = -k_{bio} * [B] * [S] \tag{4.9}$$

where [S] denotes the concentration of the substance (substrate) being degraded (moles $L^{-1}$), [B] denotes the density of microorganisms (cells $L^{-1}$) and $k_{bio}$ is the second-order rate constant for microbial degradation (L $cells^{-1}$ $h^{-1}$). The microbial density for sediment is entered in units of cells $kg^{-1}$ dry weight of sediment, but is internally converted to cells $L^{-1}$ of water through multiplying by the water content (L water $kg^{-1}$ dry weight sediment) of the sediment.

Biotransformation rate constants are entered as single values (at 20 °C) and temperature dependency is accounted for by specifying a $Q_{10}$ value (increase in biotransformation rate upon 10°C increase in temperature). Temperature independent rate constants are specified by supplying a $Q_{10}$ value of 0.

$$k_{bio,T} = k_{bio,20} * Q_{10}^{(T-20)/10} \tag{4.10}$$

The EXAMS technical documentation (Burns et al.,1982) explicitly states that 'because microbial communities frequently adapt their metabolic capacity to keep pace with slow (e.g. seasonal) changes in environmental temperatures, temperature responses measured in a laboratory setting do not always apply to environmental

conditions'. No guidance is given on how to derive biodegradation rate constants for simulation from experimental data or in situations where no experimental data are available.

PestSurf uses equations for degradation in pore water and in the water column equivalent to the equations used in EXAMS, but the user has to supply a rate constant which includes a factor accounting for density of the microorganisms, i.e. the rate equation is first-order in the substance only.

$$\frac{d[S]}{dt} = -k'_{bio} * [S] \tag{4.11}$$

The effect of temperature is accounted for by an 'Arrhenius type equation' similar to Eq. (4.10):

$$k'_{bio,T} = k'_{bio,To} * e^{A*(T-To)} \tag{4.12}$$

where T is given in degrees Centigrade. At temperatures below 5 °C, biodegradation is assumed to stop.

For ponds both an aerobic and an anaerobic degradation rate constant should be supplied, whereas for streams aerobic conditions are assumed at all times. Anaerobic degradation is considered only relevant for phytoplankton dominated ponds.

Styczen et al. (2004) give some guidance on the type of experimental degradation rates that are preferred for use in PestSurf: 'preferentially a total degradation rate for an experiment conducted as a shaking bottle experiment with suspended sediment (ISO 14952 Part 1) and the particle (suspended sediment) concentration at which the experiment was conducted should be entered. If the user prefers to use a degradation value obtained from a test without addition of suspended matter the particle concentration should be set to 0. The reference temperature for the input has to be 20 °C. If only data on ready biodegradability and/or inherently biodegradability exist then it is suggested to use the recommended data from the EU 'Technical Guidance Document' (TGD, 1996). If the substance is ready biodegradable, use a half-life of 15 days; if the substance is ready biodegradable but failing 10-day window, use a half-life of 50 days; if the substance is inherently biodegradable use a half-life of 150 days. Otherwise assume that the substance is persistent. The concentration of suspended matter should be set equal to 15 mg $L^{-1}$.

PCPF-1 also accounts for microbial degradation in sediment and in water, assuming rates are first-order in the concentration of the substance under consideration and dependent on microbial activity. Biotic and abiotic degradation (except photochemical degradation) is considered together as one process, assuming additivity of rates (Watanabe and Takagi, 2000). No mention is made of methods to account for the influence of temperature on rate constants.

In PCPF-1 the degradation in sediment can be chosen to follow biphasic first-order or single phase first-order kinetics. Biphasic kinetics are characterised by a fast phase being followed by a second, slower phase of degradation. Transfer from the first to the second phase occurs at a phase intercept concentration which is supplied by the user.

## 4.5 Experimental determinations of degradation rates

The computer model TOXSWA aims to estimate the concentrations of plant protection products to which aquatic organisms may be exposed. These exposure concentrations are influenced by transformation reactions occurring both in water and in sediment.

The degree to which biotic transformation reactions occur in water-sediment systems is often assessed on the basis of data obtained from laboratory tests, which are routinely provided during the registration procedure of plant protection products. Adriaanse et al. (2002) have discussed several test guidelines for water-sediment studies. They concluded that the OECD guideline (draft proposal guideline 308; finalised version published in 2002) was the most comprehensive guideline with respect to system characterisation and, moreover, that it was the only one enabling adequate evaluation of biotransformation rates and pathways (Adriaanse et al., 2002). The FOCUS Working Group on Surface Water Scenarios (FOCUS, 2001) describes the OECD 308 guideline as a consensus summary of the guidance provided by other guidelines and concludes that water/sediment studies performed according to OECD 308 should be considered appropriate for use in FOCUS Step 3 model scenario calculations (FOCUS, 2001).

According to OECD guidelines concerning the degradation of organic chemicals (OECD, 2006) an approach providing adequate knowledge would allow for preliminary screening of chemicals on the basis of relatively simple tests of ultimate biodegradability, identifying those chemicals for which more detailed studies are needed. According to this approach, the examination of biodegradability can be organised into a general testing strategy:

- The assessment of aerobic biodegradability in a test for ready biodegradability.
- When the substance scores a negative result in ready biodegradability, a simulation test may be used to assess biodegradation in the environment or in a biological sewage treatment plant (STP). This also applies when the substance scores a positive result but more detailed information, e.g. a precise DT50, is needed.
- When information about potential degradability under optimised aerobic conditions is needed or wanted, a screening test for inherent biodegradability may be performed.
- In addition, potential biodegradability under anoxic conditions can be examined in a screening test for anaerobic biodegradability.

**Ready biodegradability**

OECD provides several testing guidelines (TG) for the assessment of ready biodegradability (OECD TG 301A-F, TG 310 in fresh water and 1 guideline (TG 306) on the biodegradability in sea water (which consists of variants of 301 D and 301 E).

In these tests the test medium contains a relatively high concentration of the test substance compared to the concentration of biomass, and the test substance provides the sole source of organic carbon. The methods provide an indication of the extent of ultimate biodegradation (OECD, 2006).

Standardisation of the inoculum (i.e. the source of microorganisms) between the different tests may improve comparability between tests. This would reduce the number of species present and is therefore generally not aimed for, and a mixed inoculum is recommended to ensure the presence of a variety of degrading organisms. Pre-exposure of the inoculum to the test substance is not allowed in view of possible adaptation. An OECD inter-laboratory ring test was performed in 1988 to ensure the practicability and validity of the tests.

**Simulation tests**

These tests can be used for the assessment of biodegradation in a laboratory system representing either the aerobic treatment stage of an STP, or an environmental compartment such as surface water. Concerning surface water, technical guidelines were devised for aerobic and anaerobic transformation in aquatic sediment systems (TG 308) and for aerobic mineralisation in surface water (TG 309).

Generally a low concentration of the test substance is used (e.g. 1 - 100 µg/L in TG 309). In view of the temperature dependence of kinetics constants, it is recommended to perform the tests at a temperature characteristic of the simulated environment.

**Inherent biodegradability tests**

These tests have been designed to assess the potential of a substance for biodegradation under aerobic conditions, using favourable conditions. Three test guidelines are provided by the OECD (TG 302 A - 302 C), where the biodegradation capacity increases in the order C < B < A (OECD, 2006). Biodegradation > 20% is regarded as evidence of inherent, primary biodegradability, whereas biodegradation > 70% is regarded as evidence of inherent, ultimate biodegradability. The latter is indicative of potential for degradation under favourable conditions, whereas a negative result (< 20%) indicates the possibility of environmental persistence.

**Anaerobic biodegradation screening tests**

OECD TG 311 (draft) describes the assessment of the biodegradation of the test substance, which is the sole organic carbon source, under anoxic conditions. A typical test duration is 60 days, but the test may be prolonged or terminated earlier if > 60% biodegradation has been achieved before this period. The preliminary criterium for anaerobic biodegradation is 60% of the theoretical. The test is designed to assess the ultimate anaerobic degradation in heated digesters in anaerobic sludge treatment and is not necessarily applicable to anoxic environmental compartment (OECD, 2006).

**Use of data from water-sediment systems in TOXSWA**

Water-sediment studies are one type of simulation test and data on such studies are often provided in the procedures for pesticide registration. Laboratory-derived water-sediment tests thus constitute only a small part of the whole range of tests providing data on the biodegradation of organic chemicals. However, most other biodegradation tests from the preceding section employ concentrations of the test substance much higher than what would normally be expected for pesticides. Water-sediment tests, usually employing relatively low concentrations of pesticides, most closely mimic the conditions assumed in the TOXSWA model in this respect. Moreover, the presence of both sediment and water closely resembles the situation of shallow surface water like a pond or ditch.

However, a laboratory water-sediment system differs from microcosm or macrocosm systems in several respects, possibly resulting in differences between the transformation rates in the water and sediment compartments. Katagi (2006) has enumerated some of the differences between laboratory and larger-scale indoor and outdoor sediment-water systems:

– Different (and variable) pH of the water column, related to photolysis. The resulting changes in pH may affect the (abiotic) degradation of hydrolytically labile substances.
– Different composition of the surface micro-layer. Since natural water may contain organic matter differing both in amount and in composition from the organic matter present in laboratory systems, the micro-layer separating the aqueous from the gaseous phase may differ appreciably. For substances where the rate of

degradation in the micro-layer differs much from the rate in the bulk of the water compartment, this may have an effect on overall degradation rates.
- Stratification does not generally occur in laboratory water-sediment systems, but may occur in larger systems, which may affect degradation rates.
- Bioturbation in the sediment layer due to the presence of organisms may influence the degradation rate in the sediment compartment of larger systems.

Adriaanse et al. (2002) have pointed out that laboratory water-sediment tests result in dissipation rates for the water-sediment system as a whole, and do not usually distinguish between separate rate constants for water and sediment compartments. If these rate constants differ, the rate observed for the system as a whole will be influenced by the ratio of the water volume and the sediment surface area. This implies that the observed rate may not necessarily be representative of systems where this ratio is different, such as the surface water being simulated in TOXSWA. Although far from definitive in nature, examples of such discrepancies are given by e.g. Bromilow et al., who examined the distribution and degradation of eight chemicals in laboratory-scale water-sediment systems (Bromilow et al., 2003) and in larger outdoor mesocosms (Bromilow et al., 2006). Although for both types of system the distribution of the substances over sediment and water compartments was mostly governed by lipophilicity, slight differences were observed between laboratory and outdoor systems. In the outdoor systems permethrin and difenoconazole were found to be sorbed less to sediment and were much less persistent than in the laboratory-scale systems. Similarly, Rönnefahrt et al. (1997) concluded that the degradation of isoproturon as determined in a laboratory water-sediment test according to the BBA guideline IV, 5 - 1 (BBA, 1990) was significantly slower than observed in a larger (800 L) microcosm located in a greenhouse, even though degradation pathways were the same.

One should also consider that the overall degradation in water-sediment systems is partly the result of hydrolysis in the aqueous phase, a process which is usually accounted for by a separately determined hydrolysis rate constant. Adding an overall water-sediment degradation constant as a descriptor for an additional degradation route may inadvertently account for hydrolysis in the aqueous phase twice.

In view of these difficulties of using laboratory-derived whole-system degradation rates for prediction of degradation rates in systems with different dimensions, the FOCUS Working Group on Surface Water Scenarios (FOCUS, 2001) supported making a distinction between the DT50 values in the sediment, the DT50 value in the water phase and the DT50 value in the whole of the water/sediment system, providing some recommendations that should enable a reliable calculation of DT50 from water/sediment studies. Adriaanse et al. (2002) have proposed a method enabling the estimation of separate transformation rate constants in water and sediment from laboratory water-sediment tests. The applicability of the method is still subject of investigation, but Ter Horst et al. (2005) have concluded on the basis of some preliminary findings on eight hypothetical substances with varying organic matter sorption coefficients ($K_{om}$) and DT50's, that for many substances it may prove to be far from straightforward to obtain reliable estimates for separate rate constants for sediment and aqueous transformation reactions. This difficulty has been anticipated by the FOCUS work group on degradation kinetics (FOCUS, 2006) in the procedure given for the calculation of aqueous concentrations (Predicted Environmental Concentration, or PEC) using FOCUS surface water scenarios. For situations where degradation rates from water/sediment studies cannot be resolved into separate rates for sediment and water, they advise to perform two different calculations. In the first calculation the experimental overall rate constant is used as an estimate for the rate constant in water and a degradation half-life of 1,000 days is assumed for degradation in the sediment compartment. In the second calculation the experimental overall rate constant is used as an estimate for the rate constant in sediment and a degradation half-life of 1000 days is assumed for the water compartment. From the two different PEC's resulting from these calculations, the highest is chosen for risk assessment. This procedure does not address the fundamental flaw of water/sediment studies, i.e. the lack of information on separate degradation rates for

the two compartments. The goal is to derive a most reasonable (but conservative) estimate of the concentration in the water compartment on the basis of the limited information available.

## 4.6 Modelling biotic transformations in TOXSWA

Only limited information is found on general principles applicable to biotic transformation processes in surface water models. Quantitative modelling, taking into account factors such as temperature, pH and the amount of microorganisms present in surface water, appears to be far from straightforward. Therefore, as a first approximation, biotic degradation rates in TOXSWA should be based on water/sediment studies, using separate degradation rate constants for sediment and water compartments when possible. If these separate rate constants cannot be derived from the water/sediment studies at hand, overall transformation rates may be estimated according to the guidance given by FOCUS (2001). For situations where no results from water/sediment studies are available, Styczen et al. (2004) gives some guidance, which is shown in Section 4.4 of this report. However, due to the very general nature of their approach it cannot be expected that their guidance results in reliable estimates for biotic degradation rate constants. The current registration procedures for pesticides in the EU requires that data from at least two water/sediment studies are provided by the applicant, which implies that for pesticides basic data on degradation in water/sediment systems will usually be available. The guidance provided by the FOCUS working group on degradation kinetics (2006) may be the most appropriate way to account for biotic degradation where no separate rates can be established for the sediment and water compartments.

In view of the limited information available, one may choose to limit corrections for variations in pH and temperature to systems for which the actual relationship between biotic degradation rates and these parameters is available through experimental determination. However, other considerations, e.g. the regulatory aim to strive for conservative estimates of exposure concentrations, may indicate the need to apply corrections even though only limited information is available.

# 5 Temperature and pH

## 5.1 Introduction

The current versions of TOXSWA (v1.2 used in Dutch registration procedure and FOCUS-TOXSWA versions up to v 3.3.1) use average monthly temperatures for the adjustment of a transformation rate encompassing both abiotic and biotic transformation reactions. The effect of pH on transformation reactions is not taken into account and no value for pH is assumed by TOXSWA, nor does the user have to provide such a value.

Reaction rate constants are related to temperature in an exponential fashion, due to the nature of the Arrhenius equation. Similarly, pH dependent hydrolysis is governed by an exponential type of relationship between hydrolysis rate and pH. The use of average values for temperature and pH will not take into account the relatively high rates at elevated temperature and pH and may result in an underestimation of the rate of hydrolysis reactions. An example is given in Annex F, where the consequences of using a daily average values and neglecting the occurrence of daily maximum values are demonstrated. Preferably, therefore, the adjustment of transformation rates on the basis of temperature and pH should not only reflect changes in (e.g. monthly or seasonal) average values, but should also incorporate the consequences of deviations from these average values, e.g. daily maximum values.

When incorporating the influence of temperature and pH into TOXSWA, the calculations should preferably be based on realistic values for these parameters. Several surface water models employ different methods for incorporating temperature and pH, some of which are summarised in Section 5.2. Instead of using assumed 'theoretical' values, an alternative approach is to make use of values actually measured in ditches. Section 5.3 details some measurement series recorded in experimental ditches located at the experimental station 'Sinderhoeve' in Renkum, the Netherlands. The reader should be aware that the present study only serves as a first exploration into the general characteristics of pH and temperature data gathered over a relatively short (1 year) period. The data is quite limited and should therefore not be considered to be representative in any way for ditches in agricultural areas in general.

Section 5.4 describes the proposed method for the incorporation of temperature and pH in TOXSWA.

## 5.2 Temperature values used in some surface water models

For the surface water models EXAMS (Burns et al., 1982; Burns, 1997), SWAT (Neitsch et al., 2002), PestSurf (Styczen et al., 2004, 2004b) and PFAM (Young, personal communication) a short summary was made what temperature values are used in the model calculations.

In EXAMS the user has to provide monthly average water temperatures for each of the ecosystem segments. Temperatures are considered to be constant for the entire month, no diurnal of daily variation is considered.

SWAT uses average daily water temperatures which are calculated using an equation which was developed for a well-mixed stream by Stefan and Preud'homme (1993):

$$T_{water} = 5.0 + 0.75T_{av} \quad (5.1)$$

where $T_{water}$ is the water temperature for the day (°C) and $T_{av}$ is the average air temperature for that day (°C).

Due to thermal inertia of the water, the response of water temperature to a change in air temperature is dampened and delayed. Eq. (5.1) assumes that the lag time between air and water temperatures is less than one day (Neitsch et al., 2002). However, when water and air temperature are plotted for a stream or river, the peaks in the water temperature plots usually lag 3-7 hours behind the peaks in air temperature. As the depth of the river increases, this lag time can increase even further and for very large rivers the lag time can extend up to a week (Neitsch et al., 2002). Moreover, water temperature is also influenced by factors such as solar radiation, relative humidity, wind speed, water depth, groundwater inflow, artificial heat inputs, thermal conductivity of the sediments and the presence of impoundments along the stream network. SWAT assumes that the impact of these other variables on water temperature is not significant.

In a calibration study with MIKE-11, which is the water flow model used in PestSurf, temperatures measured in water during the day were used (Styczen et al., 2004b). In MIKE-11 (Graham and Butts, 2006; DHI, 2005) the user can specify more elaborate data in the temperature menu. The user can input the latitude at which the river is located and the maximum absorbed solar radiation, maximum displacement of solar radiation from noon and emitted heat radiation from the water surface can be specified by the user.

In PFAM the water temperature is estimated from the backward 30-day average of the daily air temperatures as specified in the meteorological data input provided by the user. PFAM simulates with a time step of one day and was developed for stagnant rice paddy fields. This may be representative of ditches with stagnant water, but is probably not applicable to small streams (Young, personal communication).

## 5.3 Values observed in experimental ditches

Details about the experimental ditches located at experimental station 'Sinderhoeve', including the equipment used for the measurement of water temperature, pH and oxygen content, are given by Drent and Kersting (1993). The experimental station comprises twenty stagnant ditches, twelve of which were during 1990 - 2000 used for pesticide research and eight were at that time used for research into the effects of nutrients on ditch based ecosystems. These artificial ditches (length 40 m, width 3.3 m at the water surface and 1.6 m at the sediment surface; water depth approx. 0.5 m in the central part of the ditches, sediment depth 0.25 m) have a volume of approximately 55 $m^3$ and contain both rooted and non-rooted aquatic macrophytes. Recording of data did not start until two years after the completion of the experimental facilities, ensuring equilibration of the ditches. Measurements were recorded as 15-minute averages and were collected over a seven year period (January 1990 until December 1996). Data from two ditches used for nutrient research was used.

One of the ditches had a bare sandy bottom and contained no aquatic macrophytes (ditch 18), whereas the other ditch had a silty clay sediment layer and contained a large amount of both rooted and non-rooted macrophytes (ditch 14; dominating macrophyte species: *Chara* sp. and *Elodea nutallii*). The total dry weight biomass of macrophytes is usually 0.02 kg $m^{-2}$ in spring, increasing to slightly over 0.1 kg $m^{-2}$ in autumn. For both ditches pH and temperature data, both measured at the middle of the water column, from January 1991 to December 1991 were used. Moreover, air temperature data were also collected at the experimental station, enabling a comparison between water and air temperatures at the site (Section 5.3.3).

### 5.3.1 Temperature

A typical course of daily average temperature over time is given in Figure 5.3.1 for ditch 14 (containing macrophytes). Average temperatures for each month are given in Table 5.3.1 for both ditches; the data are also shown graphically in Figure 5.3.1. Average temperatures in the ditches were quite similar, although the ditch containing macrophytes had slightly lower average temperatures during summer and also showed a slightly smaller (average) difference between minimum and maximum daily temperatures (referred to in Figure 5.3.5 as the daily temperature swing). This is most likely caused by the presence of macrophytes resulting in some shading of the water column.

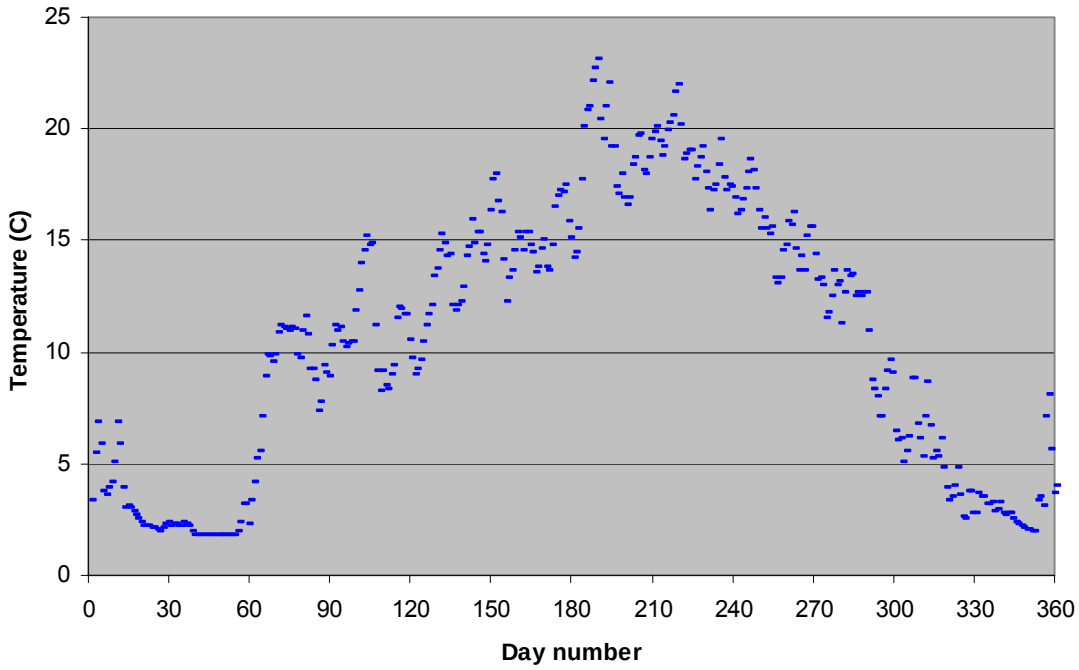


***Figure 5.3.1***
*Daily water temperatures for ditch 14 over the course of 1991.*

***Table 5.3.1***

*Average monthly temperature data for January - December 1991 for ditches with and without macrophytes.*

| Month | Average temperature (°C) | |
|---|---|---|
| | Ditch 14 (macrophytes) | Ditch 18 (no macrophytes) |
| Jan | 3.36 | 3.97 |
| Feb | 2.03 | 2.31 |
| Mar | 9.15 | 9.73 |
| Apr | 11.17 | 11.22 |
| May | 13.57 | 13.68 |
| Jun | 15.00 | 15.68 |
| Jul | 19.28 | 21.72 |
| Aug | 18.47 | 20.79 |
| Sep | 15.24 | 16.69 |
| Oct | 10.28 | 10.85 |
| Nov | 4.90 | 5.04 |
| Dec | 3.50 | 3.76 |

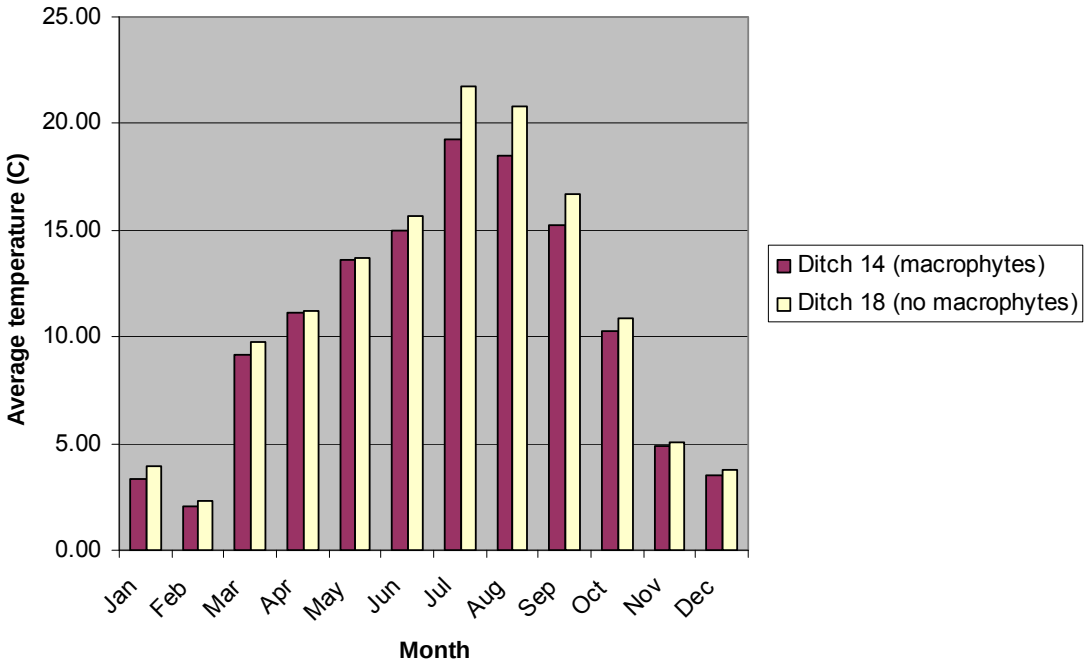


***Figure 5.3.2***

*Average monthly water temperatures for January - December 1991 for ditches with and without macrophytes.*

The level of detail in the temperature data was slightly increased by calculating average temperature data for 4 daily periods, 0 - 6h, 6 - 12h, 12 - 18h and 18 - 24h, i.e. dividing each day into four time periods. Average temperatures for each of these periods are given in Figure 5.3.3 for ditch 14, containing macrophytes, and in Figure 5.3.4 for ditch 18, not containing macrophytes. Although these graphs clearly show that average temperatures were usually highest during the afternoon and evening periods of 12 - 18h and 18 - 24h, especially in spring and summer, it is also obvious that this representation of the temperature data provides only limited extra information on the temperatures occurring in the ditches.

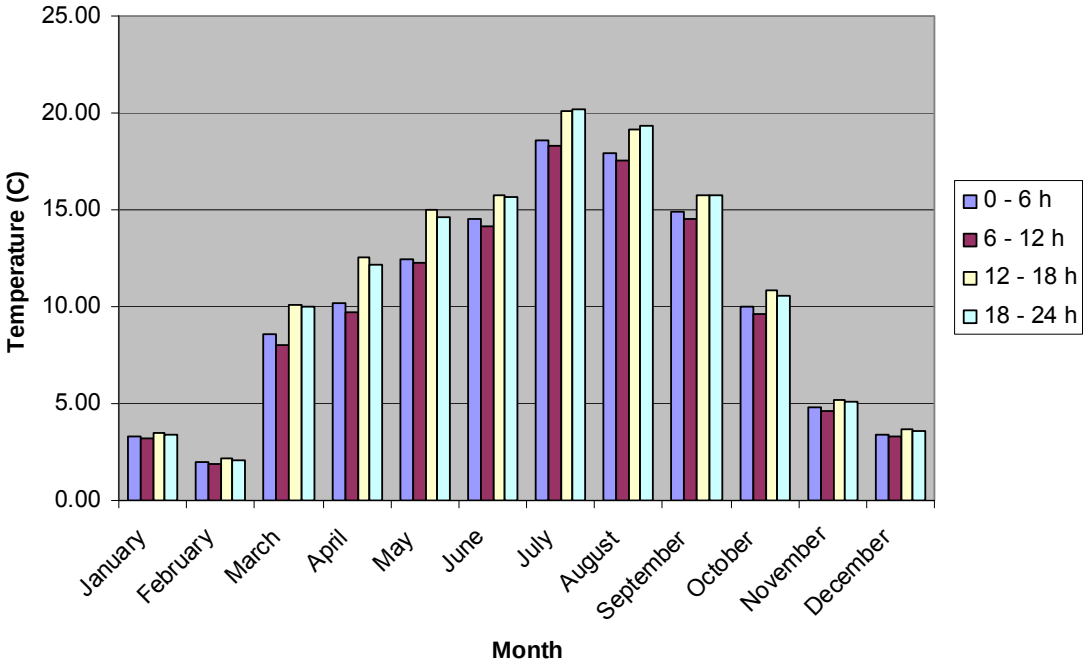


***Figure 5.3.3***

*Average monthly water temperatures for January - December 1991 for ditch 14 (containing macrophytes) separated into daily periods of 6 h.*

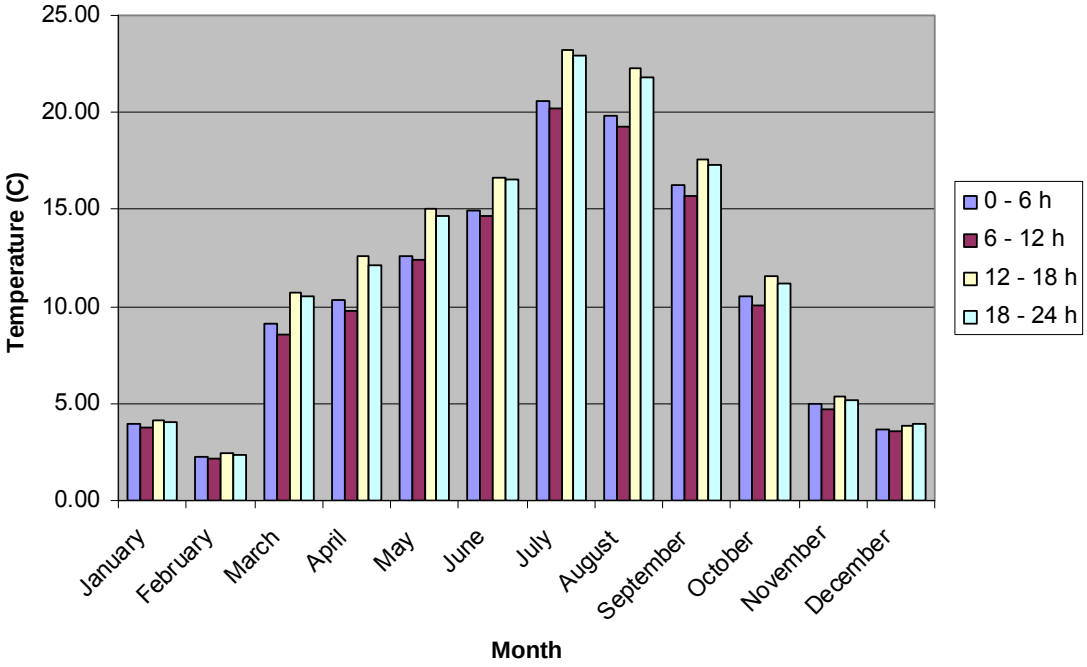


***Figure 5.3.4***

*Average monthly water temperatures for January - December 1991 for ditch 18 (not containing macrophytes) separated into daily periods of 6 h.*

More detailed information about the extreme values in temperatures occurring in the ditches can be retrieved by investigating the daily difference between minimum and maximum temperature values, i.e. the daily temperature swing or daily temperature increase. Table 5.3.2 gives some summarised information about the average, the 50-percentile (i.e. median) and the 90-percentile values of the daily temperature increase occurring in each month.

***Table 5.3.2***

*Daily temperature increase in ditches 14 and 18 for January - December 1991*

| Month | Daily temperature increase ditch 14 (macrophytes) (°C) | | | Daily temperature increase ditch 18 (no macrophytes) (°C) | | |
|---|---|---|---|---|---|---|
| | Average | 50-Percentile | 90-Percentile | Average | 50-Percentile | 90-Percentile |
| January | 0.96 | 0.69 | 1.90 | 1.06 | 0.77 | 1.95 |
| February | 0.40 | 0.06 | 0.95 | 0.49 | 0.22 | 1.17 |
| March | 3.02 | 2.93 | 4.60 | 3.00 | 2.93 | 4.56 |
| April | 4.41 | 4.54 | 5.84 | 4.29 | 4.37 | 5.98 |
| May | 4.18 | 4.05 | 6.21 | 3.99 | 3.56 | 6.38 |
| June | 2.75 | 2.12 | 4.46 | 3.58 | 3.20 | 5.43 |
| July | 3.14 | 3.17 | 4.54 | 5.19 | 5.49 | 7.72 |
| August | 2.68 | 2.74 | 3.46 | 4.37 | 4.46 | 6.03 |
| September | 2.19 | 2.02 | 3.39 | 3.01 | 2.69 | 5.27 |
| October | 2.00 | 1.95 | 2.68 | 2.30 | 2.08 | 3.30 |
| November | 1.31 | 1.19 | 2.09 | 1.40 | 1.16 | 2.28 |
| December | 0.91 | 0.53 | 2.84 | 1.06 | 0.66 | 3.04 |
| Average | 2.3 ± 1.3 | 2.2 ± 1.4 | 3.6 ± 1.6 | 2.8 ± 1.5 | 2.6 ± 1.7 | 4.4 ± 2.0 |

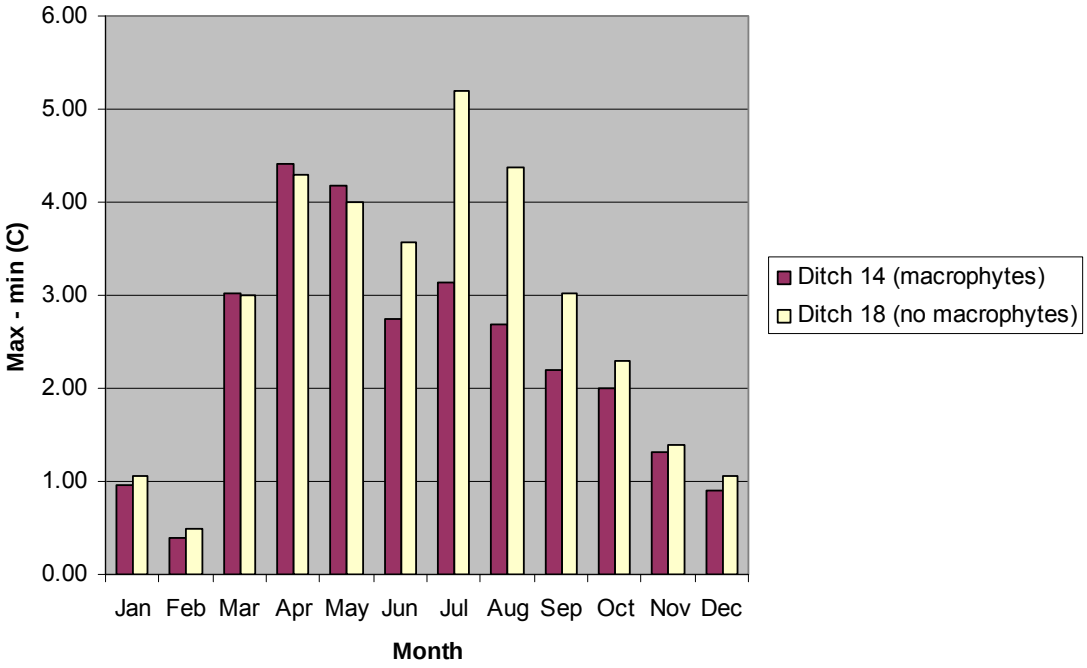


***Figure 5.3.5***

*Average difference between daily minimum and maximum water temperatures for January - December 1991 for ditches with and without macrophytes.*

Another way to obtain water temperatures is to use an estimation method to derive water temperatures from e.g. measured air temperatures, similar to the procedure in SWAT. Figure 5.3.6 shows the course of average daily air temperatures measured at the Sinderhoeve during 1991. Temperatures ranged from -8.8 °C to +25.2 °C.

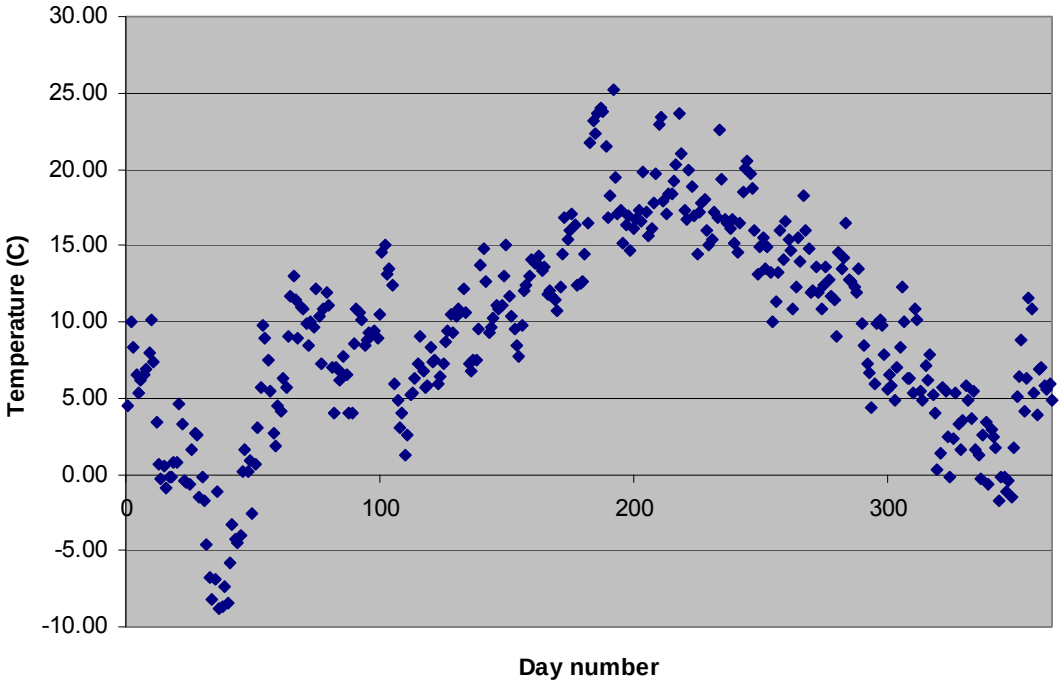


***Figure 5.3.6***

*Daily values of air temperatures measured over the course of 1991.*

The methods employed in SWAT and PFAM for estimating water temperature from measured daily average air temperatures, as given in Section 5.2, are investigated in Annex G. However, both estimation methods result in estimates of water temperature that are only poorly correlated to the actually measured water temperatures.

A simple linear relationship between measured air and water temperatures, similar to the equation used in SWAT, results in an error of estimate in the estimated water temperature of 2.2°C; this relationship is limited to water temperatures above 4 °C.

$$T_{water} = 1.85 + 1.01 T_{air} \qquad (5.2)$$

where $T_{air}$ is the average air temperature, and $T_{water}$ is the estimated daily water temperature.

Eq. (5.2) can be used to estimate water temperatures in the ditches at the Sinderhoeve from daily average air temperature, for air temperatures of 2.1 °C and higher. For lower air temperatures a constant water temperature of 2.82 °C can be assumed (main water temperature in ditch 18 when the air temperature was below 2.1 °C).

The coefficients in this equation are most likely governed to a large extent by the dimensions (surface area to volume ratio, depth etc.) of the ditch under consideration and therefore strictly apply to the ditches for which the equation was derived. Moreover, even for the ditch under consideration the equation yields a relatively large standard error of estimate of 2.2 °C. This relationship therefore does not seem a satisfactory way to estimate water temperatures for other types of ditches or other types of surface water.

Daily values for temperature can be estimated on a monthly basis from the monthly average value ± the 90-percentile of the difference between daily minimum and maximum values, as given in Tables 5.3.1 and 5.3.2. From the point of view of detail in the available data, it is probably not worthwhile to distinguish between more than three periods of eight hours each. The course of temperature over a 24 hour period may be estimated from either a sine-curve or by assuming different but constant values over three periods of eight hours each.

A more physically based procedure for the calculation of water temperatures, based on heat exchange with the atmosphere and sediment and absorption of radiation by the water, is under development and will be described in a separate report (Jacobs, in preparation).

### 5.3.2 pH

A typical course of daily average pH over time is given in Figure 5.3.7 for ditch 14 (containing macrophytes). Average values of pH for each month are given in Table 5.3.3 for both ditches; the data are also shown graphically in Figure 5.3.8. Average values of pH in the ditches were quite similar, although the ditch containing macrophytes had slightly lower average pH during summer, but had a much higher (average) difference between minimum and maximum daily pH values (Figure 5.3.11). This is most likely caused by the presence of macrophytes resulting in consumption of carbon dioxide and a subsequent increase of pH.

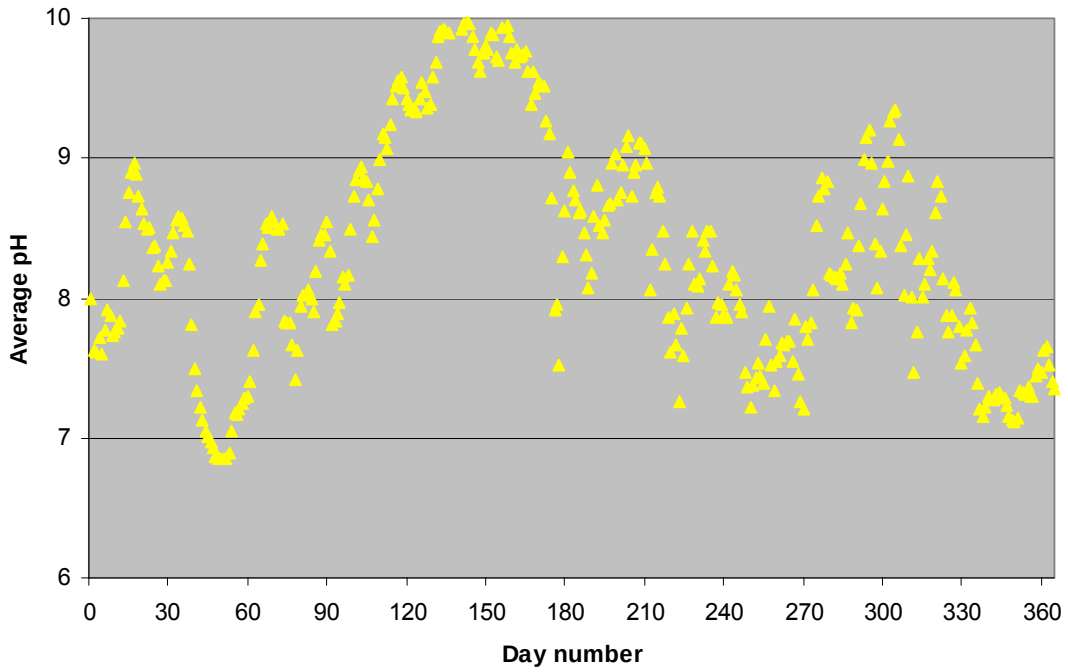


***Figure 5.3.7***

*Daily values of pH for ditch 14 over the course of 1991.*

***Table 5.3.3***

*Average monthly pH data for January - December 1991 for ditches with and without macrophytes.*

| Month | Average pH | |
|---|---|---|
| | Ditch 14 (macrophytes) | Ditch 18 (no macrophytes) |
| Jan | 8.20 | 8.65 |
| Feb | 7.45 | 9.57 |
| Mar | 8.09 | 9.52 |
| Apr | 8.76 | 9.50 |
| May | 9.73 | 9.56 |
| Jun | 9.35 | 9.32 |
| Jul | 8.72 | 9.13 |
| Aug | 8.12 | 9.24 |
| Sep | 7.61 | 9.15 |
| Oct | 8.53 | 8.91 |
| Nov | 8.17 | 7.82 |
| Dec | 7.33 | 8.50 |

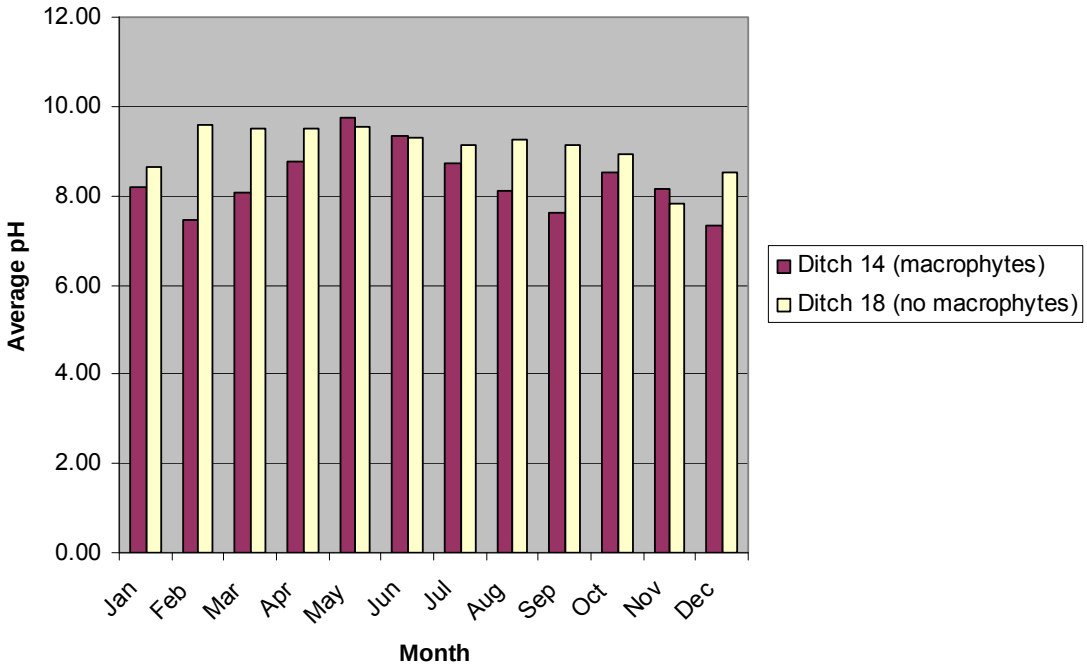


***Figure 5.3.8***

*Average monthly pH for January - December 1991 for ditches with and without macrophytes.*

The level of detail in the pH data was slightly increased by calculating average pH data for 4 daily periods, 0 - 6h, 6 - 12h, 12 - 18h and 18 - 24h, i.e. dividing each day into four time periods. Average pH for each of these periods are given in Figure 5.3.9 for ditch 14, containing macrophytes, and in Figure 5.3.10 for ditch 18, not containing macrophytes. Similar to what was observed in Section 5.3.1 for temperature data,

this representation of the monthly pH data provides only limited extra information on pH values occurring in the ditches.

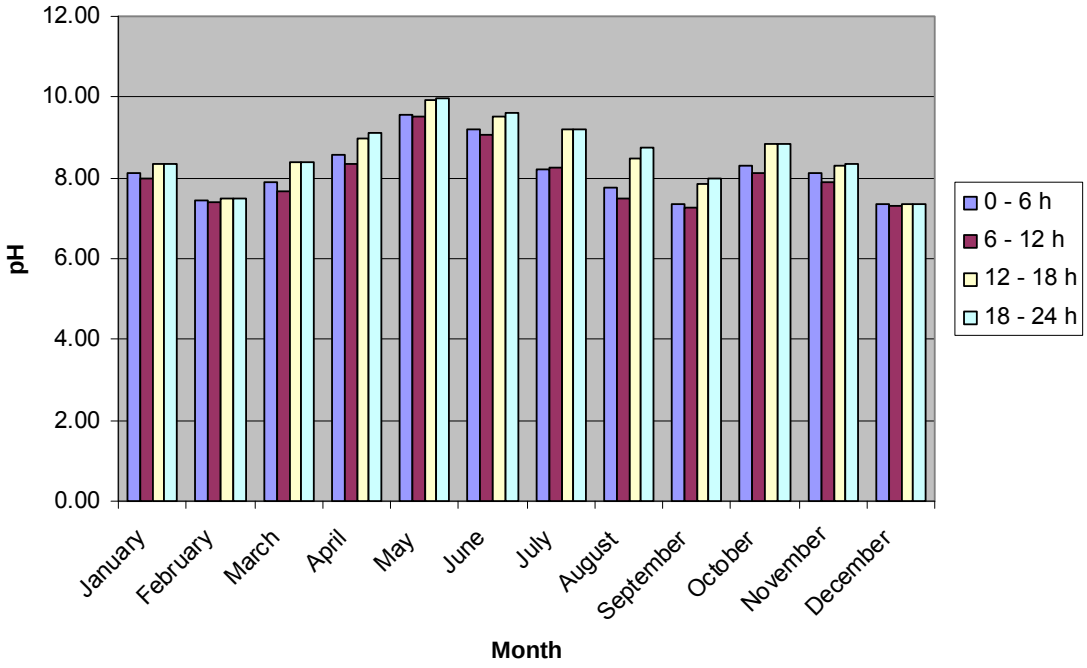


***Figure 5.3.9***

*Average monthly pH for January - December 1991 for ditch 14 (containing macrophytes) separated into daily periods of 6 h.*

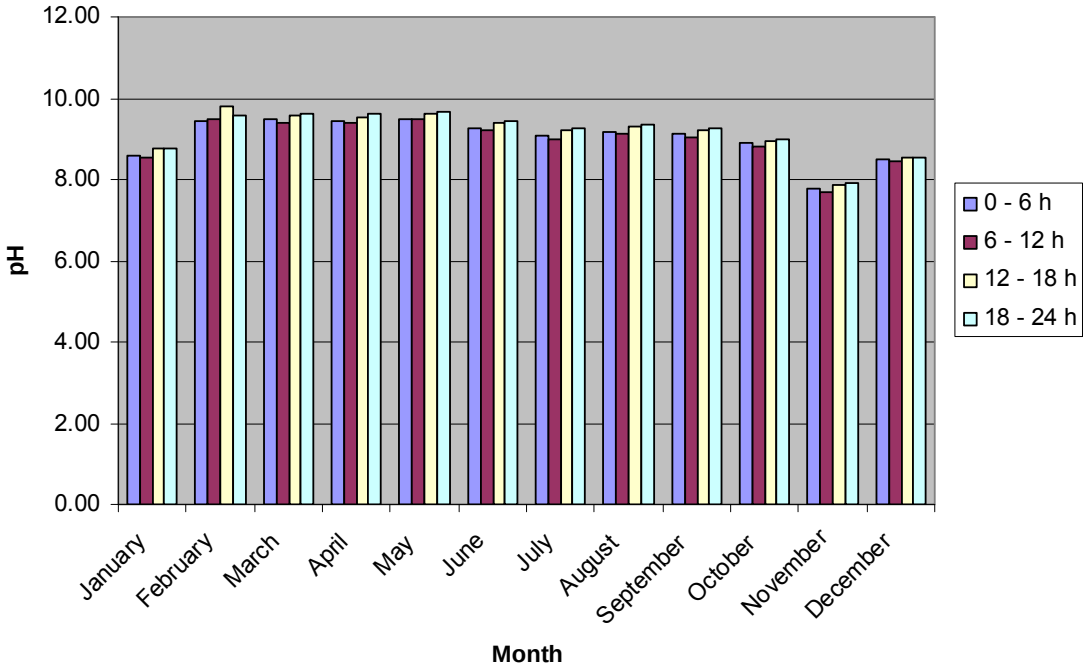


***Figure 5.3.10***

*Average monthly pH for January - December 1991 for ditch 18 (not containing macrophytes) separated into daily periods of 6 h.*

More detailed information about the extreme values in pH occurring in the ditches due to the diurnal rhythm can be retrieved by investigating the daily difference between minimum and maximum pH values, i.e. the daily pH increase also referred to as daily pH swing. Table 5.3.4 gives some summarised information about the average, the 50-percentile (i.e. median) and the 90-percentile values of the daily increase in pH occurring in each month.

***Table 5.3.4***

*Daily pH increase in ditches 14 and 18 for January - December 1991.*

| Month | Daily increase in pH ditch 14 (macrophytes) | | | Daily increase in pH ditch 18 (no macrophytes) | | |
|---|---|---|---|---|---|---|
| | Average | 50-Percentile | 90-Percentile | Average | 50-Percentile | 90-Percentile |
| January | 0.58 | 0.60 | 0.91 | 0.44 | 0.38 | 0.81 |
| February | 0.20 | 0.13 | 0.41 | 0.62 | 0.63 | 1.13 |
| March | 1.08 | 1.07 | 1.38 | 0.38 | 0.34 | 0.58 |
| April | 1.09 | 1.12 | 1.49 | 0.30 | 0.29 | 0.42 |
| May | 0.72 | 0.74 | 0.91 | 0.29 | 0.28 | 0.38 |
| June | 0.84 | 0.68 | 1.45 | 0.35 | 0.33 | 0.49 |
| July | 1.79 | 1.82 | 2.13 | 0.43 | 0.42 | 0.52 |
| August | 1.71 | 1.82 | 1.96 | 0.34 | 0.34 | 0.46 |
| September | 1.21 | 1.31 | 1.82 | 0.31 | 0.30 | 0.39 |
| October | 1.10 | 1.08 | 1.56 | 0.27 | 0.26 | 0.42 |
| November | 0.82 | 0.73 | 1.40 | 0.46 | 0.42 | 0.75 |
| December | 0.15 | 0.12 | 0.25 | 0.30 | 0.24 | 0.34 |
| Average | 0.94 ± 0.51 | 0.94 ± 0.55 | 1.31 ± 0.58 | 0.37 ± 0.10 | 0.35 ± 0.11 | 0.56 ± 0.23 |

The presence of macrophytes results in a larger daily difference between minimum and maximum observed pH than was observed in ditches without macrophytes.

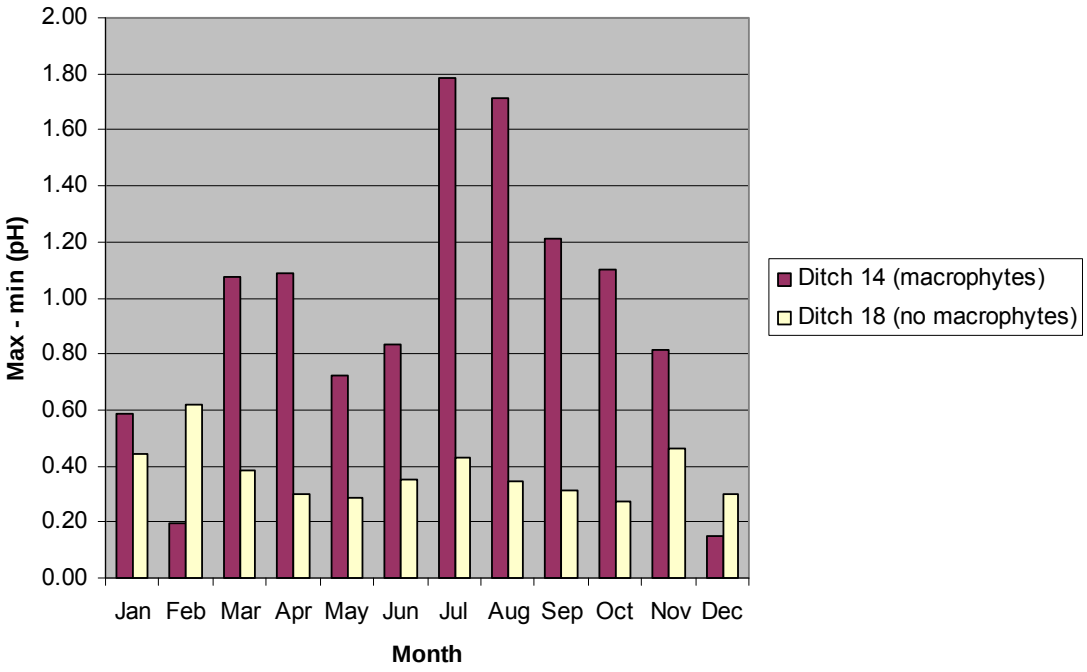


***Figure 5.3.11***

*Average difference between daily minimum and maximum water pH for January - December 1991 for ditches with and without macrophytes.*

The reader should bear in mind, however, that ditches with very similar characteristics and histories can be slightly different as far as pH, alkalinity and other parameters are concerned. Choosing other ditches would most likely have resulted in different values for pH. To demonstrate this, Figure 5.3.12 presents data on the daily average pH measured in four very similar ditches (ditches 2, 3, 5 and 11 at the Sinderhoeve, all of which contained macrophytes) over the period from March - November 1990. Although the pH is in the same range of 7.2 - 9.6 for all ditches, there can be relatively large differences between the ditches on any given day.

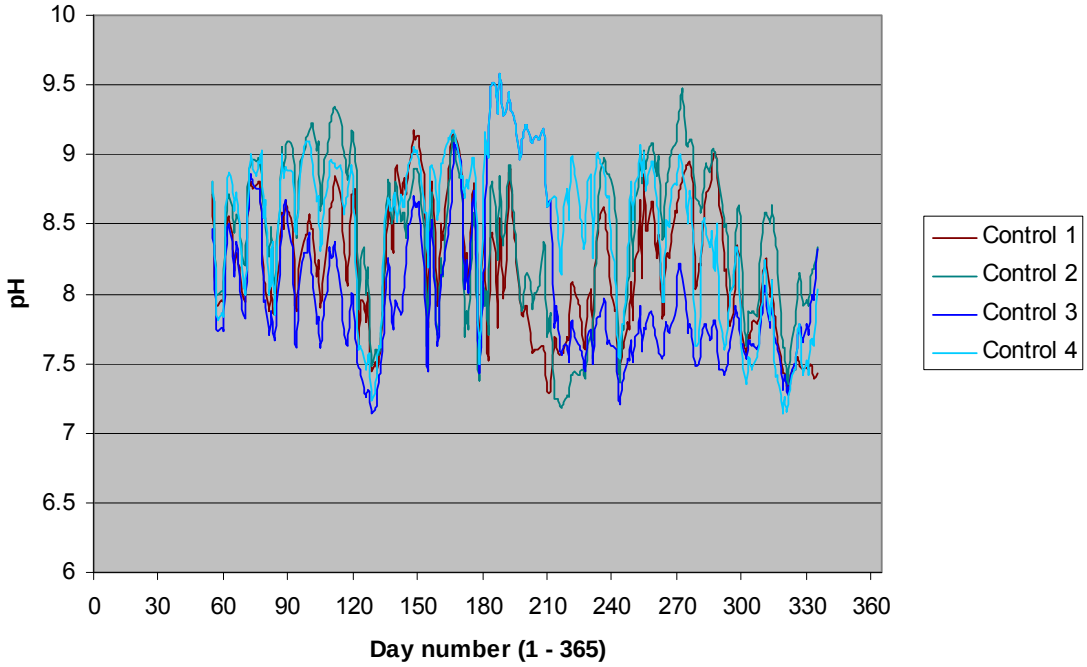


***Figure 5.3.12***

*Daily average pH in four macrophyte containing ditches located at the Sinderhoeve from March to November 1990.*

Daily values for pH can be estimated on a monthly basis from the monthly average value ± the 90-percentile of the difference between daily minimum and maximum values, as given in Tables 5.3.3 and 5.3.4. From the point of view of detail in the available data, it is probably not worthwhile to distinguish between more than three periods of eight hours each. The course of pH over a 24 hour period may be estimated from either a sine-curve or by assuming different but constant values over three periods of eight hours each.

## 5.4 Parameter values in TOXSWA

The data presented were taken from recorded measurements for two ditches at the experimental station Sinderhoeve and are only a small subset of the complete data available for all ditches over the 1990 - 1996 period. The present study does not aim to provide data representative for a broad array of ditches over a long term period. It only serves as a first exploration into the general characteristics of pH and temperature data gathered over a relatively short (one year) period. The choice of the two ditches used was based on two criteria: 1) data should be available for the entire period under study (1991) and 2) one of the ditches should contain macrophytes and the other shouldn't. This could easily have resulted in the use of data from other ditches or from another period of time. In view of differences between very similar ditches, as demonstrated for pH in Section 5.3.2 (see Figure 5.3.12), this would have resulted in different values for the parameters discussed, i.e. temperature and pH.

The reader should be aware that the presented data simply describe measurements in the two ditches used, over the period described (1991). The data relate to stagnant ditches of specific dimensions and are not easily transferrable to very different systems. Obviously, the data is quite limited and can therefore not be considered to be representative for ditches or other types of surface water in agricultural areas in general.

It is possible to estimate daily values for temperature and pH on a monthly basis from the monthly average value ± the 90-percentile of the difference between daily minimum and maximum values, as given in Tables 5.3.1 and 5.3.2 for temperatures and Tables 5.3.3 and 5.3.4 for pH resp. The course of temperature and pH over a 24 hour period may be estimated by different but constant values over three periods of eight hours each.

# 6 Modelling of transformation processes

## 6.1 Introduction

In the preceding sections general concepts for hydrolysis, photolysis and biotic transformations, and the influence of environmental conditions temperature and pH have been described. Also, some guidance for modelling is given. To illustrate the aim of the study, i.e. improvement of the simulation of transformation processes in TOXSWA, this chapter will specify in more detail how processes and environmental conditions can be modelled.

The total transformation rate in water takes into account only the dissolved substance, but not the part of a substance adsorbed to solid phases. As discussed in Chapter 1, this is a major change of concept compared to previous versions of TOXSWA. The total transformation in the water layer is given by:

$$-\frac{dc}{dt} = R_h + R_p + R_b \tag{6.1}$$

with:

$c$ = concentration dissolved in water (kg $L^{-1}$)
$t$ = time (d)
$R_h$ = rate of hydrolysis of substance in water (kg $L^{-1}$ $d^{-1}$)
$R_p$ = rate of photolysis of substance in water (kg $L^{-1}$ $d^{-1}$)
$R_b$ = rate of biotic transformation of substance in water (kg $L^{-1}$ $d^{-1}$)

The following three sections describe in more detail the modelling of each of the three processes. The final section describes the modelling of temperature and of pH in water.

## 6.2 Hydrolysis

The rate of hydrolysis is described by:

$$R_h = k_h\, c \tag{6.2}$$

with:

$k_h$ = overall rate coefficient for hydrolysis of substance ($d^{-1}$)

The rate of hydrolysis depends on pH and on temperature. The dependence of hydrolysis on pH can be modelled through (see Section 2.1):

$$k_h = k_a\left[H_3O^+\right] + k_b\left[OH^-\right] + k_n \tag{6.3}$$

with:

$k_a$ = rate coefficient for acid catalysed hydrolysis of substance ($d^{-1}$)
$k_b$ = rate coefficient for base catalysed hydrolysis of substance ($d^{-1}$)

$k_n$ = rate coefficient for neutral hydrolysis of substance ($d^{-1}$)
$[H_3O^+]$ = aqueous concentration of $H_3O^+$ (mol $L^{-1}$)
$[OH^-]$ = aqueous concentration of $OH^-$ (mol $L^{-1}$)

The effect of temperature on each of the separate hydrolysis rates is given by:

$$k_x = f_t \cdot k_{x,ref} \tag{6.4}$$

with:
$k_x$ = hydrolysis rate constant, either $k_a$, $k_b$ or $k_n$
$f_t$ = factor for the effect of temperature on the rate coefficient of transformation (-)
$k_{x,ref}$ = rate coefficient for hydrolysis ($k_a$, $k_b$ or $k_n$) in reference conditions ($d^{-1}$)

The factor for the effect of temperature on the rate coefficient for hydrolysis is calculated with the Arrhenius equation (see Section 2.3):

$$f_t = \exp\left[\frac{-\Delta H_t}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{6.5}$$

with:
$\Delta H_t$ = molar enthalpy of transformation (Arrhenius coefficient) (J $mol^{-1}$)
$R$ = molar gas constant (J $mol^{-1}$ $K^{-1}$)
$T$ = temperature (K)
$T_{ref}$ = reference temperature (K)

Usually pH is considered to be known and is assumed to be independent of temperature. Upon a change of temperature, the $[OH^-]$ associated with a given pH can be calculated from:

$$\log[OH^-] = pH - \frac{6014}{T} - 23.65 * \log(T) + 64.70 \tag{6.6}$$

Eq. (6.6) is derived from Eq. (1) in Annex B.

The hydrolysis rate in frozen water is set at zero, i.e. for T < 273 K, $f_t = 0$.

## 6.3 Photolysis

The rate of photolysis, only considering direct photolysis, can be modelled through (see Section 3.1):

$$R_p = k_p c \tag{6.7}$$

with:
$k_p$ = rate coefficient for direct photolysis of substance ($d^{-1}$)

Note that photolysis is not affected by temperature.

## 6.4 Biotic transformation

The rate of biotic transformation in water is described by (see Section 5.1):

$$R_b = k_b\, c \tag{6.8}$$

with:
$k_b$ = rate coefficient for biotic transformation of substance in water from the water layer ($d^{-1}$)

In Chapter 5 it was concluded that only the temperature affects the biotic transformation rate. The effect of temperature on the biotic transformation rate is given by:

$$k_b = f_t \cdot k_{b,ref} \tag{6.9}$$

with:
$k_{b,ref}$ = rate coefficient for biotic transformation in water from the water layer at reference conditions ($d^{-1}$)

The factor for the effect of temperature on the rate coefficient for transformation, $f_t$, is calculated using equation (6.5) given in Section 6.2.

This concept for the effect of temperature on the biotic transformation rate is most probably valid for short term variations over days or weeks. However, in the long term, months or seasons, microorganisms may adapt to the changing conditions. Hence during the gradual change from one season to the other, the capacity to transform a substance may not change, although the average temperature changes (see Section 5.2 for some background).

## 6.5 Temperature and pH

The temperature and pH can be modelled as a daily pattern, repeated during one month. The pattern of temperature and pH over a 24 hour period may be either a sine-curve or with minimum, average and maximum values over fixed periods of time.

For the temperature change during the day, the sine-curve is modelled with:

$$T = T_m + T_a \sin\left[\frac{(12+t)}{24}\cdot 2\pi\right] \tag{6.10}$$

with:
$T$ = temperature in water layer (K)
$T_m$ = mean monthly temperature in water (K)
$T_a$ = amplitude of monthly temperature swing in water (K)
$t$ = time during the day (h)

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

A daily pattern with constant temperatures over eight hours periods can be modeled with:

$$\begin{aligned} T &= T_L && 0h < t \le 8h \\ T &= T_M && 8h < t \le 16h \\ T &= T_H && 16h < t \le 24h \end{aligned} \qquad (6.11)$$

with:
$T_L$ = low temperature in water (K)
$T_M$ = middle temperature in water (K)
$T_H$ = high temperature in water (K)

The period of eight hours is only used as an example, periods of other length are possible as well, e.g. six hours.

For the pH change during the day, the sine-curve is modelled with:

$$pH = pH_m + pH_a \sin\left[\frac{(12+t)}{24} \cdot 2\pi\right] \qquad (6.12)$$

with:
$pH$ = pH in water layer (-)
$pH_m$ = mean month pH in water (-)
$pH_a$ = amplitude of month pH in water (-)
$t$ = time during the day (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.

A daily pattern with constant pH in the water over eight hours periods can be modelled with:

$$\begin{aligned} pH &= pH_L && 0h < t \le 8h \\ pH &= pH_M && 8h < t \le 16h \\ pH &= pH_H && 16h < t \le 24h \end{aligned} \qquad (6.13)$$

with:
$pH_L$ = low pH in water (K)
$pH_M$ = middle pH in water (K)
$pH_H$ = high pH in water (K)

The period of eight hours is only used as an example, periods of other length are possible as well, e.g. six hours.

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# Annex A Recently published literature on hydrolysis and photolysis of pesticides in water

Keywords in Scopus search engine

1. (hydrol* OR fotolys* OR photolys*) AND (pest*) AND (relation*)

2. (hydrol* OR fotolys* OR photolys*) AND (pest*) OR (empir*)

3. (photolys*) AND (pestic*)

were used in the search for recent literature dealing with hydrolysis and photolysis of pesticides in water that was published after 2003. Additionally, the index of contents of the Journal of Photochemistry and Photobiology (editions A: Chemistry, B: Biology, and C: Photochemistry Reviews) from January 2004 until June 2009 were checked for papers dealing with photolysis of pesticides, as was the index of contents of Photochemical and Photobiological Sciences from January 2006 until June 2009.

On the basis of the titles found a more detailed inspection of some of the papers was made. Titles applicable to the abiotic degradation of pesticides in aqueous systems were selected, whereas e.g. papers on enzymatic or biotic degradation studies were discarded. Papers were not studied in detail because of lack of time.

This query was not supposed to give an exhaustive overview of the literature published in recent years. The primary intent was to get a general impression of the type of papers recently published, and to find out whether emphasis was mostly on experimental studies or whether more theoretical considerations predominated.

Most of the papers found report the results of experimental studies dealing with the photolysis or hydrolysis of a single substance, sometimes several closely related substances. Most such studies try to elucidate the products formed, but do not involve detailed examinations of reaction pathways. As pointed out by Canle et al. (2005), there is generally a lack of detailed mechanistic studies, which is also concluded by Burrows et al. (2002).

Some studies deal with the effect of modifying agents on photolysis and/or hydrolysis. Prosen and Zupancic-Kralj (2005) studied the influence of humic acids on the abiotic breakdown of atrazine, whereas Manzanilla-Cano et al. (2008) studied the photochemical degration of methylparathion in the presence of humic acids. Nélieu et al. (2008) studied the influence of nitrate and nitrite on the phototransformation of monuron, and Vulliet et al. (2004) have studied the influence of pH and irradiation wavelength on the degradation of sulfonylureas. Garcia et al. (2005) discuss the photodegradation of a large number of hydroxylated N-heteroatomic substances (hydroxypyridines, hydroxyquinolines and hydroxypirimidines) in the presence of a synthetic dye, Rose Bengal, which acts as a sensitiser. The main aim of the study was to examine conditions maximising the photodegradation efficiency of the studied substances.

A group of pesticides represented relatively well in degradation studies is the large group of organophosphorus pesticides. Many of these substances contain ester linkages, which are prone to hydrolysis. Zamy et al. (2004a) have reported data on the hydrolysis rate and probable degradation pathways of four organophosphorus and two carbamate pesticides; the phototransformation of the same four organophosphorus substances was also investigated (Zamy et al., 2004b). The light induced transformation of several other organophosphorus insecticides have also been investigated, e.g. dimethoate (Evgenidou et al., 2005), dichlorvos (Oancea and Oncescu, 2008) and several other substances (Whiteside et al., 2006; Calza et al., 2008).

Some articles were found dealing with more general subjects related to abiotic transformations. Bracchini et al. (2005) discuss the optical properties in the coastal lagoon of Fogliano, Italy, establishing seasonal variations in the attenuation coefficient, performing in situ measurements for ultraviolet and visible light.

Review articles dealing with general principles of hydrolysis and photolysis of organic substances, and pesticides in particular, were scarce. Katagi (2004) discusses the photodegradation of pesticides on plant and soil surfaces, and the hydrolysis of pesticides in the aquatic environment (Katagi, 2002). Burrows et al. (2002) provide an excellent overview of studies dealing with the photolysis of several classes of pesticides, the substances being dissolved in water or organic solvents. The paper summarises both direct and photosensitised degradation of a large number of substances.

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# Annex B EPA equations to establish hydrolysis rate constants at any pH from experimental data on hydrolysis rates at three different values of pH

Note: when applying these equations care should be taken that the (experimental DT50) input values used to establish hydrolysis rates $k_a$, $k_b$ and $k_n$ adhere to the criterium that the DT50 values used for hydrolysis at acidic and basic conditions should at most be equal to (but not larger than) DT50 values given for neutral conditions. Failing to do so will result in inappropriate estimates for hydrolysis rates.

The equations are taken from a U.S. E.P.A. test guideline (Fate, transport and transformation test guideline OPPTS 835.2130: Hydrolysis as a function of pH and temperature). However, equation 14 of the original document, used for the calculation of $k_n$, contains a term '$- 10^{Y} * k_h$' which was replaced in the current equations by '$10^{-Y} * k_h$'. A comparison between the original and the adapted equation is given in Annex C, from which it was concluded that the original equation contained a typographical error.

The equations assume measurement of the hydrolysis reaction rate $k_h$ at three values of pH:

$i = 1$; $pH = X$; $k_h = k_{i=1}$

$i = 2$; $pH = X + Y$; $k_h = k_{i=2}$

$i = 3$; $pH = X + Y + Z$; $k_h = k_{i=3}$

($X$, $Y$ and $Z > 0$, preferably $X \geq 3$, $Y \geq 2$, $Z \geq 2$)

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

$Kw = [H_3O^+] * [OH^-]$; 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 Kw also is temperature dependent; its value is approximated by:

$$pKw = -1 * \text{Log}(Kw) = (6014/T) + 23.65 * \text{Log}(T) - 64.70 \quad (1)$$

where Log(X) denotes the logarithm to the base 10 of X, and T denotes temperature in Kelvin.

The reaction rate constants for acid catalysed, base catalysed and neutral hydrolysis ($k_a$, $k_b$ and $k_n$, resp.) are given by:

$$k_a = 10^{X} * k_{i=1} - 10^{X} * k_{i=2} + 10^{(X - Z)} * k_{i=3} \quad (2)$$

$$k_b = 10^{(pKw - X - 2Y - Z)} * k_{i=1} - 10^{(pKw - X - Y - Z)} * k_{i=2} + 10^{(pKw - X - Y - Z)} * k_{i=3} \quad (3)$$

$$k_n = 10^{(-Y)} * k_{i=1} + k_{i=2} - 10^{(-Z)} * k_{i=3} \quad (4)$$

When $k_a$, $k_b$ and $k_n$ are known, the rate constant at any value of pH can be calculated from:

$$k_h = k_a * 10^{(-pH)} + k_b * 10^{(pH - pKw)} + k_n \quad (5)$$

# Annex C A comparison between the original and the adapted EPA equation for $k_n$

The equations are taken from a U.S. E.P.A. test guideline (Fate, transport and transformation test guideline OPPTS 835.2130: Hydrolysis as a function of pH and temperature).

Equation 3 given below corresponds to Equation 14 of the original document, used for the calculation of $k_n$. This equation contains a term '$- 10^{Y} * k_{i=1}$' which is suspected to be a typographical error. Replacing this factor with '$10^{-Y} * k_{i=1}$' results in an adapted equation for the estimation of $k_n$, Equation 4.

The reaction rate constants for acid catalysed, base catalysed and neutral hydrolysis ($k_a$, $k_b$ and $k_n$, resp.) are given by:

$$k_a = 10^{X} * k_{i=1} - 10^{X} * k_{i=2} + 10^{(X - Z)} * k_{i=3} \quad (1)$$

$$k_b = 10^{(pKw - X - 2Y - Z)} * k_{i=1} - 10^{(pKw - X - Y - Z)} * k_{i=2} + 10^{(pKw - X - Y - Z)} * k_{i=3} \quad (2)$$

$$k_n = -10^{(Y)} * k_{i=1} + k_{i=2} - 10^{(-Z)} * k_{i=3} \quad (3)$$

$$k_n^{*} = 10^{(-Y)} * k_{i=1} + k_{i=2} - 10^{(-Z)} * k_{i=3} \quad (4)$$

When $k_a$, $k_b$ and $k_n$ are known, the rate constant at any value of pH can be calculated from:

$$k_h = k_a * 10^{(-pH)} + k_b * 10^{(pH - pKw)} + k_n \quad (5)$$

For a hypothetical substance values of $k_a = 1\ h^{-1}$, $k_b = 5\ h^{-1}$ and $k_n = 0.005\ h^{-1}$ were assumed. Using Eq. 5 values for $k_h$ were calculated at pH values of 3, 7 and 9. The obtained values for $k_h$ were then employed to estimate values of $k_a$ and $k_b$ from Eq. 1 and 2, and values of $k_n$ from both Eq. 3 and Eq. 4. The resulting estimates for $k_a$, $k_b$ and $k_n$ derived from $k_h$ at different values of pH are given in Table 1.

***Table 1***

*Values for $k_a$, $k_b$ and $k_n$ of a hypothetical substance, estimated using the original and adapted EPA equations 1 - 4.*

| Parameter | Assumed value ($h^{-1}$) | Estimated with original EPA equations | Estimated with adapted EPA equations |
|---|---|---|---|
| $k_a$ | 1 | 1.049 | 1.049 |
| $k_b$ | 5 | 5.022 | 5.022 |
| $k_n$ | 0.005 | -59.99 | 0.00495 |

Obviously, the negative estimate for $k_n$ obtained using the original EPA equation for $k_n$ is incorrect, whereas the estimate for $k_n$ based on the adapted EPA equation (equation 4) closely corresponds to the original value for $k_n$.

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

The equations have been kindly provided by Dr J. Molenaar of Biometris, PSG Wageningen UR (University & Research centre).

This approach assumes to have available three measured values for the hydrolysis reaction rate $k_h$ at three different pH values:

1. For pH = pH1 we have the experimental outcome $k_h = k1$
2. For pH = pH2 we have the experimental outcome $k_h = k2$
3. For pH = pH3 we have the experimental outcome $k_h = k3$

with:
pH1 << 7, acidic conditions
pH2 ≈ 7, neutral conditions
pH3 >> 7, basic conditions

From these three measurement data we want to fit the coefficients $k_a$, $k_b$, and $k_n$ in the function

$$k_h = k_a * 10^{(-pH)} + k_b * 10^{(pH - pKw)} + k_n \quad (1)$$

Since pKw is given by the temperature T dependent expression

$$pKw = -1 * \text{Log}(Kw) = (6014/T) + 23.65 * \text{Log}(T) - 64.70 \quad (2)$$

$$\text{it holds that } 10^{(-pKw)} = Kw \quad (3)$$

So, relation (1) can be written in the form

$$k_h = k_a * 10^{(-pH)} + \overline{k}_b * 10^{(pH)} + k_n \quad (4)$$

with the definition $\overline{k}_b = k_b * Kw$. It suffices to estimate $k_a$, $\overline{k}_b$, and $k_n$, after which $k_b$ follows directly from $k_b = \overline{k}_b / Kw$.

**Symmetric case**

In most practical cases one expects the data to satisfy the conditions

$$k1 \geq k2 \text{ and } k3 \geq k2 \quad (5)$$

We refer to this situation as the 'symmetric' case, since the data suggest for $k_h$ a parabolic behavior with the minimum around pH2 ≈ 7. Expression (4) is well suited to fit such data. Substituting the data we obtain the linear equations

$$\begin{aligned} k1 &= k_a * 10^{(-pH1)} + \bar{k}_b * 10^{(+pH1)} + k_n \\ k2 &= k_a * 10^{(-pH2)} + \bar{k}_b * 10^{(+pH2)} + k_n \\ k3 &= k_a * 10^{(-pH3)} + \bar{k}_b * 10^{(+pH3)} + k_n \end{aligned} \qquad (6)$$

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

$$\text{Det = Determinant} \quad \begin{bmatrix} 10^{-pH1} & 10^{+pH1} & 1 \\ 10^{-pH2} & 10^{+pH2} & 1 \\ 10^{-pH3} & 10^{+pH3} & 1 \end{bmatrix} \qquad (7)$$

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

$$\text{Det} = 10^{(pH2 - pH1)} - 10^{(pH3 - pH1)} - 10^{(pH1 - pH2)} + 10^{(pH3 - pH2)} + 10^{(pH1 - pH3)} - 10^{(pH2 - pH3)} \qquad (8)$$

The coefficients $k_a$, $k_b$ and $k_n$ are then given by equations 9, 10 and 11 resp.:

$$k_a = \frac{1}{Det} * \left\{ k1 * (10^{pH2} - 10^{pH3}) - k2 * (10^{pH1} - 10^{pH3}) + k3 * (10^{pH1} - 10^{pH2}) \right\} \qquad (9)$$

$$k_b = \frac{1}{Kw} * \frac{1}{Det} * \left\{ k1 * (10^{-pH3} - 10^{-pH2}) - k2 * (10^{-pH3} - 10^{-pH1}) + k3 * (10^{-pH2} - 10^{-pH1}) \right\} \qquad (10)$$

$$k_n = \frac{1}{Det} * \left\{ k1 * (10^{(pH3 - pH2)} - 10^{(pH2 - pH3)}) - k2 * (10^{(pH3 - pH1)} - 10^{(pH1 - pH3)}) + k3 * (10^{(pH2 - pH1)} - 10^{(pH1 - pH2)}) \right\} \qquad (11)$$

**Asymmetric cases**

Often measured values of k1, k2 and k3 will not satisfy the conditions given by Eq. 5. If one tries to fit the data with the function in Eq. 1, one finds that negative values for $k_a$, $k_b$ or $k_n$ are obtained. The reason for this unrealistic outcome is obvious: the function in Eq. 1 is not suited for the fitting purposes for which it is applied. This can be understood as follows.

Let us focus first on the asymmetric case where k1 > k2, k2 > k3 (i.e. acid catalysed hydrolysis). The function $k_h$ in Eq. 4 is a linear combination of three totally different functions: a decaying exponential $10^{-pH}$, an increasing 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 $k_n$ is nearly completely determined by the value of k2, the coefficient $k_a$ is mainly determined by the value of k1, and the coefficient $k_b$ by the value of k3. The algorithm outlined above for the symmetric case tends to take for $k_n$ a value close to k2. However, if k3 < k2, the constant in expression (4) is bigger than k3, which has as a consequence that for $k_b$ a negative value will be estimated in order to obtain a curve that passes through (pH3, k3). To avoid this, we should choose for $k_n$ a value ≤ k3. The constant contribution in Eq. 1 is then not big enough to represent the value k2 at pH2, but

since the exponentials in Eq. 1 cannot compensate for this, it is not possible to fit asymmetric data with the function in Eq. 1.

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.

*Case 1*
Consider the asymmetric case that k1 > k2, k2 > k3 (acid catalysis). From these data we conclude that the increasing exponential in Eq. 4 does apparently not contribute, so we set:

$$\bar{k}_b = 0 \tag{12}$$

This implies that for the constant $k_n$ we have to choose:

$$k_n = k3 \tag{13}$$

The decaying exponential and the corresponding coefficient ka form the only remaining degree of freedom. It is impossible to fit the data points (pH1, k1) and (pH2, k2) simultaneously with a proper choice for $k_a$. One could 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

$$k_h(k_a) = k_a\, 10^{-pH} + k3 \tag{14}$$

This function should approach (pH1, k1) and (pH2, k2) in some optimal way. The errors are:

$$\varepsilon_1 = k_a\, 10^{-pH1} + k3 - k1 \tag{15a}$$
$$\varepsilon_2 = k_a\, 10^{-pH2} + k3 - k2 \tag{15b}$$

The can be combined in the error function

$$H(k_a) = \left(\frac{\varepsilon_1}{k1}\right)^2 + \gamma * \left(\frac{\varepsilon_2}{k2}\right)^2 \tag{16}$$

The term $\varepsilon_1/k1$ accounts for the relative error at pH1, and the term $\varepsilon_2/k2$ for the relative error at pH2. The constant γ is introduced as a weighting factor: if γ = 1, both errors are equally important, but if γ >> 1, the error at pH2 gets most emphasis.

In practice:

- if γ = 0, the curve will pass through (pH1, k1), but has a considerable error at pH2;
- if γ >> 1 (say 10000) the curve will more or less pass through (pH2, k2) with a considerable error at pH1.

By minimising $H(k_a)$ with respect to $k_a$, we obtain the following estimate for $k_a$:

$$k_a = \frac{(k1-k3)*k_2^2*10^{-pH1} + \gamma*(k2-k3)*k_1^2*10^{-pH2}}{k_2^2*10^{-2*pH1} + \gamma*k_1^2*10^{-2*pH2}} \quad (17)$$

*Case 2*

Next we consider the asymmetric case where k1 < k2, k2 < k3 (base catalysis).
This case is handled similarly as the case k1 > k2 > k3. The fitting function now is:

$k_h(\overline{k}_b) = \overline{k}_b * 10^{pH} + k_n$ (18)

since the decaying exponential does not contribute and thus

$k_a = 0$ (19)

As above, we choose for the constant contribution

$k_n = k1$ (20)

i.e., we force the fitting function to pass through (pH1, k1), the lowest data point.

The estimate for $\overline{k}_b$ is now given by

$$\overline{k_b} = \frac{(k3-k1)*k_2^2*10^{pH3} + \gamma*(k2-k1)*k_3^2*10^{pH2}}{k_2^2*10^{2*pH3} + \gamma*k_3^2*10^{2*pH2}} \quad (21)$$

For γ = 0, the fitting function passes through (pH3, k3) and for γ >> 1, say (γ = 10000) the function passes more or less through (pH2, k2).

**How to choose the weighing factor γ**

In situations of either acid or base catalysed hydrolysis the DT50 may become relatively small (e.g. < 1 h). 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 is very similar), where k1 > k2 > k3. Suppose that the standard deviation in k1 is SD1, and the standard deviation in k2 is SD2. Relative standard deviations RSD1 and RSD2 are then given by SD1/k1 and SD2/k2 resp.

Because the error function H contains the squares of RSD1 and RSD2, the contribution of k1 and k2 can be weighed according to their relative standard deviations by choosing

$\gamma = \{RSD1/RSD2\}^2$

To give k1 a larger weight, γ can be chosen smaller, and to give k2 a larger weight γ can be chosen larger.

**Determining rate constants from experimental data that does not closely adhere to equation (1) of this annex**

The general description given by equation (1) in this annex assumes that the overall hydrolysis rate is the sum of an acid catalysed, a base catalysed and a neutral (non catalysed) hydrolysis rate.

When input data closely adheres to this assumption, it is expected that estimation of $k_a$, $k_b$ and $k_n$ using the set of equations 9/10/11, 12/13/17 or 19/20/21 (depending on whether both acid and base catalysed, only acid catalysed or only base catalysed hydrolysis is valid) will proceed rather straightforward and will yield values of $k_a$, $k_b$ and $k_n$ which will describe the input data rather closely. However, it is interesting to observe what happens when input data do not closely adhere to the assumptions. For this reason 3 sets of data were used to test what happens to the estimates of $k_a$, $k_b$ and $k_n$ when input data either adheres to the description, slightly deviates or badly deviates.

**Both acid and base catalysed hydrolysis**

This scenario assumes that the substance will degrade slowest at neutral pH. Using input data which are either consistent (good data), slightly deviating (bad data) or totally not in line with this assumption (very bad data), equations 9 - 11 estimate values for $k_a$, $k_b$ and $k_n$ which are given in Table F.2. Figure F.1 graphically depicts the course of rate versus pH as estimated from the 'good data'.

***Table F.1***

*Hypothetical input data for the 'symmetric' scenario which presumes both acid and base catalysed hydrolysis.*

| | DT50 (h) | | |
|---|---|---|---|
| | pH = 5 | pH = 7 | pH = 9 |
| Good data | 48 | 480 | 240 |
| Bad data | 500 | 480 | 240 |
| Very bad data | 500 | 480 | 600 |

***Table F.2***

*Rate constants estimated from the three sets of input data.*

| | Rate constants ($h^{-1}$) estimated from data in Table F.1 using equations 9 - 11 | | |
|---|---|---|---|
| | $k_a$ | $k_b$ | $k_n$ |
| Good data | 130 | 214 | 0.00142 |
| Bad data | -0.432 | 212 | 0.00143 |
| Very bad data | -0.0607 | -42.3 | 0.00145 |

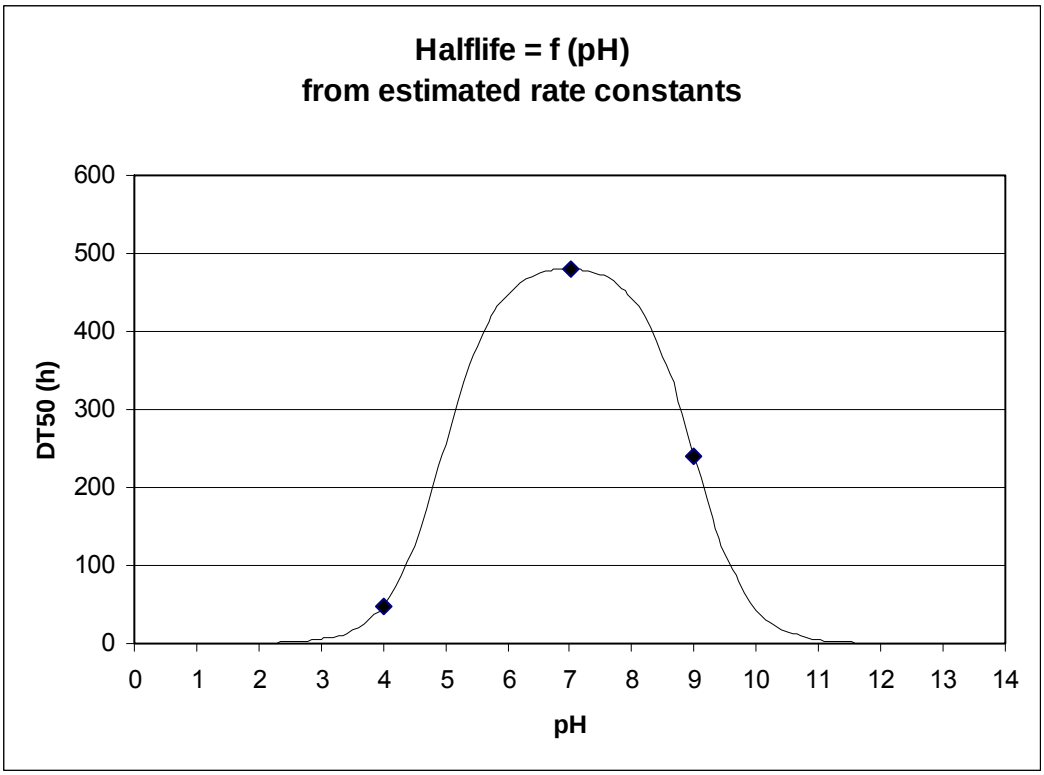



***Figure F.1***

*Calculation of DT50 from rate constants derived from experimental values (symbols represent 'good data').*

Only the use of 'good data' results in estimates of rate constants which are all > 0. As can be seen in Figure F.1 for the 'good data', the estimated rate constants closely reproduce the input data from which they were generated. When the set of equations 9 - 11 are used on input data which do not show both acid and base catalysed hydrolysis, either $k_a$ or $k_b$ will assume a negative value, making the constants unsuitable for calculation of rates at intermediate values of pH. Therefore, equations 9 - 11 should only be used in situations where both an increase of pH over 7 and a decrease of pH below 7 are accompanied by a decrease of DT50.

**Acid catalysed hydrolysis**

It is assumed that the substance will degrade fastest at low (< 7) pH. Using input data which are either consistent (good data), slightly deviating (bad data) or totally not in line with this assumption (very bad data), equations 12 - 17 estimate values for $k_a$, $k_b$ and $k_n$ (using a value of $\gamma$=1) which are given in Table F.4. Figure F.2 graphically depicts the course of rate versus pH as estimated from the 'good data'.

***Table F.3***

*Hypothetical input data for the 'asymmetric' scenario which presumes acid catalysed hydrolysis.*

| | DT50 (h) | | |
|---|---|---|---|
| | pH = 5 | pH = 7 | pH = 9 |
| Good data | 48 | 480 | 480 |
| Bad data | 48 | 480 | 520 |
| Very bad data | 960 | 480 | 360 |

***Table F.4***

*Rate constants estimated from the three sets of input data.*

| | Rate constants ($h^{-1}$) estimated from data in Table F.3 using equations 12 - 17 | | |
|---|---|---|---|
| | $k_a$ | $k_b$ | $k_n$ |
| Good data | 1286 | 0 | 0.00144 |
| Bad data | 1309 | 0 | 0.00133 |
| Very bad data | -120 | 0 | 0.00193 |

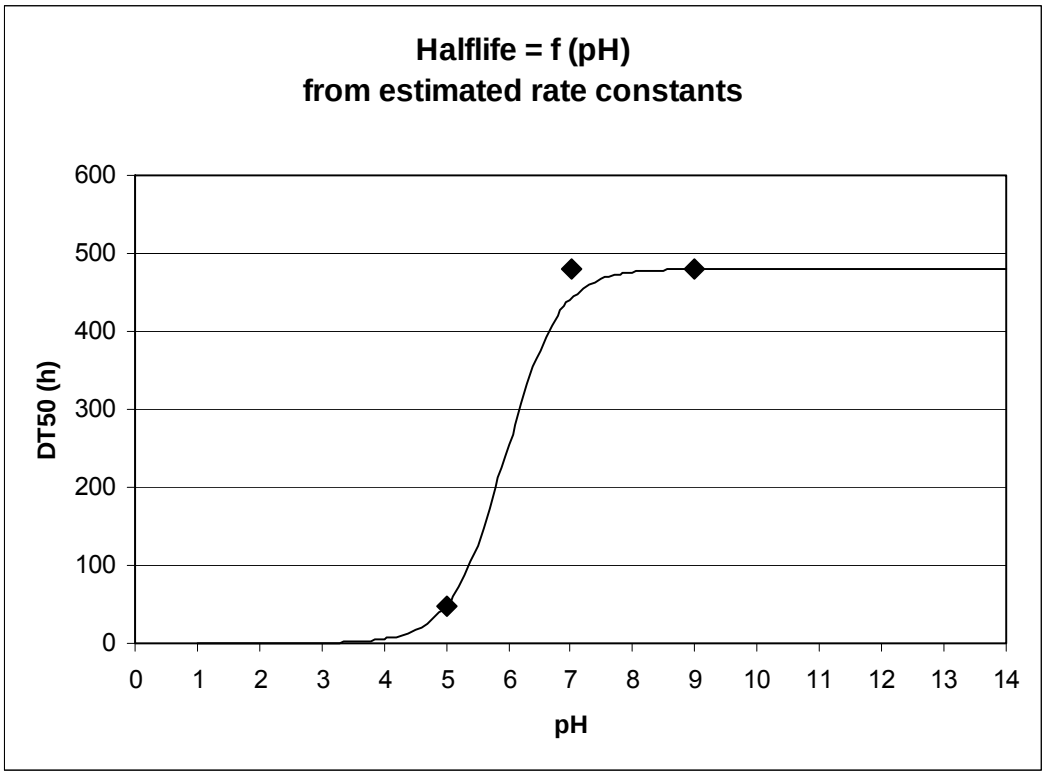



***Figure F.2***

*Calculation of DT50 from rate constants derived from experimental values (symbols represent 'good data').*

Both the use of 'good data' and of 'bad data' results in estimates of rate constants which are all > 0. As can be seen in Figure F.2 for the 'good data', the estimated rate constants closely reproduce the input data from which they were generated. Bad data represent the situation where a further decrease in speed of hydrolysis is seen at pH > 7. The estimation method responds by slightly increasing the value of $k_a$.

When the set of equations 12 - 17 are used on input data which do not show acid catalysed hydrolysis $k_a$ will assume a negative value, making the constants unsuitable for interpolation of rates at intermediate values of pH. Therefore, equations 12 - 17 should only be used in situations where a decrease of pH below 7 is accompanied by a decrease of DT50.

Similarly, for base catalysed hydrolysis the conclusion is that equations 18 - 21 should only be used in situations where an increase of pH to values above 7 is accompanied by a decrease of DT50.

# Annex E Molar absorptivities of 2,4-D, cymoxanil, isoproturon and pyrimethanil, reproduced with permission from Feigenbrugel et al. (2006)

Table 1
Molar absorptivities ε of 2,4-D, cymoxanil, fenpropidin, isoproturon and pyrimethanil measured between 240 and 344 nm using a deuterium lamp and normalized to the value determined at 253.7 nm with a Hg-lamp

| λ (nm) | ε (2,4-D) ($M^{-1}$ $cm^{-1}$)[a] | ε (cymoxanil) ($M^{-1}$ $cm^{-1}$)[a] | ε (fenpropidin) ($M^{-1}$ $cm^{-1}$)[a] | ε (isoproturon) ($M^{-1}$ $cm^{-1}$)[a] | ε (pyrimethanil) ($M^{-1}$ $cm^{-1}$)[a] |
|---|---|---|---|---|---|
| 240 | 708 | 8303 | 9 | 10053 | 0 |
| 242 | 508 | 8448 | 22 | 10164 | 934 |
| 244 | 344 | 8493 | 41 | 10251 | 2340 |
| 246 | 236 | 8417 | 63 | 10235 | 3886 |
| 248 | 174 | 8338 | 94 | 10018 | 5949 |
| 250 | 146 | 8193 | 126 | 9489 | 8135 |
| 252 | 142 | 8040 | 165 | 8429 | 10593 |
| 253.7[b] | 145 ± 6 | 7940 ± 526 | 196 ± 14 | 7334 ± 511 | 13209 ± 735 |
| 254 | 151 | 7841 | 204 | 6925 | 13315 |
| 256 | 171 | 7659 | 241 | 5366 | 15993 |
| 258 | 197 | 7461 | 272 | 4041 | 18426 |
| 260 | 232 | 7274 | 304 | 3044 | 20786 |
| 262 | 270 | 7042 | 329 | 2373 | 22525 |
| 264 | 318 | 6832 | 334 | 1955 | 24005 |
| 266 | 369 | 6583 | 308 | 1712 | 24852 |
| 268 | 425 | 6328 | 295 | 1572 | 25442 |
| 270 | 483 | 6024 | 284 | 1472 | 25371 |
| 272 | 541 | 5717 | 239 | 1400 | 24836 |
| 274 | 593 | 5376 | 168 | 1348 | 24097 |
| 276 | 635 | 4997 | 107 | 1274 | 22899 |
| 278 | 661 | 4558 | 79 | 1207 | 21373 |
| 280 | 680 | 4074 | 70 | 1126 | 19757 |
| 282 | 688 | 3604 | 66 | 1029 | 17945 |
| 284 | 690 | 3162 | 65 | 915 | 16086 |
| 286 | 680 | 2748 | 66 | 811 | 14348 |
| 288 | 668 | 2357 | 69 | 707 | 12712 |
| 290 | 650 | 1961 | 74 | 607 | 11230 |
| 292 | 631 | 1627 | 79 | 517 | 9991 |
| 294 | 594 | 1356 | 81 | 431 | 8862 |
| 296 | 508 | 1115 | 84 | 382 | 7834 |
| 296.7[b] | 449 ± 16 | 864 ± 186 | – | – | 6649 ± 690 |
| 298 | 384 | 917 | 87 | 374 | 6970 |
| 300 | 271 | 743 | 87 | 362 | 6265 |
| 302 | 170 | 608 | 89 | 356 | 5507 |
| 304 | 97 | 491 | 90 | 348 | 5127 |
| 306 | 56 | 401 | 90 | 339 | 4765 |
| 308 | 36 | 332 | 90 | 338 | 4446 |
| 310 | 27 | 283 | 90 | 339 | 4112 |
| 312 | 22 | 227 | 89 | 322 | 3755 |
| 312.6[b] | – | – | – | – | 3552 ± 479 |
| 313.2[b] | – | – | – | – | 3356 ± 417 |
| 314 | 19 | 198 | 89 | 322 | 3402 |
| 316 | 17 | 168 | 88 | 296 | 3060 |
| 318 | 15 | 149 | 86 | 279 | 2734 |
| 320 | 14 | 128 | 85 | 258 | 2394 |
| 322 | 12 | 111 | 83 | 231 | 2024 |
| 324 | 10 | 95 | 81 | 208 | 1706 |
| 326 | 9 | 87 | 79 | 177 | 1432 |
| 328 | 6 | 71 | 77 | 148 | 1157 |
| 330 | 4 | 64 | 75 | 126 | 948 |
| 332 | 2 | 53 | 74 | 95 | 734 |
| 334 | 0 | 38 | 71 | 74 | 554 |
| 336 | 0 | 34 | 70 | 53 | 400 |
| 338 | 0 | 23 | 68 | 24 | 248 |
| 340 | 0 | 13 | 67 | 9 | 164 |
| 342 | 0 | 14 | 66 | 0 | 76 |
| 344 | 0 | 9 | 65 | 0 | 29 |

[a] The reported values are averaged over 2 nm intervals in the range 240–344 nm.
[b] The values are obtained using a Hg-lamp. The quoted errors correspond to 2σ obtained from the least square fit analysis.

Molar extinction coefficients used for calculations in GCSOLAR.

| Wavelength (nm) | ε 2,4-D ($mol^{-1}$ $cm^{-1}$) | ε Pyrimethanil ($mol^{-1}$ $cm^{-1}$) |
|---|---|---|
| 295 | 559 | 8348 |
| 297.5 | 384 | 6970 |
| 300 | 271 | 6265 |
| 302.5 | 170 | 5507 |
| 305 | 76.5 | 4946 |
| 307.5 | 36 | 4446 |
| 310 | 27 | 4112 |
| 312.5 | 22 | 3552 |
| 315 | 18 | 3232 |
| 317.5 | 15 | 2734 |
| 320 | 14 | 2394 |
| 323 | 11 | 1865 |
| 330 | 4 | 948 |

# Annex F Example calculation to demonstrate the effect of inclusion of maximum temperature and pH in rate calculations

**Effect of temperature**

The calculation assumes a hypothetical substance with DT50 for hydrolysis of 48 h at a temperature of 20 °C, without any effects of pH on hydrolysis rate.

Assuming an average activation energy $E_a$ of 75 kJ mole$^{-1}$, the effect of a temperature change on the hydrolysis rate can be calculated from an Arrhenius type equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

where A is a frequency factor (h$^{-1}$), R is the gas constant (8.31 J K$^{-1}$ mole$^{-1}$)) and T is the absolute temperature.

If we assume a daily temperature regime consisting of a 6 h period with a constant temperature of 12 °C, a second 6 h period with 16 °C, a third 6 h period with 22 °C and a fourth 6 h period with an average temperature of 18 °C, the average temperature over the entire 24 h period would be 17 °C.

DT50 calculated for the four different temperatures with the aid of the Arrhenius equation is given in Table H.1.

The fraction of the substance remaining after 8 h at some temperature can be calculated from:

$$\frac{M}{M0} = e^{-kt}$$

where M is the amount remaining after time t (h), M0 is the initial amount, and k is the rate constant (h$^{-1}$) at the temperature assumed; k = ln(2)/DT50.

***Table H.1***

*DT50 for hydrolysis at various temperatures for a hypothetical substance with DT50 of 48 h at 20 °C, estimated using Arrhenius equation with $E_a$ = 75 kJ mole$^{-1}$.*

| Temperature (°C) | DT50 (h) |
|---|---|
| 20 | 48.0 (known) |
| 12 | 113.8 (estimated) |
| 16 | 73.5 (estimated |
| 22 | 39.0 (estimated) |
| 18 | 59.3 (estimated) |
| 17 | 66.0 (estimated) |

Remaining fraction of the substance after an 6 h period at 12 °C: 0.964
Remaining fraction of the substance after an 6 h period at 16 °C: 0.945
Remaining fraction of the substance after an 6 h period at 22 °C: 0.899
Remaining fraction of the substance after an 6 h period at 18 °C: 0.932
Remaining fraction of the substance after an 6 h period at 17 °C: 0.939.

After four consecutive periods of time, each of 6 h duration, with temperatures of 12, 16, 22 and 18 °C resp., the remaining fraction of the substance would be 0.964 * 0.945 * 0.899 * 0.932 = 0.763.

If the calculations had assumed that the average temperature (17 °C) would have been applicable for the full 24 h period, the remaining fraction of the substance would have been 0.939 * 0.939 * 0.939 * 0.939 = 0.777.

Eventhough the relative differences in remaining fractions after a 1-day period are limited (0.763 and 0.777 resp., a relative difference of 1.8 %), they will increase with time. After a 14-day period the remaining fractions are 0.0228 and 0.0293 resp., resulting in an relative difference of approx. 22 % between the remaining fractions.

Accounting for periods with higher than average temperatures thus results in faster degradation over the 24 h period and hence to a lower remaining amount of material, although the effect is limited when using an energy of activation of 75 kJ/mole over a temperature range of 12 - 22 °C.

**Effect of pH**

The calculation assumes a substance with DT50 for hydrolysis of twelve days at pH = 4, DT50 = 1.2 days at pH = 7 and DT50 = 0.01 d at pH = 9 (tolylfluanid); temperature is assumed constant at 20 °C.

If we assume a daily pH regime consisting of an 16 h period with pH = 7, and a 8 h period with pH = 9, the average pH over the entire 24 h period would be 7.67.

DT50 calculated for the different values of pH is given in Table H.2.

The fraction of the substance remaining after 8 h at some pH can be calculated from:

$$\frac{M}{M0} = e^{-kt}$$

where M is the amount remaining after time t (h), M0 is the initial amount, and k is the rate constant ($h^{-1}$) at the pH assumed; k = ln(2)/DT50.

***Table H.2***

*DT50 for hydrolysis at various pH for a hypothetical substance with known DT50 of twelve days at pH=4, 1.2 days at pH=7 and 0.01 days at pH=9.*

| pH | DT50 (d) |
|---|---|
| 4 | 12 (known) |
| 7 | 1.2 (known) |
| 9 | 0.01 (known) |
| 7.67 | 0.25 (estimated |

The DT50 at pH = 7.67 was estimated from known DT50's at pH 4, 7 and 9 using the procedure and equations outlined in Annex D.

Remaining fraction of the substance after an 8 h period at pH = 7.0: 0.825
Remaining fraction of the substance after an 8 h period at pH = 9.0: $9.24\ 10^{-11}$
Remaining fraction of the substance after an 8 h period at pH = 7.67: 0.397

After two consecutive periods of time, 16 h at pH=7 and 8 h at pH = 9, the remaining fraction of the substance would be $0.825 * 0.825 * 9.24\ 10^{-11} = 6.3\ 10^{-11}$.

If the calculations had assumed that the average pH (7.67) would have been applicable for the full 24 h period, the remaining fraction of the substance would have been 0.397 * 0.397 * 0.397 = 0.06.

Accounting for periods with higher than average pH thus results in faster degradation over the 24 h period and hence to a lower remaining amount of material.

# Annex G Estimation of water temperatures from air temperatures

In order to test whether water temperatures can be estimated sufficiently accurate on the basis of air temperatures, both the SWAT and the PFAM temperature estimates were calculated on the basis of air temperatures, by using either a linear transformation:

$$T_{water} = 5.0 + 0.75 T_{av} \qquad \text{(SWAT)}$$

or by using the backward 30-day average as an estimate of temperature:

$$T_{water,dayi} = \frac{1}{30} \sum_{x=i-29}^{x=i} T_{air,x} \qquad \text{(PFAM)}$$

Scatter plots of measured water temperature in ditch 18 against measured air temperature (Figure I.1, SWAT estimated water temperature (Figure I.2) and PFAM estimated water temperature (Figure I.3) are given below.

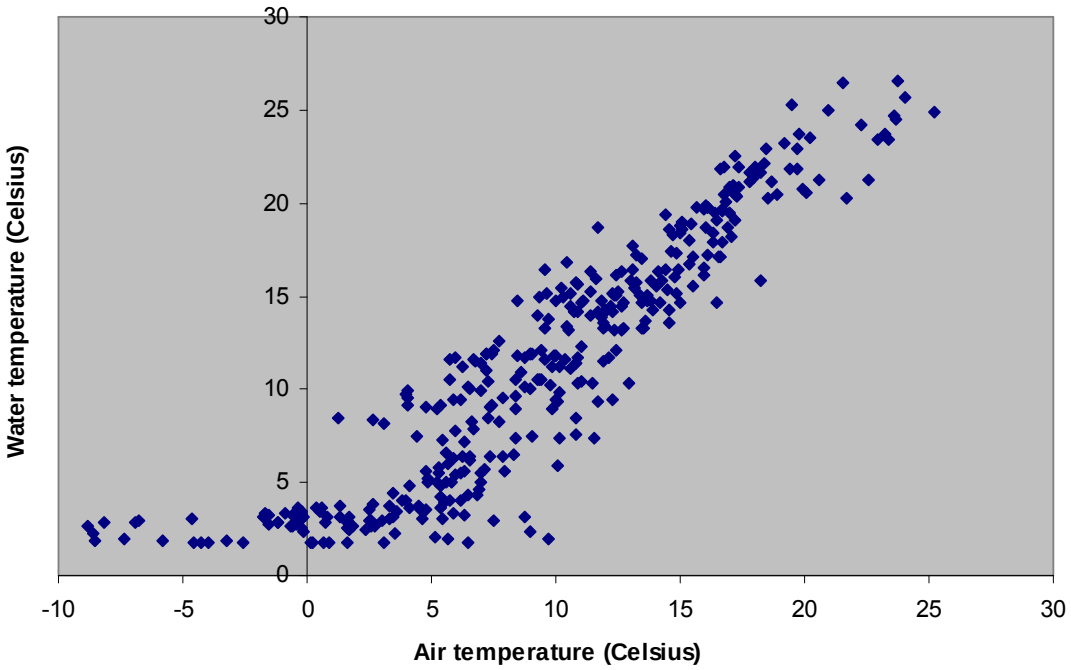



***Figure I.1***

*Water temperature in ditch 18 versus air temperature.*

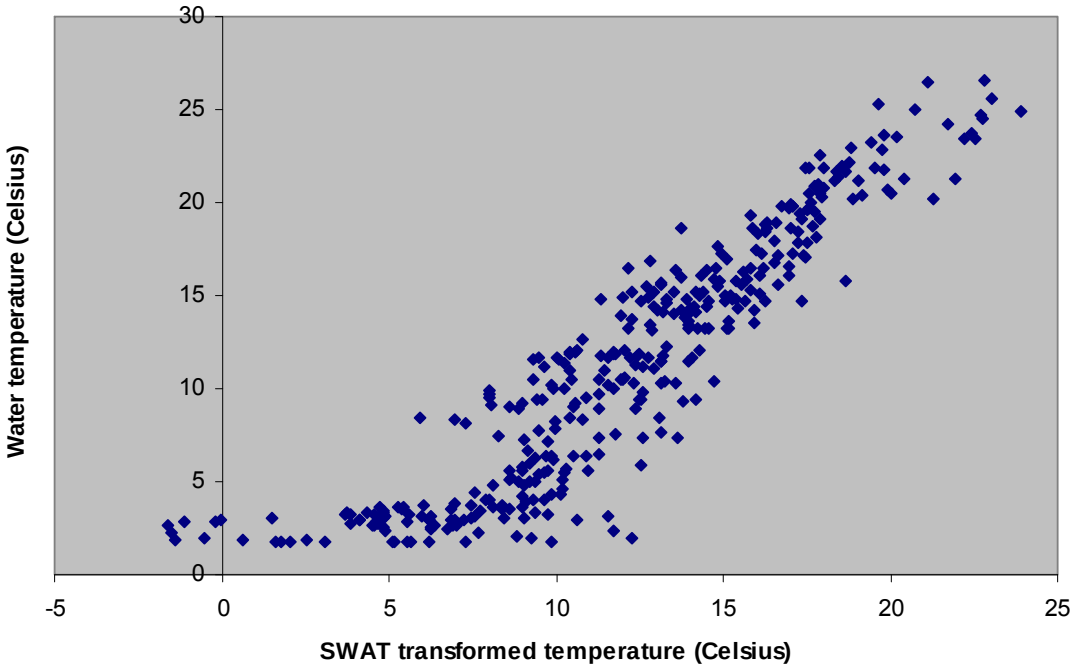



***Figure I.2***

*Water temperature in ditch 18 versus temperature estimated using the SWAT equation.*

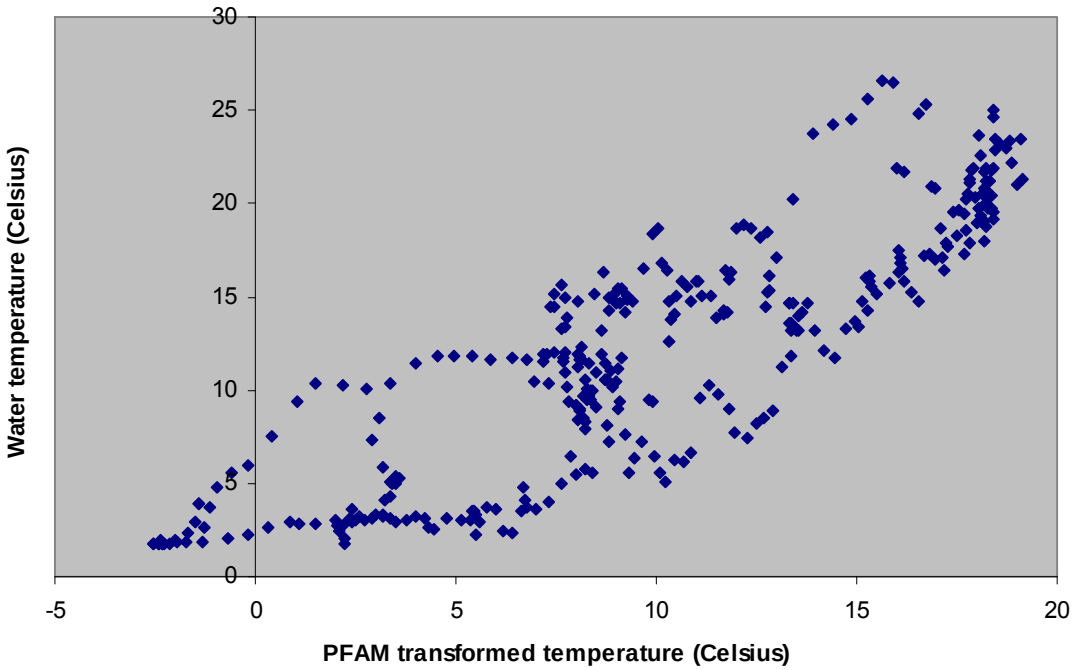



***Figure I.3***

*Water temperature in ditch 18 versus temperature estimated using the PFAM equation*

The predictive power of each conversion was tested through linear regression of the (daily average) water temperatures measured in ditch 18 against the water temperatures calculated by each of the equations, forcing a zero intercept. For reference, measured water temperatures were also regressed against the untransformed air temperature. All regressions were of the form Y = A*X (forcing a zero intercept) or Y = A * X + B, where Y was the measured water temperature in ditch 18 and X was either the air temperature or the water temperature estimated through the SWAT or PFAM conversion equation. Results are given in Table I.1 and I.2 for zero intercept and non-zero intercept resp.

***Table I.1***

*Linear regression of water temperature in ditch 18 against air temperature or SWAT/PFAM estimated water temperatures forcing zero intercept.*

| Temperature used for regression | Slope | $R^2$ | Standard error of estimate | Degrees of freedom |
|---|---|---|---|---|
| Untransformed | 1.114 ± 0.014 | 0.945 | 3.08 | 365 |
| SWAT water temp | 0.986 ± 0.012 | 0.949 | 2.97 | 365 |
| PFAM water temp | 1.568 ± 0.017 | 0.935 | 3.49 | 336 |

PFAM converted temperatures were available from day 30 onward, resulting in a slightly smaller number of data points being used in the regressions.

The use of SWAT converted temperatures results in a slightly better coefficient of variance ($R^2$) and smaller standard error of estimate than the use of untransformed air temperature data. Using PFAM converted air temperature values does not noticeably improve the relationship between measured water and air temperatures.

***Table I.2***

*Linear regression of water temperature in ditch 18 against air temperature or SWAT/PFAM estimated water temperatures, allowing non-zero intercept.*

| Temperature used for regression | Slope | Intercept | $R^2$ | Standard error of estimate | Degrees of freedom |
|---|---|---|---|---|---|
| Untransformed | 0.923 ± 0.021 | 2.70 ± 0.25 | 0.842 | 2.66 | 365 |
| SWAT water temp | 1.230 ± 0.028 | -3.45 ± 0.36 | 0.842 | 2.66 | 365 |
| PFAM water temp | 0.966 ± 0.03 | 2.55 ± 0.30 | 0.759 | 3.24 | 336 |

From Figures I.1 - I.3 the relatively low coefficient of correlation between air and water temperatures appears to be partly due to the fact that measured water temperatures do not decrease below approx. 3 °C, causing a non-linearity in the fitted relationships which starts to become apparent at water temperatures of approx. 4 °C. Removing water temperatures below 4 °C from the regression, the relationship between measured water temperature and air temperature becomes slightly better (Table I.3).

***Table I.3***

*Linear regression of water temperature in ditch 18 against air temperature or SWAT/PFAM estimated water temperatures, allowing non-zero intercept and excluding water temperatures below 4 °C.*

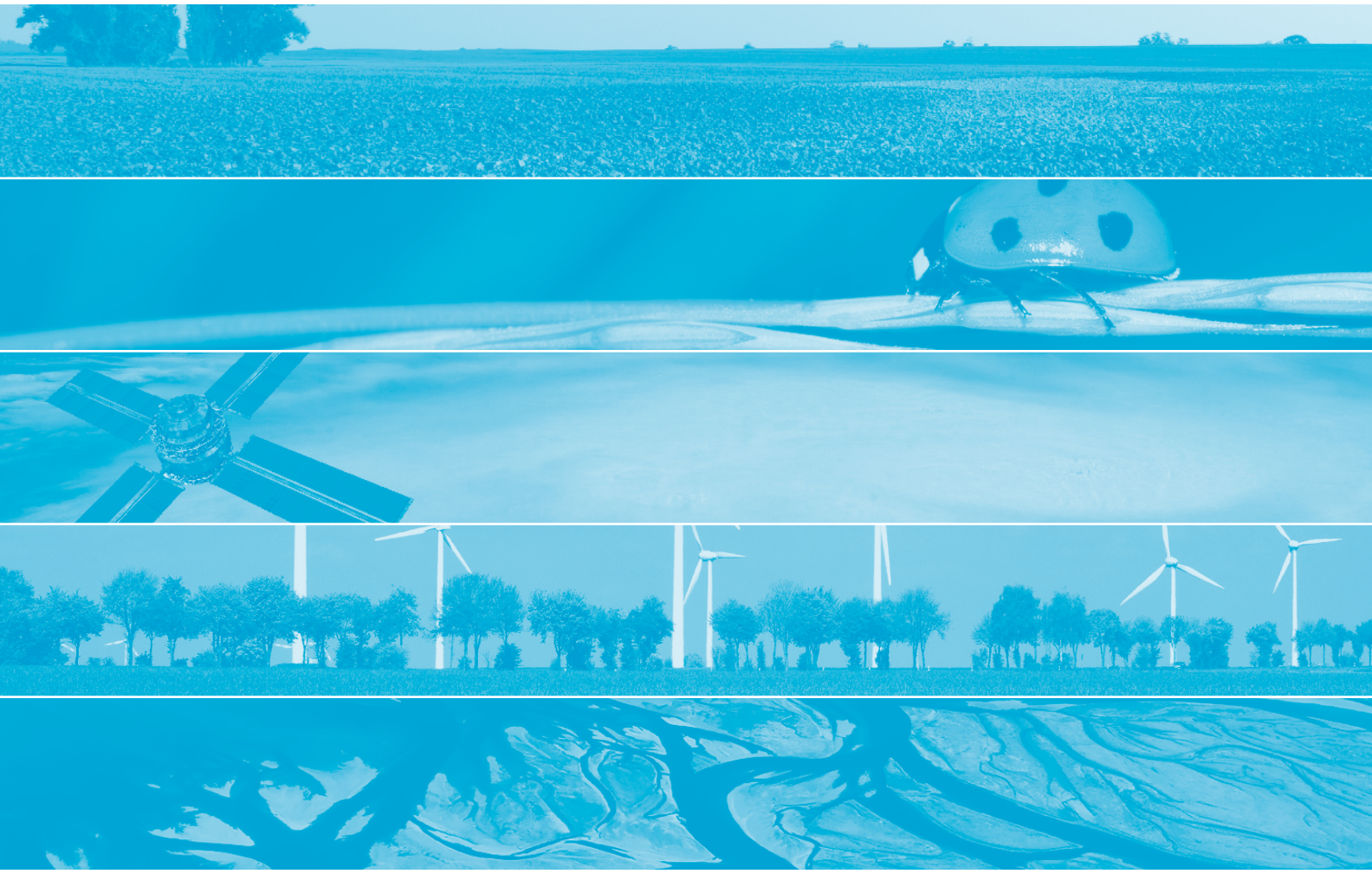
| Temperature used for regression | Slope | Intercept | $R^2$ | Standard error of estimate | Degrees of freedom |
|---|---|---|---|---|---|
| Untransformed | 1.01 ± 0.03 | 1.85 0.35 | 0.835 | 2.21 | 281 |
| SWAT water temp | 1.35 ± 0.04 | -4.9 ± 0.5 | 0.835 | 2.21 | 281 |
| PFAM water temp | 0.97 ± 0.06 | 2.7 ± 0.8 | 0.569 | 3.30 | 230 |

Obviously, the PFAM estimate of water temperature is not very well suited to estimate measured water temperatures in the ditch, which is surprising since the PFAM temperature estimate was devised for stagnant (rice paddy) systems. The relationship between measured water and (untransformed) air temperatures results in an error of estimate in the estimated water temperature of 2.2 °C, and appears to be the best variable to estimate water temperature (for water temperatures above 4 °C).

$$T_{water} = 1.85 + 1.01 * T_{air}$$

where $T_{av}$ is the average air temperature, and $T_{water}$ is the estimated daily water temperature.

This equation can be used to derive a monthly average water temperature from an monthly average air temperature. This equation is very similar to the SWAT transformation of air into water temperature, although the coefficients of slope and intercept are slightly different. It can be used to estimate water temperatures from daily average air temperature, from air temperatures of at least 2.1 °C and higher. For lower air temperatures a constant water temperature of 2.82 °C can be assumed (main water temperature in ditch 18 when the air temperature was below 2.1 °C).



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