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Rationale of a new parameterization for TOXSWA

C.M.J. Jacobs and P.I. Adriaanse

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Abstract

In the TOXSWA (TOXic substances in Surface WAters) model volatilization of pesticides from surface water is computed because it may be an important component of the mass balance of pesticides in water bodies. Here, we briefly review the physics of air-water gas exchange relevant in this context. A new parameterization of volatilization is proposed. This new TOXSWA parameterization would take into account key physical aspects of the air-water gas exchange process, while still fitting into the TOXSWA philosophy. It is recommended to cast the new parameterization into a micrometeorological framework, based on two atmospheric resistances and one aqueous resistance against gas transport. In this context, the dimensionless Henry coefficient is a crucial characteristic of the pesticides and determines whether atmospheric properties as modelled by the atmospheric resistances exert the main dynamic control on air-water gas exchange or the aqueous properties and resistance. Most pesticides will be subject to atmospherically controlled volatilization.

Keywords: TOXSWA, pesticides, volatilization, air-water gas exchange.

Alterra Report 2316
Wageningen, May 2012

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Summary

The TOXSWA (TOXic substances in Surface WAters) model has been developed to describe the behaviour of pesticides in small surface waters and to estimate their concentration as a function of time. Volatilization of pesticides from the surface waters may be an important loss term in the mass balance of pesticides in water bodies and is therefore an important component of the TOXSWA model. The present parameterization of the volatilization process in TOXSWA follows the concept of the so-called stagnant film model. It does not take into account the impact of weather on the volatilization process. Moreover, the influence of the hydrodynamic conditions in the water, also partly influenced by the weather, is not taken into account.

Here, we propose a new parameterization to compute volatilization with the TOXSWA model. Although the physics of air-water gas exchange, including volatilization, is quite complicated and contains many uncertainties relatively simple adjustments within the present TOXSWA framework can be made to significantly improve upon the present TOXSWA parameterization of volatilization. It can easily be extended to include a more detailed description of relevant processes if future new TOXSWA developments require doing so. The new parameterization proposed here fits well into the 'bulk' approach of TOXSWA, which assumes vertically well-mixed water bodies. It is recommended to cast the new parameterization in a micrometeorological framework, based upon two atmospheric resistances and one aqueous resistance against gas transport. Generally, the meteorological information required to use the proposed parameterization is readily available. It will also fit smoothly in the envisaged new temperature simulation algorithm in TOXSWA.

The dimensionless Henry coefficient k_h is a crucial characteristic of the pesticides. Broadly, depending on its value the dynamic control on gas exchange of a pesticide is either exerted by atmospheric properties (in case of low k_h) or by the properties of the water (in case of high k_h). It is shown that most pesticides are subject to atmospheric control, so that atmospheric resistance to diffusion controls volatilization. For very low values of k_h ($< 10^{-7}$) the volatilization rate is so slow (with volatilization half-life times[1] of tens to hundreds of years) that in practice pesticide loss from water bodies will be dominated by processes other than volatilization, such as biological or chemical degradation. On the other hand, in a few exceptional cases k_h is sufficiently large ($>10^{-2}$) to allow very fast volatilization (volatilization half-life times of less than a day), in the water-controlled regime.

The distribution of k_h-values among the pesticides currently applied suggests that for the problem of volatilization of pesticides from water bodies a simple but reasonable description of the aqueous resistance would give acceptable results. This is the case if $k_h < {\sim}10^{-4}$, which applies to ${\sim}85\%$ of the pesticides. Thus, it would be justifiable to put more effort in improving the parameterization of the atmospheric resistances than in improving the aqueous resistance parameterization. For the much smaller group of pesticides with $k_h > {\sim}10^{-2}$ the reverse is true. An improved parameterization of the volatilization will be most effective for pesticides with k_h-values between 10^{-6} and 10^{-3}. Pesticides with k_h-values in this range are either in the intermediate regime where atmospheric resistance and water resistance are of a similar order of magnitude (${\sim}10^{-4} < k_h < {\sim}10^{-2}$) or in the atmospherically controlled regime but with still relatively fast volatilization rates (up to tens of days, for ${\sim}10^{-6}$ $k_h < {\sim}10^{-4}$).

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[1] We define the volatilization half-life time as the time needed to volatilize half of the pesticide mass from a water body in the absence of any other mass loss term, and with an atmospheric pesticide concentration of zero.

1 Introduction

1.1 Problem definition

The TOXSWA (TOXic substances in Surface WAters) model has been developed to describe the behaviour of pesticides in small surface waters and to estimate their concentration as a function of time. Volatilization of pesticides from the surface waters may be an important loss term in the mass balance of pesticides and is therefore an important component of TOXSWA model (Adriaanse, 1996; Westein et al., 1998).

The present parameterization of the volatilization process in TOXSWA dates back to the early seventies, when Liss and Slater (1974) formulated their so-called stagnant film model. In the meantime, a lot of research has been performed into air-water gas exchange (see e.g., Wanninkhof et al., 2009). Moreover, the present implementation of the volatilization parameterization does not allow influences of weather and conditions in the water to be accounted for. This may be a serious shortcoming, since water bodies in the open air are actually influenced by the weather conditions that are known to influence gas exchange across the air-water interface.

Thus, the question arises as to whether the parameterization of TOXSWA is still up-to-date from a physical knowledge point-of-view. Furthermore, it is felt that it may be necessary to include in a new parameterization the possibility to account for the impact of weather on the volatilization. It is timely to do so, because a new parameterization for the simulation of water temperature is underway (Jacobs et al., 2010) and it is felt that a new parameterization of the volatilization process should benefit from that development.

1.2 Goal

The main goal of the present report is provide a short review of the present knowledge on air-water gas exchange and to suggest improvements of the algorithm in TOXSWA that computes the volatilization of pesticides from small surface waters.

1.3 Scope

The TOXSWA model was initially developed to describe the behaviour of pesticides in ditches with slowly moving water in The Netherlands. Extensions to simulate small streams and ponds with variable water levels and discharges were included later on. The main use of the current FOCUS_TOXSWA_2.2.1 model concerns the aquatic risk assessment for the registration procedure of pesticides at EU level. So, with respect to geographic extent the TOXSWA model is mainly applied in Europe. However, applications outside Europe, for example, in China, are at present being developed.

The new volatilization algorithm should be able to simulate volatilization from small water bodies at hourly to seasonal timescales. Improvements should take into account knowledge gained in air-water gas exchange over the past decades. Nevertheless, the new algorithm must be as simple as possible and easy to implement in the existing TOXSWA environment. Preferably, it should benefit from the algorithms that will be designed to improve the air temperature estimates (Jacobs et al., 2010). Data used to drive the model must be readily available.

We will aim to implement a one-dimensional description of air-water gas exchange, that is, a description of vertical exchange processes. This can be done by selecting a physical framework that envisages air-water gas fluxes as an exchange between two well-mixed layers, one in the air and one in the water, where turbulence dominates transport and mixing. These layers are separated by two so-called quasi-laminar layers aligned at the air-water interface. Again, one layer is located in the air and one in the water. In these layers, molecular diffusion plays an important role. However, in contrast to fully laminar layers, sometimes called stagnant film layers, some influence of turbulence is allowed as well. The short review provided in this report will focus on the use of this concept, which appears to be a widely used concept to describe air-water gas exchange.

The proposed concept corresponds well with the 'bulk' approach of TOXSWA, which assumes vertically well-mixed water bodies (Adriaanse, 1996; Adriaanse and Beltman, 2009). It also fits well into the envisaged new temperature calculation algorithm for TOXSWA (Jacobs et al., 2010). It can be viewed as an extension of the existing volatilization parameterization (Beltman and Adriaanse, 1999) and is well in line with the research on air-water gas exchange that has been performed in the past few decades (e.g. Wanninkhof et al., 2009). Although the proposed simple parameterization necessarily excludes many details of air-water gas exchange, it will be able to capture the main features of air-water gas exchange dynamics. Moreover, it can easily be extended to include more detailed descriptions if future new TOXSWA developments require doing so.

1.4   Structure of the report

The remainder of the report is structured as follows. Chapter 2 briefly reviews the physical concept underlying air-water gas exchange. In the case of pesticides it is sometimes convenient to distinguish two differing regimes: the air-controlled regime, where gas exchange is most sensitive to atmospheric processes and the water-controlled regime where the conditions in the water are more important. The regimes follow directly from the physical framework discussed in Chapter 2 and are therefore discussed in that chapter as well. It will appear convenient to cast the parameterizations in a so-called micrometeorological framework, using a so-called resistance approach. In Chapter 3, this micrometeorological framework is discussed in some detail and it is also compared with the present TOXSWA parameterization for volatilization. Next, in Chapter 4 some sample calculations are presented. Finally conclusions and recommendations are provided in Chapter 5.

2   Theory of volatilization

## 2.1   Basic theoretical framework of air-water gas exchange

Gas exchange across an air-water interface is driven by the gradient of the chemical potential of a substance across the air-water interface. For very precise calculations, the chemical potential gradient should be expressed in terms of fugacity or activity. However, for practical purposes, it is convenient and usually sufficiently accurate to assume ideal behaviour of the pesticide in the gas phase as well as in the solution, which allows expressing this gradient in terms of concentration in the air and water phase, respectively, taking into account the solubility of the gaseous substance. This can be done in various ways, but here we choose to proceed by invoking Henry's law and defining the dimensionless Henry coefficient as:

$$k_h \equiv C_a / C_w \qquad (1)$$

where C_a [kg m^{-3}] is the atmospheric concentration of a gaseous component, and C_w [kg m^{-3}] its equilibrium concentration in water.

The dimensionless Henry coefficient $k_h = H/RT$ with $H =$ [Pa m^3 mol^{-1}] the Henry coefficient, R the universal gas constant (8.314 Pa m^3 mol^{-1} K^{-1}) and T [K] the absolute temperature. It its turn, in this definition of Henry's law, $H \equiv p_x / C_{sol}$ with p_x [Pa] the partial vapour pressure of compound 'X' over the solution, and C_{sol} [mol m^{-3}] the solubility of X in water. In general compounds with low k_h will readily dissolve in water, although the vapour pressure of the compound is contained in k_h as well.

Figure 1 schematically depicts the theoretical framework that is generally used to describe gas exchange across water surfaces. Henry's law (1) is assumed to apply at the interface, so that $k_h C_{w,i} = C_{a,i}$ where the index 'i' is used to denote the interface. The concentration jump at the interface therefore depends on k_h and thus on the solubility and the vapour pressure of the compound being considered.
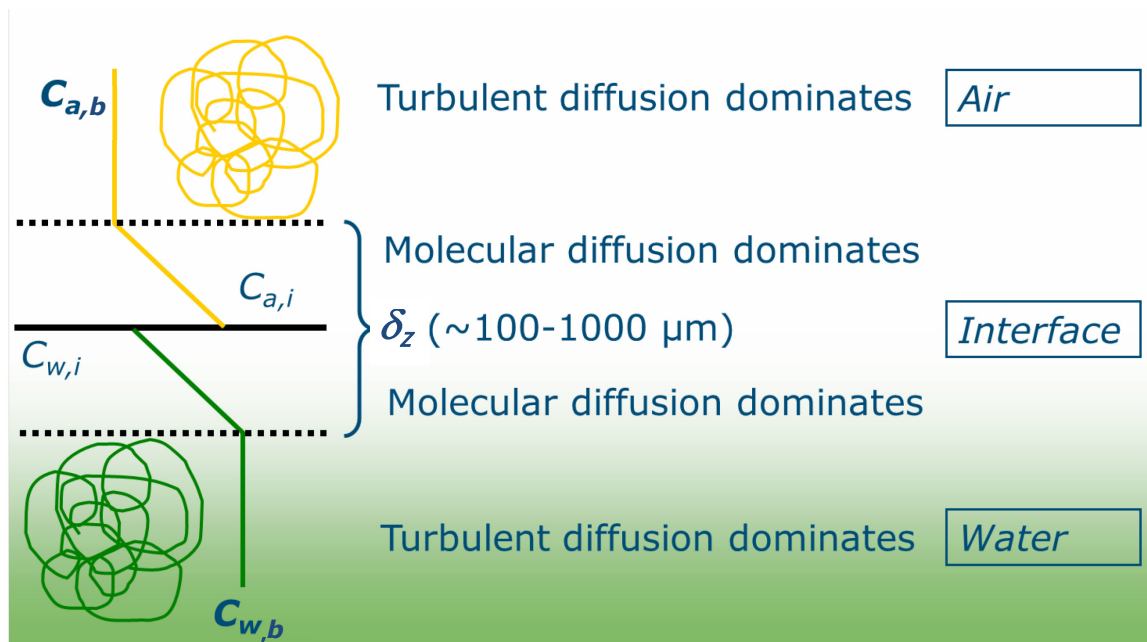
Figure 1
Conceptual view of air-water gas exchange. See the main text for an explanation.

Dynamic control is exerted on the gas exchange by the interplay of molecular and turbulent diffusion around and across the air-water interface (e.g., Donelan and Wanninkhof, 2002; Frost and Upstill-Goddard, 1999; Jähne and Haußecker, 1998; Wanninkhof et al., 2009). In the layers adjacent to the interface, molecular diffusion may dominate the transport process, while somewhat further away turbulence dominates.

The layers where molecular diffusion dominates will henceforth be called 'laminar layers.' The depth of the laminar layer at either side of the interface is typically about 100-1000 µm. In these layers, at a given concentration gradient, the molecular diffusion coefficient D_x [m^2 s^{-1}] controls the diffusion process. In the case of completely stagnant laminar layers, without the effect of turbulence, the diffusion would be linearly related to D_x. However, at natural air-water interfaces stagnant layers do rarely occur -if ever- and to some extent turbulence has an impact on the diffusion process in the laminar layers as well. As will be explained later in Section 2.3.1, this impact of turbulence has important consequences for the role of D_x in the diffusion process and hence for the parameterization and theoretical treatment of diffusion across air-water interface.

Turbulent transport and mixing is much more efficient than molecular diffusion. Thus, in the turbulent layers, which will henceforth be called 'bulk layers,' turbulent diffusion completely controls the transport and mixing processes and molecular diffusion may be neglected. That is, D_x plays no role anymore in the bulk layers. As an additional consequence it may be assumed that the bulk layers are well mixed, so that the concentration gradients are confined to the laminar layers. In combination with a completely stagnant laminar layer, this then leads to the so-called stagnant-film model, proposed by Liss and Slater (1974) and implemented in the present version of TOXSWA.

In Figure 1, the concentrations in the bulk layers are denoted with an extra subscript 'b'. Concentration gradients in the bulk layers exist in reality, but do not fundamentally affect the theoretical description of air-water gas exchange. Although such gradients may affect the interpretation of gas exchange observations in the field (Jacobs et al., 2002), they can easily be included in the theoretical framework described here (see next Section).

For some compounds the effect of chemical reactions in the water should be taken into account as well. The framework used here can in principal be extended to describe the effect of such reactions on gas exchange (e.g., Wanninkhof et al., 2009). Chemical reactions can be modelled explicitly (see Jacobs et al., 2002, for an example on the air-water exchange of CO_2). Another option is to determine k_h in (1) as an effective Henry coefficient, which implicitly includes chemical reactions. However, when considering volatilization of pesticides at sub-daily timescales effects of chemical reactions are generally of minor importance. Therefore, we will henceforth ignore such reactions for simplicity.

2.2   General description of air-water gas exchange

Within the theoretical framework sketched above, the flux F [kg m^{-2} s^{-1}, defined positive upward here[2]] across the interface can conveniently be described by analogy with Ohm's law: the flux ('current') is proportional to the concentration difference ('potential difference') with conductance or inverse resistance as the constant of proportionality. The resistance approach is illustrated in Figure 2.

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[2] This is according to micrometeorological convention. Note that in TOXSWA upward fluxes are defined negative.

Concentration differences and resistances are evaluated across the laminar layer, between the air-water interface and the well-mixed bulk layer. This can be done either in the air (see the left hand side of Figure 2), in which case

$$F = \frac{C_{a,i} - C_{a,b}}{r_g} = k_g(C_{a,i} - C_{a,b})$$ (2a),

or in the water, so that

$$F = \frac{C_{w,b} - C_{w,i}}{r_w} = k_w(C_{w,b} - C_{w,i})$$ (2b)

In (2a) r_g [s m^{-1}] denotes a transport resistance in the gaseous phase (air) and in (2b) r_w [s m^{-1}] is a transport resistance in the water phase. Their inverse, $1/r_g = k_g$ and $1/r_w = k_w$ are conductances or so-called transfer coefficients [m s^{-1}]. In particular k_w has been the subject of extensive research in the past decades (see the various aforementioned reviews). This quantity is often called the 'piston velocity.'

Since F is continuous across the air-water interface, F from (2a) must equal F from (2b). Therefore, upon invoking Henry's law according to (1) at the interface, it can be shown that

$$F = \frac{k_h C_{w,b} - C_{a,b}}{r_g + k_h r_w}$$ (3a)

or alternatively,

$$F = \frac{C_{w,b} - C_{a,b}/k_h}{r_g/k_h + r_w}$$ (3b)

Equations (3a) and (3b) are of course fully consistent. Depending on the problem, either form can be chosen. It is often convenient to consider surface fluxes in a micrometeorological framework that allows evaluating the resistances from readily available meteorological observations. From that perspective it appears to be slightly more convenient to use (3a) instead of (3b). We will do so in the present context as well.
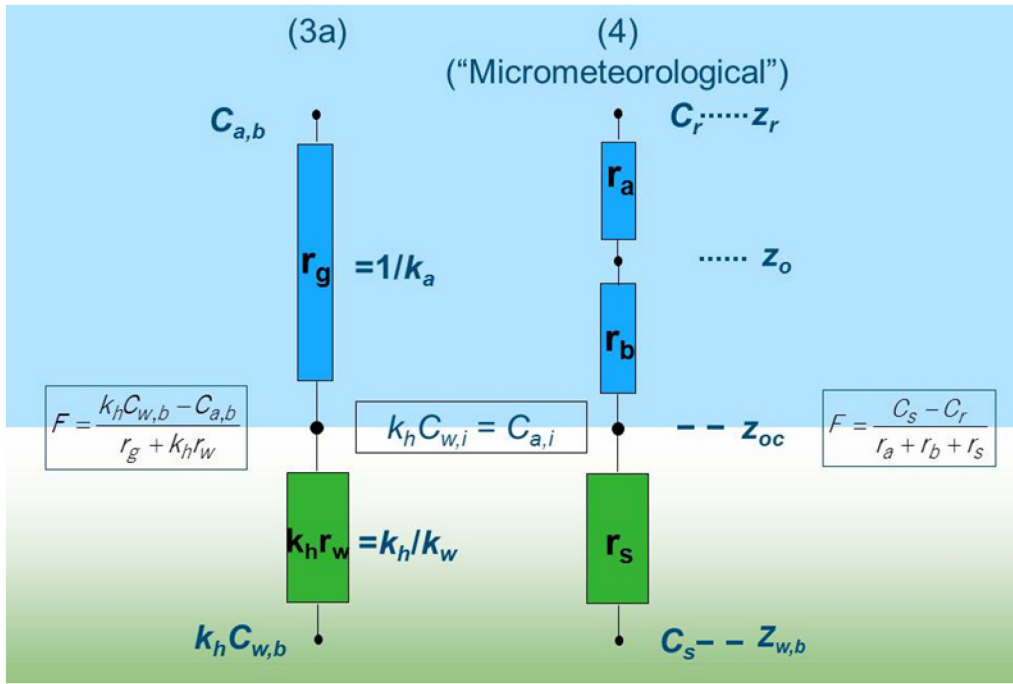
Figure 2

Comparison of Equation (3a) (left) and (4) (right) in terms of resistances and concentration difference. In the framework of (3a) the air-water interface is located at the internode between resistance r_g and $k_h r_w$. The concentration and resistance in the water follow from the definition of Henry's law by Eq. (1), which implies that at the interface $k_h C_{w,i} = C_{a,I}$ and which converts the concentration and resistances to atmospheric equivalents. Equation (4) represents the micrometeorological concept. The air-water interface is then located at z_{oc}, which can also be interpreted as an effective source or sink height of the compound. The height z_0 is the aerodynamic roughness length. It can be seen that (3a) and (4) are fully equivalent if $r_g \equiv r_a + r_b$, $r_s \equiv k_h r_w$, $C_r \equiv C_{a,b}$ and $C_s \equiv k_h C_{w,b}$.

A general micrometeorological description of the surface flux F (deposition or volatilization) of any compound is given by (see the right hand side of Figure 2 for illustration):

$$F = \frac{C_s - C_r}{r_a + r_b + r_s} \qquad (4)$$

Here, C_r [kg m^{-3}] is the concentration at a reference level in the atmosphere and C_s [kg m^{-3}] is a surface concentration to be defined later. Resistance r_a [s m^{-1}] is the aerodynamic resistance in the atmospheric layer between a reference level at height z_r [m] in the atmosphere and aerodynamic roughness length[3] z_0 [m]. It is a measure of the ability of turbulent eddies to mix the atmosphere between z_r and z_0 and therefore for the rate at which turbulent transport proceeds. Resistance r_b [s m^{-1}] is the resistance in the layer between z_0 and the roughness length for scalars, z_{0c} [m]. The latter height is usually interpreted as the effective or apparent source or sink height of the scalar under consideration. In the present context, it may also be interpreted as a virtual location of the air-water interface. Resistance r_b is a measure of mixing and transport in the atmospheric laminar boundary layer, in which molecular diffusion and turbulent transport may both be noticeable. Surface

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[3] The aerodynamic roughness length is the height where the wind speed becomes zero upon downward extrapolation of the wind speed profile in the lower atmosphere. It is generally related to the roughness of a surface.

resistance r_s [s m^{-1}] is used to describe the mixing and transport across the quasi-laminar layer, which is the result of water-atmosphere interactions as well as hydrodynamic processes. The parameterization of these various resistances is at the heart of the parameterization of volatilization and will be discussed extensively in the sections below.

Figure 2 also schematically compares Equation (3a) and (4). It can be seen that these equations are fully consistent if we define (cf. Asman et al., 2003):

1. $C_r \equiv C_{a,b}$
2. $r_a + r_b \equiv r_g\ (=1/(k_g))$
3. $C_s \equiv k_h C_{w,b}$
4. $r_s \equiv k_h r_w\ (=k_h/k_w)$

It should be noted that definitions 1-2 imply a slight concentration gradient in the layer between z_0 and z_r.

The main advantage of using Equation (4) with Definitions 1-4 is that standard meteorological variables and measurable quantities can now be used to compute the fluxes. Resistance r_a is readily derived from micrometeorological theory. Theories to describe r_b are available as well, although the uncertainties are larger than in the case of r_a. As will be explained later, even r_s can be parameterized in terms of meteorological quantities. However, the uncertainty in r_s is quite large.

By virtue of Definitions 1-4 in the micrometeorological context, the interfacial concentrations become implicit in the description of the flux. The flux can then be cast in terms of the bulk concentrations. Therefore, we henceforth drop the indices 'b' (and 'l') and write

$$ F = \frac{k_h C_w - C_a}{r_a + r_b + k_h r_w} \tag{5} $$

The flux defined by Equation (5) is valid for downward fluxes (or deposition) as well as upward fluxes (or volatilization). The difference C_w - C_a determines the flux direction. Note that upward fluxes are defined positive[2] by virtue of (5).

2.3 Air-controlled versus water-controlled gas exchange

Although the theory described in the previous section is generally applicable, provided chemical reactions may be ignored or are incorporated implicitly in k_h, it is useful to distinguish the following two regimes in air-water gas exchange:

1. The water-controlled regime: the main control of the gas exchange is exerted by processes and properties in the water.
2. The air-controlled regime: the main control of the gas exchange is exerted by processes and properties in the air.

From Equations 3a and 4 it can be seen that the first regime is in place if $k_h r_w >> r_g$ or $r_s >> r_a + r_b$. Then, changes in the atmospheric resistances hardly affect the flux. Thus, the main resistance or kinetic control is at the water side. The second regime is in place if $k_h r_w << r_g$ or $r_s << r_a + r_b$. In that case, variations in the resistance at the water side will hardly be noticeable. Thus, the main control over the gas exchange is located at the atmospheric side. Taking $r_s = 0$ s m^{-1} is a reasonable assumption in that regime.

The order of magnitude of $r_a + r_b$, and therefore r_g, is typically 100 s m^{-1}, with a range extending from ~10 s m^{-1} to ~1000 s m^{-1}, depending on the surface characteristics and the weather conditions. In contrast, r_s varies over many orders of magnitude. This is mainly because of the impact on r_s of k_h that ranges from values down to 10^{-14} for some pesticides (Westein et al., 1998; Asman et al., 2003), up to 100 and more for some atmospheric constituents and tracers like sulphur-hexafluoride (SF$_6$; Wanninkhof et al., 2009). Consequently, k_h of a gaseous substance determines whether the main control is at the water side or at the air side of the air-water interface (e.g., Donelan and Wanninkhof, 2002; Liss and Slater, 1974; Wanninkhof et al., 2009). Although k_h is determined both by the solubility and the vapour pressure, readily soluble compounds are found to have small values of k_h so that in practice the gas-exchange regime is to a large extent determined by solubility. Obviously, the two regimes are not strictly separated since there will be compounds for which r_s will be of the same order of magnitude as $r_a + r_b$ or r_g.

The impact of k_h on r_s and on the control of air-water gas exchange is illustrated in Figure 3. The figure shows resistance r_s and the ratio $(r_a+r_b)/r_s$ as a function of k_h for $r_w = 4.65 \cdot 10^4$ s m^{-1} (we will show in Section 3.3.2 that this value is appropriate for a wind speed of 6-7 m s^{-1} at a height of 2m) and $r_a + r_b = 100$ s m^{-1}. For $k_h < 1 \cdot 10^4$, $r_s < 10$ s m^{-1} and therefore becomes less than the atmospheric resistance by more than a factor of 10. As k_h becomes smaller than $1 \cdot 10^5$, $r_s < 1$ s m^{-1} and $r_s = 0$ will be a reasonable approximation. For values of k_h smaller than ~10^4 variations in r_s (or k_w) will hardly influence the gas exchange and the atmospheric resistances r_a and r_b become much more important. On the other hand, if $k_h > ~10^{-2}$, the atmospheric resistances become smaller than r_s by more than a factor of 10. Then, the gas exchange becomes very sensitive to r_s and rather insensitive to the atmospheric resistances.
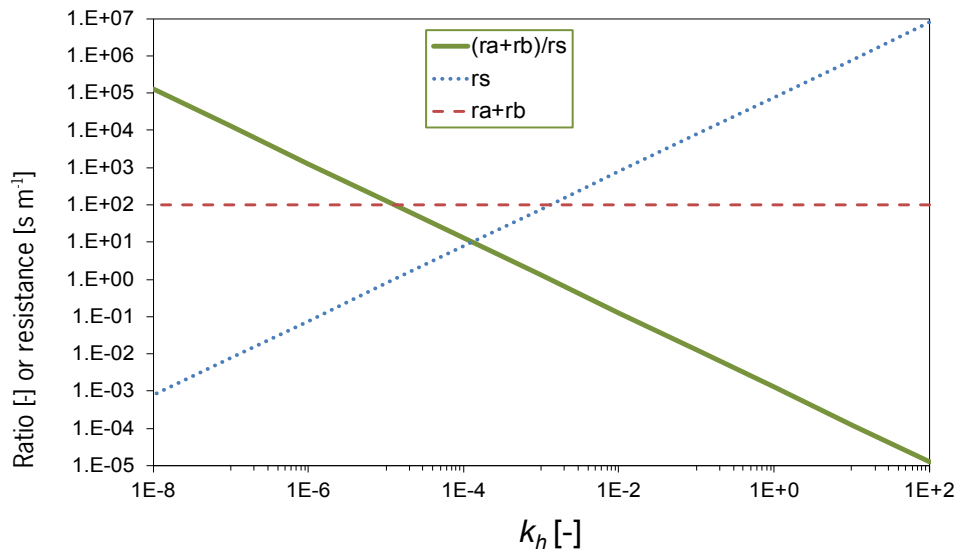
Figure 3

Resistances r_s, r_a+r_b and ratio $(r_a+r_b)/r_s$ as a function of dimensionless Henry coefficient k_h. Resistance r_w, used to compute r_s, is taken equal to $4.65 \cdot 10^4$ s m^{-1}.

2.4 Volatilization speed and volatilization half-life time

To further explore the impact of k_h and illustrate the behaviour of gas exchange in the two regimes we use a simple analytical solution to describe concentration changes in the water due to volatilization. Assuming C_a to be small enough to be considered zero (that is, we take $C_a=0$) and assuming that volatilization is the only sink term in a well-mixed water body, changes in C_w will be given by

$$\frac{dC_w}{dt} = \frac{1}{h} \cdot \frac{-k_h C_w}{r_a + r_b + k_h r_w} ,$$

from which we obtain

$$C_w(t) = C_w(0) \exp\left(-\frac{1}{h} \frac{k_h}{r_a + r_b + k_h r_w} t \right) \tag{6}$$

Here, h [m] is the depth of the well-mixed water layer and t [s] is time. Assuming the absence of any source of compound X, volatilization half-life times ($t_{0.5,V}$ [s]) are defined by $C_w(t_{0.5,V})/C_w(0) = 0.5$. That is, $t_{0.5,V}$ is the time after which half of the mass of the compound will have escaped from the water by volatilization. This is a convenient way to express the speed of volatilization in various conditions, and to allow comparison with other half-life times, such as chemical degradation half-life times.

Table 1 and Figure 4 show computed values of $t_{0.5,V}$, obtained from Eq. (6). In the calculations, mixed water depth (h), wind speed at $z_r = 10$ m (U) and atmospheric resistance (r_a+r_b) are varied independently. Wind speed U affects r_w, taking $1/r_w = k_w = 8.6 \cdot 10^{-7} U^2$ (Wanninkhof, 1992). Thus, we assume a strong quadratic dependence of k_w on wind speed, which has often been observed over oceans and seas (see, e.g., Wanninkhof et al., 2009). Note that in reality, r_a as well as r_b depend on U, but the independent variation applied here better serves our goal of illustration. The calculations are performed for $h = 0.2$, 0.5 or 1.0 m, $r_a+r_b = 40$, 100 or 200 s m^{-1} and $U = 2$, 5 or 10 m s^{-1}. In the results shown in Table 1 and Figure 4, $t_{0.5,V}$ is given in days. The regimes are explored for $10^{-8} < k_h < 10^2$.

Table 1.

Volatilization speed as a function of k_h for differing hypothetical conditions. The volatilization speed is expressed as the time needed for half of the mass to escape from a water body. This half-life time, $t_{0.5,V}$ is defined by taking $C_w(t_{0.5,V})/C_w(0)=0.5$ in Equation (6). It is given in days. The conditions assumed in the calculations are given in the top part of the table. Wind speed U is given at a height of 10 m.

h (m)	0.2	0.5	1.0	0.5	0.5	0.5	0.5	0.5	0.5
U (m s^{-1})	5	5	5	2	5	10	5	5	5
r_w (s m^{-1})	46452	46452	46452	290323	46452	11613	46452	46452	46452
r_a+r_b (s m^{-1})	100	100	100	100	100	100	40	100	200
k_h	Half life time (days)								
1.0E-08	16045	40113	80226	40114	40113	40113	16045	40113	80226
1.0E-07	1605	4011	8023	4012	4011	4011	1605	4011	8023
1.0E-06	160.5	401.3	802.6	402.3	401.3	401.2	160.6	401.3	802.4
1.0E-05	16.1	40.3	80.6	41.3	40.3	40.2	16.2	40.3	80.4
1.0E-04	1.68	4.20	8.40	5.18	4.20	4.06	1.79	4.20	8.21
1.0E-03	0.23	0.59	1.17	1.57	0.59	0.45	0.35	0.59	0.99
1.0E-02	0.09	0.23	0.45	1.20	0.23	0.09	0.20	0.23	0.27
1.0E-01	0.08	0.19	0.38	1.17	0.19	0.05	0.19	0.19	0.19
1.0E+00	0.07	0.19	0.37	1.16	0.19	0.05	0.19	0.19	0.19
1.0E+01	0.07	0.19	0.37	1.16	0.19	0.05	0.19	0.19	0.19
1.0E+02	0.07	0.19	0.37	1.16	0.19	0.05	0.19	0.19	0.19
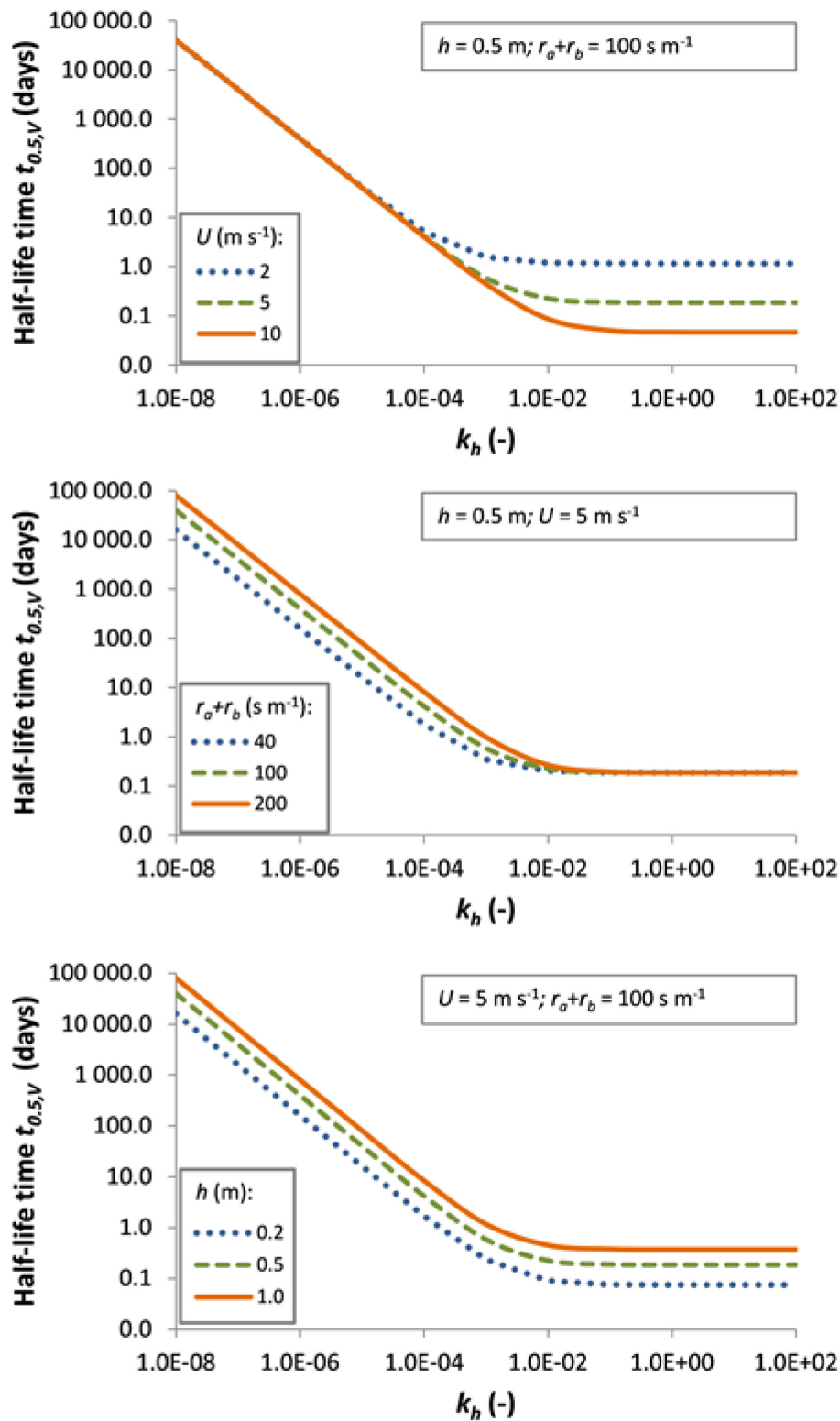
Figure 4

Volatilization speed as a function of k_h for differing hypothetical situations. The volatilization speed is expressed as the time needed for half of the mass to escape from a water body. This half-life time (in days) is defined by taking $C(t)/_w = 0.5$ in Equation (6). Upper panel: for varying wind speed at fixed water depth and atmospheric resistances; middle panel: for varying atmospheric resistances at fixed water depth and wind speed; lower panel: for varying water depth at fixed wind speed and atmospheric resistances. In all cases, the wind speed applies at a height of 10 m.

For the hypothetical conditions considered here, half-life times are found to vary between about 80000 days (or about 220 years) and 0.05 day (or slightly more than 1 hour). Low values of $t_{0.5,V}$ are obtained at the high values of k_h and U (implying lower values of r_w). Less soluble and more volatile compounds (high k_h) will readily escape to the atmosphere. The volatilization is further enhanced by a low resistance across the laminar layer at the water side, which is expected to occur at higher wind speed. On the other hand, high values of $t_{0.5,V}$ are found for low values of k_h and high values of the atmospheric resistance. Very soluble and less volatile compounds (low k_h) tend to remain in the water (or return to it once they are in the air). The concentration in the air near the surface, the equilibrium concentration, is extremely low. Concentration gradients are then virtually absent and therefore the exchange rate is low as well. The exchange rate is further impeded by low turbulence intensity in the air (high atmospheric resistances). The resistance at the water side has virtually no impact since it is nearly zero and may be ignored. Like will be shown in Section 3.2, for many pesticides the present parameterization of TOXSWA yields much higher atmospheric resistances than the values used here, resulting in longer volatilization half-life times.

The water and air controlled regimes can clearly be distinguished in the cases where the depth of the well-mixed water layer (or simply water depth in case of an entirely well-mixed water body) is constant. Compare, for example, the upper and middle panel of Figure 4. The differing cases of the atmospheric resistance (r_a+r_b) (middle panel) can clearly be distinguished if $k_h < 1 \cdot 10^{-2}$. In our calculations, the half-life time varies almost a factor of 5 in the air-controlled regime, since r_a+r_b have been chosen to vary a factor of 5, while $r_s \approx 0$ (see above). Moreover the volatilization half-life times decrease nearly exponentially with increasing k_h in this regime: it decreases from many years at $k_h = 10^{-8}$ to a few days at $k_h = 10^{-4}$. By contrast, there is hardly any effect of r_a+r_b once $k_h > 10^{-2}$. In this water-controlled regime, $t_{0.5,V}$ becomes nearly independent of k_h and may be much less than a day, down to a few hours or less. Variations in r_w through variations in U clearly affect the half-life time when $k_h > 1 \cdot 10^{-4}$. For example, if $k_h > 1$ the half-life times vary between about 1 and 28 days for U varying between 2 and 10 m s^{-1}.

The behaviour of air-water gas exchange in response to k_h has some possible implications for the parameterizations chosen to model the volatilization. In the air-controlled regime, the parameterization of $r_a + r_b$ is much more important than the parameterization of r_w or r_s, since the latter will hardly affect volatilization. On the other hand, a proper parameterization of r_w and r_s is required in this regime while the parameterization of r_a+r_b is less critical. Obviously, there is an intermediate regime ($\sim 1 \cdot 10^{-4} < k_h < \sim 1 \cdot 10^{-2}$), where both r_w and r_a+r_b have a significant effect on the air-water gas exchange. It should be noted that at very low values of k_h ($< 10^{-7}$) the volatilization is so slow, that other removal processes like chemical and biological degradation will dominate removal of pesticides from water bodies. Here, none of the resistances will exert critical control in the present context of volatilization of pesticides from small water bodies.

According to the analysis by Westein et al. (1998) and Asman et al., (2003), who examined k_h of many pesticides, k_h is less than 10^{-4} for 80-90% of the pesticides that are applied at present. This would imply that for the problem of volatilization of pesticides from water bodies a simple but reasonable description of r_w would give acceptable results in most cases. Also, it would be justifiable to put more effort in improving $r_a + r_b$ than in improving r_s. Of course, for the - much smaller - group of pesticides with $k_h > 10^{-2}$ the reverse would be the case. A quite large group of pesticides has k_h values between 10^{-6} and 10^{-3}. In particular for this group of pesticides, improved parameterizations will lead to better estimates of volatilization.

It is noted that the impact of water depth h on the half-life times does not depend on k_h and can be distinguished over the entire range of k_h values (see, e.g., the lower panel of Figure 4.). Although the physics of air-water gas exchange in this framework is independent of water depth, h affects the total amount of compound available (at a given concentration), and therefore directly affects the mass balance that is implicit in Equation (6). As such, h is obviously a quite critical characteristic of a water body. Therefore, improving estimates of h in TOXSWA will further improve the estimates of volatilization as well.

3 Parameterization of volatilization

3.1 Present TOXSWA parameterization of volatilization

At present, the parameterization of volatilization in TOXSWA (Beltman and Adriaanse, 1999) is based on the stagnant film model by Liss and Slater (1974). The approach fits in the framework discussed in the previous chapter. It is essentially similar to using Eq. (3b), but with fixed reference values for the resistances r_w and r_g. These fixed reference values for r_w and r_g are based on the resistances to transport of CO_2 in water and of H_2O in air. They are given as transport coefficients (k_l (or: k_w) = $1/r_w$; $k_g = 1/r_g$). Their values have been taken from Liss and Slater (1974) and read:

$k_{w,CO2}$ = 4.8 m day^{-1} (which equals 20 cm h^{-1} or 5.56·10^{-5} m s^{-1})
and
$k_{g,H2O}$ = 720 m day^{-1} (which equals 3000 cm h^{-1} or 8.33·10^{-3} m s^{-1})

In terms of resistances, these values correspond to $r_{w,CO2}$ = 1.8·10^4 s m^{-1} and $r_{g,H2O}$ =120 s m^{-1}, respectively.

The reference values of the transport coefficients are then scaled with the ratio of the molecular mass of the actual compound (M_X [g mol^{-1}]) and that of CO_2 (M_{CO2} [=44 g mol^{-1}]) or H_2O (M_{H2O} [= 18 g mol^{-1}]), respectively, to obtain the transport coefficients for the compound under consideration:

$$k_w = k_{w,CO2}\sqrt{\frac{M_{CO2}}{M_x}} \tag{7a}$$

$$k_g = k_{g,H2O}\sqrt{\frac{M_{H2O}}{M_x}} \tag{7b}$$

In fact, this scaling corrects for the difference in the molecular diffusion coefficient between the actual compound and that of CO_2 in water or H_2O in air, respectively. Since it may be assumed that the molecular diffusion coefficient is approximately inversely proportional to the square root of molecular mass (cf. Asman et al., 2003), the scaling method applied in TOXSWA corresponds to a linear relation of k_w with the molecular diffusion coefficient. As will be explained later, this linear scaling is only valid if the stagnant film model applies. As a final step, k_g is multiplied with k_h and C_a is divided by k_h to make the flux description consistent with Henry's law (Eq. 1; see Section 2.2 as well), which then leads to Eq. (3b) (as noted in Section 2.2 we use (3a) as a starting point for a description in the micrometeorological framework).

In the present TOXSWA approach (Beltman and Adriaanse, 1999) the transport coefficients or resistances are independent of the actual weather conditions and the conditions in the water that determine the gaseous transport across the air-water interface through their effect on turbulence. Furthermore, Liss and Slater (1974) based their estimates mainly on global studies of air-sea gas exchange. The values may therefore be less appropriate for estimates of volatilization from small water bodies surrounded by land.

In the following sections, we will consider parameterizations of the resistances in a micrometeorological framework (see Section 2.2). This framework allows including effects of weather conditions on gas exchange and will fit into improvement of temperature estimates within TOXSWA as well (Jacobs et al., 2010).

3.2 Atmospheric resistances

3.2.1 Aerodynamic resistance r_a

Aerodynamic resistance r_a can be obtained from micrometeorological theory (e.g., Monteith and Unsworth, 1990). It is defined by:

$$r_a = U / u_*^2 \tag{8a}$$

where u_* [m s^{-1}] is the friction velocity that can be obtained from the so-called logarithmic wind profile:

$$U = \frac{u_*}{\kappa}[\ln(z_r / z_0)] \tag{8b}$$

so that

$$r_a = [\ln(z_r / z_0)]^2 / (\kappa^2 U) \tag{9}$$

Here, z_r [m] is the reference height, z_0 [m] is the aerodynamic roughness length (~0.03 m for 'standard' grassland) and κ [-] is the Von Kármán constant (0.4). In the case of small water bodies, such as the ones that are modeled in TOXSWA, friction velocity u_* obtained from (9) is assumed to be valid over the water surface as well (cf. Jacobs et al., 1998). For large water bodies a correction should be made to account for the much lower roughness of water surfaces in comparison with land surfaces (Garratt, 1992).

Equation (9) is valid for neutral conditions only, but can be extended to include atmospheric stability. However, the assumption of neutral conditions is considered sufficiently accurate for the present purpose. This assumption then also allows a very simple estimate of the wind speed at z_r if U was obtained at a height other than z_r. For example, in agricultural practice the wind speed at a height of 2 m may be required while meteorological observations of the wind speed (U_{obs} [m s^{-1}]) are usually performed at an observation height (z_{obs} [m]) of 10 m. Under neutral conditions

$$U = [\ln(z_r / z_0) / \ln(z_{obs} / z_0)]U_{obs} \tag{10}$$

which results from applying (8b) for U_{obs} and z_{obs} as well as for U and z_r. Using (10) with $z_0 = 0.03$ m gives a wind speed at a height of 2 m that is 0.72 times the one obtained at 10 m (or conversely, the wind speed at a height of 10 m is 1.38 times the one at 2 m).

An additional correction may be required if the roughness in the surroundings of the site where U has to be applied deviates significantly from the standard roughness length at the meteorological station. The correction involves computing the wind speed at a height where the effect of local surface roughness may be assumed negligible. This so-called 'blending height' may be taken 60 m (Wieringa, 1986). Thus, Eq. (10) is first applied to compute the wind speed at the blending height using the roughness length at the observation site. For example, at a height of 60 m and with $z_0 = 0.03$ m, the new U_{obs} becomes about 1.31 times the original one obtained at 10 m. This new U_{obs} can now be used in (10) with $z_{obs} = 60$ m, z_0 at the site of application and using the actual height of application z_r, to obtain the desired wind speed U at z_r. For example, if z_0 of the terrain where U has to be utilized were 0.1 m instead of 0.03 m, the wind speed at 2 m would be 0.61 times the wind speed at 10 m from the original site, instead of 0.72 times that wind speed without change in roughness length. Under neutral atmospheric conditions, the factor to extrapolate the wind speed from $z_{obs} = 10$ m to $z_r = 2$ m remains within 10% of the one for $z_0 = 0.03$ m (i.e., 0.72) as long as 0.01 m < z_0 < 0.06 m.

3.2.2 Boundary-layer resistance r_b

Boundary layer resistance r_b is less well-defined than r_a. As discussed by Jacobs et al. (2007), many parameterizations of r_b are available. These authors compared three different approaches. The first one is the parameterisation of Hicks et al. (1987):

$$r_b = 2(\kappa u_*)^{-1}(Sc_a / 0.71)^{2/3} \tag{11}$$

where Sc_a [-] is the Schmidt number in air, defined as the ratio of the kinematic viscosity of the air (ν_a [$\approx 1.5 \cdot 10^{-5}$ m^2 s^{-1}]) and the molecular diffusion coefficient D_a [m^2 s^{-1}] of a compound in air. This parameterisation has been derived for *vegetated* surfaces but is often used to evaluate dry deposition to other surface types as well. It has become more or less a standard in gas exchange studies, regardless of the surface type. The second parameterization,

$$r_b = 15.2 Sc_a^{0.61} u_*^{-1} \tag{12}$$

was proposed by Deacon (1977) and has been derived specifically to describe gas exchange at water surfaces. It is based on observations in a wind-tunnel experiment, using relatively smooth surfaces and its use is probably more appropriate in the present context that the use of (11). The third one is (Garratt, 1992):

$$r_b = \frac{2.9(z_0 u_* / \nu_a)^{0.25} Sc_a^{0.5} - 2}{\kappa u_*} \tag{13}$$

which was derived from dimensional analysis for surfaces with blunt obstacles such as waves and rocks. It presumably applies to small water bodies as well.

Figure 5 shows the total atmospheric resistance $r_a + r_b$ as a function of Sc_a, using (9) plus (11), (12) or (13), respectively. The resistances have been computed for U=5 m s^{-1} at $z_r = 10$ m and $z_0 = 0.03$ m, giving $u_* = 0.34$ m s^{-1}. The range of Sc_a corresponds to a range in D_a from $3.8 \cdot 10^{-6} - 3 \cdot 10^{-5}$ m^2 s^{-1}, or an approximate range in molecular mass between 15 and 450 g mol^{-1}. The results are compared to the present parameterization in TOXSWA (Eq. (7b), Section 3.1). It can be seen that the differences between the parameterizations are quite large. For example, at $Sc_a \approx 2.5$ the differences in $r_a + r_b$ are a factor of 2-3 for (9) plus (11), (12) or (13), respectively. It is known that such differences lead to considerable differences in computed deposition, which is the reverse of volatilization (Jacobs et al., 2007).

At values of Sc_a larger than about 0.6, the present TOXSWA parameterization gives much higher estimates of $r_a + r_b$ than any of the other parameterizations used here. The difference with (9) plus (13), which yields the highest estimate of $r_a + r_b$ from the three alternatives (11)-(13), increases from a factor of 1.5 at $Sc_a = 1$ to a factor of 3.3 at $Sc_a = 4$. The difference ranges from a factor of 3.3 at $Sc_a = 1$ to a factor of 9.0 at $Sc_a = 4$ with the commonly used parameterization of Hicks et al. (1987), and from a factor of 2.3 at $Sc_a = 1$ to a factor of 5.5 at $Sc_a = 4$ for the parameterization proposed by Deacon (1977). At Sc_a=2.5 the difference is a factor of 6.6, 4.2 and 2.5 with (9) plus (11), (12) or (13), respectively. This implies that at present, TOXSWA probably underestimates volatilization rates in the atmospherically controlled regime. Moreover, because k_g in the TOXSWA parameterization is approximately proportional to D_a (see Section 3.1), $r_a + r_b = 1/k_g$ is almost linearly related to Sc_a (=ν_a / D_a), in contrast with the other parameterizations. Note that the results shown in Figure 5 are obtained at one particular wind speed (5 m s^{-1} at $z_r = 10$ m). Parameterizations (9) plus (11), (12)

or (13) would give higher values of $r_a + r_b$ at lower wind speeds and the reverse, while the results for TOXSWA would remain the same.
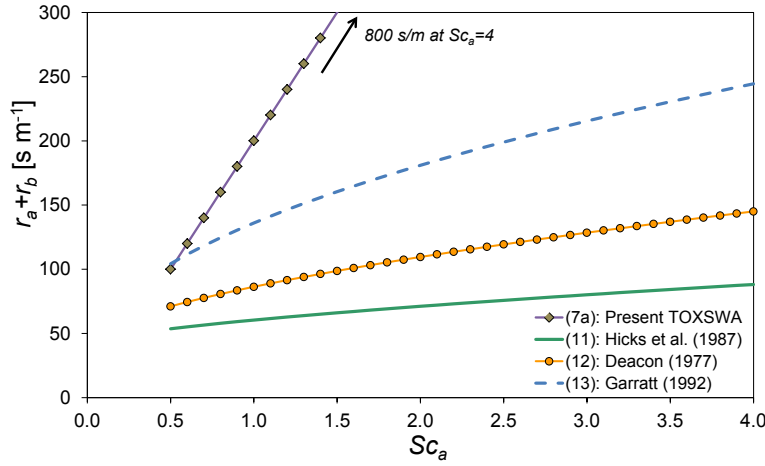
3.3 Aqueous resistance

3.3.1 Introduction

Most of the research into air-water gas exchange has been cast in terms of the transfer velocity (or piston velocity) $k_w \equiv 1/r_w$. This implies that most of the available parameterizations suitable to compute r_w and r_s are also given in terms of k_w. The discussion in this section will follow that convention, in order to avoid confusion with the available literature.

The short summary on parameterizations of k_w provided here is largely based upon various excellent reviews on the subject of air-water gas exchange (e.g., Donelan and Wanninkhof, 2002; Frost and Upstill-Goddard, 1999; Jähne en Haußecker, 1998; MacIntyre et al., 1995; Wanninkhof et al., 2009). The reader is referred these reviews for more information.

The summary starts in Section 3.3.2 with a general discussion on the impact of molecular diffusion and turbulence on k_w. These issues are connected to the so-called Schmidt number similarity, used to normalize k_w for various conditions and compounds. The Schmidt number similarity thereby also allows computing k_w for any compound, if k_w of a reference compound (usually CO_2) is known.

It is beyond the scope of the present report to describe the impact of turbulence and hydrodynamic processes in detail. Various processes like radiation exchange with the atmosphere, wave formation and breaking, momentum transfer between water and air, and velocity differences in the water are involved. Some of these processes are as yet only poorly understood. Therefore, we proceed by making a distinction between two physically differing regimes for which many parameterizations of k_w have been derived.

In the first regime it is assumed that turbulence in the water is to a large extent driven by or correlated with wind speed. This regime, discussed in Section 3.3.3, is most commonly studied in the oceanographic and related communities. Parameterizations of k_w have been cast in terms of U. In the other regime, discussed in Section 3.3.4, friction processes at the bottom of streams and rivers are assumed to be the main source of turbulence in the water column and therefore the main control on gas exchange. This regime has been extensively studied in connection with aeration and oxygen exchange between air and water. This has led to a completely different class of parameterizations, cast in terms of hydrodynamic properties of rivers and streams, such as bottom slope and water velocity.

Figure 5

Atmospheric resistances r_a+r_b as a function of Sc_a, for $U=5$ m s^1 and $z_0=0.03$ m.

3.3.2 Impact of molecular diffusion and turbulence; Schmidt number similarity

Transfer velocity k_w is determined by the properties of the aqueous laminar boundary layer. In the case of a completely stagnant laminar layer the transfer velocity is given by the molecular diffusion coefficient of the gaseous substance in water (D_w [m^2 s^{-1}]) and the thickness of the aqueous laminar layer (δ_z [m]) (see Figure 1 as well):

$$k_w = \frac{D_w}{\delta_z} \tag{14a}$$

Thus, for a given thickness δ_z the stagnant film model predicts k_w to be proportional to D_w. The present TOXSWA parameterization is based on this principle as well, albeit indirectly by utilizing the inverse square root of molecular mass to scale D_w (see Section 3.1).

In reality the laminar layer is not completely stagnant. It is affected to some extent by the turbulence in the water and therefore by the hydrodynamic features in the water layer and the interaction with the atmosphere. Various conceptual models are available to describe such interactions. One similar feature of these models is that they all express k_w in terms of D_w and some function $G()$. In its turn, the function $G()$ is given in terms of a turbulence velocity scale **V** (such as friction velocity), a length scale **L** (such as the turbulent mixing depth) and the kinematic viscosity of the water ν_w [m^2 s^{-1}], such that:

$$k_w = a(D_w)^n G(\mathbf{V},\mathbf{L},\nu_w) \tag{14b}$$

where a is a proportionality constant. Note that $G()$ can be used to describe the effective depth of the laminar layer. Then, if $G() = \delta_z^{-1}$ (14a) and (14b) become identical if $a=1$ and $n=1$.

The power n in (14b) describes the relation between k_w and D_w and therefore the ultimate impact of the latter compound property on k_w. The value of n depends on the way in which turbulence influences the laminar layer. In case there would be no impact of turbulence, such as in the stagnant film model, $n=1$, which is the value implicit in the present TOXSWA approach.

However, in reality turbulence is observed to have an impact on the laminar layer and the value of n depends on the way turbulence is able to penetrate into the laminar layer. Most of the available observational evidence is consistent with predictions of the so-called surface renewal concept (Danckwerts, 1951) according to which $n=1/2$ (e.g., Haußecker, 1996; Nightingale et al., 2000). In this concept, the water in the laminar layer is replaced completely with water from the bulk layer at time intervals dictated by the turbulence intensity in the water, which in its turn is a function of various processes such as water flow, momentum transfer between air and water, radiation exchange and wave breaking (see, e.g., the aforementioned reviews on the subject of air-water gas exchange). It is concluded that, because of the impact of turbulence, k_w is not linearly related to D_w, but it varies approximately with the square root of D_w.

The aforementioned relationship is important, since it determines the impact of a crucial compound property - D_w - on the volatilization. Also, since k_w is usually given for CO_2 or other specific tracer gases like He and SF_6, the transfer velocity k_w of any other compound must then be obtained using this relation of k_w with D_w. In the air-water gas exchange literature the scaling is usually based upon the so-called Schmidt number similarity, according to which:

$$\frac{k_{w,1}}{k_{w,2}} = \left(\frac{Sc_{w,2}}{Sc_{w,1}} \right)^n$$

(15)

where the numbered subscripts distinguish substance 1 from 2 and $Sc_w = v_w/D_w$ is the Schmidt number in water. The Schmidt number Sc_w not only includes the molecular diffusion coefficient D_w, but also the impact on the molecular diffusion process of temperature and salinity via the kinematic viscosity. Usually, k_w determined from experiments is given for $Sc_w = 600$, which is the Schmidt number for CO_2 in sweet water of 20 °C.

In the present version of TOXSWA, the square root of the ratio of molecular masses is used to scale the transfer coefficient k_w, so that $k_{w,1}/k_{w,2}=(M_2/M_1)^{0.5}$, where M [g mol^{-1}] is molecular mass (Beltman and Adriaanse, 1999; see Eq. (7a)). Like in the case of the atmospheric resistance, this scaling is based on the idea that the value of the diffusion coefficient is approximately inversely proportional to the square root of molecular mass (cf. Asman et al., 2003). Therefore, this scaling assumes k_w to be proportional to D_w. It is equivalent to using Eq. (15) with $n=1$, in which case the stagnant film model would have to apply. As has been explained above, this is usually not the case. Furthermore, effects of salt and temperature on the molecular diffusion process in the water are ignored since the present TOXSWA method does not depend on the kinematic viscosity of the water.

3.3.3 Formulations for wind driven turbulence

Since it is extremely difficult to describe k_w mechanistically many simple parameterizations have been proposed to compute k_w. The most popular one describes k_w as a function of wind speed:

$$k_w = bU^m + c$$

(16)

where b and c are constants. These parameterizations are of k_w are usually given as the value normalized to $Sc_w=600$, and denoted by k_{600} in the units of cm h^{-1}. Wind speed U is taken to be the wind speed at a height of 10 m under neutral atmospheric conditions. If wind speed is available at another height, it can be converted to a height of 10 m using Eq. (9) (see Section 3.1).

The popularity of (16) relates to the fact that - apart from its simplicity - some of the main processes dominating turbulence formation in the water and surface renewal in the laminar water layer are directly or

indirectly related to wind speed, at least in cases where water depth is large. These processes include wave formation and breaking and momentum transport. However, at low wind speed, turbulence is mainly driven by convection due to long-wave radiation exchange with the atmosphere or, during daytime, it may be suppressed by absorption of short-wave solar radiation in the water (e.g., Soloviev and Schlüssel, 1996). Such processes, of which the physical details are not yet understood very well, may be important for small water bodies in particular (Read et al., 2012). They can in principle be modeled (Soloviev and Schlüssel, 1996; Jacobs et al., 2002), but a simpler, practical alternative is to choose c > 0 in (16), so that gas transfer continues at low wind speed (e.g., Cole and Caraco, 1998; Cole et al., 2010; Wanninkhof et al., 2009).

Power m in Equation (16) typically varies between 1 and 3, depending on the conditions and the characteristics of the water body under consideration. For small water bodies with low water velocity m tends to be lower (~1.5) than for large water bodies like large lakes, seas and oceans (~2). The reason probably is that wave breaking and related bubble-mediated gas transfer at high wind speed causes extra non-linear enhancement of gas transfer of such water bodies. Tri-linear relationships and polynomial relationships can also be used to accommodate differing physical effects in various wind speed regimes.

Although subtle differences in forms of (16) may yield appreciable differences in gas exchange in a global context and at annual timescales (Wanninkhof et al., 2009), they are probably of minor importance in the case of small water bodies. Intrinsic uncertainty in the relationship (i.e., the scatter around the regression line) is probably much more important. Other main problems and uncertainties related to the use of (16) in the context of volatilization of pesticides from small water bodies are probably connected to the parameterization in the low wind speed regime. Apart from the treatment:
- Precipitation can enhance turbulence independently of wind speed and thereby increase k_w (e.g., Ho et al., 2000).
- Surfactants reduce k_w primarily by inhibiting surface turbulence (Frew, 1997).
- Since the wave field has a strong effect on gas exchange, fetch (the distance the winds blows over the water surface) is believed to have a first-order effect on the transfer (Wanninkhof et al., 2009).

In addition, most of the research has been conducted for relatively large and deep water bodies like large lakes, marginal seas and oceans. Therefore, the uncertainty of (16) is probably larger for very small water bodies over land, like ditches, than for extensive water bodies.

Figure 6 shows four parameterizations of k_{600} (i.e., k_w at Sc_w=600, the Schmidt number for CO_2 in sweet water of 20 °C) cast in some form of (16). For convenience we ignore the small difference for saline waters here. The formulations have been based on reviews of observations in wind-wave tunnels, over lakes and seas and over the oceans:

1) *Liss and Merlivat (1986)* is a tri-linear formulation, reflecting a smooth regime, a regime with an undulating surface, and a regime with breaking waves:

$$
\begin{aligned}
k_{600} &= 0.17\,U & (U < 3.6\,\mathrm{m\,s^{-1}}) \\
k_{600} &= 2.85\,U - 9.65 & (3.6 < U < 13\,\mathrm{m\,s^{-1}}) \\
k_{600} &= 5.9\,U - 49.3 & (U > 13\,\mathrm{m\,s^{-1}})
\end{aligned}
\tag{17}
$$

2) *MacIntyre et al. (1995)* is a widely used fit to observations of lakes and small water bodies:

$$
k_{600} = 0.45 U^{1.64}
\tag{18}
$$

3) *Cola and Caraco (1998)* extended the fit by MacIntyre et al. (1995) with more observations and took into account that often $k_{600} \neq 0$ at U=0:

$$k_{600} = 0.215 U^{1.7} + 2.07 \qquad (19)$$

4) *Wanninkhof (1992)* is a widely used quadratic fit to match oceanic observations. It is included here for reference and because of its popularity, but it may be less suitable for application in case of small water bodies:

$$k_{600} = 0.31 U^2 \qquad (20)$$

Details on the parameterizations can be found in the cited literature.
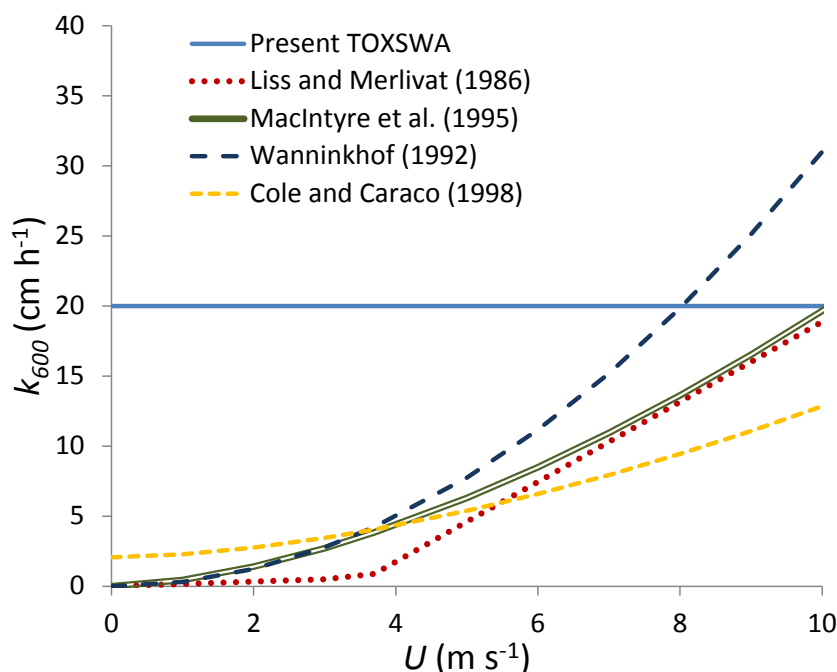
Figure 6

Comparison of four winds-speed dependent formulations for k_{600} with the current TOXSWA values.

In Figure 6, parameterizations 1-4 are compared with the present TOXSWA formulation that takes k_{600} to be constant at 4.8 m day^{-1} or 20 cm h^{-1}. It can be seen that the present TOXSWA value would be appropriate at a wind speed of 8-10 m s^{-1} at a height of 10 m (5 Beaufort), which under neutral atmospheric conditions corresponds to a wind speed of about 6-7 m s^{-1} at a height of 2 m (the latter height is often used in problems related to agricultural practice). Usually, the wind speed over land is much lower. At more typical wind speed values over land, of up to 5 m s^{-1} at a height of 10 m, the present TOXSWA method typically overestimates k_w by a factor of 4-10 in comparison with the alternatives (17)-(20). This would lead to an overestimation of volatilization in the water-controlled regime, which applies to a small minority of pesticides only.

It can be seen that for the wind speed range shown here, the formulations for the small surface waters (10)-(12) are reasonably consistent for wind speeds between 5 and 10 m s^{-1}. They clearly deviate from the much steeper relationship for oceans (13). However, for the present purpose, the behaviour at low wind speed is probably more important.

3.3.4 Formulations for bottom-driven turbulence

While relationships similar to (16) have also been found for small lakes and ponds with low water velocity (see e.g., Asman et al.,2003; Cole et al., 2010), so called bottom-driven turbulence has since long been recognized as an important contributor to surface renewal and therefore to gas exchange of shallow streams and rivers (Upstill-Goddard, 2006). Some gas exchange studies in the aforementioned wind-driven turbulence framework have been performed for Estuaries. In these systems, a combination of wind-driven and bottom-driven turbulence occurs (Borges et al., 2004; Zappa et al., 2007), leading to a current-dependent offset c in Equation (16) (Abril et al., 2009; Raymond and Cole, 2001). However, it has been postulated that in small streams over land, where the wind speed is very low, the turbulence that drives gas exchange is almost exclusively driven by hydraulic properties of the channels, such as mean water velocity u_w [m s^{-1}], total water depth d_w [m] and bottom slope I [m m^{-1}] (Moog and Jirka, 1995; Thyssen en Erlandsen, 1987). Note that $d_w = h$ in the case of fully mixed water. However, the extremely large uncertainty in the available parameterizations and their lack of predictive skill cast some doubt on the validity of the assumption that turbulence may be purely bottom-driven.

A wealth of information comes from so-called Oxygen re-aeration studies (see, e.g., Aristegi et al., 2009; Moog and Jirka, 1995; Thyssen en Erlandsen, 1987). Such studies usually report the so-called Oxygen re-aeration coefficient K_{2s} [day^{-1}], which is related to the transfer velocity of Oxygen ($k_w(O_2)$ [cm h^{-1}]) by (cf. Moog and Jirka, 1995; Asman et al., 2003):

$$k_w(O_2) = 4.17 K_{2s} d_w \qquad (21)$$

The transfer velocity so obtained can be scaled by the Schmidt number similarity (15), using appropriate temperature dependences for the diffusion coefficients and the kinematic viscosity of water.

The differences in the available parameterizations of K_{2s} are quite large and only few appear to have predictive skill (Aristegi et al., 2009; Moog and Jirka, 1995; Thyssen en Erlandsen, 1987). Moog and Jirka (1995) found that inclusion of bottom slope I is required to obtain reasonable results. For $I < 4 \cdot 10^{-4}$ m m^{-1} the fixed, average value of $K_{2s} = 1.8$ day^{-1} ($k_w(O_2) = 7.5$ cm h^{-1}) was found to describe re-aeration better than any of the predictive equations. A relationship for all slopes that was among the best of the ones studied by these authors was:

$$K_{2s} = 186\sqrt{u_w I} \cdot d_w^{-1} \qquad (22)$$

which was proposed by Cadwallader and McDonnell (1969). Note that using (21) along with (22) makes k_w independent of depth. Thyssen and Erlandsen (1987) also reviewed the available parameterizations for K_{2s} and proposed to use for small streams dominated by macrophytes:

$$K_{2s} = 8784 u_w^{0.734} \cdot I^{0.930} d_w^{-0.420} \qquad (23)$$

This parameterization has been implemented in the Danish pesticide deposition assessment model proposed by Asman et al. (2003).

Many more parameterizations for K_{2s} are available but they generally ignore possible interactions with the atmosphere. Although this may be reasonable for interaction with wind speed, since U tends to be quite low over low-lying streams, radiation exchanges may probably not be ignored. Effects of vertical walls and bends are ignored as well. Both omissions may explain part of the scatter found in the data as well as in the parameterizations.
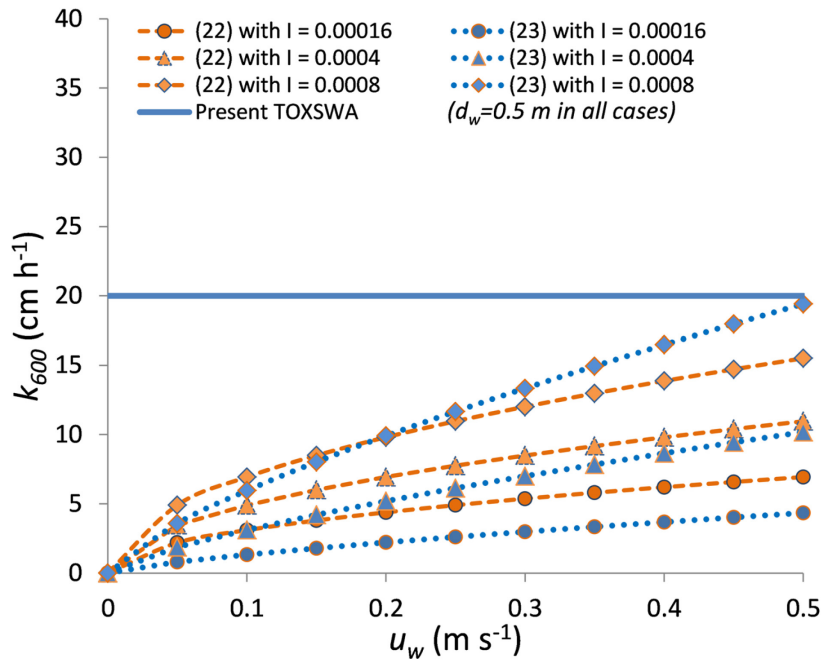
Figure 7

Comparison of k_{600} as a function of water velocity, using (22) or (23) with (21), for different bottom slopes I and assuming a water depth d_w of 0.5 m.

In Figure 7, $k_w = k_{600}$ from (22) or (23) with (21) is shown as a function of water velocity u_w for three different bottom slopes (I = 0.00016, 0.0004 and 0.0008, respectively), and assuming d_w = 0.5 m. The small difference between Sc_w for O_2 and CO_2 (~10%) has been ignored in these sample calculations. The present TOXSWA value is shown as well. As discussed before, the differences between the parameterizations are quite large and it can be seen that the impact of bottom slope is strong. It can be seen that in the context of bottom-driven turbulence parameterizations, the TOXSWA value of 20 cm h^{-1} would be appropriate for quite high slopes and water velocities. At lower water velocity and slope values, which are more appropriate in the present context, the present TOXSWA formulation typically overestimates the transfer velocity by a factor of 4 -20 in comparison with alternatives (21) to (23). This again suggests overestimation of volatilization in the water-controlled regime, which applies to a minority of pesticides.

At very low water velocity (up to ~0.2 m s^{-1}), the values obtained with parameterizations (21) to (23) would agree reasonably well with the offset of about 2 cm h^{-1} in (19) and the observations reported by Cole et al. (2010), who found k_{600} for relatively small lakes to range between about 1.5 and 3.1 cm h^{-1} at wind speeds below 3 m s^{-1}. However, at high water velocities and the steeper slope of 0.0008, the transfer velocity is larger than those obtained with most of the wind speed relations at U=10 m s^{-1}.

4 Sample calculations

4.1 General

In this chapter we will present some sample calculations showing the volatilization from a shallow water body, using the differing parameterizations presented above. The purpose is to further illustrate the principles of the air-water gas exchange, in support of a proper selection of the parameterization that will be implemented in TOXSWA, and to compare the resulting new volatilization behaviour with the one that would result from the present TOXSWA approach (see Section 3.1).
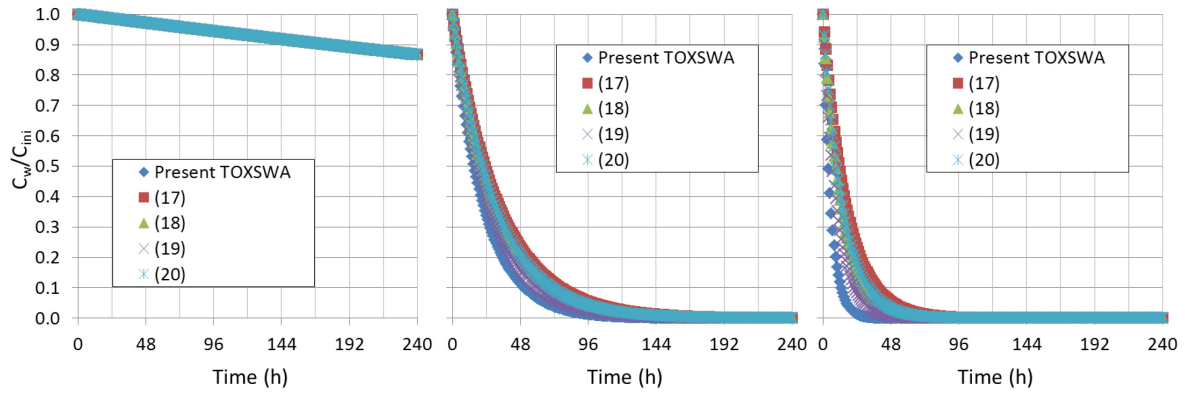
Calculations will be shown for compounds with $k_h = 1 \cdot 10^{-5}$ (air-controlled transfer), $1 \cdot 10^{-3}$ (intermediate regime) and $1 \cdot 10^{-1}$ (water-controlled transfer), respectively. For these compounds, we compute volatilization from a water body for a period of 10 days or 240 hours, taking at the reference height a constant wind speed and an atmospheric concentration of the compounds equal to zero. Since we are interested in the concentration changes in the water only, we plot the ratio of the computed instantaneous bulk concentration in the water, C_w, to the initial bulk concentration C_{ini}. For simplicity, the initial concentration in the water is taken to be 1 µg m^{-3}. Since $C_a = 0$ at all times, the computed ratio C_w/C_{ini} is insensitive to the initial concentration. Further specific details will be given in the examples given below.

4.2 Example 1: influence of k_w-formulation based on wind speed-driven turbulence

In the first set of sample calculations we apply parameterizations (17)-(20) to compute k_w assuming a wind speed of 5 m s^{-1} at a height of 10 m and $z_0 = 0.03$ m in the landscape surrounding the water body. This means $u_* = 0.34$ m s^{-1}. The wind speed chosen here corresponds to a wind speed of about 3.5 m s^{-1} at a height of 2 m. Furthermore, we take a water depth of 0.5 m. We need to specify water depth here, since it determines the total mass balance.

We take $Sc_a = 2.5$, which is appropriate for a compound with a molecular mass M_x of about 250 g mol^{-1}, assuming the diffusion coefficient to be inversely proportional to the square root of M_x, and taking the diffusion coefficient of CO_2 in air ($1.6 \cdot 10^{-5}$ m^2 s^{-1}) as a reference value. This also implies that k_w from (7a), the present TOXSWA estimate, is equal to 8.4 cm h^{-1} or $2.33 \cdot 10^{-5}$ m s^{-1} and $r_w = 1/k_w = 4.29 \cdot 10^4$ s m^{-1}. By virtue of the Schmidt scaling (15) with exponent $n=0.5$ our assumptions on the diffusion coefficient and M_x also imply that k_w of the compound is 71% of k_{600} from the parameterizations, thereby increasing r_w by 40% relative to $r_{600}=1/k_{600}$. Finally, we take atmospheric resistance $r_a+r_b=120$ s m^{-1}, which is approximately equal to the value predicted by the Deacon (1977) parameterization, Eq. (12) (see Figure 5).

The results from this example are shown in Figure 8. It can clearly be seen that the largest differences between the parameterizations occur at the larger value of k_h (water controlled regime). In addition, volatilization occurs at a much faster rate at those higher values of k_h: almost all material has volatilized after four days, in all cases. By contrast, the differences in the air-controlled case are small, and less than 15% of the material has volatilized after 240 hours (ten days). It can clearly be seen that for intermediate to large k_h values the current TOXSWA formulation of k_w tends to overestimate volatilization as compared to the alternatives investigated here.
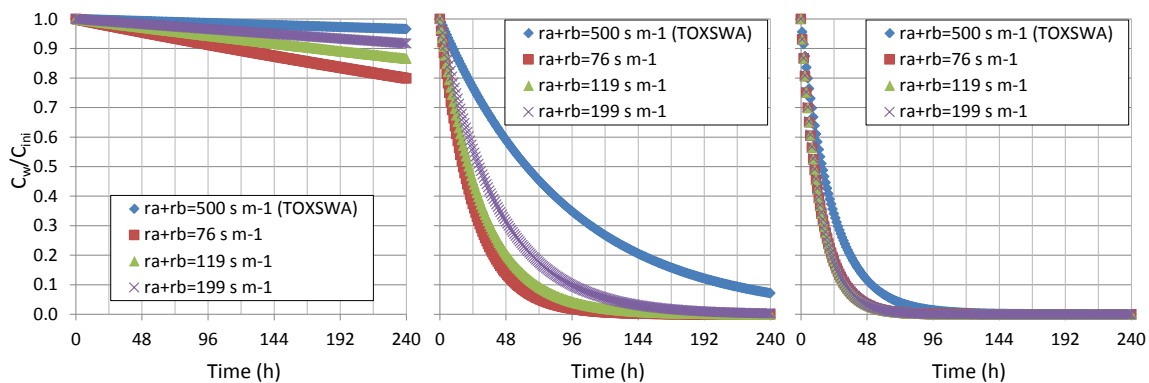
Figure 8

Computed ratio C_w/C_{ini} upon volatilization from a 0.5 m deep water body, using differing parameterizations of k_w based on wind speed. See text on Example 1 for further explanation. Left: $k_h = 1 \cdot 10^5$ (air-controlled transfer); middle: $k_h = 1 \cdot 10^3$ (intermediate regime); right: $k_h = 1 \cdot 10^1$ (water-controlled transfer).

4.3 Example 2: influence of r_b-formulation

In the second set of sample calculations we apply the same conditions as in Example 1. However, we now fix k_w and r_w using the parameterization by Cole and Caraco (1998) for a wind speed of 5 m s^{-1} at 10 m high, while taking differing parameterizations (11)-(13) for the boundary layer resistance r_b, along with Eq. (8) for aerodynamic resistance r_a. The behaviour according to the present TOXSWA parameterization is evaluated as well. The resulting value for $k_w = 1.06$ $^{-5}$ m s^{-1}, corresponding to 9413 s m^{-1} for r_w. Note that this value is smaller than the one used to compute the half-life times (Figure 4 and Table 1). Resulting values for $r_a + r_b$ are 76 s m^{-1}, 119 s m^{-1} and 199 s m^{-1} for (8) with (11), (12) and (13), respectively and 500 s m^{-1} for the present TOXSWA method.

The results from this example are depicted in Figure 9. It can clearly be seen that the largest differences between the parameterizations occur at the smaller values of k_h (air controlled and intermediate regime). Although volatilization is slow for $k_h = 1 \cdot 10^{-5}$, appreciable differences of more than 15% exist after 240 hours (ten days). Volatilization is much faster at $k_h = 1 \cdot 10^{-3}$ and the differences between the parameterizations are quite large as well. In particular the present TOXSWA approach leads to much lower volatilization rates. Like expected, volatilization rates are fastest at $k_h = 1 \cdot 10^{-1}$. The different parameterizations can hardly be distinguished anymore, except for the present TOXSWA parameterization.
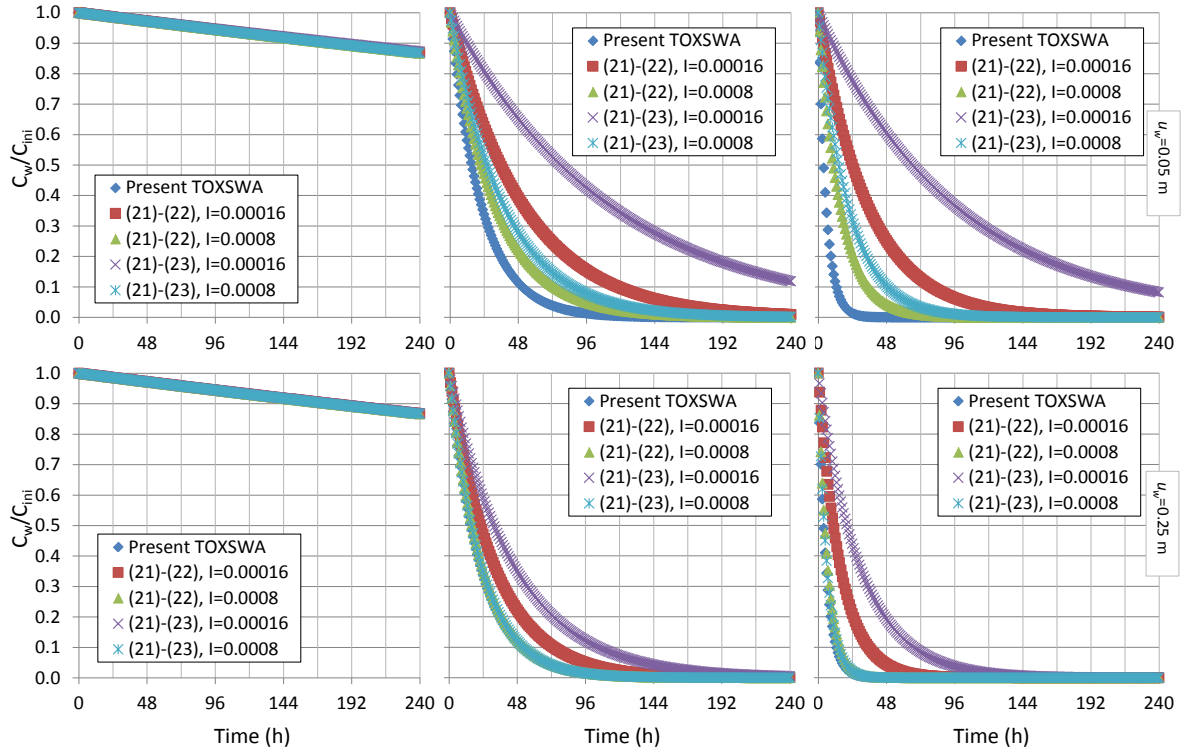

Figure 9

Computed ratio C_w/C_{ini} upon volatilization from a 0.5 m deep water body, using differing parameterizations of atmospheric resistance $r_a + r_b$. See text on Example 2 for further explanation. Left: $k_h = 1 \cdot 10^5$ (air-controlled transfer); middle: $k_h = 1 \cdot 10^3$ (intermediate regime); right: $k_h = 1 \cdot 10^1$ (water-controlled transfer).

4.4 Example 3: influence of k_w-formulation based on bottom-driven turbulence

In the third example, parameterizations of k_w assuming bottom-driven turbulence are investigated. The transfer velocity k_{600} is computed from (21) with (22) and (21) with (23), respectively. Here, wind speed plays no role anymore. Instead, we choose water velocities of 0.05 and 0.25 m s^{-1}. Also, we take slope I = 0.00016 and 0.0008, respectively. Other conditions are the same as in Example 1.

The results from this example are shown in Figure 10, in the upper panels for u_w = 0.05 m s^{-1} and in the lower panels for u_w = 0.25 m s^{-1}. The results at k_h = 1·10^5 resemble those of Example 1 and confirm that in the air-controlled regime volatilization is insensitive to the parameterization of k_w. Much larger differences occur if k_h > 1·10^{-3}, in particular at the lower water speed of 0.05 m s^{-1}. The volatilization rates are largest with k_h = 1·10^{-1} and I = 0.0008, leaving almost no material in the water after 144 h (six days) in all cases. At the larger water velocity of 0.25 ms^{-1} the results from the present TOXSWA parameterization happen to agree quite well with those of the other parameterizations at the higher bottom slope values. Indeed, at u_w = 0.05 m s^{-1} the current TOXSWA methodology yields much larger values than the other parameterizations, while the differences are smaller at u_w = 0.25 m s^{-1} (see Figure 7).

Figure 10

Computed ratio C_w/C_{ini} upon volatilization from a 0.5 m deep water body, using differing parameterizations of k_w based on water velocity, water depth and bottom slope. See text on Example 3 for further explanation. Left: k_h = 1·10^5 (air-controlled transfer); middle: k_h = 1·10^3 (intermediate regime); right: k_h = 1·10^1 (water-controlled transfer). Upper panels: u_w = 0.05 m s^{-1}; lower panels: u_w = 0.25 m s^{-1}.

5   Conclusions and recommendations

The TOXSWA (TOXic substances in Surface WAters) model has been developed to describe the behaviour of pesticides in small surface waters and to estimate their concentration as a function of time. Volatilization of pesticides from the surface waters may be an important loss term on the mass balance and is therefore an important component of TOXSWA model. The present parameterization of the volatilization process in TOXSWA follows the concept of the so-called stagnant film model. This concept can be regarded as an early member of a family of concepts that envisage air-water gas fluxes as an exchange between two well-mixed layers, one in the air and one in the water, where turbulence dominates transport and mixing. These layers are separated by two so-called quasi-laminar layers aligned along the air-water interface. The air-water gas exchange across the laminar layers is driven by the difference in chemical potential of the compound in air and water, usually formulated in terms of concentration differences and by invoking Henry's law.

One of the shortcomings of the present parameterization in TOXSWA is that it does not describe the influence of weather and the hydrodynamic conditions in the water on the volatilization process. Although the physics of air-water gas exchange is quite complicated and contains many uncertainties relatively simple adjustments can be made to include such influences in TOXSWA in a way that fits well into the 'bulk' approach of TOXSWA, which assumes vertically well-mixed water bodies. To this end, it is most convenient to cast the physics of volatilization in a micrometeorological framework. Within such a framework, the required environmental input will be readily available. It will also fit smoothly in the envisaged new temperature simulation algorithm in TOXSWA.

In a micrometeorological framework, the gas flux is given by:

$$F = \frac{k_h C_w - C_a}{r_a + r_b + k_h r_w} \qquad (5)$$

It may be assumed that the chemical potential difference of the modelled compound between the water and the air, approximated by $k_h C_w - C_a$, is known from the dynamic mass balance calculations in TOXSWA at each time step. This leaves the resistances to be further parameterized.

The dimensionless Henry coefficient k_h and therefore the aqueous resistance $k_h r_w$ varies over many more orders of magnitude than the atmospheric resistance $r_a + r_b$. This feature allows a useful distinction of two physical regimes (see Figure 4 and Table 1): the air-controlled regime where $r_a + r_b \gg k_h r_w$ and the water-controlled regime where $r_a + r_b \ll k_h r_w$. In the first regime, gas exchange is only sensitive to the parameterization of atmospheric turbulence and therefore of $r_a + r_b$. Obviously, the two regimes are not strictly separated. In an 'intermediate regime' the effects of both the atmospheric resistances and the water resistance are noticeable, since $r_a + r_b$ and $k_h r_w$ are of a similar order of magnitude.

Most pesticides (~80-90%) belong to the first, atmospherically controlled regime. In this regime, at very low values of k_h ($< 10^{-7}$) the volatilization rate is so slow - with volatilization half-life times of tens to hundreds of years - that pesticide loss from water bodies will be dominated by processes other than volatilization, such as biological or chemical degradation. If k_h becomes larger than 10^{-2} the volatilization become quite fast - with volatilization half-life times in the order of one to a few hours -, but only a small minority of pesticides belongs to this group.

The distribution of k_h-values among pesticides implies that for the problem of volatilization of pesticides from water bodies a simple but reasonable description of r_w would give acceptable results most in cases. Also, it would be justifiable to put more effort in improving $r_a + r_b$ than in improving r_w. For the much smaller group of pesticides with $k_h > 10^{-2}$ the reverse is true. An improved parameterization of volatilization will be most effective for pesticides with k_h-values between 10^{-6} and 10^{-3}. Pesticides with k_h-values in this range are either in the intermediate regime where atmospheric resistance and water resistance are of a similar order of magnitude ($\sim 10^{-4} < k_h < \sim 10^{-2}$) or in the atmospherically controlled regime but with still relatively fast volatilization rates (up to tens of days, for $\sim 10^{-6} < k_h < \sim 10^{-4}$).

The aerodynamic resistance, r_a, can be computed using

$$r_a = [\ln(z_r / z_0)]^2 / (\kappa^2 U) \tag{9}$$

Although (9) is strictly only valid for neutral atmospheric conditions, it is at present considered sufficiently accurate in the context of its use in TOXSWA. It can easily be extended to include stability effects if future developments of TOXSWA require doing so. As explained in Section 3.2.1 Some care should be taken in using U at the correct reference level z_r and for the correct roughness length z_0.

The uncertainty in boundary layer resistance r_b is quite large and many parameterizations for r_b are available. Here we recommend using

$$r_b = 15.2 Sc_a^{0.61} u_*^{-1} \tag{12}$$

which was proposed by Deacon (1977). It is considered appropriate in the present context because (12) has been derived specifically to describe gas exchange at water surfaces and was based on observations in a wind-tunnel experiment using relatively smooth surfaces. The friction velocity u_* can be obtained from the logarithmic wind profile (8b), given in Section 3.2.1.

To obtain aqueous resistance r_w we propose to use

$$1 / r_{600} = k_{600} = 0.215 U^{1.7} + 2.07 \tag{19}$$

in combination with

$$1 / r_w = k_w = k_{600} \left(\frac{600}{Sc_w} \right)^{0.5} \tag{24}$$

to convert the reference value of r_{600} at $Sc_w = 600$ to the actual r_w at Sc_w of the compound under consideration. Note that in (19), U should be given at a height of 10 m. If the wind speed is available for another height, that wind speed can be converted to yield U at 10 m (see Section 3.2.1). Also note that (24) is a specific form of (15), acknowledging that most present-day parameterizations of k_w are given for a $Sc_w = 600$.

Equation (19) belongs to the family of parameterizations that assume turbulence in the water to be directly or indirectly related to wind speed U. Another class of parameterizations assumes the turbulence to be driven by the hydrodynamic properties of the water body. From the available options within both classes of parameterizations, Eq. (19) with scaling law (15) is proposed because of the following, sometimes practical considerations:
- In practice, for most pesticides (~85%), r_w is much less important than $r_a + r_b$; sometimes it is even unimportant.
- The skill of the parameterizations based on hydrodynamic characteristics of the water bodies is extremely low; the variation between results from those parameterizations is even larger than the ones based on U in the class assuming wind-driven turbulence.

- From the available parameterizations with U, (19) is based on a review of gas exchange observations at relatively small water bodies, which is an advantage in the present context.
- There is no doubt that even small water bodies interact with the atmosphere:
  1) Through the impact of the atmospheric flow which is modeled via the relation with wind speed.
  2) Through the impact of radiation exchange. The latter process drives mixing of the water at least during the night, even in the absence of atmospheric flow. This feature, which may warrant further investigation in particular for small water bodies, is modelled using the intercept in (19).
- The atmospheric influence is absent in the class of parameterizations based on hydrodynamic characteristics. By contrast, the intercept of (19) is in the midst of the range of k_{600} values from the examples of this class of parameterization investigated in Section 3.3.4. Thus, at low wind speed and noting the fact that a fixed value of k_w was found to model the effect of bottom-driven turbulence equally well - if not better - than parameterizations based on that concept, the intercept in (19) may be viewed as a way to take bottom-driven turbulence into account as well.

In the scaling represented by Eq. (15) we suggest to use the power $n=0.5$ to take into account the impact of turbulence on the laminar layer in the water. This value of the power is consistent with the so-called surface renewal theory, and has been confirmed by many observations. The present TOXSWA approach is consistent with $n=1$, which applies to the stagnant film model.

The parameterizations proposed here fit well into the envisaged new temperature calculation algorithm for TOXSWA and can be viewed as a relatively easy-to-implement extension of the existing volatilization parameterization. It is well in line with the research on air-water gas exchange that has been performed in the past few decades. The required meteorological information is readily available at intervals of one hour. Although the proposed set of simple parameterization necessarily excludes many details of air-water gas exchange, it will be able to capture the main features of air-water gas exchange dynamics. Moreover, it can easily be extended to include more detailed descriptions if future new TOXSWA developments require doing so.

References

Abril, G., M.-V. Commarieu, A. Sottolichio, P. Bretel and F. Guérin, 2009. Turbidity limits gas exchange in a large macrotidal estuary. Estuarine, Coastal and Shelf Science 83, pp. 342-348.

Adriaanse, P.I., 1996. Fate of pesticides in field ditches: the TOXSWA simulation model. Sc-DLO Report 90. Winand Staring Centre, Wageningen, 241 pp.

Adriaanse, P.I. and W.H.J. Beltman, 2009. Transient water flow in the TOXSWA model (FOCUS versions): concepts and mathematical description. Wageningen, Statutory Research Tasks Unit for Nature and the Environment. WOt-report No. 101. Alterra, Wageningen, 78 pp.

Aristegi, L., O. Izagirre and A. Elosegi, 2009. Comparison of several methods to calculate reaeration in streams, and their effects on estimation of metabolism. Hydrobiologia 635, pp. 113-124.

Asman, W.A.H., A. Jørgensen and P.H. Jensen, 2003. Dry deposition and spray drift of pesticides to nearby water bodies. Pesticides Research 66. Danish Environmental Protection Agency, Copenhagen, Denmark.

Beltman, W.H.J. and P.I. Adriaanse, 1999. User's manual of TOXSWA 1.2. Simulation of pesticide fate in small surface waters. Technical Document 54.Winand Staring Centre, Wageningen, 112 pp.

Borges, A.V., B. Delille, L.-S. Schiettecatte, F. Gazeau, G. Abril and M. Frankignoulle, 2004. Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt, and Thames). Limnol. Oceanogr. 49, pp. 1630- 1641.

Cole, J.J., D.L. Bade, D. Bastviken, M.L. Pace and M. van de Bogert, 2010. Multiple approaches to estimating air-water gas exchange in small lakes. Limnol. Oceanogr.: Methods 8, pp. 285-293.

Cole, J.J. and N.F. Caraco, 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by addition of SF_6. Limnol. Oceanogr. 43, pp. 647-656.

Deacon, E.L., 1977. Gas transfer to and across an air-water interface. Tellus 29, pp. 363-377.

Donelan, M.A. and R. Wanninkhof, 2002. Gastransfer at water surfaces - Concepts and issues. Geophysical Monograph, 127: pp. 1-10.

Donelan, M.A., W.M. Drennan, E.S. Saltzman and R. Wanninkhof (eds.), 2002. Gas Transfer at Water Surfaces (Geophysical Monograph, 127). American Geophysical Union, Washington DC.

Frew, N.M., 1997. The role of organic films in air-sea gas exchange, 1997. In: P.S. Liss and R.A. Duce (eds.), The Sea Surface and Global Change. Cambridge Univ. Press., Cambridge, pp. 121-172.

Frost, T. and R.C. Upstill-Goddard, 1999: Air-sea gas exchange into the millennium: progress and uncertainties. Oceanography and Marine Biology: an Annual Review, 37, pp. 1-45.

Garratt, J.R., 1992. The atmospheric boundary layer. Cambridge University Press, Cambridge, pp. 90-93.

Haußecker, H., 1996. Messung und Simulation von kleinskaligen Austauschvorgängen an der Ozeanoberfläche mittels Thermographie. Ph.D-Thesis, Ruprecht-Karls-Universität, Heidelberg, 199 pp.

Hicks, B.B., D.D. Baldocchi, T.P. Meyers, R.P. Hosker Jr. and D.R. Matt, 1987. A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. Water, Air, and Soil Pollution, 36, pp. 311-330.

Ho D.T., W.E. Asher, L.F. Bliven, P. Schlosser and E.L. Gordan, 2000. On mechanisms of rain-induced air-water gas exchange. J. Geophys. Res. 105, pp. 24045-24057.

Jacobs, C.M.J., J.W. Deneer and P.I. Adriaanse, 2010. Modelling water temperature in TOXSWA. Alterra report 2099, ISSN 1566-7187. Wageningen, Alterra, 60 pp.

Jacobs, A.F.G., B.G. Heusinkveld and D.C. Lucassen, 1998. Temperature variation in a class A evaporation pan. J. Hydrol., 206, pp. 75-83.

Jacobs, C., J.-F. Kjeld, P. Nightingale, R. Upstill-Goddard, S. Larsen and W. Oost, 2002. Possible errors in CO2 air-sea transfer velocity from deliberate tracer releases and eddy covariance measurements due to near-surface concentration gradients. J. Geophys. Res., 107(C9), 3128, doi:10.1029/2001JC000983.

Jacobs, C.M.J., E. van den Berg and J.A. van Jaarsveld, 2007. Principles and main uncertainties of a methodology to assess gaseous deposition of pesticides onto small water bodies. In: A.A.M. Del Re, E. Capri, G. Fragoulis and M. Trevisan (eds.), Environmental Fate and Ecological Effects of Pesticides. La Goliardica Pavese s.r.l., Pavia, pp. 270-277.

Jähne, B., and H. Haußecker, 1998. Air-water gas exchange. Annu. Rev. Fluid Mech., 30, pp. 443-468.

Liss, P.S. and P.G. Slater, 1974. Fluxes of gases across the air-sea interface. Nature, 247, pp. 181-184.

Liss P.S. and L. Merlivat, 1986. Air-sea gas exchange rates: introduction and synthesis. In: P Buat-Menard (Ed.), The Role of Air-Sea Exchange in Geochemical Cycling, Reidel, Boston, pp. 113–129.

MacIntyre, S., R. Wanninkhof and J.P. Chanton, 1995. Trace gas exchange across the air-water interface in freshwater and coastal marine environments. In: Matson, P.A., Harriss, R.C.. Biogenic trace gases: measuring emissions from soil and water, Blackwell Science, Oxford, UK, pp. 52-97.

Monteith, J.L. and M.H. Unsworth, 1990. Principles of environmental physics. Edward Arnold, Londen.

Moog, D.B. and G.H. Jirka, 1995. Analysis of reaeration equations using mean multiplicative error. In: B. Jähne and E. Monahan (Eds.), Air-Water Gas Transfer. AEON Verlag, Heidelberg, pp. 101-111.

Nightingale, P.D., G. Malin, C.S. Law, A.J. Watson, P.S. Liss, M. I. Liddicoat, J. Boutin and R. C. Upstill-Goddard, 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers-, Global Biogeochem. Cycles, 14, pp. 373-388.

Raymond, P.A. and J.J. Cole, 2001. Gas exchange in rivers and estuaries: choosing a gas transfer velocity. Estuaries, 24, pp. 312-317.

Read, J.S., D.P. Hamilton, A.R. Desai, K.C. Rose, S. MacIntyre, J.D. Lenters, R.L. Smyth, P.C. Hanson, J.J. Cole, P.A. Staehr, J.A. Rusak, D.C. Pierson, J.D. Brookes, A. Laas and C.H. Wu, 2012. Lake-size dependency

of wind shear and convection as controls on gas exchange. Geophys. Res. Lett., 39, L09405, doi:10.1029/2012GL051886.

Soloviev, A.V. and P. Schlüssel, 1996. Evolution of cool skin and direct air-sea gas transfer coefficient during daytime. Boundary Layer Meteorol., 77, pp. 45- 68.

Thyssen, N. and M. Erlandsen, 1987. Reaeration of oxygen in shallow, macrophyte rich streams: ll. Relationship between the reaeration rate coefficient and hydraulic properties. Int. Revue ges. Hydrobiol., 72, 375-397.

Upstill-Goddard, R.C., 2006. Air-sea gas exchange in the coastal zone. Estuarine, Coastal and Shelf Science, 70, pp. 388-404.

Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res., 97, C5, 7373-7382.

Wanninkhof, R., W.E. Asher, D.T. Ho, C. Sweeney and W.R. McGillis, 2009. Advances in quantifying air-sea gas exchange and environmental forcing. Annu. Rev. Mar. Sci., 1, pp. 213-244.

Westein, E., M.W.J. Jansen, P.I. Adriaanse and W.H.J. Beltman, 1998. Sensitivity analysis of the TOXSWA model simulating fate of pesticides in surface waters. Wageningen, DLO Winand Staring Centre, 120 pp.

Wieringa, J., 1986. Roughness-dependent geographical interpolation of surface wind speed averages. Q. J. R. Met. Soc., 112, pp. 867-889.

Zappa C.J., W.R. McGillis, P.A. Raymond, J.B. Edson, E.J. Hintsa, H.J. Zemmelink, J.W.H. Dacey and D.T. Ho, 2007. Environmental turbulent mixing controls on air-water gas exchange in marine and aquatic systems. Geophys. Res. Lett., 34, L10601.
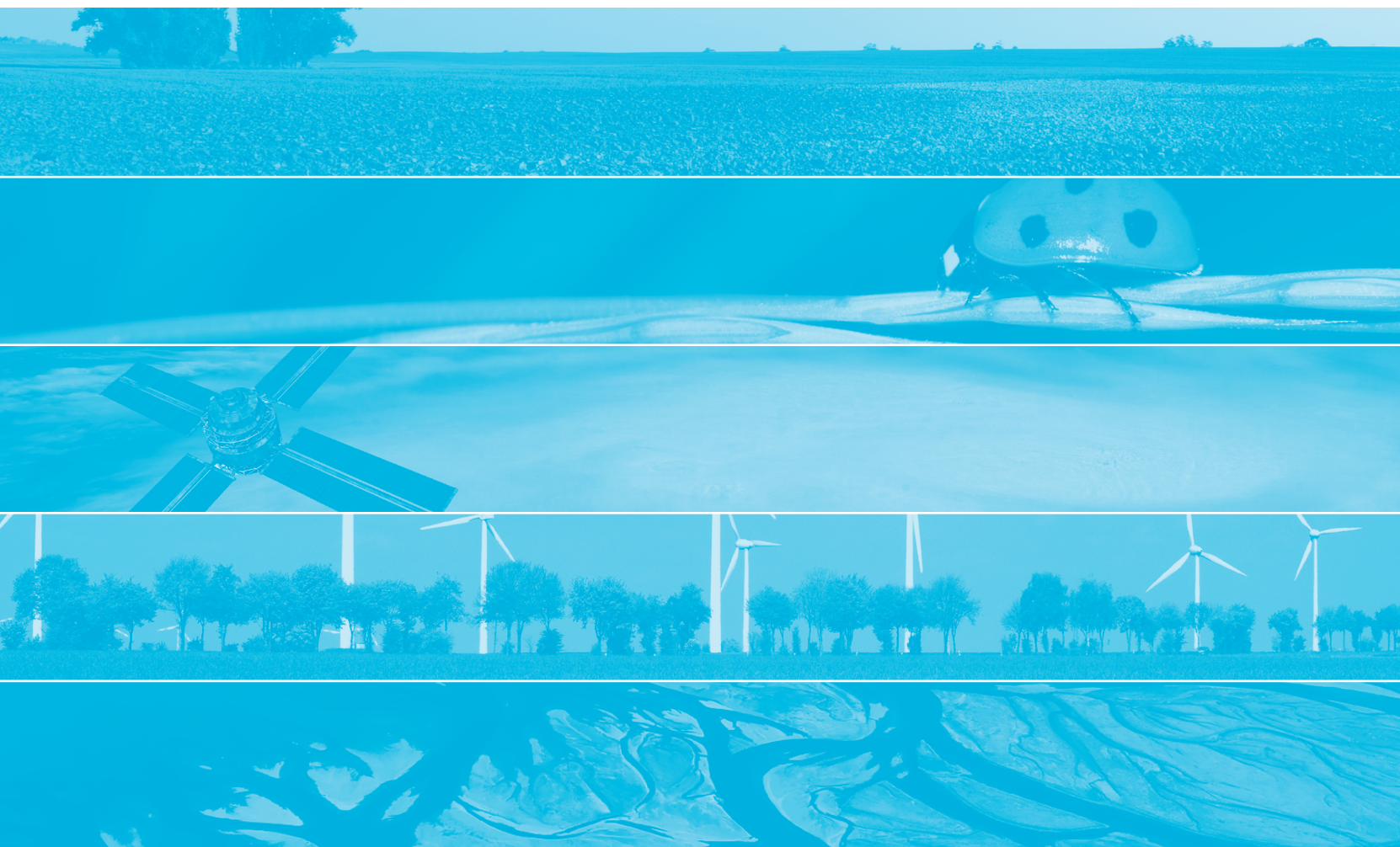
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