

Persistence of Parent Compounds and Transformation Products in a Level IV Multimedia Model

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An approach to extend the concept of persistence to transformation products of environmental chemicals is presented. First, the residence time in a steady-state scenario and the lifetime in a pulse scenario as two commonly used persistence measures are compared with respect to their mathematical formulation, and concentration functions as time-dependent solutions of a dynamic multimedia model are calculated. Second, it is shown how the model system needs to be modified in order to calculate concentration functions for any number of transformation products. On the basis of these concentration functions, two new persistence measures describing the additional exposure of the environment that is caused by the presence of transformation products are introduced. These two measures, called Joint Persistence and Secondary Persistence, are explicitly calculated for two pairs of parent compounds and transformation products, namely, methyl *tert*-butyl ether (MTBE) and atrazine and their transformation products *tert*-butyl alcohol (TBA) and desisopropyl atrazine (DIA), respectively. The suitability of both persistence definitions as measures for providing information on transformation products for regulatory purposes is discussed.

Introduction

Assessing the environmental exposure caused by anthropogenic chemicals requires a reliable understanding of the chemicals' fate in the environment. A key process determining the environmental fate of chemicals is their degradation or, more precisely, transformation behavior. Degradation does not necessarily mean that a chemical is directly mineralized. In many cases, structurally related transformation products are formed in the environment, and several examples are known where these transformation products are more persistent (e.g., refs 1–3), more toxic (e.g., ref 4), more mobile (e.g., refs 5 and 6), or more bioaccumulative (e.g., ref 7) than their parent compounds. Consequently, guidelines for the environmental risk assessment of chemicals such as the Technical Guidance Documents of the EU (8) explicitly state that transformation products should also be subject to risk assessment.

However, in many cases the transformation products are not known or only poorly characterized. Knowledge of the physicochemical properties of transformation products and the transformation kinetics is very limited. Moreover, limited

data availability is not the only obstacle to the assessment of transformation products since also the assessment procedures themselves have to be adapted to be suitable for transformation products. In this work, we focus on the environmental persistence as an important parameter in the assessment of chemicals. Persistence describes the temporal extent of the exposure of the environment to the chemical. It is frequently used in priority setting and screening of chemicals before they are admitted to a more thorough and therefore costly and time-consuming quantitative, effect-based risk assessment (9–12). Persistence is also often considered as a complement to or weighting factor for the assessment of the toxic properties of a chemical (13). In the case of a single-pulse input into the environment, persistence stands for the time span within which the chemical decays to a certain fraction of the initial concentration. This notion of lifetime is often quantified by a half-life (14) or equivalence width of the concentration function (15, 16). In those cases where the chemical is continuously released, persistence is commonly defined as the average residence time of the substance in the system under consideration (17–19).

Both persistence measures, residence time and half-life, do not cover transformation products, and even more problematic, they tend to mask the occurrence of transformation products since they give the impression that the environmental exposure ceases after the time span given by the persistence measure.

A first attempt to determine the environmental persistence of known transformation products might be to conduct a risk assessment for the transformation product in the same way as it is done for the parent compound (20). However, this approach does not take into account the kinetics of the transformation process that leads to a delayed formation of the transformation product. For this reason, we have developed measures for the persistence of parent compounds and transformation products in combination, which is a novel approach to the assessment of transformation products. In this study, we present the definitions of two new persistence measures called Joint Persistence (JP), representing the persistence of the parent compound in combination with all transformation products, and Secondary Persistence (SP), representing the persistence of each transformation product alone. To this end, we use a closed box model with the three environmental media soil, water, and air. The model is solved for the steady-state concentrations (level III) and the time-dependent concentration functions of the three media (level IV), and the relation between the persistence results obtained for steady-state and pulse release is investigated.

Next, we apply the new persistence measures to two examples with a sufficient data basis. These are atrazine and its transformation product desisopropyl atrazine (DIA) as well as methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA). DIA is a comparably short-lived transformation product (21), while TBA is more persistent than its parent compound MTBE (22). Although these examples do not cover all environmentally relevant transformation products of atrazine and MTBE, they demonstrate that inclusion of the transformation products leads to persistence values that are significantly different from those obtained for the parent compounds alone. Thus, we argue that transformation products should not be disregarded in the standard procedures of the assessment of chemicals.

Model Setup and Solutions

Model Description Including Transformation Products. The box model used for our persistence calculations consists of

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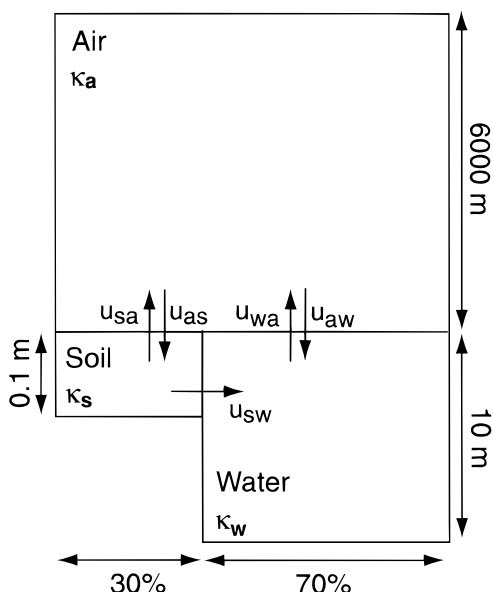


FIGURE 1. Dimensions of the evaluative model system used to calculate persistence values as adopted from Klein et al. (24). The coefficients u_{ik} represent phase transfer processes, while the degradation constants are denoted by κ_i .

the three phases soil (s), water (w), and air (a) with averaged environmental properties and dimensions (see Figure 1). The dimensions of each phase as well as the definition and quantification of the phase-transfer processes between the phases are the same as those used by Scheringer (15); see also refs 23 and 24. The processes considered in the model are abiotic and biotic first-order degradation processes, denoted by κ_i in each phase i , and diffusive and advective transfer processes between the phases, denoted by u_{ik} , where the sequence $i-k$ stands for transfer from phase i to phase k . The phase transfer parameters represent processes such as volatilization, dry and wet deposition, leaching, etc. Some of these processes are functions of the Henry's law constant K_H and the octanol–water partitioning coefficient K_{ow} . Advective transfer in to and out of the model system is not considered, so that the resulting persistence values can be compared with the persistence values calculated in global scale or other closed-system models (10, 14, 15, 18).

The following rate equation, which takes into account all degradation and interphase transfer processes between the compartments with volumes v_i and v_k , can be formulated for each of the m chemical species x in the model system:

$$\frac{dc_i^x(t)}{dt} = -\kappa_i^x c_i^x(t) - \sum_k u_{ik}^x c_i^x(t) + \sum_k u_{ki}^x \frac{v_k}{v_i} c_k^x(t) \quad i, k = s, w, a \quad (1)$$

The first term on the right-hand side of eq 1 describes degradation, the second term represents transfer from the compartment i to the other two compartments k , and the last term is the transfer from these other two compartments k into the compartment i . For each species x , this linear differential equation can also be written as

$$\dot{\mathbf{c}}^x(t) = -\mathbf{S}^x \mathbf{c}^x(t) \quad (2)$$

The 3×3 matrix \mathbf{S}^x is composed of the parameters κ_i^x and u_{ik}^x according to eq 1.

Since, except for the parent compound, each species in the system can be a transformation product y ($y = B, C, \dots$,

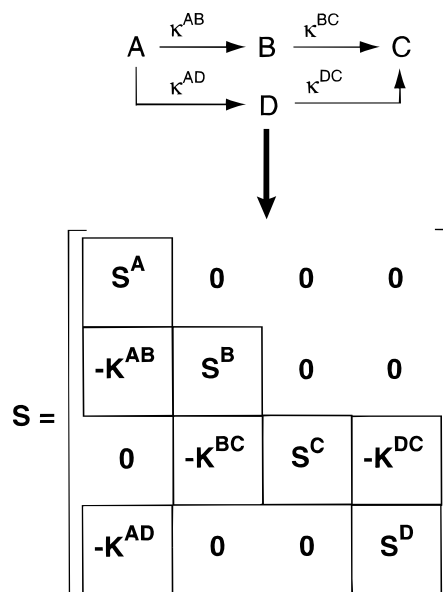


FIGURE 2. Construction of the matrix \mathbf{S} in eq 4 for an example in which parent compound A decays in two parallel reaction channels into the transformation products B and D , which are both further transformed to C , hence $m = 4$. The rate constants of the transformation processes are denoted by κ^{xy} . \mathbf{S}^x is the submatrix of the species x including its degradation and transfer processes (see eq 1). \mathbf{K}^{xy} is the transformation submatrix representing the transformation of the species x to the species y .

m) of another species x ($x = A, B, C, \dots, m; x \neq y$), a formation term

$$\frac{dc_i^y(t)}{dt} = + \sum_x \kappa_i^{xy} c_i^x(t) \quad (3)$$

has to be added to the rate equation of the transformation product y with κ_i^{xy} being the rate constant at which x is transformed to y in phase i . Thereby κ_i^{xy} is a fraction of κ_i^x , i.e., $\kappa_i^{xy} = \theta_i^{xy} \kappa_i^x$ with $0 \leq \theta_i^{xy} \leq 1$ denoting the fraction of transformation. For each pair xy of parent compound and transformation product, this additional rate equation can also be expressed by means of the diagonal formation matrix \mathbf{K}^{xy} which consists of the three rate constants of formation, κ_i^{xy} , $i = s, w, a$.

For our model system with the three phases soil, water, and air and the m chemical species, of which one is the parent compound and the others are transformation products that are formed from the other species, the various 3×3 matrixes \mathbf{S}^x and \mathbf{K}^{xy} can be used as block matrixes to construct a main matrix \mathbf{S} , see Figure 2. This results in eq 4, which stands for a system of $3m$ linear differential equations:

$$\dot{\mathbf{c}}(t) = -\mathbf{S} \mathbf{c}(t) \quad (4)$$

In eq 4, the concentrations $c_i^x(t)$ are being combined to the vector $\mathbf{c}(t) = [c_s^A(t), c_w^A(t), c_a^A(t), c_s^B(t), \dots, c_s^m(t), c_w^m(t), c_a^m(t)]$, and \mathbf{S} is built according to the following rules (also see Figure 2):

(i) All submatrixes \mathbf{S}^x and \mathbf{K}^{xy} have the dimension $p \times p$, where p is the number of phases, here $p = 3$.

(ii) The main matrix \mathbf{S} has the dimension $mp \times mp$, where m is the number of species in a parent compound–transformation product system.

(iii) The m submatrixes \mathbf{S}^x always lie on the diagonal of \mathbf{S} , while their sequence is the same as the sequence of the chemicals in $\mathbf{c}(t)$.

(iv) The \mathbf{K}^{xy} submatrixes always lie at the position xy , where x denotes the column and y denotes the row.

Persistence Definitions in Steady-State (Level III) and Dynamic (Level IV) Systems. In many approaches to calculate the persistence of a chemical, level III multimedia models are used, and the persistence is determined as the chemical's residence time in the model system given by the ratio of the mass contained in the system, M^{stst} (in kg), and the flow through the system, Q (in kg/s) (10, 14, 18, 25). Bennett et al. (18) investigated the temporal change of the ratio $M(t)/Q$ with a level IV model starting from the point in time when the substance is first emitted into the system. $M(t)$ stands for the total mass in the system at time t , i.e., the sum of the concentrations $c_i(t)$ in each compartment multiplied with the volumes v_i of the respective compartments.

To calculate the steady-state concentrations c_i^{stst} , a source vector \mathbf{q} is added to eq 4 and $\dot{\mathbf{c}}(t)$ is set to zero (see eq 5). The first three elements of the vector \mathbf{q} represent the continuous release fluxes of the parent compound into each compartment (in kg/m³·s), while the remaining elements of \mathbf{q} concerning the transformation products equal zero:

$$\dot{\mathbf{c}} = -\mathbf{S}\mathbf{c} + \mathbf{q} = 0 \quad (5)$$

From eq 5, we obtain the steady-state concentrations c_i^{stst} by inverting the matrix \mathbf{S} as

$$\mathbf{c}^{\text{stst}} = \mathbf{S}^{-1}\mathbf{q} \quad (6)$$

The residence time of the parent compound is then given by eq 7:

$$\tau^{\text{stst}} = \frac{\sum_i c_i^{\text{stst}} v_i}{\sum_i q_i v_i} = M^{\text{stst}}/Q \quad (7)$$

To determine the persistence of the parent compound alone, i.e., the way persistence is usually defined, the sum is limited to the first $p = 3$ elements of the concentration vector.

In contrast to the residence time, which is a steady-state quantity, the half-life (19) or equivalence width (15) are characteristics of the decreasing function $M(t)$ as it is obtained after a pulse emission or after a continuous release has ceased. The equivalence width τ^{equiv} of the parent compound is defined as

$$\tau^{\text{equiv}} = \frac{\sum_i v_i \int_0^\infty c_i(t) dt}{\sum_i c_{0,i} v_i} = \frac{\sum_i e_i v_i}{\sum_i c_{0,i} v_i} = \frac{1}{M_0} \int_0^\infty M(t) dt \quad (8)$$

The time integrals of the $c_i(t)$ in eq 8 are called the total exposures e_i . The vector $\mathbf{e} = [e_s^A, e_w^A, e_a^A, e_s^B, \dots, e_s^m, e_w^m, e_a^m]^T$ is calculated according to (see ref 15):

$$\mathbf{e} = \mathbf{S}^{-1}\mathbf{c}_0 \quad (9)$$

Equation 9 is obtained from eq 4 by using a vector of initial concentrations, \mathbf{c}_0 , and by taking the integral over time of $\mathbf{c}(t)$ (15). In analogy to \mathbf{q} , the vector \mathbf{c}_0 contains the amount of the parent compound released into each compartment (in kg/m³), while all elements of \mathbf{c}_0 concerning the transformation products equal zero.

Comparing eqs 6 and 7 with eqs 8 and 9 shows that the same results are obtained for the residence time τ^{stst} and the equivalence width τ^{equiv} if \mathbf{c}_0 and \mathbf{q} have the same entries (yet with different units). This means that each steady-state model can also be interpreted in terms of a pulse scenario or, in other words, that the steady-state concentrations and the residence time resulting from a continuous input are equivalent to the exposure values and the equivalence width resulting from a pulse input. [Note that if the steady-state

concentrations themselves are used as initial concentrations for a pulse scenario, the resulting equivalence width is *different* from the residence time obtained for the steady state (10).] A second important observation is that, as both $M(t)$ and M^{stst} are directly proportional to M_0 and Q , respectively, τ^{stst} and τ^{equiv} do not depend on the absolute values of M_0 or Q but only on the relative magnitude of the single elements of \mathbf{c}_0 and \mathbf{q} .

Because of this identical mathematical formalism of τ^{stst} and τ^{equiv} , the numerical values obtained for both of them can be used equivalently. In the following, we solve the model on level IV because this gives a more detailed insight into the degradation dynamics: Comparing the point in time marked by the equivalence width τ^{equiv} with the plot of the concentration function $\mathbf{c}(t)$ lends a better understanding as to how persistence values should be interpreted. Moreover, if one wants to develop an extended persistence definition including transformation products, it is crucial to understand how the concentration functions of the transformation products behave relative to those of the parent compound.

Calculation and Characterization of Concentration Functions. To investigate the position of τ^{equiv} in a given concentration profile, the system of linear, homogeneous differential equations given in eq 4 needs to be solved for $\mathbf{c}(t)$. This is done by calculating the eigenvalues $\lambda_1, \dots, \lambda_{3m}$ and eigenvectors $\mathbf{y}_1, \dots, \mathbf{y}_{3m}$ of the main matrix \mathbf{S} . The general solution of the system is then given by

$$\mathbf{c}(t) = a_1 e^{-\lambda_1 t} \mathbf{y}_1 + a_2 e^{-\lambda_2 t} \mathbf{y}_2 + a_3 e^{-\lambda_3 t} \mathbf{y}_3 + \dots + a_{3m} e^{-\lambda_{3m} t} \mathbf{y}_{3m} \quad (10)$$

[In a one-compartment system, the eigenvalues occurring in the exponential expressions are directly given by the degradation rate constants of the parent compound and its transformation products (26).] The coefficients a_i in eq 10 are chosen such that they satisfy the initial condition

$$\mathbf{c}_0 = a_1 \mathbf{y}_1 + a_2 \mathbf{y}_2 + a_3 \mathbf{y}_3 + \dots + a_{3m} \mathbf{y}_{3m} = \mathbf{Y}\mathbf{a} \quad (11)$$

where \mathbf{Y} is the $3m \times 3m$ matrix whose columns are the eigenvectors $\mathbf{y}_1, \dots, \mathbf{y}_{3m}$.

The resulting vector $\mathbf{c}(t)$ consists of all $c_i^x(t)$ for all species in all phases and characterizes the $3m$ single concentration functions. Since we do not consider back reactions, including the transformation products into the calculations does not change the dynamics of the parent compound and therefore neither its persistence.

In the following, the concentrations $c_i^x(t)$ are calculated for different release scenarios (release to soil, to water, or to air) of atrazine and methyl *tert*-butyl ether (MTBE) and their transformation products desisopropyl atrazine (DIA) and *tert*-butyl alcohol (TBA), respectively. Atrazine is one of the most often used herbicides and is found in many surface waters and groundwaters. DIA is one of its transformation products often found, besides others, in the same places as atrazine itself (21). The environmental fate of MTBE has become a subject of renewed interest because of the large quantities of this compound that are being used as an oxygenated additive in gasoline (27). TBA is one of its major degradation products with a sufficiently large resistance to further degradation in soil and groundwater so that it may accumulate as an intermediate (28, 29). The input parameters for the four substances, namely, the three degradation constants κ_i and the two partitioning coefficients K_H and K_{ow} , are given in Table 1.

For each substance, the resulting concentration functions $c_i^x(t)$ in each compartment are multiplied with the compartment's volume v_i , thus providing the mass profiles $m_i^x(t)$ for each compartment. These are then added up over all compartments to give overall mass profiles $M^x(t)$. Thus,

TABLE 1. First-Order Degradation Rates, Octanol–Water Partitioning Coefficient, and Henry's Law Constant for Atrazine, DIA, MTBE, and TBA^a

compd	k_s (s ⁻¹)	k_w (s ⁻¹)	k_a (s ⁻¹)	log K_{ow}	K_H (Pa m ³ mol ⁻¹)
atrazine	3.82×10^{-7}	2.67×10^{-7}	1.60×10^{-4}	2.68	2.51×10^{-4}
DIA	3.50×10^{-6}	2.50×10^{-6}	5.38×10^{-5}	1.15	1.18×10^{-4}
MTBE	4.46×10^{-8}	4.46×10^{-8}	7.27×10^{-7}	0.94	59.48
TBA	4.01×10^{-8}	4.46×10^{-8}	3.26×10^{-7}	0.35	1.46

^a From refs 2, 21, 22, 30, and 31.

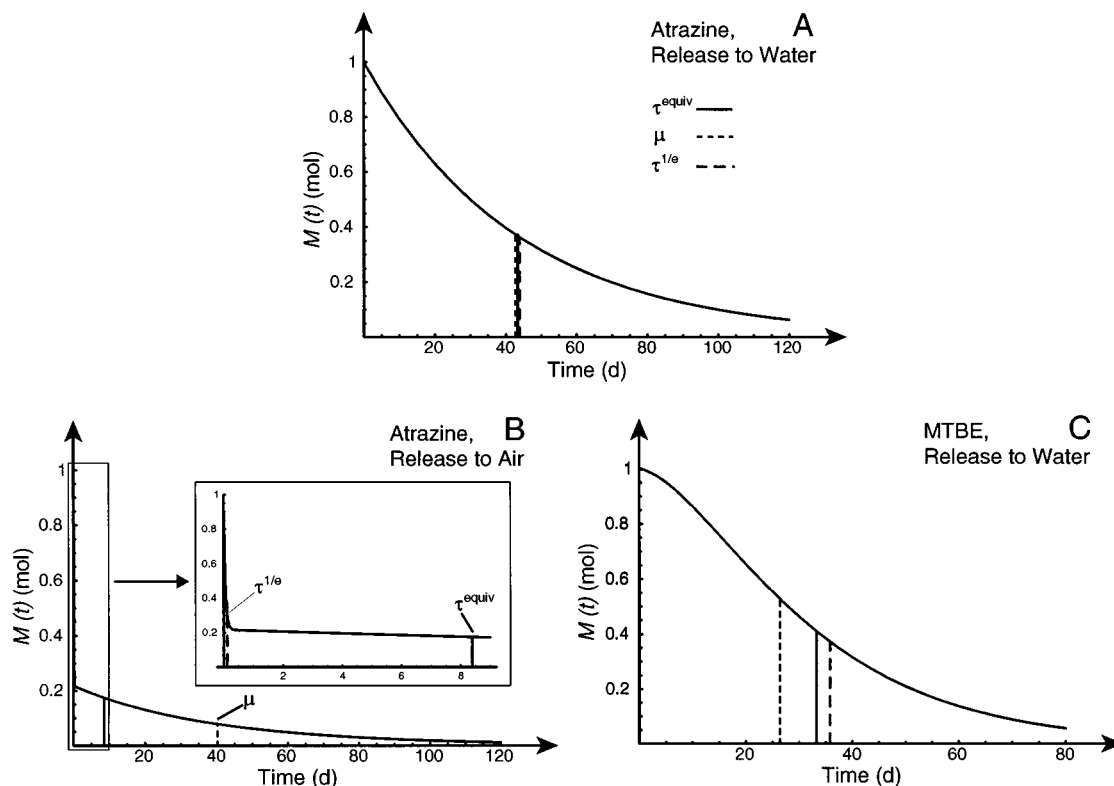


FIGURE 3. Overall mass profiles $M(t)$ of atrazine released to water (A), atrazine released to air (B), and MTBE released to water (C). $M(t)$ is the overall mass of the chemical in the model system at time t when it is summed up over all compartments. As the calculated persistence values do not depend on the absolute amount of substance in the system, M_0 can be chosen arbitrarily and was set to 1 mol in the examples given. The vertical lines indicate the three different persistence measures τ^{equiv} , $\tau^{1/e}$, and μ .

depending on the release scenario, three overall mass profiles $M^x(t)$ are obtained for each substance x . As examples of the parent compounds' mass profiles, the overall mass profiles for atrazine after release to water, atrazine after release to air, and MTBE after release to water are depicted in Figure 3, panels A–C. It shows that fairly different profiles are obtained for the different situations.

The shape and temporal extension of the calculated mass profiles can be described not only by means of τ^{equiv} as given in eq 8 but also by the time $\tau^{1/e}$ that denotes the time required for a decrease of the initial mass M_0 to a fraction of $1/e \cdot M_0$:

$$\frac{M(\tau^{1/e})}{M_0} = 1/e \approx 0.37 \quad (12)$$

or by the mean value μ , in which the masses are weighted with their respective times:

$$\mu = \frac{\int_0^\infty M(t)t \, dt}{\int_0^\infty M(t) \, dt} \quad (13)$$

These two measures provide additional information on the nature of the mass profiles $M(t)$ and are used in this section

TABLE 2. Equivalence Width, Mean Value, and Lifetime for Scenarios A–C Depicted in Figure 3 (in days)

panel	τ^{equiv}	μ	$\tau^{1/e}$
A	43.3	43.3	43.3
B	8.65	40.5	0.09
C	33.7	26.2	36.0

in addition to the equivalence width. The values for τ^{equiv} , $\tau^{1/e}$, and μ for Figure 3A–C are given in Table 2.

If atrazine is released to water as depicted in Figure 3A, the overall mass profile is dominated by the mass fraction of atrazine in the water compartment and therefore comes close to a single-exponential decay. This is due to the compound's slow degradation in and high affinity to the water compartment as compared to the other compartments. The resulting overall mass profile can be satisfactorily described as $c(t) = a e^{-k_w t}$. In this case, the equivalence width equals the values calculated for μ and $\tau^{1/e}$ with $\tau^{\text{equiv}} = \mu = \tau^{1/e} = 1/k_w$. Furthermore, τ^{equiv} here correctly predicts that after another period of the length τ^{equiv} the function $M(t)$ will have decreased to $M_0 \cdot 1/e^2$.

However, when the overall mass profile is not dominated by one single compartment, its shape may deviate signifi-

cantly from a single-exponential decay. This is the case for the release of atrazine to air and of MTBE to water (Figure 3B,C). The mass profile in Figure 3B is the sum of a fast decay in air, to which the substance has been released, and of two slow decays in water and soil, into which the substance is transported subsequently. For this type of curve the equivalence width is always bigger than $\tau^{1/e}$, indicating that the mass profile shows a distinct tailing with the substance remaining in the overall system at low concentrations for longer time periods than the time $\tau^{1/e}$ would suggest. This effect is emphasized by the value obtained for μ , which is several times bigger than $\tau^{1/e}$ and τ^{equiv} because the small amounts of substance left at long times are weighted with the respective times. Figure 3C, in contrast, is typical for situations where the emission and the nonemission compartments have similar decay rates and affinities for the chemical. In this case, the equivalence width is smaller than $\tau^{1/e}$, suggesting that the substance is degraded even faster than one expects from the value of $\tau^{1/e}$. Consequently, μ is smaller than the equivalence width for this type of mass profile.

We conclude that, especially if the chemical shows markedly different degradation rates in the various environmental compartments, it is advisable to solve the level IV system and to include information gained from the course of the mass profile into the risk assessment. Otherwise, the interpretation of the persistence value, calculated as τ^{equiv} or τ^{stst} , as the rate at which a chemical continues to disappear after several lifetime periods have elapsed, might lead to significant discrepancies between the expected concentration and the concentration calculated by solving the level IV model.

Persistence of Parent Compounds and Transformation Products

Extended Persistence Definitions. To include the temporal behavior of transformation products in the persistence definition of parent compounds, three different types of persistence, mathematically based on the equivalence width definition (see eq 8), are calculated for parent compounds and transformation products. First, the overall persistence of each separate compound, i.e., parent compound and transformation product, is determined as described in the preceding section. This overall persistence of single compounds is henceforth called Primary Persistence (PP) and is calculated according to eq 8 for each compound x :

$$\text{PP}^x = \frac{\sum_i e_i^x v_i}{\sum_i c_{0,i} v_i} = \frac{1}{M_0} \int_0^\infty M^x(t) dt \quad (14)$$

In addition to the PP, two further types of persistence are derived from the concentration vector $\mathbf{c}(t)$ that results from solving eq 4: First, the overall persistence of the sum of the masses of the parent compound and the transformation products is called Joint Persistence (JP). The JP is defined as the sum of the exposure of all substances in all compartments divided by the mass M_0 of the parent compound at $t = 0$. In eq 15, this definition is shown for the case of a parent compound A with $m - 1$ transformation products y :

$$\text{JP} = \frac{1}{M_0} \int_0^\infty (M^A(t) + \sum_y M^y(t)) dt \quad (15)$$

In a one-compartment system, the JP according to eq 15 is equal to the sum of the PPs of the parent compound A and the transformation products y . However, in a multimedia system, the JP cannot be deduced from the PPs in a straightforward manner. Note that the JP can be calculated

from the level III solutions of the system because of the equivalence between eq 15 and eq 8.

The second type of persistence derived from the concentration vector $\mathbf{c}(t)$ is the overall persistence of each transformation product alone as it is formed while the parent compound is being degraded, called Secondary Persistence (SP). In calculating the SP from the overall mass profile of the transformation product, the concept of equivalence width fails because the mass M^y at $t = 0$ equals zero. Nevertheless, in analogy to the equivalence width definition, the SP can be calculated as the integral over the entire mass profile divided by M_{max}^y , the maximum value of the mass profile of the transformation product:

$$\text{SP}^y = \frac{1}{M_{\text{max}}^y} \int_0^\infty M^y(t) dt \quad (16)$$

M_{max}^y provides a point of reference for the transformation product y that is independent of M_0 on a relative scale. (If M_0 was used instead of M_{max}^y , information on the temporal extent of the function $M^y(t)$ and on the amount of transformation product y that is formed out of M_0 would become mixed in the SP. This means that very low SPs would be obtained for long-lived transformation products that are formed in very small amounts.)

The purpose of the SP is to characterize and compare individual transformation products by a measure that explicitly reflects their formation from their precursors. It is related to the particular transformation scheme in which the chemicals occur and is therefore not a property of the chemicals alone. The SP indicates the temporal extent of the exposure of the environment to the individual transformation products. Since its calculation is based on the maximum mass, M_{max}^y , it requires the level IV solution of the system to be known.

On the basis of eqs 15 and 16, the following relationship between the JP and the SPs can be formulated for a parent compound A and its transformation products y :

$$\text{JP} = \text{PP}^A + \sum_y \frac{M_{\text{max}}^y}{M_0} \text{SP}^y \quad (17)$$

As M_{max}^y/M_0 is always smaller than 1, eq 17 leads to a lower and an upper limit of the JP, which is given in eq 18:

$$\text{PP}^A \leq \text{JP} \leq \text{PP}^A + \sum_y \text{SP}^y \quad (18)$$

Upper and lower bounds of the JP can also be expressed in terms of PPs according to the following consideration: The transformation products y are formed in all compartments that are accessible for the parent compound. Their contribution to the joint persistence (second term on the right-hand side of eq 15) is determined by the transfer processes between the compartments and by the different formation and degradation rates in the three compartments. This contribution to the JP is equal to or greater than the hypothetical contribution from the scenario where the transformation products are formed completely in those compartments where their PPs are lowest (PP_{min}^y in eq 19). In a similar way, the upper bound can be approximated by summing up the PP of the parent compound and the hypothetical contribution from the scenario where the transformation products are formed completely in those compartments where their PPs are highest (PP_{max}^y in eq 19). This leads to the following relationship:

$$\text{PP}^A + \sum_y \text{PP}_{\text{min}}^y \leq \text{JP} \leq \text{PP}^A + \sum_y \text{PP}_{\text{max}}^y \quad (19)$$

TABLE 3. Primary Persistences of Parent Compounds Atrazine and MTBE in Comparison with Primary Persistences of Their Transformation Products DIA and TBA (in days)

atrazine—DIA	PP atrazine (d)	PP DIA (d)	MTBE—TBA	PP MTBE (d)	PP TBA (d)
release to soil	31.2	3.59	release to soil	21.3	148
release to water	43.3	4.63	release to water	33.7	160
release to air	8.65	2.83	release to air	16.6	64.6

TABLE 4. Secondary Persistences of Transformation Products DIA and TBA and Joint Persistences of Pairs Atrazine—DIA and MTBE—TBA (in days)^a

atrazine—DIA	SP DIA (d)	JP atrazine & DIA (d)	LoLim (d)	UpLim (d)	MTBE—TBA	SP TBA (d)	JP MTBE & TBA (d)	LoLim (d)	UpLim (d)
release to soil	42.2	34.8	34.0	35.8	release to soil	134	87.9	85.9	181
release to water	56.6	47.9	46.1	47.9	release to water	156	105	98.3	194
release to air	5.87	11.8	11.5	13.3	release to air	123	81.5	81.2	177

^a In addition, the lower (LoLim) and upper limit (UpLim) estimates according to eq 19 are given.

The advantage of these upper and lower bounds of the JP is that they can be derived from the PP values, i.e., from results obtained by assessing the transformation products as single substances in level III models. The lower limit is always more restrictive than the PP^A given as lower limit in eq 18; the upper limit is the better estimate than the term $\sum_j SP^j$ in eq 18 the smaller the factor M'_{\max}/M_0 is.

In our concept of assigning persistence measures to transformation products, JP is the key quantity that shows the relevance of the sum of all transformation products as compared to the parent compound alone. In addition, SP provides auxiliary information if one is interested in a detailed assessment of the single chemicals occurring in the transformation scheme.

Results for Two Selected Chemicals (Atrazine and MTBE). The combinations atrazine—DIA (i) and MTBE—TBA (ii) have been chosen according to the ratio between the PPs of parent compound and transformation product, i.e., if each of them is released separately into the model system. They represent to cases of (i) a persistent parent compound and a less persistent transformation product and (ii) a persistent transformation product and a less persistent parent compound. Second, they were chosen because both parent compounds are well-known environmental chemicals with the transformation products present in the environment in considerable amounts (21, 29, 32). The PPs of the four compounds are listed in Table 3; they depend on the release scenario chosen. The ratio between the PPs of the parent compounds and the transformation products is around 10 for the pair atrazine—DIA and between 0.1 and 0.2 for the pair MTBE—TBA; see Table 3.

To cover the most extreme case, where the maximally possible amount of transformation product is present in the environment, we assumed that the parent compounds are converted entirely into their respective transformation products in each compartment ($\theta_s^{xy} = \theta_w^{xy} = \theta_a^{xy} = 1$). In a first step, this assumption is used for the sake of clarity of the results and ignores the fact that in reality the parent compounds are transformed into a multitude of different transformation products whose relative share also depends on the degradation compartment.

For the calculation of the concentration profiles of the transformation products, eq 4 was solved as shown in eqs 10 and 11 for $p = 3$ and $m = 2$. The results for JP and SP (in days) as well as the estimates of the upper and lower bounds of the JP are listed in Table 4 for the pairs atrazine—DIA and MTBE—TBA, respectively.

To illustrate the persistence values in Table 4, the mass profiles on which the calculations of JP and SP are based are

shown in Figures 4 and 5. The corresponding persistence values are marked by vertical lines.

For the two pairs of chemicals analyzed here, the JP is maximally 5 times and the SP is maximally 7 times bigger than the PP of the parent compound (Tables 3 and 4, release of MTBE to air). If the SP is compared with the PP of the transformation product, one finds that the SP surpasses the PP significantly if a long-lived parent compound leads to a short-lived transformation product ($SP \approx 12.0$ PP for the release of atrazine to water, Tables 3 and 4). In this situation, the amount of the transformation product is, after a short transient phase, directly proportional to the amount of the parent compound, which is referred to as secular equilibrium in radiochemistry (33).

In general, the SP has been found to be always bigger than the smaller one of the two PPs of the parent compound and the transformation product whereas it has no upper limit. The integration of transformation products into the risk assessment process by conducting a single substance risk assessment for them as it is done in ref 20 therefore seems questionable. The naturally occurring exposure is only represented properly if the transformation process itself is included into the calculations.

An uncertainty analysis evaluating the influence of θ_i^{xy} on the persistence values has been conducted for two scenarios, release of MTBE to water and release of atrazine to soil. For each of the three fractions of transformation, θ_s^{xy} , θ_w^{xy} , and θ_a^{xy} , a uniform distribution between 0 and 1 has been assumed, and the resulting distributions of the JP and the SP have been calculated. This assumption represents a worst case in which no information on the relative share of the reaction channel of the transformation product under consideration as compared with the reaction channels of the other transformation products is available. As expected, the PP of the parent compound remains unaffected by changing values of θ_i^{xy} because no back reactions are considered. For the JP a uniform distribution is obtained, ranging between the PP of the parent compound and the JP calculated by setting all θ_i^{xy} s to 1 (values in Table 4), which was to be expected from the mathematical definition of the JP.

The value of the SP does not change as long as the ratio of $\theta_s^{xy}:\theta_w^{xy}:\theta_a^{xy}$ is kept constant and only the absolute values of θ_i^{xy} vary. Similarly, Quartier et al. found that the magnitude of the formation constant κ^{xy} has no influence on their calculation of secondary spatial ranges (34). For changing ratios of the θ_i^{xy} values though, a distribution of SP values is obtained with a mean SP of TBA for release of MTBE to water of 159 ± 9 days and a mean SP of DIA for the release of atrazine to soil of 44.5 ± 7 days. Both distributions are skewed

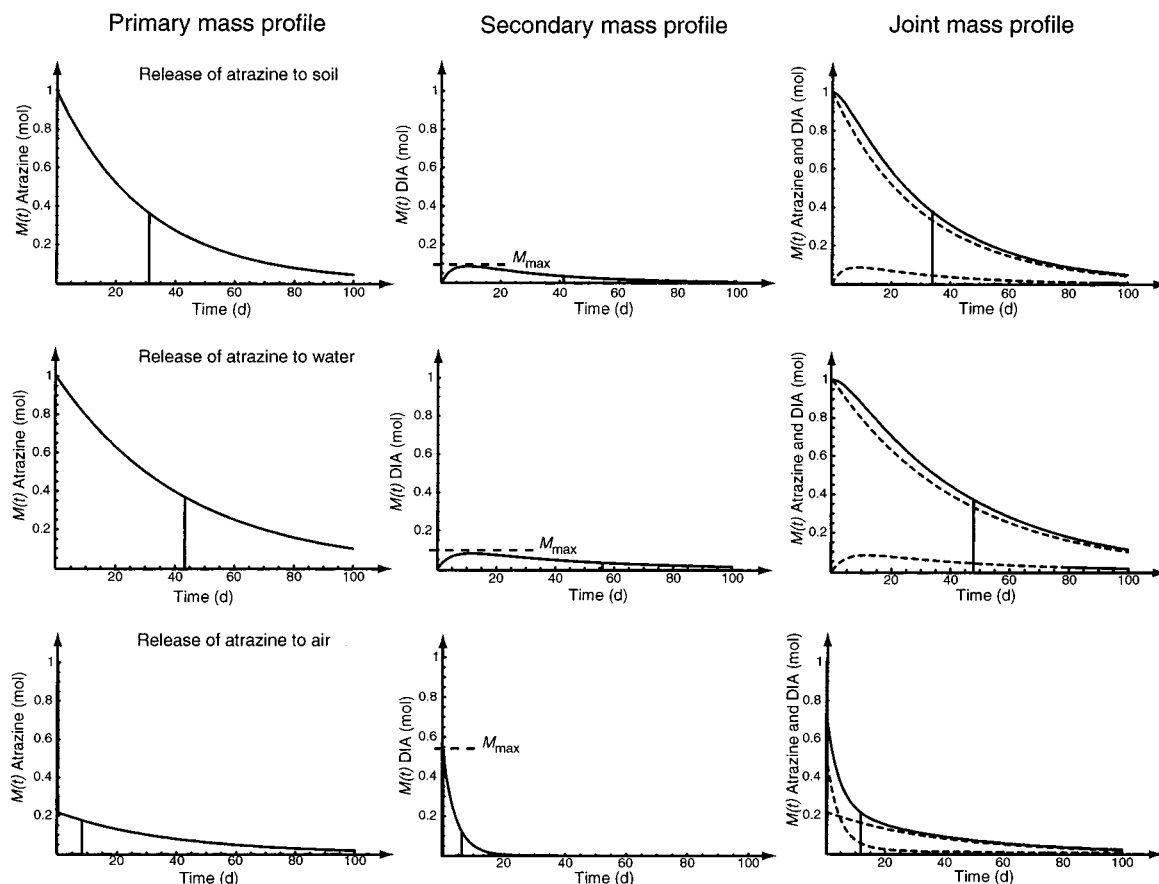


FIGURE 4. Combination of the overall mass profiles of the parent compound atrazine for three different release scenarios with the overall mass profiles of the transformation product DIA, resulting in three joint mass profiles. The vertical lines indicate the position of the three persistence measures PP, SP, and JP, respectively. In all cases, M_0 was set to 1 mol.

toward smaller SPs. In the case of DIA, considering the whole range of possible values of the SP (37–51 days) does not affect the main finding that the persistence of DIA as a transformation product is considerably enhanced as compared to the PP of DIA (3.6 days).

Discussion

The comparison of the mass profiles obtained by the model calculations presented here with mass profiles measured in field and laboratory experiments reveals congruence in some relevant aspects. A main finding of our calculations, namely, that transformation products have an enhanced potential for persistence as compared to their individual PP if the precursor compound is longer-lived than the individual transformation product, is confirmed by results presented in ref 21. There the occurrence of DIA as a transformation product of atrazine in different laboratory test systems has been measured, and the maximum of the experimental secondary mass profile lies between 7 and 275 days for different test systems. For the same series of measurements, maximal concentrations of DIA of 8% of the originally applied amount of atrazine have been found. This is consistent with our finding that, even if atrazine is entirely transformed to DIA in all compartments, the maximal concentration of a short-lived transformation product such as DIA is still low (approximately 10% of the initial concentration of atrazine for release to soil and water; see Figure 4).

Regarding the pair MTBE–TBA, several experimental studies (28, 29, 35) mention that there is evidence that TBA is at least as resistant to biodegradation as MTBE. In ref 35, the primary mass profile of MTBE, the primary mass profile of TBA, and the secondary mass profile of TBA are shown for

a mixed bacterial culture developed from microorganisms present in a chemical plant bioreactor sludge. It was found that TBA alone and TBA as transformation product of MTBE declined at a slower rate than did MTBE, which is in accordance with our findings. The maximal TBA concentration of 50% of the amount of MTBE applied corresponds well to the maximal concentrations between 45% and 50% we calculated for the long-lived transformation product TBA for all three release scenarios; see Figure 5. Further agreement can be found between laboratory soil column measurements (29), where the TBA concentration shows a maximum after 52 days and the MTBE concentration is at 20% of its original value, and our calculations for release of MTBE to soil, which indicate a maximum concentration of TBA after 50 days and at the same time a reduction of MTBE to 20%. The agreement between calculated and experimental results is a reassuring indicator that our model system is successful in reflecting the relevant features of the mass profiles of parent compounds and their transformation products.

As generally applicable measures for the persistence of transformation products, which might be used for regulatory purposes, the two quantities JP and SP have different advantages and shortcomings. The SP seems to be well suited to characterize single transformation products as they occur in the transformation scheme. It allows one to establish an exposure-based ranking among the different transformation products of one parent compound, on which, e.g., a priority list could be based that indicates transformation products that need further, effect-based testing. According to the uncertainty analysis, the variability of the SP caused by large uncertainties in the θ_i^{xy} values is not so large that a general ranking of transformation products is impeded. Drawbacks

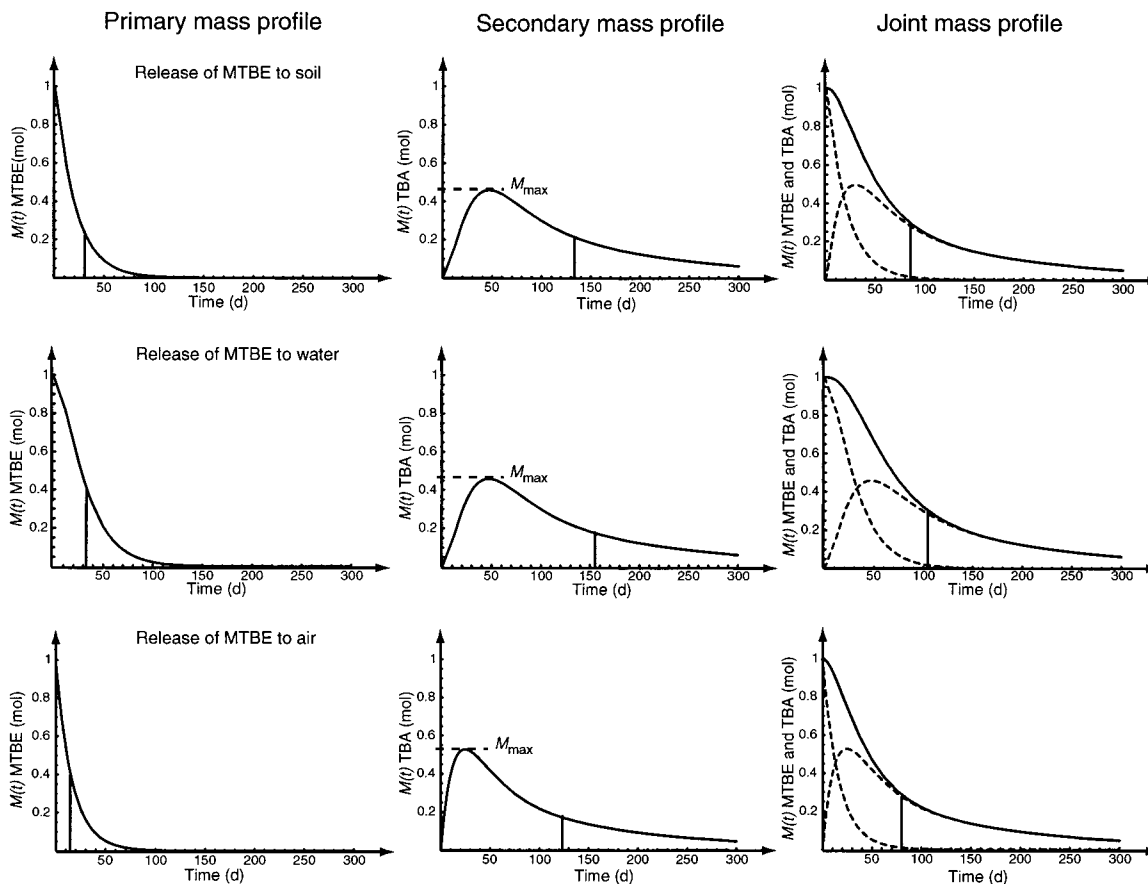


FIGURE 5. Combination of the overall mass profiles of the parent compound MTBE for three different release scenarios with the overall mass profiles of the transformation product TBA, resulting in three joint mass profiles. The vertical lines indicate the position of the three persistence measures PP, SP, and JP, respectively. In all cases, M_0 was set to 1 mol.

of the SP are that it gives no indication of the amount of transformation product present relative to the amount of the parent compound and that the level IV system has to be solved explicitly in order to calculate the SP.

The JP, in comparison, contains information about how much the transformation products contribute to the total mass in the system. It is therefore a suitable indicator of the total exposure of the environment to chemicals, caused by the release of the parent compound. A ranking of the parent compounds including transformation products according to their JP might considerably differ from a ranking based on the PP of the parent compounds only as presented in ref 16. As the JP can be calculated by means of matrix inversion, analogously to solving a level III system, customary spreadsheet programs for level III systems can be easily adopted to evaluate JPs. One reservation about the use of JPs must be mentioned though. The results of the preliminary uncertainty analysis indicate that the value of the JP depends strongly on the values of the different θ_i^{xy} . Nevertheless, the value of the JP calculated for $\theta_s^{xy} = \theta_w^{xy} = \theta_a^{xy} = 1$ can serve as an upper limit of the JP. The calculation of exact results for the JP, however, requires a sufficient accuracy of the values for θ_i^{xy} .

In conclusion, we have shown how the fate of transformation products can be included in level III and level IV multimedia models and how the resulting additional exposure of the environment can be expressed by means of JP and SP. Regarding the chemical risk assessment practice, these two quantities might be of particular importance if the transformation products have a higher toxicity than the parent compound or if their toxicity is unknown. In those cases, they might serve as useful quantities to anticipate,

in accordance with the precautionary principle, possible effects.

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