Analyzing the Limitations and the Applicability Domain of Water–Sediment Transformation Tests like OECD 308

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ABSTRACT: The assessment of chemical degradation rates from water–sediment experiments like for instance OECD 308 is challenging due to parallel occurrence of processes like degradation, sorption and diffusive transport, at different rates in water and sediment or at their interface. To systematically and quantitatively analyze this limitation, we generated artificial experiment data sets using model simulations and then used these data sets in an inverse modeling exercise to estimate degradation half-lives in water and sediment (DegT50wat and DegT50sed), which then were evaluated against their true values. Results were visualized by chemical space diagrams that identified those substance property combinations for which the OECD 308 test is fundamentally inappropriate. We show that the uncertainty in estimated degradation half-lives in water increases as the process of diffusion to the sediment becomes dominant over degradation in the water. We show that in theory the uncertainty in the estimated DegT50sed is smaller than the uncertainty in the DegT50wat. The predictive value of our chemical space diagrams was validated using literature transformation rates and their uncertainties that were inferred from real water–sediment experiments.

INTRODUCTION

An important part of the environmental risk assessment of pesticides is the calculation of predicted environmental concentrations (PEC) in surface water using system level fate models. Input parameters in these models are among others the degradation half-lives in water and sediment. Degradation half-lives in water and sediment are required data in the present European pesticide registration procedures for both risk half-lives in water and sediment are required data in the present European pesticide registration procedures for both risk half-lives in water and sediment. Degradation half-lives in water and sediment are required data in the present European pesticide registration procedures for both risk half-lives in water and sediment.

Degradation half-lives in water and sediment that are estimated in this way are used in higher tiers of the European regulatory exposure in surface water assessment (FOCUS Surface Water Step 2 and Step 3). Consequently, the estimated degradation half-lives in water and sediment need to be accurate.

Ideally, such a standardized test as OECD 308 generates unambiguous results that can be used to derive mechanistically meaningful and accurate parameters that are applicable in system level fate models. However, in the past decade, the OECD 308 protocol has received considerable criticism. The test combines water and bed sediment compartments, as well as aerobic and anaerobic conditions in one set up. Each of...
Experimental Procedure for Water–Sediment Experiments. The standard procedure for water–sediment experiments is given in the OECD 308 guideline. For a summary of the experimental approach, the reader is referred to section 1 of the Supporting Information (SI).

Model Simulation of Chemical Fate During the OECD 308 Test. The TOXSWA (TOXic substances in Surface Waters) model (version 2.1.2-F2) was used to describe the processes in the water–sediment system. Processes in TOXSWA that are relevant for water–sediment studies like OECD 308 are (i) sorption to suspended solids and sediment, which were described with the nonlinear Freundlich equation, (ii) degradation in water and sediment, covering the combined effect of hydrolysis and biodegradation, (iii) diffusion across the water–sediment interface and diffusion in the pore water of the sediment. The model as used in this paper is described in more detail in section 2 of the SI.

The conservation equations for the water and sediment are solved numerically with the aid of an explicit central finite-difference method. Sediment segmentations used as input in the TOXSWA model were optimized to match concentration profiles obtained with an analytical solution provided by Crank (1967) (see section 3 of the SI) in order to guarantee that the concentration-sediment depth profiles do not depend on the selected segment sizes. The thickness of the top ten numerical compartments was between 0.02–1 mm, dependent on the value of the Freundlich coefficient for sorption.

Parameterization of the Simulated Water–Sediment Experiments. For generation of the simulated data sets, two simulated, that is, virtual water–sediment experiments (i.e., system 1 and system 2) were defined and the most important properties of the two simulated water–sediment systems are described here.

OECD 308 recommends a sediment layer of 2.5 cm (±0.5 cm) and a water:sediment volume ratio of 3:1 per incubation vessel. Therefore, for both simulated experiments water depth, $h_{w}$, was set to 7.5 cm and sediment depth, $Z_s$, is set to 2.5 cm.

OECD 308 recommends to perform two studies: one with low organic carbon content (0.5–2.5%) and one with high organic carbon content (2.5–7.5%). Therefore, organic carbon content, $m_{oc}$, of the systems was set at the average of these ranges, that is, 1.5% and 5%, respectively.

Organic matter content ($m_{om}$), dry bulk density ($\rho_{d}$), porosity ($\epsilon$) and tortuosity ($\lambda$) were assumed to be constant with depth in the sediment. For system 1 ($m_{oc} = 1.5\%$) the four sediment layer subsections, which leaves some room for a more accurate simulation of concentration profiles that would reduce any remaining uncertainty about the accuracy of their model predictions.

The objective of our study was to identify the limitations as well as the applicability domain of OECD 308 with respect to substance properties, that is, for which substance properties can (i) the inappropriateness of the OECD 308 test be a priori proven on the basis of theory and (ii) the OECD 308 test in theory provide reliable estimates. The influence of environmental conditions (i.e., organic matter content) was addressed by comparing two different sediment types. To assess the accuracy of parameter estimates of the most relevant substance properties, it is necessary to know beforehand the true values of these parameters. Therefore, we used an approach where we first generated artificial experimental data sets using model simulations and next used these data sets in an inverse modeling exercise to estimate degradation half-lives in water and sediment, which were then evaluated against the original true values. We generated 120,000 data sets including experimental errors. The simulated data sets were generated using the TOXSWA model. TOXSWA is well suited for our purposes because it is an elaborate deterministic model based on physical process knowledge and it has been used for pesticide registration purposes in The Netherlands since 1996 and the European Union since 2003.
Policy Analysis

et al. (1987). They calculated an average CV for the water
simulated data sets were obtained.

The following Monte Carlo type procedure was used to
generate simulated data sets for each parameter set (2400) and
water–sediment system (2). In the first step, simulations with the
TOXSWA model were done to obtain the true concentrations of $c^{*}_{\text{wat}}$ and $c^{*}_{\text{sed,ave}}$ (average mass concentration of substance in the sediment) on the sampling times 0.5, 1, 3, 7, 14, 30, 60, and 100 days; that is, eight sampling times in total, which is about the average of the number of sampling times (i.e., 8, 12, 6, 5, 8) found in literature. OECD 308 recommends using at least six sampling times.

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water–sediment system (2). In the first step, simulations with the
TOXSWA model were done to obtain the true concentrations of $c^{*}_{\text{wat}}$ and $c^{*}_{\text{sed,ave}}$. In the second step, random values of these quantities were generated for the chosen sampling times as follows. It was assumed that $c^{*}_{\text{wat}}$ and $c^{*}_{\text{sed,ave}}$ were log-normal distributed with an average equal to the true value and with a coefficient of variation, CV, which was assumed to be 5%. Subsequently, values of $c^{*}_{\text{wat}}$ and $c^{*}_{\text{sed,ave}}$ for data sets were drawn from these distributions around the true values. The value of the CV (5%) is in line with values calculated from average concentrations and their standard deviation of water–sediment experiments performed by Houx et al. (1987). They calculated an average CV for the water layer of 4.4% and an average CV for the sediment of 5%. The log-normal distribution was based on the following mean, $\mu$, and standard deviation, $\sigma$, of the log transformed concentration:

$$
\mu = \ln \left( \frac{A}{\sqrt{1 + CV^2}} \right) 
$$

(1)

$$
\sigma = \sqrt{\ln(1 + CV^2)}
$$

(2)

where $A$ is the average value of either $c^{*}_{\text{wat}}$ or $c^{*}_{\text{sed,ave}}$.

Replicates of both $c^{*}_{\text{wat}}$ and $c^{*}_{\text{sed,ave}}$ were generated for each sampling time and for each combination of parameter set and water–sediment system. This was repeated such that 120 000 simulated data sets were obtained.

The generated $c^{*}_{\text{wat}}$ values were stored in g m$^{-3}$ with five decimal digits (e.g., 0.00005, which correspond to 0.5 times the LOD for the concentration in the water layer) and the $c^{*}_{\text{sed,ave}}$ values were stored in g m$^{-3}$ with four decimal digits (e.g., 0.0015, which corresponds to 0.5 times the LOD for the concentration in the sediment). Precision of the generated concentrations was chosen such that it corresponds to the accuracy of measurements of real water–sediment experiments.

The LOD for the concentration in the water layer, $c^{*}_{\text{wat}}$ was set to the European drinking water standard of 0.0001 g m$^{-3}$ (0.1 $\mu$g L$^{-1}$). The LOD for the concentrations in the sediment, $c^{*}_{\text{sed,ave}}$ was chosen to be 0.003 g m$^{-3}$ (3 $\mu$g L$^{-1}$), based on literature. In case that per compartment (i.e., water or sediment) one or more concentrations in the simulated data set were below the limit of detection, the data set for that compartment was handled using the standard procedure recommended by FOCUS. It implies that the first concentration in a particular compartment below the LOD was set to 0.5 times the LOD and that subsequent concentrations in that particular compartment below the LOD were discarded from the simulated data set.

Procedures for Inverse Modeling. For each simulated data set, DegT50$_{\text{wat}}$ and DegT50$_{\text{sed}}$ were estimated simultaneously through inverse modeling using the automatic parameter estimation model PEST in combination with TOXSWA. The model was fitted to the individual replicate artificial measurements of $c^{*}_{\text{wat}}$ and $c^{*}_{\text{sed,ave}}$. PEST uses the Gauss-Marquardt–Levenberg method to minimize the difference between simulated and measured values. The sum of the squared residuals is used as objective function. The procedure for calculating the objective function, $\Phi$, including weighting factors used is described in section 6 of the SI.

The outcome of the estimation may be influenced by the starting values of the parameters, the specified range of variation of the parameter and several optimization control variables of the PEST program. In a first round of inverse modeling, four sets of starting values of the DegT50$_{\text{wat}}$ and DegT50$_{\text{sed}}$ as specified in section 7 of the SI were used. From these fits, the fit with the smallest value of the objective function, $\Phi$ (eq S15), was selected and the other fits were discarded and not used. The optimization control variables were fine-tuned for one particular case and it was assumed that their values are suitable as well for the other simulated data sets.

Some parameter sets appeared to cause discontinuities in the inverse modeling results. As this was caused by the relatively low number of sets of starting values, inverse modeling for these cases was repeated using 13 instead of four sets of starting values (see section 7 of the SI).

Collected Output and Post Processing. As described before, 25 data sets were generated for each parameter set and each data set was fitted four times with four different sets of starting values. After the selection of the best fit out of four, 25 parameter estimates were available for DegT50$_{\text{wat}}$ and DegT50$_{\text{sed}}$. From these 25 values the coefficients of variation (CV) of DegT50$_{\text{wat}}$ and DegT50$_{\text{sed}}$ were calculated.

We aimed at a CV that represents an exact measure of the accuracy of the estimated parameter. To this end we used the true values of the DegT50$_{\text{wat}}$ and DegT50$_{\text{sed}}$ as the population mean. Using the population mean instead of the sample mean, the standard deviation ($s$) is calculated as

$$
s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \mu_{\text{pop}})^2}{n}}
$$

(3)

where, $X_i$ is an observation of $X$ (i.e., one of the 25 optimized parameter values), $n$ is the number of observations (i.e., number of parameter estimates), $\mu_{\text{pop}}$ is the population mean of variable $X$ (i.e., the true parameter value) and $s$ is the standard deviation of population $X$. The coefficient of variation of the population is calculated as

$$
CV_{\text{pop}} = \frac{s}{\mu_{\text{pop}}}
$$

(4)

Contrary to standard inverse modeling studies (i.e., using experimental data) which provide a probability of the accuracy of the estimated parameter (e.g., confidence interval), our study gives an exact measure of the accuracy (i.e., $CV_{\text{pop}}$). This is possible because we exactly know the true parameter values, which is an important merit of the present approach. The $CV_{\text{pop}}$ combines information about (i) the accuracy of the estimated parameter (i.e., in this study this indicates the deviation of the estimated value from the true value) and (ii) the amount of variability in the estimated parameters from 25 data sets. Small values of $CV_{\text{pop}}$ are obtained if the estimated
value is close to the true value and if the variability between the 25 parameter estimates is small. The following three different situations result in large values of the CV pop: (1) the 25 parameter estimates are found around the true value but the variability is large, (2) the 25 parameter estimates are found around a wrong value (e.g., an upper or lower boundary) and the variability is small or (3) the 25 parameter estimates are found around a wrong value and the variability is large.

**RESULTS AND DISCUSSION**

**Effect of Pesticide Properties on the Accuracy of the Estimated Degradation Half-Lives.** Chemical space diagrams of the CV pop of DegT50wat and DegT50sed for two values of the KF,om (L/kg). Note that a logarithmic scale is used on the vertical and horizontal axes starting at 1 (x-axis) of 10 (y-axis) and finishing at 500 days. The purple/blue colors indicate accurate parameter estimates and the red colors indicate inaccurate parameter estimates.

Large CV pop values of the DegT50wat are found for large KF,om values (>1000 L kg⁻¹) in combination with large values of the DegT50wat (roughly >50 days). The CV pop of the DegT50wat decreases with decreasing KF,om and DegT50wat, indicating that the inverse modeling exercise was more likely to return parameter estimates close to the true values of the DegT50wat for substances with low or negligible partitioning to organic matter and rather rapid degradation in the water.

Large CV pop values of the DegT50sed are found for all tested KF,om and DegT50wat values in combination with DegT50sed values of about >300 days, but for KF,om = 1 L kg⁻¹ large CV pop values are found for DegT50sed values from about 30 days and onward. The observed trend is decreasing CV pop values of the DegT50sed for decreasing DegT50sed values, indicating that parameter estimates of the DegT50sed are more accurate for substances degrading rather fast in the sediment.

**Figures 1 and 2 can also be used to illustrate the limitations of OECD 308 for determining persistence indicators for the assessment of Persistent Bioaccumulative Toxic chemicals (PBT) and very Persistent and very Bioaccumulative chemicals (vPvB).** To this end, imagine two vertical lines at DegT50wat 40 and 60 days (representing respectively, PBT and vPvB criteria in freshwater) and imagine two horizontal lines at DegT50sed 120 and 180 days (representing respectively the PBT and vPvB criteria in freshwater sediment).
Effect of Sediment Properties. Chemical space diagrams of the two different water–sediment system types are very alike, but for system 2 higher values of the CV pop of the DegT50 wat are found at slightly lower DegT50 wat values. The relation between sediment properties and the diffusion into the sediment is not straightforward and it is therefore difficult to predict the effect of sediment properties on the parameter estimation of the DegT50 wat (this is explained into more detail in section 9 of the SI).

Explanation of Observed Trends in the Accuracy. It was our objective to systematically test the hypothesis that the determination of degradation half-lives might be fundamentally impossible for pesticides that are—at the same time—subject to other dissipation processes than degradation. We therefore established and visualized the relation between the accuracy of the parameter estimate and the contribution of degradation to the overall dissipation in the compartment under consideration (water or sediment). The latter was based upon the mass balances of the two major dissipation processes in each compartment. Figure S9 in section 10 of the SI shows a graphic image of such mass balances. The area under each curve represents the total change in mass of the concerning process in time and is calculated by numerical integration. The measure for the contribution of degradation to the overall dissipation in the concerning compartment (water or sediment) was defined as the total change in mass by degradation divided by the total change in mass of the overall dissipation:

\[ F_{\text{deg-wat}} = \frac{\int_{i=0}^{n} M_{\text{deg-wat}(i)} \, di}{\int_{i=0}^{n} M_{\text{deg-wat}(i)} \, di + \int_{i=0}^{n} M_{\text{deg-sed}(i)} \, di} \]  

(5)

where \( F_{\text{deg-wat}} \) is the fraction of the mass degraded in the water layer to the overall mass dissipated from the water layer (−), \( M_{\text{deg-wat}(i)} \) is the mass degraded in the water layer for hour \( i \) (g), \( M_{\text{deg-sed}(i)} \) is the mass transported from the water layer to the sediment layer for hour \( i \) (g), and \( n \) is the total number of hours within 100 day time.

Analogous for the sediment compartment the contribution of degradation to the overall dissipation was defined as

\[ F_{\text{deg-sed}} = \frac{\int_{i=0}^{n} M_{\text{deg-sed}(i)} \, di}{\int_{i=0}^{n} M_{\text{deg-sed}(i)} \, di + \int_{i=0}^{n} M_{\text{back-dif}(i)} \, di} \]  

(6)

where \( F_{\text{deg-sed}} \) is the fraction mass degraded in the sediment to the overall mass dissipated from the sediment (−), \( M_{\text{deg-sed}(i)} \) is the mass degraded in the sediment for hour \( i \) (g), \( M_{\text{back-dif}(i)} \) is the mass transported from the sediment to the water layer by diffusion for hour \( i \) (g).

\( F_{\text{deg-wat}} \) and \( F_{\text{deg-sed}} \) values are between 0 and 1. Values close to 1 indicate that the contribution of mass degraded in the concerning compartment is large compared to the contribution of other processes causing dissipation and values close to zero indicate that dissipation of substance from the concerning compartment happens mainly by other processes than degradation.

The \( F_{\text{deg-wat}} \) was plotted against the CV pop values of the DegT50 wat for all six tested \( K_{\text{Fom}} \) values and for all sets of true DegT50 wat and DegT50 sed (Figure S10). The \( F_{\text{deg-sed}} \) was plotted against the CV pop values of the DegT50 sed for all six tested \( K_{\text{Fom}} \) values and for all sets of true DegT50 wat and DegT50 sed (Figure S11). In both plots, each dot represents one of the combinations of 20 DegT50 wat values and 20 DegT50 sed values (in total 400 dots). In Figure S9, dots with the same color depict one (true) DegT50 wat value and 20 different (true) DegT50 sed values. In Figure S11, dots with the same color depict one (true) DegT50 wat value and 20 different (true) DegT50 sed values. Figures S10 and S11 are only made using the results of water–sediment study 1. The results will be very similar for water–sediment study 2, because the contour diagrams of the CV pop are very much alike.

From Figures S10 and S11, the plots for \( K_{\text{Fom}} = 1000 \, \text{L} \, \text{kg}^{-1} \) are shown in Figure 3. These plots are discussed here briefly. A more detailed discussion of the plots for all six \( K_{\text{Fom}} \) values is given in section 11 of the SI.

The plot on the left-hand site of Figure 3 shows a clear pattern. For the true values of DegT50 wat between 1 and 70 days (dots in the color range red to blue) we observe a trend of increasing CV pop of the DegT50 wat for decreasing \( F_{\text{deg-wat}} \). This means that estimates of the parameters quantifying the degradation in water are less accurate when partitioning to the sediment strongly influences the fate of the chemical in the test.
system (the latter is indicated by mass disappearing by diffusion to the sediment). This trend supports our explanation that estimated parameters are more uncertain in cases where there is a limited contribution of degradation in water to the data. The trend is interrupted for the largest tested values of the DegT50wat (97-500 days; purple-pink colored dots). In fact an opposing trend is observed; decreasing CVpop of the DegT50wat for decreasing F_{mdeg-wat} (an explanation is given in section 11 of the SI). This opposing trend is clearer and starts at lower values of the true DegT50wat as the K_{fom} value increases (Figure S10). This opposing trend is only observed in the domain of CVpop values close to 1 or larger than 1, so undoubtedly indicating inaccurate parameter estimates, and for lower values of F_{mdeg-wat}. This means that our hypothesis that accurate parameter estimates are not possible for substances which are—at the same time—subject to other dissipation processes than degradation (indicated by low F_{mdeg-wat} values) is confirmed for the case of estimating degradation half-lives in the water layer of a water—sediment experiment.

The plot on the right-hand side of Figure 3 shows that many DegT50 sets resulted in a F_{mdeg-sed} of 1, despite the value of the CVpop of the DegT50sed. This indicates that for many substances, diffusion from the sediment to the water is not a very important dissipation process. Only some of the sets with lower DegT50wat values resulted in lower values of the F_{mdeg-sed} however not necessarily in combination with a high CVpop of the DegT50wat. This means that for the half-life in the sediment it is not possible to demonstrate that inaccurate parameter estimates are found for those substances which are - at the same time - subject to other dissipation processes than degradation.

Testing the Predictive Value of Our Chemical Space Diagrams. Honti and Fenner (2015) assessed the uncertainties in estimated transformation rates in water and sediment using 41 real experimental OECD 308 data sets for 23 different substances. We provide a more generalized approach using space diagrams. In such diagrams, chemicals represent specific cases, like for instance the 23 chemicals considered by Honti and Fenner (2015). In this section we test the predictive value of our chemical space diagrams with respect to results obtained from analyzing concrete experimental data sets, that is, those used by Honti and Fenner (2015).

Honti and Fenner (2015) used Bayesian parameter estimation and four different models to estimate transformation rates in water and sediment. Table S4 in the SI of Honti and Fenner (2015) gives a regression for each system-substance set the 5%, 50%, and 95% quantile of the posterior marginal distribution of the transformation rates (their k_{water} k_{sed} and k_{sed}) in Table S4 in the SI of Honti and Fenner (2015), to estimate a CV for each of the 41 substance—systems (see section 12 of the SI for the method). For calculating this CV we assumed a normal distribution. The posterior marginal distributions calculated for the 41 system-substance sets of Honti and Fenner (2015) are very likely not normally distributed and the CV values calculated by us for their data are not accurate and can therefore only be used in a qualitative sense.

Despite this rather rough method for comparing uncertainties, Table 1 and Figures S16 and S17 in the SI show that on average the uncertainty of the estimates as provided by Honti and Fenner (2015) increases when the substance—system set is found in a location in our chemical space diagram with a higher CVpop value, which illustrates their predictive value.

Table 1. Comparing Uncertainties of Our Chemical Space Diagrams (CVpop) with Recalculated Uncertainties Based on 5%, 50%, and 95% Quantiles of the Posterior Marginal Distribution of the Transformation Rates (k_{water} k_{sed}) Estimated by Honti and Fenner (2015)

| CVpop category in chemical space diagram | DegT50wat | DegT50sed |
|-----------------------------------------|-----------|-----------|
|                                          | DegT50wat | DegT50sed |
| below 0.5                                | 0.69      | 0.32      |
| 0.5−0.75                                | 0.89      | 0.23      |
| >0.75                                   | 0.88      | 0.25      |

"Equation S19. *Equations S19 and S21.

average the uncertainty of the estimates as provided by Honti and Fenner (2015) increases when the substance—system set is found in a location in our chemical space diagram with a higher CVpop value, which illustrates their predictive value.

GENERAL DISCUSSION AND IMPLICATIONS

Degradation in the Water Layer. The TOXSWA model implementation that we applied simulated chemical transport in the sediment more accurate than Model D of Honti and Fenner (2015), because TOXSWA used a much higher resolution in modeling vertical transport into the sediment. Aiming at concentration profiles that are as accurate as possible, we tuned our sediment segmentation such that the resulting profiles exactly matched those calculated with an analytical solution to the diffusion-transport equation reported by Crank (1967). Whereas we used in total 15 to 45 numerical segments with 10 numerical segments in the top layer of the sediment with thicknesses varying from 0.02 mm (K_{fom} value of 100 000 L kg⁻¹) to 1 mm (K_{fom} value of 1 L kg⁻¹), Honti and Fenner (2015) used only four numerical compartments with thicknesses of respectively 1.7, 3.3, 6.7, and 13.3 mm (assuming a 2.5 cm thick sediment layer; see section 13 in the SI for details). The effect of the choice of sediment segmentation on the calculated concentration profiles is demonstrated in Figures S18–S21 (section 13 in the SI) for a few selected yet representative DegT50wat−DegT50sed sets and all six K_{fom} values. The simulations use the parametrization of our “water−sediment study 1” and compare simulation results obtained with a sediment segmentation as used by TOXSWA in our study, with those obtained with the sediment segmentation.
as used by Honti and Fenner (2015). This comparison shows that concentration profiles (both in water and sediment) might differ considerably for higher $K_{Pam}$ values, dependent on the number of segments used. In case concentration profiles are not accurately simulated, the estimated transformation rates and their uncertainty will very likely be less reliable as well. It is difficult to predict the exact effect of this limitation on the estimated transformation rates and their uncertainty because this depends very much on the chemical properties (see section 13 in the SI).

Both our study and the study of Honti and Fenner (2015) show that the uncertainties surrounding estimated DegT$_{50_{out}}$ values are rather large for many substances. Adriaanse et al. (2013) and Honti and Fenner (2015) provide reasons for this large uncertainty, but it was not their explicit objective to mechanistically assess the cause of these uncertainties. Using a more generic approach we showed that the uncertainty surrounding estimated DegT$_{50_{out}}$ values increases as the process of diffusion to the sediment becomes dominant over degradation in the water layer. In terms of substance properties, this means that for very hydrophobic substances that degrade slowly in water, (high DegT$_{50_{out}}$ and high $K_{Pam}$), the estimated DegT$_{50_{out}}$ values will be associated with larger uncertainties. The relation between substance properties and the potential for successful parameter estimation, as demonstrated by the chemical space diagrams indicates that a tiered framework approach could be developed for the assessment of degradation halflives from OECD 308 experiments. The chemical space diagrams in this paper could be used to decide on (i) using a simple model and/or simple inverse modeling technique as a first tier, or (ii) jump to a higher tier by using a more complex model in combination with a more complex inverse modeling technique (e.g., a Bayesian parameter estimation approach). Special attention should be paid to the selection of the sediment segmentation when parametrizing the model. Another higher tier option is considering the found uncertainty quantitatively in surface water fate models. This can be done by performing Monte Carlo simulations, that is, repeatedly drawing a DegT$_{50_{out}}$ value from the posterior distribution resulting from the inverse modeling exercise and using this as input in the surface water fate model, followed by assessing the resulting distribution of the PEC. A third option for a higher tier is to estimate degradation halflives in water from outdoor experimental systems. In an outdoor system the proportion of applied mass transferred to the sediment is much smaller than in a water—sediment study for similar initial concentrations. Consequently, an outdoor system seems better suited for assessment of degradation halflives in water. Degradation in the Sediment. Like any model exercise, our modeling approach represents a simplified version of reality. Nevertheless, our chemical space diagrams show that in theory the uncertainty in the estimated DegT$_{50_{out}}$ is smaller than the uncertainty in the DegT$_{50_{out}}$. This is not in line with the results of Honti and Fenner (2015) who found more or less comparable uncertainties for the DegT$_{50_{out}}$ and the DegT$_{50_{out}}$. One of the explanations for this difference might be that we assume an average experimental error of 5% for all sampling times. Comparison to an error structure based on data from a series of water—sediment experiments with different chemicals and performed at different facilities can indicate whether our assumption is appropriate. In case halflives are derived from data of real water—sediment experiments main uncertainties relate to the location and timing of transformation in the sediment (penetration depth as a function of time), whether the transformation at a certain location in the sediment and time is aerobic or anaerobic and NER formation. Different penetration patterns of a chemical into the sediment can still result in identical average concentrations over the upper 5 cm. Future research could focus on the measurement of the penetration patterns and the redox state as a function of depth in water—sediment systems. Further research could also explore to what extent the different degradation processes can be modeled separately; that is, hydrolysis, NER formation, and biodegradation. Instead of determining biodegradation halflives for water and sediment separately, the concept of one overall half-life per unit of biofilm surface may be promising.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge via Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02906.

A summary of the experimental approach of a water—sediment study, detailed description of the TOXSWA model in case used for simulating a stagnant water—sediment system, details on the parametrization of the TOXSWA model, details on the generation of simulated data sets for the inverse modeling and the inverse modeling method, details on the approach for creating chemical space diagrams and several details and results of different type of analyses used to support our conclusions (PDF)

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**Notes**

The authors declare no competing financial interest.

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