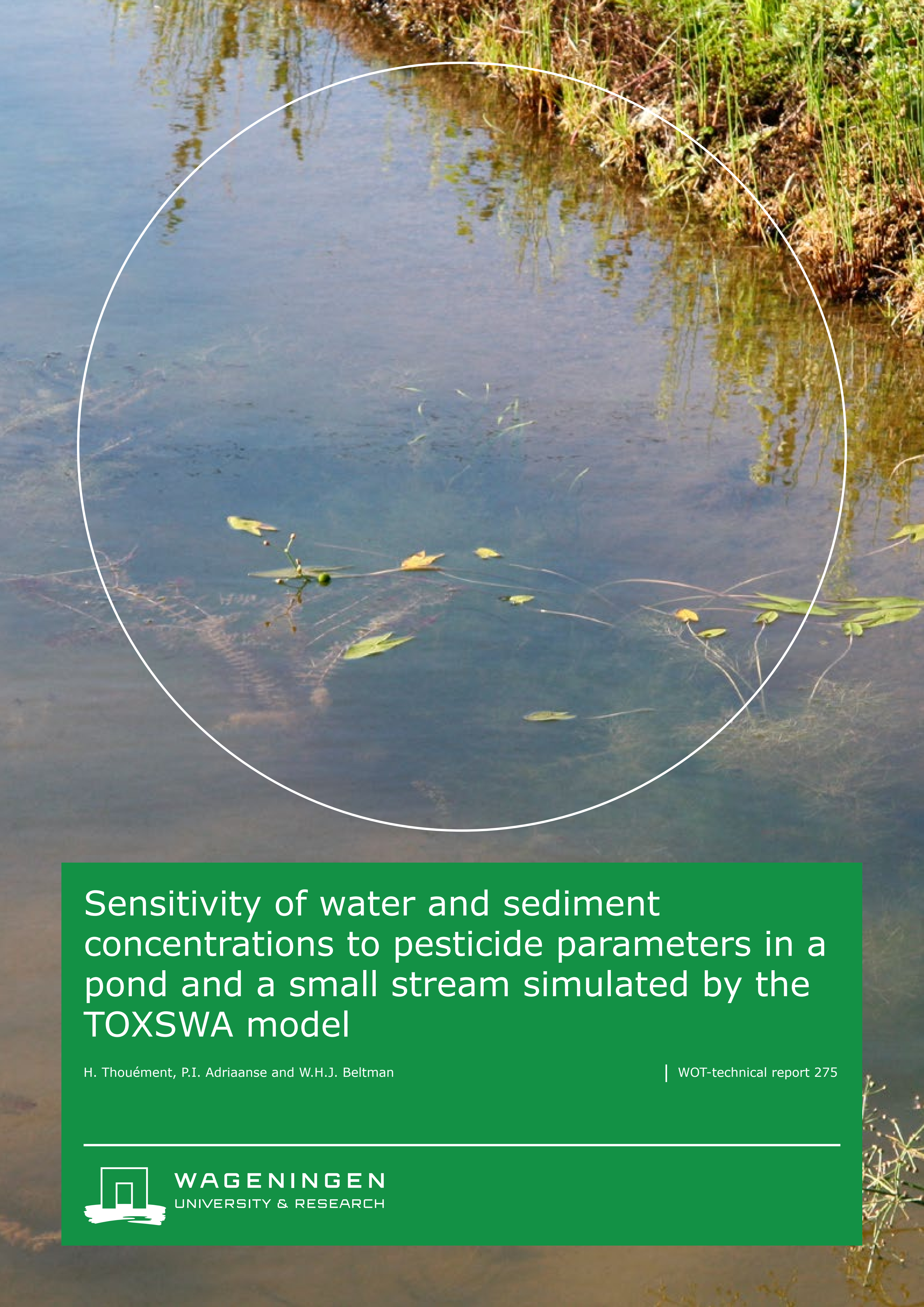

Sensitivity of water and sediment concentrations to pesticide parameters in a pond and a small stream simulated by the TOXSWA model

H. Thouément, P.I. Adriaanse and W.H.J. Beltman

WOT-technical report 275

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Sensitivity of water and sediment concentrations to pesticide parameters in a pond and a small stream simulated by the TOXSWA model

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Sensitivity of water and sediment concentrations to pesticide parameters in a pond and a small stream simulated by the TOXSWA model

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Abstract

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A sensitivity analysis has been performed for the TOXSWA model, which simulates pesticide behaviour in surface waters. For 11 pesticide input parameters, including degradation rates, sorption coefficients, saturated vapor pressure and solubility, the influence on predicted peak concentrations in water (PEC_{wat}) and sediment (PEC_{sed}), as well as Time-Weighted Averages in water (TWA7 and TWA28) have been evaluated. Advanced global sensitivity methods, including Saltelli's Sobol sequence for sampling input parameters, were applied to ponds and streams, representing low and high flow systems, respectively. Results show that sorption coefficients are the most sensitive parameters for TWA concentrations in ponds. In addition, degradation rates are sensitive parameters. The findings refine our understanding of pesticide behaviour, enabling more targeted parameterisation, and can contribute to improving guidance for regulatory exposure assessments. Compared to prior analyses, this study incorporates variable hydrology and sediment concentrations. It is recommended to extend the analysis to system parameters and pesticide entries.

Keywords: surface water, pesticide, exposure concentrations, sensitivity analysis

Photo cover: Wim Beltman

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Preface

This report builds upon earlier work by Westein in 1998, who carried out a sensitivity analysis of the TOXSWA model. In addition to considering water concentrations, this sensitivity analysis now also considers sediment concentrations for systems with a variable hydrology. The TOXSWA model is used in the Netherlands as well as the EU for exposure assessments in the framework of regulatory aquatic risk evaluation of pesticides. The insights derived from this sensitivity analysis are helpful to develop guidelines for determining pesticide input parameters.

We would like to thank George van Voorn and Sjoerd Boersma from the Biometris Group of Wageningen Plant Research for providing their statistical expertise. They suggested and helped us to use state-of-the-art methods for global sensitivity analyses of models, i.e. the Saltelli’s method for sampling and use of Sobol indices for quantifying sensitivity.

Contents

Summary

This report presents how physico-chemical parameters of pesticides influence predicted pesticide concentrations in surface water systems, as calculated using the TOXSWA model. TOXSWA was developed to simulate pesticide transport, transformation, sorption, and volatilization. It is used in the pesticide registration procedure for evaluating exposure of aquatic ecosystems. This study includes a comprehensive sensitivity analysis designed to identify the most critical pesticide properties input parameters that affect four selected model outputs. In doing so, the research aims to guide improvements in methods for determining pesticide properties and, thus, improve regulatory decision-making processes.

The TOXSWA model is applied to simulate pesticide behaviour in small surface water bodies, such as ponds, ditches and streams. Ponds, which are characterized by static water and longer residence times, differ fundamentally from ditches and streams, which have dynamic water flow and shorter residence times. These contrasting hydrological systems influence pesticide fate. The study utilised this variation in assessing the sensitivity of model outputs to input parameters. The target outputs analysed were the peak Predicted Environmental Concentrations in water (PEC_{wat}) and sediment (PEC_{sed}), as well as the highest Time-Weighted Average concentrations (TWA) in water over seven days (TWA7) and 28 days (TWA28). These are the metrics used to characterize pesticide exposure in the assessment of risks to aquatic organisms and sediment-dwelling species.

The sensitivity analysis employed advanced computational methods, including Saltelli’s extension of the Sobol sequence, which was used in sampling input parameters. This approach efficiently explores the parameter space, and ensures statistical reliability, while minimizing computational demands. It generates robust insights by considering the effects of individual parameters and their interactions. The Sobol indices, which were used to quantify sensitivity, were first-order indices S_1 (related to the direct effect of a single parameter), second-order indices S_2 (related to interactions between two parameters), and total-order indices S_T (related to the combined effects of a parameter, including all interactions). These indices provided a detailed breakdown of how variations in input parameters influence model predictions.

Sensitivity analysis of TOXSWA can be performed for three categories of input parameters: process parameters (pesticide properties); system parameters (e.g. watercourse dimensions, sediment properties, hydrological characteristics); and entry-route parameters (e.g. mechanisms of pesticide introduction into the system, such as spray drift or runoff/drainage). The current study was done for the process parameters, for 11 key parameters, molecular mass, degradation rates in water and sediment, Freundlich coefficients and exponents for sorption to suspended solids and to sediment, saturated vapour pressure, water solubility, diffusion coefficient in water, and sorption to macrophytes. Sampling from realistic parameter distributions was conducted using data from the Pesticide Properties Data Base (PPDB). For each waterbody, approximately 50,000 simulations were performed and the Sobol indices of the target outputs determined.

The study examines two representative waterbody systems to capture the variability in hydrodynamics and exposure scenarios that TOXSWA is designed to simulate. The first system is a pond, characterized by stagnant or low-flow conditions (depth 1 m, discharge 0.07 L s^{-1}, residence time 157 d). The second system is a stream, representative of water bodies with higher flow velocities (depth 0.41 m, discharge 2.22 L s^{-1}, residence time 21 d when no runoff entry occurs). For the pond, a spray drift event was applied (entry of pesticide solely). For the stream, 1 mm runoff with 0.5 mg m^{-2} during the 8-hour event (hence, water and pesticide entries).

The results show that the most sensitive parameters for the pond are in terms of first-order Sobol index values (the direct effect of single parameters), as given here in percentages:

- PEC_{wat} - The Freundlich sorption coefficient for organic matter in suspended solids (89%).
- PEC_{sed} - The Freundlich sorption coefficient for organic matter in sediment (69%), and to a lesser extent the half-lives in water and in sediment (6% and 4% respectively).
- TWA7 and TWA28 - Half-lives in water (43% and 53% respectively), the Freundlich sorption coefficient on organic matter in sediment (16% and 14% respectively), and to a lesser extent, the saturated vapour pressure (5% and 7% respectively), and solubility (6% and 5% respectively).

And for the stream:

- PEC_{wat} - The Freundlich sorption coefficient for organic matter in suspended solids (96%).
- PEC_{sed} - The Freundlich sorption coefficient for organic matter in sediment (96%).
- TWA7 and TWA28 - The Freundlich sorption coefficient for organic matter in suspended solids (61% and 57% respectively), and the Freundlich sorption coefficient for organic matter in sediment (21% and 25% respectively).

In summary, for the pond, which represents the low flow velocity domain, the most sensitive parameters are the sorption coefficients for suspended solids and for sediment for the selected target outputs. There is also a lower sensitivity to dissipation parameters represented by transformation and volatilization parameters (saturated vapour pressure and solubility). For the stream, which represents the high flow velocity domain, the most sensitive parameters are the sorption coefficients for suspended solids and for sediment.

The results of the sensitivity of the concentrations in the pond to pesticide process parameters were also valid for the ditch simulations by TOXSWA 1.2, because its flow velocity of 10 md^{-1} was similar to the pond.

The main difference in the sensitive parameters between the low- and high flow velocity domains, is that time-dependent (dissipation) parameters contribute less to the sensitivity of the studied outputs for the stream. This is understandable, because the high flow velocity leads to short residence times of the pesticide in water and also in the sediment.

An assumption when using Saltelli's method for analyzing the sensitivity of a model is that the model is linear. With respect to the $PEC_{wat,}$ some non-linearity exists but it is not pronounced. While for the PEC_{sed}, TWA7 and TWA28, the non-linearity is more pronounced. Although the only non-linear process in TOXSWA is the equilibrium sorption according to the Freundlich isotherm to suspended solids and to sediment, the total water layer-sediment system may behave in a significant non-linear way. This happens especially, when two subsystems behave at different time scales, i.e. a fast-reacting water layer with instantaneous mixing over water depth, and a slower reacting sediment with mass transport via diffusion in sediment pore water. So, in fact, the (local) sensitivities studied may not apply to the entire parameter domain. However, the results were sufficiently satisfactory for our purpose, particularly for qualitative use, as results agree well internally and can be explained from the TOXSWA model descriptions.

The current sensitivity analysis is performed for the input of pesticide properties parameters only, given two sets of system parameters, entries and initial conditions. Assessment of the sensitivity to system parameters, such as watercourse dimensions, sediment properties, etc., was not performed, nor to the entry route parameters, such as pesticide entries via spray drift or runoff/drainage, were also not included in the analysis. The system- and entry route parameters are, however, important in the definition of standard scenarios for the pesticide registration procedure. As the FOCUS surface water scenarios used at EU level for pesticide registration, are already more than 20 years old, and no specific sediment scenarios have been defined, the issue is still relevant. Therefore, we recommend study of the sensitivity of selected output variables to these input parameters.

The sensitive parameters identified indicate which pesticide properties input parameters need to be determined with the highest accuracy in order to obtain robust output. Therefore, special attention is required in obtaining accurate input for the sorption coefficients (suspended solids $K_{F,om,ss}$ and sediment $K_{F,om,sed}$), as well as dissipation processes, such as volatilization (i.e. the saturated vapour pressure P_{sat} and solubility c_{slb}), and degradation in water and in sediment. In light of this, accurate measurement of these parameters is absolutely essential to reduce uncertainty in model outputs and ensure robustness of exposure predictions in pesticide regulation.

Samenvatting

Dit rapport beschrijft hoe de fysisch-chemische eigenschappen van pesticiden de berekende concentraties in oppervlaktewater, berekend door het TOXSWA-model, beïnvloeden. TOXSWA is ontwikkeld om het transport, de omzetting, de sorptie en de vervluchtiging van pesticiden te simuleren. TOXSWA wordt gebruikt voor het berekenen van de blootstelling van aquatische ecosystemen in de registratieprocedure van pesticiden. Deze studie betreft een uitgebreide gevoeligheidsanalyse om de meest kritische parameters (fysisch-chemische eigenschappen) van pesticiden te identificeren die van invloed zijn op de modeluitvoer; vier geselecteerde blootstellingsconcentraties. Hiermee beoogt deze studie bij te dragen aan verbetering van methodieken om fysisch-chemische eigenschappen van pesticiden te bepalen, en daarmee de besluitvorming in het beoordelingsproces te verbeteren.

Het TOXSWA-model wordt toegepast om het gedrag van pesticiden in kleine oppervlaktewateren, zoals vijvers, sloten en beken, te simuleren. Vijvers, die worden gekenmerkt door stilstaand water en langere verblijftijden, verschillen fundamenteel van sloten en beken, die sneller stromen en kortere verblijftijden hebben. Deze contrasterende hydrologische systemen bepalen het gedrag van pesticiden. In deze studie is deze variatie gebruikt om de gevoeligheid van modeluitvoer voor invoerparameters te beoordelen. De geanalyseerde modeluitvoer zijn de piekconcentraties in water (PEC_{wat}) en in sediment (PEC_{sed}), evenals de hoogste tijdgewogen gemiddelde concentraties (TWA) in water over zeven (TWA7) en 28 dagen (TWA28). Deze uitvoer karakteriseert de blootstelling aan pesticiden die wordt gebruikt bij het beoordelen van de risico's voor aquatische organismen en soorten die in het sediment leven.

De gevoeligheidsanalyse maakte gebruik van geavanceerde methoden, waaronder Saltelli's uitbreiding van de Sobol-reeks voor het trekken van invoerparameters. Deze aanpak onderzoekt efficiënt de parameterruimte, waardoor statistische betrouwbaarheid wordt bevorderd en de rekenbehoefte worden geminimaliseerd. Het genereert robuuste inzichten door rekening te houden met de effecten van individuele parameters en hun interacties. De Sobol-indices die in deze studie worden gebruikt om de gevoeligheid te kwantificeren zijn de eerste-orde-indices S_1 (het directe effect van een enkele parameter), de tweede-orde indices S_2 (interacties tussen twee parameters) en de totale-orde-indices S_T (de gecombineerde effecten van een parameter, inclusief alle interacties). Deze indices gaven een gedetailleerd overzicht van de manier waarop variaties in invoerparameters modelvoorspellingen beïnvloeden.

Een gevoeligheidsanalyse van TOXSWA kan worden uitgevoerd voor drie categorieën invoerparameters: procesparameters (fysisch-chemische eigenschappen van pesticiden), systeemparameters (bijv. afmetingen van de waterloop, sedimenteigenschappen, hydrologische kenmerken) en aanvoerrouteparameters (bijv. voor drift en afspoeling/drainage). Het huidige onderzoek werd uitgevoerd voor de procesparameters, voor 11 sleutelparameters: molecuulmassa, afbraaksnelheden in water en sediment, Freundlich-coëfficiënten en exponenten voor sorptie aan zwevende stof en aan sediment, verzadigde dampdruk, wateroplosbaarheid, diffusiecoëfficiënt in water, en sorptie aan waterplanten. Trekking op basis van realistische parameterverdelingen werd uitgevoerd met behulp van gegevens uit de Pesticide Properties Database (PPDB). Voor elk waterlichaam werden ongeveer 50.000 simulaties uitgevoerd en werden de Sobol-indices van de beoogde uitvoer bepaald.

Twee representatieve watersystemen zijn onderzocht om de variabiliteit in hydrodynamica en blootstellingsscenario's vast te leggen die TOXSWA moet simuleren. Het eerste systeem is een vijver, gekenmerkt door stilstaand water of lage stromingscondities (diepte 1 m, afvoer 0,07 L s^{-1} verblijftijd 157 d), terwijl het tweede systeem een beek is, representatief voor waterlichamen met hogere stroomsnelheden (diepte 0,41 m, afvoer 2,22 L s^{-1}, verblijftijd 21 d wanneer er geen afvoer plaatsvindt). Voor de vijver werd een drift toegepast (alleen pesticide aanvoer), en voor de beek 1 mm afvoer met 0,5 mg m^{-2} pesticide tijdens de 8 uur durende afspoelgebeurtenis (aanvoer van water en pesticiden).

Uit de resultaten blijkt dat de meest gevoelige parameters (eerste orde Sobol-indexwaarde, direct effect van de enkele parameter, hier weergegeven in %), voor de vijver zijn;

- PEC_{wat}; de Freundlich-sorptiecoëfficiënt voor organisch materiaal in zwevende stof (89%),
- PEC_{sed}; de Freundlich-sorptiecoëfficiënt voor organisch materiaal in sediment (69%) en in mindere mate de halfwaardetijden in water en sediment (6% en 4%), en
- TWA7 en TWA28; halfwaardetijd in water (43% en 53%), de Freundlich-sorptiecoëfficiënt voor organisch materiaal in sediment (16% en 14%) en in mindere mate de verzadigde dampdruk (5 en 7%) en oplosbaarheid (6% en 5%) voor beide TWA's,

en voor de beek;

- PEC_{wat}; de Freundlich-sorptiecoëfficiënt voor organisch materiaal in zwevende stof (96%),
- PEC_{sed}; de Freundlich-sorptiecoëfficiënt voor organisch materiaal in sediment (96%), en
- TWA7 en TWA28; de Freundlich-sorptiecoëfficiënt voor organisch materiaal in zwevende stof (61% en 57%) en de Freundlich-sorptiecoëfficiënt voor organisch materiaal in sediment (21% en 25%).

Samenvattend: voor de vijver, die het domein met lage stroomsnelheid vertegenwoordigt, zijn de meest gevoelige parameters de sorptiecoëfficiënten voor zwevende stof en voor sediment voor de geselecteerde blootstellingsconcentraties. Er is een beperkte gevoeligheid voor verwijderingsparameters; omzettings- en vervluchtigingsparameters (verzadigde dampdruk en oplosbaarheid). Voor de beek die het hoge stroomsnelheidsdomein vertegenwoordigt, zijn de meest gevoelige parameters de sorptiecoëfficiënten voor zwevende stof en voor sediment.

De resultaten van de gevoeligheid van de concentraties in de vijver voor pesticide-eigenschappen gelden ook voor de slootsimulaties met TOXSWA 1.2, omdat de stroomsnelheid van 10 m d^{-1} vergelijkbaar is met die van de vijver.

Het belangrijkste verschil in de gevoelige parameters tussen het lage en hoge stroomsnelheidsdomein is dat tijdsafhankelijke (verwijderings)parameters minder bijdragen aan de gevoeligheid van de blootstellingsconcentraties voor de beek. Dit is begrijpelijk omdat de hoge beeksnelheid leidt tot korte verblijftijden van het pesticide in water en ook voor het sediment.

Een aanname bij het gebruik van Saltelli's methode voor het analyseren van de gevoeligheid van een model is dat het model lineair is. Wat de PEC_{wat} betreft is er sprake van enige niet-lineariteit, maar deze is niet groot, terwijl bij de PEC_{sed}, TWA7 en TWA28 de niet-lineariteit groter is. Hoewel het enige niet-lineaire proces in TOXSWA de evenwichtssorptie volgens de Freundlich-isotherm is voor zwevende stof en sediment, kan het totale waterlaag-sedimentsysteem zich op een significante niet-lineaire manier gedragen. Dit gebeurt vooral wanneer twee subsystemen zich op verschillende tijdschalen gedragen, dat wil zeggen een snel reagerende waterlaag met onmiddellijke menging over de waterdiepte en een langzamer reagerend sediment met massatransport via diffusie in sediment poriënwater. Het is dus mogelijk dat de bestudeerde (lokale) gevoeligheden niet gelden voor het gehele parameterdomein. Omdat de resultaten echter intern goed overeenkomen en kunnen worden verklaard uit de TOXSWA-modelbeschrijvingen, zijn de resultaten voldoende bevredigend voor ons doel van vooral kwalitatief gebruik.

De huidige gevoeligheidsanalyse is alleen uitgevoerd voor de invoer van parameters voor de eigenschappen van pesticiden, gegeven twee sets systeemparameters, aanvoerroutes en initiële voorwaarden. De gevoeligheid voor de systeemparameters (zoals afmetingen van de waterloop, sedimenteigenschappen, enz.) is niet uitgevoerd, noch voor de parameters van de aanvoerroutes (zoals de belasting van pesticiden via spuitdrift of afspoeling/drainage). De systeem- en aanvoerrouteparameters zijn belangrijk bij het definiëren van scenario's voor de pesticide registratieprocedure. Omdat de FOCUS-oppervlaktewaterscenario's die op EU-niveau worden gebruikt voor de registratie van pesticiden al meer dan twintig jaar oud zijn en er geen specifieke sedimentscenario's zijn gedefinieerd, is kennis over de gevoeligheid van systeemparameters en aanvoerroutes nog steeds relevant. Daarom raden we aan om de gevoeligheid van deze parameters te testen.

De geïdentificeerde gevoelige parameters geven aan welke fysisch-chemische eigenschappen van pesticiden met de hoogste nauwkeurigheid moeten worden bepaald om een robuuste uitvoer (blootstellingsconcentraties) te verkrijgen. Daarom is speciale aandacht vereist bij het verkrijgen van nauwkeurige eigenschappen, met name voor de sorptiecoëfficiënten (zwevende stof $K_{F,om,ss}$ en sediment $K_{F,om,sed}$), evenals verwijderingsprocessen zoals vervluchtiging (d.w.z. de verzadigde dampspanning P_{sat} en oplosbaarheid c_{slb}) en de afbraak in water en in sediment. Een nauwkeurige meting van deze eigenschappen is essentieel om de onzekerheid in modeluitvoer te verminderen en de robuustheid van berekende blootstellingsconcentraties in pesticiden risico beoordeling te garanderen.

1 Introduction

1.1 General background and aim

The application of pesticides to agricultural fields may result in their entry into surface waters. The TOXSWA model (Adriaanse, 1996; Adriaanse et al., 2013; Adriaanse et al., 2022) describes the fate and behaviour of pesticides in small surface waters, that enter by e.g. spray drift deposition, via drain pipes or surface runoff and erosion after agricultural use. The model was introduced in 1996 and has been adopted for use in assessing the exposure of the aquatic and sediment ecosystem to evaluate pesticide risks in the registration procedure. TOXSWA has been used in The Netherlands since June 1999 (Ctgb, 2020); at EU level since May 2003 (FOCUS, 2001; European Food Safety Authority (EFSA), 2020); and for pesticide use in greenhouses that discharge into small surface waters (incorporated in the GEM software) in The Netherlands since May 2016 (van der Linden et al., 2015). In the near future, it will be applied for improved scenarios for arable- and fruit crops and avenue trees in The Netherlands (incorporated in the DRAINBOW software (Boesten et al., 2021; Wipfler et al., in prep.)).

The model calculates acute and time-weighted average concentrations in water and sediment for relevant scenarios. These are compared to imposed concentration levels in ecotoxicological experiments to assess the acute and chronic effects of pesticides.

Performing a sensitivity analysis allows for a better understanding of the behaviour of the model and of which input parameters determine most the model output. This is **useful for**:

1. Validation of the model, i.e. by comparing the measured distribution of pesticide in the field to model simulations, the accuracy of model predictions for actual situations can be assessed. To do so, it is necessary to know which of the model inputs need to be measured with high accuracy (because to a large extent, they determine the output) and which inputs are less important for the model output and can, thus, be determined in a less detailed way.
2. Definition of standard scenarios for pesticide registration, e.g. for aquatic organisms or amphibians. Knowing which input parameters have a significant effect on the exposure concentrations helps to focus attention on the most important input parameters, e.g. while designing a scenario selection procedure and thereafter, in parameterising exposure scenarios.

A previous sensitivity analysis was performed in 1998 (Westein et al. 1998). The motivation for renewing sensitivity analysis of the TOXSWA model in 2023 and 2024 is to consider the latest modifications of the model, notably the multiplication of water flow descriptions, including dynamic flows. Also, in earlier sensitivity analysis, only water concentrations were considered as output of the model: the present study also includes sediment concentrations.

The **aim** of the sensitivity analysis is to assess which input parameters contribute most to the variation in model output for the TOXSWA model, for a range of realistic input parameter values. Model output considered in the sensitivity analysis are exposure concentrations in water and sediment.

Different **sources of sensitivity** can be distinguished. In the TOXSWA model, the output depends upon the following sources of sensitivity:

i. Process parameters: Coefficients (parameters) that characterize the dynamic behaviour of the modelled processes. In TOXSWA, the corresponding input parameters are the parameters that describe the properties of the pesticide.
ii. System parameters: Coefficients (parameters) that describe the dimensions and properties of the system. In TOXSWA, these are the watercourse, the sediment characteristics, and the hydrology.
iii. Entries: These represent the influence of the external 'environment' on the system, e.g. sources such as seepage, drainage, or runoff of water.
iv. Initial conditions: For example, at the start of the simulations, the sediment does not contain pesticides.

Process parameters are considered in this sensitivity analysis. In addition, system parameters and pesticide entries were considered in the analysis, but only to a limited extent, and in so far as they have substantial influence on the system. The system is studied through a sensitivity analysis for a pond and a stream. A spray drift entry is studied for the pond, and a runoff entry for the stream. Note that entries of drainage and runoff water affect the hydrology of the waterbody and thus the system dimensions and properties.

Seepage is zero in all scenarios used in the registration procedure, therefore it is not considered in the sensitivity analysis. The entry of eroded soil has not been described in TOXSWA and thus it cannot be considered in the sensitivity analysis. The entry of pesticide mass with eroded soil is described by TOXSWA.

Finally, the initial conditions are not considered in the sensitivity analysis, because in the regulatory use of TOXSWA, initial water (and/or sediment) concentrations are zero or pre-defined. In some cases, the initial sediment concentration may be obtained by simulating a number of years ahead of the intended scenario simulations, (a so-called "warming up period") to obtain a steady state. By means of example, in the FOCUS scenarios, such a relatively fixed plateau concentration in sediment is obtained after six years (FOCUS, 2020).

Climate change, which entails more extreme minimum and maximum values for temperature and precipitation particularly, as well as their duration and increased precipitation intensity, is not specifically included in this sensitivity analysis. The rationale for this was that climate change mostly influences the entry route models for drainage and surface runoff, and the TOXSWA model itself to a much lesser extent. Originally, we intended, therefore, to study an intermediate and higher runoff water entry, but we finally executed only the analysis for an intermediate entry (1 mm runoff distributed over eight hours, see Chapter 6).

There are three different routes of entry of pesticides into systems:

1. Through spray drift deposition and atmospheric deposition: Only pesticide mass enters the water layer of the waterbody.
2. Through eroded soil: Pesticide mass is sorbed into eroded soil. In the TOXSWA model, it is assumed to enter the upper 1-cm layer of sediment. So, only pesticide mass enters the sediment layer of the waterbody, not the eroded soil. And
3. Through drainage or runoff: pesticide mass accompanied by non-negligible water fluxes, affecting system properties water depth and flow velocity/discharge.

Entry of pesticide mass is an external condition, i.e. a boundary condition. The magnitude and timing of these entries are not part of the TOXSWA model but determined by other models. Therefore, the magnitude and timing of the entries were not included in the sensitivity analysis. In addition, the entries of pesticide mass were not considered in definition of the standard scenarios for the pesticide registration procedure.

It is known from previous analysis (European Food Safety Authority (EFSA) et al., 2020) that the output of TOXSWA is very sensitive to the date of application of the pesticide on adjacent field (relative to rainfall events) and resulting pesticide entries. However, the aim of this sensitivity analysis is to test the **sensitive components of TOXSWA**, and not pesticide entries or the models that simulate pesticide entries (such as PAT - the Pesticide Application Timer module, or the MACRO and PEARL models for drainage, and the PRZM model for runoff). The testing of application timing is outside the scope of this sensitivity analysis. Therefore, for the entry of pesticide mass, some example cases have been defined. These are characterized in more detail in Chapter 4.4.

Sensitivity within the model structure (i.e. in the form of the mathematical equations which constitute the model) or the applied computational scheme within which the model is implemented (i.e. model operation) are not considered within this sensitivity analysis of the TOXSWA model. So, it is assumed that sensitivities are solely introduced via model inputs.

The target model outputs used in this sensitivity analysis are the peak Predicted Environmental Concentration (PEC) in water (PEC_{wat}), as well as in sediment (PEC_{sed}), and maximum values of Time-Weighted Average concentrations (TWA) over seven (TWA7) and 28 days (TWA28) for water. The peak PECs and maximum TWA values are determined per calendar year. The xth percentile value of the annual values is the target used in the regulatory risk assessment. As in this sensitivity analysis, the model is run for three months, only one annual maximum value is available. The time of occurrence of the target concentration has not been considered in this sensitivity analysis, although in some cases. the time window of the concentrations may be restricted in refined risk assessments, e.g. to account for the fact that in the winter, the sensitive aquatic organism is not present.

Peak PEC values are important model outputs. They are the main exposure concentrations used in aquatic and sediment risk assessment[1], and they are also used to develop scenario selection procedures. The time-weighted average concentrations are taken over the exposure periods of the standard aquatic and sediment test organisms in lower-tier chronic effect tests. For sediment, the thickness over which the concentration is averaged is either 1 cm (sediment-dwelling organisms) or 5 cm (aquatic macrophytes). As toxicity for sediment organisms is usually expressed in terms of initial exposure concentration (resulting from 'spiking' the overlying water layer), the default approach is to use peak concentrations in the sediment for the risk assessment. We limit the sensitivity analysis to the 1-cm sediment layer, as this is expected to have higher concentrations than the 5-cm layer and react more dynamically than the average over 5 cm depth. TWA values would need to be considered if the field exposure concentrations would be *"demonstrated to be sufficiently variable during a time frame smaller than the duration of the sediment-spiked toxicity tests."* (EFSA, 2015- Ch. 9.2 in the Scientific Opinion on effect assessment of sediment organisms). We limited our analysis to the sediment peak concentrations.

The proposed **method** for executing the sensitivity analysis was a single-input sensitivity analysis.

In this study, we determine the first-order, second-order, and total-order Sobol indices for the target output variables (i.e. a positive characterization of the sensitivity with respect to the considered parameter(s)). This made it possible to assess:

- How well the target output variables could be approximated by a function that depends only upon the considered parameters (S_1).
- Or, whether interaction between some parameters contribute to the variance of the selected outputs:
  - Through a one-to-one approach, assessing how each parameter is correlated to every other parameter (S_2).
  - Or by presenting the total variance related to one input parameter and its correlations to all other parameters (S_T).

The prior sensitivity analysis (Westein et al., 1998) used a group-of-input analysis approach to tackle computational issues when studying interactions. However, due to improved computational power during the past 25 years, this was not considered necessary anymore, and the more recent and widely used, Saltelli's extension of the Sobol sequence, was selected[2].

In a sensitivity analysis for TOXSWA, the following **groups of parameters** were considered:

1. Process parameters i.e. the pesticides' properties.
2. System parameters, such as water depth and flow velocity.
3. Entry route parameters, i.e. incoming pesticide and water fluxes via the upstream boundary, or laterally.

The TOXSWA model is used to predict exposure concentrations for all pesticides, intended to be released on the market. Therefore, a sensitivity analysis must take all pesticides into account. For this purpose, a sensitivity analysis is performed first to identify which process parameters contribute most to the variation in the target model output.

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[1] In Section 7.2.5.1 of the Aquatic Guidance Document:
When accumulation of an a.s. in aquatic sediment is indicated or predicted by environmental fate studies, the impact on a sediment-dwelling organism shall be assessed. The chronic risk to *Chironomus riparius* (OECD 218, 219) or *Lumbriculus* spp. (OECD 225) shall be determined.
Maximum duration of tests mentioned (so not indicating whether acute or chronic exposure is tested) for sediment dwelling organisms: e.g. 28 days for *Chironomus Riparius* and *Chironomus Yoshimatisui* and 65 days for *Chironomus Dilutus*.

[2] In the group-of-input analysis, first the analysis was initially performed with a sample from distributions of all parameters, and then, with a sample based on distributions of parameters identified sensitive and average values for parameters identified as not sensitive. A limited number of simulations could be applied (180 simulations in both steps). For the current analysis, the full parameter space can be used in the analysis.

Therefore, the aim of this sensitivity analysis was to identify **which process parameters** contribute most to the variation in the target model output. This was examined for the domain of properties of selected pesticides, for which data were obtained from the PPDB (Pesticide Properties DataBase), a database that is filled with data from EU registration dossiers, along with other data (see Section 5.2 for more details), and given two sets of system parameters, entries and initial conditions.

We focused on sets of system parameters and entries that differed from those studied in Westein et al. (1998). In this previous analysis, the sensitivity analysis was performed for a simple hydrology (constant flow velocity). TOXSWA can now simulate transient hydrology resulting from variable water depths and variable flow velocities. Furthermore, scenarios are available that represent how TOXSWA is used. Therefore, this new sensitivity analysis is carried out using existing scenarios with variable hydrology.

We aim to identify a limited set of process parameters that account for most of the variation in model output. By varying this limited set of process parameters over the total range of these parameters, as expressed by the pesticides from the PPDB, it is possible to determine the variation in the target model output as a function of the most sensitive process parameters. This variation will be used as an approximation for all pesticides, for which sufficient data were available, including pesticides which are no longer registered in the EU anymore but still in use in other parts of the world.

In this study, sensitivity to the process parameters has been studied, for a fixed set of system parameters (a pond and a stream), and an instantaneous mass entry (in the pond) or a runoff water and mass entry during a couple of hours (in the stream).

The sensitivity analysis has been done with TOXSWA model version[3] 3.3.8 of 11-Aug-2022, which has been developed for use with the repaired FOCUS surface water scenarios (EFSA, 2020).

The sensitivity analysis is restricted to the simulation of parent substances, hence metabolite formation, degradation and metabolite fate are not considered.

1.2 Reading guide

In Chapter 2 a brief description of the TOXSWA model is given. The method and the statistical principles used to perform a global sensitivity analysis are described in Chapter 3. In Chapter 4, we identified which process parameters contribute most the variation in model output, and distributions of these parameter values are determined in Chapter 5. In Chapter 6, the pond system used for the sensitivity analysis is described and the results are given. In Chapter 7, this is applied for the stream. In Chapter 8, the conclusions of the sensitivity analysis have been summarized and discussed, and some recommendations for further research are given. A complete list of symbols and units used in this report is provided in Annex 1.

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[3] In the analysis of results of the stream, a 'bug' was found in TOXSWA. The adsorption to macrophytes was not simulated correctly when the water depth changes during the simulation period. The 'bug' was repaired in the 11-Aug-2022 version and the analysis for the stream was carried out with the repaired version of 30-Sep-2024. The earlier prepared results of the pond were still valid because the water depth does not change during the simulation.

2 Description of the TOXSWA model

2.1 Introduction

In this Chapter, a brief overview is presented of the concepts of the TOXSWA model. A complete description can be found in Adriaanse (1996) and Ter Horst et al. (2016).

The TOXSWA model calculates pesticide behaviour in waterbodies at the edge-of-field scale, i.e. waterbodies with a maximum length of a few hundred metres adjacent to a single, treated field (Adriaanse, 1996; Adriaanse et al., 2014; Ter Horst et al., 2016; Adriaanse et al., 2017; Adriaanse, 2022). The hydrological sub-model of TOXSWA, therefore, focuses on the same scale, i.e. that of a single edge-of-field waterbody.

The waterbody setup is used to simulate ponds, as well as ditches and streams. The modelled system consists of two types of subsystems: The water layer containing suspended solids and macrophytes, and the sediment. The properties of the sediment, i.e. porosity, organic matter content and bulk density, may vary with depth. In the water layer, concentrations vary in the horizontal direction. Whereas in the sediment, concentrations vary in the horizontal and the vertical directions.

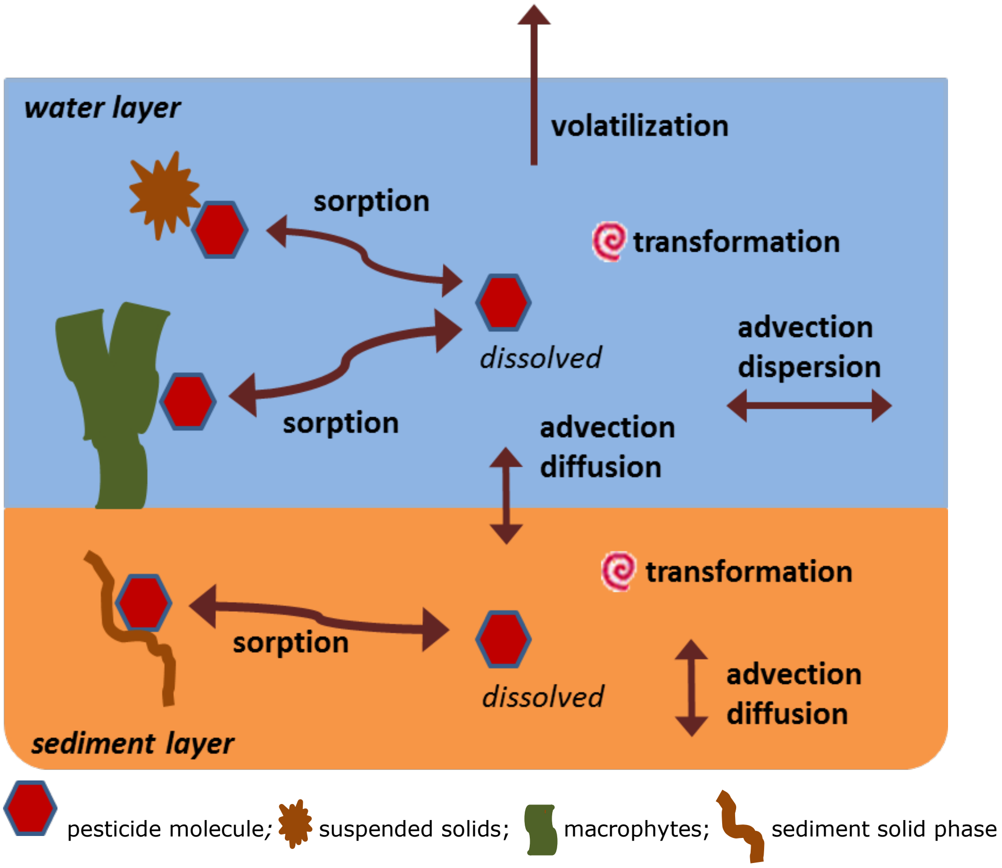

Figure 2-1 *Processes in TOXSWA.*

TOXSWA considers four processes for the parent substance and its metabolites: (i) transport, (ii) transformation, (iii) sorption and (iv) volatilization (see Figure 2-1). In the water layer, substances are transported by advection and dispersion, dissolved in the water phase, or sorbed to suspended solids. In the sediment, substances are transported[4] by advection, dispersion and diffusion in the liquid phase, i.e. via the pores. Exchanges across the water-sediment interface are facilitated by advection (upward seepage or downward infiltration) and by diffusion. Transformation is simulated in the water layer, as well as in the sediment. Up to TOXSWA version 3.3, the transformation rate covers the combined effects of hydrolysis, photolysis, and biodegradation. The transformation rates are assumed to be temperature-dependent. The Arrhenius equation is applied to describe the temperature dependence of the rate coefficient of transformation. Sorption to suspended solids and to sediment is described by the Freundlich isotherm. Sorption to macrophytes is described by a linear sorption isotherm.

In the following Sections, the equations for the processes occurring in the water layer and in the sediment, for the hydrology and for the entries are presented. The equations have been retrieved from the technical report 84: *"The TOXSWA model version 3.3 for pesticide behaviour in small surface waters."* (Ter Horst, 2016), in which full information about model equations and their background can be found.

2.2 Hydrology

The hydrological sub-model of TOXSWA simulates watercourses (ditches and streams) and ponds. Differences between the modelled ponds and watercourses basically relate only to the dimensions. The length and width of ponds are generally of a similar order, whereas for water courses, the length is often of a 10 to 100 larger factor than the width. The descriptions of the different types of hydrology summarized in this section are as those provided by Adriaanse et al. (2017), Adriaanse (1996), Adriaanse and Beltman (2009) and Ter Horst et al. (2016).

Constant flow
The system is a watercourse, in which the discharge and the water depth, thus, also the wetted area (hence Q and A in Eq. (4)), are constant over the whole length of the waterbody, and constant in time. Hence, Q and A in Eq. (4) are constant as f(distance, time). Therefore, also the flow velocity of water is constant over the full length of the watercourse, and in time. This type of hydrology has been used for the Dutch scenario with spray drift entries only (Beltman & Adriaanse, 1999).

Simple ditch
A version of the model for gradually varied flow was developed for slow-flowing watercourses, using another numerical solution of the water balance than the one in Adriaanse & Beltman (2009). This is the so-called 'simple ditch' model. This model approximates the discharge-water depth relationship by assuming that $\delta Q(x,t)/\delta x$ (and thus the water depth) is constant over the entire length of the watercourse. Hence, similar to Adriaanse & Beltman (2009) Q in Eq. (4)) is f(distance, time) and A in Eq. (4) is f(time). This type of hydrology has been used in the Dutch greenhouse scenario (Van der Linden et al., 2015).

Transient flow for ponds and for watercourses
Transient flow is characterized by varying discharge and water depth in time and along the length of the waterbody. In TOXSWA 3.3, the transient flow is modelled with a constant water depth along the length of the 100-m FOCUS watercourse. Hence, A in Eq. (4) is a f(time) only, while Q in Eq. (4)) is f(distance, time) because there are water fluxes entering laterally. This type of hydrology has been used for the FOCUS pond, ditch and stream scenarios (EFSA, 2020).

In this report, we study the sensitivity of the exposure concentrations in a FOCUS-type pond and small stream for pesticide parameters, and thus the description for the transient flow is the relevant description for the sensitivity analysis studied.

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[4] Advection and dispersion in sediment are not included in the sensitivity analysis because seepage is not modelled in the current scenarios applied in risk assessment.

2.3 Processes in the water layer

The mass conservation equation for the pesticide in the water layer is:

$$\frac{\partial(c_{wat}^{*}A)}{\partial t} = -\frac{\partial(A\,J_{wat})}{\partial x} - k_{wat}c_{wat}^{*}A + J_a W_w - J_{sed}P_0 \tag{1}$$

with:

c_{wat}^{*} = mass concentration in the water layer (dissolved and sorbed to suspended solids and macrophytes) (kg m^{-3})
A = wetted cross-sectional area of flow (m^2)
t = time (d)
J_{wat} = areic mass flux of substance in water layer by advection and dispersion (kg m^{-2} d^{-1})
x = distance in the direction of flow (m)
k_{wat} = rate coefficient for transformation of the parent substance in water (d^{-1})
J_a = areic[5] mass flux of substance across the water-air interface (kg m^{-2} d^{-1}) [the flux is negative in the upward direction]
W_w = width of water surface (m)
J_{sed} = areic mass flux of substance across the water-sediment interface (kg m^{-2} d^{-1})
P_0 = length of wetted perimeter at depth z = 0, via which exchange between water and sediment occurs (m)

The total mass concentration of pesticide in the water layer, c_{wat}^{*}, is given by:

$$c_{wat}^{*} = c_{wat} + \frac{m_{mp}P_0}{A}X_{mp} + m_{ss}X_{ss} \tag{2}$$

with:

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

Transport in water

The flux J_{wat} of the conservation equation describes the transport of the substance, both dissolved in water and sorbed to the suspended solids. It consists of an advective- and a dispersive component (which are assumed to be identical for the dissolved- and sorbed substances).

$$J_{wat} = u(c_{wat} + m_{ss}X_{ss}) - E_{phys}\frac{\partial(c_{wat} + m_{ss}X_{ss})}{\partial x} \tag{3}$$

with:

u = flow velocity of the water (m d^{-1})
E_{phys} = longitudinal dispersion coefficient (in the direction of flow) (m^2 d^{-1})

The term $\partial(AJ_w)/\partial x$ in the conservation equation equals:

$$\frac{\partial\left(A\left[u_x(c_{wat}+m_{ss}X_{ss}) - E_{phys}\frac{\partial(c_{wat}+m_{ss}X_{ss})}{\partial x}\right]\right)}{\partial x} = \frac{\partial\left(Q(c_{wat}+m_{ss}X_{ss}) - AE_{phys}\frac{\partial(c_{wat}+m_{ss}X_{ss})}{\partial x}\right)}{\partial x} \tag{4}$$

---

[5] Areic means that it is divided by the surface area concerned.

In which, Q is the discharge, i.e. volume flux of water passing through a vertical cross-section of the waterbody (m^3 d^{-1}), expressed as:

$$Q = A\, u \tag{5}$$

and A, the wetted cross-sectional area, is calculated from the water depth h as:

$$A = bh + s_1 h^2 \tag{6}$$

with:
b = bottom width of the waterbody (m)
s_1 = side slope (horizontal/vertical) (-)
h = water depth of the waterbody (m)

The longitudinal dispersion, E_{phys}, is calculated using Fischer's equation (Fischer et al., 1979):

$$E_{phys} = c_F \frac{u^2 W_w^2}{h\, u^*} \tag{7}$$

with:
u^* = shear velocity (m d^{-1})
c_F = coefficient (-)

Note that in Fischers' original equation u reads $\bar{u}$ (average cross-sectional flow velocity in m d^{-1}). In TOXSWA the water layer is assumed to be ideally mixed horizontally and vertically, therefore $\bar{u}$ can be replaced by u.

The shear velocity is calculated according to Fischer et al. (1979), as:

$$u^* = 0.1\, u \tag{8}$$

Transformation in water

The transformation rate coefficient of the substance in the water layer, k_{wat}, is a measure of the (entire) transformation of the substance in the water layer. The substance may be dissolved in water, or it may be sorbed to suspended solids or to macrophytes.

The three most important transformation processes in the water layer are photolysis, hydrolysis, and biotic degradation (Thomann and Mueller, 1987). Photolysis depends mainly upon the light intensity in the water layer. Hydrolysis depends especially upon the pH and on temperature. Biotic degradation is mainly determined by the extent and composition of the microorganism community and temperature.

Transformation of the parent pesticide in water is described by the following first-order rate equation:

$$R_{t,p,wat} = k_{wat} c_{wat}^* \tag{9}$$

with:
$R_{t,p,wat}$ = rate of transformation if parent in water (kg m^{-3} d^{-1})

Similar rate equations are used for each transformation product.

Sorption to suspended solids

The sorption of pesticides to organic matter in suspended solids is instantaneous (equilibrium sorption), described with a Freundlich sorption isotherm:

$$X_{ss} = m_{om,ss} K_{F,om,ss} \, c_{ss,r} \left(\frac{c_{wat}}{c_{ss,r}} \right)^{N_{ss}} \tag{10}$$

with:

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

Using the Freundlich sorption equation, the partitioning between the solid and liquid phases is dependent upon concentration c_{wat}. c_{wat} cannot be expressed in explicit way as a function of the other quantities. The implicit equation must then be solved by iteration, as described in Annex 3 of Ter Horst et al. (2016).

Sorption to macrophytes

The sorption of pesticides to macrophytes is instantaneous (equilibrium sorption), and is described with a linear sorption isotherm:

$$X_{mp} = K_{mp} c_{wat} \tag{11}$$

with:

K_{mp} = distribution coefficient for substance between macrophytes and water, i.e., the slope of the linear sorption isotherm on the mass of dry macrophytes (m^3 kg^{-1})

Exchange between water and atmosphere

The exchange flux of the pesticide between the water layer and the atmosphere is described by:

$$J_a = -k_{t,l} \left(c_{wat} - \frac{c_a}{K_H} \right) \tag{12}$$

with:

$k_{t,l}$ = overall transfer coefficient for the air-water interface based on the liquid phase (m d^{-1})
c_a = mass concentration of substance in the air (kg m^{-3})
K_H = Henry coefficient (-)

in which:

$$\frac{1}{k_{t,l}} = \frac{1}{k_l} + \frac{1}{K_H k_g} \tag{13}$$

with:

k_l = exchange coefficient of substance in the liquid phase (m d^{-1})
k_g = exchange coefficient of substance in the gas phase (m d^{-1})

Henry's coefficient is calculated from Henry's law, which describes the partitioning of the pesticide between the liquid and the gas phase:

$$K_H = \frac{c_a}{c_I} \tag{14}$$

with:

c_I = equilibrium mass concentration of substance at the water-gas interface in the water phase (kg m^{-3})

Henry's coefficient is calculated form the ratio of saturated concentration in air and the solubility of the substance in water. The saturation concentration in air is calculated with Boyle's law for ideal gases, from the saturated vapour pressure. Both, vapour pressure and solubility in water are dependent on the temperature, so the same holds for the Henry coefficient. The Henry coefficient is calculated as follows:

$$K_H = \frac{P_{sat} M_m}{R\, T_m} \frac{1}{c_{slb}} \tag{15}$$

with:

P_{sat} = saturated vapour pressure of substance (Pa)
M_m = molar mass (kg mol^{-1})
R = universal gas constant (J mol^{-1} K^{-1})
T_m = temperature at which the saturated vapour pressure, the solubility and the exchange coefficients are defined (K)
c_{slb} = solubility of substance in water (kg m^{-3})

The temperature has much effect on the partitioning of the pesticide between the gas and liquid phases because the saturated vapour pressure and the solubility are both temperature-dependent. Hence, the effect of temperature on these properties should be considered.

Exchange between water and sediment

The mass flux at the water-sediment interface is based on diffusion, hence, for the water layer:

$$J_{sed} = -\, \varepsilon\, D_{l,sed} \frac{\partial c_{l,sed}}{\partial z} \tag{16}$$

with:

ε = volume fraction of pore water (-)
$c_{\mathrm{l,sed}}$ = mass concentration of substance in liquid phase in the sediment (kg m^{-3})
$D_{\mathrm{l,sed}}$ = diffusion coefficient in pore water (m^2 d^{-1})
z = depth in the sediment from the water-sediment interface to area concerned (m)

It is assumed that diffusion across the water-sediment interface is rapid compared to diffusion in sediment. This implies that the interface resistance is negligible and that the mass concentration of the substance in the water layer equals that in the outer sediment pores, hence: $c_{\mathrm{wat}} = c_{\mathrm{l,sed}}$ (at $z = 0$).

For the sediment, the mass flux is calculated by:

$$J_{l,sed} = J_{sed} \tag{17}$$

with:

$J_{l,sed}$ = areic mass flux by diffusion in the liquid phase of the sediment (kg m^{-2} d^{-1})

The condition at the surface of the sediment is that the concentration in the pore water in the sediment is equal to the concentration in the water, hence: $c_{l,sed}$ (at $z = 0$) = c_w.

Note that TOXSWA also simulates advective and dispersive transport in sediment, but no dispersive transport between the water layer and the sediment. As advective transport in sediment is not applied in the scenarios currently used in risk assessment, advective and dispersive transport in sediment is not included our sensitivity analysis.

2.4 Processes in sediment

The mass conservation equation for the pesticide in sediment is:

$$P \, \frac{\partial c_{sed}^*}{\partial t} = \frac{\partial \left(P \, J_{l,sed}\right)}{\partial z} - k_{sed} c_{sed}^* P \tag{18}$$

with:

c^*_{sed} = total mass concentration in the sediment (kg m^{-3})

z = depth in sediment (m)

P = length of perimeter (m)

k_{sed} = rate coefficient for transformation of parent substance in sediment (d^{-1})

The total mass concentration of pesticide in sediment, c_{sed}^*, is given by:

$$c_{sed}^* = \varepsilon \, c_{l,sed} + \rho_b X_{sed} \tag{19}$$

with:

$c_{l,sed}$ = mass concentration of substance in liquid phase in the sediment (kg m^{-3})

ρ_b = bulk density of dry sediment, i.e., volumic mass of dry sediment material (kg m^{-3})

X_{sed} = mass sorbed to sediment (kg kg^{-1}).

Transport in sediment

In the pore water the substance is transported by diffusion. This flux, $J_{l,sed}$, is described by:

$$J_{l,sed} = \varepsilon \, D_{l,sed} \frac{\partial c_{l,sed}}{\partial z} \tag{20}$$

with:

$D_{l,sed}$ = diffusion coefficient in pore water (m^2 d^{-1})

The diffusion coefficient of the substance in the liquid phase of the sediment, $D_{l,sed}$, is calculated as:

$$D_{l,sed} = \lambda \, D_{wat} \tag{21}$$

with:

λ = relative diffusion coefficient (or tortuosity) (-)

D_{wat} = diffusion coefficient in water (m^2 d^{-1})

Note that TOXSWA also simulates advective and dispersive transport in sediment. As advective transport in sediment is not applied in the scenarios currently used in risk assessment, advective and dispersive transport in sediment is not included in our sensitivity analysis.

Transformation in sediment
The transformation rate coefficient of the substance in the sediment, k_{sed}, is a measure of the entire transformation of the substance in pore water, as well as in sorbed form. The main transformation processes in the sediment are hydrolysis and biodegradation.

Transformation of the parent pesticide in sediment is described by the following first-order rate equation:

$$R_{t,p,sed} = k_{sed} c^{*}_{sed} \tag{22}$$

with:
$R_{t,p,sed}$ = rate of transformation of parent in sediment (kg m^{-3} d^{-1})

Similar rate equations are used for each transformation product.

Sorption to sediment organic matter
The sorption of pesticides to sediment is instantaneous (equilibrium sorption), as described with a Freundlich sorption isotherm:

$$X_{sed} = m_{om} K_{F,om,sed}\ c_{s,r} \left(\frac{c_{l,sed}}{c_{sed,r}}\right)^{N_{sed}} \tag{23}$$

with:
$m_{om,sed}$ = mass fraction of organic matter in sediment (kg^{-1} kg^{-1})
$K_{F,om,sed}$ = Freundlich coefficient for sorption to organic matter in sediment (m^3 kg^{-1})
$c_{sed,r}$ = reference concentration in the liquid phase for sorption to the sediment (kg m^{-3})
$c_{l,sed}$ = mass concentration of substance in liquid phase in the sediment (kg m^{-3})
N_{sed} = Freundlich exponent for sorption to sediment (-)

Using the Freundlich sorption equation, the partitioning between the solid and liquid phases is dependent upon concentration $c_{l,sed}$. $c_{l,sed}$ cannot then be expressed in an explicit way as a function of the other quantities. For further detail, please refer to the technical report of TOXSWA 3.3 (ter Horst, 2016).

2.5 Entries

TOXSWA can simulate three different types of entries of pesticides; spray drift and atmospheric deposition (not elaborated here), erosion, and drainage, or runoff. The erosion entry is not described because it is not included in our sensitivity analysis.

Spray drift deposition on the water layer
Only pesticide mass enters the water layer of the waterbody (so not accompanied by water flows).

Spray drift is modelled as a distributed pulse input. It is assumed that the supplied lineic mass of substance m_L (kg m^{-1}) is instantaneously and ideally mixed over the cross-sectional area of the water layer at the time of entry.

$$m_L = W_w\ m_{drift} \tag{24}$$

with:
m_L = lineic mass of substance entering the watercourse (kg m^{-1})
m_{drift} = spray drift mass deposited at the water layer (kg m^{-2})

Drainage or runoff into the water layer

Pesticide mass, which is accompanied by non-negligible water flows, affects system properties, such as water depth and flow velocity/discharge).

Drainage and runoff inputs are modelled for the water layer as:

$$m_{LT}(t,x) = q_F w_F c_{wat,F} \tag{25}$$

with:

m_{LT} = lineic mass of substance entering the watercourse per unit of time (kg m^{-1} d^{-1})

w_F = width of the adjacent field (perpendicular to the waterbody) discharging drainage or runoff water into the waterbody (m)

q_F = areic volume flux of excess water from the adjacent field (m^3 m^{-2} d^{-1})

$c_{wat,F}$ = concentration in water in lateral discharge, by drainage or runoff (kg m^{-3})

Note that in the FOCUS runoff scenarios, the excess water from contributing areas with runoff consists of surface runoff plus a fraction of the smaller subsurface drainage flow at 1 m depth in the soil. For the sensitivity analysis, this subsurface drainage flow is set to zero. Therefore, it is not included in the descriptions here.

3 Method of sensitivity analysis

3.1 Introduction

Sensitivity analysis allows the identification of the parameters, or sets of parameters that have the greatest influence on the model output (Zhang, 2015). The application of sensitivity analysis serves to enhance understanding of the relationship between inputs and outputs of the model, to determine how the uncertainty of the input influences the variability of the results, and to identify the most crucial input parameters.

Sensitivity analysis relies on the fact that variations in the input parameters can usually be characterized by their distribution functions and their correlations. Usually, a random sample is generated from these distributions, resulting in a set of values for the various input parameters. Next, simulations are carried out with these randomly selected set of parameter values, and their influence on the selected model output is assessed.

There are two main approaches to analyze the sensitivity of the model parameters on an output: local and global approaches. A local sensitivity analysis addresses sensitivity relative to change of a single parameter value (differential sensitivity). While a global analysis examines sensitivity with regard to some domain of the model inputs characterized by their distribution. We are most interested in global sensitivity analysis to assess which input parameters contribute most to the variation in the output, over the entire domain of realistic values of the input parameters.

In the sensitivity analysis of TOXSWA, three different types of input parameters can be analyzed on their sensitivity on output. These parameter types are the process, system, and entry route parameters.

The following questions are subsequently answered by the analysis:
1. Which process parameters contribute most to variations in the model output for a standard set of system parameters, entries, and initial conditions?
2. In TOXSWA, the process parameters are those that describe the properties of the pesticide. They are listed in Section 7b of the TOXSWA input file.
3. Which system parameters contribute most to variations in the model output for the total domain of process parameters (characterized by the limited set of sensitive process parameters that are found in Step 1), and standard entries and initial conditions? This can be done for e.g. two systems - a pond and a ditch/stream.
4. Which entry route parameters contribute most to variations in the model output for the total domain of process parameters (characterized by the limited set of sensitive parameters found in Step 1), and for the total domain of two sets of system parameters (each characterizsed by the limited sets of sensitive parameters found in Step 2), and standard initial conditions.

TOXSWA is applied to a low flow velocity domain and a high flow velocity domain. Therefore, sensitivity analyses can be performed for two systems for each of the preceding three questions, as below:

- One for a pond, which is representative of the low flow velocity domain of TOXSWA.
- One for a ditch or stream, which represents the high flow velocity domain of TOXSWA.

Thus, the total number of different sensitivity analyses performed would be six, at least, but more if more than one type of entry route is studied.

A clear delimitation is required in view of project budget and available time.

Finally, in this report, we studied the sensitivity of the process parameters for two standard sets of system parameters, a pond and a stream, for an instantaneous mass entry (in the pond), and a runoff water and mass entry during a number of hours (in the stream).

The current sensitivity analysis follows the approach of Westein et al. (1998), but some methods are updated and a wider domain of the TOXSWA model with respect to the types of water flow is analyzed.

The theory considering the sampling of the input values and the indicators of sensitivity or uncertainty of outputs of the model are presented in Section 3.2. The general approach of the sensitivity analysis for TOXSWA, as used in the context of the report, is presented step by step in Section 3.3. The implementation of the steps using the existing Python tools for sensitivity analysis is presented in Section 3.4.

3.2 Theoretical background for sensitivity analysis

3.2.1 Sampling from distribution of parameters

The number of simulations required to obtain statistically significant sensitivity analysis results depends partly upon the applied sampling method within the parameter's distribution. In the previous sensitivity analysis (Westein et al. 1998), sampling within the distributions was carried out according to the Latin Hypercube method. In this sensitivity analysis, we use the Saltelli's extension of the Sobol sequence, which is a more efficient sampling method that is now commonly used in this kind of analysis.

Saltelli's sampling method usually requires less samples from the distribution (i.e. less simulations) to obtain statistically significant results compared to the Latin Hypercube method. In addition, this method allows for sampling across the different distributions of the parameters and avoids repetitive sampling from the same areas. This is how the method reduces the number of simulations required for the sensitivity analysis while providing statistically significant results. Moreover, the randomization of sampling within each parameters' distribution eliminates existing correlations between the process parameters (for example, the different sorption coefficients). However, while it offers enhanced speed and lighter calculation, the method is prone to spurious results, such as negative variances (Thiele et al., 2014, Ten Broeke et al., 2016b). The theoretical background for Saltelli's sampling method has been outlined by Saltelli (2002).

Saltelli's sampling method for parameters with known distributions is based on the following steps:

- Generate two sets of samples (as matrices A and B) uniformly distributed from 0 to 1 (using a quantum random number generator). For our analysis, every matrix had 11 columns - one for each parameter.
- Saltelli's method then requires sampling the two matrices obtained above for each parameter, as well as their recombination matrices, B_A and A_B (B_A and A_B are explained in Section 3.2.2).
- Apply a scale function to scale the samples obtained with Saltelli's method on the basis of the distribution of the original values. In the present study, the scale is based on the distribution of the log10 of each TOXSWA input parameter, characterized by their Mean and Standard Deviation, as reported in Annex 1.

Through the normalization process of model output, it is possible to compare the sensitivity of the output to all the input parameters considered. Therefore, it enables evaluation of the impact of variation of input parameters on the output, i.e. input parameters that have different ranges and units.

The number of samples is a function of the number of parameters (N_p) for which the sensitivity will be assessed. The user provides a number, *N,* which must be to a power of two. For instance, a recommended value for *N* for 10 parameters is 2^{10} = 1024, and the number of samples will be calculated by the tool provided by the SALib library as $n = N \times (2N_p + 2)$. The power two-rule ensures that a sufficient number of drawings from both matrices are included to make statistically significant inferences on the parameter sensitivities. Selection of a higher value for *N* will result in a higher number of samples that provide more reliable results, but it will increase computational time. In this study, we used a *N* value of 2048 (2^{11}). With a number of parameters (N_p) of 11, this yields a number of runs *n* to about ~50,000, which was judged to be a good compromise between computational time and results reliability.

The Saltelli sampling tool is provided from the Python SALib library (Herman and Usher, 2017; Iwanaga et al., 2022).

3.2.2 Global sensitivity analysis and its measures

This section regarding global sensitivity analysis is based on Ten Broeke et al. (2016a).

We did not apply a local sensitivity analysis (see e.g. Westein et al., 1998). Local sensitivity analysis is a useful method for assessing which parameters have the greatest influence on an output around a nominal point. It has the advantage of being computationally cheap relative to a global sensitivity analysis. As local sensitivity analysis entails a linearization of output response around a nominal point, it implicitly assumes that the local response holds true for the entire parameter domain, while in reality there may be interactions with other parameters at other locations in the parameter space. Thus, it omits non-local interaction effects. As knowledge about these interaction effects is also desired in this study, another approach was chosen, namely a global sensitivity analysis.

Global sensitivity analysis considers the effect of simultaneous variations in more than one model parameter. Each parameter changes over a relatively large area of the parameter space, and consequently a global sensitivity analysis includes non-local interaction effects. The range of the parameters is defined by the assigned probability density functions of the parameters that are included in the sensitivity analyses. Hence, the chosen model output will vary when the input parameter varies within its range (probability distribution). This variation in the chosen output variables over the range of the input parameters is then attributed to the variations in the different input parameters.

The Sobol method (Sobol, 2001) is one of the most commonly used methodologies for global sensitivity analysis. This method assumes that all input parameters are independent. That is, a parameter x is not determined based on parameter y. However, interactions might occur (Jansen, 1999; Saltelli et al., 2010).

In the presented sensitivity analysis, independence of the parameter space is ensured. For instance, by randomly selecting from the distributions of real pesticide values (see Chapter 5 for more details).

The Sobol method is based on a decomposition of the output variance:

$$V(Y_j) = \sum_i V_i + \sum_{l>i} V_{i,l} + \cdots + V_{1,2,\ldots,N_p} \tag{26}$$

with $V(Y_j)$ the total output variance over the considered parameter (j is the number of the state variable), i.e. output analyzed: in this sensitivity analysis, we four outputs, so, j takes a value 1, 2, 3 or 4. They are: predicted peak exposure concentrations in sediment and in water, and highest time-weighted average concentration in water over a period of seven days, and over a period of 28 days.

Y_j is the chosen model output that depends upon the model input parameter θ_i (with *i* being the number of input parameter, 1 up to 11 included; note that input parameters θ_i are not in the equation).

V_i is the part of the variance that is attributed to the parameter θ_i and $V_{i,l}$ is the part that is attributed to the interaction between parameter θ_i and θ_l, where the number of parameters runs from 1 to N_p, the number of input parameters (for example, in this sensitivity analysis, we have 11 process parameters which will vary).

Sensitivity indices (or Sobol indices) are defined by normalizing the terms of the equation above by dividing these by the total variance. The normally reported sensitivity indices are the first-order index and the total-order index (Saltelli et al. 2008).The first-order index estimates the variance that is explained by a single parameter θ_i excluding interaction effects, and is defined as:

$$S_{i,j} = \frac{V_i}{V(Y_j)} \tag{27}$$

In addition to the single parameter variance (i.e. first order), the total-order sensitivity ($\tilde{S}$) for one parameter θ_i and for the output Y_j, includes all the interaction effects (including all higher than first order) with other parameters in addition to the single parameter variance (i.e. first order), and is defined as:

$$\tilde{S}_{i,j} = \frac{1}{V(Y_j)} \left(V_i + \sum_{l>i} V_{i,l} + \cdots + V_{1,2,\ldots,N_p} \right) \tag{28}$$

Each first-order index for a parameter θ_i always attains a value between 0 and 1. However, the sum of the total-order indices (sum over the number of parameters N_p) can exceed 1, if the model has interaction effects. A large difference between (27) and (28) indicates that interaction effects are influential.

An estimation of (27) and (28) for each given output j is found by sampling the parameter space, as described below, and running simulations for all these samples of the parameter space. The numerical method described in Saltelli et al. (2010) is applied to estimate (27) and (28), and is based on the generation of two sample matrices, A and B. Each contains the same number of sample points N_s, drawn independently from the probability density functions of the parameters.

Subsequently, N_p recombination matrices A_B^i and B_A^i are generated from the two sampling matrices, where A_B^i and B_A^i are identical to A and B, respectively, except for its i^{th} column that is taken from B and A, respectively.

The model is then run for each sample, generating a vector of the chosen model outputs of size $2N_s*(N_p+1)$. When the samples are from the sample matrix A, this output vector is defined as Y_A and so forth. The first-order index (27) can then be estimated as:

$$S_{i,j} \approx S_i^A = \frac{1}{V(Y)} \left(\frac{1}{N_s} Y_A^T \cdot Y_{B_A} - E(Y)^2 \right) \tag{29}$$

with Y_A^T the transpose of Y_A, and $\cdot$ denotes the inner product. The total-order index (28) can be estimated as:

$$\tilde{S}_{i,j} \approx \tilde{S}_i^A = 1 - \frac{1}{V(Y)} \left(\frac{1}{N_s} Y_A^T \cdot Y_{A_B} - E(Y)^2 \right) \tag{30}$$

To calculate the $E(Y)^2$ and $V(Y)$, they are approximated by the sample variance.

The squared sample mean $E(Y)^2$ can be approximated by $E(Y)^2 \approx \frac{1}{N_s} Y_A^T Y_B$ and sample variance $V(Y)$ by $V(Y) \approx \frac{1}{2}\left(V(Y_A) + V(Y_B)\right)$.

Finally, the second-order sensitivity indices are used to measure the fractional contribution of parameter interactions to the output variance (Zhang et al., 2015). Second-order indices are, therefore, included in the total-order indices. Similarly, the second-order indices are calculated following Saltelli (2002). The equations can be retrieved from Saltelli's publication.

The estimations of the first-order, second-order and total-order indices are calculated by the SAlib Python library (Herman and Usher, 2017; Iwanaga et al., 2022). In summary, those different indices represent the following (examples are provided for system with three input parameters: A, B and C):

- First-order indices (S_1): These measure the contribution to the output variance through a single model input. They hold similarities with the top marginal variance used in the previous sensitivity analysis of Westein et al. (1998). *Example: S_1 calculated for the parameter A provides the contribution of the variations of A to the variance of the output. The sum of the three values (for A, B and C) of S_1 represents the variance of the output which can be explained by variations of the single model inputs A, B and C.*
- Second-order indices (S_2): These measure the contribution to the output variance caused by the interaction of two model inputs. Each combination is calculated. *For example: S_2 will be calculated for the pairs of parameters (A, B), (A, C) and (B, C).*

- Total-order index (S_T): This measures the contribution to the output variance caused by a model input, including both its first-order effects (the input varying alone) and all higher-order interactions. *Example: S_T will be equivalent for A to the sum of the S_1 value calculated for the input parameter A, plus the S_2 values for the pairs (A, B) and (A, C), plus higher-order interactions. In this case, with three parameters, only a third-order value is calculated for (A, B, C) (no details here).*

Provided the model used is linear, we expect that:

- The contribution to the output variance of each parameter, when summed up together (sum of all values of S_1 for all considered model parameters), should reach 1 (100%), or be close to 1. This would mean that the model is linear or near-linear. If parameters display interactions, then this sum will decrease. Note that this is independent of the linearity of the parameters.
- On the other hand, S_T is the sum of the contribution of a given parameter, including first-order effects and all higher-orders interactions. It is supposed to be equal to S_1 if there are no interactions, otherwise S_T will increase above S_1.
- Second-order indices should be 0 if there is no interaction of second order between parameters, and will increase otherwise. Otherwise, the interaction between the two parameters must be considered to appropriately interpret the analysis output.

Confidence intervals
Confidence intervals are provided from the Python tool, with the values S_1, S_2 and S_T. These confidence intervals should be as low as possible for the corresponding value to be trusted. A confidence interval of 10% of the S_1 or S_T index value is usually aimed for the most sensitive parameter (Zhang, 2015).

3.3 Sensitivity analysis of TOXSWA

For **each sensitivity analysis, the following general steps are performed.** This approach is illustrated in the test of sensitivity of process parameters in the second part of this Section.

1. Select the parameters from the set that are part of the analysis and determine their distributions. Perform a curve fit for each of the distributions of these parameters.
2. Determine parameter values for the set of fixed parameters that are not part of the analysis (e.g. the system, entry route parameters).
3. Sample parameter values from the distributions determined in (1) using Saltelli's method. This is described in Section 3.2.
4. For each sampled set of (3) run the model with the sampled set (3) and the fixed set (2) of input parameters.
5. Analyze the results by using the distribution of the process parameters and calculated targets to determine the Sobol indices of each of the process parameters.

For Steps 3 – 5, a program was written in Python, in which, Python scripts are incorporated for sampling with Saltelli's method and for calculation of Sobol indices.

The analysis is carried out through calculation of the Sobol indices for each process parameter of the problem. Note that the word 'problem' is used in Python to name the dictionary (a collection of information) which contains for each parameter, the necessary information to model its distribution: number of parameters, name of parameter, Mean, Standard Deviation, and the name of type of distribution (see example in Annex 1). The theory of this method is shortly described in Section 3.2.2.

The approach described above is illustrated for **the sensitivity analysis of the process parameters for the pond and a single spray drift entry**. As process parameters are environmental data, their values often present a so-called lognormal distribution. For such data, it is common to use the logarithm (here, log10) of the data for statistical treatment. This is the choice that we made here.

1. Select from all process parameters (pesticide properties) which parameters will be part of the analysis. Determine the distribution characteristics of each of these parameters using a curve fit. *Note that for process parameters, the curve fit is performed on the log10 of the parameter's values.* Determine the fixed value for the remaining process parameters, not tested on their sensitivity. See Chapter 5.

2. Determine a set of system parameters, i.e. the pond, and a set of entry route parameters, i.e. spray drift entry. See Section 6.1.
3. Sample values of the process parameters from the distributions of (1). *Note that for the process parameters the sampling will be performed within the distribution of the log10 of the data*.
4. Run TOXSWA with the sampled process parameters with the pond system and spray drift entry to calculate PEC in water and PEC in sediment. *Note that the values are transformed back using* $x = 10^{(log10(x))}$ *to obtain the model input.*
5. Use the sampled process parameter distributions. For the process parameters here, we use the distribution of the *log10* of the values as determined in (1) to determine the Sobol indices for each of the process parameters for the different output chosen, i.e. the peak PEC in water, peak PEC in sediment and highest TWA in water for seven and 28 days. See Section 3.2.

3.4 Implementation of the sensitivity analysis of TOXSWA with Python

In this Section, the Python programs used for the sensitivity analysis of TOXSWA are explained. The same code can be used for assessing the sensitivity to the system parameters (Step 2). For Step 3 (sensitivity to the entry parameters). The code requires some extension for reading and adapting the file with hourly lateral entries of water and pesticide.

The code produces an output file with the peak PECs (water and sediment) and highest TWAs in water after seven and 28 days for each set of parameters:
- For the pond, the water layer consists of a single node.
- For the ditch or stream, the last node of ditch or stream.

The peaks PECs and TWAs represent the maximum values over the simulation time, which is three months here.

3.4.1 Sampling

Sampling for sensitivity analysis is carried out using the sampling tool that applies Saltelli's method from the SAlib library (as presented in Section 3.2). The tool inputs are the characteristics of the distributions of each parameter (see below). The output is generated using Saltelli's extension of the Sobol sequence, and consists of a table with N_p columns (in this example, with the process parameters, $N_p = 11$) and n rows (here, approximately 50,000, which is the number of runs).

For instance, for the process parameters, the distributions provided were the distribution of the log10 of the values (see Section 3.3), which were all normal distributions. The only values necessary to describe normal distributions are the respective Mean and Standard Deviation, which were, therefore, the information provided to the tool. Those values are provided in the shape of a "dictionary", which is referred to as the "problem" description in the SALib examples. For the process parameters, once sampled within the distribution of the log10 of the values, the sampled values were transformed back to real parameter values to provide them as input for TOXSWA.

3.4.2 Execution of TOXSWA runs

A template TOXSWA input file ('ref.txw') is prepared in which the process values that are part of the sensitivity analysis in this study were replaced by a text field (example: '<KomSed>'). A simple text search and replace command allows to attribute to each parameter the selected input value. Process parameters which are not included in this sensitivity analysis are given as fixed values.

The code running TOXSWA for each sample proceeds as follows:
- Creation of a folder with the sample number as name for each sample containing the necessary input files including the adapted template file ('ref.txw') filled with the sampled input values.

- Running the TOXSWA simulations for each sample (in parallel on several cores of the computer) using the parameter values obtain with Saltelli sampling above.
- Getting the desired model output from the output files ('.sum') in a summary file.

The TOXSWA simulations are done once, and from the results a sensitivity analysis is done for each of the four model outputs.

3.4.3 Determination of SOBOL indices

The Sobol indices (introduced in Section 3.2.2) are calculated using the analysis tool provided in the SAlib library. For this calculation, the following information is provided:

- the "problem", as defined in the Sampling section above, i.e. using the distributions of the sampled parameters.
- the values from one of the output values, i.e. the maximum PEC_{wat}, PEC_{sed}, or TWA over seven or 28 days in water.

The analysis is done for each output separately and the Sobol indices are stored in a summary Excel file.

4 Identification of pesticide properties parameters contributing most to the variation in the model output

4.1 Introduction

As described in Chapter 3.1 three different types of input parameters can be analyzed with respect to their influence on the variance of the output. These types are the process, system and entry route parameters. The process parameters are the parameters describing the properties of the pesticide, listed in Section 7b of the TOXSWA input file.

In this report, we studied the influence of the process parameters on the output variance. To sample these, we performed the following two steps:

1. Preparation of an overview of pesticide properties parameters in the TOXSWA model with indication as to whether each is important for selected target output variables PEC_{wat}, TWA7, TWA28 and PEC_{sed} or not. Two tables were made, one with properties sensitivity is determined for (see Section 4.1), and another with properties considered less important on the basis of expert judgement (see Section 4.2).

2. Determination of ranges and distribution of values of pesticide properties parameters (Chapter 5). The data were obtained from the PPDB (Lewis et al., 2016) Pesticide Properties Database (herts.ac.uk).

In addition, we provided an overview of the system parameters (Section 4.3) and the pesticide entry route parameters (Section 4.4), that were set for this sensitivity analysis.

In this report, we studied the variance of output to the pesticide properties parameters for two systems: One with low flow (a pond) and one with higher flow (a stream). The R1 pond and R1 stream were selected, respectively.

The initial intention was to study two types of mass entry for both the R1 pond and R1 stream: an instantaneous mass entry, and a distributed type of entry of mass fluxes (accompanied by water fluxes), representing a moderate runoff event of 1 mm runoff that lasted eight hours (Chapter 6). We finally opted for only studying the effect of an instantaneous mass entry in the R1 pond, and the distributed mass and water fluxes entering the R1 stream over eight hours.

Pesticides are often applied multiple times within one growing season or year. Through testing, multiple applications dependencies are created that differ in time interval between applications and transformation rate in water. This adds complexity in the selection of options and analysis of output. Therefore, we adhere to analysis of the influence of the pesticide properties parameters on the TOXSWA output within a single application only, assuming this will cover most of sensitivity of the pesticide properties parameters.

The variance of four output parameters are studied. These are the peaks in time of the PEC_{wat}, PEC_{sed}, and of the TWA7 and TWA28 in water. The PEC_{wat} and PEC_{sed} represent the maximum momentaneous concentration values on the hour (in the water layer and sediment, respectively). For the water layer, the concentration from spray drift is the dissolved concentration calculated, i.e. after instantaneous processes sorption to suspended solids and macrophytes, but without the time-dependent processes of transformation, volatilization and diffusion into sediment.

Spatially, the PEC_{sed} represents the segment thickness weighted average concentration of all nodes (used in the numerical solution of the CDE in sediment) located in the 1-cm upper sediment layer, and thus not the 5-cm upper layer (which is relevant for its effects on rooted macrophytes). The TWA7 and TWA28 represent the maximum average concentrations in the water layer of hourly values over a rolling time window of 7seven and 28 days, respectively.

4.2 Pesticide properties parameters

In the present sensitivity analysis the variance of the studied output by the input of the pesticides properties (the process parameters) is studied. Pesticide properties are set in Section 7b of the input file for TOXSWA.

4.2.1 Parameters included in the sensitivity analysis

The pesticide properties parameters included in the sensitivity analysis are given in Table 4-1. Further details are provided in Chapter 5.

Table 4-1 *The eleven process parameters of the TOXSWA model included in the sensitivity analysis.*

Process parameter	**Symbol**	**Name in TOXSWA**	**Unit**[6]
Molar mass	M_m	MolMas	g mol^{-1}
Saturated vapour pressure	P_{sat}	PreVapRef	Pa
Water solubility	c_{slb}	SlbWatRef	mg L^{-1}
Half-life for transformation in water and in sediment at reference temperature	$DT_{50,wat}$ $DT_{50,sed}$ Half-life DT_{50} = Ln(2)/k for k_{wat} and k_{sed}	DT50WatRef DT50SedRef	d
Diffusion coefficient in water	D_w	CofDifWatRef	m^2 d^{-1}
Freundlich coefficient for equilibrium sorption to organic matter in suspended solids or sediment	$K_{F,om,sed}$ $K_{F,om,ss}$	KomSed KomSusSol	L kg^{-1}
Freundlich exponent for sorption to organic matter suspended solids or sediment	N_{sed} N_{ss}	ExpFreSed ExpFreSusSol	-
Coefficient for linear sorption to macrophytes	K_{mp}	CofSorMph	L kg^{-1}

4.2.2 Parameters not included in the sensitivity analysis

The process parameters not included in the sensitivity analysis are given in Table 4-2. The rationale for not including these parameters is discussed below the table.

Table 4-2 *Process parameters of the TOXSWA model which were not varied in the sensitivity analysis.*

Process parameter	**Symbol**	**Name in TOXSWA**	**Unit**
Reference concentration in liquid phase for Freundlich coefficient for sorption to organic matter in suspended solids or sediment	$c_{ss,r}$ $c_{sed,r}$	ConLiqRedSusSol ConLiqRefSed	mg L^{-1}
Molar enthalpy for vaporization, dissolution in water, transformation in water and transformation in sediment	-	MolEntVap MolEntSlb MolEntTraWat MolEntTraSed	kJ mol^{-1}
Reference temperature for saturated vapour pressure, for water solubility and for transformation in water and in sediment	-	TemRefVap TemRefSlb TemRefTraWat TemRefTraSed	°C

Reference concentration
The reference concentration defines the concentration at which the Freundlich coefficient K_F has been estimated. The K_F value depends on the curvature of the sorption isotherm and this curvature differs according to its location in the isotherm. A K_F value for Eqs (12) and (23) is therefore only valid at a location somewhere located within the measured concentration range. However, the PPDB does not specify the reference concentration applied to define the K_F. So, this reference concentration has not been included in the sensitivity analysis and it has been assumed that it has the default value of 1 mg L^{-1}.

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[6] Unit as in the TOXSWA input files.

Enthalpies

Enthalpy values for state changes and for transformation rate are substance-dependent. However, the values per substance are usually not available and therefore the values used in the models are average values from Smit et al. (1997) for state changes and EFSA recommendations (EFSA, 2007) for transformation rate.

It may be useful to analyze the sensitivity of the target variables (acute and chronic PECs in surface water and in sediment) to the value of the enthalpies for transformation in water and sediment and for dissolution and volatilization, e.g. for a subset of pesticides. However, this is not within the scope of this study.

Reference temperature

The reference temperature is the temperature at which the state change or transformation rate is expressed or measured. This is usually 20˚C, this is also the default value when it is not known. Therefore a fixed 20˚C is used as the reference temperature.

4.3 System parameters

The system parameters used as input for TOXSWA are listed in Table 4-3. System parameters are general parameters that describe the waterbody supplemented with parameters that describe the hydrology of the pond or stream.

Table 4-3 *System parameters in TOXSWA.*

Description	Symbol	Name in TOXSWA	Unit
General			
Mass concentration of suspended solids	ss	ConSus	$g\ m^{-3}$
Mass fraction of organic matter of suspended solids	$m_{om,ss}$	CntOmsusSol	-
Dry mass of macrophytes per m^2 sediment	DW	AmaMphWatLay	$g\ m^{-2}$
Bulk density of dry sediment material	ρ_{sed}	Rho	$kg\ m^{-3}$
Volume fraction of pore water	ε	ThetaSat	-
Mass fraction of organic matter of sediment	$m_{om,sed}$	CntOm	-
Air temperature, applied for water and sediment	T	-	°C
Bottom width	b	WidWatSys	m
Side slope, horizontal/vertical	s_1	SloSidWatSys	-
Water depth defining the exchanging perimeter $P_{z=0}$	h_{wat}	DepWatDefPer	m
Pond			
Size of surrounding area discharging excess water into the pond	$A_{contr,pond}$	AreaSurPndInp	ha
Base flow, i.e. inflow into pond	Q_{base}	QBasPndInp	$m^3\ d^{-1}$
Height of the weir crest at outflow	h_{weir}	HgtCrePnd	m
Width of the weir crest at outflow	b_{crest}	WidCrePnd	m
Size of the eroding area around the pond (only for runoff/PRZM)	$A_{erosion}$	AreaErsSurPndInp	ha
Watercourse: ditch and stream			
Area of upstream catchment	A_{up}	AreaUpsWatCrsInp	ha
Slope bottom representative channel	G	SloBotRepCha	-
Height of the weir crest	h_{weir}	HgtCreRepCha	m
Width of the weir crest	b_{crest}	WidCreRepCha	m
Length representative channel	$L_{d\text{-}w}$	LenRepCha	m
Coefficient defining Manning's coefficient for channel roughness in a channel with a 1 m water depth	$K_{M,1m}$	CofRghRef	d^{-1}
Energy coefficient due to non-uniform distribution of flow velocities in cross section[7]	α	CofVelHea	$m\ d^{-1}$
Base flow from upstream catchment	Q_{base}	QBasWatCrsInp	$m^3\ d^{-1}$

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[7] Note that that for the hydrology of the watercourse the energy coefficient due to non-uniform distribution of flow velocities in cross section, α (see Annex 1 of Adriaanse and Beltman, 2009), needed to calculate the so-called backwater curve, is input for TOXSWA, while the discharge coefficient of the weir, C_{weir}, is not an input parameter but its values of 1.7 $m^{1/2}\ s^{-1}$ is hardcoded in TOXSWA.

4.4 Entries

We identified three types of entries that could be considered.

The first two types of entries consist of (i) an instantaneous mass entry, represented by a spray drift deposition event, and (ii) a distributed type of mass entry (accompanied by substantial water fluxes and lasting a number of hours), represented by a runoff event.

A third type of entry, distributed type of mass input in sediment (= pesticide mass sorbed to eroded soil) is not considered in the sensitivity analysis for process parameters, as these types of entry in the TOXSWA model do not play an important role with respect to the studied output parameters. The reason is that erosion fluxes entering the TOXSWA waterbody are modelled by adding the pesticide mass sorbed to eroded soil to a discrete layer of the sediment (upper 1 cm in FOCUS scenarios). Therefore, often in scenarios with runoff and erosion, the maximum content in sediment occurs at the time of the erosion event, which only lasts a few hours. In such cases, the processes of transformation in sediment and diffusion from the sediment into the water layer are often more important than diffusion from the fast-flowing water layer into the sediment and subsequent sorption in sediment. Thus, the initial maximum concentration in sediment will often not increase, and originates from an entry into the TOXSWA model, and thus it is not related to the behaviour of the TOXSWA model itself. Therefore, a sensitivity analysis of TOXSWA for such an erosion mass entry has not carried out within this project.

So, for the first two types of entries mentioned above (instantaneous mass entry represented by a spray drift deposition event, and distributed type of mass entry, accompanied by substantial water fluxes that lasts a number of hours, represented by a runoff event), five simulation options have been determined in total:

Spray drift deposition event
For the spray drift entry, all mass fluxes in the runoff entry file are set to zero, and combined with:

1. Only baseflow, with all other water fluxes zero.
2. Baseflow plus runoff event of intermediate size, represented by 1 mm runoff (~ 10-20 mm rain, see Adriaanse et al., 2017) at Day 7, runoff water fluxes distributed over six to eight hours.
3. Baseflow plus event with high runoff, represented by 10 mm runoff (~ 40 mm rain) at Day 7, runoff water fluxes distributed over 20-24 hours.

Runoff event
For the runoff mass entry, the pesticide mass flux is equally distributed between the hours with water fluxes, and combined with the water fluxes of:

1. The runoff event of intermediate size, see 2.
2. The high runoff event, see 3.

Note that a runoff mass entry does not occur when there is no water flux, therefore, the situation with only baseflow is not relevant for a runoff entry. Thus, only two instead of three options are relevant.

The pond was selected to represent waterbodies with low flow velocities. The most logical approach would be to select two of the five simulation options for executing the sensitivity analysis with a pond, because other options lead to a (higher) increase of flow velocity, and therefore these options are expected to decrease the sensitivity of the process parameters. So, the most logic approach is to study options 1 and 4, for the pond, so with an instantaneous mass entry and with a distributed type of mass entry (accompanied by water fluxes). However, we were able to execute only the sensitivity of an instantaneous mass entry (Option 1), in the selected R1 pond (Chapter 6). To get insight into the effect of type of mass entry, a distributed type of mass (and water) entries during a number of hours was studied, so Option 4. A stream, representing waterbodies with higher flow velocities than those in a pond, was selected (Chapter 7).

The parameters related to the entries are given in Table 4-4.

__Table 4-4__ Entries in TOXSWA.

Description	Symbol	Name in TOXSWA	Unit
Start of stretch of waterbody loaded	-	LoaStrSta	m
End of stretch of waterbody loaded	-	LoaStrEnd	m
Date and time of application	-	-	
Drift deposition	m_{drift}	-	mg m^{-2}
Width of treated plot, contributing drainage (Dra) or runoff (Rnf) fluxes	w_F	WidFldDra WidFldRnf	m
Ratio of upstream catchment treated	-	RatAreaUpsApp	-

Not input of TOXSWA, but relevant when set for the sensitivity analysis are the magnitude of runoff events (e.g. 0.1, 1 or 10 mm) and the length of the period in which this event occurs (e.g. 1, 6 or 10 hours).

5 Creation of the sample of pesticide properties parameters

5.1 Introduction

The aim of the sensitivity analysis is to assess for the TOXSWA model which input parameters contribute most to the variation of the selected model outputs, for a realistic range of input parameter values (Section 1.2). This Section describes the construction of the distributions of the eleven processes parameters selected for this sensitivity analysis (see Table 4-1). Towards this aim, multiple simulations are run while varying the values of selected input parameters within their range of distribution.

The following sections present how distributions of the eleven processes parameters were obtained. Characterization was required as input for the Python tool that prepares the TOXSWA simulations.

Realistic distributions of the parameters were based, as far as possible, on values determined for existing pesticides. For most parameters, such data were obtained from the Pesticide Properties DataBase (PPDB) (Lewis et al., 2016), which includes all pesticides that are currently registered in the EU, as well as those that are no longer registered in the EU (but might still be used elsewhere, in e.g. Africa or China). The distribution characteristics for the eleven process parameters were obtained directly or derived from this database and were otherwise obtained through calculations or expert judgement, as described in this Chapter.

5.2 Selection of pesticide data from the PPDB

The process parameters (pesticide properties used as input in TOXSWA) were, as far as possible, obtained or derived from the PPDB database. We selected a set of parameters that we wanted to obtain from the PPDB, as presented below, with the process(es) they relate to:

- Molar mass M_m, used for calculation of volatilization and also for calculation of the diffusion coefficient D_{wat} (see Section 5.3.3).
- Saturated vapour pressure P_{sat}, used for calculation of volatilization.
- Solubility in water c_{slb}, used for calculation of volatilization and also to calculate the coefficient for linear sorption to macrophytes K_{mp} (see Section 5.3.6).
- Degradation half-life in water-sediment systems (used to derive the half-lives of transformation in water $DT_{50,wat}$ and in sediment $DT_{50,sed}$, see 5.3.2).
- Sorption coefficient (either linear sorption or Freundlich) based on the organic carbon content in soil (used to derive the Freundlich coefficient for equilibrium sorption, based on the organic matter content, of suspended solids $K_{F,om,ss}$ and of sediment $K_{F,om,sed}$, see Section 5.3.4).
- Degradation half-life in soil. The latter was not necessary for the sensitivity analysis of the process parameters, but it was selected in view of a possible use when simulating the system and runoff/drainage entries. This parameter is used for the selection of the input values of pesticides, but is not further discussed in this Section.

We selected pesticides from the PPDB based upon two criteria:

- All the parameters mentioned above were available in the PPDB for the given pesticides.
- The pesticide use should be one of the following: herbicides, fungicides, insecticides, nematicides, or growth regulators.

The selection process described above reduced the number of pesticides to 416, while the PPDB contained more than 2,000 entries. For the remaining pesticides, about half (223) were approved in the EU. The non-approved pesticides contained a number of pesticides which have been used previously in the EU, or that are still used in countries outside the EU. It was decided to not reduce further the pesticide list, but to also include values of pesticides that are not used in the EU. We used data from the 416 pesticides to determine the characteristics of the distribution of each parameter. The ranges for the values provided by the PPDB that were directly available from the database, are presented in Table 5-1. However, this concerns only five of the eleven parameters. Half-life DT50 in soil is not necessary for determining process parameters in TOXSWA and, therefore, does not appear in the table. The following sections describe how the parameters used as input for TOXSWA were obtained, either from the PPDB values or from using other approaches.

Table 5-1 *Summary of the parameters of 416 pesticides selected from the PPDB database: Minimum, 25th, 50th (= Median), 75th percentile and maximum values.*

Description[8]	**Minimum**	**25th**	**50th**	**75th**	**Maximum**
Molar mass (g mol^{-1})	32	248	319	381	1,089
Saturated vapour pressure (Pa)	$5.1 \cdot 10^{-15}$	$3.6 \cdot 10^{-7}$	$9.6 \cdot 10^{-6}$	$1.5 \cdot 10^{-4}$	3,000
Solubility (mg L^{-1})	0.0002	1.14	29.2	1424	$6 \cdot 10^{6}$
Half-life for transformation in water-sediment systems (d)	0.02	5.9	28.6	100	2,400
Coefficient for sorption to organic carbon content in soil (linear and Freundlich coefficients together) (L kg^{-1})	0.06	87	358.5	2063	$5.94 \cdot 10^{6}$

5.3 Deriving the values of the pesticide properties parameters

The following sections present how the values of all the eleven process parameters for which the sensitivity of the model is tested (as listed in Table 4-1) were derived. The final versions of distributions determined have been summarized in Annex 1 and Figure 5-1. Note that the distributions of the selected 416 pesticides presented in Figure 5-1 differ from the distributions of the approved pesticides (EC regulation 1107/2009 status) presented for reference in Annex 7. The distributions in Annex 7 represent a slightly smaller group of 379 pesticides (details in the Annex). The differences between the distributions are not discussed in this report.

5.3.1 Molar mass, solubility, and saturated vapour pressure

The molar mass M_m, the solubility c_{slb} and the saturated vapour pressure P_{sat} were obtained directly from the database. The latter two properties are already standardized to 20°C in the PPDB and did not require further treatment.

5.3.2 Half-life of transformation in water and sediment

The half-life of transformation of pesticides in the water-sediment system of 416 pesticide values is used to derive the transformation rate coefficient in the water (k_{wat}) and in sediment (k_{sed}), used in the Eqs (9) and (22), respectively. The general relation between a rate k and the half-life DT_{50} is given by:

$$k = \frac{ln(2)}{DT_{50}} \qquad (31)$$

with:

k = transformation rate coefficient (d^{-1})

DT_{50} = half-life time (d)

The water-sediment experiments executed for test-tube sized water-sediment systems result in an overall system degradation rate. This does not allow for differentiation between a separate degradation rate in the water and degradation rate in the sediment (Ter Horst and Koelmans, 2016).

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[8] Unit as used in TOXSWA input files.

For the sensitivity analysis, the distribution of the values in water and in sediment are taken equal (but uncorrelated). And the range and distribution of the DT_{50} of the water-sediment system was used to characterize the distribution of the half-life in water ($DT_{50,wat}$) and in the sediment ($DT_{50,sed}$).

Note that when TOXSWA is used for regulatory purposes, the water-sediment DT_{50} obtained from laboratory experiments will be attributed either to sediment or to water, while the other DT_{50} will be set to 1,000 days, and vice versa. The worst case PEC in water of the two simulations is to be used in the aquatic risk assessment. Further information is available in FOCUS (2006).

5.3.3 Diffusion coefficient

Two methods were tested to calculate the diffusion coefficient of the pesticide in water (D_{wat}).

The previous sensitivity analysis used the Hayduk & Laudie method to estimate diffusion. This method is recommended by Lyman (1982) for estimating the diffusion coefficient for organic compounds in water. The Hayduk & Laudie equation is written as:

$$D_{wat} = \frac{13.26 \cdot 10^{-5}}{\eta_{wat}^{1.14} \cdot V_B^{0.589}} \cdot 8.64 \cdot 10^6 \tag{32}$$

with:

D_{wat} = diffusion coefficient in water (mm^2 d^{-1})

η_{wat} = (dynamic) viscosity of water (kg m^{-1} s^{-1})

V_B = molar volume (LeBas method) (cm^3 mol^{-1})

The viscosity of water was taken at 20 °C ($\approx 10^{-3}$ kg m^{-1} s^{-1} or Pa s) [9]. The molar volume of the pesticide was estimated from the chemical structure of the pesticide and the additive volume increments of the individual atoms. The volume increments of some atoms (C, H, O, N, Br, Cl, F, I, and S) for calculating the LeBas molar volume are listed in Reid et al. (1977). Unknown volume increments of atoms (P, Zn) were estimated by interpolation on basis of their molecular mass. For simplification (and, as it was performed in Westein et al., 1998), volumes estimates calculated here did not consider the geometry of the molecule, although geometry has an influence on the volume. Diffusion coefficients are typically in the order of 30 to 50 mm^2 d^{-1} (Annex 2).

Another method to calculate the diffusion coefficient requires only the molar mass, the viscosity and the temperature (Worch, 2004):

$$D_{wat} = \frac{3.595 \cdot 10^{-14} \cdot T \cdot 8.64 \cdot 10^{10}}{\eta_{wat} M_m^{0.53}} \tag{33}$$

with:

T = water temperature (K), set at 293 K

To use this empirical equation, the molar mass must be provided in g mol^{-1} and the dynamic viscosity of water in Pa s (or kg m^{-1} s^{-1})[10].

For this study, both methods gave comparable results (see Annex 2). In the following, the distribution of the coefficient D_{wat} was obtained with the Worch method applied to the distribution of the molar fractions obtained from the PPDB. This method was preferred over the method of Hayduk & Laudie for its simplicity.

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[9] Note that to express the diffusion coefficient (originally in cm^2 s^{-1}) in mm^2 d^{-1}, the factor $8.64 \cdot 10^6$ accounts for the adaptation from cm^2 to mm^2 (100) and for seconds to days (86400).

[10] Note that to express the diffusion coefficient in mm^2 d^{-1} (originally in m^2 s^{-1}), the factor $8.64 \cdot 10^{10}$ accounts for the adaptation from m^2 to mm^2 (10^6) and for seconds to days (86400).

5.3.4 Coefficients for Freundlich sorption to sediment and suspended solids

In TOXSWA, sorption to sediment and to suspended solids is described with a Freundlich sorption isotherm. The input parameter for the model is the Freundlich coefficient for sorption, based on the organic matter content in the suspended solids ($K_{F,om,ss}$, in Eq.(9)) and in the sediment ($K_{F,om,sed}$ in Eq.(23)).

In literature, very few data are available for sorption of pesticides specifically to suspended solids or sediments. Therefore, both coefficients are estimated to be equal to their counterpart obtained for soils. This is in line with how the sorption coefficients are determined in pesticide registration.

Two coefficients for sorption to soil are provided in the PPDB database: sorption coefficients for linear sorption (K_{oc}) and for non-linear, Freundlich sorption ($K_{F,oc}$), both based upon organic carbon content of the soil. Both were not always provided simultaneously, and the choice for using one or the other coefficient as input for the model was based on the rationale published in Oh et al. (2021). In this rationale, K_{oc} is preferred over $K_{F,oc,}$ as explained below:

The definition of the K_{oc} is based on a linear sorption isotherm:

$$X = m_{oc} K_{oc} C \tag{34}$$

with:

X = mass of pesticide sorbed per mass of dry soil (mg kg^{-1})

m_{oc} = mass fraction of organic carbon of the soil (kg kg^{-1})

K_{oc} = organic-carbon/water distribution coefficient (L kg^{-1})

C = mass concentration in the liquid phase (mg L^{-1})

The definition of the $K_{F,oc}$ in the PPDB differs from the one given in Eqs (10)and (23) used by the TOXSWA model, although both these equations and Eq. (35) are based on the Freundlich sorption isotherm:

$$X = m_{oc} K_{F,oc} C^{N} \tag{35}$$

with:

$K_{F,oc}$ = Freundlich coefficient for distribution over organic carbon and water (L^{N} kg^{-1} mg^{1-N})

N = Freundlich exponent (-)

So, whereas, the unit of K_{oc} depends only upon the unit used for the mass of dry soil (kg) and the volume of liquid (L), the unit of $K_{F,oc}$ is also a function of the unit used for the mass of pesticide (mg) and also of N. This has the consequence that the value of $K_{F,oc}$ depends upon the unit used for the mass of pesticide. E.g. the $K_{F,oc}$ value obtained by fitting of data with X expressed in mg kg^{-1} and C expressed in mg L^{-1} will differ from the $K_{F,oc}$ value obtained by fitting of the same data with X expressed in µg kg^{-1} and C expressed in µg L^{-1} (see the calculation examples in the reference). As the PPDB does not indicate for which units the $K_{F,oc}$ has been determined, the listed $K_{F,oc}$ values are judged to be not reliable. Note that the definition of $K_{F,oc}$ as given the PPDB differs from Eq. (10) for $K_{F,om}$ that TOXSWA uses.

As a result the distribution of model inputs $K_{F,om,ss}$ and $K_{F,om,sed}$ were based on the K_{oc} values of the pesticides, except when the latter was not available. In those cases, the $K_{F,oc}$ was included to estimate the distribution of $K_{F,om,ss}$ and $K_{F,om,sed}$, although they are clearly less reliable as explained above. In approximately 50% of the substances, a K_{oc} value was available in the PPDB. In the other 50%, we had to use the $K_{F,oc}$ values. (And in the latter case, we set the required reference concentration in the liquid phase in the TOXSWA input file at 1 mg L^{-1}).

The Freundlich coefficients for sorption to suspended solids and sediment based on the organic matter content (i.e. $K_{F,om,ss}$ and $K_{F,om,sed}$ the inputs required by TOXSWA) were then obtained by pooling the $K_{F,oc}$ and K_{oc} for soil values, as these were the only data available in the PPDB. Before determining the distribution of the input values, the sorption coefficients were expressed on the basis of the organic matter content (which is the required input for TOXSWA), by converting them following the relation between sorption coefficient based organic carbon content and based on organic matter content:

$$K_{om} = \frac{K_{oc}}{1.724} \tag{36}$$

5.3.5 Freundlich exponents for suspended solids and sediment

It was decided not to use the Freundlich exponent values available in the PPDB. One reason is that the available data for the Freundlich exponent for sorption in the PPDB presented numerous impossible values (>1). Calvet et al. (1980) reported a range of 0.7-1.0 for the Freundlich exponent for pesticide sorption to organic matter in soils for different pesticides. Values above 1 are considered unrealistic for the soil matrix (Boesten et al., 2015).

Usually, when TOXSWA is used for regulatory purpose, a standard value of 0.9, derived from the average reported by these authors, is taken. To verify if this approach is reasonable, considering the sensitivity of the relevant outputs of the model to the Freundlich exponents, we need to vary the values of the Freundlich exponents. Therefore, (similar to Westein et al., 1998), we multiplied the standard value of 0.9 by a randomly drawn value for a log-normal distribution function with Mean 1 and Standard Deviation τ (so, the variation coefficient also equals τ). This log-normal distribution was obtained by trial and error with the aim to contain as much as possible the minimum and maximum values within the range (0.7-1.0) reported by Calvet et al. (1980). In this way, log-normal distributions with an average value of 0.9 were created for both the Freundlich exponent for suspended solids (N_{ss}) and for sediment (N_{sed}).

5.3.6 Sorption to macrophytes

No consistent dataset is yet available for the sorption of pesticides to macrophytes. A relationship between the value for the sorption coefficient to macrophytes (K_{mp}) and the solubility was determined, however, the set of pesticide values used was limited, and did not include herbicides or strongly sorbing pesticides (Crum et al., 1999). To our knowledge, no other estimate is available. Therefore, we applied this relationship to all pesticides including herbicides and highly sorbing pesticides, which we wanted to include in the study. The distribution coefficient for pesticides between water and macrophytes, K_{mp}, (i.e. the slope of the sorption isotherm based on dry weight of macrophytes) was calculated using the relationship below:

$$\log\left(K_{mp}\right) = 3.2 - 0.65 \cdot \log\left(C_{slb}\right) \tag{37}$$

with:

K_{mp} = distribution coefficient between macrophyte and water (L kg^{-1})

C_{slb} = solubility (mg L^{-1})

As the relationship above was derived for pesticides that did not include strongly sorbing pesticides, it may be possible that the K_{mp} range is somewhat underestimated by Eq. (37).

5.4 Lumped volatilization parameter: Henry coefficient (K_H)

The sensitivity analysis is carried out for input parameters of the TOXSWA model. However, the volatilization process is often characterized by the dimensionless Henry coefficient, K_H, to characterize the pesticide, e.g. volatile or not volatile. As we might want to compare the results of this sensitivity analysis to the results of the former sensitivity analysis of Westein et al. (1998), who used the dimensionless Henry coefficient, K_H, we here define it as well.

The dimensionless Henry coefficient, K_H, is a generally known parameter that is used to rank pesticides based on their volatilization capacity (e.g. Lyman et al., 1982). In the prior sensitivity analysis of Westein et al. (1998), the sensitivity to the Henry coefficient was analysed (instead of the individual parameters of solubility and vapour pressure. We analysed the sensitivity of the output to these two parameters in the current sensitivity analysis, therefore, we were unable to compare the results of the two sensitivity analysis for the Henry coefficient *versus* solubility and vapour pressure. However, we did calculate the distribution for the Henry coefficient for our parameter drawings, and compared it to the one by Westein et al. (Section 5.5.1).

Henry coefficient
The Henry coefficient is calculated using:

$$K_H = \frac{P_{sat} \cdot M_m}{R \cdot T} \cdot \frac{1}{C_{slb}} \tag{38}$$

with:
K_H = dimensionless Henry coefficient (-)
P_{sat} = saturated vapour pressure of pesticide (Pa)
M_m = molecular mass (g mol^{-1})
R = universal gas constant (J mol^{-1} K^{-1})
T = temperature at which the saturated vapour pressure and the solubility are defined (K)
c_{slb} = solubility of pesticide in water (g m^{-3})

5.5 How representative are the pesticide properties parameter values?

5.5.1 Comparison with the values used in the prior sensitivity analysis

Here we compare the ranges and distributions of the input parameters used in the current sensitivity analysis with the values used in the previous sensitivity analysis of Westein et al. (1998).

The range and distributions of the current analysis were based on 416 pesticides, while those of Westein et al. (1998) were based on 180 pesticides. We carried out the comparison, because ranges and distributions of the input parameters have a significant influence on the results of the sensitivity analysis. In this way it will thus be easier to explain possible differences in outcome between the two sensitivity analyses.

The comparison was performed for parameters that we consider relevant for the interpretation of the results:

- Input parameters of the current TOXSWA model. transformation in water and sediment, the diffusion coefficient in water, the Freundlich coefficients and exponents for sorption to suspended solids and sediment based on organic matter, and the coefficient for linear sorption to macrophytes (eight of the eleven parameters).
- The lumped parameter that characterizes volatilization, i.e., the Henry coefficient, K_H, is not currently used as input in the current TOXSWA model sensitivity analysis, but is used in the prior sensitivity analysis of Westein et al (1998). Note that Westein et al (1998) calculated this value based on the M_m, P_{sat}, c_{slb} provided for each specific pesticide as randomized values for P_{sat}, c_{slb} would not yield realistic values for K_H. However, for this sensitivity analysis we opted to study the sensitivity of the individual parameters, and performed this for all parameters in this study e.g. sorption to sediment and sorption to suspended solids
- As the lumped parameter K_H was used, the values of M_m, P_{sat}, c_{slb} were not input of the previous sensitivity analysis, and, therefore, their ranges could not be directly compared with the values used in the current sensitivity analysis.

Table 5-2 presents the ranges of parameters provided in the previous sensitivity analysis, as well as the corresponding values extracted (or calculated) from the PPDB in the current analysis. The graphical representations of the distributions of the parameters of the 416 pesticides of this analysis are provided in Figure 5-1, as well as the minimum and maximum values. The graphical representations of Westein et al. (1998) can be found in Figure 5-2. Note that in the table, the units were adapted to be comparable to the units used in the current report (those units are consistent with the units in the input file of TOXSWA).

Table 5-2 *Comparison between the values extracted from the database for 180 pesticides for the previous sensitivity analysis (Westein et al., 1998), and obtained or calculated for 416 pesticides in the current sensitivity analysis. Only the parameters presented in the previous sensitivity analysis have been included.*

		Previous sensitivity analysis (1998, values obtained from 180 pesticides data)		**Current sensitivity analysis (2023-2024, values obtained from 416 pesticides data)**	
Symbol	**Description**	**min**	**max**	**min**	**max**
k_{wat}	Transformation rate coefficient in the water layer (d^{-1})[11]	$6.9 \cdot 10^{-5}$	77	$2.9 \cdot 10^{-4}$	35
k_{sed}	Transformation rate coefficient in sediment (d^{-1})	$4.9 \cdot 10^{-4}$	77	$2.9 \cdot 10^{-4}$	35
D_{wat}	Diffusion coefficient in water ($m^2\ d^{-1}$)	$2.9 \cdot 10^{-5}$	$8.28 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$
$K_{F,om,sed}$ $K_{F,om,ss}$	Freundlich coefficient for sorption on suspended solids and sediment based on organic matter ($L\ kg^{-1}$)	0.1	$1.8 \cdot 10^5$	0.058	$5.9 \cdot 10^6$
N_{sed} N_{ss}	Freundlich exponent for sorption to suspended solids and sediment based on organic matter (-)[12]	0.606 0.694	1.212 1.151	0.67	1.2
K_{mp}	Slope of sorption isotherm for macrophytes ($L\ kg^{-1}$)	0.1	$1.8 \cdot 10^5$	0.3	290
Lumped coefficient (see Section 5.4)					
K_H	Henry coefficient (-)	$1.2 \cdot 10^{-16}$	2.58	$8.8 \cdot 10^{-19}$	0.222

Through comparison of the minimum and maximum values in Table 5-2, and the distributions in Figure 5-1 (current sensitivity analysis) and Figure 5-2 (previous sensitivity analysis), we observe the following:

- The ranges for transformation rates of Westein et al. (1998) are of the same magnitude as the ranges that we extracted from the PPDB database (Table 5-2), with a minimum degradation rate in the range of $6.9 \cdot 10^{-5}$ to $4.9 \cdot 10^{-4}$ d^{-1} and a maximum degradation rate in the range of 35 to 77 d^{-1}. Note the minimum transformation rates in the water layer and in sediment differ from each other in the former sensitivity analysis ($6.9 \cdot 10^{-5}$ d^{-1} and $4.9 \cdot 10^{-4}$ d^{-1} for water and sediment, respectively), but not in our study ($2.9 \cdot 10^{-4}$ d^{-1} for both water and sediment). This may be related to the fact that Westein et al. (1998) also included information on hydrolysis/photolysis rates or soil degradation rates when the degradation rate in the water-sediment studies was missing, while we only took water-sediment degradation rates. The overall distributions for the rate in water and in sediment in the study of Westein et al. (1998) and in this sensitivity analysis are also relatively similar. However, the majority of data from Westein et al. (1998) were below a rate of 1 d^{-1} (Figure 5-2), as we also found (See Figure 5-1, note that a log10 of the half-life of degradation DT_{50} above 0 days corresponds to a rate value, k, of approximately smaller than 1 d^{-1}).
- The distribution for diffusion coefficient of Westein et al. (1998) and ours are similar, with a minimum in the order of magnitude of 10^{-5} $m^2\ d^{-1}$ (Table 5-2). Although the range of diffusion coefficients is about twice as large in our study as in the former study (Table 5-2), this large range is explained by a few large values above $8 \cdot 10^{-5}$ $m^2\ d^{-1}$ in our estimates for diffusion (Figure 5-1). The values are otherwise distributed around a peak at about $4 \cdot 10^{-5}$ $m^2\ d^{-1}$ (see where the maximum of the number of pesticides is situated for diffusion on Figure 5-1 and Figure 5-2 (40 $mm^2\ d^{-1} = 4 \cdot 10^{-5}\ m^2\ d^{-1}$)).
- For sorption to suspended solids and sediment, the range of Freundlich coefficients in our sensitivity analysis is slightly larger (up to $5.9 \cdot 10^6$ $L\ kg^{-1}$ instead of $1.8 \cdot 10^5$ $L\ kg^{-1}$, Table 5-2). This indicates that slightly stronger sorbing pesticides are included in our analysis. Besides the maximum values, the distributions are similar, with most values around 10^{-1} $m^3\ kg^{-1}$ for the previous sensitivity analysis (Figure 5-2), which is in agreement with the values of around 10^2 $L\ kg^{-1}$ in the current sensitivity analysis (Figure 5-1 - Note that different units are used between the two figures, $10^3\ L\ kg^{-1} = 1\ m^3\ kg^{-1}$).
- For the Freundlich exponents for sediment and suspended solids, the values in both sensitivity analyses were obtained by creating a log-normal distribution with an average value of 0.9. The minimum values are

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[11] The relation between the rate coefficient and the half-life (Eq. (31)) was applied.

[12] Values in both studies are not obtained from the data base but through creating a distribution, see Section 5.3.5. They are presented here for comparison of the input values of both sensitivity analysis

similar with a minimum value of 0.67 (close to the 0.7 value as reported by Calvet et al. (1980)) (Table 5-2). However, the distributions (Figure 5-1 and Figure 5-2) differ as the distribution used in the current sensitivity analysis has less values above one than in the prior sensitivity analysis.

- For the sorption coefficient to macrophytes, Westein et al. (1998) took them equal to sorption to sediment and suspended solids. We apply a relation between K_{mp} and c_{slb} that is based on a study with three macrophytes and six pesticides. The relation that we use yields much lower values than the ones that Westein et al. (1998) applied, with a maximum value of 290 L kg^{-1} in this study vs. $1.8 \cdot 10^5$ L kg^{-1} in the previous study (Table 5-2).
- The range of Henry coefficient from Westein differs from ours, notably with a much lower minimum of $8.8 \cdot 10^{-19}$ (unitless) vs a minimum of $1.2 \cdot 10^{-16}$ (unitless) in the previous sensitivity analysis. However, the general distribution of the values is comparable, for both the majority of occurrences are between 10^{-5} to 10^{-10} (unitless)(see Figure 5-1 and Figure 5-2).

5.5.2 Running the sensitivity analysis on uncorrelated parameters

Process parameters are pesticides properties and therefore they may present correlations, for instance high sorption (to suspended solids or sediment) might correlate with low solubility. Additionally, a direct correlation can occur from the way that the values are estimated, e.g. the diffusion coefficient is calculated from the molar mass.

In a sensitivity analysis, each parameter must vary independently, so, it needs to be uncorrelated to other parameters. Therefore, input values of process parameters were drawn randomly from each process parameter distribution. Each sampling through the range of all eleven process parameters created a new hypothetical pesticide (referred to as hypothetical, because the combination of the parameters is fictitious). While the ranges, and the distributions of the values of the process parameters for the new hypothetical pesticides correspond to those of existing pesticides, there can be unlikely combinations of process parameters for the hypothetical pesticides (for instance, high sorption to suspended solids but not to sediment). The sampling method is explained in Section 3.4.1.

5.6 Distributions of the pesticide properties parameters values and lumped parameter K_H

The above sections presented how data were selected for the purpose of obtaining representative distributions of the pesticide properties parameters. In this Section, we explain how the characteristics of the distributions were obtained.

As presented in Section 3.3., the process parameters, i.e. the pesticide properties, are environmental data, and therefore their values often present a so-called lognormal distribution. For such data, it is common to use the logarithm (here, log10) of the data for statistical treatment. A reasonable fit for the log10 of all values of each parameter was obtained for each parameter based on the Kolmogorov-Smirnov test[13] both using a normal and a lognormal distribution (not shown). For simplicity, a normal distribution is preferred. Using a fitting tool from the statistics library in Python[14], the characteristics of the normal distributions of the log10 of the process parameters and lumped parameter K_H was obtained. The characteristics of the obtained distributions are presented in Annex 1.

After sampling the obtained distributions (Annex 1) approximately 50,000 times, and then, transforming the sampled values back to process parameters values (by $x = \log10(10^x)$), we obtained the following distribution as input for the model (Table 5-3). In Figure 5-1 we present the distributions, as well as the fitted curves on the distributions of the pesticide parameters for the 416 pesticides used as input. Considering the large number of samples, approximately 50,000, the samples taken within the distribution represented the fitted curves well.

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[13] https://docs.scipy.org/doc/scipy/reference/generated/scipy.stats.kstest.html

[14] https://scipy.github.io/devdocs/reference/generated/scipy.stats.fit.html

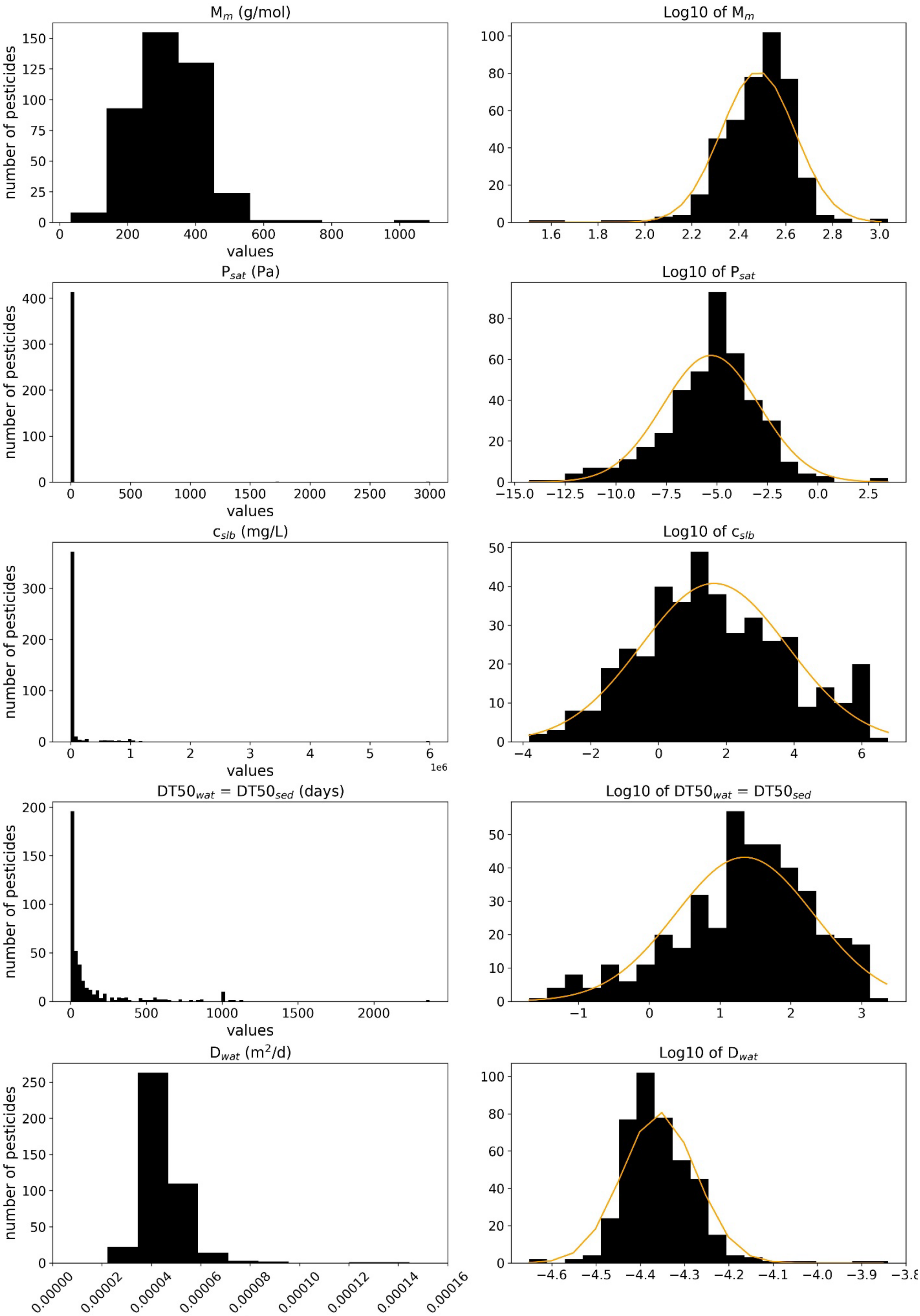
Table 5-3 *Distribution of the input and of the lumped process parameter K_H. The values were obtained through sampling ~$50\cdot10^3$ times the fitted distributions of the log10(x) of the parameter values of the 416 pesticides and transformed back to parameter values ($x = 10^{log10x}$).*

Name	**Process parameter (as in TOXSWA)**	**minimum**	**25-percentile**	**median**	**75-percentile**	**maximum**
Molar mass M_m (g mol^{-1})	MolMas	85.9	237.8	303.5	387	1,071.8
Saturated vapour pressure P_{sat} - (in water at 20°C) (Pa)	PreVapRef	$2.6\cdot10^{-14}$	$1.3\cdot10^{-7}$	$5.2\cdot10^{-6}$	$2.1\cdot10^{-4}$	$1.1\cdot10^{3}$
Solubility c_{slb} - (in water at 20°C) (mg L^{-1})	SlbWatRef	$1.3\cdot10^{-6}$	1.5	43.6	1244	$1.5\cdot10^{9}$* $1.0\cdot10^{6}$
Half-lives of transformation in water and sediment (at 20°C)** $DT_{50,wat}$ and $DT_{50,sed}$ (d)	DT50WatRef & DT50SedRef	$8.8\cdot10^{-3}$* $1\cdot10^{-2}$	4.9	22.2	101	$5.6\cdot10^{4}$
Diffusion coefficient in water D_{wat} (m^2 d^{-1})	CofDifWatRef	$2.2\cdot10^{-5}$	$3.9\cdot10^{-5}$	$4.4\cdot10^{-5}$	$5.0\cdot10^{-5}$	$8.6\cdot10^{-5}$
Freundlich sorption coefficient on organic matter in suspended solids and in sediment $K_{F,om,ss}$ and $K_{F,om,sed}$ (L kg^{-1})	KomSusSol KomSed	0.1	82.7	470.5	2677	$3.8\cdot10^{6}$
Freundlich exponent to suspended solids and sediment based upon organic matter content N_{ss} and N_{sed} (-)	ExpFreSusSol ExpFreSed	0.67	0.8	0.9	0.9	1.2
Coefficient for linear sorption on macrophytes K_{mp} (L kg^{-1})	CofSorMph	0.1	3.3	8.4	21.8	1,126.2
Lumped parameter		**minimum**	**25-percentile**	**median**	**75-percentile**	**maximum**
Henry coefficient K_H (-)	-	$1.7\cdot10^{-20}$	$1.0\cdot10^{-10}$	$1.5\cdot10^{-8}$	$2.2\cdot10^{-6}$	$3.6\cdot10^{6}$

* Maximum values of $1\cdot10^6$ mg L^{-1} for solubility and of minimum value of 0.01 d for half-lives of transformation (both water and sediment) were applied because these are the threshold values that can be entered in the TOXSWA model. Values were adjusted for the 1056 largest solubility values and for the 24 smallest values for each half-lives (i.e., ~2.2% of the runs). This change also lowered the mean values, which is not reported in this table. Note that the range of the Henry coefficient in this table is much larger than when using values calculated from real data (Table 5-2: $9.9\cdot10^{-19}$ to $2.2\cdot10^{-1}$ (-)) as the random selection of solubility and vapour pressure to calculate the K_H yields unlikely combinations of values, resulting in a higher range.

** The PPDB does not give the temperature at which the water-sediment studies are done. For the sensitivity analysis it is implicitly assumed that the temperature is 20°C, and therefore used as a reference temperature in TOXSWA.

Distributions of the parameters' values are shown in Figure 5-1 The data do not follow a Gaussian distribution and, therefore they are presented with a percentile distribution, which is more appropriate than Mean and Standard Deviation. On the left, the values themselves are shown. While log10 values of the process parameter are shown on the right, as well as a normal distribution fitted on the log10 of the values (orange) of the sampled input for the 50,000 simulations. The x-axis shows the interval boundaries of distributions shown, and on the y-axis the number of values for each interval. Note that the distribution of $DT_{50,wat}$ is the same as $DT_{50,sed}$, and similarly the pairs $K_{F,om,ss}$ and $K_{F,om,sed}$, N_{ss} and N_{sed} are taken equal. Hence, the eight distributions shown represent the distributions for the eleven process parameters considered in our sensitivity analysis. In addition, the distribution of the lumped parameter K_H has been included. N_{ss} and N_{sed}, were not extracted from the database but calculated, see Section 5.3.5. Furthermore, note that in some of the graphs (e.g. solubility in water), the x-axis has a very broad range, up to 10^6, but values are visible only in the lower range. However, there are a few large values, not visible in the graph, that justify the broad range on the x-axis.


M_m (g/mol)
number of pesticides
0
25
50
75
100
125
150
0
200
400
600
800
1000
values
Log10 of M_m
0
20
40
60
80
100
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
P_sat (Pa)
number of pesticides
0
100
200
300
400
0
500
1000
1500
2000
2500
3000
values
Log10 of P_sat
0
20
40
60
80
−15.0
−12.5
−10.0
−7.5
−5.0
−2.5
0.0
2.5
c_slb (mg/L)
number of pesticides
0
100
200
300
0
1
2
3
4
5
6
1e6
values
Log10 of c_slb
0
10
20
30
40
50
−4
−2
0
2
4
6
DT50_wat = DT50_sed (days)
number of pesticides
0
50
100
150
200
0
500
1000
1500
2000
values
Log10 of DT50_wat = DT50_sed
0
10
20
30
40
50
−1
0
1
2
3
D_wat (m2/d)
number of pesticides
0
50
100
150
200
250
0.00000
0.00002
0.00004
0.00006
0.00008
0.00010
0.00012
0.00014
0.00016
Log10 of D_wat
0
20
40
60
80
100
−4.6
−4.5
−4.4
−4.3
−4.2
−4.1
−4.0
−3.9

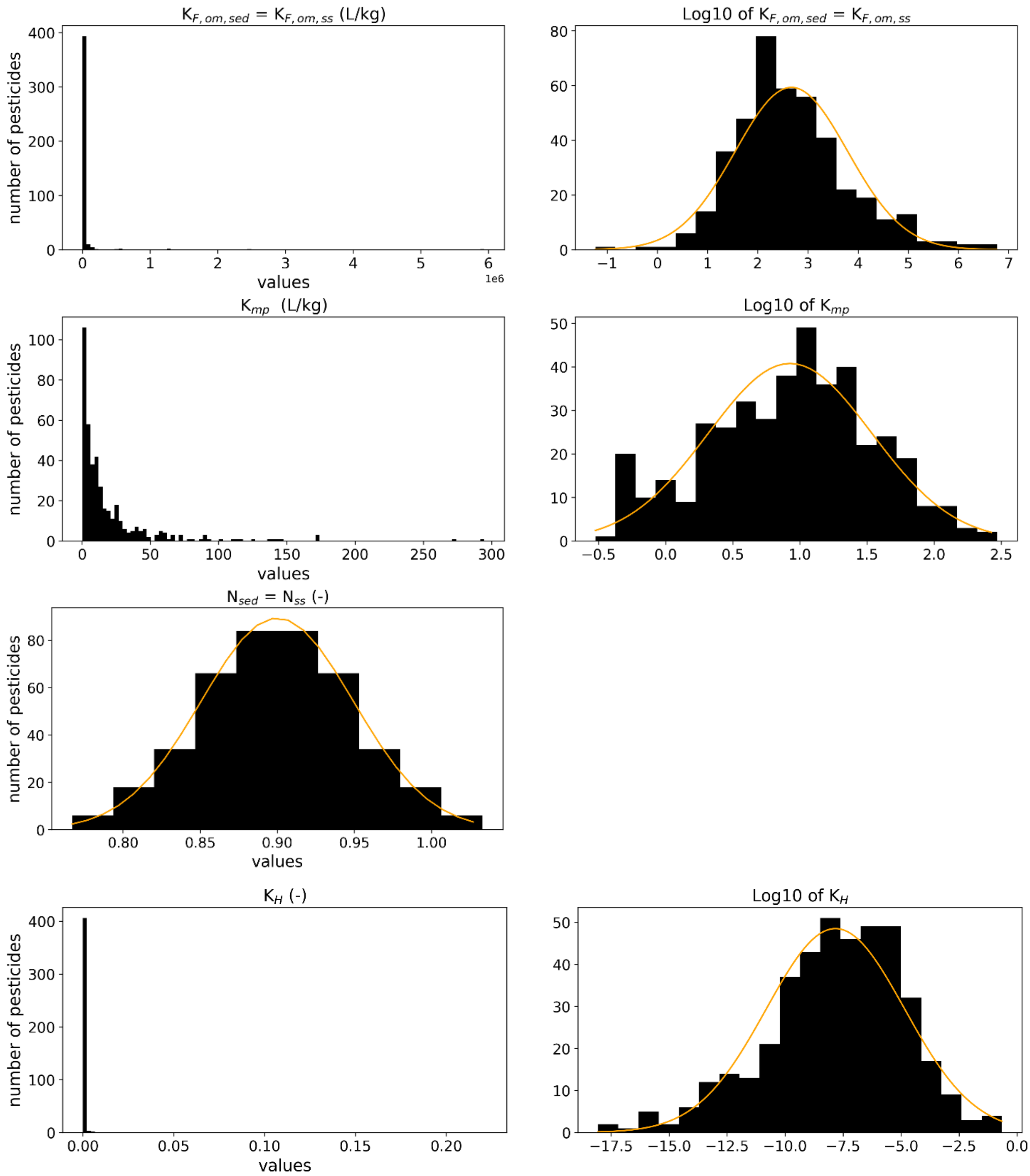


Figure 5-1 *Distribution of the process parameters of the 416 pesticides from the PPDB, in this study. Original values: left, log10 values, plus fitted distribution of the sampled input for the 50,000 simulations (orange): right.*

Figure 5-2 shows p.32 of Westein et al. (1998). From top right to bottom left: k (d^{-1}) is the transformation rate in the water layer, $K_{om,ss}$ (m^3 kg^{-1}) is the sorption coefficient for suspended solids, n_{ss} (-) is the Freundlich exponent for sorption to suspended solids, K_{mp} (m^3 kg^{-1}) is the sorption coefficient for macrophytes, K_H is the Henry coefficient, D_w (note that the unit is be corrected to mm^2 d^{-1} and not mm d^{-1}) is the diffusion coefficient, k_b (d^{-1}) is the transformation rate in sediment, $K_{om,wb}$ (m^3 kg^{-1}) is sorption coefficient for sediment and n_{wb} (-) the Freundlich exponents for sorption to the sediment.

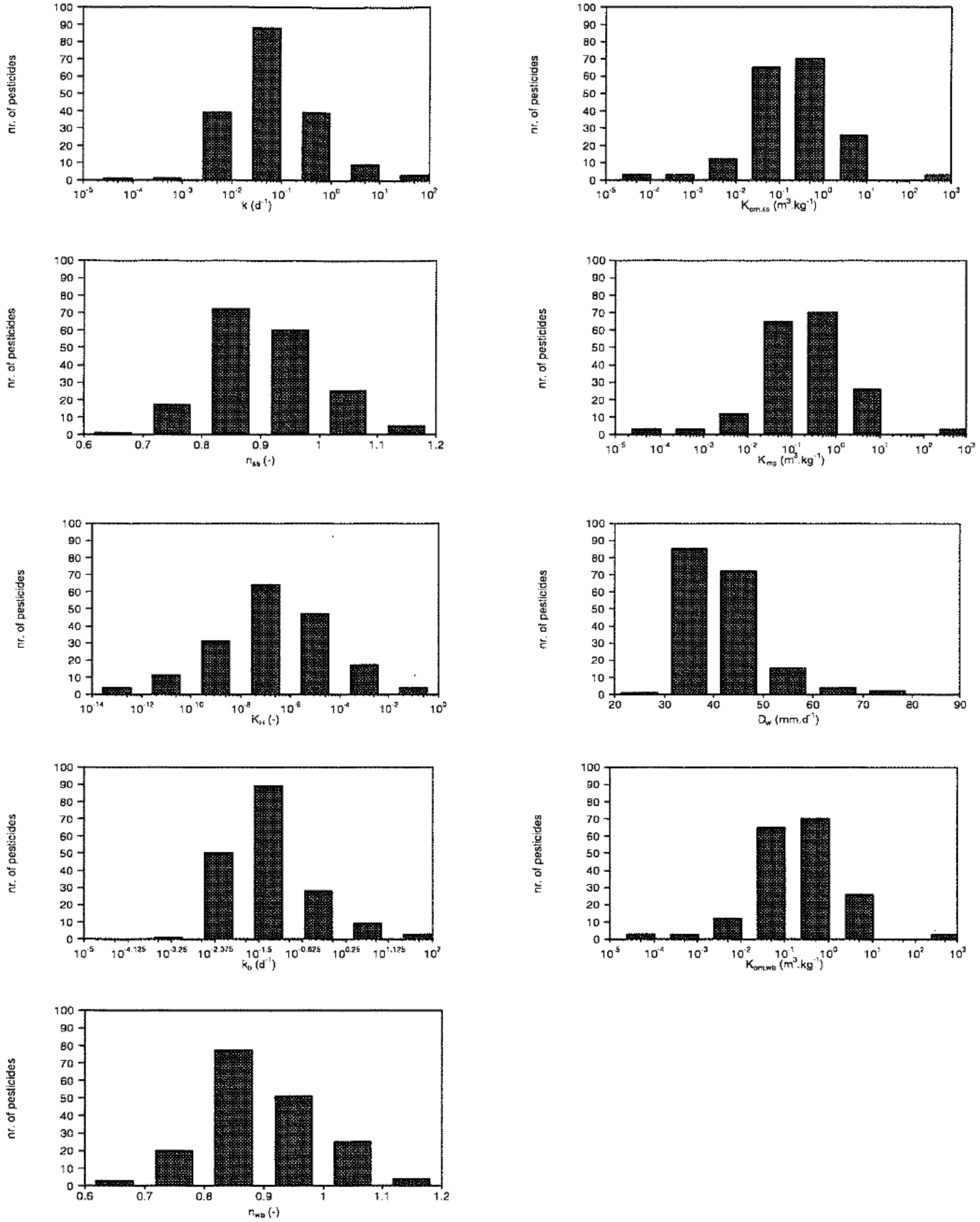


Figure 5-2 *Distribution of the process parameters of the 180 pesticides of Westein et al. (1998).*

6 Sensitivity for the pond system

In this Chapter, the sensitivity to eleven selected pesticide parameters of the exposure in a pond system with spray drift entry is described. The parameterisation of the pond and of the spray drift entry is described in Section 6.1. The results of the sensitivity analysis are described in Section 6.2, and summarised in Section 6.3.

So, numerous simulations were run with a different set of pesticide properties parameters for each simulation, i.e. a hypothetical pesticide. The pesticide properties parameters which were not selected for the sensitivity analysis, and the system parameters, entries and initial conditions were unchanged during the simulations. A standard set was therefore created. The standard set was used to run TOXSWA for each of the hypothetical pesticides using the pesticide properties parameters values obtained through sampling the parameter distributions (Section 5.6). In Section 6.1 this standard set is described.

6.1 Standard set of system parameters, entries and initial conditions

In Sections 6.1.1 up to 6.1.3 the studied system and its initial conditions and entries are described.

6.1.1 The pond system

For the simulation of a pond system a FOCUS scenario was selected in which as well instantaneous mass entries by drift deposition as distributed mass or water entries are possible (see Section 4.4). This is the R1 pond, because it is the only pond in the FOCUS scenarios being able to receive instantaneous mass entries by spray drift deposition as well as distributed mass and water entries by runoff. The depth of the pond is 1 m, the discharge is 0.07 L s^{-1} and the hydraulic residence time is 157 d (only baseflow).

Upward or downward seepage in the sediment is not considered, because this is not considered in current EU and NL scenarios.

In this Chapter 6 we performed a sensitivity analysis for an instantaneous mass entry - a spray drift deposition event, with only baseflow entering. So, all other water fluxes were zero, and there were no runoff water fluxes entering the R1 pond. In Chapter 7 we performed a sensitivity analysis for the distributed mass and water entry by runoff, in addition to the baseflow.

Although macrophytes, which may sorb pesticide mass, are currently not included in any regulatory scenario, at EU level or at Member State level, we included these in the sensitivity analysis, as they may play an important role in field experiments used for model validation (e.g. Adriaanse et al., 2022). A density of macrophytes of 200 g DW m^{-2} is used in our simulations here: 200 g DW m^{-2} represents a moderate macrophyte biomass per area of ditch bottom for shallow oligotrophic waters (Brock, 1988, Adriaanse et al., 2022). All other values of the system parameters were equal to those of the R1 pond (FOCUS, 2001).

TOXSWA version 3.3.8 (part of FOCUS_TOXSWA 6.6.4 and of DRAINBOW 2.2) is used for the R1 pond for the most recently developed EU-FOCUS scenarios, running 20 years (EFSA, 2020). The sensitivity is tested based on a single entry in one year only, and not for the series of 20 years. So, the standard simulation period of one year (FOCUS, 2001) or 26 years (six years warming up + 20 simulation years in EFSA (2020)) is shortened to three months from 1st March onwards in the first simulation year (1969), using temperature data of 1969 of the scenario. Temperature is the only weather effect included in the simulation. And 1969[15] is the first year simulated (EFSA, 2020).

This is sufficient for peaks in the water layer because mass entries generally have flowed out within a couple of days up to weeks and thus, they do not accumulate over the years. However, in the sediment, concentrations may accumulate by transfer from the water layer into the sediment, as long as the water concentration is higher than the sediment pore water concentration. However, this behaviour does not change after a mass entry in the water layer, the following year. So, equally for the sediment, a series of years is not required. However, the simulation period should be sufficiently long to reach the peak exposure before the end of the three months' simulation (i.e. date of PEC_{sed} should not be the last day of the simulation). As it would be very cumbersome to check this for all simulations, we verified this hypothesis for simulations with extreme values for the sorption coefficient for sediment. The PEC_{sed} were found between the 4th and the 10th of March, well before the end of the simulation (31st May). So peaks occurred well before the end of the simulations. The application date was set to the 4th March, because Spring is a season generally many pesticide applications occur.

The template (txw input file) used for TOXSWA for the pond system is shown in Annex 4. Note that for large adsorption coefficients in the sediment ($K_{om,sed}$ > 17,400 L kg^{-1} or K_{oc} > 30,000 L kg^{-1}), the FOCUS fine sediment segmentation is used (see Section 4.4.4 in Beltman et al., 2018). This is applied to ensure convergence of the numerical solution.

6.1.2 Initial conditions for pond system

For the sensitivity analysis it was assumed that the water layer and the sediment are free of pesticides at the start of the simulation.

6.1.3 Pesticide entry for pond system

One type of entry is of tested; an instantaneous mass entry represented by a spray drift event.

The spray drift mass entry is set to 0.38617 mg m^{-2}, which would follow from a rather high application rate of 1,763 g ha^{-1} and spray drift of 0.8106% to the pond from a field crop, such as Winter cereals (drift percentage from FOCUS (2001) for the water edge close to the treated field). The application is set on Day 4 of the simulation, corresponding to only baseflow and lateral inflow of water via interflow. In the whole simulated period from 1 March - 31 May 1969 there is no runoff. (Note that the year 1969, the first warming-up year, is in reality the year 1983, a relatively 'average' year with respect to runoff-causing rainfall events (FOCUS, 2020). The interflow varies per day resulting in small variations in flow velocity. This is an extreme situation for a spray drift event regarding maximum PEC in water, PEC in sediment, TWA7 and TWA28 in water, because without runoff water flowing in the residence time of water in the pond is longest.

6.2 Results

The model was run 49,152 times[16] varying the input parameters to evaluate the sensitivity of the selected outputs. The sensitivity of the output was obtained through the calculation of Sobol's indices. The results of the simulations and of the analysis of the output variance are presented in this section for the case of spray drift entries in the pond scenario.

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[15] Temperature data for 1969 were not available, based on runoff data analysis, data of 1983 are applied for 1969 (see Section 3.1.2 in EFSA (2020).

[16] 18 of these runs were not finalized because a numerical solution for the sediment resulted in negative concentrations (run stop with negative concentration error). For these 18 runs the outputs of the (successful) run performed for preceding sampled parameters () were used as result. Hence, for 18 runs incorrect results were used in the analysis. This is only 0.04% of the runs, hence, we expect the failure of these runs has no effect on the results of the study.

6.2.1 Predicted Environmental Concentrations in water (PEC$_{wat}$)

The deposition of 0.386 mg m^{-2} on the water surface, resulted in a theoretical maximum concentration of 0.386 µg L^{-1} in the 1-m deep pond (not considering instantaneous sorption to suspended solids and to macrophytes). Figure 6-1 shows the distribution of PEC$_{wat}$ values from the simulations. The values show a limited variation, the large majority lies between 0.35 µg L^{-1} and the maximum concentration of 0.386 µg L^{-1}. This can be understood by realizing that the PEC$_{wat}$ occurs immediately after the spray drift deposition and instantaneous sorption to suspended solids and to macrophytes. So, lowering of the maximum concentration only occurs when these sorption processes are significant.

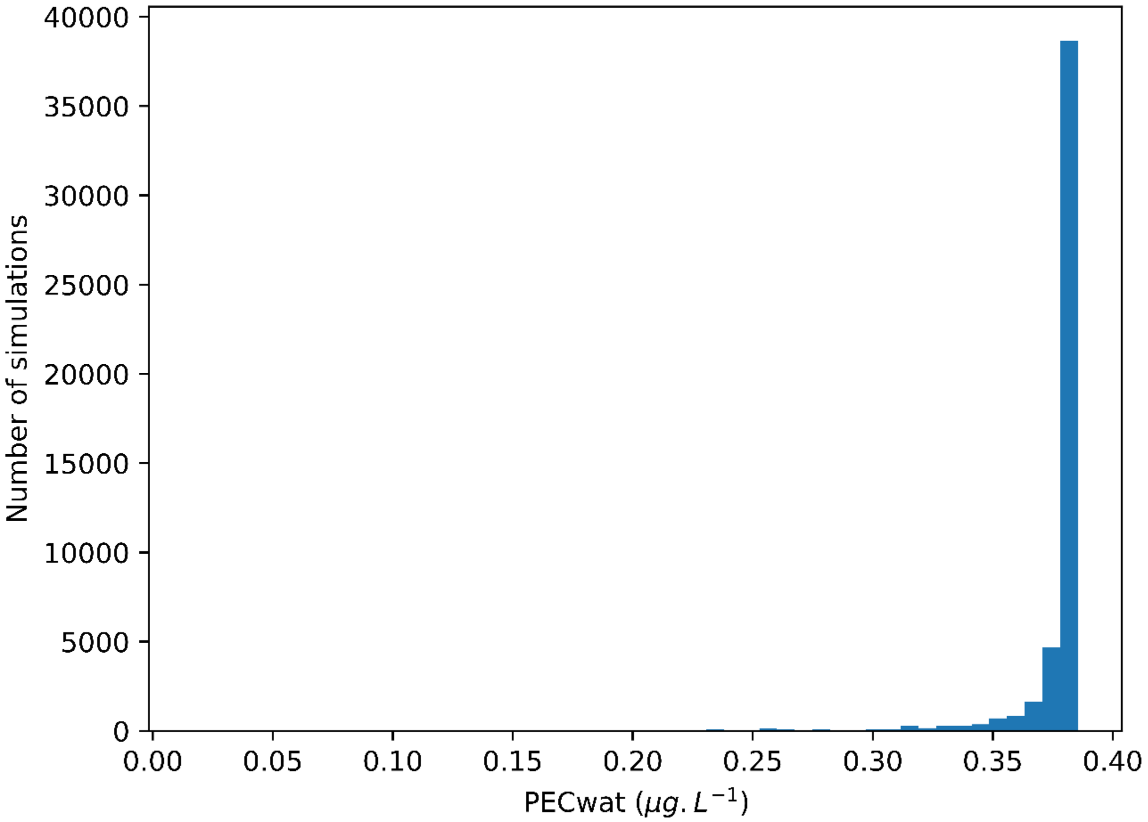

Figure 6-1 *Distribution of the maximum PEC$_{wat}$ in the R1 pond after spray drift entry.*

The three Sobol indices of pesticide process parameters for the PEC$_{wat}$ are shown in Figure 6-2. Values of the S_1 and S_T indices are provided in Table 6-1 and of the S_2 index in Annex 6.

The first-order indices S_1 indicate the contribution of the single process parameters, independently, to the variance of the calculated PEC$_{wat}$. The PEC$_{wat}$ variance is explained to 91% by the independent variation of single process parameters of which 89% by the sorption coefficient of suspended solids, $K_{F,om,ss}$ (Table 6-1).

As stated above, the values of the PEC$_{wat}$ show a skewed distribution: indeed, a decrease of the PEC$_{wat}$ occurs only for very high sorption coefficients, e.g. for pyrethroids with extreme $K_{F,om,ss}$ values of 100,000 L kg^{-1} or higher. Back-of-the envelope calculations demonstrate that these lead to PEC$_{wat}$ values as low as 0.016 µg L^{-1} (not visible on the graph due to the limited amount of data). For sorption coefficients $K_{F,om,ss}$ in the more commonly found range of approximately 100-10,000 L kg^{-1}, relatively few mass is sorbed to suspended solids and PEC$_{wat}$ values are hardly influenced.

The remaining S_1 indices indicate that the coefficient for linear sorption to macrophyte K_{mp} and the Freundlich exponent for sorption to suspended solids N_{ss} contribute negligibly to the variation of the PEC$_{wat}$ (S_1 values of 2% and 1%, respectively). So, surprisingly, sorption to macrophytes does not contribute significantly to the variance of the PEC$_{wat}$. The reason is not that the process is less important than the other instantaneous sorption process, i.e. sorption to suspended solids, but rather that the range for the K_{mp} input parameter is small compared to the range for the sorption coefficient $K_{F,om,ss}$: 0.1- 1,126.2 L kg^{-1} for K_{mp} compared to 0.1 – 3.8.10^{6} L kg^{-1} for the $K_{F,om,ss}$ (Table 5-3). Note that the range in K_{mp} is not based upon K_{mp} values in the PPDB database, as is the case for all other input parameters, but that it has been estimated based upon a relationship between the log(solubility) and the log(K_{mp}) found in experiments run with only six pesticides (Crum et al., 1999). So, in fact the uncertainty in the range may be significantly higher than the uncertainty in the range of other input parameters but this was not specifically considered in the sensitivity analysis.

Despite the strong influence of the sorption to suspended solids on the variance of PEC_{wat} (as shown by the S_1 index of 89% for the $K_{F,om,ss}$ parameter), the N_{ss} parameter hardly contributes to the variation of the PEC_{wat} (S_1 index of 1%), probably also because of its very limited range (0.67-1.2, Table 5-3). All other process parameters do not influence the PEC_{wat}, i.e., the peak concentration immediately after application, and their contribution to the PEC_{wat} variation is smaller than 1%.

The sum of all S_1 indices is 91%, whereas for a linear model with no interaction this is expected to be near 100% (see Section 3.2.2). Hence, 9% variation of PEC_{wat} may not be attributed to single parameters independently. The S_2 and S_T indices allow to evaluate which parameters show interactions relevant to explain the variation in the output.

The total-order index S_T indicates the contribution of a process parameter input to the variance of the calculated PEC_{wat}, including both its first-order effects (S_1, the process parameter varying alone) and all higher-order interactions. Hence S_T given for $K_{F,om,ss}$ and N_{ss} are higher than S_1 of the same process parameters (Table 6-4) because second and higher order interactions are included (which is confirmed by S_2 values >0 in Figure 6-2). The increase from S_1 to S_T is from 89% to 98% and 1% to 9% for $K_{F,om,ss}$ and N_{ss}, respectively. The value of S_T for the K_{mp} is equal to its value of S_1, i.e. 2%, indicating that there is no additional significant interaction with other input parameters. For all other process parameters S_1 and S_T are 0%, indicating there is no interaction. Because second-order and higher-order interactions are included in S_T, the sum of S_T is expected to be higher than the sum of S_1 (91%). Indeed, the sum of all S_T values is 108%. As stated in Section 3.2.2 a S_T sum above 100% indicates interactions, i.e. non-linearity. Here the non-linearity of the PEC_{wat} output is mainly driven by interactions with the two parameters for sorption to suspended solids, $K_{F,om,ss}$ and N_{ss}.

The second-order index S_2 indicates the contribution of interactions between any two process parameters to the variance of the calculated PEC_{wat}. In Figure 6-2 it can be seen that S_2 between the sorption parameters to suspended solids, $K_{F,om,ss}$ and N_{ss} is relatively large (6%, see Annex 6) with a large confidence interval (approx. -40% to 50%). Figure 6-2 also presents a large uncertainty for the S_2 index for $K_{F,om,ss}$ and N_{sed}, but no visible index value (= 0.00, see Annex 6). The reason lies in Saltelli's sampling method, which is very efficient (i.e. few drawings are needed), but has the drawback that sampling may be too sparse, resulting in large confidence intervals. In addition, and more importantly, the estimators used in the SALIB implementation of Saltelli to calculate the S_2 values (based on Saltelli et al., 2010, referred to in the SALIB coding) show small errors and can lead to negative variance calculations (pers. comm. G van Voorn). For the pair $K_{F,om,ss}$ and N_{sed} the high uncertainty with no associated S_2 index value related to it, indicates that the statistical reliability is too low here.

All other parameters do not show any influence on the PEC_{wat}.

We conclude that the Sobol indices found for PEC_{wat} are quite satisfactory, as expected and indicated by the S_1 and S_T indices the most sensitive parameter for the PEC_{wat} is the $K_{F,om,ss}$. The other sensitive parameters (K_{mp} and N_{ss}) can be well understood, as explained above. With respect to the PEC_{wat} model outcome, the TOXSWA model behaves slightly non-linearly, as indicated by the sum of S_1 of 91% and of S_T of 108%. The non-linear Freundlich isotherm description for the process of sorption to suspended solids in the water layer may explain this non-linearity.

Finally, the confidence interval of S_1 for the sorption coefficient for suspended solids $K_{F,om,ss}$ is 26% of S_1 (Table 6-1), which is clearly above 10%. For a robust result of the sensitivity analysis the number of simulations should be increased to aim for a smaller confidence interval, below 10%, as Zhang (2015) stated for the Saltelli sampling method. However, the number of simulations required may be quite high due to the current, large confidence interval of the $K_{F,om,ss}$ parameter. As the results are sufficiently understood with respect to the processes described in the TOXSWA model and the S_1, S_T and S_2 results agree well internally, no further analyses were performed with an increased number of simulations. In addition, we intend to use the outcome of this sensitivity analysis especially in a qualitative way, indicating to us which process parameters matter most for the PEC_{wat}, PEC_{sed}, TWA7 and TWA28 model output, and not in a quantitative way such as e.g. determining relative weight in a model calibration. Therefore, we chose not to increase the number of approximately 50,000 simulations and are satisfied with the results obtained.

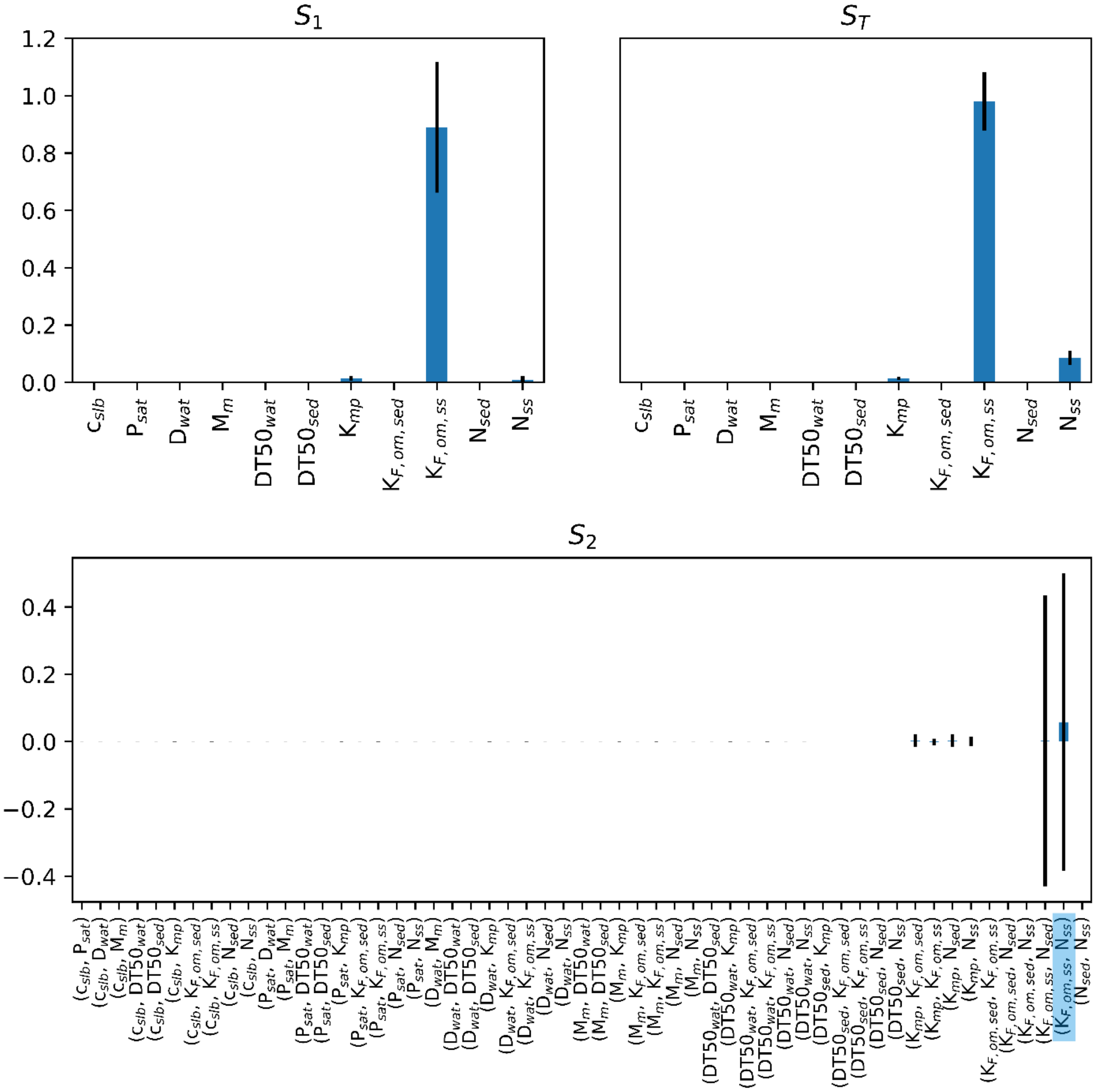

Figure 6-2 *Values of the Sobol sensitivity indices S_1, S_T, S_2 (resp. first-order, total-order and second-order, y-axis) of the pesticide properties parameters (x-axis) for PEC_{wat} in the R1 pond with spray drift entry. The index values are given in blue and their confidence intervals in black. The description in the S_2 graph marked in blue is the KomSusSol/ExpFreSusSol pair with a S_2 of 6%.*

Table 6-1 *First-order (S_1) and total-order (S_T) Sobol index values and their confidence intervals (±) for PEC_{wat} of the R1 pond with spray drift entry.*

Parameter	S_1	S_1 ±	S_T	S_T ±
KomSusSol	0.89	0.23 (26%)[17]	0.98	0.10 (10%)
CofSorMph	0.02	0.01	0.01	0.01
ExpFreSusSol	0.01	0.01	0.09	0.03
SlbWatRef	0.00[18]	0.00	0.00	0.00
PreVapRef	0.00	0.00	0.00	0.00
CofDifWatRef	0.00	0.00	0.00	0.00
MolMas	0.00	0.00	0.00	0.00
DT50WatRef	0.00	0.00	0.00	0.00
DT50SedRef	0.00	0.00	0.00	0.00
KomSed	0.00	0.00	0.00	0.00
ExpFreSed	0.00	0.00	0.00	0.00
sum	0.91		1.08	

Comparison to sensitivity analysis of Westein et al. (1998)

The very low sensitivity of PEC_{wat} to sorption to macrophytes (K_{mp}) reported in this study differs from the previous sensitivity analysis, which attributed more weight to the K_{mp} on the PEC_{wat} variance compared to the $K_{F,om,ss}$ parameter for sorption to suspended solids (see Section 6.2 of Westein et al., 1998). Based on the model equations, the process parameters related to sorption to suspended solids and to macrophytes can all contribute to the variation in PEC_{wat}, particularly the following parameters:

- Freundlich sorption coefficient to organic matter in suspended solids $K_{F,om,ss}$ (KomSusSol).
- Freundlich exponent for suspended solids N_{ss} (ExpFreSusSol).
- Sorption coefficient for macrophytes K_{mp} (CofSorMph).

The reason for the PEC_{wat} variance to show relatively less sensitivity to K_{mp} in this study is likely that the studied range for K_{mp}, which is 0.1 to 1,126 L kg^{-1}, while for the $K_{F,om,ss}$ the range is 0.1 to $3.80 \cdot 10^6$ L kg^{-1}, so more than a factor 3000 larger. Note that in Westein et al. (1998) the studied range for the K_{mp} and $K_{F,om,ss}$ parameters was equal, 0.1 to 180,000 L kg^{-1}. The difference in the quantity of sorbing matrix of suspended solids (here 0.09 (OM content) x 15 g m^{-2} of ditch bottom (=1.35 g OM m^{-2} of ditch bottom) for the 1-m deep R1 pond in this study[19]) and of macrophytes (200 g DW m^{-2} bottom) is smaller than the difference for the sorption coefficients, thus the sorbing matrix quantities have a lesser influence than the difference in range of the K_{mp} on the result.

The ranges for K_{mp} differ between the two studies, as for the present sensitivity analysis. The range is based upon the relationship (for linear sorption isotherms) between the log(solubility) and the log(K_{mp}), provided by experiments run with six pesticides (Crum et al., 1999). Of the six pesticides, chlorpyrifos was the pesticide with the highest sorption coefficient to soil organic matter ($K_{oc,soil}$ 5,509 L kg^{-1}, PPDB, May 2023). So, a much smaller sorption coefficient than pyrethroids which present the highest $K_{oc,soil}$ values (several 100,000 L kg^{-1}). Such highly sorbing compounds would likely have made the range for K_{mp} larger. If the studied range for the K_{mp} would be larger, we expect the sensitivity of the PEC_{wat} for the K_{mp} would be significantly larger. This expectation is confirmed by the findings of Westein et al. (1998) for the sensitivity of the PEC_{wat} and the TWA4 (called AEC0 and AEC4 respectively, see Figure 6.1 and the TMV, Top Marginal Variance, in the Table 4.4 of this report, respectively), where, based upon equal ranges for K_{mp} and $K_{F,om,ss}$, the sensitivity for the single process parameter of K_{mp} ranked significantly higher than the $K_{F,om,ss}$.

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[17] For the highest S_1 and S_T values confidence intervals are also given (between brackets) as a percentage of the S_1 and S_T index as required for evaluating the statistical reliability according to Zhang (2015), see Section 3.2.2.

[18] Values written as "0.00" indicate values < 0.005 µg/L.

[19] Note that 15 g m^{-2} of ditch bottom in 1 m deep water corresponds to the input value of 15 g m^{-3} for suspended solids in the water layer.

6.2.2 Predicted Environmental Concentrations in sediment (PEC$_{sed}$)

The predicted environmental concentration in sediment (PEC$_{sed}$) is the maximum concentration of pesticide in sediment (total of sorbed and pore water concentrations) in time calculated for the top layer of the sediment of the pond. In this study PEC$_{sed}$ is calculated as the average of the sediment concentrations in the top 1 cm of sediment. PEC$_{sed}$ is expressed in mass of substance per dry mass of sediment.

Figure 6-3 presents the distribution of PEC$_{sed}$ values of the ~50,000 simulation runs for the sensitivity analysis. The distribution of the PEC$_{sed}$ values is very skewed. Obviously, the minimum cannot be smaller than zero. It takes time for the compound to enter the sediment. In the meantime degradation and volatilization from water occur and slow down the build-up in the sediment. Therefore, for most compounds the PEC$_{sed}$ remains relatively low, and large PEC$_{sed}$ values are only found for very strongly sorbing compounds. The maximum concentration is 45.5 µg (kg DW)$^{-1}$.

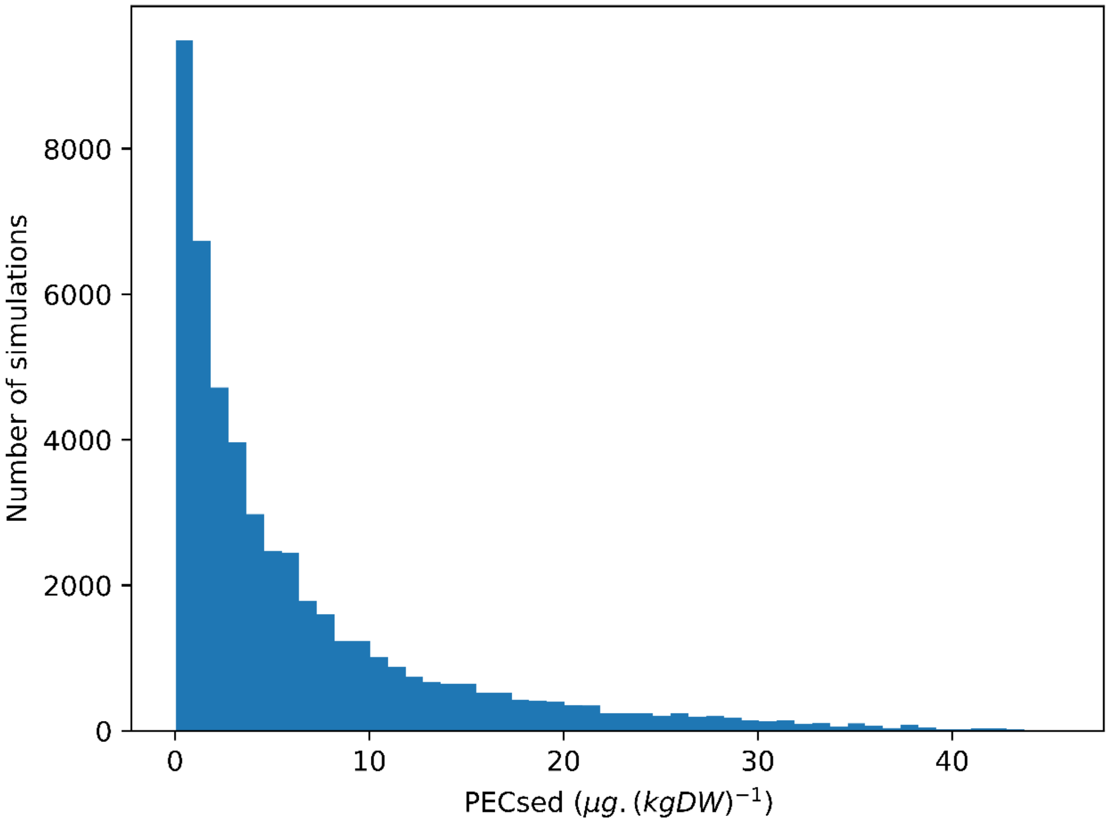

Figure 6-3 *Distribution of the maximum PEC in sediment in the R1 pond with spray drift entry.*

Figure 6-4 shows the three Sobol indices (S_1, S_T and S_2, presented in Section 3.2) characterizing the influence of the 11 selected pesticide properties parameters on the variance of PEC$_{sed}$. Values of the S_1 and S_T indices are provided in Table 6-2. Values of the S_2 index are provided in Annex 6.

The first-order index S_1 indicates the contribution of the single process parameters, independently, to the variance of PEC$_{sed}$. The values of S_1 indices are provided in Table 6-2. The PEC$_{sed}$ variance is explained to 84% by the sum of single process parameters independent variation, of which the S_1 of the Freundlich sorption coefficient to organic matter in sediment $K_{F,om,sed}$ (KomSed) contributes most (S_1 of 69%). Three other parameters show some contribution: degradation half-life in water $DT_{50,\mathrm{water}}$ (DT50WatRef) for 6%, degradation half-life in sediment $DT_{50,sed}$ (DT50SedRef) for 4%, and the Freundlich exponent for sorption to sediment N_{sed} (ExpFreSed) for 3%. Two more parameters have a nearly negligible contribution, P_{sat} (PreVapRef) and solubility in water c_{slb} (SlbWatRef), with an S_1 value of 1%. The contribution of the five other process parameters is null. The S_1 values indicate that two groups of process parameters influence the variance of PEC$_{sed}$ through their independent variation: processes directly occurring in the sediment explaining in total 76% ($K_{F,om,sed}$ (KomSed), N_{sed} (ExpFreSed) and $DT_{50,sed}$ (DT50SedRef) and processes occurring in the water layer explaining only 7% ($DT_{50,wat}$ (DT50WatRef) and the saturated vapour pressure P_{sat} (PreVapRef) and solubility in water c_{slb} (SlbWatRef). Below we consider these results in relation to what we expect in view of TOXSWA model process descriptions.

The sensitivity is highest for sediment parameters describing sorption. This can be explained by considering that the pesticide enters the sediment by diffusion across the water-sediment interface into the pore water of the sediment, driven by the difference in concentration in the water layer (where concentrations are initially highest) and in pore water (initially zero) (Eq. (16)). The pesticide in the pore water then sorbs instantaneously to the sediment (Eq. (23)). Sorption to sediment decreases concentrations in the pore water and therefore maintains a concentration gradient between the water layer and the pore water, which drives diffusion into the sediment. As a consequence, sorption (determined by $K_{F,om,sed}$ and N_{sed}) plays a major role for increasing the PEC_{sed}. When the concentration in water decreases due to clean water flowing into the pond (or fast dissipation by degradation or volatilization), the concentration gradient reverses and the pesticide diffuses back from the pore water into the water layer. Degradation in the sediment (characterized by $DT_{50,sed}$) has significantly less influence on the variance of the observed peak concentration, PEC_{sed}, than $K_{F,om,sed}$ as demonstrated by Table 6.2 (69 vs 4%).

Next, three processes that diminish the water concentration, also contribute to the variation in PEC_{sed}: degradation in water, $DT_{50,wat}$ (DT50WatRef, S_1 of 6%, Table 6.2) and with nearly negligible contributions, volatilization by P_{sat} (PreVapRef, 1%) and c_{slb} (SlbWatRef, 1%) (Eq(15)).

Surprisingly, the diffusion coefficient in water D_{wat} (CofDifWatRef), determining pesticide transport across the water-sediment interface and transport in the sediment pore water, is not a sensitive parameter. While diffusion is a relevant process, very probably, the range of D_{wat} values in this study (See Table 5.3: $2.2.10^{-5}$ to $8.6.10^{-5}$ m^2 d^{-1}) is too small in relation to the range of other parameters, to contribute in a significant way to the PEC_{sed} variance.

So, overall, the ranking of the S_1 of the different process parameters is considered plausible considering their expected influence on the PEC_{sed}.

The sum of the S_1 indices is 84% (see Table 6-2), whereas for a linear model all the variance of the output would be explained by the independent variation of input parameters. For a linear model the sum of the S_1 indices would therefore be 100% (see Section 3.2.2). In the next paragraphs, we investigate (using the Sobol indices S_T and S_2) which interactions between process parameters would be relevant to explain the non-linearity of the model and the 16% of PEC_{sed} variance not yet attributed.

The total index S_T (Table 6-2) reflects the contribution of a process parameter input to the variance of PEC_{sed}, including its first-order effects (S_1, the process parameter varying alone) and all higher-order interactions. Hence S_T given for $K_{F,om,sed}$ (KomSed, 80%) is higher than it first-order index S_1 (69%) because second-order and higher-order interactions are included (which is confirmed by S_2 values >0 in Figure 6-4 and Annex 6). Similarly, for the three other process parameters with S_1 values of 6, 4 or 3%, S_T is approximately 2-3 times higher than their respective S_1 values (12, 13 and 5%), so while these parameters contribute rather little to moderately to the variance of PEC_{sed} when they vary independently, their interactions with other process parameters contribute more significantly to the variance in PEC_{sed}. Additionally, a contribution of interactions is seen for P_{sat} and c_{slb}: their respective independent contribution is 1% (S_1), but their total contribution including interactions (S_T) is 4%. Their contribution of 4% can be explained, because saturated vapour pressure and solubility contribute both to the Henry coefficient (see Eq. (15)). The Henry coefficient determines the overall transfer to the gas phase/air, and therefore it influences the concentration in the water, which in turn influences the concentration in the sediment. The sum of S_T is 119%, so clearly above 100%, which indicates that the system is not linear due to the identified interactions.

Note that, while the TOXSWA model consists of two mainly linear parts (the simulated subsystems of the water layer and of the sediment, linked by transport across the water-sediment interface), the overall model may behave in a non-linear way (as demonstrated for the PEC_{sed} above). This occurs especially when two subsystems behave on different time scales, i.e. the water layer with possibly fast flowing pesticide-containing water and the sediment with slow pesticide diffusion and transport. Moreover, TOXSWA has one non-linear process: sorption to sediment or suspended solids according to the non-linear Freundlich isotherm, and especially sorption to sediment plays a major role in the ultimate value of the maximum PEC_{sed}. So, a S_T index clearly above 100% is possible for this PEC_{sed} output of the TOXSWA model. As can be expected, the non-linearity for the PEC_{sed} is clearly higher than the non-linearity for the PEC_{wat}, which is demonstrated by the sums of S_1 of 84% and of S_T of 119% for the PEC_{sed} compared to the sums of S_1 of 91% and of S_T of 108% for the PEC_{wat} that are closer to 100% (Section 5.3.1).

The second-order indices S_2 characterize the contribution of interactions between any pair of process parameters to the variance of the output PEC_{sed}. Figure 6-4 shows that for two pairs of process parameters, S_2 is 3-5%, otherwise other interactions are 1% to 2% (values in Annex 6). For several pairs, the confidence intervals of the S_2 values are relatively large, above 10%. These large confidence intervals of more than 10% signal that the values of S_2 are not reliable statistically. However, the two relatively high S_2 values point to interactions between pairs of process parameters which are consistent with the previous observations on S_1 and S_T as shown below, or can be physically explained, as we also explain below.

For the PEC_{sed}, the S_2 value is highest for pairs of $K_{F,om,sed}$, the most sensitive process parameter, with one of the other process parameters found to be sensitive by both the S_1 and S_T indices: $DT_{50,sed}$ (5%) and $DT_{50,wat}$ (3%) (S_2 values are in Annex 6). This seems logical, as degradation in water will influence the concentration in water, thus diffusion into the sediment, thus sorption in sediment, and degradation in sediment will also influence the amount pesticide present in the sediment.

The only other pair of parameters with a relatively high S_2 (1%, Annex 6) is P_{sat} with c_{slb} (Figure 6-4 and Annex 6). Together, they determine volatilization to the air (Eqs (14) and (15)) from the water layer, which leads to a decrease in the water concentration and a lowered diffusion into the sediment, thus contributing to the variance in PEC_{sed}.

For the other pairs, S_2 values are 1% or less (some are negative), these values are too low to justify any conclusions.

Based upon the process descriptions incorporated in TOXSWA, D_{wat} and K_{mp} might be able to contribute to the variance in PEC_{sed} (by increasing/decreasing transport into sediment, or lowering the water concentration, respectively), but this does not appear in this sensitivity analysis. Regarding diffusion, this means that the range of possible D_{wat} values for the pesticides considered in this sensitivity analysis i.e. from $2.2.10^{-5}$ to $8.6.10^{-5}$ m^2 d^{-1}, is apparently too low to create significant concentration differences across the water-sediment interface for transport of pesticides to the sediment. Regarding sorption to macrophytes, we explained in Section 6.2.1 that the influence of this parameter is low, also probably because of its small range.

We conclude that the Sobol indices found for PEC_{sed} are quite satisfactory: as expected and indicated by the S_1 and S_T indices, the most sensitive parameter for the PEC_{sed} is the $K_{F,om,sed}$ (KomSed). The other sensitive parameters ($DT_{50,wat}$, $DT_{50,sed}$, N_{sed}, and the interactions between P_{sat} and c_{slb}) can be well understood, as explained above. With respect to the PEC_{sed} model outcome, the TOXSWA model behaves quite non-linearly, as indicated by the sum of S_1 of 84% and of S_T of 119%. We did not expect this high extent of non-linearity, but as the PEC_{sed} is the result of the interplay of two different model parts (the water layer and sediment subsystems) behaving at different time scales, and one of the main sediment processes, sorption to sediment, is non-linear, this is in fact plausible.

For a robust result of the sensitivity analysis the number of simulations should be sufficient to obtain confidence intervals below 10%, as Zhang (2015) stated for the Saltelli sampling method. The confidence interval for the most sensitive parameter $K_{F,om,sed}$ (KomSed) is 12% for S_1 (and 7% for S_T), so above 10% for $K_{F,om,sed}$. Hence, the confidence intervals is not sufficiently low, and according to Zhang (2015) the study is not reliable from a statistical point of view. However, the results of our PEC_{sed} analysis agree well internally (S_1, S_T and S_2), as well as with our knowledge about the importance of processes in the TOXSWA model. Therefore, we do not increase the number of approximately 50,000 simulations and are satisfied with the results obtained.

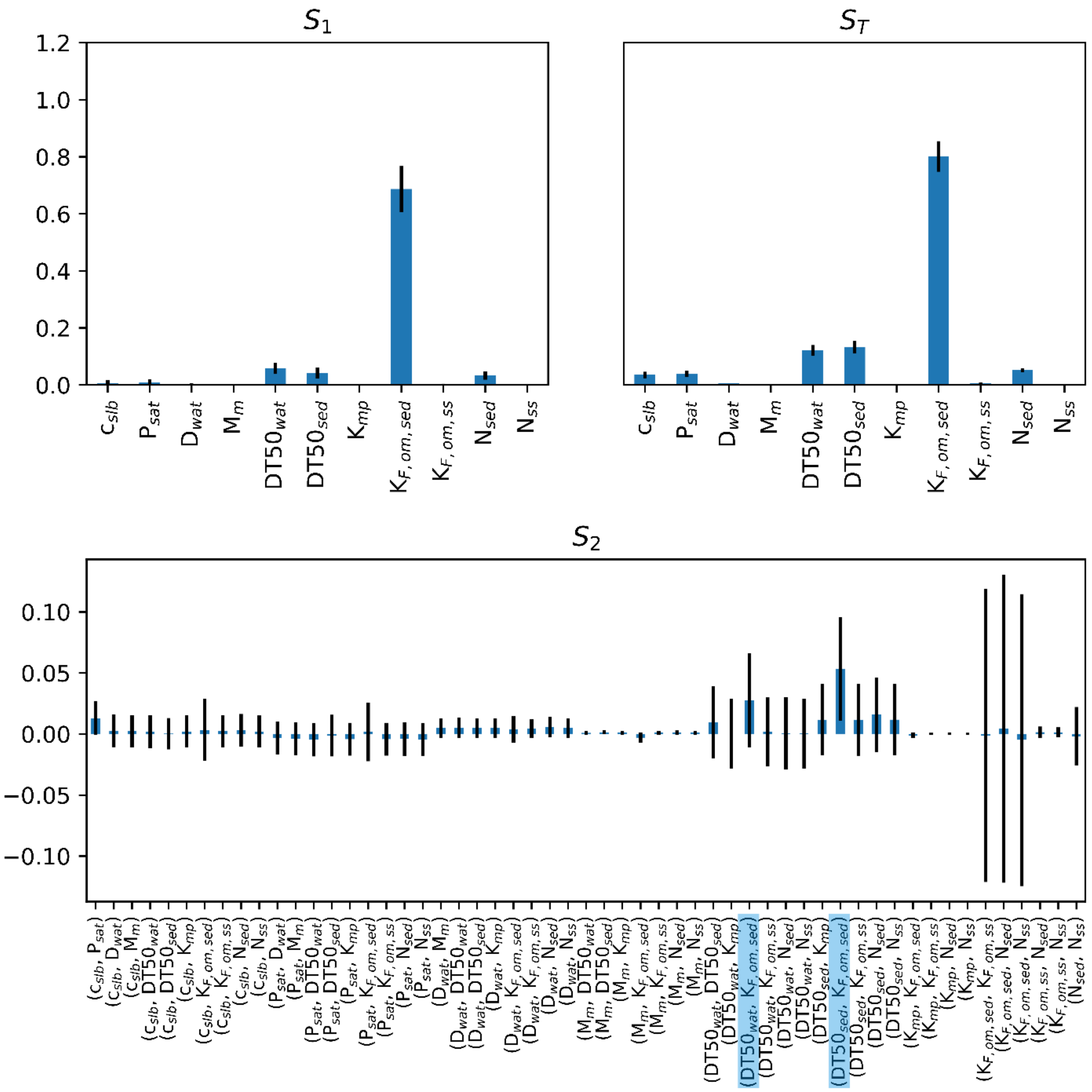

Figure 6-4 *Values of the Sobol sensitivity indices S_1, S_T, S_2 (y-axis) of the pesticide properties parameters (x-axis) for PEC$_{sed}$ in the R1 pond. The index values are given in blue and their confidence intervals in black. Descriptions in the S_2 graphs are marked in blue for pairs that include KomSed and have S_2 > 0.03.*

Table 6-2 *First-order (S_1) and total order (S_T) Sobol index values and their confidence intervals (±) for PEC$_{sed}$ of the R1 pond with spray drift entry.*

Parameter	**S_1**	**S_1 ±**	**S_T**	**S_T ±**
KomSed	0.69	0.08 (12%)	0.80	0.05 (7%)
DT50WatRef	0.06	0.02	0.12	0.02
DT50SedRef	0.04	0.02	0.13	0.02
ExpFreSed	0.03	0.01	0.05	0.01
PreVapRef	0.01	0.01	0.04	0.01
SlbWatRef	0.01	0.01	0.04	0.01
KomSusSol	0.00	0.00	0.01	0.00
CofDifWatRef	0.00	0.005	0.01	0.00
CofSorMph	0.00	0.00	0.00	0.00
MolMas	0.00	0.00	0.00	0.00
ExpFreSusSol	0.00	0.00	0.00	0.00
Sum	0.84		1.19	

6.2.3 Time-Weighted Average concentrations in water over a period of seven days (TWA7)

The distribution of the maximum time-weighted average concentration values over a period of seven days (TWA7) obtained from the 49,152 simulations is shown in Figure 6-5. After the spray drift entry, two types of processes influence the pesticide concentration in water over the period of days: (i) instantaneous processes operating as soon as the pesticide enters the water and (ii) continuous processes requiring a longer duration to have an effective impact on concentration. As for the PEC_{wat}, for pesticides with high sorption coefficients to organic matter in suspended solids or to macrophytes, sorption causes an instantaneous decrease of the dissolved concentration in water. Continuous processes such as volatilization to the air, degradation in water, and diffusion to sediment will have an influence on concentration over the course of the seven days.

Note that the hydraulic residence time in the R1 pond is long (151 d in period TWA7 is calculated, March 1969 in simulation) and thus outflow does not cause any significant lowering of the concentration over the seven days. Figure 6-5 shows a larger number of results towards higher values compared to average values, with a long tail approaching 0 μg L^{-1}. High values close to the maximum PEC_{wat} of 0.386 μg L^{-1} (see section 6.2.1, PEC_{wat}) correspond to conditions with limited processes able to reduce dissolved concentrations (hence, both (i) and (ii)). As the initial concentrations are mostly close to the maximum value 0.386 μg L^{-1}, for low values close to 0 μg L^{-1}, processes decreasing water concentration (hence (ii)) must dominate; hence, possibly degradation in water, volatilization to the air and diffusion into sediment. This initial interpretation was verified with the Sobol indices of Figure 6-6, discussed below. It demonstrates that degradation in water and volatilization are important processes determining the TWA7, and diffusion into sediment is not.

The TWA7 results show a slightly bimodal distribution as there is a small increase in number of TWA7 concentrations close to zero. For the Sobol analysis it is assumed that the analyzed model is linear and a symmetric distribution of the results is expected and exceptions should be understood and explained. TWA7 is the highest value obtained when averaging the hourly concentrations over a rolling window of seven consecutive days. As a result, the low TWA7 corresponds to systems with strong attenuation processes leading to relatively quick attenuation. The attenuation processes can be for instance degradation, volatilization, but it could also be due to mass flowed out of the pond. The explanation for the bimodal distribution is the large range of values for solubility, vapor pressure and degradation that can lead to the same low TWA7 values. This is elaborated in Section 6.2.4 for TWA28, in which the bimodal distribution is more pronounced.

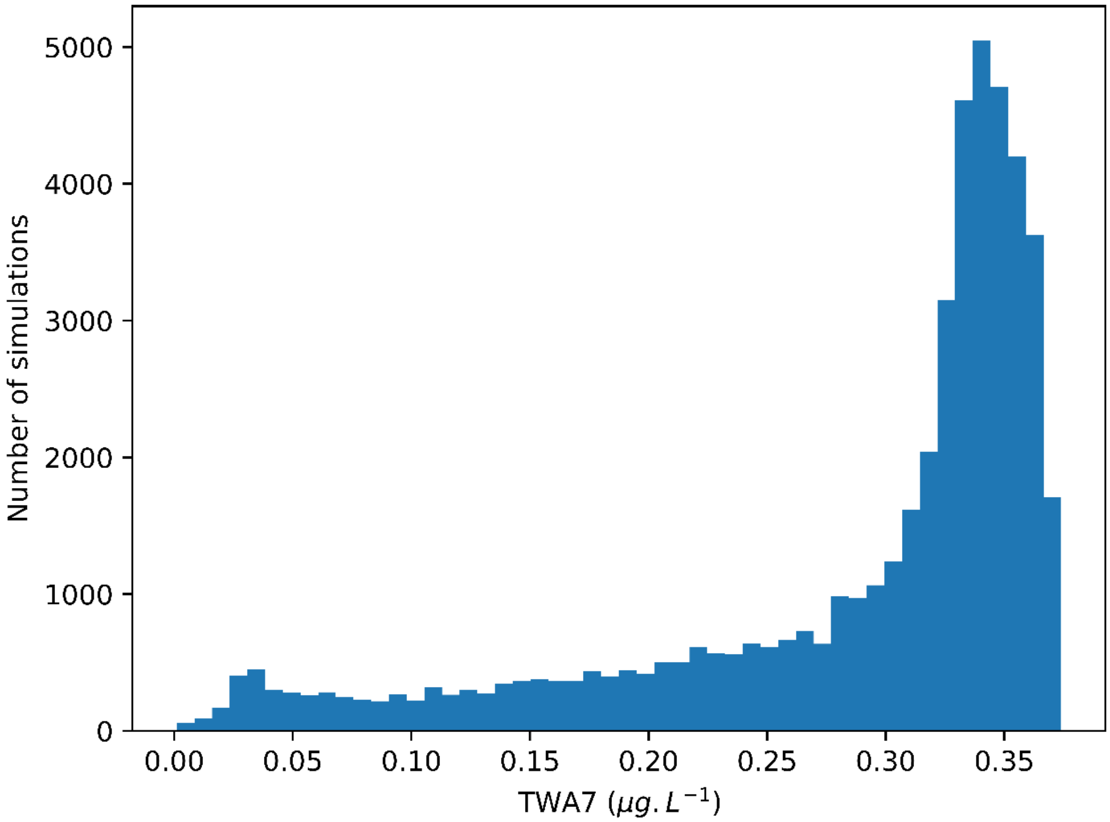

Figure 6-5 *Distribution of the maximum average exposure concentrations over seven days (TWA7) in the R1 pond with spray drift entry.*

The three Sobol indices of pesticide process parameters for TWA7 are given in Figure 6-6. Values of the S_1 and S_T indices are provided in Table 6-3. Values of the S_2 index are provided in Annex 6.

The first-order index S_1 indicates the contribution of the single process parameters, independently, to the variance of calculated TWA7. The TWA7 variance is explained to 81% by the independent variation of single process parameters, of which 43% by the degradation rate in water $DT_{50,wat}$ (DT50WatRef), 16% by the sorption to sediment, 9% by the saturated vapour pressure P_{sat} (PreVapRef), 6% by the solubility in water c_{slb} (SlbWatRef) and 5% by the sorption coefficient to suspended solids (KomSusSol). All other input parameters have a contribution of less than 1% to the TWA7 variance.

The sum of S_1 is 81%, whereas for a linear model this is expected to be 100% (see Section 3.2.2). Hence 19% variation of TWA7 may not be attributed to single parameters independently. The S_2 and S_T indices presented below allow evaluation of which parameters show interactions relevant to explain the output.

The total index S_T indicates the contribution of a process parameter input to the variance of calculated TWA7, including both its first-order effects (S_1, the process parameter varying alone) and all higher-order interactions. For two sensitive parameters, P_{sat}, saturated vapour pressure, and c_{slb}, solubility in water, the total-order indices are more than twice as large as the first-order indices (S_1 of 9% and 6%, vs S_T of 24% and 22%, respectively), which indicates that the interactions of those parameters with other parameters is relevant to explain the variance. The other parameters (incl. the $DT_{50,wat}$ with the highest S1 index of 43%) show minor differences between their S_1 and their S_T, indicating a lesser influence of interaction for those parameters. The sum of S_T is 120%, which indicates a non-linear response, as was already indicated by the S_1 value of 81%.

The second-order index S_2 indicates the contribution of interactions between two process parameters to the variance of the calculated TWA7. In Figure 6-6 it can be seen that S_2 between the saturated vapour pressure, P_{sat}, and the solubility, c_{slb}, is high, 12% (values are provided in Annex 6), which indicates that this interaction is relevant to explain the variance. The interaction is understandable, as saturated vapour pressure and solubility contribute both to the Henry coefficient (see Eq. (15)) which determines the overall transfer to the gas phase/air. This latter process is therefore influencing the variance of TWA7. All other second-order interactions are low, less than 0.5% or negative.

We conclude that the Sobol indices found for TWA7 are satisfactory: as expected and indicated by the S_1 and S_T indices, the most sensitive parameters for the TWA7 are $DT_{50,wat}$, $K_{F,om,sed}$, P_{sat}, c_{slb}, and $K_{F,om,ss}$. As explained above, this can be understood. With respect to the TWA7 model outcome, the TOXSWA model behaves non-linearly, as indicated by the sum of S_1 of 81% and of S_T of 120%. This might be explained by the relatively high interaction (12%, Annex 6) between P_{sat} and c_{slb}.

The confidence intervals for the most sensitive parameter, $DT_{50,wat}$, are 16% and 10% for the S_1 and S_T index, respectively (Table 6-3). Hence, the S_1 confidence interval is above 10% and thus the study is insufficiently reliable, from a statistical point of view (Zhang, 2015). However, the results of our TWA7 analysis agree well internally (S_1, S_T and S_2), as well as with our knowledge about the importance of processes in the TOXSWA model. Therefore, we do not increase the number of approximately 50,000 simulations and are satisfied with the results obtained.

Comparison to sensitivity analysis of Westein et al. (1998)
Maximum time-weighted averages were considered outputs in the previous sensitivity analysis by Westein et al. (1998), and the analysis was carried out for a 300 m ditch with slowly moving water (10 m d^{-1}). In this previous sensitivity analysis, the sensitivity for the sorption coefficient to macrophytes, K_{mp}, degradation rate in water, k_{wat} (=ln2/$DT_{50,wat}$) and the Henry coefficient (which combines solubility, c_{slb}, and saturated vapour pressure, P_{sat}) were highest with contributions (TMV-Top Marginal Variance, i.e. similar to the first-order interaction S_1) of 34.0%, 32.3% and 19.6%, respectively, for the AEC4, Time-Weighted Average concentration over four days (Table 4.4 of Westein et al., 1998).

We now discuss the main differences with our study, namely:
for K_{mp} a TMV of 34.0% vs a S_1 of 0% on the TWA7 in this study.
for k_{wat} a TMV of 32.3% vs for the $DT_{50,wat}$ a S_1 of 43% on the TWA7 in this study.
for K_H a TMV of 19.6% vs for c_{slb} and P_{sat} S_1 indices of 6% and 9%, respectively, on the TWA7 in this study.

K_{mp}: TMV of 34.0% on the AEC4 vs S_1 of 0% on the TWA7
As stated previously, the absence of any sensitivity for the sorption coefficient to macrophyte (K_{mp}) in our study very probably relates to the range of K_{mp} which is much smaller in our study than in the prior sensitivity analysis. Indeed, K_{mp} was given a much larger range in the study by Westein et al. (1998) as K_{mp} was taken equal to the sorption coefficient to organic matter (0.1 to 180,000 L kg^{-1} in Westein et al., vs 0.1 to 1126 L kg^{-1} in our study, so, six orders *vs* four orders of magnitude). This corresponds with our findings for the TWA7 (S_1 and S_T indices 0% for K_{mp}).

k_{wat}: a TMV of 32.3% on AEC4 vs $DT_{50,wat}$: S_1 of 43% on the TWA7
The higher sensitivity of the degradation half-life in water, $DT_{50,wat}$, in our study (S_1 of 43%) compared to the sensitivity to the k_{wat} in the study of Westein et al. (TMV of 32.3% for the AEC4) could be related to the fact that sorption to macrophyte has here no influence on the variance, the other parameters influencing the variance would then have a larger weight in explaining the variance of the result than their weight in Westein et al. (1998). Moreover, the duration over which the concentration is calculated is larger in this study (seven days, versus four days in Westein et al., 1998), which might lead to a stronger influence of degradation here. Note that the range of $DT_{50,wat}$ values in Westein et al.'s study was 0.009 – 10 046 d (calculated from the rates values of the 180 values in Westein et al., 1998) and in our study 0.0088 – 56 000 d (generated in Sobol from parameters fitted on the distribution of half-lives of the 416 pesticide values in our study) so, the range in Westein et al's study is quite similar to the range in our study, so, a difference in range does not contribute significantly to the difference in variance.

K_H: a TMV of 19.6% on the AEC4 vs for c_{slb} and P_{sat}: S_1 indices of 6% and 9%, respectively, on the TWA7
In the study of Westein et al. (1998), the variance of the AEC4 outcome was evaluated with respect to the Henry coefficient K_H, which is (as presented our section 2.3 Eq. (15)) a lumped parameter that is calculated from the solubility, the saturated vapour pressure and the molar mass – the latter having relatively little

influence on K_H values due to its limited range. In the present study, K_H was not a studied process parameter as it is not an input of the model. So, one might expect that the first-order effect of K_H would be quite similar as the sum of the first-order effects of the three process parameters involved. Indeed the total S_1 index for the solubility, the saturated vapour pressure and the molar mass is 15% according to Table 6-3, which is close to the *TMV* of 19.6% for the K_H of Westein et al. (1998).

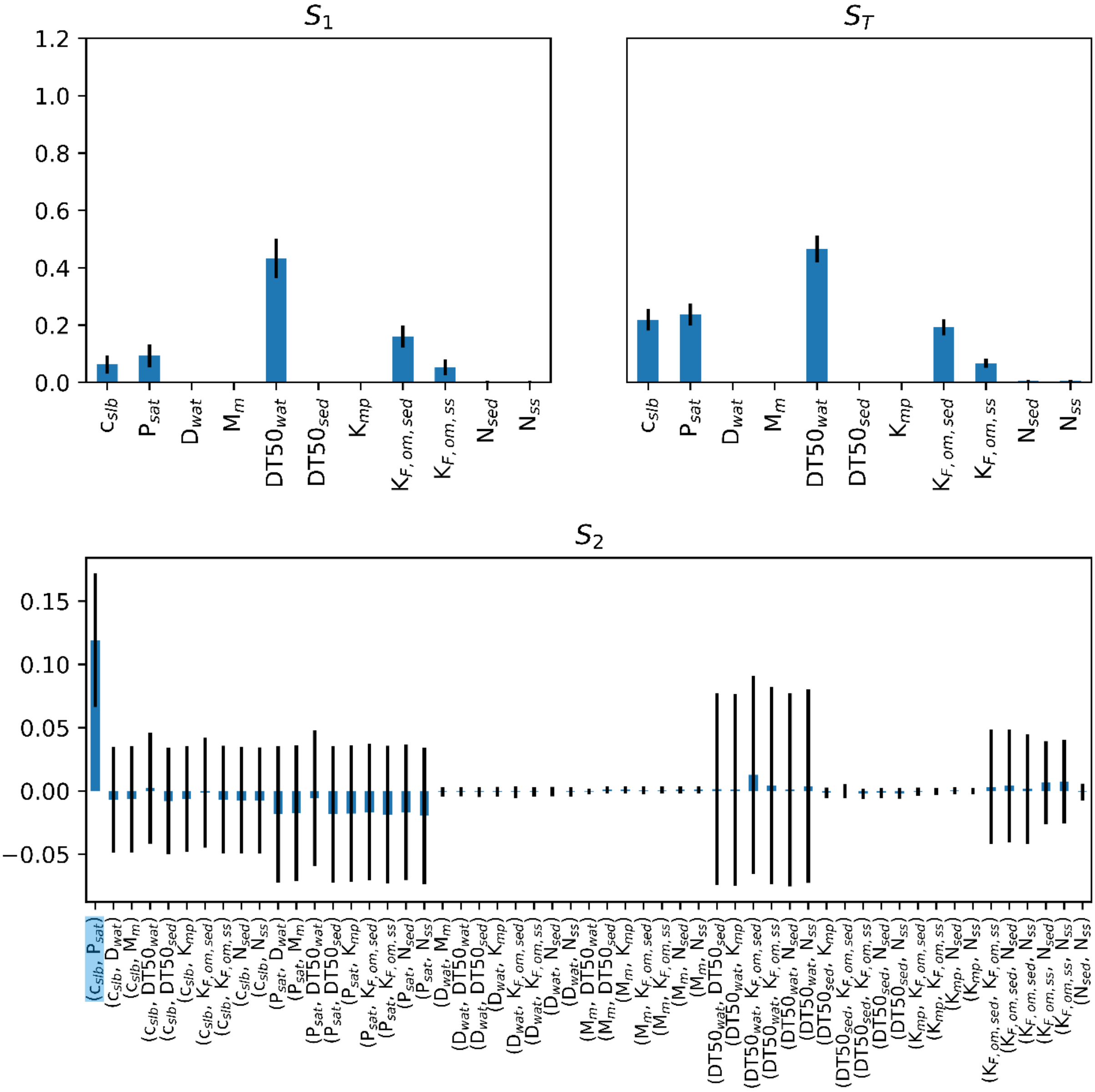

Figure 6-6 *Values of the Sobol sensitivity indices* S_1, S_T, S_2 *(y-axis) of the pesticide properties parameters (x-axis) for maximum time weighted average concentrations in water over seven days (TWA7) in the R1 pond with spray drift entry. Index values are given in blue and their confidence intervals in black. Descriptions in the* S_2 *graphs are marked in blue for the pair* C_{slb}/P_{sat} *with* S_2 *of 0.12. All other pairs show* S_2 *values of 0.01 or less.*

Table 6-3 *First-order (S_1) and total order (S_T) Sobol index values and their confidence intervals (±) for TWA7 of the R1 pond with spray drift entry.*

Parameter	S_1	S_1 ±	S_T	S_T ±
DT50WatRef	0.43	0.07 (16%)	0.47	0.05 (10%)
KomSed	0.16	0.04	0.19	0.03
PreVapRef	0.09	0.04	0.24	0.04
SlbWatRef	0.06	0.03	0.22	0.04
KomSusSol	0.05	0.03	0.07	0.02
DT50SedRef	0.00	0.00	0.00	0.00
ExpFreSed	0.00	0.00	0.01	0.00
CofDifWatRef	0.00	0.00	0.00	0.00
ExpFreSusSol	0.00	0.01	0.01	0.00
CofSorMph	0.00	0.00	0.00	0.00
MolMas	0.00	0.00	0.00	0.00
sum	0.81		1.20	

6.2.4 Time-Weighted Average concentrations in water over a period of 28 days (TWA28)

Figure 6-7 shows the distribution of TWA28 values from the simulations. Similarly to the TWA7, after the spray drift entry instantaneous as well as continuous processes decrease the concentration during 28 days: instantaneous for pesticides with high sorption coefficients for organic matter in suspended solids or to macrophytes and more continuous for volatilization to the air, degradation in water and diffusion to sediment.

The TWA28 results show a bimodal distribution, as there is a clear increase in number of TWA28 concentrations close to zero, as was observed (to a lesser extent) for the TWA7 values. As the Sobol analysis assumes that the model is linear, a symmetric distribution of the results was expected and exceptions should be understood and explained. TWA28 is the highest value obtained when averaging the hourly concentrations over a rolling window of 28 consecutive days. As a result, the low TWA28 values correspond to systems with strong attenuation processes leading to quick attenuation. The attenuation processes can be for instance degradation, volatilization, but it could in principle also be due to mass flowed out of the pond. This is elaborated into detail at the end of this Section.

The three Sobol indices of pesticide process parameters for TWA28 are shown in Figure 6-9. Values of the S_1 and S_T indices are provided in Table 6-4 and of the S_2 index in Annex 6.

The first order indices S_1 indicate the contribution of the single process parameters, independently, to the variance of calculated TWA28. The TWA28 variance is explained to 83% by the independent variation of single process parameters of which 53% by degradation rate in water $DT_{50,wat}$ (DT50WatRef), 14% by sorption to the sediment (KomSed), 7% by saturated vapour pressure P_{sat} (PreVapRef), and 5% by solubility in water c_{slb} (SlbWatRef) (Table 6-4). Of all other input parameters only the $K_{F,om,ss}$ and $DT_{50,sed}$ have non-negligible contributions to the TWA28 variance, with values of 2 and 1%, respectively.

The sum of S_1 is 83%, whereas for a linear model this is expected to be 100% (see Section 3.2.2). Hence 17% variation of TWA28 is not attributed to the variation of single parameters. The S_2 and S_T indices presented below allow evaluation of which parameters show interactions relevant to explain the output.

The total index S_T indicates the contribution of a process parameter input to the variance of calculated TWA28, including both its first-order effects (S_1, the process parameter varying alone) and all higher-order interactions. For two sensitive parameters, P_{sat}, saturated vapour pressure, and c_{slb}, solubility in water, the total-order indices are more than twice as large as the first-order indices (S_1 of 7% and 5%, vs S_T of 18% and 17%, respectively), which indicates that the interactions of those parameters with other parameters contribute significantly to the variance in TWA28. Interactions with the parameter of $DT_{50,wat}$, having the highest S_1 index of 53%, contribute only moderately to the overall variance of the TWA28 (increase from S_1 of 53% to S_T of

60%). The other input parameters do not display significant differences between S_1 and S_T values. The sum of S_T is 118%; this indicates a non-linear response, as was already indicated by the S_1 value of 83%.

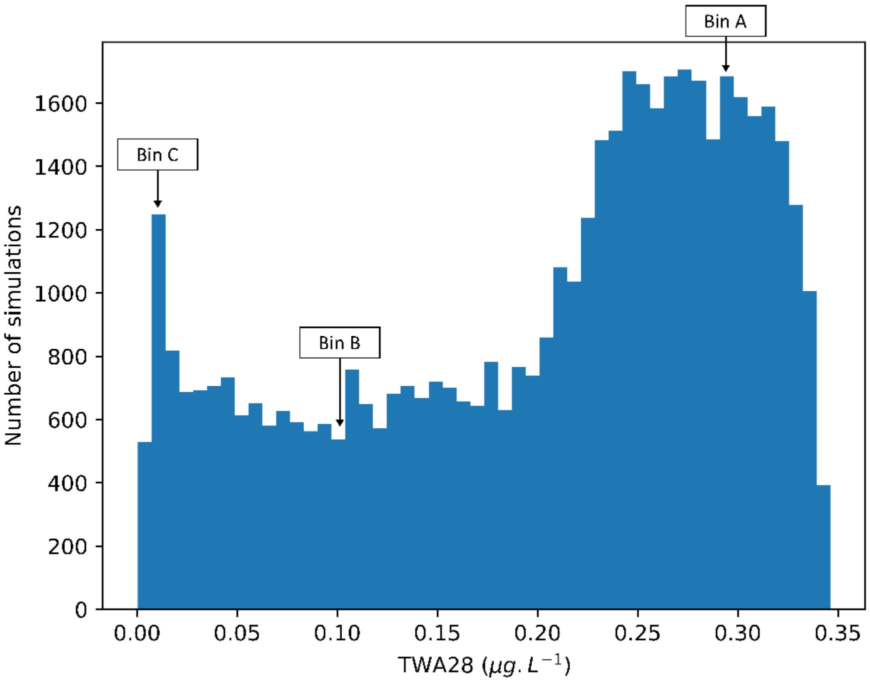

Figure 6-7 *Distributions of the maximum average exposure concentrations over 28 days (TWA28) in the R1 pond with spray drift entry. The bins Bin A, Bin B and Bin C correspond to ranges of TWA28 in the main peak, the valley and the second, smaller peak, respectively.*

The second order index S_2 indicates the contribution of interactions between two process parameters to the variance of the calculated TWA28. In Figure 6-9 it can be seen that S_2 is highest, 7%, for the second-order interaction between the saturated vapour pressure P_{sat} and the solubility c_{slb}. This interaction is expected as saturated vapour pressure and solubility contribute both to the Henry coefficient (see Eq. (15)) which determines the overall transfer to the gas phase/air and therefore the output TWA28. All other second-order interactions are rather low, with a S_2 of 2% or less. Confidence intervals are relatively high, they are approximately 5-6% for interactions with the $DT_{50,wat}$, and thus still below the required 10% to be statistically reliable.

We conclude that the Sobol indices found for TWA28 are satisfactory: as expected and indicated by S_1 and S_T the most sensitive parameters for the TWA28 are and to a lesser extent $DT_{50,wat}$, $K_{F,om,sed}$, P_{sat}, and c_{slb}. The four most sensitive parameters are similar to the four most sensitive parameters found for the TWA7. The sum of S_1 and S_T for the TWA28 are quite similar to those for the TWA7: 83% and 118% for the TWA28 *vs* 81% and 120% for the TWA7. So, again, this indicates that the TOXSWA model behaves non-linearly. Compared to the TWA7 for the TWA28, the relative influence of the $DT_{50,wat}$ slightly increased, both for S_1 as S_T, while it decreased for P_{sat} and c_{slb}.

The confidence intervals of the S_1 and S_T index for the most sensitive parameter, the degradation half-life in water, $DT_{50,wat}$, are 11% and 7%, respectively (Table 6-4). Hence, the S_1 confidence interval is just above 10% and thus the study would in principle be insufficiently reliable, from a statistical point of view (Zhang, 2015). However, the value is close to 10% and the results of our TWA28 analysis agree well internally (S_1, S_T and S_2) as well as with our knowledge about the importance of processes in the TOXSWA model. Therefore, we do not increase the number of approximately 50,000 simulations and are satisfied with the results obtained.

To explore how the driving processes, degradation in water and volatilization (by the combination of saturated vapour pressure and solubility, lead to the bimodal shape of the TWA28 values, we illustrate how these input parameters lead to selected ranges of TWA28 values. To that purpose, we plotted in Figure 6-8 the distribution of the most relevant process parameters, but we chose to use the lumped parameter Henry coefficient (K_H), which is calculated from the vapour pressure and the solubility and represents volatilization (see Section 5.4).

On the left (a), all the (~50,000) hypothetical pesticides are represented, the distribution corresponds to the combinations of two Gaussian distributions: most values are in the centre and less at the edges. On the right (b), we selected the hypothetical pesticides which lead to three specific ranges of TWA28 values, representative of the main peak in the higher TWA28 value range (Bin A: 0.2972 – 0.3041 μg.L^{-1}), in the valley (Bin B: 0.0972 – 0.1041 μg.L^{-1}) and the second peak in the lower TWA28 range (Bin C: 0.0072 – 0.0141 μg.L^{-1}).

For Bin A, where attenuation is weak, the input parameters are found within a large range of values which correspond to limited or no attenuation. Many combinations of the parameters can lead to TWA28 within the Bin A (i.e. the black dots). The input parameters leading to TWA28 with values within Bin C (the blue dots, 1058 dots) cover a very large range of extreme values for either volatilization or for degradation and they are numerous: 1,058 simulations. The quick attenuation required to fall in this TWA28 range seems to be driven either by relatively fast degradation (i.e. the blue dots forming the vertical line in Figure 5-10 b) or by relatively fast volatilization (i.e. the blue dots forming the horizontal line).

For volatilization specifically, the range for K_H to reach such fast attenuation covers a very large space: from about 10^{-2} to 10^{7} (-). In contrast, for Bin B (the red dots, 535 dots), less combinations lead to the TWA28 values in this bin: only 535 simulations. For bin B only a very narrow space of input parameters can lead to the same TWA28 values in this bin: the system needs to be finely tuned to reach precisely those values. The peak forming at the low values is therefore understood by the large range of values for solubility, vapour pressure (combined here in the Henry coefficient) and degradation that can lead to the same low TWA28 values of Bin C, compared to less combinations leading to TWA28 values of Bin B. This explanation can also be given for the (weaker) bimodal distribution found for TWA7.

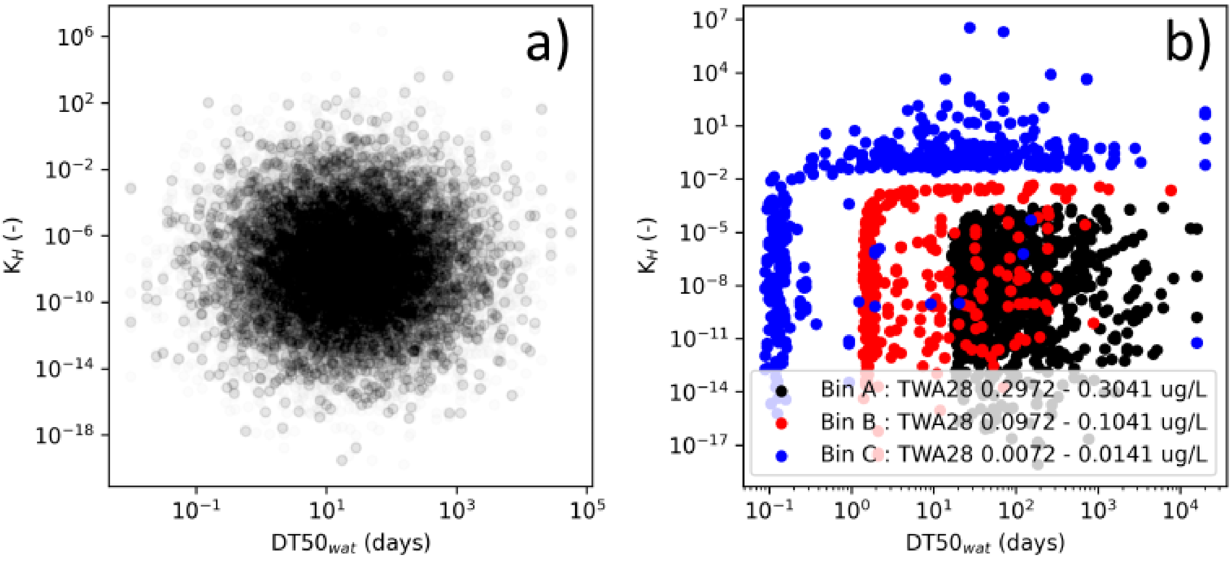

Figure 6-8 *a) (left): Distribution of the degradation half-life in water (*DT50$_{wat}$*) and Henry coefficient (*K_H*) for the ~50,000 hypothetical pesticides. b) (right): On the same axis, only the input for the Bin A, B and C as presented on Figure 6-7 are plotted.*

Table 6-4 *First order (S_1) and total order (S_T) Sobol index values and their confidence intervals (±) for TWA28 of the R1 pond with spray drift entry.*

Parameter	**S_1**	**S_1 ±**	**S_T**	**S_T ±**
DT50WatRef	0.53	0.06 (11%)	0.60	0.04 (7%)
KomSed	0.14	0.03	0.19	0.02
PreVapRef	0.07	0.03	0.18	0.03
SblWatRef	0.05	0.03	0.17	0.03
KomSusSol	0.02	0.01	0.03	0.01
DT50SedRef	0.01	0.01	0.01	0.00
ExpFreSed	0.00	0.01	0.01	0.00
CofDifWatRef	0.00	0.00	0.00	0.00
ExpFreSusSol	0.00	0.00	0.00	0.00
CofSorMph	0.00	0.00	0.00	0.00
MolMas	0.00	0.00	0.00	0.00
sum	0.83		1.18	

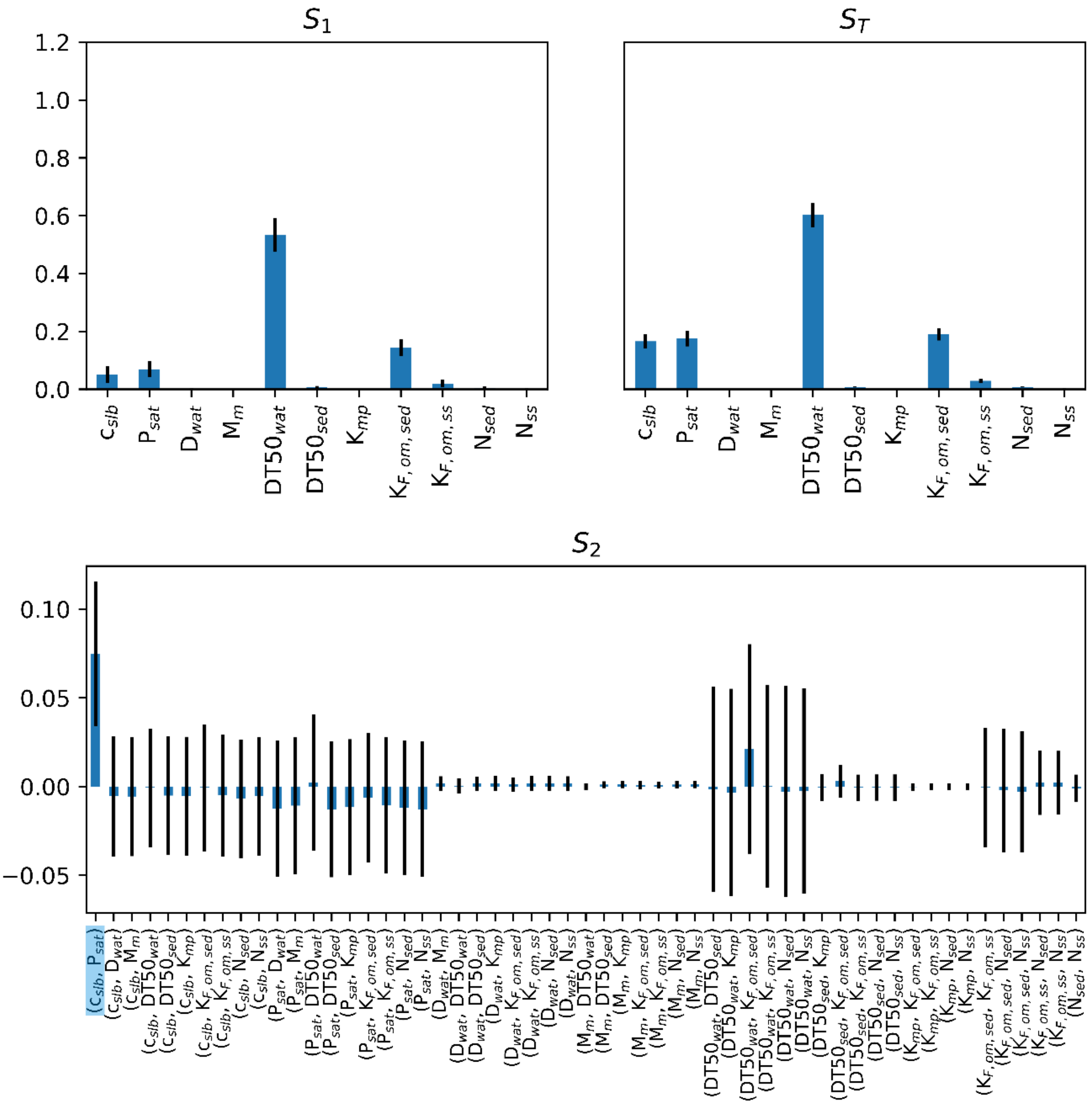

Figure 6-9 *Values of the Sobol sensitivity indices S_1, S_T, S_2 (y-axis) of the pesticide properties parameters (x-axis) for maximum time weighted average concentrations in water over 28 days (TWA28) in the R1 pond with spray drift entry. Index values are given in blue and their confidence intervals in black. Descriptions in the S_2 graphs are marked in blue for the pair C_{slb}/P_{sat} with S_2 of 0.07. All other pairs show S_2 values of 0.02 or less (also negative values).*

Comparison to sensitivity analysis of Westein et al. (1998)
Maximum time-weighted averages were studied outputs in the previous sensitivity analysis by Westein et al. (1998), and the analysis was done for a 300-m ditch with slowly moving water (10 m d^{-1}). In their Table 4.4 they present the TMV-Top Marginal Variance (similar to our first-order interaction S_1) for the AEC28, Time-Weighted Average Concentration over 28 days. Below we compare their TMV results to our S_1 results for the 28 days average concentrations.

For K_{mp} a TMV of 17.7% vs a S_1 of 0%.
For k_{wat} a TMV of 49.5%, vs for the $DT_{50,wat}$ a S_1 of 53%.
For K_H a TMV of 12.0% vs for P_{sat} and c_{slb} S_1 indices of 7% and 5%, respectively.

The differences between the results of Westein et al. (1998) and our study are related to the same four parameters as those for the TWA7, explained above in Section 5.3.3. They point in the same direction; regarding the parameters related to volatilization (P_{sat}, c_{slb}), their shares in the variance of the results are even more logical than for TWA7, i.e. slightly larger than in the former study, which is expected due to the absence of influence of sorption to macrophytes in the present study. Therefore we refer to this previous section of the TWA7 for an explanation of the differences.

6.3 Sensitive process parameters for the pond-summary

The sensitivity analysis has been run for a FOCUS-type pond with a single pesticide entry by spray drift deposition on the 4th of March at 9 a.m.. The selected pond is based on the FOCUS R1 pond, but in this study, the pond contains macrophytes, a moderate to high biomass of 200 g DW m^{-2} sediment area (the R1 pond scenario does not include macrophytes). Its hydraulic residence time is 157 d, so water flow is very low. The aim was to determine the most sensitive pesticide properties parameters used as input for the TOXSWA model. Hence, the results indicate which pesticide properties parameters contribute most to the variation of the model outputs and should thus be determined carefully. The four selected outputs for which the sensitivity has been studied are the maximum values in time for the Predicted Exposure Concentration in water, (PEC_{wat}), and in sediment, (PEC_{sed}), and for the Time Weighted Average concentrations over seven and 28 days (TWA7 and TWA28).

The PEC_{wat} represents the maximum value in time of the Predicted Exposure Concentration in the water layer, observed during the simulation of three months. The nominal PEC_{wat} value corresponds to the concentration after dissolution of the spray drift deposition in the pond, all processes occurring next lower the nominal concentration. Thus, the maximum PEC_{wat} occurs immediately at the start of the simulation with its spray drift event at the time of the spray drift entry. However, the nominal PEC_{wat} value of 0.386 μg.L^{-1} may be lowered by instantaneous sorption to suspended solids or macrophytes (which is assumed to also occur immediately after the spray drift deposition). Figure 6-1 shows that the variation in the PEC_{wat} is relatively low: the large majority lies between 0.35 μg L^{-1} and its maximum value of 0.386 μg L^{-1}. This demonstrates that the instantaneous sorption to macrophytes or suspended solids have a relatively low influence on the PEC_{wat} value.

The S_1 value of 89% for the coefficient for sorption to suspended solids, $K_{F,om,ss}$, indicates that this parameter is by far the most sensitive one, explaining the variation of the PEC_{wat}. The influence of sorption to macrophytes on the PEC_{wat} variation is extremely small (S_1 of 2%), which is caused by the studied, small range of this input parameter. Note that the applied range in K_{mp} input parameter was not based upon K_{mp} values in the PPDB database, as is the case for all other input parameters, but that it has been estimated based upon a relationship between the log(solubility) and the log(K_{mp}) found in experiments run with only six pesticides (Crum et al., 1999). So, in fact the uncertainty in the range may be significantly higher than the uncertainty in the range of other input parameters, this has not been considered in the sensitivity analysis and is expected to have contributed to its low importance. The influence of the Freundlich exponent of sorption to suspended solids N_{ss} equally is extremely small (S_1 of 1%), also probably due to its small input range. All other parameters have a S_1 value below 1%, thus have negligible influence on the PEC_{wat} variation.

The PEC_{sed} is the maximum concentration (averaged over the upper 1-cm sediment layer) observed during the simulation period of three months. As diffusion into the sediment and next, sorption onto sediment take some time the PEC_{sed} will not occur at time of the spray drift deposition, but some time later. Figure 6-3 shows that approximately 60% of the PEC_{sed} values lie between 0 and 4 µg (kg DW)$^{-1}$ and only few values are around 30 µg (kg DW)$^{-1}$. These highest concentrations result from simulations with high coefficients for sorption to sediment, $K_{F,om,sed}$. This corresponds with the fact that the $K_{F,om,sed}$ parameter has the highest S_1 value of 46%%, explaining the variation in PEC_{sed}. Lower S_1 values are attributed to the parameters degradation half-life in water, $DT_{50,wat}$ (6%), in sediment, $DT_{50,sed}$ (4%), Freundlich exponent in sediment N_{sed} (3%), saturated vapour pressure, P_{sat} (1%), and solubility in water, c_{slb} (1%). The latter two parameters determine the Henry coefficient, describing the partitioning between the water and gas (i.e. air) phases. Hence, also processes that determine the dissipation of the pesticide from the water layer, such as degradation in water and partitioning (i.e. volatilization), slightly contribute to the variation of the PEC_{sed}.

For the TWA7 most values are between 0.30 and 0.38 µg L^{-1}. Thus the majority of the TWA7 concentration values are relatively high and close to the majority of concentrations observed for the PEC_{wat} in Figure 6-1 (0.35 to 0.386 µg L^{-1}), in which no continuous processes occurred, but only the instantaneous sorption processes lowered the studied PEC_{wat} output. The most sensitive parameters for the TWA7 are degradation half-life in water, $DT_{50,wat}$ (S_1 of 43%), sorption to sediment, $K_{F,om,sed}$ (S_1 of 16%), saturated vapour pressure, P_{sat} (S_1 of 9%), solubility in water, c_{slb} (S_1 of 6%, both of them strongly interacting as shown by their S_2 value of 12% in Annex 6), and sorption to suspended solids $K_{F,om,ss}$ (S_1 of 5%). All other parameters have S_1 values below 1%. So, the pesticide dissipation processes from the water layer, degradation in water, instantaneous sorption to suspended solids and volatilization, determine most the TWA7 output variance.

The TWA28 concentrations are the maximum values in time of the time-weighted average concentrations in water over 28 d. Contrary to the PEC_{wat} and PEC_{sed} concentrations the TWA28 concentrations show a clear bimodal distribution, while Sobol analyses, assuming a linear model, are expected to result in a symmetric distribution of the calculated output. A closer look at the unexpected peak at TWA28 values close to 0 µg L^{-1} showed that there were many input parameter combinations, of the K_H (composed of P_{sat} and c_{slb}) and the $DT_{50,wat}$, leading to such low concentrations, while there were only few combinations leading to the higher TWA28 values of approximately 0.02 to 0.20 µg L^{-1}. So, this explains the bimodality.

Generally, the TWA28 values are spread over the range 0.00 and 0.35 µg L^{-1}. (The spread over the wide range of 0.00 and 0.35 µg L^{-1} indicates that there has been ample time (28 d) for the continuous processes to lower the initial concentrations, as observed for the PEC_{wat} in Figure 6-1 (0.35 to 0.38 µg L^{-1}). The most sensitive parameters for the TWA28 are degradation half-life in water, $DT_{50,wat}$ (S_1 of 53%), sorption to sediment $K_{F,om,sed}$ (S_1 of 14%), saturated vapour pressure, P_{sat} (S_1 of 7%), and solubility in water, c_{slb} (S_1 of 5%). P_{sat} and c_{slb} again interact as shown by their S_2 value of 7% in Annex 6. All other parameters have S_1 values of 2% or lower. So, the pesticide dissipation processes from the water layer degradation in water, continuous sorption to sediment and volatilization, determine most of the TWA28 output variance.

So, overall, we conclude that the Sobol S_1, S_2 and S_T indices found agree well internally and can be well understood from the TOXSWA model description and thus that the results are satisfactory.

However, for a significant number of Sobol indices (S_1, S_T and S_2 indices) the confidence intervals are quite high, above 10%. Zhang (2015) states that for the most sensitive parameter the confidence intervals for S_1 and S_T need to be below 10% of the S_1, respectively S_T index values, to sufficiently explain the variances. Regarding the most relevant parameters (explaining more than 40 to 50% of the variance), this was not the case for (i) the $K_{F,om,ss}$ parameter explaining the PEC_{wat} variation (confidence interval of S_1 of 26%), (ii) the $K_{F,om,sed}$ parameter explaining the PEC_{sed} variation (confidence interval of S_1 of 12%), (iii) the $DT_{50,wat}$ parameter explaining the TWA7 variation (confidence interval of S_1 of 16%), and (iv) the $DT_{50,wat}$ parameter explaining the TWA28 variation (confidence interval of S_1 of 11%). However, the results of our analyses agree well internally (S_1, S_T and S_2) as well as with our knowledge about the importance of processes in the TOXSWA model. Moreover, we intend to use the outcome of this sensitivity analysis especially in a qualitative way, to indicate which pesticide properties parameters matter most for the PEC_{wat}, PEC_{sed}, TWA7 and TWA28 model output, and not in a quantitative way, such as e.g., determining relative weights in a model calibration. Therefore, we do not increase the number of approximately 50,000 simulations and are satisfied with the results obtained.

An assumption when using Saltelli's sampling method for analyzing the sensitivity of a model is that the model is linear. The resulting Sobol indices inform on the presumed linearity: the sum of first-order indices S_1 as well as the sum of the total-order indices S_T should be 1 (100%) for a linear model. With respect to the PEC_{wat} (S_1 of 91% and S_T of 108%), non-linearity exists but is not pronounced, while for the PEC_{sed} (S_1 of 84% and S_T of 119%), TWA7 (S_1 of 81% and S_T of 120%) and TWA28 (S_1 of 83% and S_T of 118%) the non-linearity is more pronounced. Although the only non-linear process in TOXSWA is the equilibrium sorption according to the Freundlich isotherm to suspended solids and to sediment, the total water layer-sediment system may behave in a significant non-linear way. This happens especially, when two subsystems behave at different time scales, i.e., a fast-reacting water layer with instantaneous mixing over water depth and a slower reacting sediment with mass transport via diffusion in sediment pore water. So, in fact the studied (local) sensitivities may not hold true for the entire parameter domain. However, as stated above, results agree well internally and can be explained from the TOXSWA model descriptions and therefore the results are sufficiently satisfactory for us. Note that in the current literature, the tendency is not to test for models' linearity anymore (oral communication from S. Boersma, Biometris).

We compared our results to the results of the sensitivity analysis for the TOXSWA model, performed by Westein et al., in 1998. They did not study sensitivities for sediment concentrations (as we did with the PEC_{sed}), but only sensitivities for the maximum water concentrations, AEC0, AEC4, and AEC28. i.e., our PEC_{wat},TWA over four days and over 28 days. The most important difference between the two studies is related to the (surprising) absence of any sensitivity for the coefficient for sorption to macrophytes, K_{mp} parameter in our study, while it was the most sensitive parameter with respect to the AEC4/AEC28 and one of the two most sensitive parameters with respect to the AEC0 in Westein et al., (1998). The difference very probably relates to the range of K_{mp} which is much smaller in our study than in the prior sensitivity analysis. Indeed, in Westein et al., (1998) the range for the K_{mp} was taken equal to the range for the coefficient for sorption to organic matter (0.1 to 180,000 L kg^{-1}), while we had a range of 0.1 to 1,126 L kg^{-1} for the K_{mp}, so, approximately two orders of magnitude smaller. This smaller range resulted in the absence of any detectable sensitivity to the K_{mp} in our study.

7 Sensitivity for the stream

In this Chapter the sensitivity analysis of 11 selected pesticide parameters (Section 4.2) for the watercourse system with runoff entry is described. The parameterisation of the watercourse and of the runoff entry is described in Section 7.1. The results of the sensitivity analysis are described in Section 7.2, and summarized in Section 7.3.

7.1 Standard set of system parameters, entries and initial conditions

7.1.1 The stream system

For the simulation of a watercourse system a FOCUS scenario was selected in which a distributed mass with water entries during a certain lapse of time are possible. We selected a FOCUS stream scenario (instead of a ditch) to cover the highest flow velocities applied in scenarios used in pesticide authorization. We selected a runoff scenario instead of a drainage scenario because runoff entries are in general higher than entries by macropore flow that are simulated in FOCUS drainage scenarios, Dutch GEM-soil-bound or Dutch DRAINBOW scenarios. The FOCUS R1 stream is selected because, regarding minimum discharge (2.22 L s^{-1}) and maximum residence time (0.21 d). It represents an average situation for the four FOCUS R streams *(FOCUS, 2001; EFSA, 2020)*. The minimum discharge occurs when only baseflow enters the stream, The discharge of the stream only changes during runoff events. With only baseflow the water depth in the R1 stream is 0.41 m.

Similar to the pond, a density of macrophytes of 200 g DW m^{-2} is used in our simulations (see 6.1.1). All other values of the system parameters were equal to those of the R1 stream (FOCUS, 2001).

The sensitivity is tested based on a single entry in a three-month period, and not one entire year (FOCUS, 2001) or a series of 20 years (EFSA, 2020). So, the standard simulation period is shortened to three months from 1 March onwards in the first simulation year of the warming-up period (1969-1974 included, note that 1969 corresponds to 1984 in reality[20]). In the three-month period, all runoff and erosion entries were removed, except for the event for the sensitivity analysis that is described in Section 7.1.3. Hence, temperature is the only weather effect in the simulation. The three-month period is sufficient for peaks in the water layer because mass entries generally have flowed out within a couple of days to weeks, and thus, they do not accumulate over the years. However, in the sediment, concentrations may accumulate by transfer from the water layer into the sediment, as long as the water concentration is higher than the sediment pore water concentration. However, this behaviour does not change after a mass entry in the water layer, the next year, so, equally for the sediment a series of years is not required. However, the simulation period should be sufficiently long to reach the peak exposure before the end of the three-months' simulation (i.e. date of PEC_{sed} should not be the last day of the simulation). As it would be very cumbersome to check this for all simulations, we verified this hypothesis for simulations with extreme values for the sorption coefficient for sediment. The PEC_{sed} for these simulations was found on the 4th of March, well before the end of the simulation (31st May).

The spray drift entry to the stream is set to zero, because the focus of this sensitivity analysis is the runoff mass entry accompanied with water. The upstream catchment of the FOCUS stream scenarios is 100 ha, of which 20 h is treated.

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[20] See Section 3.1.2 in EFSA (2020).

The template (txw input file) used for TOXSWA for the watercourse system is shown in Annex 5. Note that for sediment $K_{F,om,sed}$ > 17,400 L kg^{-1} (K_{oc} > 30,000 L kg^{-1}) the FOCUS fine sediment segmentation is used (see Section 4.4.4 in Beltman et al., 2018). This is applied to ensure convergence of the numerical solution.

7.1.2 Initial conditions for stream system

For the sensitivity analysis it was assumed that the water layer and the sediment are free of pesticides at the start of the simulation. Upward or downward seepage in the sediment is not considered, because this is not taken into account in current EU and NL scenarios.

7.1.3 Pesticide entry for stream system

One type of entry is tested; a mass plus accompanying water flux entry by runoff on a spring oil seed field (FOCUS, 2001). The simulation runs for three months between the 1st of March and the 31st of May 1969, and the runoff event occurs on the 4th day of the simulation, March 4th. The event is 1 mm runoff in total containing 0.5 mg m^{-2} pesticide mass in total entering during a period of eight hours. Hence the hourly fluxes are 0.125 mm h^{-1} and 0.0625 mg m^{-2} h^{-1}. We set the eroded soil mass entries to zero, so there is no pesticide mass entering via eroded soil. There is also no spray drift entry.

During the runoff event, runoff water from the one hectare adjacent field and from the 100 ha upstream catchment enters the R1 stream. The volume of water passing the last node of the stream (95-100m) during one hour is 8.0 m^3 baseflow plus the runoff from the one hectare field and 100 ha upstream catchment. The runoff event of 1 mm in eight hours (hence 0.125 mm h^{-1}) corresponds to: 101 ha x 10,000 m^2 ha^{-1} x 0.000125 m^3 m^{-2} h^{-1} = 126.25 m^3 h^{-1}. Hence the total volume including the baseflow is 134.25 m^3 h^{-1}.During the runoff event lasting eight hours, pesticide mass from the one hectare field and from 20 of the 100 ha upstream catchment (20% treated) enters the stream. The pesticide mass passing the last node of the stream during one hour is 21 ha x 10,000 m^2 ha^{-1} x 0.0625 mg m^{-2} h^{-1} = 13 125 mg h^{-1}. In eight hours, this is 105 g. Hence, in the absence of attenuation processes, the concentration in the node is 13,125 / 134.25 = 97.76 mg m^{-3} (= 97.76 µg L^{-1}). The water depth in the R1 stream is 0.409 m and the flow velocity is 19.5 m h^{-1} before the runoff event and during the runoff event these are 0.544 m and approximately 247 m h^{-1}, corresponding to hydrological residence times of 0.21 and 0.017 d in the 100-m long stream. Hence there is hardly time for any decline in the stream during these eight hours.

An excerpt of the PRZM p2t file providing the input for the runoff entry, used for the simulations is given in Annex 5.

7.2 Results

The model was run 49,152 times[21] varying the input parameters to evaluate their sensitivity to the variance of selected outputs. The sensitivity of the variance was obtained through the calculation of Sobol's indices. The results of the simulations and of the analysis of the variance are presented in this Section for the case of runoff entries in the stream scenario.

7.2.1 Predicted Environmental Concentrations in water (PEC$_{wat}$)

The PEC$_{wat}$ is the maximum predicted environmental concentration of pesticide in water in time. In this study, the PEC$_{wat}$ is given for the last node of the stream (95-100 m). The distribution of PEC$_{wat}$ values from

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[21] 69 of these runs were not finalized; 48 because the restriction indicated in a footnote of Table 5-3 regarding a lower limit for entry of DT50 (water and sediment) which would be set when the selected DT50 < 0.01 d, was not implemented for the stream (runs stop with input error) and 21 because a numerical solution for the sediment resulted in negative concentrations (run stop with negative concentration error). For these 69 runs the outputs of the preceding (successful) run were used as result. Hence, for 69 runs, incorrect results were used in the analysis. This is only 0.14% of the runs, hence, we expect the failure of these runs has negligible effect on the results of the study.

the simulations is presented in Figure 7-1. The values show little variation, the large majority[22] lies above 95 µg L^{-1}. So, lowering of the maximum concentration only occurs when instantaneous attenuation processes are significant and the results show that this occurs in less than 38% of the simulations.

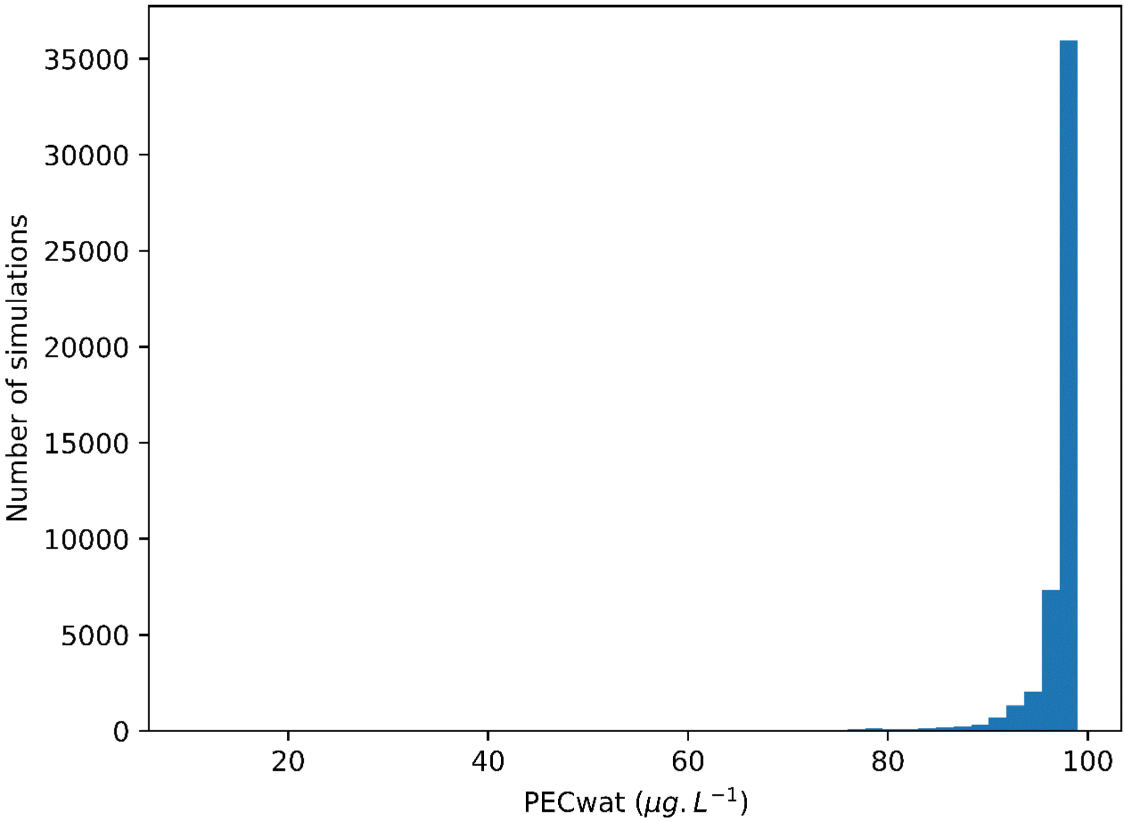

Figure 7-1 *Distribution of the maximum PEC_{wat} in the R1 stream after a runoff entry.*

The three Sobol indices of pesticide process parameters for the PEC_{wat} are shown in Figure 7-2. Values of the S_1 and S_T indices are provided in Table 7-11 and of the S_2 index in Annex 6.

The first-order indices S_1 indicate the contribution of the single process parameters, independently, to the variance of the calculated PEC_{wat}. The PEC_{wat} variance is explained to 98% by the independent variation of single process parameters, of which 96% by the sorption coefficient of suspended solids, $K_{F,om,ss}$ (Figure 7-2).

As stated above, the value of the PEC_{wat} shows little variation: only very high sorption coefficients lead to a decrease of the PEC_{wat}, e.g. for pyrethroids with extreme $K_{F,om,ss}$ values of 100,000 L kg^{-1} or higher. For sorption coefficients $K_{F,om,ss}$ in the more commonly found range of approximately 100-10,000 L kg^{-1}, relatively few mass is sorbed to suspended solids and PEC_{wat} values are hardly influenced.
The remaining S_1 indices indicate that P_{sat}, $DT_{50,wat}$, and $K_{F,om,sed}$ contribute negligibly to the variation of the PEC_{wat} (all with S_1 values of 1%). The negligible, yet visible contribution of these processes relate to the position where the PEC_{wat} is calculated: the value is given for the last node representing the stream, which is of 100 m, i.e. at 97.5 m. These processes of degradation in water ($DT_{50,wat}$), volatilization (where saturated vapour pressure P_{sat} plays a role) and sorption to sediment organic matter ($K_{F,om,sed}$) have this negligible influence on the water concentration of the substance during transport to the last node, which is less than 0.5h.

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[22] Approximately 62% of the PEC_{wat} values are above the maximum estimated concentration of 97.76 µg L^{-1}, up to 98.94 µg L^{-1}. These higher values are due to a small internal discrepancy between the hydrology and pesticide module in TOXSWA, reported in the release notes of FOCUS_TOXSWA 4.4.3, and illustrated in Annex 8. Note that the hydraulic residence time in the R1 stream with 1 mm runoff over 8 h is of less than 1 h (flow velocity of 247 m h^{-1}).

All other process parameters do not influence the PEC_{wat}, as their contribution to the PEC_{wat} variation is less than 1%.

The sum of all S_1 indices is 98%, therefore close to the value of 100%, which indicates that the model is linear for the PEC_{wat} in the R1 stream (see Section 3.2.2). In addition to the S_1 which presents the influence of the parameters when they vary independently, the S_2 and S_T indices presented below should provide information which parameters show interactions relevant to explain the variation in the output. However, the sum of S_1 indices reaching 100%, no interactions are expected as verified below.

The total index S_T indicates the contribution of a process parameter input to the variance of the calculated PEC_{wat}, including both its first-order effects (S_1, the process parameter varying alone) and all higher-order interactions. S_T values are provided Table 7-1 and show that the respective values of S_1 and S_T of the 3 first parameters are nearly equal (only for $K_{F,om,ss}$ there is a slight difference: the S_1 is 96% and S_T 97%), which indicates there is no relevant contributions from interaction between the parameters. The sum of all S_T indices is 103%, i.e. close to the sum of all S_1 indices.

The second-order index S_2 indicates the contribution of interactions between any two process parameters to the variance of the calculated PEC_{wat}. Figure 7-2 presents six small, negative sensitivities for interactions with $K_{F,om,ss}$, two of which have a very large confidence interval (approx. 60%). This high uncertainty with negative associated S_2 index values related to it, indicates that the statistical reliability is too low here. The reason lies in Saltelli's sampling method, which is very efficient (i.e. few drawings are needed), but has the drawback that sampling may be too sparse, resulting in large confidence intervals. All other parameters do not show any influence on the PEC_{wat} from their interactions.

We conclude that the Sobol indices found for PEC_{wat} are quite satisfactory: as expected and indicated by the S_1 and S_T indices, the most sensitive parameter for the PEC_{wat} is the $K_{F,om,ss}$. The other (negligibly) sensitive parameters (P_{sat}, $DT_{50,wat}$ and $K_{F,om,sed}$) can be clearly understood, as explained above. With respect to the PEC_{wat} model outcome, the TOXSWA model behaves linearly, as indicated by the sum of S_1 of 98% and of S_T of 103%.

Finally, the confidence interval of S_1 for the sorption coefficient for suspended solids $K_{F,om,ss}$ is 29% of S_1 (Table 7-1), which is clearly above 10%. For a robust result of the sensitivity analysis, the number of simulations should be increased to aim for a smaller confidence interval, below 10%, as Zhang (2015) stated for the Saltelli sampling method. However, the number of simulations required may be quite high due to the current, large confidence interval of the $K_{F,om,ss}$ parameter. As the results are sufficiently well understood with respect to the processes described in the TOXSWA model and the S_1, S_T and S_2 results agree well internally, no further simulations were carried out with an increased number of simulations.

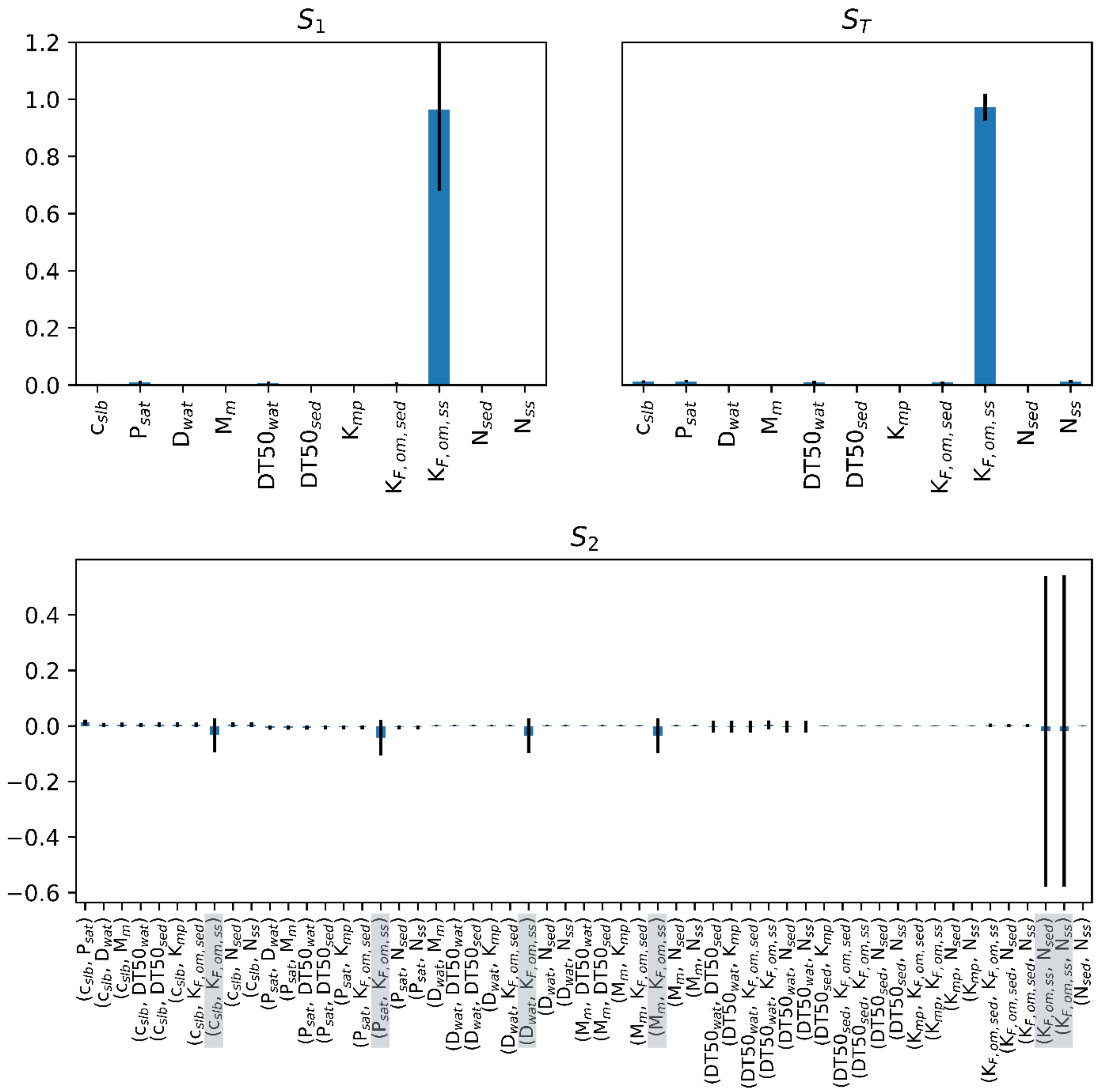

Figure 7-2 *Values of the Sobol sensitivity indices* S_1, S_T, S_2 *(resp. first-order, total order and second-order, y-axis) of the pesticide process parameters (x-axis) for* PEC_{wat} *in the R1 stream after a runoff entry. The index values are given in blue and their confidence intervals in black. Pairs in grey have a negative* S_2 *of -0.02 to -0.04.*

Table 7-1 *First order* (S_1) *and total order* (S_T) *Sobol index values and their confidence intervals (±) for* PEC_{wat} *in the R1 stream after runoff entry (values sorted by* S_1 *value).*

Parameter	S_1	S_1 ±	S_T	S_T ±
KomSusSol	0.96	0.28 (29%)[23]	0.97	0.05 (5%)
PreVapRef	0.01	0.01	0.01	0.00
DT50WatRef	0.01	0.01	0.01	0.00
KomSed	0.01	0.00	0.01	0.00
SlbWatRef	0.00	0.00	0.01	0.00
CofDifWatRef	0.00	0.00	0.00	0.00
MolMas	0.00	0.00	0.00	0.00
CofSorMph	0.00	0.00	0.00	0.00
DT50SedRef	0.00	0.00	0.00	0.00
ExpFreSed	0.00	0.00	0.00	0.00
ExpFreSusSol	0.00	0.00	0.01	0.01
sum	0.98		1.03	

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[23] For the highest S_1 and S_T values confidence intervals are as a percentage of the S_1 and S_T index given between brackets as required for evaluating the statistical reliability according to Zhang (2015), see Section 3.2.2.

7.2.2 Predicted Environmental Concentrations in sediment (PEC_{sed})

The PEC_{sed} is the maximum predicted environmental concentration of pesticide in sediment (total of sorbed and pore water concentrations) in time calculated for the top layer of the sediment. In this study, the PEC_{sed} is calculated as the average of the sediment concentrations in the top 1 cm of sediment under the last node of the stream (95-100m). PEC_{sed} is expressed in mass of substance per dry mass of sediment.

The distribution of PEC_{sed} values of the ~50,000 simulations run for the sensitivity analysis is presented in Figure 7-3. For PEC_{sed}, the range is from 9.9 µg (kg DW)$^{-1}$ up to a maximum concentration of 8141 µg (kg DW)$^{-1}$. The Median value is 141.2 µg (kg DW)$^{-1}$. The distribution of PEC_{sed} is slightly bimodal, showing a second 'peak' around 2000 µg (kg DW)$^{-1}$. The reason for this bimodal result is the use of two sediment segmentations, a coarse and a fine segmentation. The second peak results from simulations performed with the fine segmentation. The fine segmentation is applied for sediment sorption coefficients $K_{om,sed}$ > 17,400 L kg^{-1}. For the coarse segmentation (i.e. used up to $K_{F,om,sed}$ < 17,400 L kg^{-1}) the maximum PEC_{sed} calculated is 328.1 µg (kg DW)$^{-1}$. For the 24 simulations with $K_{F,om,sed}$ 17,542 L kg^{-1} (= first value > 17,400) the PEC_{sed} values are in the range 1219 to 1498 µg (kg DW)$^{-1}$. This is a jump of approximately a factor of four between the PEC_{sed} from coarse and from fine segmentation. Hence, the distribution of PEC_{sed} being bimodal is due to the change in segmentations applied for the sediment. So, in fact the slight bimodality is caused by an artefact of the TOXSWA model.

In the R1 pond the nominal concentration in the water was 0.386 µg L^{-1} and concentrations in the sediment ranged from close to zero up to 45.5 µg (kg DW)$^{-1}$, while for the R1 stream the nominal concentration in the water was 98.7 µg L^{-1} and concentrations in the sediment ranged from 9.9 µg (kg DW)$^{-1}$ up to a maximum concentration of 8141 µg (kg DW)$^{-1}$. The difference in highest values for the two waterbodies can be explained by the difference in concentration in water; the concentration in water is approximately a factor 250 higher and the highest PEC_{sed} is approximately a factor 200 higher, so approximately similar to the factor for concentration in water.

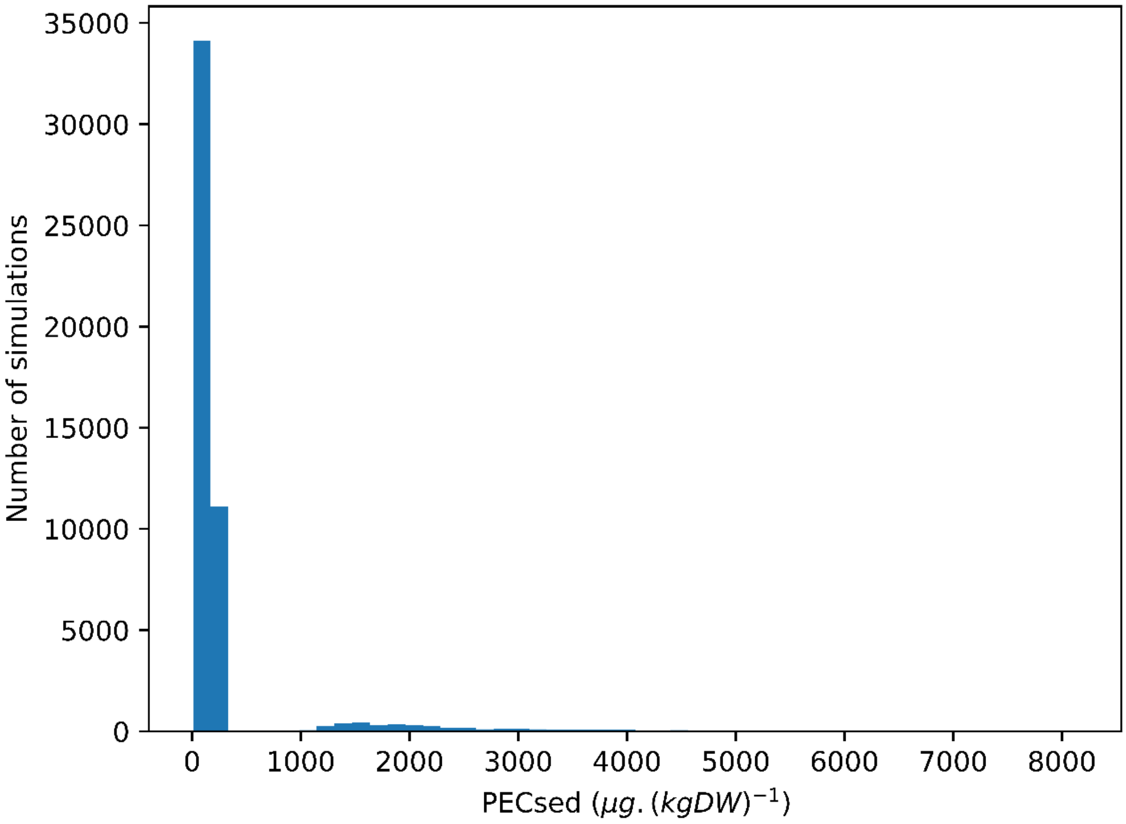

Figure 7-3 *Distribution of the maximum PEC_{sed} in the R1 stream after a runoff entry.*

The three Sobol indices of pesticide properties parameters for the PEC_{sed} are presented in Figure 7-4. Values of the S_1 and S_T indices are provided in Table 7-2. Values of the S_2 index are provided in Annex 6.

The first-order index S_1 indicates the contribution of the single process parameters, independently, to the variance of PEC_{sed}. The PEC_{sed} variance is explained to 96% by the sum of single process parameters independent variation, of which the S_1 of the Freundlich sorption coefficient to organic matter in sediment $K_{F,om,sed}$ (KomSed) dominates (S_1 of 96%). The contribution of the other process parameters is less than 1% each. Hence, PEC_{sed} variance is not explained by those parameters. The S_1 values indicates that parameters related to processes in the sediment influence the variance of PEC_{sed} through their independent variation, explaining in total 96% ($K_{F,om,sed}$ (KomSed)). Below, we consider these results in relation to what we expect in view of TOXSWA model process descriptions.

The sensitivity is determined by sorption to sediment organic matter. This can be explained by considering that the pesticide enters the sediment via the water-sediment interface by diffusion into the pore water of the sediment, driven by the difference in concentration in water (where concentrations are initially highest) and in pore water (initially zero) (Eq. (16). The pesticide in the pore water then sorbs instantaneously to the sediment (Eq. (23)). Sorption to sediment decreases concentrations in the pore water and therefore maintains a concentration gradient between the water layer and the pore water, which drives diffusion into the sediment. As a consequence, sorption (determined by $K_{F,om,sed}$ and N_{sed}) plays a major role in increasing the PEC_{sed}.

The sum of all S_1 indices is 96%, whereas for a linear model with no interaction this is expected to be near 100% (see Section 3.2.2). Hence, 4% variation of PEC_{sed} may not be attributed to single parameters independently. The S_2 and S_T indices allow evaluation of which parameters show interactions that can explain a fraction of the variation in the output.

The total index S_T (Table 7-2) indicates the contribution of a process parameter input to the variance of PEC_{sed}, including its first-order effects (S_1, the process parameter varying alone) and all higher-order interactions. Hence, S_T given for $K_{F,om,sed}$ (KomSed, 100%) is higher than its first-order index S_1 (96%) because second and higher-order interactions are included (which is confirmed by S_2 values >0 in Figure 7-4 and Annex 6). Similarly, for diffusion in water S_T is a few percent higher than the S_1 value, so interaction with other process parameters contributes, albeit little, to the variance in PEC_{sed}. The sum of S_T is 103%, so close to 100%, which indicates that the system is close to, but not entirely linear.

The S_T index for the coefficient for diffusion in water, D_{wat}, is 2%, indicating it has a small influence on the variance in PEC_{sed}. This can be explained by realising that the transport across the water-sediment interface, as well as within the sediment pores is an important process for mass entering the sediment.

The second-order indices S_2 characters the contribution of interactions between any pair of process parameters to the variance of the output PEC_{sed}. It appears on Figure 7-4 that for the pair $K_{F,om,sed}/D_{wat}$, which are the two parameters with highest S_2 of 1%, explaining the higher S_T value for both parameters (values are given in Annex 6). $K_{F,om,sed}$ pairs show large confidence intervals of more than 20%. These large confidence intervals of more than 10% signal that the values of S_2 are not reliable from a statistical point of view. However, most of the relatively high S_2 values point to interactions between pairs of process parameters which are consistent with the previous observations on S_1 and S_T as shown above.

So, we conclude that the Sobol indices found for PEC_{sed} are quite satisfactory: as expected and indicated by the S_1 and S_T indices the most sensitive parameter for the PEC_{sed} is the $K_{F,om,sed}$ (KomSed). With respect to the PEC_{sed} model outcome, the TOXSWA model behaves close to, but not entirely linearly, as indicated by the sum of S_1 of 96% and of S_T of 103%. As the PEC_{sed} is the result of the interplay of two different model parts (the water layer and sediment subsystems) and one of the main sediment processes, sorption to sediment, is non-linear, some extent of non-linearity is plausible.

The confidence interval for the most sensitive parameter $K_{F,om,sed}$ (KomSed) is 14% for S_1 and 7% for S_T. For S_1, the confidence interval is greater than the threshold of 10% and the results are not reliable from a statistical point of view for the Saltelli sampling method (Zhang, 2015). However, the number of simulations required to obtain statistical significance may be quite high in view of the current, large confidence interval of the $K_{F,om,ss}$ parameter. As the results are sufficiently well understood with respect to the processes described in the TOXSWA model, and the S_1, S_T and S_2 results agree well internally, no further simulations were performed with an increased number of simulations.

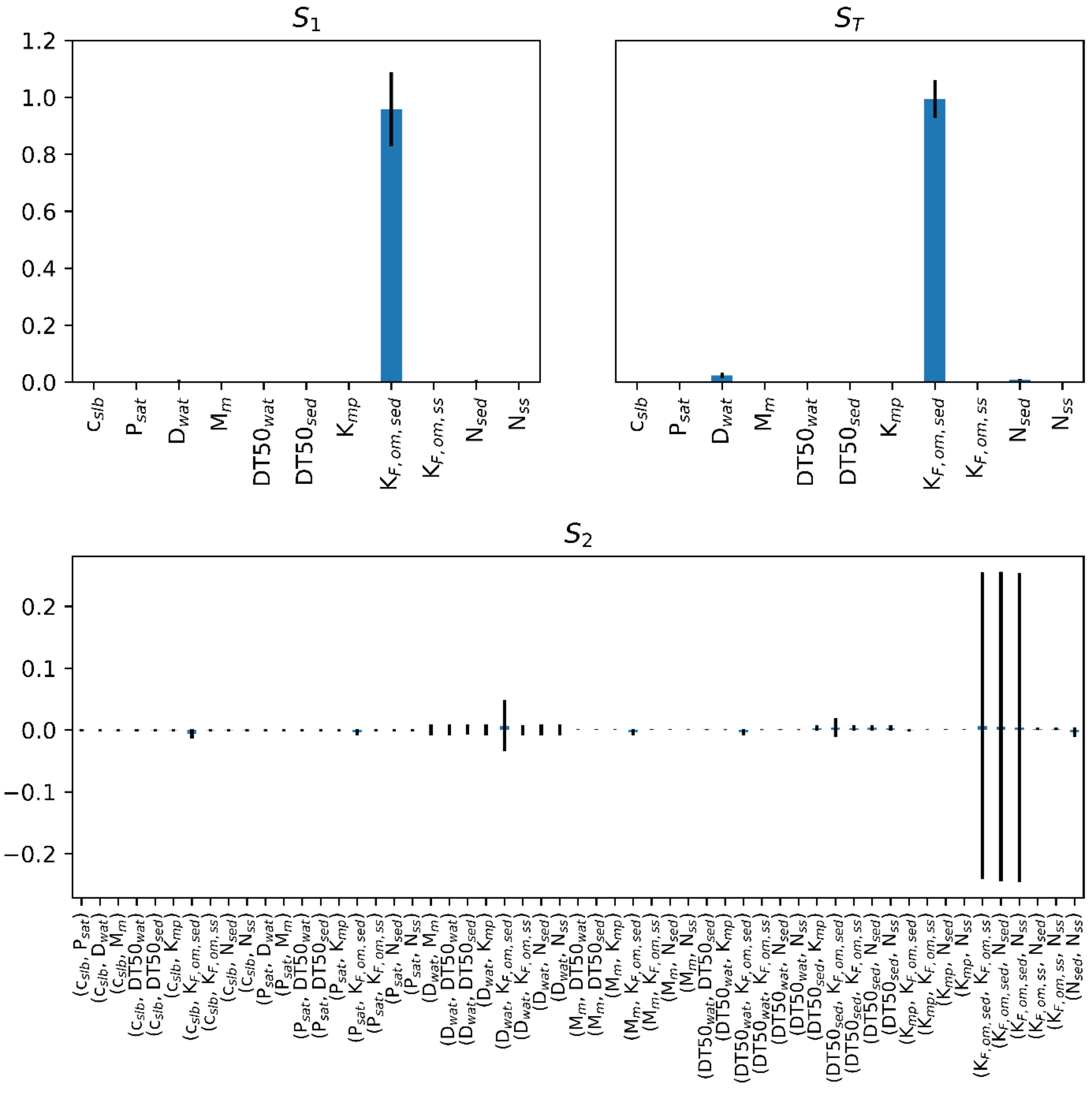

Figure 7-4 *Values of the Sobol sensitivity indices S_1, S_T, S_2 (resp. first-order, total order and second-order, y-axis) of the pesticide properties parameters (x-axis) for PEC_{sed} in the R1 stream after a runoff entry. The index values are given in blue and their confidence intervals in black.*

Table 7-2 *First order (S_1) and total order (S_T) Sobol index values and their confidence intervals (±) for PEC_{sed} in the R1 stream after a runoff entry (values sorted by S_1 value).*

Parameter	S_1	S_1 ±	S_T	S_T ±
KomSed	0.96	0.13 (14%)	1.00	0.07 (7%)
CofDifWatRef	0.00	0.01	0.02	0.01
ExpFreSed	0.00	0.00	0.01	0.00
SlbWatRef	0.00	0.00	0.00	0.00
PreVapRef	0.00	0.00	0.00	0.00
DT50WatRef	0.00	0.00	0.00	0.00
MolMas	0.00	0.00	0.00	0.00
ExpFreSusSol	0.00	0.00	0.00	0.00
KomSusSol	0.00	0.00	0.00	0.00
CofSorMph	0.00	0.00	0.00	0.00
DT50SedRef	0.00	0.00	0.00	0.00
sum	0.96		1.03	

7.2.3 Time-Weighted Average concentrations in water over a period of seven days (TWA7)

The distribution of the maximum time-weighted average concentration values over a period of seven days (TWA7) obtained from the 49,152 simulations is shown in Figure 7-5. Note that the hydraulic residence time in the R1 stream during the 1-mm runoff in 8-h event is less than 0.5 h (flow velocity of 247 m h^{-1}), and is 5 h in the absence of runoff (velocity of 19.5 m h^{-1}). So, when the runoff stops, the water flow velocity decreases from 247 m h^{-1} to 19.5 m h^{-1}. The rolling window of seven days therefore contains the entire period of the runoff event of eight hours, the period where the stream flow flushes the pesticide mass downstream, and once the water is clean, the period where pesticide is back-diffusing from the sediment into the water layer due to the concentration gradient change As for the PEC_{wat}, processes leading to instantaneous decrease of the dissolved concentration in water are expected to influence TWA7 most. However, the distribution shows a second small peak near 8 µg L^{-1} (hence bimodality). This is again due to the use of two sediment segmentations (see Section 7.2.2). When plotting TWA7 values as a function of $K_{F,om,sed}$ there is jump from approximately 7 µg L^{-1} to approximately 8 µg L^{-1} at $K_{F,om,sed}$ 17,400 L kg^{-1}. The relatively higher content in sediment for the fine segmentation ($K_{F,om,sed}$ > 17,400 L kg^{-1}) with back-diffusion thereafter leads to prolonged higher concentrations in water leading to higher TWA7.

The three Sobol indices of the pesticide properties parameters for TWA7 are given in Figure 7-6. Values of the S_1 and S_T indices are provided in Table 6-4. Values of the S_2 index are provided in Annex 6.

The first-order index S_1 indicates the contribution of the single process parameters, independently, to the variance of calculated TWA7. The TWA7 variance is explained to 92% by the independent variation of single process parameters, of which 61% by sorption to suspended solid $K_{F,om,ss}$ (KomSusSol), 21% by sorption to the sediment $K_{F,om,sed}$ (KomSed), 4% by the degradation rate in water $DT_{50,wat}$ (DT50WatRef), 3% by the saturated vapour pressure P_{sat} (PreVapRef) and 2% by the solubility in water, c_{slb} (SlbWatRef). Of all other input parameters only the sorption coefficient to macrophyte K_{mp} (CofSorMph) has some (but close to negligible) contribution to the TWA7 variance, of 1%.

The sum of S_1 is 92%, whereas for a linear model this is expected to be 100% (see Section 3.2.2). Hence, 8% variation of TWA7 may not be attributed to single parameters independently. The S_2 and S_T indices presented below allow evaluation of which parameters show interactions relevant to explain the output.

The total index S_T indicates the contribution of a process parameter input to the variance of calculated TWA7, including both its first-order effects (S_1, the process parameter varying alone) and all higher-order interactions. For two sensitive parameters, P_{sat}, saturated vapour pressure, and c_{slb}, solubility in water, the total-order indices are three and five times as large as the first-order indices (S_1 of 3% and 2%, *vs* S_T of 9% and 8%, respectively), which indicates that the interactions of those parameters with other parameters is relevant to explain the variance. The other input parameters which had shown to be relevant with S_1 values above 1% have S_T values similar to their S_1 values. The sum of S_T is 110%, which indicates a non-linear response.

The second order index S_2 indicates the contribution of interactions between two process parameters to the variance of calculated TWA7. In Figure 7-6 it can be seen that S_2 between the saturated vapour pressure, P_{sat}, and the solubility, c_{slb}, is high, 6% (values are provided in Annex 6), which indicates that this interaction is relevant to explain the variance. The interaction is understandable, as saturated vapour pressure and solubility contribute both to the Henry coefficient (see Eq. (15)), which determines the overall transfer to the gas phase/air. Over the short duration of the transport in the stream, volatilization from the stream plays a (relatively small) role, influencing the variance of TWA7. All other second-order interactions are lower, with S_2 values of 1% or less (also small negative values reported, as stated before, this is linked to the relatively low numbers of samples associated with the Saltelli sampling method).

We conclude that the Sobol indices found for TWA7 are satisfactory: as expected and indicated by the S_1 and S_T indices the most sensitive parameters for the TWA7 is sorption to suspended solids $K_{F,om,ss}$ as for PEC_{wat}, with additional processes which show a lesser influence: $K_{F,om,sed}$, $DT_{50,wat}$, P_{sat}, c_{slb}, and K_{mp}. As explained above, this can be well understood. With respect to the TWA7 model outcome, the TOXSWA model behaves non-linearly, as indicated by the sum of S_1 of 92% and of S_T of 110%. This might be explained by the relatively high interaction (6%, Annex 6) between P_{sat} and c_{slb}.

The confidence intervals for the most sensitive parameter, $K_{F,om,ss}$ (KomSusSol) are 32% and 14% for the S_1 and S_T index, respectively (Table 7-3). Hence, the confidence intervals are above 10% and thus the study is insufficiently reliable, from a statistical point of view (Zhang, 2015). However, the results of our TWA7 analysis agree well internally (S_1, S_T and S_2), as well as with our knowledge about the importance of processes in the TOXSWA model. Therefore, we do not increase the number of approximately 50,000 simulations and are satisfied with the results obtained.

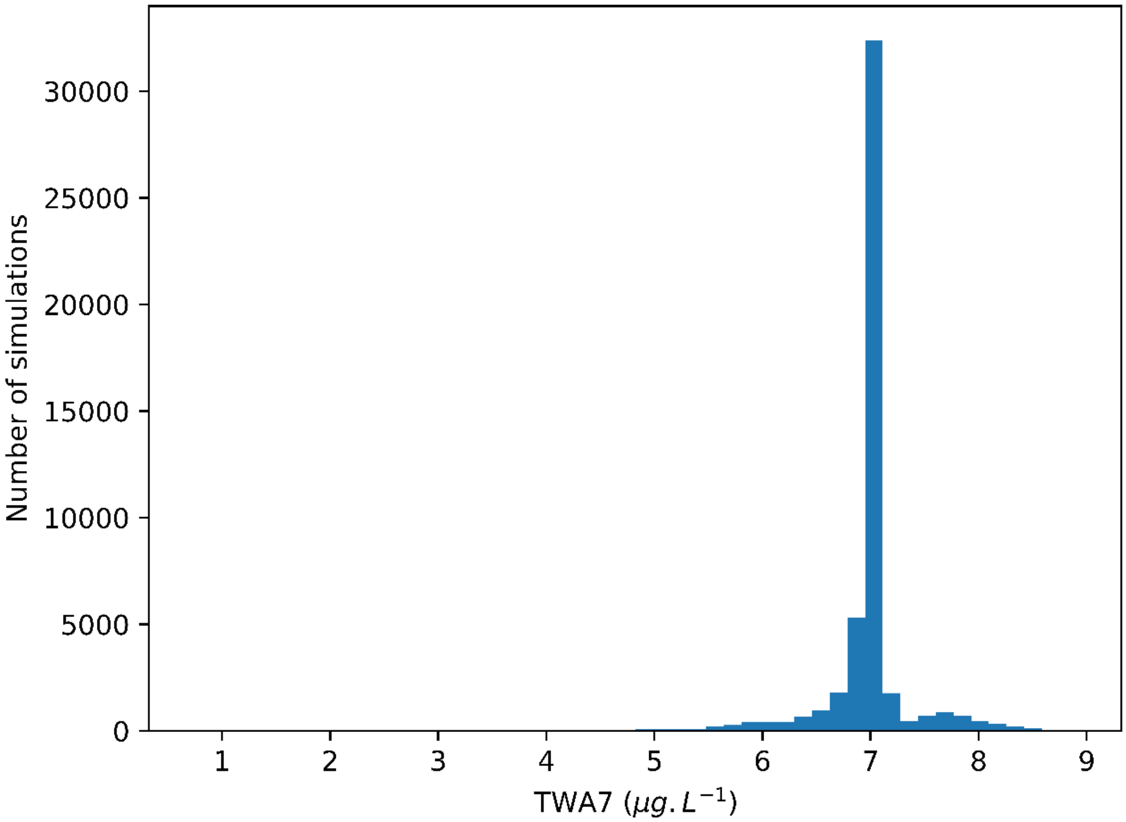

Figure 7-5 *Distribution of the maximum average exposure concentrations over seven days (TWA7) in the R1 stream after a runoff entry.*

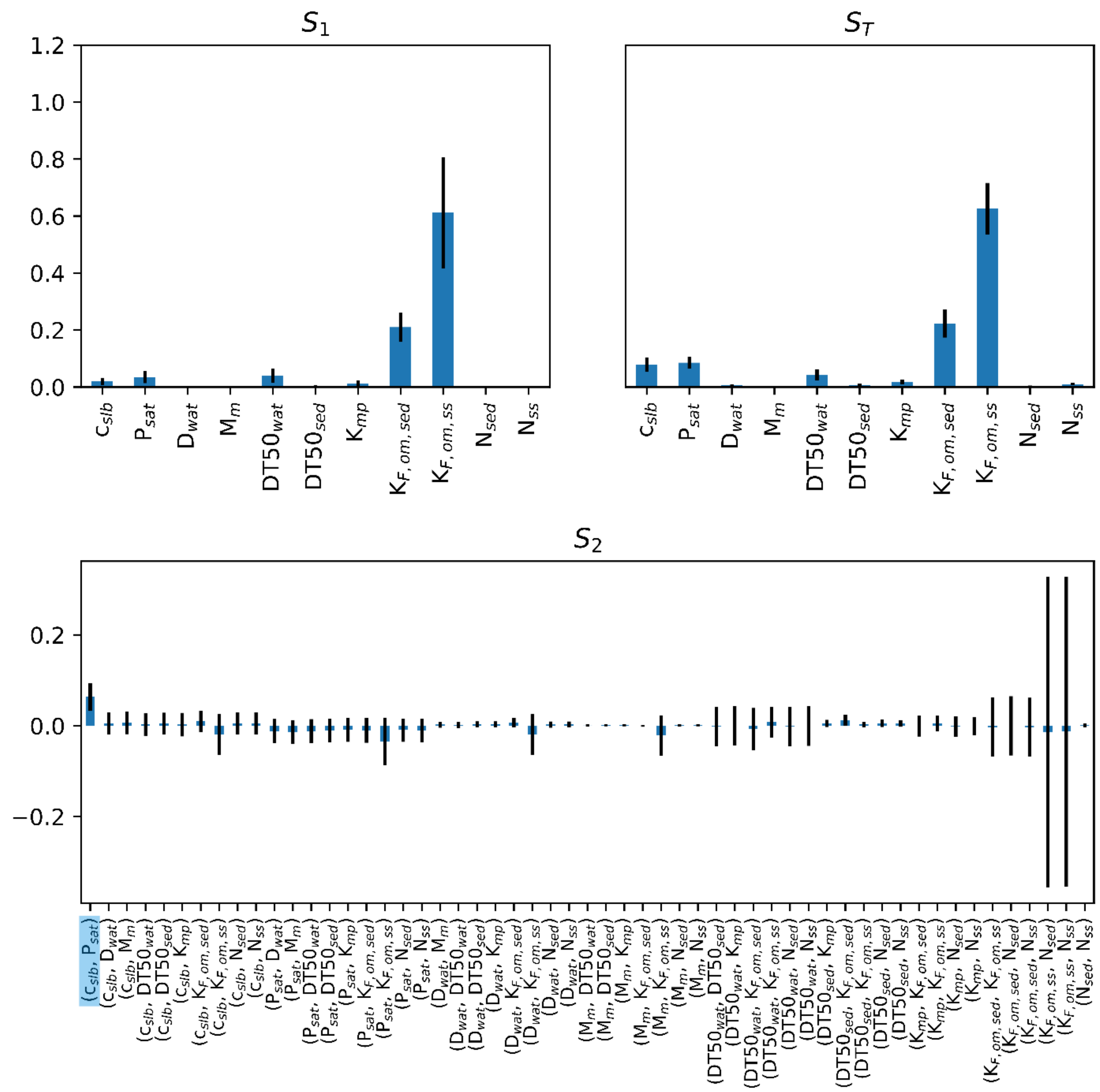

Figure 7-6 *Values of the Sobol sensitivity indices* S_1*,* S_T*,* S_2 *(resp. first-order, total order and second-order, y-axis) of the pesticide properties parameters (x-axis) for time weighted average concentrations in water over seven days (TWA7) in the R1 stream after a runoff entry. The index values are given in blue and their confidence intervals in black. The description in the* S_2 *graph marked in blue is the* c_{slb}/P_{sat} *pair with a* S_2 *of 0.06.*

Table 7-3 *First-order (*S_1*) and total-order (*S_T*) Sobol index values and their confidence intervals (±) for TWA7 in the R1 stream after a runoff entry (values sorted by* S_1 *value).*

Parameter	**S_1**	**S_1 ±**	**S_T**	**S_T ±**
KomSusSol	0.61	0.20 (32%)	0.63	0.09 (14%)
KomSed	0.21	0.05	0.22	0.05
DT50WatRef	0.04	0.02	0.04	0.02
PreVapRef	0.03	0.02	0.09	0.02
SlbWatRef	0.02	0.01	0.08	0.03
CofSorMph	0.01	0.01	0.02	0.01
DT50SedRef	0.00	0.01	0.01	0.00
ExpFreSed	0.00	0.00	0.00	0.00
MolMas	0.00	0.00	0.00	0.00
CofDifWatRef	0.00	0.01	0.01	0.00
ExpFreSusSol	0.00	0.00	0.01	0.00
sum	0.92		1.10	

7.2.4 Time-Weighted Average concentrations in water over a period of 28 days (TWA28)

The distribution of maximum TWA28 values from the simulations is similar to the distribution of TWA7. Most values are in the range of 1.3 to 2.2 µg L^{-1}. Similarly to the maximum TWA7 with its relevant S_1 indices of instantaneous as well as continuous processes here instantaneous as well as continuous processes decrease the concentration after the runoff entry over the following 28 days: instantaneous processes for pesticides with high sorption coefficients for organic matter in suspended solids or to macrophytes and more continuous processes for diffusion into sediment (plus next adsorption), volatilization to the air, and degradation in water. The distribution shows a slight decrease near 1.8 µg L^{-1} (hence a slight bimodality). This is again due to the use of two different sediment segmentations (see Section 7.2.2). When plotting TWA28 values as a function of $K_{F,om,sed}$ there is jump from approximately 1.8 µg L^{-1} to approximately 2 µg L^{-1} at $K_{F,om,sed}$ 17,400 L kg^{-1}. The relatively higher content in sediment for the fine segmentation ($K_{F,om,sed}$ > 17,400 L kg^{-1}) with back-diffusion thereafter leads to prolonged higher concentrations in water and higher TWA28 than for the coarser segmentation.

Similarly to the maximum TWA7, the rolling window of 28 days covers entirely the period when the concentrations in water are high. Therefore, the distribution of the TWA28 is very similar to the one of the TWA7, only with lower values as the TWA28 values have been averaged over a longer period and therefore with more time steps where concentration is very low or 0 µg L^{-1}. Median and most frequent values for TWA7 were approximately 7 µg L^{-1}, they are approximately 1.8 µg L^{-1} for TWA28 values.

The three Sobol indices of pesticide process parameters for the maximum TWA28 are shown in Figure 7-7. Values of the S_1 and S_T indices are provided in Table 7-4 and of the S_2 index in Annex 6. There are only slight differences between the relevant parameters for TWA7 and TWA28, but the latter show a slightly lower effect of instantaneous processes (such as sorption to suspended solids) *versus* time-dependent processes. This similarity signifies that no other processes occur within this longer period of 28 days that influence the output, for the reasons explained in the paragraph above. Therefore, we refer to the explanations given for TWA7 for the results for the sensitivity analysis for TWA28.

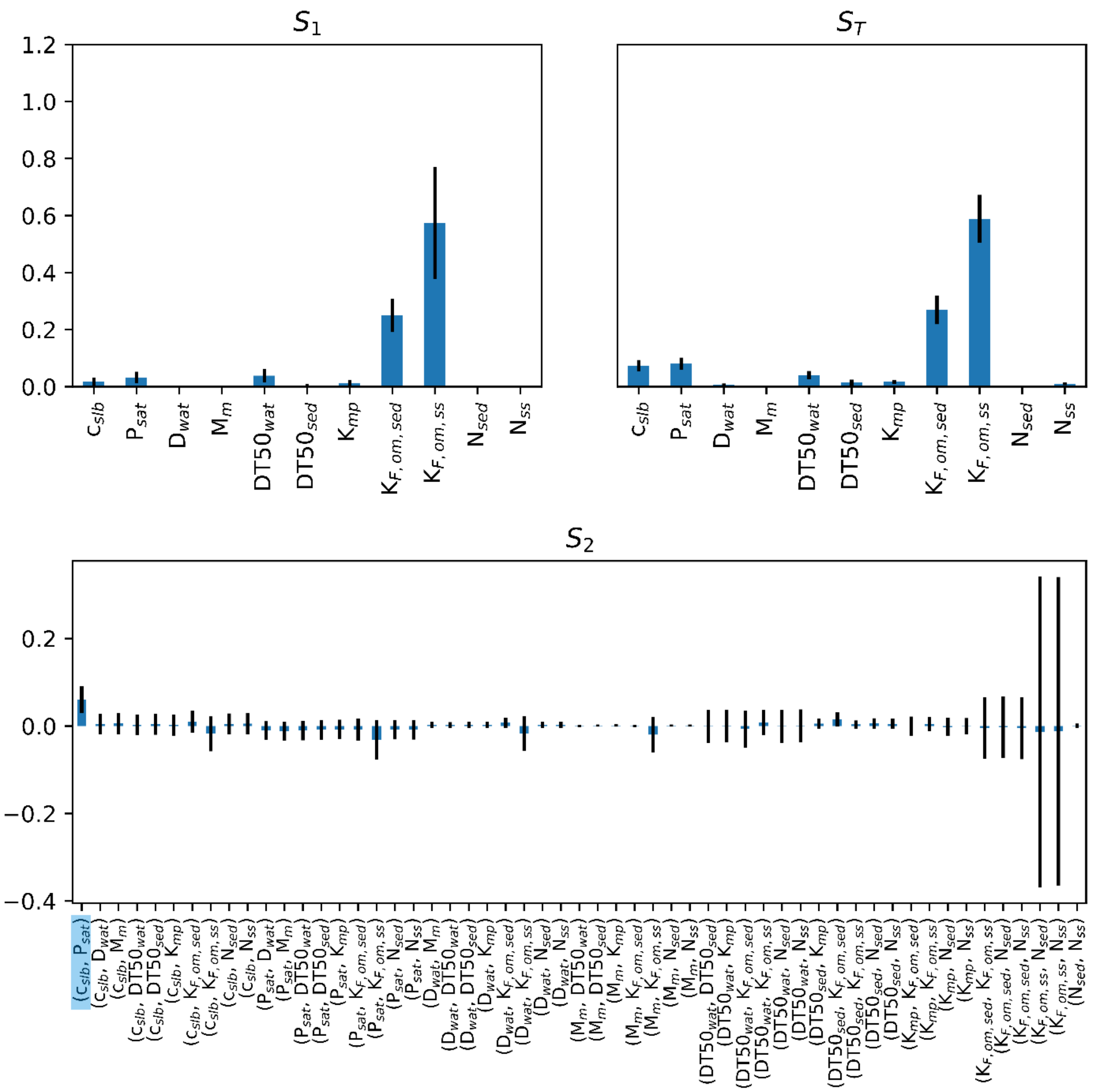

Figure 7-7 *Values of the Sobol sensitivity indices* S_1, S_T, S_2 *(resp. first-order, total order and second-order, y-axis) of the pesticide properties parameters (x-axis) for time weighted average concentrations in water over 28 days (TWA28) in the R1 stream after a runoff entry. The index values are given in blue and their confidence intervals in black. The description in the* S_2 *graph marked in blue is the* c_{slb}/P_{sat} *pair with a* S_2 *of 0.06.*

Table 7-4 *First order* (S_1) *and total order* (S_T) *Sobol index values and their confidence intervals (±) for TWA28 in the R1 stream after a runoff entry (values sorted by* S_1 *value).*

Parameter	**S_1**	**S_1 ±**	**S_T**	**S_T ±**
KomSusSol	0.57	0.20 (34%)	0.59	0.08 (14%)
KomSed	0.25	0.06	0.27	0.05
DT50WatRef	0.04	0.02	0.04	0.01
PreVapRef	0.03	0.02	0.08	0.02
SlbWatRef	0.02	0.01	0.07	0.02
CofSorMph	0.01	0.01	0.02	0.01
DT50SedRef	0.00	0.01	0.01	0.01
ExpFreSed	0.00	0.00	0.00	0.00
MolMas	0.00	0.00	0.00	0.00
CofDifWatRef	0.00	0.01	0.01	0.00
ExpFreSusSol	0.00	0.00	0.01	0.00
sum	0.92		1.10	

7.3 Sensitive process parameters for the stream - Summary

The sensitivity analysis has been run for a FOCUS-type stream with a pesticide entry by a single runoff event lasting eight hours on the 4th of March from 0 a.m. onwards. The selected stream is based on the FOCUS R1 stream, but in this study, the stream contains macrophytes, a moderate to high biomass of 200 g DW m^{-2} sediment area (the FOCUS R1 stream scenario does not include macrophytes). Its flow velocity is 247 m h^{-1} during runoff and 19.5 m h^{-1} without runoff, so water flow is relatively fast during the runoff event, and low thereafter. Corresponding hydraulic residence times are 0.21 d and approximately 0.017 d. The aim was to determine the most sensitive pesticide properties parameters used as input for the TOXSWA model. Hence, the results indicate which process parameters contribute most to the variation of the model outputs and should thus be determined carefully. The four selected outputs of which the sensitivity has been studied are the maximum values in time for the Predicted Exposure Concentration in water, (PEC_{wat}), and in sediment, (PEC_{sed}), and for the Time Weighted Average concentrations over seven and 28 days (TWA7 and TWA28) for the most downstream node in the stream (segment 95-100 m).

The PEC_{wat} represents the maximum value in time of the Predicted Exposure Concentration in the water layer, observed during the simulation of three months. The maximum PEC_{wat} occurs immediately at the runoff entry. At the time of the runoff entry, instantaneous sorption processes, such as sorption to suspended solids or macrophytes lower the nominal concentration of approximately 98.7 µg L^{-1}. Most PEC_{wat} values are located between 95 and 98.7 µg L^{-1}. Processes that need time, such as diffusion followed by sorption to sediment, degradation in water or volatilization, are not expected to influence the PEC_{wat}.

The S_1 value of 96% for the coefficient for sorption to suspended solids, $K_{F,om,ss}$, indicates that this parameter is by far the most sensitive one, explaining the variation of the PEC_{wat}. The parameters P_{sat}, $DT_{50,wat}$, and $K_{F,om,sed}$ contribute negligibly to the variation of the PEC_{wat} (S_1 values of 1%), as only the very little travel time up (less than 0.5 hours) to the end of the stream allows them to act upon the stream concentration. The sum of all S_1 indices is 98%, therefore close to the value of 100% which indicates that the model is linear for the PEC_{wat} in the R1 stream.

As the sum of all S_1 indices is very close to 100% the independent variation of the input parameters explains practically all variation in the PEC_{wat} output, therefore we do not expect any influence of interactions of input parameters, or second-order, or higher order interactions. This is confirmed by the sum of all S_T indices being 103%, i.e. very close to the sum of all S_1 indices.

So, the Sobol indices found for PEC_{wat} are very satisfactory: as expected and indicated by the S_1 and S_T indices, the most sensitive parameter for the PEC_{wat} is the $K_{F,om,ss}$. The other (negligibly) sensitive parameters (P_{sat}, $DT_{50,wat}$, and $K_{F,om,sed}$) can be well understood, as explained above. With respect to the PEC_{wat} model outcome, the TOXSWA model behaves close to linearly, as indicated by the sum of S_1 of 98% and of S_T of 103%.
However, the confidence interval of S_1 for the sorption coefficient for suspended solids $K_{F,om,ss}$ is 29% of S_1 (Table 7-1), which is clearly above the desired 10%, required for robust results of the sensitivity analysis (Zhang, 2015). To obtain robust results, a larger number of samples and simulations is recommended. As the results are sufficiently well understood with respect to the processes described in the TOXSWA model and the S_1, S_T and S_2 results agree well internally, we are satisfied with the results.

The PEC_{sed} is the maximum concentration in time (total of sorbed and pore water concentrations, averaged over the upper 1-cm sediment layer) observed during the simulation period of three months. Most PEC_{sed} values were in the range 9-328 µg (kg DW)$^{-1}$, but larger values of 1,000-2,500 µg (kg DW)$^{-1}$ and up to 8141 µg (kg DW)$^{-1}$ occur for simulations with a large sorption coefficient to sediment.

The PEC_{sed} results show a bimodal distribution, with a large peak for smaller values of 9 - 328 µg (kg DW)$^{-1}$, and a second much smaller peak for values around 1,000-2,500 µg (kg DW)$^{-1}$ corresponding to PEC_{sed} values computed with the fine sediment discretization. The PEC_{sed} results show a bimodal distribution, with a large peak for values around 1.2 µg (kg DW)$^{-1}$, and a second much smaller peak for values around 2000 µg (kg DW)$^{-1}$. This is due to higher concentrations in sediment computed with the fine sediment discretization leading to prolonged higher concentrations from back-diffusion to water (see Section7.2.2).

The first-order S_1 indices of the Freundlich sorption coefficient to organic matter in sediment $K_{F,om,sed}$ explains virtually all the variation in the PEC_{sed} (S_1 of 96%), with the sum of all S_1 indices being 96%. The S_T is 100%, indicating that there are some second-order and higher order interactions. The sum of S_T is 103%, so close to 100%, which indicates that the system is close to, but not entirely linear.

The confidence interval for the most sensitive parameter $K_{F,om,sed}$ is 14% for S_1 and 7% for S_T, which is above the threshold of 10% for the S_1 index. Thus the value is not reliable from a statistical point of view for the Saltelli sampling method (Zhang, 2015).

The TWA7 represents the maximum value in time of the Predicted Exposure Concentration in the water layer over a rolling time window of seven days, observed during the simulation of three months. They are 7 to 8 µg L^{-1}. The maximum TWA7 values are lower than the PEC_{wat} values of 90-100 µg L^{-1}, as for the former the concentration peaks in water are averaged with close to zero concentrations after the runoff water has flowed out of the stream.

The TWA7 results show a bimodal distribution, with a large peak for values around 7 µg L^{-1}, and a second much smaller peak for values around 8 µg L^{-1}. This is again due to higher concentrations in sediment computed with the fine sediment discretization leading to prolonged higher concentrations from back-diffusion to water.

The TWA7 variance is explained by the independent variation of the single process parameters of sorption to suspended solid $K_{F,om,ss}$ (61%), by sorption to the sediment $K_{F,om,sed}$ (21%), by the degradation rate in water $DT_{50,wat}$ (4%), as well as by the saturated vapour pressure P_{sat} (3%) and the solubility c_{slb} (2%). The sum of all S_1 indices is 92%, whereas for a linear model this is expected to be 100%. Hence, 8% variation of TWA7 cannot be attributed to single parameters independently.

The S_T indices for sorption to suspended solid $K_{F,om,ss}$ and the degradation rate in water $K_{F,om,sed}$ do hardly change from their S_1 indices (S_T indices of 63% and 22% vs S_1 indices of 61% and 21% respectively). However, the S_T indices for P_{sat}, saturated vapour pressure, and c_{slb}, solubility in water, are three and four times as large as their first-order indices (S_1 of 3% and 2%, vs S_T of 9% and 8%, respectively). This indicates that the interactions of these two parameters explain to a significant extent the total variance in the TWA7 output. The sum of all S_T indices is 110%, which indicates a non-linear response.

The confidence intervals for the most sensitive parameter, $K_{F,om,ss}$ are 32% and 14% for the S_1 and S_T index, respectively. The confidence intervals are clearly above 10% and thus the study is judged to be insufficiently reliable from a statistical point of view (Zhang, 2015). However, the results of our TWA7 analysis agree well internally, as well as with our knowledge about the importance of processes in the TOXSWA model. Therefore, we do not increase the number of approximately 50,000 simulations and are satisfied with the results obtained.

The results for the maximum TWA28 are close to those of the maximum TWA7, including the slight bimodality, but with clearly lower concentrations due to the longer averaging time window of 28 days instead of seven days with near zero concentrations. Most TWA28 values are in the range of 1.3 to 2.2 µg L^{-1} compared to 7-8 µg L^{-1} for the TWA7 concentration values. We refer to the sections on TWA7 above to explain all sensitivity analysis results. For TWA28 the effect of time-dependent processes *versus* instantaneous processes is slightly stronger due to the longer time period the TWA28 is calculated for.

Considerations on the assumed linearity of the studied (TOXSWA) model and confidence intervals of S_1 and S_T indices above 10% have been discussed in Section 5.4 with the summary for the R1 pond, and are not repeated here.

8 General discussion and conclusions

8.1 Used methods

In the present study of the sensitivity analysis of the pesticide properties parameters (process parameters) of the TOXSWA model, we used the Sobol/Saltelli methods (named after Sobol and Saltelli who participated to the development of the method and development of its use). This approach developed in the 1990s is currently commonly used for sensitivity analysis. The general approach is similar in both the current and the former (Westein et al., 1998) sensitivity analyses of TOXSWA, with first a **sampling** of the input parameter values within the possible range, followed by a **study of the variance of the studied outputs** generated by the TOXSWA software using the sampled inputs.

The Sobol/Saltelli method assumes that the investigated model is linear. If the model output does not show (near) linear behaviour, Saltelli is not the best option. Although we used many samples (~50,000), the confidence interval of S_1 and S_T indices were above 10% in several instances, indicating the analysis to be insufficiently reliable from a statistical point of view. However, the sensitive parameters indicated on the basis of S_1 and S_T were judged to be plausible, as well as acceptable for a qualitative analysis, and we concluded that the model is sufficiently linear for the Saltelli's sampling method and the Sobol analysis to be useful. Therefore, we did put no further effort in extending the number of simulations.

Concerning S_2 values, S_2 values show a large variability and sometimes negative values (which are not reliable). This is related to (i) the number of simulations is likely insufficient (now 50,000 on 11 parameters), but more importantly to (ii) the estimators used in the SALIB implementation of Saltelli to calculate the S_2 values (based on Saltelli et al., 2010, referred to in the SALIB coding, pers. comm. G. van Voorn, Biometris), which show small errors and can lead to negative variance calculations. However, we will use the results of this sensitivity analysis for qualitative purposes, and not quantitative purposes, such as e.g. determining relative weight in a model calibration. As the results were in agreement with each other and could be well explained, they were judged satisfactory and sufficient. SALIB samples from input space (the Python library used for the sensitivity analysis to draw values and determine S indexes) were applied by using Saltelli's extension of the Sobol' sequence. This type of sampling is aimed at avoiding bias but assumes again a (near) linear model. Therefore, we checked the histograms of the outputs for modality and skewness visually as to whether the assumptions of linearity hold, in which case we expected a normal distribution of the outputs or whether we could explain the non-normal distribution of the outputs. For most outputs, the distribution was not normally distributed, but we were able to explain the distribution observed.

Note that for the inputs studied, the pesticide properties parameters, the distributions of the inputs are strongly skewed. In order to create representative samples, we preferred to sample within the log10 of the values (see Section 3.3) which were all (near) normal distributions. This sampling technique ensures that extremes in the Gaussian distribution are sampled. For the process parameters, once sampled within the distribution of the log10 of the values, the sampled values were transformed back to real parameter values to provide them as input for TOXSWA.

8.2 Results

This sensitivity analysis of pesticide properties parameters of TOXSWA is done for two systems:

- A pond, representative for the low flow velocity domain of TOXSWA.
- A stream, representing the high flow velocity domain of TOXSWA.

The parameterisations of a FOCUS pond and a FOCUS stream were used. For the pond an instantaneous mass entry (spray drift) was applied, and for the stream a short distributed type entry of mass flux (runoff) over eight hours was applied.

The results for the FOCUS pond (see Table 8-1) show that most sensitive parameters are:

- PEC$_{wat}$; the Freundlich sorption coefficient on organic matter in suspended solids $K_{F,om,ss}$.
- PEC$_{sed}$; the Freundlich sorption coefficient on organic matter in sediment $K_{F,om,sed}$, and to a lesser extent for half-lives in water and in sediment, $DT_{50,wat}$ and $DT_{50,sed}$.
- TWA7 and TWA28; half-life in water $DT_{50,wat}$, the Freundlich sorption coefficient on organic matter in sediment $K_{F,om,sed}$, and to a lesser extent for saturated vapour pressure P_{sat} and for solubility c_{slb} for both TWAs.

The results for the FOCUS stream (see Table 8-2) show that most sensitive parameters are;

- PEC$_{wat}$; the Freundlich sorption coefficient on organic matter in suspended solids $K_{F,om,ss}$.
- PEC$_{sed}$; the Freundlich sorption coefficient on organic matter in sediment $K_{F,om,sed}$.
- TWA7 and TWA28; the Freundlich sorption coefficient on organic matter in suspended solids $K_{F,om,ss}$, and the Freundlich sorption coefficient on organic matter in sediment $K_{F,om,sed}$.

In summary, for the FOCUS pond, representing the low flow velocity domain, the most sensitive parameters are the sorption coefficients (suspended solids $K_{F,om,ss}$ and sediment $K_{F,om,sed}$) for the selected target outputs, there is a lower sensitivity to dissipation parameters represented by transformation and volatilization parameters (saturated vapour pressure P_{sat} and for solubility c_{slb}). For the FOCUS stream, representing the high flow velocity domain, the most sensitive parameters are the sorption coefficients (suspended solids $K_{F,om,ss}$ and sediment $K_{F,om,sed}$).

The main difference in the sensitive parameters between the low and high flow velocity domain, is that time-dependent (dissipation) parameters contribute less to the sensitivity of the studied outputs for the stream. This is understandable because the high flow velocity leads to short residence times of the pesticide in water and also for the sediment.

The sensitive parameters identified indicate which pesticide properties input parameters need to be determined with the highest accuracy in order to obtain robust output. So, special attention in obtaining accurate input is required for especially the sorption coefficients (suspended solids $K_{F,om,ss}$ and sediment $K_{F,om,sed}$), as well as dissipation processes such as volatilization (i.e. the saturated vapour pressure P_{sat} and solubility c_{slb}) and the degradation in water and in sediment. So, accurate measurement of these parameters is essential for reducing uncertainty in model outputs and ensuring robustness of exposure predictions in pesticide regulation.

Table 8-1 *Sensitive pesticide parameters for a FOCUS pond, indicated by first-order Sobol index S_1. Most sensitive parameter per type of exposure concentration is given in bold ($S_1 > 0.05$), and "–" indicates $S_1 < 0.005$.*

Parameter	Description and units	name in TOXSWA	PECwat	PECsed	TWA7	TWA28
M_m	Molar mass (g mol^{-1})	MolMas	-	-	-	-
P_{sat}	Saturated vapour pressure in water at 20°C (Pa)	PreVapRef	-	0.01	**0.09**	**0.07**
c_{slb}	Solubility in water at 20°C (mg L^{-1})	SlbWatRef	-	0.01	**0.06**	0.05
D_{wat}	Diffusion coefficient in water (m^2 d^{-1})	CofDifWatRef	-	-	-	-
$DT_{50,wat}$	Half-life of transformation in water at 20°C (d)	DT50WatRef	-	**0.06**	**0.43**	**0.53**
$DT_{50,sed}$	Half-life of transformation in sediment at 20°C (d)	DT50SedRef	-	0.04	-	0.01
$K_{F,om,ss}$	Freundlich sorption coefficient on organic matter in suspended solids (L kg^{-1})	KomSusSol	**0.89**	-	0.05	0.02
N_{ss}	Freundlich exponent to suspended solids based upon organic matter content (-)	ExpFreSusSol	0.01	-	-	-
$K_{F,om,sed}$	Freundlich sorption coefficient on organic matter in in sediment (L kg^{-1})	KomSed	-	**0.69**	**0.16**	**0.14**
N_{sed}	Freundlich exponent to sediment based upon organic matter content (-)	ExpFreSed	-	0.03	-	-
K_{mp}	Coefficient for linear sorption on macrophytes (L kg^{-1})	CofSorMph	0.02	-	-	-

***Table 8-2** Sensitive pesticide parameters for a FOCUS stream, indicated by first-order Sobol index S_1. Most sensitive parameter per type of exposure concentration is given in bold ($S_1 > 0.05$), and "–" indicates $S_1 < 0.005$.*

Parameter	**Description and units**	**name in TOXSWA**	**PECwat**	**PECsed**	**TWA7**	**TWA28**
M_m	Molar mass (g mol^{-1})	MolMas	-	-	-	-
P_{sat}	Saturated vapour pressure in water at 20°C (Pa)	PreVapRef	0.01	-	0.03	0.03
c_{slb}	Solubility in water at 20°C (mg L^{-1})	SlbWatRef	-	-	0.02	0.02
D_{wat}	Diffusion coefficient in water (m^2 d^{-1})	CofDifWatRef	-	**-**	-	-
$DT_{50,wat}$	Half-life of transformation in water at 20°C (d)	DT50WatRef	0.01	-	0.04	0.04
$DT_{50,sed}$	Half-life of transformation in sediment at 20°C (d)	DT50SedRef	-	-	-	-
$K_{F,om,ss}$	Freundlich sorption coefficient on organic matter in suspended solids (L kg^{-1})	KomSusSol	**0.96**	-	**0.61**	**0.57**
N_{ss}	Freundlich exponent to suspended solids based upon organic matter content (-)	ExpFreSusSol	-	-	-	-
$K_{F,om,sed}$	Freundlich sorption coefficient on organic matter in in sediment (L kg^{-1})	KomSed	0.01	**0.96**	**0.21**	**0.25**
N_{sed}	Freundlich exponent to sediment based upon organic matter content (-)	ExpFreSed	-	-	-	-
K_{mp}	Coefficient for linear sorption on macrophytes (L kg^{-1})	CofSorMph	-	-	0.01	0.01

An assumption when using Saltelli's method for analyzing the sensitivity of a model is that the model is linear. With respect to the PEC_{wat} some non-linearity exists, but is not pronounced, while for the PEC_{sed}, TWA7 and TWA28 the non-linearity is more pronounced. Although the only non-linear process in TOXSWA is the equilibrium sorption according to the Freundlich isotherm to suspended solids and to sediment, the total water layer-sediment system may behave in a significant non-linear way. This happens especially, when two subsystems behave at different time scales, i.e. a fast-reacting water layer with instantaneous mixing over water depth and a slower reacting sediment with mass transport via diffusion in sediment pore water. So, in fact, the studied (local) sensitivities may not hold true for the entire parameter domain. However, as stated above, results agree well internally and can be explained from the TOXSWA model descriptions and, therefore the results are sufficiently satisfactory for our purpose of especially qualitative use.

We compared our results to the results of the sensitivity analysis for the TOXSWA model, performed by Westein et al., in 1998. They did not study sensitivities for sediment concentrations (as we did with the PEC_{sed}), but only sensitivities for the water concentrations, PEC_{wat} and TWA. The most important difference between the two studies is related to the (surprising) absence of any sensitivity for the coefficient for sorption to macrophytes, K_{mp}, while it was the found to be the most sensitive parameter with respect to TWA and one of the two most sensitive parameters with respect to the PEC_{wat} in Westein et al., (1998). The difference is explained by the range of K_{mp} which is much smaller in our study than in the prior sensitivity analysis (for details see Section 6.3). This smaller range resulted in the absence of any detectable sensitivity to the K_{mp} in our study.

The results of the sensitivity of the concentrations in the pond of this study to the pesticide process parameters correspond well with the findings in Westein et al. (1998) for the ditch with low flow velocity of 10 m d^{-1}. Thus the results of this study are also valid for the ditch simulations by TOXSWA 1.2.

8.3 Recommendations

The sensitivity analysis is performed only for the input of pesticide properties parameters (see Section 1.1, first group of parameters, here called aim S_i), given two sets of system parameters, entries and initial conditions. We were not able to also study the sensitivity to the system parameters (such as watercourse dimensions, sediment properties, etc), or the entry route parameters (such as pesticide entries via spray drift or runoff/drainage), or the influence of the input uncertainty on the output uncertainty for a specific situation (given pesticide and 'system'). The system and entry route parameters are important in defining standard scenarios for the pesticide registration procedure. As the EU FOCUS surface water scenarios are

already more than 20 years old, and no specific sediment scenarios have been defined, the issue is still relevant and, therefore, we recommend study of the sensitivity of selected outputs variables to these input parameters.
The aims for the other two groups of parameters and a fourth aim have been elaborated.

In a second step, the system parameters are involved in the sensitivity analysis. It can be identified which of the system parameters contribute most to the variation in the target model output. So, it can be assessed how important the choice of the set of system parameters is. The second aim of a sensitivity analysis for TOXSWA is therefore:
S2. *Identify which system parameters contribute most to the variation in the target model output. This is examined again for the total domain of pesticide properties derived from the pesticides in PPDB (now characterized by the limited set of sensitive process parameters found in S1).*

From S2, the system parameters that contribute most to the variation in model output are determined. Especially, these system parameters need to be quantified properly in defining standard scenarios for the registration procedure. This test can be performed with e.g. two types of waterbodies, a pond and a watercourse, representing the domain of waterbodies that are simulated by TOXSWA.

In a third step, the entry route parameters are involved in the sensitivity analysis. It can be identified which of the entry route parameters contribute most to the variation in the target model output. So, it can be assessed how important the choice of the set of entry route parameters is. The third aim is, therefore:
S3. *Identify which entry route parameters contribute most to the variation in the target model output. This is examined again for the total domain of pesticide properties derived from the pesticides in PPDB (now characterized by the limited set of sensitive process parameters found in S1) and given one (or two) set(s) of system parameters and initial conditions.*

From S3 the entry route parameters are determined that contribute most to the variation in model output. Especially, these entry route parameters need to be quantified properly in defining standard scenarios for the registration procedure.

A fourth aim can be defined as:
S4. *Identify the influence of the input uncertainty on the output uncertainty for a specific situation (given pesticide, 'system' incl. entry routes and initial conditions).*

For this fourth aim, we are not interested in the uncertainty in process or system parameters over their entire possible range, but, for a given pesticide and system, we are interested in the natural (spatial and temporal) variation and/or imperfect knowledge of their values. We are particularly interested in those uncertainty sources that can be measured with a higher precision by improved measurement techniques. In this way, it becomes apparent which model inputs need to be measured with high accuracy, to diminish the uncertainty in the calculated target model output as much as possible. This is useful for performing e.g. validation experiments.

The influence of the input uncertainty on the output uncertainty is interesting not over their entire possible range, but specifically for a given pesticide and system. So, we are interested in the natural (spatial or temporal) variation and imperfect knowledge of these values, especially those that can be measured with a high accuracy. This is useful for performing e.g. validation experiments for the TOXSWA model. So, a second recommendation is to also perform the sensitivity analysis of input parameters on selected output parameters for a situation within the desired TOXSWA validation domain.

From the current study, it is concluded that the sorption coefficient for macrophytes is not a sensitive parameter, whereas in the previous study (Westein et al., 1998) it was concluded differently. At the time of the previous study, there were no data on sorption of pesticides to macrophytes. Since then, sorption studies with pesticides and macrophytes were done, and two relationships were derived that estimate sorption coefficients for three types of macrophytes based on (i) the solubility in water, and (ii) the octanol-water partition coefficient of the pesticide (Crum et al., 1999). The first relationship performed best and has been applied in the current study. However, the number of pesticides on which the relation is based is quite small

- only nine pesticides. In addition, only sorption to three types of macrophytes was studied, *Chara globularis*, *Elodea nuttallii* and *Lemna gibba*. Therefore, we recommend more studies to improve the relations for deriving sorption coefficients for macrophytes. In the sensitivity analysis for the runoff entry in the stream PEC_{sed} and to a lesser extent TWA, concentrations were affected by the numerical discretization of sediment in the scenario. It is recommended to investigate in which situations exactly the observed phenomenon occurs and how this can be remediated, as it is unwanted that the simulated concentrations depend on the discretization used to solve the advection-diffusion equation for the sediment Solutions might be to decrease the value of the sorption coefficient for sediment, $K_{F,om,sed}$ of 17,400 L kg^{-1} to a lower value to start using the finer discretization or to use even more fine sediment discretizations.

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Justification

WOT-technical report: 275
BAPS-project number: WOT-04-008-024

Wageningen Environmental Research (WENR) values the quality of our end products greatly. A review of the reports on scientific quality by a reviewer is a standard part of our quality policy.

The report has been reviewed and approved by Pavan Cornelissen (WENR). This study was supervised by Erwin van Boekel (Wot N&M, theme Agri-environment)] and Hans Schollaart Ministry of Agriculture, Fisheries, Food Security and Nature). George van Voorn and Sjoerd Boersma from the Biometris group of Wageningen Plant Research provided advice on the statistical methods.

Approved by External contact person

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date: 15 January 2025

Annex 1 List of symbols and units

Table A1 *List of symbols and units.*

Symbol	Description[24]	Units
ε	volume fraction of pore water	-
$\kappa_{M,1m}$	coefficient defining Manning's coefficient for channel roughness in a channel with a 1 m water depth	d^{-1}
λ	relative diffusion coefficient (or tortuosity)	-
ρ_b	bulk density of dry sediment, i.e. volumic mass of dry sediment material	kg m^{-3}
A	wetted cross sectional area of flow	m^2
$A_{contr,pond}$	area next to the pond contributing water to the pond	m^2
A_{up}	size of the upstream catchment area	ha
b	bottom width of the waterbody	m
b_{crest}	width of weir crest	m
C_{weir}	discharge coefficient, depending on weir characteristics	m$^{1/2}$ d^{-1}
c_a	mass concentration of substance in the air	kg m^{-3}
$c_{ss,r}$	reference concentration in the liquid phase for sorption to suspended solids	kg m^{-3}
$c_{sed,r}$	reference concentration in the liquid phase for sorption to sediment	kg m^{-3}
c_F	coefficient	-
c_I	equilibrium mass concentration of substance at the water-gas interface in the water phase	kg m^{-3}
$c_{l,sed}$	mass concentration of substance in liquid phase in the sediment	kg m^{-3}
c^*_{sed}	Total mass concentration in the sediment	kg m^{-3}
c_{slb}	solubility of substance in water	kg m^{-3}
c^*_{wat}	mass concentration of substance in water layer, including substance sorbed to suspended solids and to macrophytes	kg m^{-3}
c_{wat}	mass concentration of substance in the water phase (excluding substance sorbed to suspended solids and to macrophytes)	kg m^{-3}
$c_{wat,F}$	concentration in water in lateral discharge, by drainage or runoff	kg m^{-3}
$D_{l,sed}$	diffusion coefficient in pore water of sediment	m^2 d^{-1}
$DT_{50,sed}$	half-life of degradation in sediment	d^{-1}
$DT_{50,wat}$	half-life of degradation in water	d^{-1}
D_{wat}	diffusion coefficient in water	m^2 d^{-1}
E_{phys}	longitudinal dispersion coefficient (in the direction of flow)	m^2 d^{-1}
h	water depth of the waterbody	m
h_{wat}	depth defining perimeter for exchange between water and sediment	m
h_{weir}	water depth immediately in front of weir	m
J_a	areic mass flux of substance across the water-air interface (kg m^{-2} d^{-1}) [the flux is negative in upward direction]	kg m^{-2} d^{-1}
$J_{l,sed}$	areic mass flux by advection, dispersion and diffusion in the liquid phase of the sediment	kg m^{-2} d^{-1}
J_{sed}	areic mass flux of substance across the water-sediment interface	kg m^{-2} d^{-1}
J_{wat}	areic mass flux of substance in water layer by advection and dispersion	kg m^{-2} d^{-1}
$K_{F,sed}$	Freundlich coefficient for sorption to sediment	m^3 kg^{-1}
$K_{F,ss}$	Freundlich coefficient for sorption to suspended solids	m^3 kg^{-1}
K_H	Henry coefficient	-
K_{mp}	distribution coefficient for substance between macrophytes and water, i.e. the slope of the linear sorption isotherm on the mass of dry macrophytes	m^3 kg^{-1}
$K_{F,oc}$	Freundlich coefficient for distribution over organic carbon and water	m^3 kg^{-1}
$K_{F,om,sed}$	Freundlich coefficient of equilibrium sorption on organic matter in sediment	m^3 kg^{-1}
$K_{F,om,ss}$	Freundlich coefficient of equilibrium sorption on organic matter in suspended solids	m^3 kg^{-1}
k_g	exchange coefficient of substance in the gas phase	m d^{-1}
k_l	exchange coefficient of substance in the liquid phase	m d^{-1}

---

[24] When the symbol differs from the symbol given by Ter Horst et al (2016), the symbol used by Adriaanse (1996) is added to the description between square brackets.

Symbol	Description[24]	Units
k_{sed}	rate coefficient for transformation of parent substance in sediment	d^{-1}
$k_{t,l}$	overall transfer coefficient of substance in the liquid phase	$m\ d^{-1}$
k_{wat}	rate coefficient for transformation of parent substance in water	d^{-1}
L	length of the pond	m
M_m	molar mass of substance m	$kg\ mol^{-1}$
m	mass of substance [M]	kg
m_{atm}	mass atmospheric deposition on the water layer	$kg\ m^{-2}\ d^{-1}$
m_{drift}	spray drift mass deposited on the water layer	$kg\ m^{-2}$
m_L	lineic mass of substance	$kg\ m^{-1}$
m_{LT}	lineic mass of substance entering the watercourse per unit of time	$kg\ m^{-1}\ d^{-1}$
m_{mp}	dry weight of macrophytes per area of sediment [DW]	$kg\ m^{-2}$
$m_{om,sed}$	mass fraction of organic matter in sediment	$kg^{-1}\ kg^{-1}$
$m_{om,ss}$	mass fraction of organic matter in suspended solids	$kg^{-1}\ kg^{-1}$
m_{ss}	mass concentration of suspended solids in the water layer	$kg\ m^{-3}$
N_{sed}	Freundlich exponent for sorption to sediment	-
N_{ss}	Freundlich exponent for sorption to suspended solids	-
P	length of perimeter	m
P_{sat}	saturated vapour pressure of substance	m
P_0	length of wetted perimeter at depth z = 0 (from the perspective of the sediment), via which exchange between water and sediment occurs	m
Q	discharge, i.e. volume flux of water passing through a vertical cross-section of the waterbody	$m^3\ d^{-1}$
Q_{base}	discharge or volume flux of the base flow delivered by the upstream catchment	$m^3\ d^{-1}$
q_F	areic volume flux of excess water from the adjacent field	$m^3\ m^{-2}\ d^{-1}$
R	universal gas constant	$J\ mol^{-1}\ K^{-1}$
s_1	side slope (horizontal/vertical)	-
T	temperature	K
t	time	d
u	flow velocity of the water	$m\ d^{-1}$
u^*	shear velocity	$m\ d^{-1}$
w_F	width of the adjacent field (perpendicular to the waterbody) discharging drainage or runoff water into the waterbody	m
W_w	width of water surface	m
X_{mp}	content of substance sorbed to macrophytes	$kg\ kg^{-1}$
z	depth in the sediment from the water-sediment interface to area concerned	m

Annex 2 Distribution characteristics used for sampling of process parameters

Table A2 gives characteristics of the normal distributions of the log10 of the pesticide properties parameters values from which the parameters are sampled by The SAlib library. The table below specifies the input for the sensitivity analysis as provided in Python. The values below represent the fitted distributions of the log10 of the parameters. The parameters values are sampled in those distributions, before being transformed back to parameter values presented in Table 5-3 using the relation $x = 10^{(log10(x))}$.

Table A2 *Mean and standard deviation of the normal distributions of the log10 of the pesticde properties parameters values.*

Parameter	**Name in TOXSWA**	**Mean**	**Standard-deviation**
Molar mass	MolMas	2.48	0.16
Saturated vapour pressure	PreVapRef	-2.28	2.38
Water solubility of substance	SlbWatRef	1.64	2.16
Half-life transformation in water at reference temperature	DT50WatRef	1.35	0.98
Half-life transformation in sediment at reference temperature	DT50SedRef	1.35	0.98
Diffusion coefficient in water	CofDifWatRef	-4.36	0.08
Freundlich coefficient of equilibrium sorption on organic matter in sediment	KomSed	2.67	1.12
Freundlich coefficient of equilibrium sorption on organic matter on suspended solids	KomSusSol	2.67	1.12
Freundlich exponent for sediment	ExpFreSed	-0.11	0.08
Freundlich exponent for suspended solids	ExpFreSusSol	-0.11	0.08
Coefficient for linear sorption on macrophytes	CofSorMph	0.93	0.61

The dictionary provided to the SAlib library in the Python tool is given below:

Description of the terms in the dictionary:

- ‘num_vars’ provides the number of variable,
- ‘names’ provides the name of the variables provided here as in the TOXSWA input files,
- ‘bounds’ are the mean and standard deviation of the distribution, and
- ‘dists’ refers to the type distribution: here all selected as being normal (‘norm’)).

```
{'num_vars': 11, 'names': ['SlbWatRef', 'PreVapRef', 'CofDifWatRef', 'MolMas', 'DT50WatRef',
'DT50SedRef', 'CofSorMph', 'KomSed', 'KomSusSol', 'ExpFreSed', 'ExpFreSusSol'], 'bounds':
[[1.6397715545840224, 2.158474909132504], [-2.283139091661541, 2.382811028517235], [-
4.357548233691261, 0.08328119380202487], [2.48216950262161, 0.15713432792834875],
[1.3457766333500618, 0.9752220194467246], [1.3457766333500618, 0.9752220194467246],
[0.9268489125608633, 0.609318932535865], [2.672579517834069, 1.1201868128033292],
[2.672579517834069, 1.1201868128033292], [-0.109, 0.08], [-0.109, 0.08]], 'dists': ['norm',
'norm', 'norm', 'norm', 'norm', 'norm', 'norm', 'norm', 'norm', 'norm', 'norm']}
```

Annex 3 Comparison of diffusion coefficients calculated with the LeBas method and with the Worch method

Two methods to calculate the diffusion coefficient in water are compared; the LeBas method using LeBas volume (used in Westein et al., 1998) and the Worch method using molar mass.

LeBas volumes are either known or estimated (see Table A3). Known values were obtained from Reid et. al (1977) (see Table A4). Estimated values were calculated from an estimated linear relation between LeBas volumes[25] and molar masses. The known and estimated values are presented in Figure A1. The diffusion coefficients estimated using LeBas and Worch method correspond reasonably well, as shown in Figure A2.

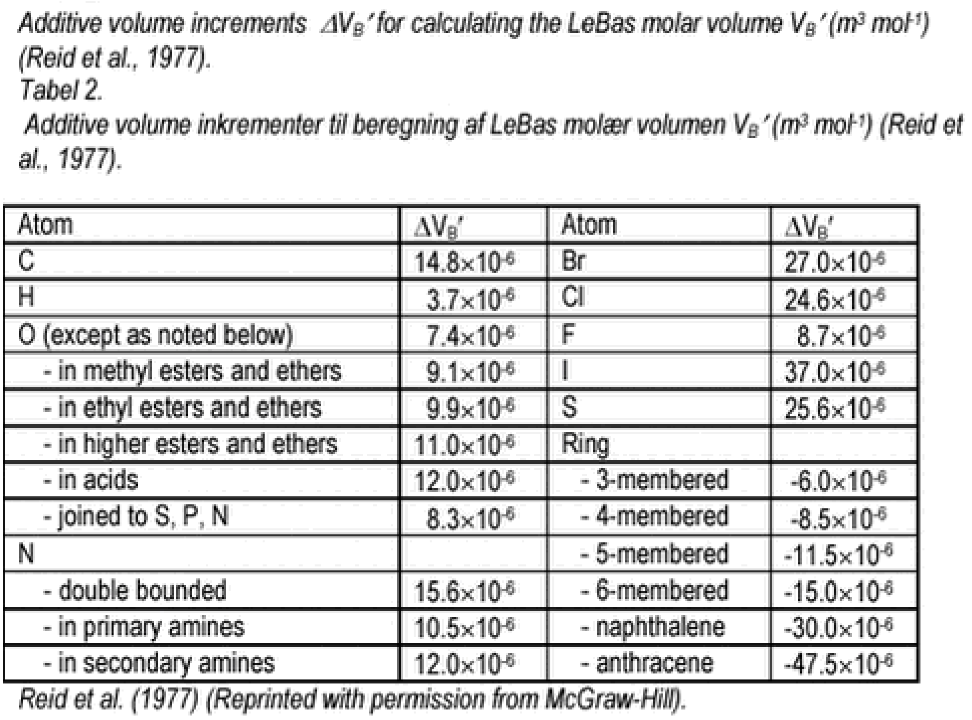
Table A3 *Known and estimated LeBas volumes (for LeBas method) and molar masses (for calculation of interpolated LeBas method, and for Worch method) of the different atoms.*

Atom	**Known Lebas volume (·10^{-6} m^{3}·mol^{-1})**	**Molar mass (g mol^{-1})**
H	2	1
O	5.48	16
N	5.69	14
F	8.7	19
C	16.5	12
S	17	32
Cl	19.5	35
Br	27	80
I	37	126
Atom	Estimated Lebas volume (·10^{-6} m^{3}·mol^{-1})	Molar mass (g mol^{-1})
Al	12.3	27
Br	27.0	80
C	16.5	12
Ca	16.3	40
Cl	19.5	35
F	8.7	19
H	2.0	1
I	37.0	126
K	16.0	39
Mn	20.9	55
N	5.7	14
Na	72.1	223
O	5.5	16
P	13.6	31
S	17.0	32
Si	12.6	28
Sn	40.1	118
Zn	23.9	65

---

[25] Note that in the estimation of the LeBas volumes applied in Westein et al. (1998), no correction was applied to the volumes to account for the type of bonds or presence of cycles (aromatic or not aromatic).

Table A4 *LeBas volume as obtained from Reid et al. (1977).*



Additive volume increments $\Delta V_B'$ for calculating the LeBas molar volume V_B' ($m^3\ mol^{-1}$) (Reid et al., 1977).
Tabel 2.
Additive volume inkrementer til beregning af LeBas molær volumen V_B' ($m^3\ mol^{-1}$) (Reid et al., 1977).

Atom	$\Delta V_B'$	Atom	$\Delta V_B'$
C	14.8×10^{-6}	Br	27.0×10^{-6}
H	3.7×10^{-6}	Cl	24.6×10^{-6}
O (except as noted below)	7.4×10^{-6}	F	8.7×10^{-6}
- in methyl esters and ethers	9.1×10^{-6}	I	37.0×10^{-6}
- in ethyl esters and ethers	9.9×10^{-6}	S	25.6×10^{-6}
- in higher esters and ethers	11.0×10^{-6}	Ring	
- in acids	12.0×10^{-6}	- 3-membered	-6.0×10^{-6}
- joined to S, P, N	8.3×10^{-6}	- 4-membered	-8.5×10^{-6}
N		- 5-membered	-11.5×10^{-6}
- double bounded	15.6×10^{-6}	- 6-membered	-15.0×10^{-6}
- in primary amines	10.5×10^{-6}	- naphthalene	-30.0×10^{-6}
- in secondary amines	12.0×10^{-6}	- anthracene	-47.5×10^{-6}

Reid et al. (1977) (Reprinted with permission from McGraw-Hill).

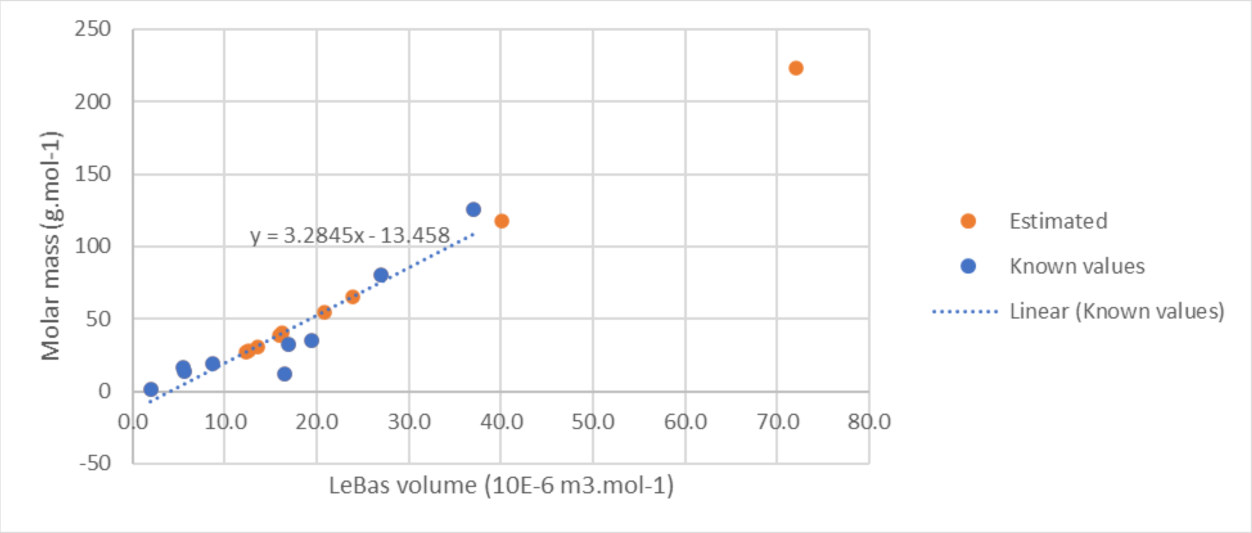


Figure A1 *Known and estimated LeBas volumes for the different atoms.*

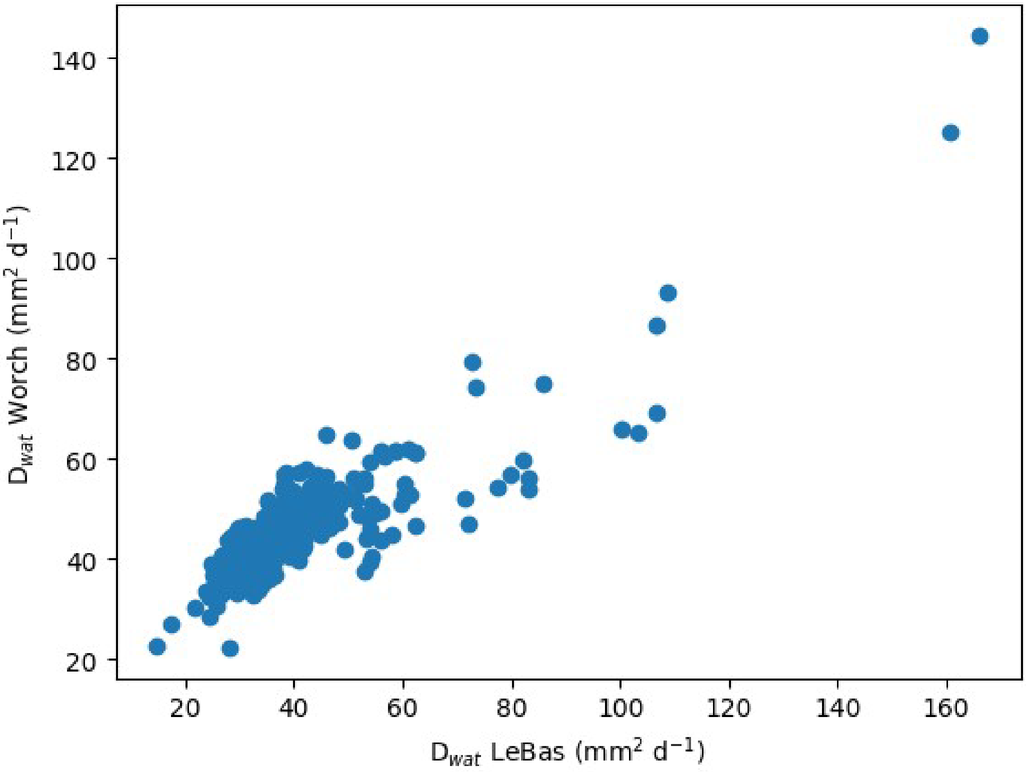


Figure A2 *Comparison of diffusion coefficients in water calculated with LeBas method (x-axis) and with Worch method (y-axis).*

References

Reid, R. C., J. M., Prausnitz, and T. K. Sherwood (1977), The Properties of Gases and Liquids, McGraw-Hill, New York.

Westein, E., M.J.W. Jansen, P.I. Adriaanse, W.H.J. Beltman (1998). Sensitivity analysis of the TOXSWA model simulating fate of pesticides in surface waters. DLO Winand Staring Centrum. Report 154.

Worch, E. (1993). Eine neue gleichung zur berechnung von diffusionskoeffizienten gelöster stoffe. Vom Wasser 81: 289-297.

Annex 4 Template of the TOXSWA input file used for the pond with spray drift entry

```
*-----------------------------------------------------------------------------------------------
* Input file for TOXSWA
*
* This file is intended to be used by expert users.
*
* E-mail: toxswa@pesticidemodels.nl
*-----------------------------------------------------------------------------------------------
* (c) Wageningen University & Research
*

* Section 0: Run identification
* Section 1: Control
* Section 2: Waterbody
* Section 3: Hydrology
* Section 4: Sediment
* Section 5: Weather
* Section 6: Temperature
* Section 7: Substance
* Section 8: Loadings
* Section 9: Initial and boundary conditions for mass balance equations
* Section 10: Output control

* This input file considers the current scenario. Input that is not needed for
* this scenario is omitted. For a description of the full input file, see the
* user manual for the FOCUS & ascii version or in your TOXSWA download package.

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 0: Run identification
*
*-----------------------------------------------------------------------------------------------

R1_Pond                  Location          ! Name of the location [1|25 characters]
R1_POND                   WaterbodyID       ! ID of the water body [1|25 characters]
Cereals_winter            CropName          ! Name of the crop [1|25 characters]
FOCUS                     SedimentTypeID    ! Name of sediment type [1|25 characters]
SA_template               SubstanceName     ! Name of parent substance [1|25 characters]
SA_spray_drift            ApplicationScheme ! Name of the application scheme [1|25 characters]


*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 1: Control
*
*-----------------------------------------------------------------------------------------------

FOCUS       CallingProgram        ! Release type of scenario [FOCUS]
6.6.4       CallingProgramVersion ! Version numbers for model, interface and database,
                                  ! respectively

   * If CallingProgram is 'FOCUS',then specify path and file name for intermediate data files
   D:\SWASH\TOXSWA\data          DirData ! Path and directory for data files
   R1_Pond_pome_stone_fruit         HydFile ! Name of .hyd file with hydrology of waterbody
   R1NOIRR                          TemFile ! Name of .tem file with temperature of waterbody

01-Mar-1969 TimStart   ! Start date of simulation [01-Jan-1900 - 31-Dec-9999]
31-May-1969 TimEnd     ! End date of simulation [01-Jan-1900 - 31-Dec-9999]

Hourly      OptInp     ! Option for hourly or daily input data of lateral entries [Hourly, Daily]

* OptHyd: options for hydrology simulation
* Only      Simulate only hydrology
* OnLine    Simulate hydrology and substance
* OffLine   Assumption hydrology has been simulated, runID.hyd file must be present
* Automatic TOXSWA checks if hydrology file (runID.hyd) exists; so, hydrology
*           simulation is skipped
Automatic   OptHyd     ! Option selected for hydrology simulation
                       ! [Only, OnLine, OffLine, Automatic]

600.        TimStpHyd (s)    ! Calculation time step for hydrology [0.001|3600]

* OptTem: options for temperature simulation
* Only      Simulate only temperature
* OnLine    Simulate temperature and substance
* OffLine   Assumption temperature has been simulated, runID.tem file must be present
* Automatic TOXSWA checks if the temperature file (runID.tem) exists; so, temperature
```

```
*           simulation is skipped
Automatic   OptTem    ! Option selected for temperature simulation
                      ! [Only, OnLine, OffLine, Automatic, ExtModel]

Calc        OptTimStp                ! Time step substance simulation options (Input, Calc)
Yes         OptCalcStabilityWater    ! Option for check of stability of the numerical solution for
                                     ! the water layer
Yes         OptCalcStabilitySediment ! Option for check of stability of the numerical solution for
                                     ! the sediment [Yes, No]
                                     ! Yes = Full check on stability
                                     ! No = Check on positivity

    * If OptTimStp is 'Calc' then specify
    3600.       MaxTimStpWat (s) ! Maximum calculation time step in water layer [0.001|3600]
    600.        MaxTimStpSed (s) ! Maximum calculation time step in sediment [0.001|3600]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 2: Waterbody
*
*-----------------------------------------------------------------------------------------------

* WaterBody table: description of waterbody
* Len           Length [0.05|]
* NumSeg        Number of segments [1|]
* WidWatSys     Width of the bottom of water system [0.05|100]
* SloSidWatSys  Side slope  of the water system [0|10]
* DepWatDefPer  Water depth defining perimeter for exchange between water layer
*               and sediment [0|lowest water depth]

table WaterBody
Len       NumSeg    WidWatSys SloSidWatSys DepWatDefPer
(m)       (-)       (m)       (-)          (m)
30.       1         30.       1E-005       0.01
end_table

15.         ConSus (g.m-3)       ! Concentration of suspended solids [0|100000]
0.09        CntOmSusSol (g.g-1)  ! Mass ratio of organic matter in suspended solids [0|1]
200          AmaMphWatLay (g.m-2) ! Dry mass of macrophyte biomass per m2 bottom [0|1000]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section  3: Hydrology: general
*   Section 3a: General
*-----------------------------------------------------------------------------------------------

Transient           OptFloWat             ! Option for water flow (Constant, Transient)
    * If OptFloWat is 'Transient' then specify
    Pond        OptWaterSystemType  ! Water system type [Pond, WaterCourse]


*-----------------------------------------------------------------------------------------------
* Section 3b: Constant water flow
*
* If OptFloWat is 'Constant'
*-----------------------------------------------------------------------------------------------


*-----------------------------------------------------------------------------------------------
* Section 3c: Variable water flow: pond
*
* If OptFloWat is 'Transient' and OptWaterSystemType is 'Pond'
*-----------------------------------------------------------------------------------------------

0.45        AreaSurPndInp (ha)  ! Size of surrounding area discharging excss water into the pond
                               ! [0|100]
5.754       QBasPndInp (m3.d-1) ! Base flow, i.e. inflow into pond [0|50]
1.          HgtCrePnd (m)       ! Height of the weir crest at outflow [0.1|5]
0.5         WidCrePnd (m)       ! Width of the weir crest at outflow [0.01|10]

    * If application option OptLoa is 'PRZM' then specify
    0.06        AreaErsSurPndInp (ha)  ! Size of the eroding area around the pond [0|100]

*-----------------------------------------------------------------------------------------------
* Section 3d: Variable water flow: watercourse
*
* If OptFloWat is 'Transient' and OptWaterSystemType is 'WaterCourse'
*-----------------------------------------------------------------------------------------------


*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 4: Sediment
*
*-----------------------------------------------------------------------------------------------

*SedimentProfile table: thickness and number of segments in horizon
* ThiHor  Thickness of horizon [0.0001|-]
* NumSeg  Number of segments in horizon [1|500]
table SedimentProfile
```

```
ThiHor    NumSeg
(m)
0.004     4
0.006     3
0.01      2
0.03      3
0.02      1
0.03      1
end_table

Input       OptSedProperties   ! Sediment properties for ThetaSat and CofDifRel [Input, Calc]

* SedimentProperties table: properties for each horizon:
* Nr        Number horizon [1|500]
* Rho       Bulk density [10|3000]
* CntOm     Organic matter mass content [0|1]
* If OptSedProperties 'Input' then specify ThetaSat and CofDifRel
* ThetaSat  Saturated water content [0.001|0.999]
* CofDifRel Relative diffusion coefficient [0|1]
table  horizon SedimentProperties
Nr        Rho       CntOm     ThetaSat  CofDifRel
          (kg.m-3)  (kg.kg-1) (m3.m-3)  (-)
1         800.      0.09      0.6       0.6
2         800.      0.09      0.6       0.6
3         800.      0.09      0.6       0.6
4         800.      0.09      0.6       0.6
5         800.      0.09      0.6       0.6
6         800.      0.09      0.6       0.6
end_table

0.          FlwWatSpg (m3.m-2.d-1) ! Percolation rate through the sediment [-0.01|0.01]


*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 5: Weather section
*
*-----------------------------------------------------------------------------------------------

R1NOIRR.MET    MeteoStation ! Name of file with meteo data (*.met)

DailyAir            OptMetInp ! Input data [MonthlyAir, DailyAir]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 6: Temperature
*
*-----------------------------------------------------------------------------------------------

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section  7: Substance
*   Section 7a: general
*-----------------------------------------------------------------------------------------------

* Compounds table: first entry is parent, next entries are metabolites [1|15 characters]
table compounds                      ! List of substances
EXSW2_2020
end_table

* FraPrtDauWat table: parent-daughter relationships transformation in water
* Column 1: fraction formed from parent into daughter [0|]
* Column 2: name of parent
* Column 3: name of daughter
table FraPrtDauWat (mol.mol-1)
end_table

* FraPrtDauSed table: parent-daughter relationships transformation in sediment
* Column 1: fraction formed from parent into daughter [0|]
* Column 2: name of parent
* Column 3: name of daughter
table FraPrtDauSed (mol.mol-1)
end_table

*-----------------------------------------------------------------------------------------------
* Section 7b: Substance properties for parent EXSW2_2020
* (note extension of parameter name is substance code)
*-----------------------------------------------------------------------------------------------

<MolMas>        MolMas_EXSW2_2020 (g.mol-1)         ! Molar mass of parent substance [10.0 - 10000]

* Volatilization from water layer
<PreVapRef>      PreVapRef_EXSW2_2020 (Pa)           ! Saturated vapour pressure of substance [0|2e5]
20.         TemRefVap_EXSW2_2020 (C)            ! Reference temperature for saturated vapour pressure
                                                     ! [0|40]
95.         MolEntVap_EXSW2_2020 (kJ.mol-1)     ! Molar enthalpy of vaporization [-200|200]
<SlbWatRef>         SlbWatRef_EXSW2_2020 (mg.L-1)       ! Water solubility of substance [0.001|1e6]
20.         TemRefSlb_EXSW2_2020 (C)            ! Reference temperature for water solubility [0|40]
27.         MolEntSlb_EXSW2_2020 (kJ.mol-1)     ! Molar enthalpy of dissolution  [-200|200]
```

```
* Diffusion in liquid phase
<CofDifWatRef>      CofDifWatRef_EXSW2_2020 (m2.d-1)    ! Reference diffusion coefficient in water [0|2E-3]

* Sorption
<KomSed>         KomSed_EXSW2_2020 (L.kg-1)          ! Freundlich coefficient of  equilibrium sorption for
                                                     ! sediment [0|1e7]
1.          ConLiqRefSed_EXSW2_2020 (mg.L-1)    ! Reference concentration in liquid phase for
                                                     ! Freundlich coefficient for sediment [0.001|100]
<ExpFreSed>          ExpFreSed_EXSW2_2020 (-)            ! Freundlich exponent  in sediment [0.1|1.5]
<KomSusSol>         KomSusSol_EXSW2_2020 (L.kg-1)       ! Freundlich coefficient of  equilibrium sorption
                                                     ! for suspended solids [0|1e7]
1.          ConLiqRefSusSol_EXSW2_2020 (mg.L-1) ! Reference concentration in liquid phase
                                                     ! for Freundlich sorption coefficient for
                                                     ! suspended solids [0.001|100]
<ExpFreSusSol>          ExpFreSusSol_EXSW2_2020 (-)         ! Freundlich exponent suspended solids [0.1|1.5]
<CofSorMph>          CofSorMph_EXSW2_2020 (L.kg-1)       ! Coefficient for linear sorption on
                                                     ! macrophytes [0|1e7]

* Transformation in water
<DT50WatRef>        DT50WatRef_EXSW2_2020 (d)           ! Half-life transformation in water at reference
                                                     ! temperature [0.1|1e5]
20.         TemRefTraWat_EXSW2_2020 (C)         ! Reference temperature for half-life measured in
                                                     ! water [5|30]
65.4        MolEntTraWat_EXSW2_2020 (kJ.mol-1)  ! Molar activation enthalpy of transformation in
                                                     ! water [0|200]

* Transformation in sediment
<DT50SedRef>        DT50SedRef_EXSW2_2020 (d)           ! Half-life transformation in sediment at reference
                                                     ! temperature [0.1|1e5]
20.         TemRefTraSed_EXSW2_2020 (C)         ! Reference temperature for half-life in sediment
                                                     ! [5|30]
65.4        MolEntTraSed_EXSW2_2020 (kJ.mol-1)  ! Molar activation enthalpy of transformation in
                                                     ! sedment [0|200]

* If CallingProgram is 'FOCUS' and substance is parent, then specify
* transformation in soil parameters entered in SWASH for soil models MACRO/PRZM
* for reporting in summary file (parameters not used by TOXSWA)
300.        DT50SoilRef_EXSW2_2020 (d)           ! Half-life transformation in sediment at reference
                                                 ! temperature [0.1|1e5]
20.         TemRefTraSoil_EXSW2_2020 (C)         ! Reference temperature for half-life in soil [5|30]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 8: Loadings
*
*-----------------------------------------------------------------------------------------------

* OptLoa options for loading type
* DriftOnly  spray drift only entry route
* MACRO      drainage calculated by MACRO
* PRZM       runoff and erosion calculated by PRZM
PRZM        OptLoa         ! Loading option [DriftOnly, MACRO, PRZM]

* Stretch for all loading types
Yes     OptLoaStr   ! Loading to full stretch of water body [Yes|No]

* Loadings table: details loading
* Column 1  Date and time of application
* Column 2  Application type []
* Column 3  Mass of loading [kg.ha-1) [0|]
* Column 4  Crop interception fraction [-) [0|1]
* Column 5  Drift deposition (mg.m-2) [0|]
* Column 6  Atmospheric deposition (mg.m-2) [0|]
* Note that the info in columns 2 - 4 is not used in the calculation
table Loadings
04-Mar-1969-09h00       air_blast      0.1      0.6    3.8617E-001    0
end_table

    * If OptLoa is 'PRZM' then specify details of runoff
    0.          WidFldRnf (m)       ! Width of field contributing runoff [0|1000]
    0.          WidFldErs (m)       ! Width of field contributing erosion [0|1000]
    0.1         RatInfDir (-)       ! Ratio of infiltraton water added to runoff water [0|1]
    0.01        ThiLayErs (m)       ! Thickness of upper sediment layer to which erosion mass
                                    ! is added [1e-5|1]

    * If OptLoa is 'MACRO' or OptLoa is 'PRZM' then specify path and file names of files
    * Table lateral entries files of soil substances, including metabolites (path+name)

    table Soil Substances
    00028-C1.p2t
    end_table

    * If OptHyd is 'transient' and OptWaterSystemType is 'WaterCourse' then specify details of catchment
    No          OptUpsInp           ! Upstream catchment treated [Yes, No]
    0.          RatAreaUpsApp (-)   ! Ratio of upstream catchment treated [0|1]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 9: Initial and boundary conditions for mass balance equations
*
*-----------------------------------------------------------------------------------------------
```

```
* Initial conditions

0.          ConSysWatIni (g.m-3)  ! Initial total concentration in water layer [0|-]

* CntSysSedIni table: initial total substance content in sediment
* If metabolites are included then initail contents for these substances are set to zero
* Column 1  Depth in sediment (m) [0|-]
* Column 2  Substance content (mg.kg-1) [0|-]
table interpolate CntSysSedIni (mg.kg-1)
end_table

* Boundary conditions
0.          ConAir (g.m-3)        ! Concentration  in air [0|-]

0.          ConWatSpg (g.m-3)     ! Concentration in incoming seepage water [0|-]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section  10: Output control
*   Section 10a: General
*-----------------------------------------------------------------------------------------------

No          OptDelOutFiles   ! Remove *.out file after simulation [Yes|No]
* DateFormat: options for format of date and time in the output file
* DaysFromSta   Print number of days since start of simulation
* DaysFrom1900  Print number of days since 1900
* Years         Print years
DaysFromSta           DateFormat       DateFormat [DaysFromSta, DaysFrom1900, Years]

* RealFormat: format of the ordinary output - use FORTRAN notation:
* e is scientific notation, g  is general notation,
* then the number of positions, then the number of digits
e14.6                 RealFormat       ! Format of ordinary output

* OptDelTimPrn: options for output time step
* Hour,Day,Decade,Month,Year  Time step for output
* Automatic                   Length of simulation period
* Other                       User defined
Hour        OptDelTimPrn  ! Output time step [Hour|Day|Decade|Month|Year|
                          ! Automatic|Other]

0.01        ThiLayTgt1 (m)   ! Depth defining the thickness of the target sediment layer 1
                             ! for output of (averaged) content [1e-5|1]

No          OptOutputThiLayTgt2  ! Output of contents in 2nd target layer of sediment [Yes|No]

None      OptOutputDistances ! Options for distances of water layer grid points at which
                             ! output can be obtained[None, All, table]

* Specify dates for output of additional profiles; options set via OptOutputDistances and
* OptOutputDepths are used
* HorVertProfiles table: profiles in horizontal direction for water layer and in vertical
* direction for sediment are given; values given are:
* Water layer: output distance, water depth, total and dissolved concentration,
* Sediment: output node water layer, output depth, pore volume, total and dissolved
* concentration.
table HorVertProfiles
end_table

* Specify type of summary report
FOCUS                 OptReport        ! [FOCUS]
Yes                   ExposureReport   ! Exposure report [Yes|No]

* Specify warming-up period
0           InitYears (-)    ! Length of warming-up period in years [0|]

* Target percentile in time, and target period for selection
0           TargetPercentile (%) ! Target percentile resulting in selected year [0|100]
01-Jan      StaTimPrdTgt         ! Start date of target period for selection of
                                 ! year with target percentile [01-Jan|31-Dec]
31-Dec      EndTimPrdTgt         ! End date of target period for selection of
                                 ! year with target percentile [01-Jan|31-Dec]

*  ! Print column oriented output files (csv format)
No          ConcentrationsTgt  ! Concentration in water FOCUS target segment and contents in
                               ! FOCUS target sediment layers
No          MassBalWaterLayer  ! Mass balance of substance in water layer
No          MassBalSediment    ! Mass balance of substance in sediment
No          Distribution       ! Distribution of substance in water body
No          Hydrology          ! Water depth and discharge
No          LateralFluxes      ! Lateral water flows and substance fluxes from drainage
                               ! runoff and erosion
*-----------------------------------------------------------------------------------------------
* Section 10b: Print variables in *.out file
* State variables, fluxes and rates given as momentary values.
*-----------------------------------------------------------------------------------------------

* Specify for all print variables whether output is wanted [Yes, No]
* When print variable is not in file; TOXSWA assumes 'No'

* PrintCumulatives: options for printing cumulatives of volume, energy and mass fluxes
```

```
* Yes   : cumulative terms have been summed up from start of simulation and have been
*         allocated to the last moment of the period considered
* No    : cumulative terms have been summed up from start of user defined output time step
*         OptDelTimPrn and have been allocated to the last moment of the period
*         considered
No          PrintCumulatives ! [Yes, No]

* Hydrology

* Lateral entries (expressed per m2 adjacent field)

* Concentrations and contents in water layer segments as specified by
* OptOutputDistances

* Concentrations and contents in sediment below water layer segments as specified by
* OptOutputDistances and OptOutputDepths

* Distribution in entire water layer

* Distribution in entire sediment

* Mass balance for entire water layer

* Mass balance sediment

*-----------------------------------------------------------------------------------------------
* End of TOXSWA input file
*-----------------------------------------------------------------------------------------------
```

Annex 5 Template of TOXSWA input file used for the stream with runoff entry and excerpt of PRZM p2t file with runoff entries

Template of TOXSWA input file

```
*-----------------------------------------------------------------------------------------------
* Input file for TOXSWA
*
* This file is intended to be used by expert users.
*
* E-mail: toxswa@pesticidemodels.nl
*-----------------------------------------------------------------------------------------------
* (c) Wageningen University & Research
*

* Section 0: Run identification
* Section 1: Control
* Section 2: Waterbody
* Section 3: Hydrology
* Section 4: Sediment
* Section 5: Weather
* Section 6: Temperature
* Section 7: Substance
* Section 8: Loadings
* Section 9: Initial and boundary conditions for mass balance equations
* Section 10: Output control

* This input file considers the current scenario. Input that is not needed for
* this scenario is omitted. For a description of the full input file, see the
* user manual for the FOCUS & ascii version or in your TOXSWA download package.

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 0: Run identification
*
*-----------------------------------------------------------------------------------------------

R1_Stream                 Location          ! Name of the location [1|25 characters]
R1_STREAM                 WaterbodyID       ! ID of the water body [1|25 characters]
oil_seed_rape_spring      CropName          ! Name of the crop [1|25 characters]
FOCUS                     SedimentTypeID    ! Name of sediment type [1|25 characters]
EXSW2_2020                SubstanceName     ! Name of parent substance [1|25 characters]
FOCUS_EXAMPLE             ApplicationScheme ! Name of the application scheme [1|25 characters]


*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 1: Control
*
*-----------------------------------------------------------------------------------------------

FOCUS       CallingProgram        ! Release type of scenario [FOCUS]
6.6.4       CallingProgramVersion ! Version numbers for model, interface and database,
                                  ! respectively

   * If CallingProgram is 'FOCUS',then specify path and file name for intermediate data files
   D:\SA_code\SA2412        DirData ! Path and directory for data files
   R1_Stream_oil_seed_rape_spring   HydFile ! Name of .hyd file with hydrology of waterbody
   R1NOIRR                          TemFile ! Name of .tem file with temperature of waterbody

01-Mar-1969 TimStart   ! Start date of simulation [01-Jan-1900 - 31-Dec-9999]
15-Apr-1969 TimEnd     ! End date of simulation [01-Jan-1900 - 31-Dec-9999]

Hourly      OptInp     ! Option for hourly or daily input data of lateral entries [Hourly, Daily]

* OptHyd: options for hydrology simulation
* Only      Simulate only hydrology
* OnLine    Simulate hydrology and substance
* OffLine   Assumption hydrology has been simulated, runID.hyd file must be present
* Automatic TOXSWA checks if hydrology file (runID.hyd) exists; so, hydrology
*           simulation is skipped
Automatic   OptHyd     ! Option selected for hydrology simulation
                       ! [Only, OnLine, OffLine, Automatic]

600.        TimStpHyd (s)    ! Calculation time step for hydrology [0.001|3600]
```

```
* OptTem: options for temperature simulation
* Only      Simulate only temperature
* OnLine    Simulate temperature and substance
* OffLine   Assumption temperature has been simulated, runID.tem file must be present
* Automatic TOXSWA checks if the temperature file (runID.tem) exists; so, temperature
*           simulation is skipped
Automatic   OptTem    ! Option selected for temperature simulation
                       ! [Only, OnLine, OffLine, Automatic, ExtModel]

Calc        OptTimStp                ! Time step substance simulation options (Input, Calc)
No          OptCalcStabilityWater   ! Option for check of stability of the numerical solution for
                                     ! the water layer
Yes         OptCalcStabilitySediment ! Option for check of stability of the numerical solution for
                                     ! the sediment [Yes, No]
                                     ! Yes = Full check on stability
                                     ! No = Check on positivity

    * If OptTimStp is 'Calc' then specify
    3600.       MaxTimStpWat (s) ! Maximum calculation time step in water layer [0.001|3600]
    600.        MaxTimStpSed (s) ! Maximum calculation time step in sediment [0.001|3600]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 2: Waterbody
*
*-----------------------------------------------------------------------------------------------

* WaterBody table: description of waterbody
* Len           Length [0.05|]
* NumSeg        Number of segments [1|]
* WidWatSys     Width of the bottom of water system [0.05|100]
* SloSidWatSys  Side slope  of the water system [0|10]
* DepWatDefPer  Water depth defining perimeter for exchange between water layer
*               and sediment [0|lowest water depth]

table WaterBody
Len       NumSeg    WidWatSys SloSidWatSys DepWatDefPer
(m)       (-)       (m)       (-)          (m)
100.      20        1.        1E-005       0.01
end_table

15.         ConSus (g.m-3)       ! Concentration of suspended solids [0|100000]
0.09        CntOmSusSol (g.g-1)  ! Mass ratio of organic matter in suspended solids [0|1]
200.          AmaMphWatLay (g.m-2) ! Dry mass of macrophyte biomass per m2 bottom [0|1000]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section  3: Hydrology: general
*   Section 3a: General
*-----------------------------------------------------------------------------------------------

Transient           OptFloWat             ! Option for water flow (Constant, Transient)
    * If OptFloWat is 'Transient' then specify
    WaterCourse OptWaterSystemType  ! Water system type [Pond, WaterCourse]

    * If OptWaterSystemType is 'WaterCourse' then specify
    Fischer     OptDis   ! Dispersion calculation method [Input, Fischer]


*-----------------------------------------------------------------------------------------------
* Section 3b: Constant water flow
*
* If OptFloWat is 'Constant'
*-----------------------------------------------------------------------------------------------


*-----------------------------------------------------------------------------------------------
* Section 3c: Variable water flow: pond
*
* If OptFloWat is 'Transient' and OptWaterSystemType is 'Pond'
*-----------------------------------------------------------------------------------------------


*-----------------------------------------------------------------------------------------------
* Section 3d: Variable water flow: watercourse
*
* If OptFloWat is 'Transient' and OptWaterSystemType is 'WaterCourse'
*-----------------------------------------------------------------------------------------------

100.        AreaUpsWatCrsInp (ha)  ! Area of upstream catchment [0|1e4]
191.8       QBasWatCrsInp (m3.d-1) ! Base flow from upstream catchment [0|1e4]
0.001       SloBotRepCha (-)       ! Slope bottom representative channel [0|0.01]
0.5         HgtCreRepCha (m)       ! Height of the weir crest [0.01|5]
0.5         WidCreRepCha (m)       ! Width of the weir crest [0.01|10]
110.        LenRepCha (m)          ! Length representative channel [10|2000]
1.          WidBotRepCha (m)       ! Width bottom representative channel [0.1 - 10]
11.         CofRghRef (s-1)        ! Value Manning coefficient for bottom roughness at 1 m
                                   ! water depth in water body [1|100]
1.2         CofVelHea (m.s-1)      ! Energy coefficient due to non-uniform distribution of
                                   ! flow velocities in cross section [1.1|1.5]
```

```
*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 4: Sediment
*
*-----------------------------------------------------------------------------------------------

*SedimentProfile table: thickness and number of segments in horizon
* ThiHor  Thickness of horizon [0.0001|-]
* NumSeg  Number of segments in horizon [1|500]
table SedimentProfile
ThiHor    NumSeg
(m)
0.004     4
0.006     3
0.01      2
0.03      3
0.02      1
0.03      1
end_table

Input       OptSedProperties   ! Sediment properties for ThetaSat and CofDifRel [Input, Calc]

* SedimentProperties table: properties for each horizon:
* Nr        Number horizon [1|500]
* Rho       Bulk density [10|3000]
* CntOm     Organic matter mass content [0|1]
* If OptSedProperties 'Input' then specify ThetaSat and CofDifRel
* ThetaSat  Saturated water content [0.001|0.999]
* CofDifRel Relative diffusion coefficient [0|1]
table  horizon SedimentProperties
Nr        Rho       CntOm     ThetaSat  CofDifRel
          (kg.m-3)  (kg.kg-1) (m3.m-3)  (-)
1         800.      0.09      0.6       0.6
2         800.      0.09      0.6       0.6
3         800.      0.09      0.6       0.6
4         800.      0.09      0.6       0.6
5         800.      0.09      0.6       0.6
6         800.      0.09      0.6       0.6
end_table

0.          FlwWatSpg (m3.m-2.d-1) ! Percolation rate through the sediment [-0.01|0.01]


*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 5: Weather section
*
*-----------------------------------------------------------------------------------------------

R1NOIRR.MET MeteoStation ! Name of file with meteo data (*.met)

DailyAir            OptMetInp ! Input data [MonthlyAir, DailyAir]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 6: Temperature
*
*-----------------------------------------------------------------------------------------------

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section  7: Substance
*   Section 7a: general
*-----------------------------------------------------------------------------------------------

* Compounds table: first entry is parent, next entries are metabolites [1|15 characters]
table compounds                      ! List of substances
EXSW2_2020
end_table

* FraPrtDauWat table: parent-daughter relationships transformation in water
* Column 1: fraction formed from parent into daughter [0|]
* Column 2: name of parent
* Column 3: name of daughter
table FraPrtDauWat (mol.mol-1)
end_table

* FraPrtDauSed table: parent-daughter relationships transformation in sediment
* Column 1: fraction formed from parent into daughter [0|]
* Column 2: name of parent
* Column 3: name of daughter
table FraPrtDauSed (mol.mol-1)
end_table

*-----------------------------------------------------------------------------------------------
* Section 7b: Substance properties for parent EXSW2_2020
* (note extension of parameter name is substance code)
*-----------------------------------------------------------------------------------------------
```

```
<MolMas>        MolMas_EXSW2_2020 (g.mol-1)         ! Molar mass of parent substance [10.0 - 10000]

* Volatilization from water layer
<PreVapRef>      PreVapRef_EXSW2_2020 (Pa)           ! Saturated vapour pressure of substance [0|2e5]
20.         TemRefVap_EXSW2_2020 (C)            ! Reference temperature for saturated vapour pressure
                                                     ! [0|40]
95.         MolEntVap_EXSW2_2020 (kJ.mol-1)     ! Molar enthalpy of vaporization [-200|200]
<SlbWatRef>         SlbWatRef_EXSW2_2020 (mg.L-1)       ! Water solubility of substance [0.001|1e6]
20.         TemRefSlb_EXSW2_2020 (C)            ! Reference temperature for water solubility [0|40]
27.         MolEntSlb_EXSW2_2020 (kJ.mol-1)     ! Molar enthalpy of dissolution  [-200|200]

* Diffusion in liquid phase
<CofDifWatRef>      CofDifWatRef_EXSW2_2020 (m2.d-1)    ! Reference diffusion coefficient in water [0|2E-3]

* Sorption
<KomSed>         KomSed_EXSW2_2020 (L.kg-1)          ! Freundlich coefficient of  equilibrium sorption for
                                                     ! sediment [0|1e7]
1.          ConLiqRefSed_EXSW2_2020 (mg.L-1)    ! Reference concentration in liquid phase for
                                                     ! Freundlich coefficient for sediment [0.001|100]
<ExpFreSed>          ExpFreSed_EXSW2_2020 (-)            ! Freundlich exponent  in sediment [0.1|1.5]
<KomSusSol>         KomSusSol_EXSW2_2020 (L.kg-1)       ! Freundlich coefficient of  equilibrium sorption
                                                     ! for suspended solids [0|1e7]
1.          ConLiqRefSusSol_EXSW2_2020 (mg.L-1) ! Reference concentration in liquid phase
                                                     ! for Freundlich sorption coefficient for
                                                     ! suspended solids [0.001|100]
<ExpFreSusSol>          ExpFreSusSol_EXSW2_2020 (-)         ! Freundlich exponent suspended solids [0.1|1.5]
<CofSorMph>          CofSorMph_EXSW2_2020 (L.kg-1)       ! Coefficient for linear sorption on
                                                     ! macrophytes [0|1e7]

* Transformation in water
<DT50WatRef>        DT50WatRef_EXSW2_2020 (d)           ! Half-life transformation in water at reference
                                                     ! temperature [0.1|1e5]
20.         TemRefTraWat_EXSW2_2020 (C)         ! Reference temperature for half-life measured in
                                                     ! water [5|30]
65.4        MolEntTraWat_EXSW2_2020 (kJ.mol-1)  ! Molar activation enthalpy of transformation in
                                                     ! water [0|200]

* Transformation in sediment
<DT50SedRef>        DT50SedRef_EXSW2_2020 (d)           ! Half-life transformation in sediment at reference
                                                     ! temperature [0.1|1e5]
20.         TemRefTraSed_EXSW2_2020 (C)         ! Reference temperature for half-life in sediment
                                                     ! [5|30]
65.4        MolEntTraSed_EXSW2_2020 (kJ.mol-1)  ! Molar activation enthalpy of transformation in
                                                     ! sedment [0|200]

* If CallingProgram is 'FOCUS' and substance is parent, then specify
* transformation in soil parameters entered in SWASH for soil models MACRO/PRZM
* for reporting in summary file (parameters not used by TOXSWA)
300.        DT50SoilRef_EXSW2_2020 (d)           ! Half-life transformation in sediment at reference
                                                 ! temperature [0.1|1e5]
20.         TemRefTraSoil_EXSW2_2020 (C)         ! Reference temperature for half-life in soil [5|30]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 8: Loadings
*
*-----------------------------------------------------------------------------------------------

* OptLoa options for loading type
* DriftOnly  spray drift only entry route
* MACRO      drainage calculated by MACRO
* PRZM       runoff and erosion calculated by PRZM
PRZM        OptLoa         ! Loading option [DriftOnly, MACRO, PRZM]

* Stretch for all loading types
Yes     OptLoaStr   ! Loading to full stretch of water body [Yes|No]

* Loadings table: details loading
* Column 1  Date and time of application
* Column 2  Application type []
* Column 3  Mass of loading [kg.ha-1) [0|]
* Column 4  Crop interception fraction [-) [0|1]
* Column 5  Drift deposition (mg.m-2) [0|]
* Column 6  Atmospheric deposition (mg.m-2) [0|]
* Note that the info in columns 2 - 4 is not used in the calculation
table Loadings
end_table

    * If OptLoa is 'PRZM' then specify details of runoff
    100.        WidFldRnf (m)       ! Width of field contributing runoff [0|1000]
    20.         WidFldErs (m)       ! Width of field contributing erosion [0|1000]
    0.1         RatInfDir (-)       ! Ratio of infiltraton water added to runoff water [0|1]
    0.01        ThiLayErs (m)       ! Thickness of upper sediment layer to which erosion mass
                                    ! is added [1e-5|1]

    * If OptLoa is 'MACRO' or OptLoa is 'PRZM' then specify path and file names of files
    * Table lateral entries files of soil substances, including metabolites (path+name)

    table Soil Substances
    00010-C1.p2t
    end_table
```

```
    * If OptHyd is 'transient' and OptWaterSystemType is 'WaterCourse' then specify details of catchment
    Yes         OptUpsInp           ! Upstream catchment treated [Yes, No]
    0.2         RatAreaUpsApp (-)   ! Ratio of upstream catchment treated [0|1]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section 9: Initial and boundary conditions for mass balance equations
*
*-----------------------------------------------------------------------------------------------

* Initial conditions

0.          ConSysWatIni (g.m-3)  ! Initial total concentration in water layer [0|-]

* CntSysSedIni table: initial total substance content in sediment
* If metabolites are included then initail contents for these substances are set to zero
* Column 1  Depth in sediment (m) [0|-]
* Column 2  Substance content (mg.kg-1) [0|-]
table interpolate CntSysSedIni (mg.kg-1)
end_table

* Boundary conditions
0.          ConAir (g.m-3)        ! Concentration  in air [0|-]

0.          ConWatSpg (g.m-3)     ! Concentration in incoming seepage water [0|-]

*-----------------------------------------------------------------------------------------------
*-----------------------------------------------------------------------------------------------

* Section  10: Output control
*   Section 10a: General
*-----------------------------------------------------------------------------------------------

No          OptDelOutFiles   ! Remove *.out file after simulation [Yes|No]
* DateFormat: options for format of date and time in the output file
* DaysFromSta   Print number of days since start of simulation
* DaysFrom1900  Print number of days since 1900
* Years         Print years
DaysFromSta           DateFormat       DateFormat [DaysFromSta, DaysFrom1900, Years]

* RealFormat: format of the ordinary output - use FORTRAN notation:
* e is scientific notation, g  is general notation,
* then the number of positions, then the number of digits
e14.6                 RealFormat       ! Format of ordinary output

* OptDelTimPrn: options for output time step
* Hour,Day,Decade,Month,Year  Time step for output
* Automatic                   Length of simulation period
* Other                       User defined
Hour        OptDelTimPrn  ! Output time step [Hour|Day|Decade|Month|Year|
                          ! Automatic|Other]

0.01        ThiLayTgt1 (m)   ! Depth defining the thickness of the target sediment layer 1
                             ! for output of (averaged) content [1e-5|1]

No          OptOutputThiLayTgt2  ! Output of contents in 2nd target layer of sediment [Yes|No]

table      OptOutputDistances ! Options for distances of water layer grid points at which
                             ! output can be obtained[None, All, table]
table OutputDistances (m)
97.5
end_table
* Specify dates for output of additional profiles; options set via OptOutputDistances and
* OptOutputDepths are used
* HorVertProfiles table: profiles in horizontal direction for water layer and in vertical
* direction for sediment are given; values given are:
* Water layer: output distance, water depth, total and dissolved concentration,
* Sediment: output node water layer, output depth, pore volume, total and dissolved
* concentration.
table HorVertProfiles
end_table

* Specify type of summary report
FOCUS                 OptReport        ! [FOCUS]
Yes                   ExposureReport   ! Exposure report [Yes|No]

* Specify warming-up period
0           InitYears (-)    ! Length of warming-up period in years [0|]

* Target percentile in time, and target period for selection
0           TargetPercentile (%) ! Target percentile resulting in selected year [0|100]
01-Jan      StaTimPrdTgt         ! Start date of target period for selection of
                                 ! year with target percentile [01-Jan|31-Dec]
31-Dec      EndTimPrdTgt         ! End date of target period for selection of
                                 ! year with target percentile [01-Jan|31-Dec]

*  ! Print column oriented output files (csv format)
No          ConcentrationsTgt  ! Concentration in water FOCUS target segment and contents in
                               ! FOCUS target sediment layers
No          MassBalWaterLayer  ! Mass balance of substance in water layer
No          MassBalSediment    ! Mass balance of substance in sediment
```

```
No          Distribution       ! Distribution of substance in water body
No          Hydrology          ! Water depth and discharge
No          LateralFluxes      ! Lateral water flows and substance fluxes from drainage
                               ! runoff and erosion
*-----------------------------------------------------------------------------------------------
* Section 10b: Print variables in *.out file
* State variables, fluxes and rates given as momentary values.
*-----------------------------------------------------------------------------------------------

* Specify for all print variables whether output is wanted [Yes, No]
* When print variable is not in file; TOXSWA assumes 'No'

* PrintCumulatives: options for printing cumulatives of volume, energy and mass fluxes
* Yes   : cumulative terms have been summed up from start of simulation and have been
*         allocated to the last moment of the period considered
* No    : cumulative terms have been summed up from start of user defined output time step
*         OptDelTimPrn and have been allocated to the last moment of the period
*         considered
No          PrintCumulatives ! [Yes, No]

* Hydrology

* Lateral entries (expressed per m2 adjacent field)

* Concentrations and contents in water layer segments as specified by
* OptOutputDistances

* Concentrations and contents in sediment below water layer segments as specified by
* OptOutputDistances and OptOutputDepths

* Distribution in entire water layer
Yes print_ConLiqWatLay
Yes print_VvrLiqRnf
Yes print_QBou
Yes print_VelWatFlw
Yes print_ConSysSed

* Distribution in entire sediment

* Mass balance for entire water layer

* Mass balance sediment

*-----------------------------------------------------------------------------------------------
* End of TOXSWA input file
*-----------------------------------------------------------------------------------------------
```

Excerpt of PRZM p2t file with runoff entry

On 4 March 1969 a runoff volume flux of 1 mm containing 0.5 mg m^{-2} enters the stream in a period of eight hours (00:00 h – 08:00h). Hence, the hourly fluxes are 0.125 mm h^{-1} and 0.0625 mg m^{-2} h^{-1}. This period is shown in the exerpt. The whole file covers the period 1 March 1969 – 31 May 1969, all fluxes are zero for dates not shown.

```
*       p2tmaker v1.2021.115.2
*       Started on      "Monday,"       January "22,"   2024
*       at      8:55:22 AM
*       on      machine D0160759 (12    CPUs)
*       OS      Microsoft       Windows NT      6.2.9200.0
*       Culture en-US
*
*       Working directory       :       D:\SWASH6projects\project_SA_R1\PRZM\oil_seed_rape_spring

*       PRZM    file    (*.ZTS) :       R1-OS-.ZTS
*       Crop    :       Oil     seed    "rape," spring
*       Scenario :      "R1,"   Weiherbach      pond/stream
*       Tier    :       Step    3
*       Sim     start   :       01-Jan-69
*       end     :       31-Dec-94
*       Applns  per     season  :       1
*  Chemical:  EXSW2_2020
*       Parent  run
*
*       Total   number  of      applns
#       0
*
*
*       Number  of      Time    Mass
*       Application     dd-MMM-YYYY-hh:mm       (g      ai/ha)

*
*               Runoff  Runoff  Erosion Erosion
*       Time    Volume  flux    Mass    Flux    Infiltration
*       dd-MMM-YYYY-hh:mm       (mm/h)  (mg as/m2/h)    (kg/h)  (mg as/m2/h)    (mm/h)          (mm/h)
        01-Mar-1969-01:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        .
        .
        03-Mar-1969-24:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-01:00       1.25E-01 6.25E-02 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-02:00       1.25E-01 6.25E-02 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-03:00       1.25E-01 6.25E-02 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-04:00       1.25E-01 6.25E-02 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-05:00       1.25E-01 6.25E-02 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-06:00       1.25E-01 6.25E-02 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-07:00       1.25E-01 6.25E-02 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-08:00       1.25E-01 6.25E-02 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-09:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-10:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-11:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-12:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-13:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-14:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-15:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        04-Mar-1969-16:00       0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
        .
        .
```

Annex 6 Second-order Sobol index values

A6.1. Second-order Sobol index S2, values for pond with spray drift

Second-order index values of the sensitivity analysis ran for the pesticide properties parameters for the pond system with spray drift entry. The colour scale from white to dark visualises the range of the values across the four outputs: maximum PEC$_{wat}$, PEC$_{sed}$,TWA7 and TWA28. The colours vary from white to dark blue, with white values for negative values. ≤-0.02. The dark blue corresponds to values ≥ 0.12.

Table A1 *Second-order index values for the process parameters calculated for PEC$_{wat}$ in the R1 pond with spray drift entry.*

PEC$_{wat}$	SlbWatRef	PreVapRef	CofDifWatRef	MolMas	DT50WatRef	DT50SedRef	CofSorMph	KomSed	KomSusSol	ExpFreSed	ExpFreSusSol
SlbWatRef		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PreVapRef			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CofDifWatRef				0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MolMas					0.00	0.00	0.00	0.00	0.00	0.00	0.00
DT50WatRef						0.00	0.00	0.00	0.00	0.00	0.00
DT50SedRef							0.00	0.00	0.00	0.00	0.00
CofSorMph								0.00	0.00	0.00	0.00
KomSed									0.00	0.00	0.00
KomSusSol										0.00	0.06
ExpFreSed											0.00
ExpFreSusSol											

Table A2 *Second-order index values for the process parameters calculated for PEC_{sed} in the R1 pond with spray drift entry.*

PEC_{sed}	SlbWatRef	PreVapRef	CofDifWatRef	MolMas	DT50WatRef	DT50SedRef	CofSorMph	KomSed	KomSusSol	ExpFreSed	ExpFreSusSol
SlbWatRef		0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PreVapRef			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CofDifWatRef				0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00
MolMas					0.00	0.00	0.00	0.00	0.00	0.00	0.00
DT50WatRef						0.01	0.00	0.03	0.00	0.00	0.00
DT50SedRef							0.01	0.05	0.01	0.02	0.01
CofSorMph								0.00	0.00	0.00	0.00
KomSed									0.00	0.00	0.00
KomSusSol										0.00	0.00
ExpFreSed											0.00
ExpFreSusSol											

Table A3 *Second-order index values for the process parameters calculated for TWA7 in the R1 pond with spray drift entry.*

TWA7	SlbWatRef	PreVapRef	CofDifWatRef	MolMas	DT50WatRef	DT50SedRef	CofSorMph	KomSed	KomSusSol	ExpFreSed	ExpFreSusSol
SlbWatRef		0.12	-0.01	-0.01	0.00	-0.01	-0.01	0.00	-0.01	-0.01	-0.01
PreVapRef			-0.02	-0.02	-0.01	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02
CofDifWatRef				0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MolMas					0.00	0.00	0.00	0.00	0.00	0.00	0.00
DT50WatRef						0.00	0.00	0.01	0.00	0.00	0.00
DT50SedRef							0.00	0.00	0.00	0.00	0.00
CofSorMph								0.00	0.00	0.00	0.00
KomSed									0.00	0.00	0.00
KomSusSol										0.01	0.01
ExpFreSed											0.00
ExpFreSusSol											

Table A4 *Second-order index values for the process parameters calculated for TWA28 in the R1 pond with spray drift entry.*

TWA28	SlbWatRef	PreVapRef	CofDifWatRef	MolMas	DT50WatRef	DT50SedRef	CofSorMph	KomSed	KomSusSol	ExpFreSed	ExpFreSusSol
SlbWatRef		0.07	-0.01	-0.01	0.00	-0.01	-0.01	0.00	0.00	-0.01	-0.01
PreVapRef			-0.01	-0.01	0.00	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
CofDifWatRef				0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MolMas					0.00	0.00	0.00	0.00	0.00	0.00	0.00
DT50WatRef						0.00	0.00	0.02	0.00	0.00	0.00
DT50SedRef							0.00	0.00	0.00	0.00	0.00
CofSorMph								0.00	0.00	0.00	0.00
KomSed									0.00	0.00	0.00
KomSusSol										0.00	0.00
ExpFreSed											0.00
ExpFreSusSol											

A6.2. Second-order Sobol index S2, values for stream with run off entry

Second-order index values of the sensitivity analysis ran for the pesticide properties parameters for the stream system with a runoff entry are given in Table A5 to Table A8. The colour scale from white to dark visualises the range of the values across the four outputs: maximum PEC_{wat}, PEC_{sed},TWA7 and TWA28. The colours vary from white to dark blue, with white values for negative values ≤-0.04. This is met three or four times for the PECs in water. The dark blue corresponds to values ≥ 0.06, met once for PEC_{sed} and for the two TWAs.

Table A5 *Second-order index values for the process parameters calculated for PEC_{wat} in the R1 stream with runoff entry.*

PECwat	**SlbWatRef**	**PreVapRef**	**CofDifWatRef**	**MolMas**	**DT50WatRef**	**DT50SedRef**	**CofSorMph**	**KomSed**	**KomSusSol**	**ExpFreSed**	**ExpFreSusSol**
SlbWatRef		0.01	0.00	0.00	0.00	0.00	0.00	0.00	-0.03	0.00	0.00
PreVapRef			-0.01	-0.01	-0.01	0.00	0.00	-0.01	-0.04	0.00	-0.01
CofDifWatRef				0.00	0.00	0.00	0.00	0.00	-0.04	0.00	0.00
MolMas					0.00	0.00	0.00	0.00	-0.04	0.00	0.00
DT50WatRef						0.00	0.00	0.00	0.00	0.00	0.00
DT50SedRef							0.00	0.00	0.00	0.00	0.00
CofSorMph								0.00	0.00	0.00	0.00
KomSed									0.00	0.00	0.00
KomSusSol										-0.02	-0.02
ExpFreSed											0.00
ExpFreSusSol											

Table A6 *Second-order index values for the process parameters calculated for PEC_{sed} in the R1 stream with runoff entry.*

PEC_{sed}	**SlbWatRef**	**PreVapRef**	**CofDifWatRef**	**MolMas**	**DT50WatRef**	**DT50SedRef**	**CofSorMph**	**KomSed**	**KomSusSol**	**ExpFreSed**	**ExpFreSusSol**
SlbWatRef		0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.00
PreVapRef			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CofDifWatRef				0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
MolMas					0.00	0.00	0.00	0.00	0.00	0.00	0.00
DT50WatRef						0.00	0.00	0.00	0.00	0.00	0.00
DT50SedRef							0.00	0.00	0.00	0.00	0.00
CofSorMph								0.00	0.00	0.00	0.00
KomSed									0.01	0.01	0.00
KomSusSol										0.00	0.00
ExpFreSed											0.00
ExpFreSusSol											

Table A7 *Second-order index values for the process parameters calculated for TWA7 in the R1 stream with runoff entry.*

TWA7	**SlbWatRef**	**PreVapRef**	**CofDifWatRef**	**MolMas**	**DT50WatRef**	**DT50SedRef**	**CofSorMph**	**KomSed**	**KomSusSol**	**ExpFreSed**	**ExpFreSusSol**
SlbWatRef		0.06	0.01	0.01	0.00	0.00	0.00	0.01	-0.02	0.01	0.01
PreVapRef			-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.03	-0.01	-0.01
CofDifWatRef				0.00	0.00	0.00	0.00	0.01	-0.02	0.00	0.00
MolMas					0.00	0.00	0.00	0.00	-0.02	0.00	0.00
DT50WatRef						0.00	0.00	-0.01	0.01	0.00	0.00
DT50SedRef							0.01	0.01	0.00	0.01	0.00
CofSorMph								0.00	0.00	0.00	0.00
KomSed									0.00	0.00	0.00
KomSusSol										-0.01	-0.01
ExpFreSed											0.00
ExpFreSusSol											

Table A8 *Second-order index values for the process parameters calculated for TWA28 in the R1 stream with runoff entry.*

TWA28	**SlbWatRef**	**PreVapRef**	**CofDifWatRef**	**MolMas**	**DT50WatRef**	**DT50SedRef**	**CofSorMph**	**KomSed**	**KomSusSol**	**ExpFreSed**	**ExpFreSusSol**
SlbWatRef		0.06	0.00	0.01	0.00	0.00	0.00	0.01	-0.02	0.01	0.01
PreVapRef			-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.03	-0.01	-0.01
CofDifWatRef				0.00	0.00	0.00	0.00	0.01	-0.02	0.00	0.00
MolMas					0.00	0.00	0.00	0.00	-0.02	0.00	0.00
DT50WatRef						0.00	0.00	-0.01	0.01	0.00	0.00
DT50SedRef							0.01	0.01	0.00	0.01	0.01
CofSorMph								0.00	0.00	0.00	0.00
KomSed									0.00	0.00	-0.01
KomSusSol										-0.01	-0.01
ExpFreSed											0.00
ExpFreSusSol											

Annex 7 Distribution of pesticides properties

A7.1. Selected pesticides and properties

A7.1.1. Introduction

This section provides an overview of the distribution of selected physico-chemical properties, for the pesticides currently approved at the EU level. The pesticide properties data is taken from the Pesticide Properties Database (PPDB) (Lewis et al., 2016), which includes all synthetic pesticides currently registered in the EU, as well as those no longer registered in the EU, but which may still be used in e.g. Africa or China. For this work, we selected only the synthetic pesticides approved at the EU level, this selection resulted in 379 entries.

A7.1.2. Material and methods

A7.1.2.1. Pesticides approved in the EU in the pesticides properties database (PPDB)
The PPDB is: *"a comprehensive relational database of pesticide physicochemical, toxicological, ecotoxicological, human health and other related data. It contains data relating to synthetic pesticides and their metabolites"* and is developed by the University of Hertfordshire's (UH) Agriculture & Environment Research Unit (AERU) (Lewis et al., 2016). We used the version of the 10th of March 2023, which contains more than 2,500 entries.

A7.1.2.2. Difference between the entries in the PPDB and EU database
The number of pesticides listed in the PPDB as approved in the EU is less than the official number of pesticides approved in the EU. In the PPDB, the information relative to the approval status (at EU level) was retrieved from the columns *"EC Regulation 1107/2009 status"* (the value should be *"approved"* or contain "approved", such as *"approved as kaolin").* This selection process yielded 379 entries[26]. This is less than the 445 active substances approved at EU level (EU Pesticide Database[27] at date 19/10/2023). The differences between the numbers of approved active substances in both databases results from their different purposes: the EU Pesticide Database presents all approved active substances, while the PPDB focusses on the synthetic chemicals, as explained below.

The PPDB was initially constructed for synthetic pesticides and does not contain all approved active substances found in EU Pesticide Database, notably when they stem from biological sources, for instance microorganisms. Regarding approved active substances, the PPDB is here less complete than the EU Pesticide Database which explains the lesser number of entries for the approved substances in the PPDB.

The PPDB has a second specificity which makes it different from the EU Pesticide Database. The salts of a given approved active substance may be registered as *"approved"* in the PPDB as a separated entry, while the EU Pesticide Database only contains the approved active substance and does not provide a separate entry for its salt. Therefore, when selecting substances based on their approval status in the PPDB, the salts of such substances may be included in the selection as an individual entry, while it would not be accounted for in the EU Pesticide Database. This inflates the number of entries in the PPDB compared to the EU Pesticide Database. However, because the number of approved substances in the PPDB is already much lower than in the EU Pesticide Database as explained above, the number of approved substances in the PPDB is less than the 445 approved substances of the EU Pesticide Database.

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[26] Note that this selection differs from the selection made earlier in this report which contains additional criteria: the selection process applied in the report is detailed in Section 5.2.

[27] EU Pesticide Database: https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/start/screen/active-substances

A7.1.2.3. Selection of properties

The 10 selected pesticides properties are presented in the Table A9 below. This table provides the preferred name for the property, the unit, as well as the name provided in the PPDB database. We selected eight pesticide properties present in the PPDB and calculated two lumped properties often used to characterize the volatilization process: the dimensionless Henry coefficient (K_H), and the overall transfer coefficient ($TC_{wat-air}$).

The selected set of properties obtained directly from the PPDB is presented below:

- Molar mass M_m,
- Saturated vapour pressure P_{sat},
- Solubility in water c_{slb},
- Degradation half-life in soil $DT_{50,soil}$,
- Degradation half-life in water-sediment systems $DT_{50,wat-sed}$,
- Sorption coefficient (either linear sorption or Freundlich) based upon the organic carbon content in soil K_{oc} and $K_{F,oc}$,
- Freundlich exponent (N), additional property to describe the sorption isotherm, required for pesticides for which the Freundlich sorption coefficient is provided (further detail about potential confusion regarding the Freundlich exponent is provided in the Box A1).

The volatilization process is often characterized by some lumped property to characterize the pesticide, e.g. volatile or not volatile. Using the data from the PPDB, we also calculated two lumped properties:

- Dimensionless Henry coefficient, K_H, a generally known property used to rank pesticides based on their volatilization capacity (e.g., Lyman et al., 1982)
- Overall mass transfer coefficient (called $TC_{wat-air}$ in Adriaanse et al. (2022)).

The method to calculate these properties is presented below Table A9.

Table A9 *List of the 10 properties. The data is obtained from the PPDB database except if indicated otherwise.*

Property	Symbol	Unit	Calculated/name in PPDB
Molar mass	M_m	g mol^{-1}	Molecular mass
Saturated vapour pressure at 20°C	P_{sat}	mPa	Vapour pressure at 20 °C (mPa)[28]
Water solubility of substance at 20°C	c_{slb}	mg L^{-1}	Solubility - In water at 20 °C (mg/L)[28]
Half-life transformation in soil (lab)	$DT_{50,soil}$	d	Soil DT50 - Lab (days)[29]
Half-life transformation in water-sediment	$DT_{50,wat-sed}$	d	Water-sediment DT50 (days)[29]
Linear sorption coefficient to organic carbon	K_{oc}	L kg^{-1}	Koc (mL/g)
Freundlich sorption coefficient to organic carbon	$K_{F,oc}$	L kg^{-1}	Kfoc (mL/g)
Freundlich exponent for soil in relation to the Freundlich sorption coefficient	N	-	Freundlich exponent (1/n)
Henry coefficient	K_H	-	*Calculated using eq. 1*
Overall mass transfer coefficient water-air	$TC_{wat-air}$	M d^{-1}	*Calculated using eq. 2*

Lumped property's calculation

The Henry coefficient is calculated from the data provided in the PPDB database via:

$$K_H = \frac{P_{sat} \cdot M_m}{R \cdot T} \cdot \frac{1}{C_{slb}} \qquad (1)$$

with:

K_H = dimensionless Henry coefficient (-)
P_{sat} = saturated vapour pressure of pesticide (Pa)
M_m = molar mass (g mol^{-1})
R = universal gas constant (J mol^{-1} K^{-1})
T = temperature at which the saturated vapour pressure and the solubility are defined (K)
c_{slb} = solubility of pesticide in water (g m^{-3})

---

[28] The PPDB provides the values for c_{slb} and P_{sat} adjusted to the temperature of 20°C.

[29] The PPDB does not provide information relative to the temperature at which the data are provided.

The overall mass transfer coefficient $TC_{wat-air}$ is also calculated from the PPDB database data, via:

$$TC_{wat-air} = \frac{1}{\frac{1}{k_l} + \frac{1}{K_H \cdot k_g}} \qquad (2)$$

The values for the transport coefficients of pesticides in water (k_l) and air (k_g) were not available from literature but can be calculated using other properties of the pesticides. They can be derived from (Liss and Slater 1974):

$$k_l = k_{l,CO_2} \frac{\sqrt{M_{CO_2}}}{\sqrt{M_m}} \qquad (3) \qquad \text{and} \qquad k_g = k_{g,H_2O} \frac{\sqrt{M_{H_2O}}}{\sqrt{M_m}} \qquad (4)$$

with:

k_{l,CO_2} = transport coefficient CO_2 in liquid phase (= 4.8 m d^{-1})
M_{CO_2} = molar mass CO_2 (= 44 g mol^{-1})
M_m = molar mass pesticide (g mol^{-1})
k_{g,H_2O} = transport coefficient H_2O in gas phase (= 720 m d^{-1})
M_{H_2O} = molar mass H_2O (= 18 g mol^{-1})

A7.1.2.4. Completeness of the PPDB regarding the selected properties and impact on the number of available values

For several properties, the total number of values (first row of the summary Table A12 which summarises the characteristics of the distribution of the values) is significantly less than the total number of active substances approved in the PPDB, which is 379 (see Section A7.1.2.2). For instance, the number of values available varied from at most 375 (for the molar mass) to 153 (for the linear sorption coefficient based upon organic carbon in soil K_{oc}). The reason is that not all properties have been specified or are applicable to all pesticides of the list. E.g.:

- For some pesticides, the properties (such as sorption coefficient, saturated vapour pressure) are applicable to organic pesticides, but are unapplicable or make little sense for other types of pesticides. For instance, for three examples:
  - Vapour pressure for talc E553B or aluminum sulphate.
  - Sorption coefficient for beer or Bordeaux mixture.
  - Molar mass for beer.
- When the properties mentioned above (saturated vapour pressure, solubility, molar mass) are missing, the lumped properties (Henry coefficient and overall mass transfer coefficient), cannot be calculated (see equations in the Section A7.1.2.3), which yields a lower number of values for the lumped properties.
- For some pesticides, the data is not available, as approval is based on another approved active substances, and therefore, the data is provided only for this other active substance. Three examples include:
  - The insecticide, kappa-tefluthrin, was approved based on the data provided for tefluthrin.
  - different salts of picloram (picloram-trolamine, picloram-potassium, etc.) have been approved based on available data for picloram or for one of its salts.
  - Similarly, the 11 dicamba-based chemicals which are in this selection of 379 substances have been approved based on dicamba properties; however the properties of those salts are not consistently reported in the PPDB with the exception of their molar mass.
- Both K_{oc} and $K_{F,oc}$ values can be equally used in the approval process. So, one or the other property needs to be provided in the database. For 153 pesticides, the K_{oc} value is available (of which, 48 pesticides are not provided a $K_{F,oc}$), and for 228 values the $K_{F,oc}$ is available (of which, 123 are not provided a K_{oc}). So, for 105 pesticides, both K_{oc} and $K_{F,oc}$ values are available. When summing the compounds for which a sorption coefficient is specified in the PPDB, this yields the total of 276 compounds (105 which are provided both sorption coefficients, plus 48 which have only a K_{oc}, plus 123 which have only a $K_{F,oc}$).
- Surprisingly, although the Freundlich sorption coefficient $K_{F,oc}$ is always defined with a corresponding exponent (called Freundlich exponent), this exponent was not provided for two of the pesticides for which a Freundlich sorption coefficient was defined, which explains the difference between the counts (228 for $K_{F,oc}$ and 226 for the Freundlich exponent). The database seems to be uncomplete here.

- More surprisingly, but maybe explained in the approval documents, no values for DT_{50} in water-sediment are available for some organic compounds such as isofetamid (fungicide), triflusulfuron (herbicide), or penoxsulam (aquatic herbicide). The database seems to be uncomplete here.

Box A1 Possible confusion regarding the Freundlich exponent

Possible confusion regarding the definition of the Freundlich exponent
Note that the Freundlich exponent is provided in the database as "Freundlich coefficient (1/n)" and the notation can be confusing as explained below. The document "Background and support" which is provided with the PPDB database informs that the Freundlich exponent corresponds in this case to the relationship:

$$Q = KC^{1/n} \tag{5}$$

with:
Q = absorbed amount of pesticide (µg/kg)
C = the equilibrium concentration (µg/L)
K = sorption coefficient, experimental parameter unique to the Freundlich isotherm ($L^{1/n}µg^{1-1/n}kg^{-1}$)*
n = experimental parameter unique to the Freundlich isotherm (-)*

*No detailed information related to the definition and the unit of the sorption coefficient was provided in the Background information of the PPDB, the information reported here are derived by the authors of this report.

In the documents describing the processes modelled in TOXSWA (for instance in the section 2.2 and 2.3 of this report), the Freundlich exponent N is defined as presented here with the example of sorption to sediment:

$$\boldsymbol{X_{sed}} = \boldsymbol{m_{om,sed} K_{F,om,sed}\, c_{sed,ref}} \left(\frac{\boldsymbol{c_{l,sed}}}{\boldsymbol{c_{sed,ref}}} \right)^{\boldsymbol{N_{sed}}} \tag{6}$$

with:
X_{sed} = mass content sorbed to sediment ($mg^{-1}\ kg^{-1}$)
$m_{om,sed}$ = mass fraction of organic matter in sediment ($kg^{-1}\ kg^{-1}$)
$K_{F,om,sed}$ = Freundlich coefficient for sorption to organic matter in sediment ($L\ kg^{-1}$)
$c_{sed,ref}$ = reference concentration in the liquid phase for sorption to the sediment ($mg\ L^{-1}$)
$c_{l,sed}$ = mass concentration of substance in liquid phase in the sediment ($mg\ L^{-1}$)
N_{sed} = Freundlich exponent for sorption to sediment (-)

The value 1/n provided in the PPDB corresponds therefore to the values of the parameter N (and not 1/ N).

A7.1.2.5. Data preparation

In the PPDB, some numerical values (approximately 10 values) were not entered as numbers and were therefore not directly usable. We adjusted the data to be able to include them in our dataset when possible. Examples of actions taken to clean the database are presented in Table A10.

Table A10 *Actions taken to prepare the pesticide data when they were not provided.*

Non numerical data	Action	Example
Data containing a sign '<', '>'	The signs were removed, attributing the threshold value to the data	'<150' becomes '150'
DT50 is provided as being 'Stable'	The pesticide does not degrade, a high DT50 is provided.	'Stable' becomes '1000'
Two values are provided	The average value is used	'2450 / 2520' becomes '2485'
Value is indicated as mean	The value is used	'754.0 (mean)' becomes '754'
Values are not provided 'nd', '0', 'Not calculated'	Cell is emptied	'0' becomes '' (empty cell)
Additional words or letters are in the cell	Those words or letters are removed	'332 typical' becomes '332'

To obtain a regular bin width, the bin width of the histograms was constrained for the plots presented on a log scale. To that aim, the interval between the minimum and maximal value was divided in equal intervals on the log scale. For intervals that are not easily readable (i.e. not a power of 10), the intervals are provided in the table below on a linear scale as shown in Table A11. Note that some of the bins indicated below might be empty.

Table A11 *Bin widths of the histograms for DT50 in soil and DT50 in water-sediment (log10 scale, translated to linear scale), molar mass and Freundlich exponent (linear scale).*

Property	Bin width
DT50 water-sediment	[0.01, 0.02, 0.04, 0.08, 0.16, 0.3, 0.6, 1.3, 2.5, 5, 10, 20, 40, 79, 158, 316, 631, 1259, 2512, 5011, 10000, 19953]
DT50 soil	[0.001, 0.002, 0.004, 0.008, 0.016, 0.03, 0.06, 0.13, 0.25, 0.50, 1.0, 2.0, 4.0, 8.0, 16, 32, 63, 126, 251, 501, 1000 (999.9), 1995]
Molar mass	[32, 102, 173, 243, 314, 384, 455, 525, 595, 666, 736, 807, 877, 948, 1018, 1089]
Freundlich exponent (1/n)	[0.095, 0.17, 0.25, 0.33, 0.41, 0.50, 0.57, 0.64, 0.72, 0.80, 0.88, 0.95, 1.04, 1.11, 1.19, 1.27]

A7.1.3. Tabular and graphical distribution

The distributions of properties related to the pesticides properties are presented through their characteristics (Table A12) and are also presented graphically (Figure A3). Physico-chemical properties, as the ones presented here, often follow a lognormal distribution. This is why the graphical visualisation of the data on a log-scale facilitates the reading of the data. No metabolite is part of the selection, unless it is approved as an active substance itself.

A7.1.3.1. Characteristics of the distributions of the properties

Table A12 presents the distributions characteristics (for instance percentiles, minimum and maximum, and number of values available) of the 10 properties for the selected active substances, i.e. synthetic chemicals approved for use in the EU.

The number of values (first row) does not always comply with the number of approved substances in the PPDB, which was of 379. This is explained in Section A7.1.2.4. The number of values corresponds to the number of pesticides on the left axis of Figure A3.

Table A12 *Distributions characteristics of the properties relative to the properties of active substances approved for use in the EU.*

	Molar mass M_m	**Solubility in water at 20°C** C_{Slb}	**Vapour pressure at 20°C** P_{Sat}	**Soil DT_{50} (lab)** $DT_{50,soil}$	**Water-sediment DT_{50}** $DT_{50,wat,sed}$	**Linear sorption coefficient** K_{oc}	**Freundlich sorption coefficient** $K_{F,oc}$	**Freundlich exponent** $(1/n)$	**Henry coefficient** K_H[30]	**Mass transfer Coefficient** $TC_{wat\text{-}air}$[16]
Number of values	*375*	*314*	*288*	*296*	*229*	*153*	*228*	*226*	*285*	*285*
unit	(g/mol)	(mg/L)	(mPa)	(days)	(days)	(L/kg)	(L/kg)	(-)	(-)	(m/d)
mean	307	84888	$7.55 \cdot 10^{6}$	68	139	4440	58365	0.90	1.9	$1.2 \cdot 10^{-1}$
standard deviation	130	$3.2 \cdot 10^{5}$	$9.7 \cdot 10^{7}$	140	278	21865	$6.8 \cdot 10^{5}$	0.10	25	$5.7 \cdot 10^{-1}$
minimum	32	$1.0 \cdot 10^{-9}$	$1.9 \cdot 10^{-12}$	0.001	0.02	0.1	1	0.10	$2.2 \cdot 10^{-19}$	$3.7 \cdot 10^{-17}$
25% percentile	227	1	$8.0 \cdot 10^{-5}$	2.0	5.2	27	85	0.85	$4.8 \cdot 10^{-11}$	$9.1 \cdot 10^{-9}$
50% percentile (median)	306	37.5	$6.6 \cdot 10^{-3}$	19.7	27	162	415	0.91	$1.0 \cdot 10^{-8}$	$1.9 \cdot 10^{-6}$
75% percentile	379	3040	$1.4 \cdot 10^{-1}$	58.4	141	1424	2643	0.95	$2.2 \cdot 10^{-6}$	$3.7 \cdot 10^{-4}$
maximum	1089	$4.0 \cdot 10^{6}$	$1.6 \cdot 10^{9}$	1000	2369	$2.5 \cdot 10^{5}$	$1.0 \cdot 10^{7}$	1.27	423	4.8

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[30] As stipulated above, both K_H and $TC_{wat\text{-}air}$ are calculated based on the PPDB data, using the equations (1) and (2), respectively.

A7.1.3.2. Distributions of the properties

The distributions of the selected properties are presented in Figure A3 below (see next pages).

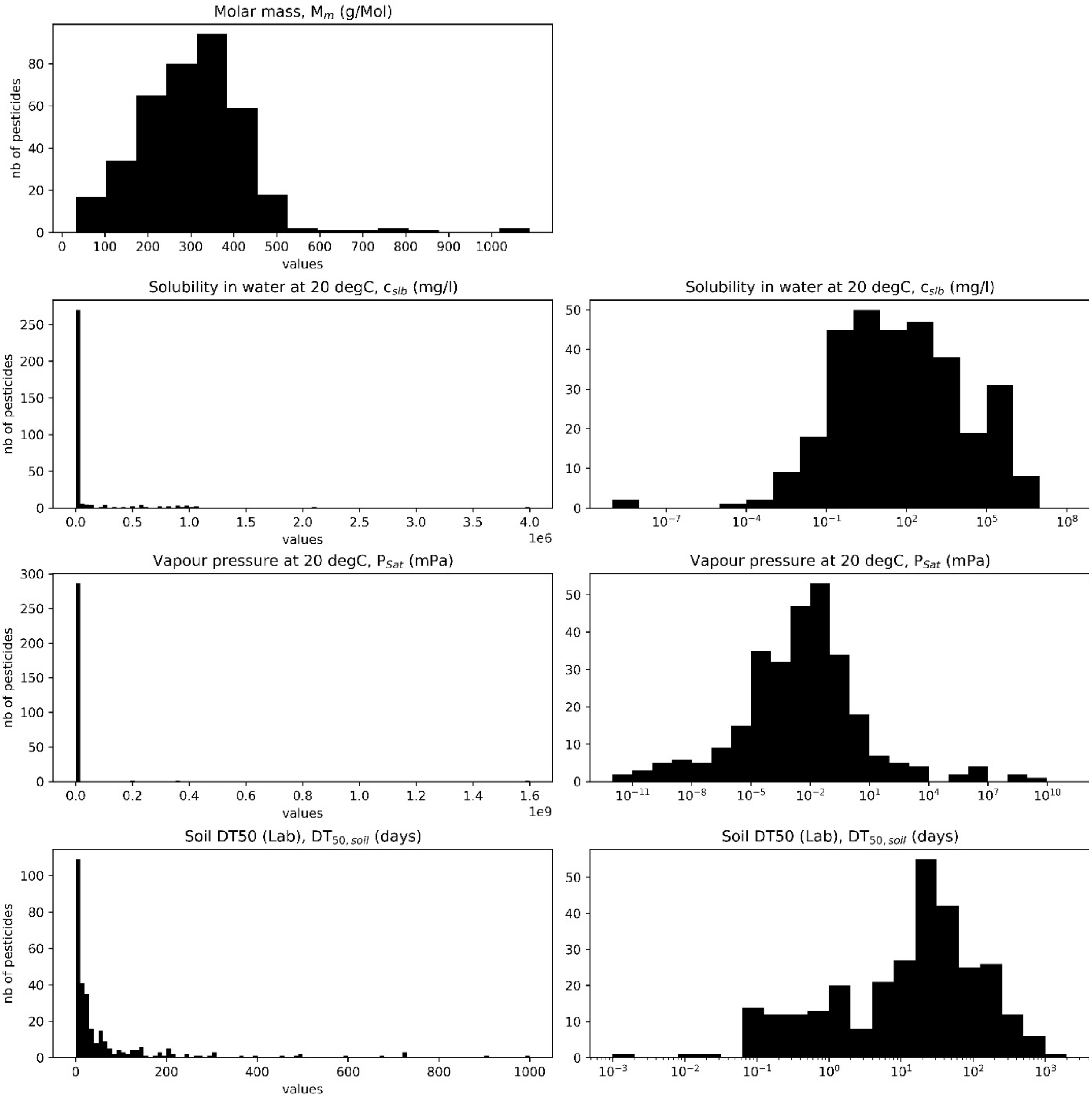

Figure A3 *Distribution of pesticides properties (source: PPDB). Left, normal x-axis, right log10 x-axis. For the log10 data, the bin width is a power of 10 except for the DT50 in water-sediment and in soil. The bin widths for both DT50 in soil and DT50 in the water-sediment system are provided in Table A11. The bin widths for the Freundlich exponent and the molecular mass, not presented for a log 10 x-axis, are also provided in Table A11.*

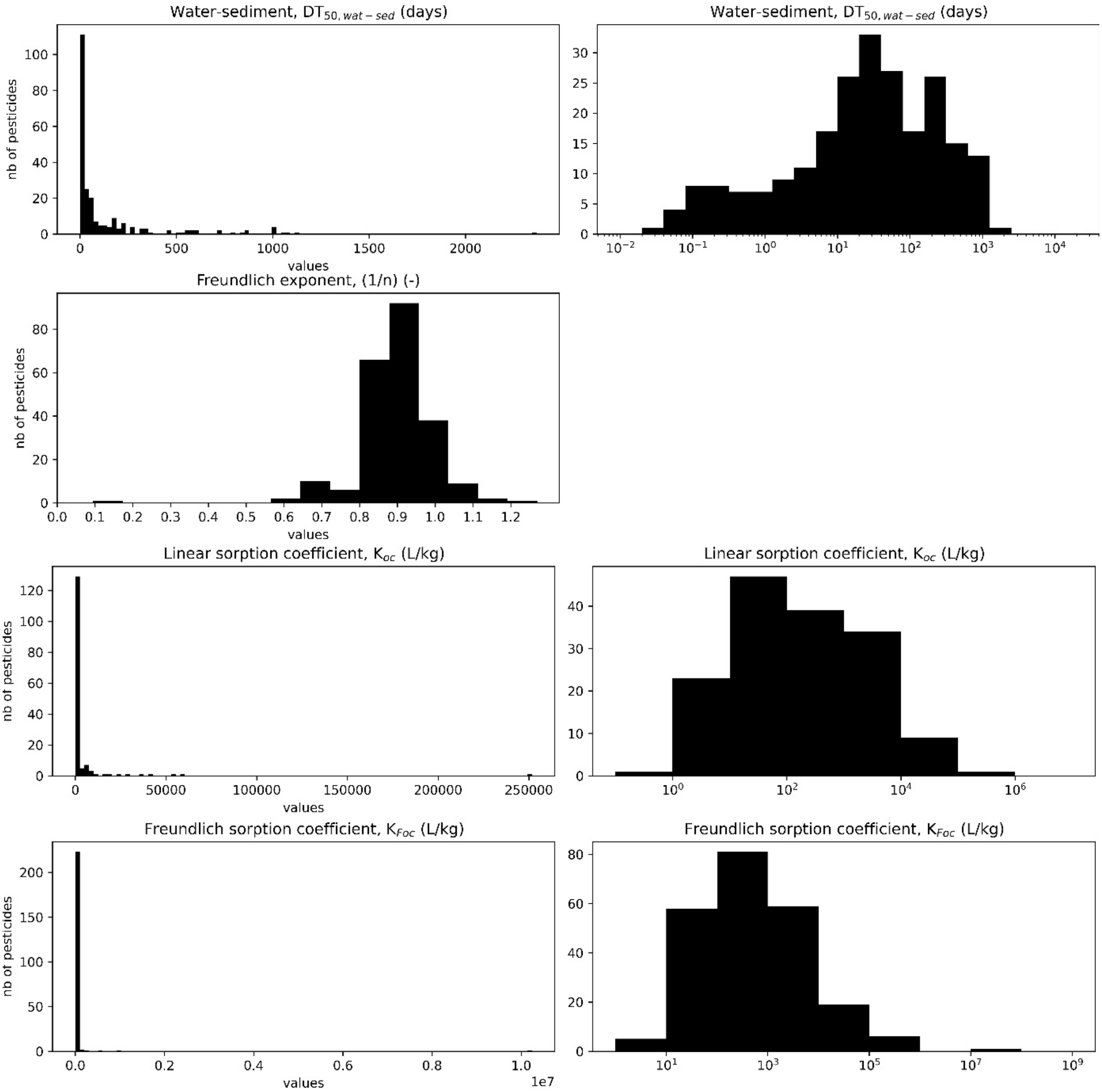

***Figure A3** (continued). Distribution of selected properties (source: PPDB). Left, normal x-axis, right log10 x-axis. For the log10 data, the bin width is a power of 10 except for the DT50 in water-sediment and in soil. The bin widths for both DT50 in soil and DT50 in the water-sediment system are provided in Table A11. The bin widths for the Freundlich exponent and the molecular mass, not presented for a log 10 x-axis, are also provided in Table A11.*

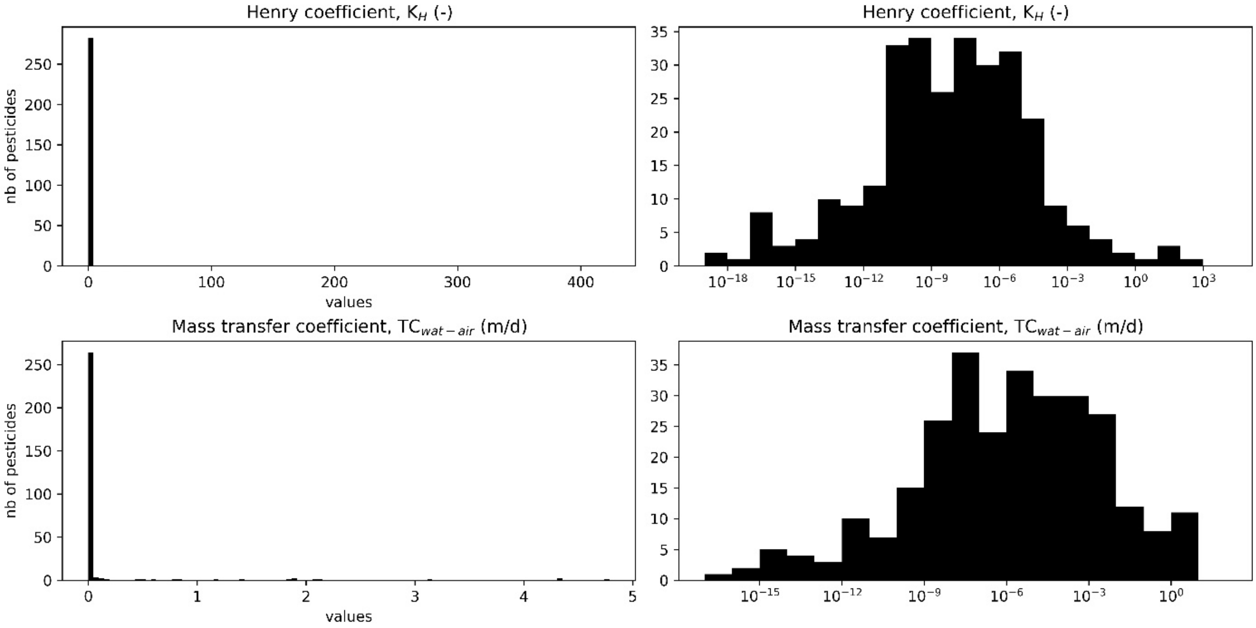

Figure A3 *(continued). Distribution of selected properties (source: PPDB). Left, normal x-axis, right log10 x-axis. For the log10 data, the bins width is a power of 10 except for the DT50 in water-sediment and in soil. The bin widths for both DT50 in soil and DT50 in the water-sediment system are provided in Table A 15. The bin widths for the Freundlich exponent and the molecular mass, not presented for a log 10 x-axis, are also provided in Table A 15.*

A7.2. Selection of pesticides, requested by WG Blootstelling

A7.2.1. Introduction

The workgroup *WG Blootstelling* requested to identify the number of active substances for which the Predicted Environmental Concentrations (PEC) in water is highly sensitive to the application date. This concerns active substances having a relatively low sorption coefficient and/or fast degradation in soil. The WG identified the following relevant ranges: $K_{F,oc}$ / K_{oc} < 10 L/kg or 10-100 L/kg for the sorption coefficient in soil and/or $DT_{50,soil}$ < 3 days or 3-30 days for the degradation in soil. Note that these substances are sensitive to the application date because they may or may not drain in small surface waters if the application date is just before, or several weeks before a rain event. Indeed, they might degrade in soil before the rainfall event.

A7.2.2. Material and method

For the sorption property, as the two sorption coefficients $K_{F,oc}$ / K_{oc} can be provided, we apply the same reasoning as explained in the report in Section 5.3.4: the K_{oc} is used unless not available, in which case the $K_{F,oc}$ is used. When this method is applied, 276 of 379 approved active substances possess a sorption coefficient (below called $K_{sorption}$, encompassing both $K_{F,oc}$ and K_{oc}). Of those 276 active substances, 269 are also provided a $DT_{50,soil}$.

For the 269 pesticides for which both properties are available, we created four categories based on the ranges of interest for the *WG Blootstelling*:

- $K_{F,oc}$ / K_{oc} < 10 L/kg and $DT_{50,soil}$ < 3 days.
- $K_{F,oc}$ / K_{oc} in 10-100 L/kg interval and $DT_{50,soil}$ < 3 days.
- $DT_{50,soil}$ in 3-30 days interval and $K_{F,oc}$ / K_{oc} < 10 L/kg.
- $DT_{50,soil}$ in 3-30 days interval and $K_{F,oc}$ / K_{oc} in 10-100 L/kg interval.

In the next Section we present which pesticides fall into each category, expressed in percentages of the 269 approved active substances for which both properties are available in the PPDB. We also list the pesticides which are in none of those categories, either because the values are outside those selected ranges, or because the properties values were not available.

A7.2.3. Overview of pesticides in $DT_{50,soil}$- $K_{sorption}$ categories

Out of the 379 active substances approved listed in the PPDB:

- 69 fall into one of the four categories of interest for the *WG Blootstelling*.
- 200 do not fall in any of those categories.
- 109 cannot be sorted in any category as at least one property ($DT_{50,soil}$ or $K_{sorption}$) is missing.

A7.2.3.1. Pesticides for which PEC might be sensitive to the application date

The distribution of the active substances in the indicated categories of interest for the *WG Blootstelling* is presented in Table A13: 69 active substances fall into one of the categories. In the more detailed Table A14, the names of the active substances are provided.

Table A13 *Number of active substances in the categories selected by the workgroup WG Blootstelling (absolute numbers and in brackets percentage of the 269 approved substances for which both $DT_{50,soil}$ and $K_{sorption}$ are available in the PPDB).*

$DT_{50,soil}$ / $K_{sorption}$ (i.e. K_{oc} or $K_{F,oc}$, see explication)	**$K_{sorption}$ < 10 L/kg**	**10 L/kg < / $K_{sorption}$ < 100 L/kg**
$DT_{50,soil}$ < 3 d	9 (3.3%)	17 (6.3%)
3 d < $DT_{50,soil}$ < 30 d	7 (2.6%)	36 (13.3%)

Table A14 *Details regarding the active substances in the categories selected by the workgroup WG Blootstelling (see explanation provided for Table A13).*

Name	**Soil DT_{50} (lab) (days)**	**Selected sorption coefficient (L/kg)**	**K_{oc} (L/kg)**	**$K_{F,oc}$ (L/kg)**
$K_{sorption} < 10$ L/kg **$DT_{50,soil} < 3$ d** **9 substances**				
1-naphthylacetamide	0.29	2	2	
acetamiprid	1.6	2	2	106.5
captan	0.8	2	2	
copper oxychloride	0.1	1	1	
dazomet	0.52	1	1	260
flonicamid	1.1	1.6	1.6	
fosetyl-aluminium	0.018	0.1	0.1	
potassium bicarbonate	0.1	1		1
sulfoxaflor	2.2	4.8	4.8	35
10 L/kg < $K_{sorption} < 100$ L/kg **$DT_{50.soil} < 3$ d** **17 substances**				
benzoic acid	0.5	25	25	547
clethodim	0.55	22.7		22.7
copper (II) hydroxide	0.1	12	12	
copper sulphate	0.1	95	95	
cycloxydim	0.65	59	59	
cymoxanil	1.7	19.6		19.6
daminozide	0.12	26.6		26.6
dichlorprop-P-etexyl	1.1	36		36
florasulam	1.85	22	22	20.37
fluroxypyr	1	68		68
folpet	1.65	34	34	
iodosulfuron-methyl-sodium	2.7	45		45
malathion	0.17	18	18	217
maleic hydrazide	0.8	45.8	45.8	28.16
MCPA-thioethyl	0.08	74	74	3430
metam-sodium	0.01	17.8	17.8	
thifensulfuron-methyl	1.39	28.3	28.3	9
$K_{sorption} < 10$ L/kg **3 d < $DT_{50.soil} < 30$ d** **7 substances**				
clomazone	22.6	3	3	128.3
clopyralid	23.2	5	5	
dicamba	9.62	5.28		5.28
nicosulfuron	16.4	3	3	21
rimsulfuron	24.3	5.3	5.3	47
triclopyr-triethylammonium	23.05	2	2	
tritosulfuron	18.1	8.9		8.9
10 L/kg < $K_{sorption} < 100$ L/kg **3 d < $DT_{50.soil} < 30$ d** **36 substances**				
1-methylcyclopropene	15	42.7	42.7	
2.4-D	4.4	39.3	39.3	24
2.4-D-dimethylammonium	4.4	39.3	39.3	24
MCPA	12.07	73.88	73.88	57.96
MCPB	3.65	14.7	14.7	101.95
amidosulfuron	14.4	29.3	29.3	31.1
bentazone	20	55.3	55.3	59.6

Name	Soil DT_{50} (lab) (days)	Selected sorption coefficient (L/kg)	*K_{oc} (L/kg)*	*$K_{F,oc}$ (L/kg)*
clodinafop	12.35	57.1		57.1
dichlorprop-P	12	44	44	36
dimethachlor	6.5	69		69
flufenacet	19.7	41	41	273.3
foramsulfuron	25.3	78.4		78.4
halosulfuron-methyl	26.7	19	19	
hymexazol	17.8	56.5		56.5
iprovalicarb	10.5	16	16	
mecoprop-P	5.24	59.8		59.8
mecoprop-P etexyl	3.04	59.8		59.8
metalaxyl-M	6.5	78.9		78.9
metaldehyde	5.1	24	24	77
metamitron	19	77.7	77.7	86.4
metazachlor	10.8	54	54	79.6
metribuzin	7.03	48.3		48.3
metsulfuron-methyl	23.2	12		12
oxamyl	5.3	14.91	14.91	13.59
penoxsulam	21.7	73.2	73.2	94
picloram	23	13	13	19.6
pyroxsulam	3.3	33.22	33.22	28.31
quinmerac	16.3	86	86	86
spiromesifen	4.1	39	39	
sulcotrione	25.3	36		36
tembotrione	14.5	66		66
tribenuron-methyl	9.1	35	35	31.6
triclopyr	18.81	27	27	57.95
triflusulfuron	6.5	60		60
triflusulfuron-methyl	14.6	58		58
urea	5	14	14	

A7.2.3.2. Pesticides that do not fall into the selected categories

Out of the 269 pesticides for which both properties DT50,soil and Ksorption are available, 200 do not fall in any of the categories based on the desired DT50,soil and Ksorption values.

Roughly a dozen of those substances is not found in the EU Pesticide Database as independent entry, while they are listed in the PPDB. An example are the glyphosate – derived compounds (eight derived compounds are in this list). Glyphosate is registered in the EU Pesticide Database, but glyphosate-isopropylamine for instance does not have an independent entry in the EU Pesticide Database. Both are listed below.

List of Pesticides that do not fall into any of the four categories

1-naphthylacetic acid
2,4-DB
2-phenylphenol
8-hydroxyquinoline
acequinocyl
acibenzolar-S-methyl
aclonifen
aluminium ammonium sulphate
ametoctradin
aminopyralid
amisulbrom
azoxystrobin
beflubutamid
beflubutamid-M
benalaxyl-M
bensulfuron
bensulfuron-methyl
benthiavalicarb-isopropyl
benzovindiflupyr
bifenazate
bifenox
bixafen
boscalid
bromuconazole
bupirimate
buprofezin
carfentrazone-ethyl
chlorantraniliprole
chlormequat
chlormequat chloride
chlorotoluron
chromafenozide
clodinafop propargyl
clofentezine
clopyralid-dimethylammonium
clopyralid-methyl
clopyralid-olamine
clopyralid-potassium
clopyralid-tripromine
cyantraniliprole
cyazofamid
cyflufenamid
cyflumetofen
cyhalofop
cyhalofop-butyl
cypermethrin
cyprodinil
deltamethrin
diclofop
diclofop-methyl
difenoconazole
diflufenican
dimethenamid-P
dimethomorph
dimoxystrobin
disodium phosphonate
dithianon
dodemorph
dodemorph acetate
dodine
esfenvalerate
ethephon
ethofumesate
etofenprox
etoxazole
fenazaquin
fenhexamid
fenoxaprop-P
fenoxaprop-P-ethyl
fenpicoxamid
fenpropidin
fenpyrazamine
fenpyroximate
flazasulfuron
florpyrauxifen
florpyrauxifen-benzyl
fluazifop-P-butyl
fluazinam
flubendiamide
fludioxonil
flumetralin
flumioxazin
fluometuron
fluopicolide
fluopyram
fluoxastrobin
flupyradifurone
flurochloridone
fluroxypyr-meptyl
flutianil
flutolanil
fluxapyroxad
forchlorfenuron
formetanate
formetanate hydrochloride
fosthiazate
gamma-cyhalothrin
glyphosate
glyphosate-diammonium
glyphosate-dimethylammonium
glyphosate-isopropylamine
glyphosate-monoammonium
glyphosate-monopotassium
glyphosate-sesquisodium
glyphosate-sodium
glyphosate-trimesium
halauxifen
halauxifen-methyl
hexythiazox
imazalil
imazamox
ipconazole
isofetamid
isoxaben
isoxaflutole
kresoxim-methyl
lambda-cyhalothrin
lenacil
mandestrobin
mandipropamid
mefentrifluconazole
mepanipyrim
mepiquat chloride
meptyldinocap
mesosulfuron
mesosulfuron-methyl
mesotrione
metaflumizone
metalaxyl
metconazole
methoxyfenozide
metiram
metobromuron
metrafenone
napropamide
oxathiapiprolin
oxyfluorfen
paclobutrazol
paraffin oil (CAS No: 8042-47-5)
pelargonic acid
penconazole
pendimethalin
penflufen
penthiopyrad
pethoxamid
phenmedipham
picolinafen
pinoxaden
pirimicarb
potassium phosphonates
prohexadione
prohexadione-calcium
propamocarb hydrochloride
propaquizafop
propoxycarbazone-sodium
propyzamide
proquinazid
prosulfocarb
prosulfuron
prothioconazole
pyraclostrobin
pyraflufen-ethyl
pyridaben
pyridalyl
pyridate
pyrimethanil
pyriofenone
pyriproxyfen

quizalofop-P-ethyl
quizalofop-P-tefuryl
sedaxane
silthiofam
sintofen
sodium 5-nitroguaiacolate
sodium o-nitrophenolate
sodium p-nitrophenolate
spinetoram
spirotetramat
spiroxamine
sulfosulfuron
sulphur
tau-fluvalinate
tebuconazole
tebufenozide
tebufenpyrad
tefluthrin
terbuthylazine
tetraconazole
thiabendazole
thiencarbazone
thiencarbazone-methyl
thifensulfuron
tolclofos-methyl
tri-allate
trifloxystrobin
trinexapac-ethyl
triticonazole
valifenalate
ziram

A7.2.3.3. Approved active substance with missing properties

Some approved active substances have not been attributed a sorption coefficient (no K_{oc} and no $K_{F,oc}$) or a $DT_{50,soil}$ in soil (sometimes, both properties values are not provided) and are, therefore, not listed in any category but could be present in one of them. This concerns 109 substances out of the 379 approved substances listed in the PPDB.

The active substances for which one of the properties (or both) is missing are listed below. Some compounds might appear in both lists (missing $DT_{50,soil}$ and missing sorption coefficient).

About 30-40 of those substances are not found in the EU Pesticide Database as an independent entry, while they are listed in the PPDB. An example are the dicamba – derived compounds (10 derived compounds are in this list, for instance: dicamba trolamine). Dicamba is registered in the EU Pesticide Database and is listed in, but dicamba biproamine which is listed below for instance does not have an independent entry in the EU Pesticide Database, and the PPDB was not completed for this compound as both $DT_{50,soil}$ and sorption coefficients were not provided.

Below are listed the names of the active substances, approved in the PPDB, for which no soil DT50 or no sorption coefficient is provided in the PPDB:

Missing DT50 soil

1,4-dimethylnaphthalene
1-decanol
1-dodecanol
acibenzolar
aluminium silicate
aminopyralid-dimethylammonium
aminopyralid-potassium
aminopyralid-tripromine
beer
bentazone-sodium
benthiavalicarb
bispyribac
Bordeaux mixture
caprylic acid potassium salt
carbon dioxide
dazomet-sodium
diammonium phosphate
dicamba biproamine
dicamba diglycolamine
dicamba dimethylammonium
dicamba diolamine
dicamba isopropyammonium
dicamba methyl
dicamba olamine
dicamba potassium
dicamba sodium
dicamba trolamine
dodemorph benzoate
ferric pyrophosphate
fructose
heptamaloxyloglucan
hydrogen peroxide
imazalil nitrate
imazalil sulfate
kaolin
kaolin calcined
kappa-tefluthrin
lavandulyl senecioate
maleic hydrazide choline
maleic hydrazide potassium
maleic hydrazide sodium
maltodextrin
MCPA-butotyl
MCPA-butyl
MCPA-dimethylammonium
MCPA-diolamine
MCPA-ethyl
MCPA-isobutyl
MCPA-isoctyl
MCPA-isopropyl
MCPA-methyl
MCPA-olamine
MCPA-potassium
MCPA-sodium
MCPA-trolamine
mecoprop-P dimethylammonium
mecoprop-P isobutyl
mecoprop-P potassium
mepiquat
metam
metam-ammonium
metam-potassium
metsulfuron
myristyl alcohol
paraffin oil (CAS No. 72623-86-0)
paraffin oil (CAS No: 64742-46-7)
paraffin oil (CAS No: 97862-82-3)
picloram-trolamine
QRD-460 Terpenoid blend
quartz sand
sodium ortho-phenylphenoxide
sodium silver thiosulphate
sucrose
talc E553B
urea sulphate
vinegar

Missing sorption coefficient

24-epibrassinolide
aluminium phosphide
aluminium sulphate
1,4-dimethylnaphthalene
1-decanol
1-dodecanol
acibenzolar
aluminium silicate
aminopyralid-dimethylammonium
aminopyralid-potassium
calcium carbide
calcium carbonate
calcium hydroxide
aminopyralid-tripromine
beer
carfentrazone
copper (I) oxide
bentazone-sodium
benthiavalicarb
bispyribac
Bordeaux mixture
caprylic acid potassium salt
carbon dioxide
dazomet-sodium
diammonium phosphate
dicamba biproamine
dicamba diglycolamine
dicamba dimethylammonium
dicamba diolamine
dicamba isopropyammonium
ferric phosphate
dicamba methyl
dicamba olamine
fosetyl
dicamba potassium
dicamba sodium
dicamba trolamine
dodemorph benzoate
ferric pyrophosphate
fructose
iron sulphate
heptamaloxyloglucan
hydrogen peroxide
imazalil nitrate
kieselgur
imazalil sulfate
lime sulphur
magnesium phosphide
kaolin
kaolin calcined
kappa-tefluthrin
lavandulyl senecioate
maleic hydrazide choline
maleic hydrazide potassium
maleic hydrazide sodium
maltodextrin
MCPA-butotyl
MCPA-butyl
MCPA-dimethylammonium
MCPA-diolamine
MCPA-ethyl
MCPA-isobutyl
MCPA-isoctyl
MCPA-isopropyl
MCPA-methyl
MCPA-olamine
MCPA-potassium
MCPA-sodium
MCPA-trolamine
mecoprop-P dimethylammonium
mecoprop-P isobutyl
mecoprop-P potassium
mepiquat
metam

metam-ammonium
metam-potassium
metsulfuron
myristyl alcohol
phosphane
picloram-dimethylammonium
picloram-etexyl
picloram-isoctyl
picloram-methyl
picloram-olamine
picloram-potassium
picloram-triethylammonium
picloram-tripromine
paraffin oil (CAS No. 72623-86-0)
propamocarb
paraffin oil (CAS No: 64742-46-7)
paraffin oil (CAS No: 97862-82-3)
picloram-trolamine
sodium hydrogen carbonate
QRD-460 Terpenoid blend
quartz sand
sodium ortho-phenylphenoxide
sodium silver thiosulphate
sucrose
talc E553B
triclopyr-butotyl
urea sulphate
vinegar
zinc phosphide

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Annex 8 Illustration of concentrations in water and in sediment for the stream for two sorption coefficients

To show some examples of concentrations in water and sediment in the stream, simulations were carried out with K_{om} 1,000 L kg^{-1} and with K_{om} 100,000 L kg^{-1} (both for suspended solids and for sediment). All other process parameters were set to their Median values (Table 5-3). For the simulation of K_{om} 100,000 L kg^{-1} the FOCUS fine sediment segmentation was used.

For K_{om} 1,000 L kg^{-1} the runoff entry of substance for eight hours leads to a total concentration between 79.4-98.5 µg L^{-1} from one to nine hours after start of the entry and a dissolved concentration of 79.0-98.0 µg L^{-1} during these hours (Figure A4). Firstly, the concentration shows a small peak slightly higher than the plateau value thereafter. This peak is due to a numerical artefact, the discrepancy between hydrology and mass modules of TOXSWA, mentioned in Footnote 22 (p. 74). The plateau concentration represents the steady state during the runoff entry, water and substance entry are constant. When the entry of water and substance stopped a first small decrease is a drop to a value somewhat lower than the plateau, due to the same numerical reason at the initial small peak. The further decrease is a steep drop due to this stop of entry runoff water (leading to a drop in water depth of the stream and slower flow velocity) and substance. The further slower decrease of concentrations is due to dilution by entry of clean water and back diffusion from the sediment to water. The concentration decrease being slower is due to the lower discharge from only baseflow. The total concentration and the dissolved concentration in water are similar, because only a small fraction of the substance is adsorbed to suspended solids and to macrophytes (K_{mp} 8.4 L/kg).

These higher values are due to a small internal discrepancy between the hydrology and pesticide module in TOXSWA, reported in the release notes of FOCUS_TOXSWA 4.4.3, and illustrated in Annex 8.

For K_{om} 1,000 L kg^{-1}, the runoff entry of substance leads to a peak concentration of 1,930 µg (kg OM)$^{-1}$ at 16 hours after start of the entry in sediment (Figure A5). Thereafter the concentrations in sediment decrease steadily, first quickly during the first approximately 7 to 10 days, and next, more slowly in the period thereafter. The decrease of concentration is due to diffusion out of the sediment to the water layer being flushed with clean water.

For K_{om} 100,0000 L kg^{-1}, the runoff entry of substance for eight hours leads to a total concentration in water of 76.9-97.7 µg L^{-1} from 1 to 9 hours after start of the entry and a dissolved concentration of 65.1-82.3 µg L^{-1} during these hours (Figure A6). The increase and decrease of concentration is explained as described for the K_{om} 1,000 L kg^{-1} substance (above). Compared to the simulation for a K_{om} value of 1,000 L kg^{-1}, the total concentration and the dissolved concentration in water differ strongly, because a substantial fraction of the substance is adsorbed to suspended solids.

For K_{om} 100,000 L kg^{-1}, the runoff entry of substance leads to a peak concentration in sediment of 28,865 µg (kg OM)$^{-1}$ at 13 hours after start of the entry (Figure A7). Thereafter, the concentrations in sediment decrease steadily, first quickly during the first 7 to 10 days, and next, more slowly in the period thereafter. The decrease of concentration is due to diffusion from the sediment to the water layer being flushed with clean water.

Comparing the two simulations shows the impact of the difference in sorption coefficients. For water, the impact of a sorption coefficient of 1,000 L kg^{-1} for suspended solids has a negligible effect on the dissolved concentration (= PEC_{wat}). For the very high sorption coefficient of 100,000 L kg^{-1}, the decrease of dissolved concentration is in the order of 15%. For sediment, the difference in the two sorption coefficients of a factor 100 leads to a decrease in the PEC_{sed} in sediment of a factor of 10.

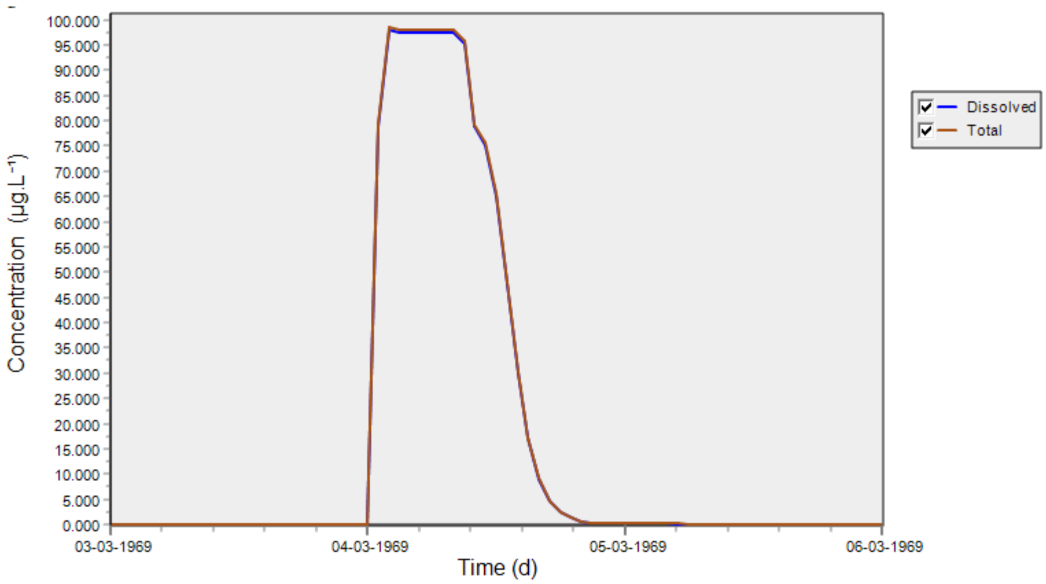

Figure A4 *Total (incl. sorbed to suspended solids and to macrophytes) and dissolved concentration in water in the segment 95-100 m in the stream for* K_{om} *1,000 L* kg^{-1}*.*

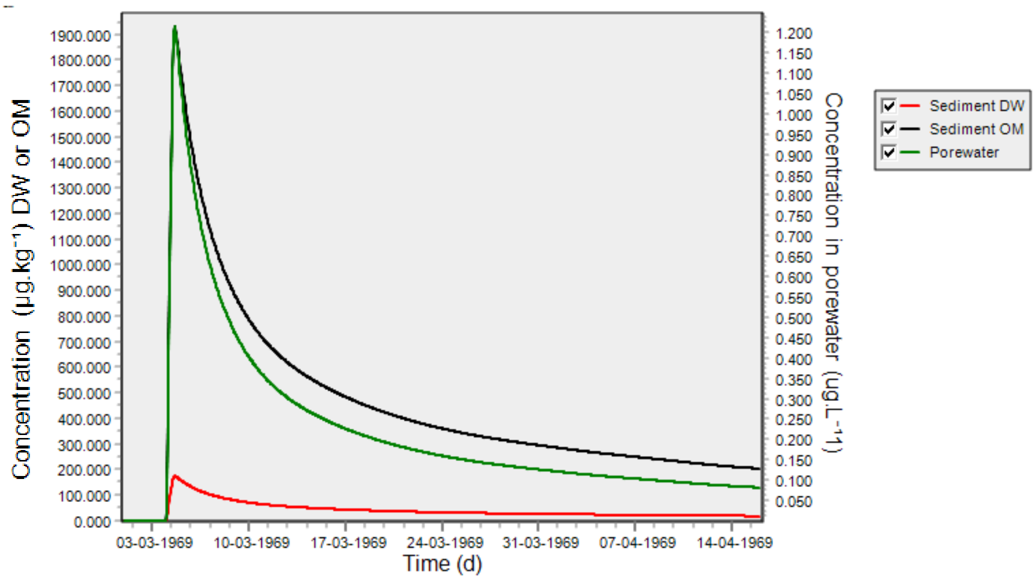

Figure A5 *Concentration in sediment per kg dry weight (DW), and per kg organic matter (OM) (left y-axis) and dissolved in pore water (right y-axis) below the segment 95-100 m in the stream for* K_{om} *1,000 L* kg^{-1}*.*

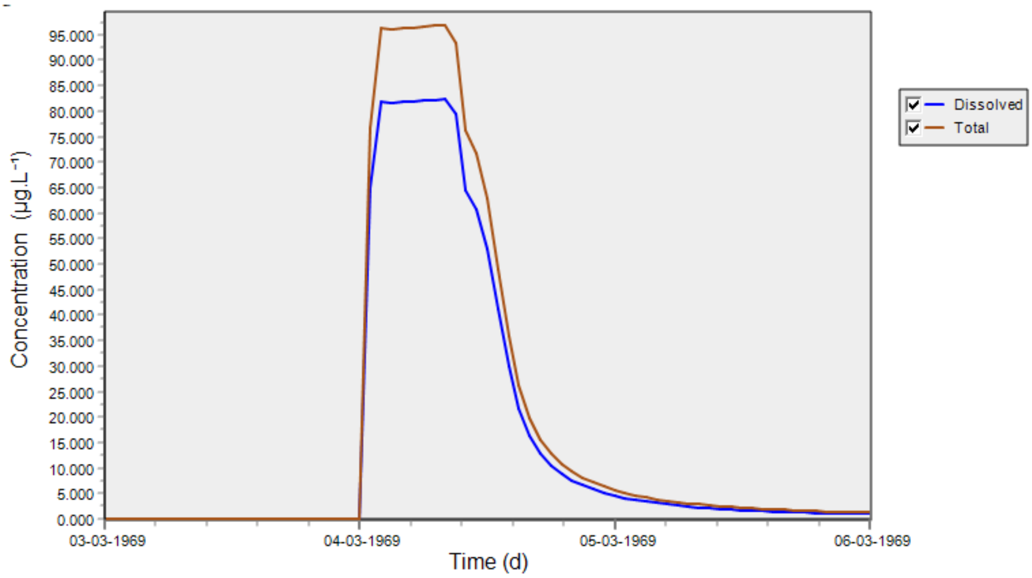

Figure A6 *Total (incl. sorbed to suspended solids and to macrophytes) and dissolved concentration in water in the segment 95-100 m in the stream for* K_{om} *100,000 L* kg^{-1}.

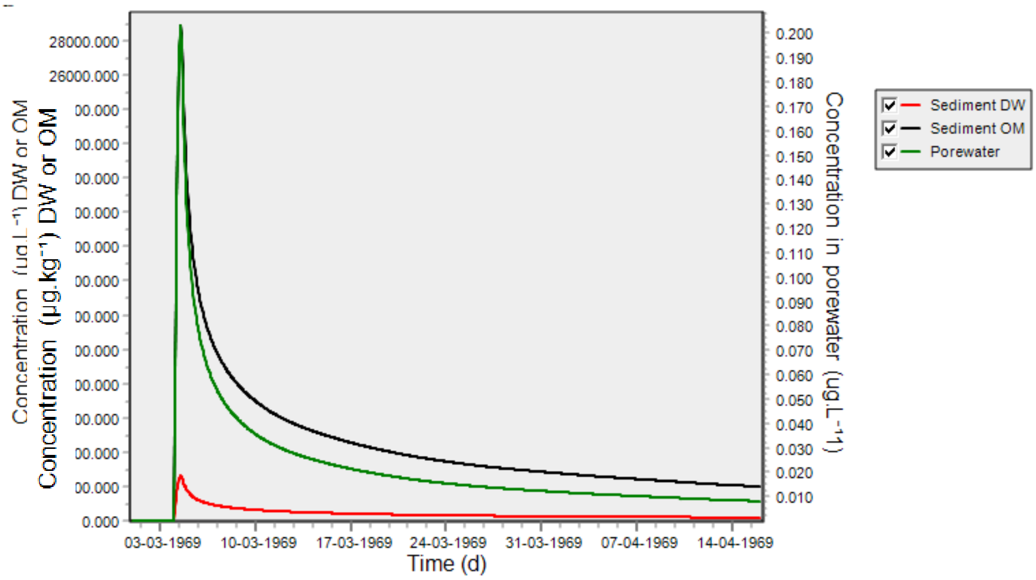

Figure A7 *Concentrations in sediment in mass kg dry weight (DW), mass per kg organic matter (OM) (left y-axis) and dissolved in pore water (right y-axis) below the segment 95-100 m in the stream for* K_{om} *100,000 L* kg^{-1}.

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