



The TOXSWA model version 3.3 for pesticide behaviour in small surface waters

Description of processes

M.M.S. ter Horst, W.H.J. Beltman & F. van den Berg

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The TOXSWA model version 3.3 for pesticide behaviour in small surface waters

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Abstract

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In the European Union (EU) the risk of plant protection products to aquatic organisms is assessed according to regulation 1107/2009. For this assessment the FOCUS Surface Water Scenarios have been developed. The TOXSWA model is included in the FOCUS Surface Water Software tools to calculate the exposure concentration in the water systems defined in those scenarios. At the national level the TOXSWA model is used to assess the exposure concentration in the water system defined in national scenarios. In this report a description is given of the hydrology in the Dutch and EU water body systems and the fate of pesticides and their metabolites in water and sediment. The pesticide can enter the system by spray drift and/or drainage and run-off. The transport in the water system is described by advection, dispersion and diffusion. The exchange at the water-sediment interface is described based on advection/diffusion. Other processes are sorption, volatilisation at the water – air interface and transformation in both the water layer and the sediment. The formation and transformation of metabolites in both compartments are described. The report presents an outlook on the improvements in the next version as well as on future developments.

Keywords: pesticides, modelling, exposure, surface water, aquatic ecosystem, drainage, runoff, spray drift, plant protection product, FOCUS Surface Water

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Preface

Since 1999 TOXSWA 1.2 has been applied in the Dutch registration procedure for plant protection products to calculate exposure concentrations for an edge-of-field ditch with constant flow rates. Since 2003 TOXSWA 2.1 and onwards has been applied in the FOCUS_TOXSWA software tools (versions 1.1.1, 2.2.1 and 3.3.1) that are used in the EU registration procedure to calculate exposure concentrations in ponds, ditches and streams with transient flow conditions. This document describes the concepts of the TOXSWA kernel 3.3 that is implemented in the FOCUS_TOXSWA v.4.4.3 software tool. We would like to thank Dr. Jos Boesten and Ir. Paulien Adriaanse for the internal review of (parts) this document.

Mechteld ter Horst

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Contents

Preface	5
Contents	7
Summary	9
Samenvatting	11
1 Introduction	13
2 Model for water flow	15
2.1 Introduction	15
2.2 System description – general	15
2.2.1 Geometric elements	15
2.2.2 Elements of the water balance	16
2.3 Hydrology of watercourses	18
2.3.1 Constant flow	18
2.3.2 Transient flow; constant water depth along length of modelled watercourse	19
2.4 Pond systems	23
2.4.1 No flow	23
2.4.2 Transient flow	23
3 Temperature for the modelled system	25
4 Pesticide system and conservation equations	27
4.1 Water layer	27
4.1.1 System description - general	27
4.1.2 Conservation equation	29
4.2 Sediment	29
4.2.1 System description - general	29
4.2.2 Conservation equation	32
5 Pesticide entry routes	33
5.1 Introduction	33
5.2 Entry routes at the boundaries	33
5.2.1 Entries at the upper boundary	33
5.2.2 Into sediment via upward seepage	33
5.3 Lateral entries in the waterbody - type of inputs	33
5.4 Spray drift	34
5.5 Drainage, runoff and erosion	34
5.5.1 Water layer: drainage and runoff	34
5.5.2 Sediment: erosion	35
5.6 Considerations	35
6 Pesticide process of partitioning	37
6.1 Water layer	37
6.2 Sediment	37

7	Pesticide transport and emission	39
7.1	Water layer	39
7.1.1	Transport by advection and dispersion	39
7.1.2	Transport by advection to downstream waterbody	39
7.2	Sediment	40
7.2.1	Transport by advection, dispersion and diffusion	40
7.2.2	Transport by advection to soil	42
7.3	Water-sediment interface: advection and diffusion	42
7.4	Volatilization from the water layer	43
7.5	Effect of temperature	44
7.5.1	Saturated vapour pressure	44
7.5.2	Solubility	44
8	Pesticide transformation processes	45
8.1	Metabolites: reaction scheme and kinetics	45
8.2	Water layer	46
8.3	Sediment	46
8.4	Effect of temperature on transformation rate	47
9	General discussion	49
9.1	Model sensitivity, verification, use and testing	49
9.1.1	Sensitivity and uncertainty analysis	49
9.1.2	Verification	49
9.1.3	Model use and testing	49
9.2	Ongoing developments	49
9.2.1	Introduction	49
9.2.2	Hydrology	50
9.2.3	Atmospheric deposition	50
9.2.4	Temperature	50
9.2.5	Volatilisation	50
9.2.6	Bioturbation	51
9.2.7	Transformation	51
9.3	Landscape scale modelling	51
	References	53
	Justification	55
Annex 1	List of symbols and units	57
Annex 2	Lateral entries in the waterbody	61
A2.1	Introduction	61
A2.2	Point-type pulse input	62
A2.3	Point-type distributed input	63
A2.4	Continuous point release	64
A2.5	Continuous distributed release	64
Annex 3	Iteration solution of the Freundlich sorption equation	67

Summary

Pesticides are applied in agricultural fields to control a wide range of pests that would otherwise reduce the quantity and quality of crops. Pesticides may enter surface waters by various routes such as surface runoff, leaching to drains and spray drift deposition. To assess the exposure of aquatic organisms simulation models have been developed to be used in the pesticide regulation at the European level as well as the national level. In the nineties of the last century the TOXSWA model has been developed to assess the behaviour of pesticides in a water-sediment system at the edge-of-field scale. The TOXSWA model has been adopted to be used in the Dutch registration procedure in 1999 (version 1.2) in conjunction with Dutch Surface Water scenarios. For the use of the FOCUS Surface Water Scenarios in the EU authorization procedure TOXSWA versions 2.1 up to 3.3 have been developed and used by the FOCUS-TOXSWA software tools since 2003. The FOCUS-TOXSWA software tools also include ten FOCUS Surface Water scenarios for which the TOXSWA model is run. The latest version of the software tool, i.e. FOCUS-TOXSWA 4.4.3, uses TOXSWA version 3.3. TOXSWA 3.3 includes an option to assess the fate of metabolites formed in either the water layer or the sediment compartment. This report describes the processes for the flow of water in several types of waterbody systems and the processes considered describing the fate of the pesticide in these systems. Descriptions are constrained to those processes used for simulations with the Dutch (excluding the greenhouse scenarios) and FOCUS Surface Water Scenarios.

The hydrology of the waterbody systems depends on their geometry, the elements of the water balance and the procedure to determine the discharge and the water depth. A distinction is made between watercourses and ponds. Two types of water flow regimes are defined for the watercourses: a constant water flow regime and a transient flow. Transient flow means varying discharge and water depth in time and along the length of the waterbody. In TOXSWA the transient flow is modelled for a watercourse of which a stretch has a constant water depth along the length of the waterbody. This watercourse is located adjacent to a treated, agricultural field delivering water originating from drainage or surface runoff to the watercourse. Furthermore, the watercourse is fed by a small catchment. A weir located downstream maintains the water level at a preferred minimum depth. For the ponds the situation of no flow or transient flow can be simulated.

Transient flow in a pond system is simulated by assuming the pond is a reservoir having an incoming and an outgoing water flow. The total incoming flow consists of a constant base flow plus the excess water from the contributing area, delivered into the pond. The contributing area consists of fields located at its banks. The pond outflow occurs across a weir. The incoming excess water from the contributing area originates from e.g. drain pipes or surface runoff and varies in time. For the Dutch Surface Water scenarios a watercourse has been defined with a constant flow system. In this system the flow velocity of water is constant in time and space. For the FOCUS Surface Water scenarios, three types of water bodies have been defined, i.e. ditches, streams and ponds. Hydrology in the FOCUS ditches and streams are simulated according the concept of transient flow with a constant water depth along the length of the modelled water course. The FOCUS pond is simulated using the concept for transient flow in a pond system. The 'no flow' hydrology in a pond system can be used for the simulation of water-sediment systems and microcosms.

For the description of the temperature in the waterbody in the TOXSWA model, a simple approach has been implemented. The temperature in the waterbody system (water layer and sediment) is assumed to remain constant during periods of one month.

The pesticide can enter the waterbody systems in different ways in relation to time and space. The lateral entry can be described by a pulse input or a continuous input (time). For both types the entry can occur at a specific point in the system or it can be distributed over a certain length of the system. Of the in total four types of input, two are actually implemented in TOXSWA (distributed, pulse and distributed, continuous). In addition to the lateral entries, entry routes at the boundaries i.e. upstream

entries in the waterbody or entries in the sediment via upward seepage can be simulated. In the Dutch scenario only the entry into the water layer by drift (distributed, pulse) is considered. In the FOCUS scenarios, the entry routes for the water layer are the entry from the upstream catchment, the lateral entry (distributed, continuous) due to drainage and runoff and the entry due to spray drift (distributed, pulse). For the sediment compartment the entry types are due to erosion by runoff (distributed, continuous).

In the water layer, sorption of pesticide can be to suspended solids or macrophytes. Sorption of the pesticide to suspended solids is described by a Freundlich sorption equation. The sorption to macrophytes is described using a linear sorption isotherm. The sorption of pesticides to the solid phase of the sediment is described with a Freundlich sorption equation.

The transport of the pesticide in the water layer is described by an equation including advection and dispersion in the horizontal direction. The exchange with the atmosphere is described by diffusion across the water-atmosphere interface. The exchange of pesticide between the water layer and the sediment is described using equations for transport of substance through advection and diffusion across the water-sediment interface. The transport of the pesticide in the sediment is described by an equation including advection, dispersion and diffusion in the vertical direction.

For transformation of the pesticide, the scheme of reactions of the pesticide and its transformation products is translated into a matrix of the molar fractions involved in each of the reactions. Two matrices are defined, one for the water layer and one for the sediment. The rate of transformation of the substances in both compartments is described by first-order kinetics. Pesticide transformation is highly dependent on temperature, which is described by the Arrhenius equation.

The TOXSWA model is an important tool in the evaluation of risks of agricultural pesticide use to the aquatic ecosystem. It can be used for different purposes. TOXSWA calculates exposure concentrations in surface water systems via running scenarios defined in the evaluation tiers of registration procedures at the national and EU levels. TOXSWA can also be applied for specific computations, for example to assess the effect of mitigation measures on exposure concentrations.

Further work on the development of the model has been done in recent years. Currently, the TOXSWA development team is working on the next version: 3.4. One of the improvements that has been implemented in this version of the TOXSWA model is related to the description of the variation in time of the water temperature. As the temperature in small water bodies can vary strongly by changing weather conditions, a 1-D bulk approach has been adopted to describe the terms constituting the energy balance of the waterbody. This new procedure allows taking into account temperature variations at time scales of 1 hour. Furthermore, the team is currently working on implementation of improved concepts for transformation in water. This is done by splitting transformation in water into three separate processes: hydrolysis, photolysis and biotic transformation. Describing these underlying processes enables a better quantification of the overall transformation rate, and thus improves the description of the pesticides' behaviour.

Other improvements are the inclusion of bioturbation as a particle dispersion process and the inclusion of atmospheric deposition as a pesticide entry pathway. Deposition of pesticide on the surface water can occur as a result of volatilisation of pesticide after application to the adjacent field.

At the landscape level, the CASCADE-TOXSWA model has been developed. This model is based on the TOXSWA model, but it only considers the water layer in a system of interconnected water courses. The transport processes considered are advection and dispersion. At present the only entry route considered is deposition due to spray drift. Further improvement of the model would require the inclusion of the sediment compartment. The CASCADE-TOXSWA model could be developed further to assess exposure and the resulting effects of pesticide use at the catchment scale.

Samenvatting

Pesticiden worden in de landbouw gebruikt tegen een breed scala aan plagen dat anders zou resulteren in een afname in de gewasopbrengst en de kwaliteit van deze opbrengst. Pesticiden kunnen op verschillende wijzen in het oppervlaktewater terecht komen, bijv. via run-off, uitspoeling naar het oppervlaktewater via drains en depositie van spuitdruppeltjes. Voor de beoordeling van de blootstelling van waterorganismen zijn simulatiemodellen ontwikkeld om te gebruiken in de toelatingsprocedure op zowel nationaal als Europees niveau. In de jaren negentig van de 20^e eeuw is het TOXSWA-model ontwikkeld waarmee het gedrag van pesticiden in een water-sediment systeem op veldschaal kan worden beoordeeld. Het TOXSWA-model (versie 1.2) wordt samen met de Nederlandse oppervlaktewatersscenario's sinds 1999 in de Nederlandse toelatingsprocedure gebruikt.

Om de FOCUS oppervlaktewatersscenario's in de EU-toelatingsprocedure toe te passen, zijn TOXSWA-modelversies ontwikkeld, van versie 2.1 tot aan versie 3.3, als onderdeel van de sinds 2003 uitgebrachte FOCUS-TOXSWA-softwarepakketten. De FOCUS-TOXSWA-softwarepakketten bevatten ook de tien FOCUS-oppervlaktewatersscenario's waarvoor berekeningen met TOXSWA gedaan kunnen worden. In de recentste versie van dit softwarepakket, FOCUS-TOXSWA 4.4.3, wordt TOXSWA versie 3.3 gebruikt. TOXSWA 3.3 bevat een optie om het gedrag van metabolieten te beoordelen die in de waterlaag dan wel in het sediment gevormd worden. Dit rapport beschrijft de processen voor waterstroming in verschillende oppervlaktewatersystemen en de processen die het gedrag van pesticiden in deze systemen bepalen. De procesbeschrijvingen zijn beperkt tot de processen die relevant zijn in combinatie met de Nederlandse en de FOCUS-oppervlaktewater-scenario's (m.u.v. de NL-glastuinbouwscenario's).

De hydrologie van de watersystemen hangt af van de geometrie van het systeem, de elementen van de waterbalans en de procedure om de waterafvoer en de waterdiepte in het systeem te bepalen. Hierbij wordt een onderscheid gemaakt tussen beken en poelen. Voor beken zijn twee typen waterstromingsregime gedefinieerd: een regime met constante waterstroming en een regime met niet-stationaire waterstroming. Niet-stationaire stroming houdt in dat de afvoer en waterdiepte in de gesimuleerde waterloop veranderen in de tijd en over de lengte van de waterloop. In TOXSWA wordt de niet-stationaire stroming in een waterloop beschreven met een constante diepte over de gehele waterloop. Deze waterloop is gelegen naast een behandeld landbouwkundig perceel, waarvan het drainagewater of de afvoer via run-off in deze waterloop terechtkomt. De waterloop wordt ook gevoed met water uit een bovenstrooms gebied. Aan de benedenstroomse zijde van de waterloop bevindt zich een stuw om een gewenste minimumwaterdiepte in de waterloop te handhaven.

Voor poelen kan TOXSWA een stagnante situatie en niet-stationaire stroming simuleren. Niet-stationaire stroming in een poel wordt gesimuleerd door aan te nemen dat de poel een waterreservoir is met een inkomende en een uitgaande waterstroom. De totale aanvoer van water bestaat uit een basisstroom en het overtollig water van het gebied dat op de poel afwatert. Dit afwaterend gebied wordt gevormd door velden die aan de oever van de poel grenzen. De afvoer van water vanuit de poel gaat via een stuw. Het overtollig water dat vanaf de omringende velden in de poel terechtkomt, bestaat uit afvoer via drainpijpen of oppervlakkige afvoer via run-off en de mate van deze afvoer varieert in de tijd. Voor de Nederlandse oppervlaktewater-scenario's is een waterloop gedefinieerd met een constante waterstroming. In dit systeem is de waterstroming zowel in plaats als in tijd constant.

Voor de FOCUS-oppervlaktewatersscenario's zijn drie watersystemen gedefinieerd, d.w.z. sloten, beken en poelen. De hydrologie in de FOCUS-sloten en -beken wordt beschreven via het concept voor niet-stationaire stroming met een constante waterdiepte over de gehele lengte van de waterloop. De hydrologie in de FOCUS-poel wordt beschreven met het concept voor niet-stationaire stroming in een poelsysteem. De hydrologisch stagnante situatie in een poel kan gebruikt worden voor de simulatie van water-sediment en microkosmos-systemen

Om de temperatuur in het watersysteem van het TOXSWA-model te beschrijven, wordt een simpele benadering gebruikt. De temperatuur in het watersysteem (waterlaag en sediment) wordt aangenomen constant te zijn gedurende perioden van één maand.

Het pesticide kan in het watersysteem terechtkomen op verschillende wijzen in tijd en plaats. De laterale aanvoer kan worden beschreven als een pulsbelasting of als een continue belasting (tijd). Voor beide typen aanvoer kan de belasting plaatsvinden op een specifiek punt in de waterloop of over een deel van de waterloop. Van de vier mogelijke aanvoerroutes zijn er twee geïmplementeerd in TOXSWA, nl. lijn-puls en lijn-continu. Naast de laterale aanvoer zijn er aanvoerroutes aan de grenzen van het watersysteem, nl. door aanvoer van bovenstrooms water en aanvoer via kwel in het sediment-subsysteem. In het Nederlandse scenario wordt alleen de belasting van de waterlaag via drift (lijn, puls) in rekening gebracht. In de FOCUS-scenario's zijn de aanvoerroutes voor de waterlaag de aanvoer vanuit het gebied bovenstrooms, laterale aanvoer (lijn, continu) door drainage en run-off en de aanvoer als gevolg van spuitdrift (lijn, puls). Voor het sediment-subsysteem is de aanvoerroute beperkt tot de aanvoer via erosie van bodemdeeltjes (lijn, continu).

In de waterlaag kan de sorptie plaatsvinden aan gesuspendeerde deeltjes en macrofyten. De sorptie aan gesuspendeerde deeltjes wordt beschreven met een sorptievergelijking van Freundlich. De sorptie aan macrofyten wordt beschreven met een lineaire adsorptie-isotherm. De sorptie aan de vaste fase van het sediment-subsysteem wordt beschreven met een sorptievergelijking van Freundlich.

Het transport van het pesticide in de waterlaag wordt beschreven met een vergelijking met termen voor advectie en dispersie in de horizontale richting. De uitwisseling met de atmosfeer wordt beschreven met diffusie over het water-atmosfeer grensvlak. De uitwisseling van pesticide tussen de waterlaag en het sediment wordt beschreven met vergelijkingen voor transport via advectie en diffusie over het grensvlak water-sediment. Het transport van het pesticide in het sediment wordt beschreven met een vergelijking voor advectie, dispersie en diffusie in de verticale richting.

Om het pesticide om te zetten, wordt het reactieschema voor het pesticide en de omzettings-producten vertaald naar een matrix voor de molaire fracties voor elk van de beschouwde reacties. Twee matrices worden gedefinieerd, één voor de waterlaag en één voor het sediment. De snelheid van de omzetting in beide compartimenten wordt beschreven met eerste-orde kinetiek. De omzetting van het pesticide hangt in hoge mate af van de omgevingstemperatuur en dat effect wordt beschreven door de Arrhenius-vergelijking.

Het TOXSWA-model is een belangrijk instrument in de risico-evaluatie van landbouwkundig gebruik van pesticiden voor aquatische systemen. Het model kan gebruikt worden voor verschillende doeleinden. TOXSWA berekent de blootstellingsconcentratie in oppervlaktewatersystemen door gebruik van de scenario's zoals die zijn opgenomen in de beoordelingsniveaus van de toelatingsprocedure op nationaal en EU-niveau. Het TOXSWA-model kan ook worden gebruikt voor specifieke doeleinden, bijvoorbeeld om het effect van emissie-reducerende maatregelen op de blootstellingsconcentraties in oppervlaktewater te beoordelen.

Verdere ontwikkeling van het model heeft de laatste jaren plaatsgevonden. Momenteel werkt het TOXSWA-ontwikkelteam aan de volgende versie, nl. 3.4. Een van de verbeteringen die gerealiseerd is in deze versie van het TOXSWA model betreft de beschrijving van de variatie in de tijd van de watertemperatuur. Aangezien in kleine watersystemen de temperatuur sterk kan variëren onder invloed van de verandering van de weersomstandigheden, is een 1-D bulkbenadering gebruikt om de termen te beschrijven die onderdeel zijn van de energiebalans van het watersysteem. Deze nieuwe benadering maakt het mogelijk om met temperatuurvariaties op een tijdschaal van één uur rekening te houden. Verder werkt het ontwikkelteam momenteel aan de verbetering van de concepten voor de beschrijving van de omzetting in water. Bij de omzetting in water wordt dan rekening gehouden met de bijdragen van afzonderlijke omzettingsmechanismen, hydrolyse, fotolyse en biotische omzetting. Door deze afzonderlijke processen te beschrijven, wordt de totale omzettings-snelheid beter gekwantificeerd en wordt aldus de beschrijving van het gedrag van het pesticide verbeterd.

Andere verbeteringen betreffen de uitbreiding van het model met een beschrijving van bioturbatie als een dispersieproces voor deeltjes en het opnemen van atmosferische depositie als aanvoerroute van het pesticide. Depositie van het pesticide op het oppervlaktewater kan het gevolg zijn van vervluchtiging na toepassing van het middel op het naastgelegen veld.

Op landschapsniveau is het CASCADE-TOXSWA-model ontwikkeld. Dit model is gebaseerd op het TOXSWA-model, maar het beschrijft alleen het transport van het pesticide in de waterlaag van een stelsel van onderling verbonden waterlopen. Het transport in de waterlaag wordt beschreven door advectie en dispersie. Tot nu toe is de enige aanvoerroute de aanvoer als gevolg van spuitdrift. Verdere ontwikkeling van het model vereist het inbouwen van een sedimentcompartiment. Het CASCADE-TOXSWA-model kan verder ontwikkeld worden om het mogelijk te maken dat de blootstelling en de daardoor veroorzaakte effecten op stroomgebied niveau beoordeeld kan worden.

1 Introduction

World-wide pesticides are applied in agricultural fields to control a wide range of pests that would otherwise reduce the quantity and quality of crops. Pesticides may enter surface water by various routes such as surface runoff, leaching to drains and spray drift deposition. Pesticides may have a negative effect on the aquatic environment (e.g. acute toxicity for aquatic organisms) and may threaten the quality of drinking water abstracted from surface water. Therefore, most countries regulate pesticides via legislation prescribing among others environmental risk assessment procedures for aquatic ecosystems (for instance Regulation (EC) No. 1107/2009 in the EU). An important part of these risk assessment procedures is the calculation of Predicted Environmental Concentrations (PEC) and Time Weighted Average exposure concentrations (TWAs), in both the water layer and the sediment of surface waters using fate models.

In the second half of the nineties, the TOXSWA model, that simulates pesticide behaviour in a water-sediment system at the edge-of-field scale, was developed (Adriaanse, 1996). Versions 1.0 and 1.2 simulate constant water depths and discharges and consider only spray drift deposition as entry route of pesticides in the waterbody. From version 2.1 onwards the hydrology has been further developed i.e. simulating a transient flow regime with rapidly varying discharges and water levels in small water courses adjacent to agricultural fields. Furthermore, next to spray drift deposition, pesticide fluxes and water fluxes resulting from drainage and surface runoff (including erosion) can be handled by the model as well (Figure 1). TOXSWA version 3.3 facilitates the formation of metabolites in water and sediment.

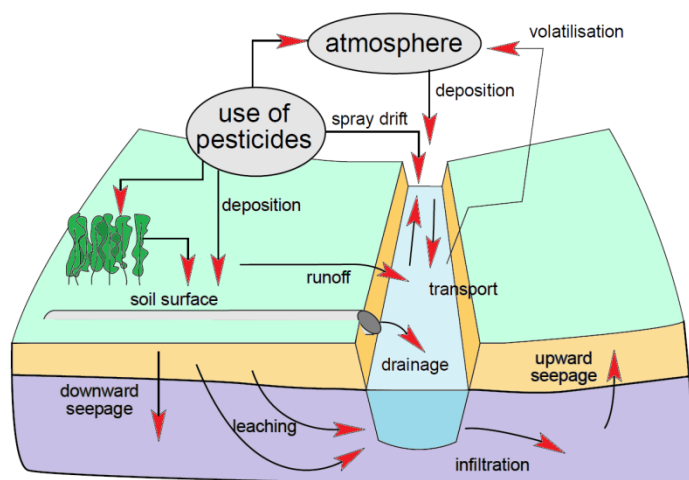


Figure 1 Possible entry routes of pesticides to a waterbody at the edge-of-field scale.

TOXSWA 1.2 has been applied in the Dutch registration procedure for first and higher tier exposure assessments since 1999. Higher tier assessments include the interpretation of field studies for pesticide registration as well as the interpretation of water-sediment studies to determine transformation rates in water and in sediment.

TOXSWA versions 2.1 and onwards are incorporated in the different FOCUS_TOXSWA software tools that have been used in the EU pesticide registration process since 2003. The FOCUS-TOXSWA software tools include ten so-called FOCUS surface water scenarios for which the TOXSWA model is run.

In the FOCUS stream and ditch scenarios, the field-scale system (i.e. waterbody and adjacent field treated with pesticides) is characterized as the downstream part of a catchment. The upstream catchment of the FOCUS stream is partly treated with pesticides; the upstream catchment of the

FOCUS ditch is not treated. The field-scale system of the FOCUS pond scenario is characterized as a waterbody with an adjacent field that is treated with pesticides. The pond receives a constant inflow of water that is free of pesticides.

This report describes the mathematical concepts of TOXSWA version 3.3 i.e. the TOXSWA kernel that is incorporated in the latest FOCUS_TOXSWA software tool (version 4.4.3; for the manual of this software tool we refer to Beltman *et al.*, 2014). Only those concepts in TOXSWA that are relevant for simulations with the FOCUS surface water scenarios and the Dutch scenarios (TOXSWA 1.2; Beltman and Adriaanse, 1999) are described in Chapter 2-8. Mathematical concepts are described independent of specific scenario properties. Elaboration of these concepts using the specific parameterizations of the FOCUS Surface Water scenarios can be found in Adriaanse and Beltman (2009) and Adriaanse *et al.* (in press) considering the hydrology and in Adriaanse *et al.* (2014) for metabolite formation in the partly treated upstream catchment of the FOCUS stream scenarios.

Furthermore, we limited this report to the description of the processes only i.e. descriptions of the numerical solutions used are not given. Considering the numerical solution used to solve the water conservation equations we refer to Adriaanse and Beltman (2009). Considering the numerical solution used to solve the mass conservation equations for pesticide in water and sediment we refer to Adriaanse (1996).

Chapter 2 of this report describes the different model concepts of TOXSWA used for simulating the hydrology of the waterbody.

Chapter 3 gives the concept for simulating the waterbody temperature.

Chapter 4 is subdivided in a part for the water layer and a part for the sediment. Each part starts with a general description of the processes considered in the specific compartment. This is followed by a section giving the conservation equation, which describes the total mass balance for the pesticide in the compartment considered.

In Chapter 5 pesticide entry routes at the boundaries of the waterbody and entry routes representing lateral entries in the waterbody are described. With respect to the lateral entries, four types of inputs are distinguished. The mathematical elaboration in a general sense is given for each of the four types. However not all four types are implemented in TOXSWA. For those types that are implemented in TOXSWA, the mathematical elaboration of the corresponding specific entry route(s) (e.g. drainage, runoff etc.) is given as well.

Equilibrium partitioning between the solid and the liquid phase is described in Chapter 6. In the water layer, the solid phase is defined by suspended solids and macrophytes. In the sediment the pore water represents the liquid phase and the sediment particles the solid phase.

Processes considering pesticide transport and emission are described in Chapter 7. First, the transport processes of advection, dispersion, and transport across the downstream end of the water layer are discussed. Next, transport processes in the sediment are discussed (advection, dispersion, diffusion and transport of pesticide across the downward-facing boundary of the sediment). Subsequently, transport processes at the water-sediment interface are specified. Volatilization from the water layer to the atmosphere is included as well in this chapter.

The formation of reaction products in water and sediment and the rates of the transformations are described in Chapter 8.

In Chapter 9 provides information about model sensitivity, verification and use and testing of the TOXSWA model. Furthermore, ongoing model developments are discussed and attention is paid to the role of the TOXSWA model considering assessing pesticide fate in an interconnected system of water courses (landscape modelling)

2 Model for water flow

2.1 Introduction

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 field. 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 watercourses and also ponds. Differences between the modelled ponds and water courses basically relate only to the dimensions. Length and width of a pond are in the same order whereas for water courses the length is a factor 10 to 100 larger than the width. This chapter describes how the water flow in the water layer is modelled. The descriptions are based on Adriaanse *et al.* (2017), Adriaanse (1996) and Adriaanse and Beltman (2009).

In Section 2.2 a general description of the waterbodies and their hydrology simulated by TOXSWA is given. The different options for simulation of water flow of watercourses are described in Section 2.3, and the different options for the simulation of water flow of ponds in Section 2.4. For each of the options first the position of the modelled system in the landscape is described, secondly the elements of the water balance that are considered in the system, and finally how discharge and water depth in the waterbody are determined.

2.2 System description – general

2.2.1 Geometric elements

The waterbody system is characterized as follows (see *Figure 2*):

- the cross section of the waterbody is shaped as an isosceles trapezium¹ and the wetted perimeter separates the water layer from the neighbouring soil,
- discharge and water level in the waterbody varies in time and along its length,
- upward, downward and lateral flow occur through the bottom and walls of the waterbody.

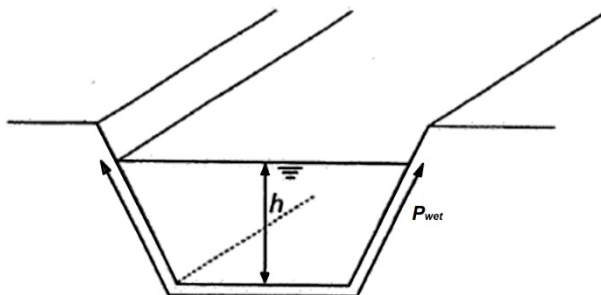


Figure 2 Outline of model system.

with

h = water depth of the waterbody (m)

P_{wet} = length of wetted perimeter of a waterbody (m)

¹ Note that a rectangle is a special form of a trapezium-shape. For the FOCUS waterbodies this rectangular shape was used. For ponds it is common to use the rectangular shape.

The coordinate system is defined as follows (*Figure 3*):
 x-axis: positive in the most frequent direction of flow in the waterbody;
 z-axis: positive with depth, zero at the sediment surface;
 y-axis: perpendicular to the x-axis and the z-axis.

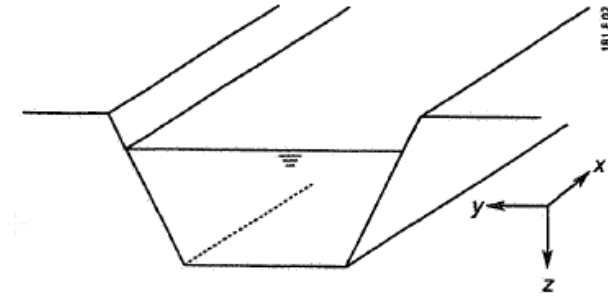


Figure 3 Definition of the coordinate system.

The shape of the wetted cross-section of the waterbody is shown in *Figure 4*.

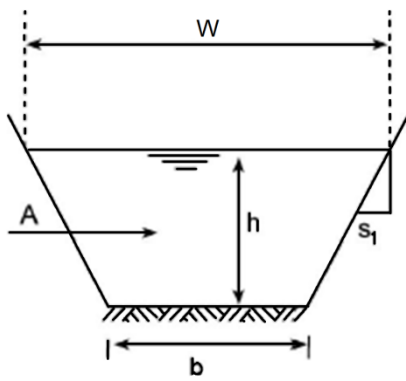


Figure 4 Cross-section of the waterbody.

with

- A = wetted cross sectional area for water flow (m^2)
- b = bottom width of the waterbody (m)
- s_1 = side slope (horizontal/vertical) (-)
- W = width of water surface (m)

The cross-sectional area A of water flow is given by:

$$A = bh + s_1 h^2 \quad (1)$$

The width of the water surface W equals (*Figure 4*):

$$W = b + 2s_1 h \quad (2)$$

2.2.2 Elements of the water balance

The inflow across the upper boundary can vary in time and consists of two components: (i) a base flow, which may be constant and (ii) a variable excess water flow from the catchment.

In addition to the inflow of water across the upper boundary, there is a lateral inflow, consisting of the excess water from the adjacent field. The excess water originates from e.g. drain pipes or surface runoff from the adjacent field. It is a function of precipitation, soil type, land use etc.

Because excess water from the adjacent field enters the watercourse, the flux of water is a function of the distance in the direction of flow. A one-dimensional water conservation equation can be developed for the elemental volume $A\Delta x$, in which A represents the cross-sectional surface area perpendicular to the direction of flow (*Figure 5*).

The water conservation equation for the water layer in the edge-of-field waterbody is:

$$\frac{\partial A}{\partial t} = -\frac{\partial Q}{\partial x} + \Phi + P_r \cdot W + E \cdot W - S \cdot P_{wet} \quad (3)$$

with:

- t = time (d)
- Q = discharge, i.e. volume flux of water passing through a vertical cross-section of the waterbody ($\text{m}^3 \text{d}^{-1}$)
- x = distance in the direction of flow (m)
- Φ = lineic volume flux of water, that is lateral inflow originating from drainage or runoff and drainage subsurface flow from the adjacent field ($\text{m}^3 \text{m}^{-1} \text{d}^{-1}$)
- P_r = areic volume flux from precipitation, i.e. volume of precipitation divided by an appropriate waterbody surface area and by time; the flux is positive in a downward direction ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)
- E = areic volume flux from evaporation; the flux is negative in an upward direction ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)
- S = areic volume flux from seepage expressed per appropriate sediment surface area, i.e. volume of water seeping upward or downward; the flux is positive in a downward direction ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)

The lineic volume flux from the adjacent field equals:

$$\Phi = w_F \cdot q_F \quad (4)$$

with:

- 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 ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)

The (upward or downward) seepage in the sediment equals:

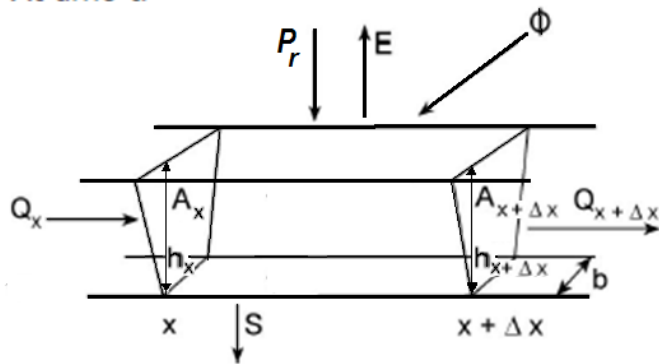
$$S = \frac{w_F}{P_{wet}} q_{F,s} \quad (5)$$

with

- $q_{F,s}$ = areic volume flux from seepage flow² from the adjacent field, expressed per surface area adjacent field ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)

² The seepage flux $q_{F,s}$ is a flux of the adjacent field that results in a flux through the water-sediment interface. Upwards seepage results in a negative $q_{F,s}$.

At time t



At time $t + \Delta t$

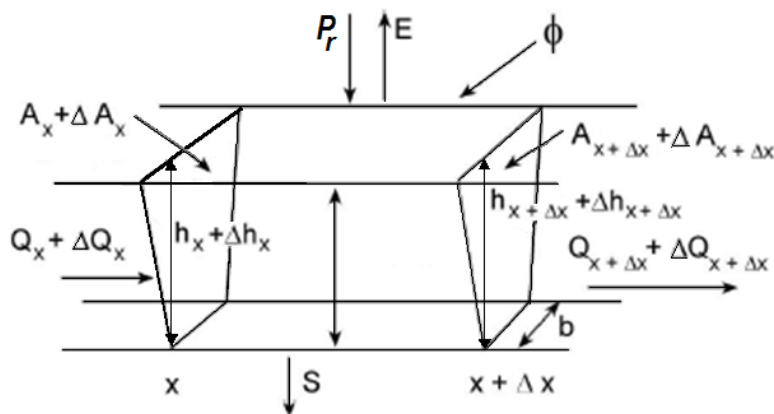


Figure 5 Elemental volume in the edge-of-field waterbody at times t and $t + \Delta t$, with its main water balance components.

- A_x = wetted cross sectional area of flow at location x (m^2)
- Q_x = discharge, i.e. volume flux of water passing through a vertical cross-section of the waterbody at location x ($\text{m}^3 \text{d}^{-1}$)
- h_x = water depth of the waterbody at location x (m)

2.3 Hydrology of watercourses

2.3.1 Constant flow

This type of hydrology has been used for the Dutch scenario with spray drift entries only (Beltman & Adriaanse, 1999).

The system is a watercourse in which the discharge and the water depth are constant over the whole length of the waterbody and also constant in time. Hence also the flow velocity of water is constant over the full length of the watercourse, and in time.

For this system all terms in the water conservation equation are zero, except the inflow and outflow of water which are equal.

2.3.2 Transient flow; constant water depth along length of modelled watercourse

Introduction

This type of hydrology has been used for the FOCUS ditch and the FOCUS stream scenarios (FOCUS, 2001). The two FOCUS watercourses are 100 m long and have a rectangular cross-section, so $s_l = 0$.

Transient flow means 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 waterbody. However, a concept for gradual, varied flow (discharge and water depth vary in time and along the length of the waterbody) is available (Opheusden *et al.*, 2011), but not yet implemented.

In the next section it is explained how the discharge and the water depth in the modelled watercourse are calculated for the type of hydrology defined here as "transient flow; constant water depth along the length of the modelled water course". With "modelled watercourse" we refer to that part of the watercourse that is situated along an agricultural field and of which simulated concentrations are used in exposure assessment of pesticide registration procedures. The text of the next sections is based upon Adriaanse *et al.* (2017).

Position of the watercourse in the landscape

The modelled watercourse is located at the downstream end of a small catchment, enabling simulation of a realistic transient flow regime. The size of the catchment may vary from a few to a few hundred hectares. A small weir located downstream in the watercourse maintains the water level next to the adjacent field at a specified minimum depth (Figure 6). It is assumed that excess water fluxes (e.g. drainage, surface runoff) of the agricultural fields in the upstream catchment equal the excess water fluxes from the adjacent field.

The water flow in the modelled watercourse is described by assuming the water depth to be constant over the length of this watercourse, so the water depth only varies in time.

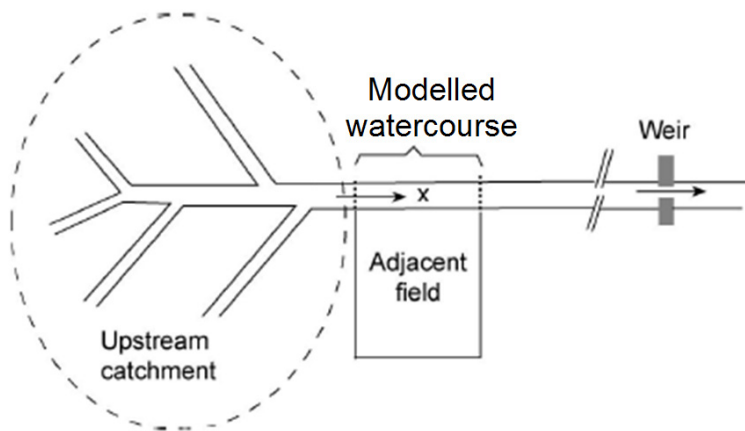


Figure 6 Schematic layout of the modelled watercourse along the adjacent field, including upstream catchment and weir.

Elements of water balance

The water balance is set up for the modelled watercourse along the total length of the adjacent agricultural field where x ranges from 0 to the total length of the adjacent agricultural field. The water conservation equation of Eq. (3) is simplified to³:

$$\frac{\partial Q}{\partial x} = -\frac{\partial A}{\partial t} + \Phi + SP_{wet} \quad (6)$$

³ The precipitation and evaporation terms of the general water balance (see section 2.2.2) were not implemented for the modelled watercourse. The seepage term is implemented in TOXSWA. However, in the parameterization of the FOCUS Surface Water scenarios the seepage flux, $q_{F,s}$ is set to zero.

The upstream boundary condition of Eq. (6) is the water flow rate coming out of the upstream catchment. This consists of (i) a small constant base flow from the upstream catchment, and (ii) either variable drainage water fluxes from the agricultural fields of the upstream catchment or highly variable runoff water fluxes and (iii) subsurface drainage water fluxes, both from the agricultural fields of the upstream catchment. Hence:

$$Q_u = Q_{base} + 10^4 q_F A_{up} \quad (7)$$

with

- Q_u = total discharge or volume flux of water entering the waterbody at the upstream boundary ($\text{m}^3 \text{d}^{-1}$)
- Q_{base} = discharge or volume flux of the base flow delivered by the upstream catchment ($\text{m}^3 \text{d}^{-1}$)
- A_{up} = size of the upstream catchment area (ha)
- 10^4 = factor to convert $\text{m} \cdot \text{ha}$ into m^3 ($\text{m}^3 (\text{m ha})^{-1}$)

In case runoff fluxes are supplemented with subsurface drainage water fluxes, the flux of excess water from the adjacent field, q_F is calculated with:

$$q_F = q_{F,r} + f_d \cdot q_{F,down} \quad (8)$$

with

- $q_{F,r}$ = areic volume flux of surface runoff excess water from the adjacent field, ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)
- f_d = fraction of downward areic volume flux of water at 1 m soil depth that is drained into the modelled water course (-)
- $q_{F,down}$ = areic volume flux of excess water at 1 m soil depth originating from the adjacent field, ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)

Note that the flux of excess water from the adjacent field, q_F is to calculate Φ in Eq. (4).

Discharge and water depth

To be able to solve the water balance (Eq. (6)) in the modelled watercourse we need to determine one of the two unknown variables of this equation, A or Q . We opted for A , *i.e.* the water depth h in the watercourse (see *Figure 5*). Thus, by imposing a water depth h as a function of time it is theoretically possible to calculate the discharge Q as a function of distance in the modelled watercourse.

To do so, we calculated the water depth h for the entire watercourse, *i.e.* from the weir up to the upper boundary of the entire watercourse. The modelled water course is found somewhere between the weir and the upper boundary of the entire watercourse. Uniform flow conditions prevail at the upper boundary of the entire watercourse (*Figure 7*).

We first simplified the stream flow into a flow with a constant discharge along the total length of the entire watercourse by excluding the lateral water inflow from the adjacent field. Only the water flow delivered by the upstream catchment (Q_u) is considered. The simplification is adequate when the lateral inflow is small compared to the water flow delivered by the upstream catchment Q_u (e.g. for FOCUS stream scenarios with its 100 ha size upstream catchment and 1 ha agricultural field adjacent the 100 m FOCUS stream the lateral inflow adds only 1% to the main stream flow). In case the lateral inflow is in the same order of magnitude as the water flow delivered by the upstream catchment Q_u (e.g. for FOCUS ditch scenarios with its 2 ha size upstream catchment and 1 ha agricultural field adjacent to the 100 m FOCUS ditch), the simplification into a constant discharge may impact the calculated water depth in the watercourse. As the numerical solution of the pesticide mass conservation equation for the water layer does take lateral water inflow into account, the impact on calculated pesticide concentrations is expected to be minor (especially for FOCUS ditch scenarios with its water depth varying between approximately 0.3 and 0.36 m).

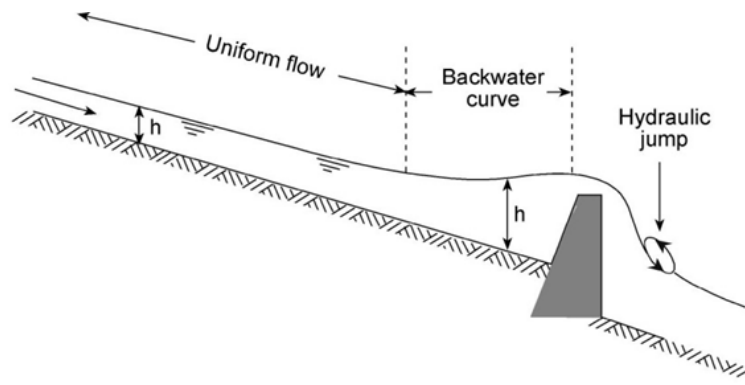


Figure 7 Schematic representation of the water level in the watercourse. At some distance upstream of the weir, the backwater curve has reached the uniform flow depth. The water depth increases travelling in a downstream direction towards the weir. Note that the vertical scale is exaggerated compared to the horizontal scale.

The water depth h as a function of Q_u is calculated in four steps:

- (1) calculation of the uniform flow depth at the upper boundary of the entire watercourse, h_{uni} ;
- (2) calculation of the water depth in front of the weir at the downstream end of the watercourse, h_{weir} ;
- (3) interpolation of the water depth as function of distance between h_{uni} and h_{weir} and
- (4) selection of the water depth at the entrance of the modelled watercourse, *i.e.* at $x = 0$ m.

The value of the water depth at the entrance of the modelled watercourse calculated in step 4 is taken to be the water depth for the full length of the modelled watercourse.

Calculation of uniform flow depth

At some distance upstream in the watercourse the water flow is not influenced anymore by the weir (Figure 7), and there is equilibrium between the friction forces and the gravitation forces on the waterbody; assuming constant watercourse properties, such as width, bottom slope and bottom roughness this so-called uniform flow is characterized by a water depth and discharge that are constant along the watercourse length. Because the discharge equals the known Q_u the constant uniform flow depth can be calculated by the widely used Chézy-Manning formula (e.g. Vennard and Street, 1976):

$$Q_u = A R_{wet}^{2/3} \kappa_M G^{1/2} \quad (9)$$

with

- R_{wet} = hydraulic radius of the wetted cross-section (m)
- κ_M = Manning's coefficient of channel roughness ($m^{1/3} d^{-1}$)
- G = slope of the energy line, for uniform flow equal to the hydraulic gradient (difference in water surface level at two locations divided by their distance), which is for uniform flow also equal to the bottom slope (-).

The hydraulic radius R_{wet} equals:

$$R_{wet} = \frac{A}{P_{wet}} \quad (10)$$

The wetted perimeter of the waterbody P_{wet} equals:

$$P_{wet} = b + 2h\sqrt{s_1^2 + 1} \quad (11)$$

For small watercourses Manning's coefficient for channel roughness is a function of water depth according to the empirical relationship:

$$\kappa_M = \kappa_{M,1m} h_{uni}^{1/3} \quad (12)$$

with

$\kappa_{M,1m}$ = coefficient defining Manning's coefficient for channel roughness in a channel with a 1 m water depth (d^{-1}) (Querner, 1993)

h_{uni} = uniform flow depth, *i.e.* water depth at uniform flow (m)

Eq. (9) needs to be solved in combination with Eq. (1), (10), (11) and (12) to find the uniform flow depth h_{uni} . Using this set of equations h must be replaced by h_{uni} .

Calculation of the water depth in front of the weir

At the downstream end of the watercourse a freely-outflowing weir is located, raising or lowering the uniform flow depth immediately in front of the weir. As the weir has a free outflow its downstream water level does not influence its upstream water level and therefore the water level over the weir crest can be calculated by the so-called head-discharge relation⁴, relating the upstream water level over the crest to the discharge over the weir (Bos, 1976). Hence:

$$Q_{weir} = C_{weir} b_{crest} h_{crest}^{3/2} \quad (13)$$

with

Q_{weir} = discharge at the location of the weir ($m^3 d^{-1}$)

C_{weir} = discharge coefficient, depending on weir characteristics ($m^{1/2} d^{-1}$)

b_{crest} = width of weir crest (m)

h_{crest} = upstream water level over the weir crest, also called head (m)

As we simplified the watercourse flow into a flow constant over the entire watercourse, the upstream water level over the weir crest h_{crest} can be calculated by using Q_u in the head-discharge relation, so by substituting Q_u for Q_{weir} in Eq. (13).

The water depth h_{weir} immediately in front of the weir equals:

$$h_{weir} = p_{weir} + h_{crest} \quad (14)$$

with

h_{weir} = water depth immediately in front of weir (m)

p_{weir} = height of weir crest above waterbody bottom (m)

Interpolation of the water depth as function of distance

The water depth as a function of distance for the entire watercourse is obtained by interpolation between h_{uni} and h_{weir} . At the upper end uniform flow prevails and thus, the water depth equals the constant uniform flow depth, h_{uni} . Going downstream the uniform flow regime is disturbed by the weir. For small discharges the weir may dam up, *i.e.* raise the water level, while for large flows the weir may draw down, *i.e.* lower the water level in front of the weir. The disturbed water level profile, a so-called backwater curve, is obtained by interpolation using the Direct Step method (e.g. Chow, 1959; Akan, 2006). The Direct Step method starts with h_{weir} at the weir and moves in upstream direction until h_{uni} is reached. It is characterized by dividing the total water depth change into small steps, corresponding to short watercourse sections and is based upon the assumption that within the short sections energy is lost by friction only (so not by e.g. turbulences). For a given watercourse, the length of the backwater curve is a function of discharge as well as the difference between h_{uni} and h_{weir} . The length of the backwater curve varies in time and generally equals a few tens to hundreds of meters.

⁴ The relation is valid for a weir with a rectangular shaped opening

Selection of the water depth at the entrance of the watercourse

Out of the obtained water level profile we finally select the water depth h at a distance L_{d-w} (scenario dependent) upstream of the weir, corresponding to the entrance of the modelled watercourse, *i.e.* at $x = 0$ m. We thus obtain a constant water depth (h at $x = 0$ m) for the modelled watercourse as a function of time. This value of h is used to solve the water conservation equation, Eq. (6)⁵ which results in Q_u as a function of x .

Note that the distance L_{d-w} is a scenario property with a fixed value for the entire simulation period. The distance between h_{uni} and h_{weir} is variable in time. Consequently, it may happen that for a certain time h at a distance L_{d-w} equals h_{uni} . However, h at a distance L_{d-w} can also equal a water depth somewhere between h_{uni} and h_{weir} *i.e.* a water depth found somewhere in the backwater curve.

2.4 Pond systems

2.4.1 No flow

This type of hydrology is used for simulation of water-sediment systems (Ter Horst and Koelmans, 2016; Beltman *et al.*, 2015) and microcosms (Deneer *et al.*, 2016). These water-sediment systems have a rectangular cross-section, *i.e.* $s_1 = 0$.

The system is a pond in which the water depth has a fixed value and there is no flow, hence $A =$ constant and $Q = 0$ in *Figure 5*.

In the water conservation for this system all terms are zero. Because the discharge is zero, also the flow velocity is zero.

2.4.2 Transient flow

Introduction

This type of hydrology has been used for the FOCUS pond scenarios (FOCUS, 2001). These ponds have a rectangular cross-section, *i.e.* the side slope; horizontal/vertical is zero. The concept for transient flow in ponds presented here is only valid in case incoming base flows and excess water fluxes from the contributing areas are small compared to the pond volume and consequently a head over the weir crest that is in the order of a few centimetres.

Position of the pond in the landscape

A pond is a reservoir having an incoming and an outgoing water flow. Fields that may be located at its bank deliver their excess water into the pond; these fields are called the contributing area (*Figure 8*). The total incoming flow consists of a constant base flow plus the excess water from the contributing area, delivered into the pond. The pond outflow occurs across a weir. The incoming excess water from the contributing area originates from *e.g.* drain pipes or surface runoff. Since it is a function of precipitation, soil type, land use *etc.*, the excess water fluxes vary in time. The water depth in the pond only varies in time.

⁵ Next to the hourly h values TOXSWA calculates values of h at time step divisions of the hour for linearly interpolated values of the hour values of Q_u . The water balance equation is numerically solved with the aid of an explicit finite-difference solution scheme. The hourly input values of drainage/runoff are interpolated with time steps divisions of the hour to transform the sudden large, discontinuous increases in inflow Q_u into more realistic smooth increases in Q_u : for instance an increase of the base flow of around 10-20 m³/h up to a Q_u of 2000 m³/h, *i.e.* 2 mm/h from 100 ha, is subdivided into *e.g.* six steps with 2000 m³/h being the highest value. Because the inflow Q_u is not linearly related to h (Eq. 9-11), the water depth h is not linearly interpolated within each hour. Instead it is *e.g.* six times within the hour calculated with the aid of the interpolated Q_u and the backwater curve in front of the weir and thus, within each hour six times the Q profile (Eq. 7) is obtained. In this way the highly dynamic flow is represented more realistically. Finally, hourly values of Q and h are transferred to the numerical solutions of the mass balances (Adriaanse and Beltman, 2009).

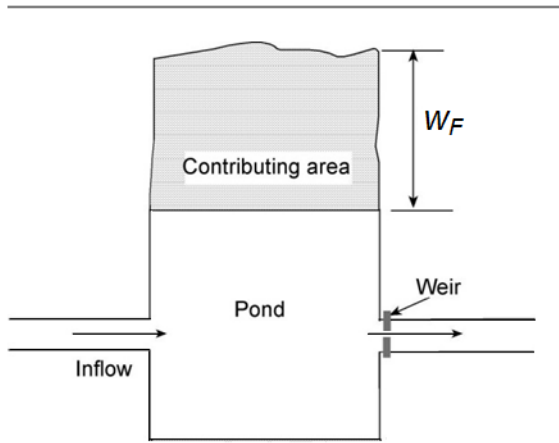


Figure 8 Schematic layout of the pond with inflow, contributing area with total width w_F and weir.

When the area of the contributing area to the pond is given, the width of the adjacent field, w_F , is calculated with:

$$w_F = \frac{A_{contr,pond}}{L} \quad (15)$$

with:

$A_{contr,pond}$ = area next to the pond contributing water to the pond (m²)
 L = length of the pond (m)

Elements of water balance

The water balance is set up for the pond. The water conservation equation of Eq. (3) is simplified to⁶:

$$\frac{\partial Q}{\partial x} = -\frac{\partial A}{\partial t} + \Phi + SP_{wet} \quad (16)$$

The upstream boundary condition of Eq. (6) corresponds to the incoming water flow:

$$Q_u = Q_{base} \quad (17)$$

Discharge and water depth

A weir, located at the outlet of the pond, governs the pond's discharge (see Figure 9). The discharge of the pond at the location of the weir Q_{out} is calculated with:

$$Q_{out} = Q_u + L \cdot \Phi \quad (18)$$

We use Q_{out} in the head-discharge relation of Eq. 13. Hence by filling in Q_{out} for Q_{weir} in Eq. (13), then combined with Eq. (14) h_{weir} is calculated. This value of h_{weir} is used for the water depth in the pond, h . This h is used to solve the water conservation equation, Eq. (16) which results in Q_u as a function of x .

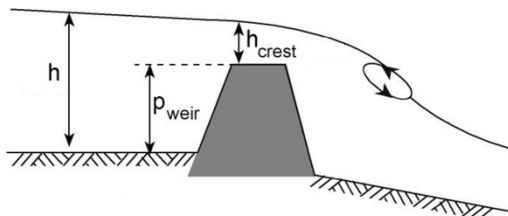


Figure 9 Schematic representation of the water depth in the pond.

⁶ The precipitation and evaporation terms of the general water balance (see section 2.2.2) were not implemented for the modelled watercourse. The seepage term is implemented in TOXSWA. However, in the parameterization of the FOCUS Surface Water scenarios the seepage flux, $q_{F,s}$ is set to zero.

3 Temperature for the modelled system

The temperature in the water layer and in the underlying sediment system depends on the meteorological conditions. This temperature can be expected to vary with the depth in the water layer and the depth in the sediment layer, but also with the horizontal position in the water layer. To include the effect of weather conditions on the course of the temperature with time, depth and distance would require descriptions of the terms and fluxes that contribute to the energy balance of the system. In TOXSWA version 3.3, a simple approach has been implemented. Using this approach, the temperature in the waterbody system (water layer and sediment) is assumed to remain constant during periods of one month. Monthly average water temperatures can be calculated from daily measurements of water temperature. However, if measurements are not available, the monthly temperature can be obtained from daily averages of the air temperature:

$$T_{wb} = T_{a,m} \quad (19)$$

with

T_{wb} = temperature of the waterbody (K)

$T_{a,m}$ = monthly average of the air temperature at 2 m above the ground (K)

When the calculated monthly temperature is below 277.15 K (4°C), the temperature in the TOXSWA simulation remains at 277.15 K. Reasoning for this minimum temperature of 277.15 K (4°C) is as follows. When freezing conditions occur and sustain, ice is formed at the top and grows downwards. During this freezing process, the temperature of the water at the bottom of the waterbody remains around 277.15 K (De Bruin and Wessels, 1988).

4 Pesticide system and conservation equations

4.1 Water layer

4.1.1 System description - general

In the water layer, the substance is subject to the following processes (see Figure 10).

- Advection and dispersion in x-direction.
- Exchange with the atmosphere, through a diffusive flux across the water-atmosphere interface.
- Exchange with the sediment, through advection, dispersion and diffusion across the wetted perimeter.
- Sorption to suspended solids and to macrophytes.
- Transformation, described as overall transformation of substance dissolved, sorbed to suspended solids and sorbed to macrophytes.

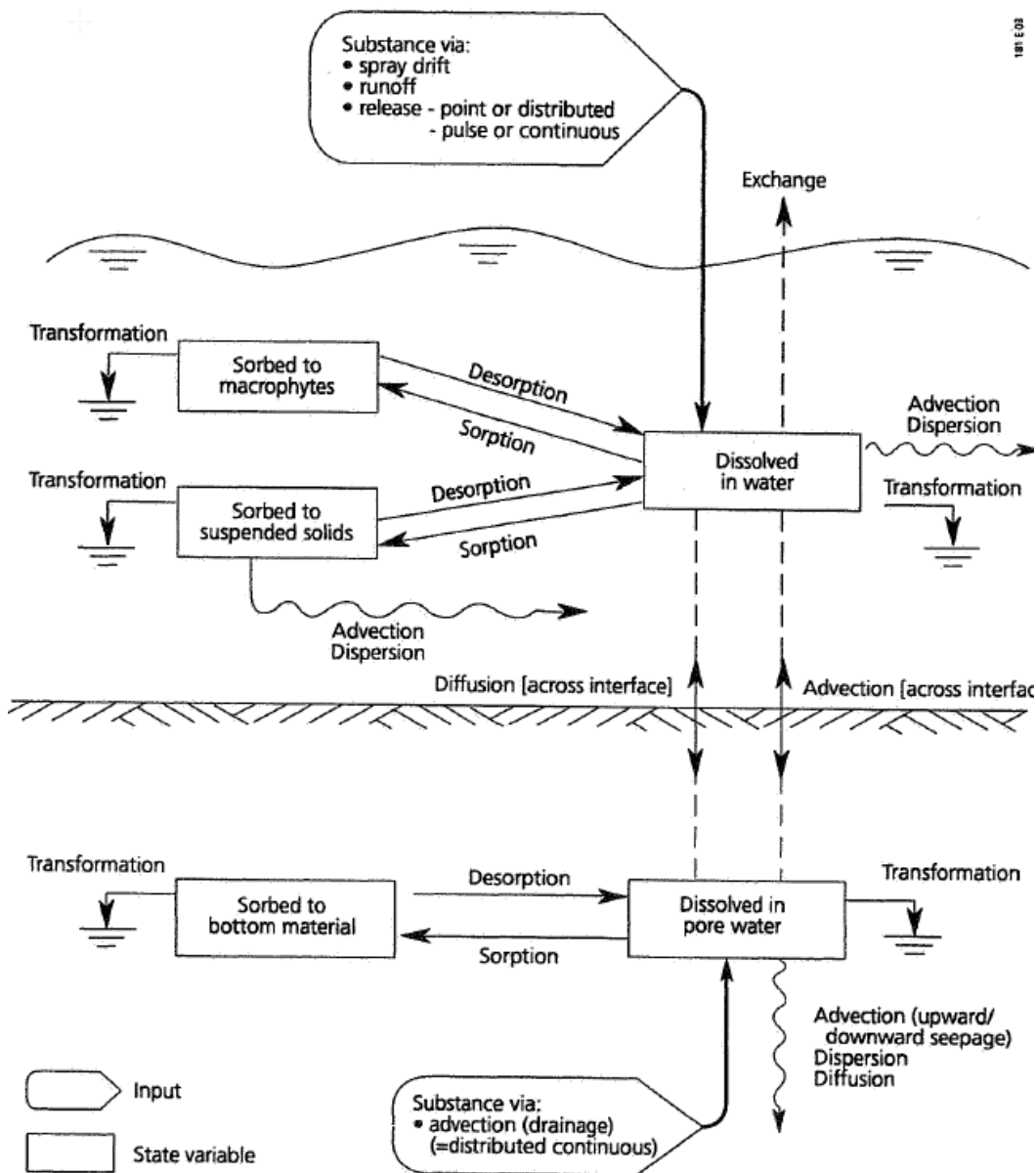


Figure 10 Diagram of modelled processes.

Diffusion in the x -direction has not been included, as dispersion prevails; the dispersion process exists even in stagnant waters, due to e.g. wind effects and inversion of the water layer caused by temperature changes between day and night.

The suspended solids concentration is assumed to be constant. The suspended solids flow along with water. Assuming a constant suspended solids concentration implies that when water is entering the waterbody (from upstream, from drains, by precipitation etc.) suspended solids will enter as well. These incoming suspended solids do not contain pesticides upon entering the waterbody. However, immediately the total mass of pesticide present in the water layer is redistributed in the model and the pesticides sorb to the incoming suspended solids. Consequently the concentration of pesticides dissolved in the water phase will decrease (that is, not only by dilution, but also by sorption to the incoming suspended solids). Pesticides sorbed to suspended solids are subject to the same advection and dispersion as pesticides dissolved in the water phase.

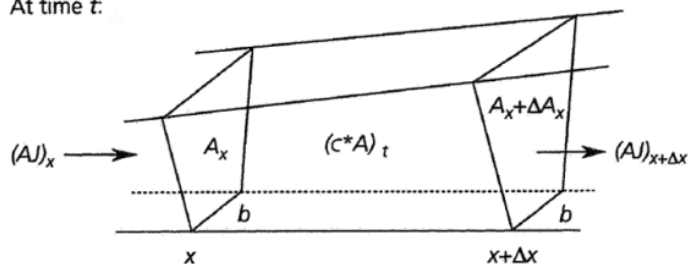
The sedimentation or resuspension of suspended solids is not taken into account. This describes well the following two cases: (i) weakly to moderate pesticide sorption and/or small mass of suspended solids and (ii) relatively short periods, or over somewhat longer periods in clear, moderately eutrophic waterbodies. For these cases pesticide remain mainly in the dissolved phase and the mass on the suspended solids is negligibly small. However, for strongly sorbing pesticides and or simulation of turbid hypertrophic waterbodies for longer periods sedimentation and resuspension cannot be disregarded.

The water layer is assumed to be ideally mixed horizontally and vertically (y - and z -directions; *Figure 3*) and the substance shows a concentration gradient only in the direction of flow (hence, only x -direction and not in y - and z -direction). This means that a one-dimensional mass balance can be drawn up for the elemental volume $A\Delta x$, in which A represents the wetted surface perpendicular to the direction of flow.

The mass balance for the substance in the water layer is depicted *Figure 11*, with

- c_w^* = mass concentration of substance in water layer, including substance sorbed to suspended solids and to macrophytes (kg m^{-3})
- J_w = areic mass flux of substance in water layer by advection and dispersion ($\text{kg m}^{-2} \text{d}^{-1}$)
- $P_{0,x}$ = length of wetted perimeter at the water-sediment interface ($z = 0$ from the perspective of the sediment) at location x (m)

At time t :



At time $t+\Delta t$:

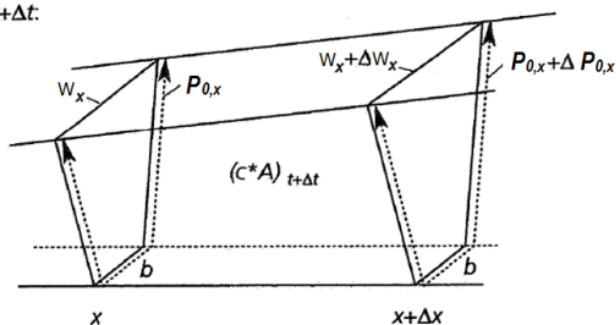


Figure 11 Mass balance at times t and $t+\Delta t$ in the water body; c^*A is the mass above a unit of length Δx ; note that A , $P_{0,x}$ and W_x at $t+\Delta t$ are different from those at time t .

Note that for the exchange between the water layer and sediment the symbol P_{wet} has been used for exchange of water, and the symbols P_0 , P_z and P_D are used for the exchange of pesticide.

Only the length of the waterbody and the width of the waterbody bottom, b , are constant values. All other parameters shown in *Figure 11* can change in time, and can vary along the length of the waterbody.

4.1.2 Conservation equation

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

$$\frac{\partial(c_w^* \cdot A)}{\partial t} = - \frac{\partial(A \cdot J_w)}{\partial x} - R_{t,p} \cdot A + J_a W - J_s \cdot P_0 \quad (20)$$

with:

- $R_{t,p}$ = rate of transformation of substance in the water layer (i.e. in water phase, sorbed to suspended solids and sorbed to macrophytes) ($\text{kg m}^{-3} \text{d}^{-1}$)
- J_a = areic⁷ mass flux of substance across the water-air interface ($\text{kg m}^{-2} \text{d}^{-1}$) [the flux is negative in upward direction]
- J_s = areic mass flux of substance across the water-sediment interface ($\text{kg m}^{-2} \text{d}^{-1}$)
- P_0 = length of wetted perimeter at depth $z = 0$, via which exchange between water and sediment occurs (m)

For each of the transformation products an extra term is added to the right-hand side of Eq. (20):

$$\frac{\partial(c_w^* \cdot A)}{\partial t} = - \frac{\partial(A \cdot J_w)}{\partial x} - R_{t,p} \cdot A + J_a \cdot W - J_s \cdot P_0 + R_{f,p} \quad (21)$$

with:

- $R_{f,p}$ = rate of formation of substance in the water layer ($\text{kg m}^{-3} \text{d}^{-1}$)

The total pesticide concentration in the water layer, c_w^* , is given by:

$$c_w^* = c_w + \frac{m_{mp} \cdot P_0}{A} X_{mp} + m_{ss} X_{ss} \quad (22)$$

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_w = mass concentration of substance in the water phase (kg m^{-3})

4.2 Sediment

4.2.1 System description - general

In the sediment the substance is subject to the following processes (see *Figure 10*).

- Advection, dispersion and diffusion in z-direction.
- Exchange with the water layer by advection and diffusion.
- Sorption to the solid phase of the sediment.
- Transformation, described as overall transformation of substance dissolved and sorbed to the solid phase of the sediment.

⁷ areic means that it is divided by the surface area concerned.

In small waterbodies (beside the bottom of the waterbody) the walls account for an important part of the total exchange area between water and sediment. Therefore the wetted perimeter instead of the bottom width is modelled as the exchange area.

Perpendicular to the wetted perimeter, the substance is transported between water layer and sediment. Per unit of length in the direction of flow this transport takes place through an area $P_0 \cdot 1$ (m^2).

The perimeter at the water-sediment interface, P_0 , is given by:

$$P_0 = b + 2h_w \sqrt{s_1^2 + 1} \quad (23)$$

with:

h_w = depth defining perimeter for exchange between water and sediment (m)

At distance z from the water-sediment interface transport in the sediment takes place through the area $P_z \cdot 1$ (see *Figure 12* and *Figure 14*), where

$$P_z = b + 2z \cdot \tan\left(\frac{1}{2}\beta\right) + 2(h_w + z) \sqrt{s_1^2 + 1} \quad (24)$$

with:

P_z = length of perimeter at depth z from the water-sediment interface (m)

β = $\arctan(1/s_1)$ (rad)

z = depth in the sediment from the water-sediment interface to area concerned (m)

Transport perpendicular to the wetted perimeter occurs in two dimensions, the z -direction and the y -direction. It has been assumed that the substance is ideally mixed horizontally (i.e. y -direction) in the sediment. Furthermore, it has been assumed that transport in the x -direction in the sediment is so small that it can be neglected. Hence the three-dimensional transport has been simplified to the one-dimensional transport in the z -direction. This implies also that transport 'around corners' is neglected; the waterbody walls are straightened and the flow pattern has been simplified to one-dimensional transport in a widening sediment column.

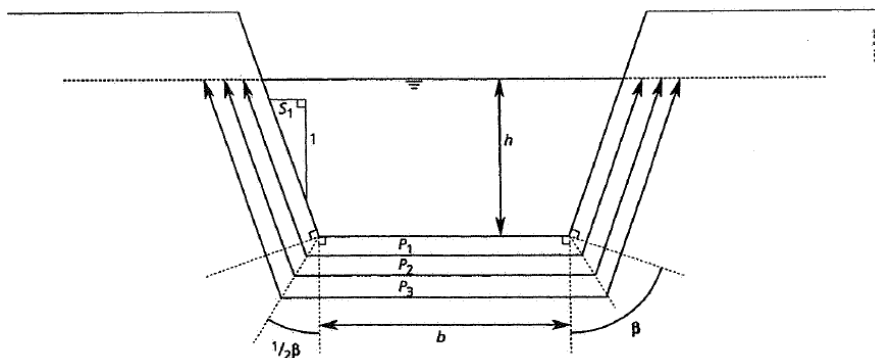


Figure 12 Cross section of a waterbody and the sediment below this body with the shape of stacked trapezia (in the figure it is assumed that $h_w = h$). The lines in the sediment are the perimeters whose length increases with depth in the sediment.

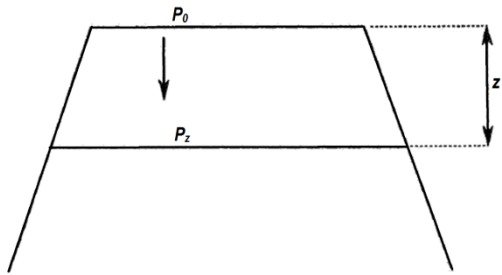


Figure 13 The sediment subsystem simplified to one dimension.

Hence the assumption is that the two-dimensional transport can be calculated by means of a one-dimensional description of mass transport in a sediment column widening with depth. This one-dimensional description has been applied to the sediment subsystem situated below the exchange area between water layer and sediment; this area has a constant size. The assumption has been made that the size of the exchange area is constant, and does not depend on the varying water level in the waterbody.

The size of the exchange area per unit of length in the x direction equals the wetted perimeter of the waterbody corresponding to a particular water level h_w (Figure 14). This fixed value of h_w can be for instance the minimal water level occurring in the waterbody. The mass transport thus takes place in a trapezium-shaped sediment column underneath the area of constant size P_0 , per unit of length.

Note that when $h_w = 0$ the perimeter still increases with depth (see Eq. (24)), which can be seen in Figure 14. For simulation of water-sediment studies (e.g. Ter Horst & Koelmans, 2016) or mesocosms with vertical artificial walls (e.g. Deneer *et al.*, 2016) this is not realistic because sediment is only present directly below the water layer. For these types of systems Eq. (24) has been simplified to:

$$P_z = b \tag{25}$$

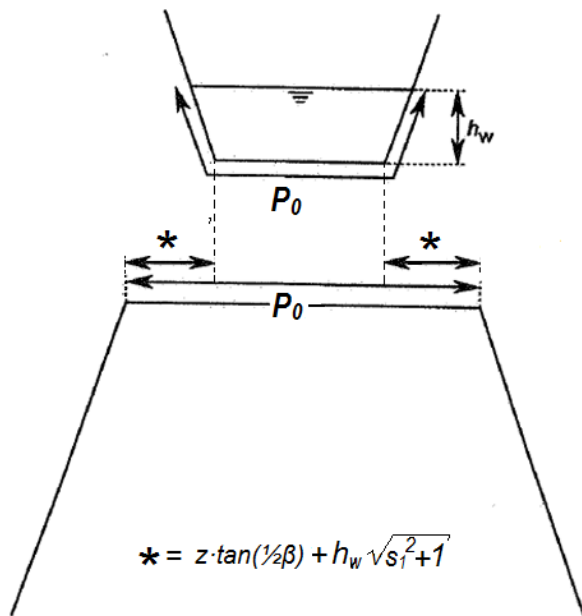


Figure 14 The sediment subsystem situated below an area of constant size, through which exchange of pesticide between water layer and sediment occurs.

The mass balance for the substance in the sediment is depicted in Figure 15

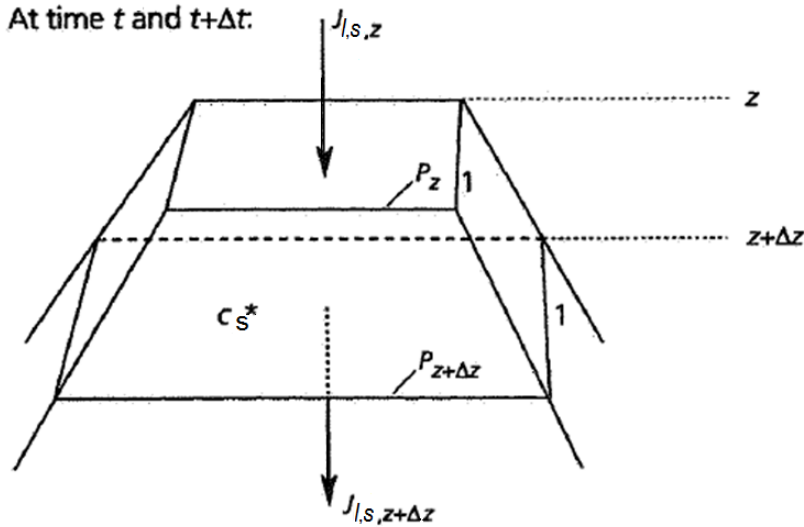


Figure 15 Mass balance for the sediment subsystem. c_s^* is the mass above a unit of length Δx

4.2.2 Conservation equation

The mass conservation equation for the pesticide in sediment is:

$$P \frac{\partial c_s^*}{\partial t} = \frac{\partial(P \cdot J_{l,s})}{\partial z} - R_{s,t,p} \cdot P \quad (26)$$

with:

- c_s^* = mass concentration in the sediment (kg m^{-3})
- z = depth in sediment (m)
- $J_{l,s}$ = areic mass flux by advection, dispersion and diffusion in the liquid phase of the sediment ($\text{kg m}^{-2} \text{d}^{-1}$)
- $R_{s,t,p}$ = rate of transformation of parent substance in the sediment ($\text{kg m}^{-3} \text{d}^{-1}$)
- P = length of perimeter (m)

For each of the transformation products an extra term is added to the right-hand side of Eq. (26) which results in:

$$P \frac{\partial c_s^*}{\partial t} = \frac{\partial(P \cdot J_{l,s})}{\partial z} - R_{s,t,p} \cdot P + R_{s,f,p} \cdot P \quad (27)$$

with:

- $R_{s,f,p}$ = rate of formation of parent substance in the sediment ($\text{kg m}^{-3} \text{d}^{-1}$)

The total pesticide concentration in sediment, c_s^* , is given by:

$$c_s^* = \varepsilon c_{l,s} + \rho_b X_s \quad (28)$$

with:

- ε = volume fraction of pore water (-)
- $c_{l,s}$ = 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_s = mass sorbed to sediment (kg kg^{-1}).

5 Pesticide entry routes

5.1 Introduction

In this chapter we discuss pesticide entry routes entering the waterbody at the boundaries and entry routes representing lateral entries in the waterbody. The entries at the boundaries are discussed in Section 5.2. Lateral entries can be divided in to four types of inputs. Not all four types of input are operational in TOXSWA 3.3, however for all four types the mathematical elaboration for the generic case of the input type is given in Annex 2. This is not given for the sediment because its elaboration is analogous to that of the water layer.

For those lateral input entries that are operational in TOXSWA the specific implementation for the corresponding entry route(s) is given in Sections 5.3 – 5.5 (including the mass conservation equation for the pesticide).

5.2 Entry routes at the boundaries

5.2.1 Entries at the upper boundary

Water entering at the upper boundary ($x=0$) of the waterbody may contain pesticide. The pesticide is transported into the waterbody. Here only advection is considered:

$$J_w = Q_u c_u^* \quad (29)$$

with

c_u^* = mass concentration in water discharging into the waterbody at the upstream end of the waterbody (kg m^{-3})

5.2.2 Into sediment via upward seepage

When upward seepage occurs (hence $q_{F,s} < 0$) at the lower end of the sediment (lower boundary) pesticide mass may be transported into the sediment. Here only advection is considered:

$$J_{l,s} = \frac{w_F}{P_D} q_{F,s} c_{spg} \quad (30)$$

with:

c_{spg} = mass concentration in seepage water (kg m^{-3})

P_D = perimeter at lower boundary of sediment, at depth $z=D$ (m)

5.3 Lateral entries in the waterbody - type of inputs

Lateral entries of pesticides into the waterbody are inputs that are included as options in the conservation equation.

In TOXSWA 3.3, the mass conservation equation for the pesticide in the water layer that is extended with two types of entries of pesticide is:

$$\frac{\partial(c_w^*A)}{\partial t} = -\frac{\partial(A \cdot J_w)}{\partial x} - R_{t,p}A + J_a W_x - J_s P_0 + S_{p,d}A + S_{c,d}A \quad (31)$$

with:

$S_{p,d}(t,x)$ = distributed pulse input ($\text{kg m}^{-3} \text{d}^{-1}$)

$S_{c,d}(t,x)$ = distributed source with continuous input ($\text{kg m}^{-3} \text{d}^{-1}$)

Distributed pulse type inputs are released into the water layer in an infinitesimally small period of time, so a certain mass of substance is released into the water layer (e.g. spray drift event).

Distributed sources with a continuous input are released into the waterbody as flux, i.e. mass released during a time interval as a rate (e.g. series of discharging drains in an agricultural field).

The mass conservation equation for the pesticide in the sediment that is extended with one type of entry of pesticide is:

$$P \frac{\partial c_s^*}{\partial t} = \frac{\partial(P \cdot J_{L,s})}{\partial z} - R_{s,t,p}P + S_{c,d}P \quad (32)$$

with:

$S_{c,d}(t,z)$ = distributed source with continuous input ($\text{kg m}^{-3} \text{d}^{-1}$)

Considering the sediment the distributed source with continuous input (e.g. erosion) has been implemented in TOXSWA.

5.4 Spray drift

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 in the water layer at the time of release. The mathematical elaboration for the generic case of a distributed pulse input is given in Annex 2 (Section A2.3).

The equations (82) and (85) (both equations can be found in Annex 2) have been implemented in TOXSWA for the simulation of spray drift entry, where

$$m_L = W \cdot m_{drift} \quad (33)$$

with

m_L = lineic mass of substance (kg m^{-1})

m_{drift} = spray drift mass deposited at the water layer (kg m^{-2})

5.5 Drainage, runoff and erosion

Releases via drainage and runoff are examples of continuous distributed releases into the water layer. Release via erosion is an example of a continuous distributed release into the sediment. The mathematical elaboration for the generic case of a continuous distributed input in the water layer is given in Annex 2 (Section A2.5).

5.5.1 Water layer: drainage and runoff

Drainage and runoff inputs according to Eq. (88) (Annex 2) are modelled in TOXSWA for the water layer with

$$m_{LT}(t, x) = q_F \cdot w_F c_{w,F} \quad (34)$$

with

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

m_{LT} = lineic mass of substance ($\text{kg m}^{-1} \text{d}^{-1}$)

5.5.2 Sediment: erosion

Erosion inputs according to Eq. (89) (Annex 2) are modelled in TOXSWA for the sediment with

$$m_{LT}(t, z) = J_{er} w_{er} \quad (35)$$

with

J_{er} = mass flux of substance associated with eroded soil ($\text{kg m}^{-2} \text{d}^{-1}$)

w_{er} = width of the adjacent field of which soil is eroded (m)

The increase in total sediment concentration by entry of eroded soil is based on the assumption that the waterbody receives the mass flux of substance in eroded sediment from a strip with width F_{er} from the adjacent field. It is furthermore assumed that this mass flux is instantaneously distributed over a top layer of the sediment with thickness z_{mix} , in such a way that the increase of the concentrations is constant over z_{mix} .

5.6 Considerations

The Greenhouse Emission Model (GEM) software tool uses TOXSWA 3.3 in conjunction with other models (e.g. PEARL, SEM) and Dutch greenhouse horticulture exposure scenarios (Wipfler *et al.*, 2015a; Wipfler *et al.*, 2015b) for calculation of pesticide exposure in watercourses adjacent a greenhouse. A release from a water basin of a greenhouse, adding water with a constant concentration of the substance to the adjacent watercourse is an example of a continuous point release. However this type of a lateral entry is not implemented in TOXSWA 3.3. Therefore, for simulating the water and substance inputs from the greenhouses to the adjacent watercourse in the Dutch greenhouse scenarios the following approach was adopted. Discharge from greenhouses to the adjacent watercourse was simulated as a point source at the upper boundary of the watercourse by adding the discharge volume flux to the water flux entering the water layer at the upper boundary of the water body. The pesticide mass that is discharged by the greenhouse was simulated as an incoming mass flux at the upper boundary of the watercourse (Wipfler *et al.*, 2015a).

6 Pesticide process of partitioning

6.1 Water layer

Sorption to suspended solids

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

$$X_{SS} = K_{F,SS} c_{SS,r} \left(\frac{c_w}{c_{SS,r}} \right)^{N_{SS}} \quad (36)$$

with:

- X_{SS} = mass content sorbed to suspended solids ($\text{kg}^{-1} \text{kg}^{-1}$)
- $K_{F,SS}$ = Freundlich coefficient for sorption to suspended solids ($\text{m}^3 \text{kg}^{-1}$)
- $c_{SS,r}$ = 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 on concentration c_w . Then c_w cannot be expressed in explicit way as a function of the other quantities. The implicit equation has to be solved by iteration, as described in Annex 3.

If the pesticide is mainly sorbed to the organic matter of the suspended solids, the Freundlich coefficient for sorption to suspended solids, $K_{F,SS}$, is calculated from

$$K_{F,SS} = m_{om,ss} K_{om,ss} \quad (37)$$

with:

- $m_{om,ss}$ = mass fraction of organic matter in suspended solids ($\text{kg}^{-1} \text{kg}^{-1}$)
- $K_{om,ss}$ = coefficient of equilibrium sorption on organic matter in suspended solids ($\text{m}^3 \text{kg}^{-1}$)

Sorption to macrophytes

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

$$X_{mp} = K_{mp} c_w \quad (38)$$

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 ($\text{m}^3 \text{kg}^{-1}$)

6.2 Sediment

Sorption to sediment

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

$$X_S = K_{F,S} c_{S,r} \left(\frac{c_{l,S}}{c_{S,r}} \right)^{N_S} \quad (39)$$

with:

$K_{F,s}$ = Freundlich coefficient for sorption to sediment ($\text{m}^3 \text{kg}^{-1}$)

$c_{s,r}$ = reference concentration in the liquid phase for sorption to the sediment (kg m^{-3})

N_s = Freundlich exponent for sorption to sediment (-)

Using the Freundlich sorption equation, the partitioning between the solid and liquid phases is dependent on concentration $c_{l,s}$. Then $c_{l,s}$ cannot be expressed in explicit way as a function of the other quantities. The implicit equation has to be solved by iteration, as described in Annex 2.

If the pesticide is mainly sorbed to the organic matter of the sediment, the Freundlich coefficient for sorption to sediment, $K_{F,s}$, is calculated from

$$K_{F,s} = m_{om,s} K_{om,s} \quad (40)$$

with:

$m_{om,s}$ = mass fraction of organic matter in sediment ($\text{kg}^{-1} \text{kg}^{-1}$)

$K_{om,s}$ = coefficient of equilibrium sorption on organic matter in sediment ($\text{m}^3 \text{kg}^{-1}$)

7 Pesticide transport and emission

7.1 Water layer

7.1.1 Transport by advection and dispersion

The flux J_w 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 identical for the dissolved and sorbed substance).

$$J_w = u(c_w + m_{ss}X_{ss}) - E_{phys} \frac{\partial(c_w + m_{ss}X_{ss})}{\partial x} \quad (41)$$

with:

u = flow velocity of the water (m d⁻¹)

E_{phys} = longitudinal dispersion coefficient (in the direction of flow) (m² d⁻¹)

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

$$\frac{\partial\left(A\left[u_x(c_w+m_{ss}X_{ss}) - E_{phys}\frac{\partial(c_w+m_{ss}X_{ss})}{\partial x}\right]\right)}{\partial x} = \frac{\partial\left(Q(c_w+m_{ss}X_{ss}) - AE_{phys}\frac{\partial(c_w+m_{ss}X_{ss})}{\partial x}\right)}{\partial x} \quad (42)$$

in which

$$Q = A \cdot u \quad (43)$$

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

$$E_{phys} = c_F \frac{u^2 W^2}{h \cdot u^*} \quad (44)$$

with:

E_{phys} = physical dispersion coefficient (m² d⁻¹)

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 as (Fischer *et al.*, 1979):

$$u^* = 0.1u \quad (45)$$

7.1.2 Transport by advection to downstream waterbody

Water discharging at the downstream end (lower boundary) of the waterbody transports the pesticide out of the waterbody. Here only advection is considered:

$$J_w = Q_{out} c_w^* \quad (46)$$

with

Q_{out} = discharge of water at the downstream end of the waterbody ($m^3 d^{-1}$)

7.2 Sediment

7.2.1 Transport by advection, dispersion and diffusion

In the pore water the substance is transported by advection, dispersion. This flux, $J_{l,s}$, is described by:

$$J_{l,s} = \frac{w_F}{P} \cdot q_{F,s} \cdot c_{l,s} - \varepsilon (E_{l,s} + D_{l,s}) \frac{\partial c_{l,s}}{\partial z} \quad (47)$$

with

$E_{l,s}$ = dispersion coefficient in pore water ($m^2 d^{-1}$)

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

The dispersion coefficient is taken to be proportional to the volume flux of the liquid phase:

$$E_{l,s} = L_{dis} |\omega| \quad (48)$$

with:

L_{dis} = dispersion length (m)

ω = average flow velocity of pore water (i.e. $w_F q_{F,s} / P \varepsilon$) ($m d^{-1}$)

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

$$D_{l,s} = \lambda \cdot D_w \quad (49)$$

with:

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

D_w = diffusion coefficient in water ($m^2 d^{-1}$)

A special problem may occur in the sediment. Very sharp concentration gradients may exist here. The magnitude (and direction) of the diffusive and dispersive fluxes are calculated with the aid of concentration gradients (see e.g. Eq. (47)). Dispersion of the substance originates in the unequal flow velocities of pore water (i.e. in the velocity distribution) and is thus caused by advection. It then logically follows that the combined material flux resulting from advection and its ensuing dispersion, should have the same direction as the advection. Otherwise the effect would cancel out its cause (Bolt, 1979, pp. 301 and 346).

Figure 16 shows the four possible situations, occurring in the sediment. In situations 1 and 3, the advective and dispersive fluxes have the same direction, so the above mentioned problem does not arise. In situation 2 as well in situation 4, the advective and dispersion fluxes have opposite directions, so it is possible that the dispersive flux cancels out or even exceeds the advective flux. This is prevented as by the procedure described below.

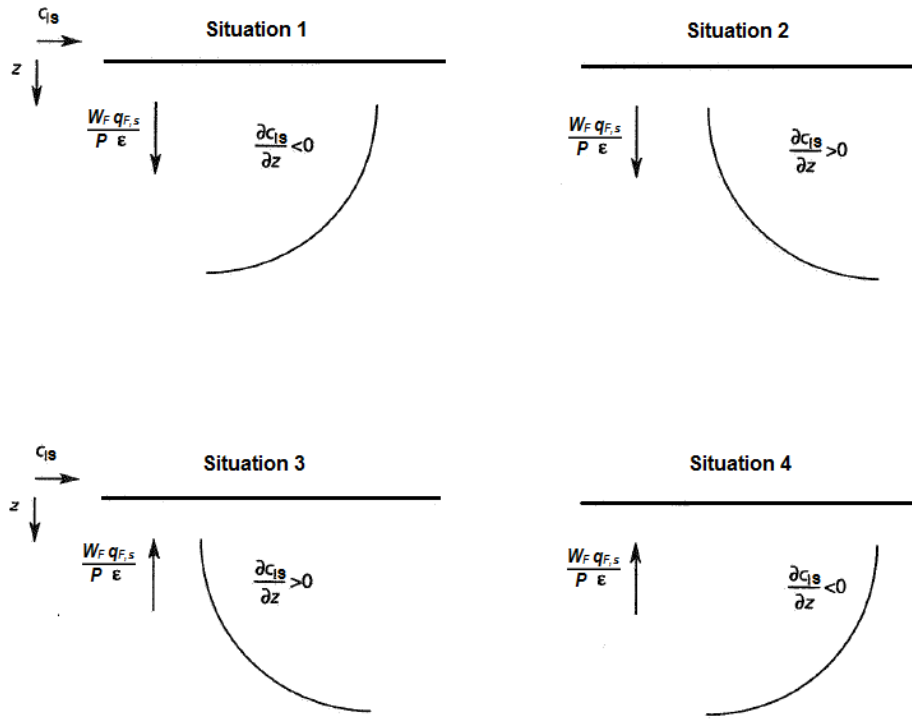


Figure 16 Four situations in the sediment, depicting the possible combinations of the directions of the advection flow (i.e. $w_F q_{F,s} / P \epsilon$) and the concentration gradient ($\partial c_{l,s} / \partial z$).

For situation 2:

$$q_{F,s} > 0 \text{ and } \partial(c_{l,s}) / \partial z > 0.$$

According to Eq. (48), with $q > 0$:

$$E_{l,s} = L_{dis} \frac{W_F q_{F,s}}{P \epsilon} \quad (50)$$

The dispersive flux should not exceed the advective flux, hence:

$$\left| \frac{W_F}{P} q_{F,s} c_{l,s} \right| > \left| \epsilon E_{l,s} \frac{\partial c_{l,s}}{\partial z} \right| \quad (51)$$

giving ($q_{F,s}$ is positive):

$$c_{l,s} - L_{dis} \frac{\partial c_{l,s}}{\partial z} > 0 \quad (52)$$

For situation 4:

$$q_{F,s} < 0 \text{ and } \partial(c_{l,s}) / \partial z < 0.$$

According to Eq. (48), with $q_{F,s} < 0$:

$$E_{l,s} = L_{dis} \frac{-W_F q_{F,s}}{P \epsilon} \quad (53)$$

The dispersive flux should not exceed the advective flux, hence:

$$\left| \frac{w_F}{P} q_{F,s} c_{l,s} \right| > \left| \varepsilon E_{l,s} \frac{\partial c_{l,s}}{\partial z} \right| \quad (54)$$

giving ($-q_{F,s}$ is positive):

$$c_{l,s} - L_{dis} \frac{\partial c_{l,s}}{\partial z} > 0 \quad (55)$$

This means that the dispersive flux is smaller than the advective flux if the following conditions are fulfilled:

$$\text{for } q_{F,s} > 0, \text{ and } \frac{\partial c_{l,s}}{\partial z} > 0 : \quad c_{l,s} - L_{dis} \frac{\partial c_{l,s}}{\partial z} > 0 \quad (56)$$

and

$$\text{for } q_{F,s} < 0, \text{ and } \frac{\partial c_{l,s}}{\partial z} < 0 : \quad c_{l,s} + L_{dis} \frac{\partial c_{l,s}}{\partial z} > 0 \quad (57)$$

When the dispersion flux would exceed the advective flux, it has been assumed that the dispersive flux will only cancel out the advective flux. Hence, only the diffusive flux is left in these cases (see also De Heer, 1979, p. 122).

7.2.2 Transport by advection to soil

The downward water flow ($q_{F,s} > 0$) from the lower end of the simulated sediment system transports the pesticide in the (saturated) soil. Here only advection is considered:

$$J_{l,s} = \frac{w_F}{P_D} \cdot q_{F,s} \cdot c_{l,s} \quad (58)$$

If there is upward seepage from the soil below the waterbody, pesticide mass can enter the sediment. This is described in Section 5.2.2.

7.3 Water-sediment interface: advection and diffusion

The mass flux at the water-sediment interface is composed of an advective and diffusive component (there is no dispersive component across the interface), hence for the water layer:

$$J_s = \frac{w_F}{P_0} \cdot q_{F,s} \cdot c_{l,s} - \varepsilon D_{l,s} \frac{\partial c_{l,s}}{\partial z} \quad (59)$$

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 $c_w = c_{l,s}$ (at $z = 0$).

The advective component of the exchange flux (first term) consists either of a supply of water with substance towards the waterbody due to drainage the neighbouring field (entering via the bottom of the waterbody) or infiltrating water from the water towards the neighbouring fields (leaving via the bottom of the waterbody).

For the sediment the mass flux is calculated by:

$$J_{l,s} = J_s \quad (60)$$

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. $c_{l,s}$ (at $z = 0$) = c_w .

7.4 Volatilization from the water layer

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

$$J_a = -k_{t,l} \left(c - \frac{c_a}{K_H} \right) \quad (61)$$

with:

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

in which

$$\frac{1}{k_{t,l}} = \frac{1}{k_l} + \frac{1}{K_H \cdot k_g} \quad (62)$$

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 describing the partitioning of the pesticide between the liquid and the gas phase:

$$K_H = \frac{c_a}{c_l} \quad (63)$$

with:

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

Henry's coefficient is calculated from 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 with:

$$K_H = \frac{P_{sat} \cdot M_m}{R \cdot T_m} \cdot \frac{1}{c_{slb}} \quad (64)$$

with:

- P_{sat} = saturated vapour pressure of substance (Pa)
- M_m = molar mass (kg mol^{-1})
- R = universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
- 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 both are temperature dependent. Hence the effect of temperature on these properties should be considered.

7.5 Effect of temperature

7.5.1 Saturated vapour pressure

The effect of temperature on the saturated vapour pressure of the pesticide is described by the Van 't Hoff equation:

$$P_{sat} = P_{sat,r} \exp \left[\frac{-\Delta H_v}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right] \quad (65)$$

with:

- $P_{sat,r}$ = saturated vapour pressure at reference temperature (Pa)
- ΔH_v = molar enthalpy of vaporization (J mol^{-1})
- T = temperature (K)
- T_r = reference temperature (K)

The default value for ΔH_v is taken to be 95 kJ mol^{-1} , which is the average of available measurements as collected by Smit *et al.* (1997). Their data show a range from 58 to 146 kJ mol^{-1} .

7.5.2 Solubility

The effect of temperature on the solubility of the pesticide (c_{slb}) is described by an equation similar to the Van 't Hoff equation:

$$c_{slb} = c_{slb,r} \exp \left[\frac{-\Delta H_d}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right] \quad (66)$$

with:

- $c_{slb,r}$ = solubility at reference temperature (kg m^{-3})
- ΔH_d = molar enthalpy of dissolution in water (J mol^{-1})

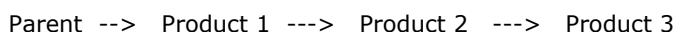
The default value for ΔH_d is taken to be 27 kJ mol^{-1} , which is the average of available measurements as collected by Smit *et al.* (1997). Their data show a range from -17 to 256 kJ mol^{-1} .

8 Pesticide transformation processes

8.1 Metabolites: reaction scheme and kinetics

The transformation of pesticides results in reaction products that can also have effects on the aquatic ecosystem. Therefore the formation and fate of transformation products are included in the model, in both the water layer and the sediment.

A pesticide may be subject to a chain of reaction in water, and/or in sediment, the so-called consecutive reactions:



Besides that, there are usually branches in the reaction scheme, representing the so-called simultaneous reactions. An example of a reaction scheme is presented in Figure 17.

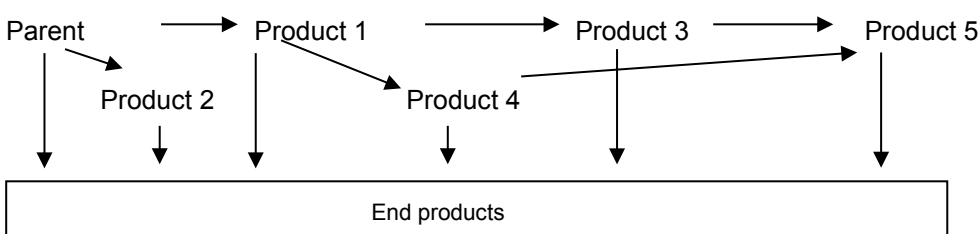


Figure 17 Example reaction scheme of parent decomposed into various metabolites. From Leistra et al. (2001).

The reaction scheme can be represented in a general way in a matrix, as shown in Table 1. The matrix indicates that a compound is usually transformed into various products. Furthermore, a product may be formed from one or more precursor compounds. Various couples of substances are connected by a reaction, but other substances are not connected directly to each other.

Table 1

Example of a matrix which represents the reactions between the substances included in the reaction scheme of a pesticide. 0 = no reaction. χ = molar fraction of a substance transformed into a specific product. From Leistra et al. (2001).

Scenario	Parent	Product 1	Product 2	Product 3	Product 4	Product 5
Parent	0	$\chi_{p,1}$	$\chi_{p,2}$	0	0	0
Product 1	0	0	0	$\chi_{1,3}$	$\chi_{1,4}$	0
Product 2	0	0	0	0	0	0
Product 3	0	0	0	0	0	$\chi_{3,5}$
Product 4	0	0	0	0	0	$\chi_{4,5}$
Product 5	0	0	0	0	0	0

The molar fractions χ are not restricted to the above-diagonal part of the matrix in the table. If Product 3 and Product 4 in the reaction scheme would be transformed partly to Product 2, the coefficients $\chi_{3,2}$ and $\chi_{4,2}$ would appear below the diagonal.

The rate of formation of reaction products can be described by first-order kinetics. For product 1, formed from the parent compound:

$$R_{f,p,1} = \chi_{p,1} \frac{M_1}{M_p} R_{t,p} \quad (67)$$

with:

$R_{t,p,1}$ = rate of formation of product 1 from the parent compound ($\text{kg m}^{-3} \text{d}^{-1}$)

$\chi_{p,1}$ = molar fraction of parent transformed to product 1 (-)

M_1 = molar mass of product 1 (kg mol^{-1})

M_p = molar mass of parent compound (kg mol^{-1})

For the transformation of product 1:

$$R_{t,1} = k_1 c_1^* \quad (68)$$

with:

$R_{t,1}$ = rate of transformation of the product 1 ($\text{kg m}^{-3} \text{d}^{-1}$)

k_1 = rate coefficient for transformation of product 1 (d^{-1})

c_1^* = mass concentration of product 1 (kg L^{-3})

A similar equation holds for each of the reaction products of the reaction scheme.

8.2 Water layer

The transformation rate coefficient of the substance in the water layer, k_w , is a measure of the (entire) transformation of the substance. 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 on the light intensity in the water layer, hydrolysis depends especially on the pH and also on temperature, and biotic degradation is mainly determined by the extent and type of microorganism community and temperature.

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

$$R_{t,p} = k_w c_w^* \quad (69)$$

with:

k_w = rate coefficient for transformation of the parent substance in water (d^{-1})

c_w^* = mass concentration of parent pesticide in water (kg m^{-3})

Similar rate equations are used for each transformation product.

8.3 Sediment

The transformation rate coefficient of the substance in the sediment, k_s , 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:

$$R_{s,t,p} = k_s c_s^* \quad (70)$$

with:

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

c_s^* = mass concentration of parent substance in sediment ($kg\ m^{-3}$)

Similar rate equations are used for each transformation product.

8.4 Effect of temperature on transformation rate

The effect of temperature on the transformation rate coefficient is given by:

$$k_1 = f_T \cdot k_{1,ref} \quad (71)$$

with:

f_T = factor for the effect of temperature on the rate coefficient (-)

$k_{1,ref}$ = rate coefficient for transformation at reference conditions (d^{-1})

Both the transformation of substance in the water layer and in the sediment depends on the temperature. The factor for the effect of temperature on the rate coefficient of transformation, f_T , is calculated with the Arrhenius equation:

$$f_T = \exp \left[\frac{-\Delta H_t}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right] \quad (72)$$

with:

ΔH_t = molar enthalpy of transformation (Arrhenius activation energy) ($J\ mol^{-1}$)

R = universal gas constant ($J\ mol^{-1}\ K^{-1}$)

T = temperature (K)

T_r = reference temperature (K)

The reference temperature, T_r , is taken to be 293.15 K. The lowest temperature that is simulated by TOXSWA is 4°C, hence the minimum temperature used in the Arrhenius equation is 4°C. There is no upper limit for the temperature and therefore also not for the maximum temperature used in the Arrhenius equation.

9 General discussion

9.1 Model sensitivity, verification, use and testing

9.1.1 Sensitivity and uncertainty analysis

Westein *et al.* (1998) performed a sensitivity analysis for a watercourse with constant flow and spray drift entry only with TOXSWA 1.0. The exposure concentrations calculated by TOXSWA were most sensitive to the following parameters: half-life of the substance in the water layer, coefficient for sorption to macrophytes, Henry coefficient, flow velocity and water depth. TOXSWA 2.1 (kernel implemented the FOCUS_TOXSWA 1.1.1 software) was briefly evaluated on the uncertainties related to the calculated exposure concentrations calculated in waterbodies with transient flow. The timing of application of the pesticide versus rainfall event is the most important factor affecting the calculated exposure concentrations in FOCUS surface water scenarios (p. 216-224 in FOCUS, 2001).

9.1.2 Verification

The accuracy of the numerical approximations for the pesticide were tested against analytical solutions (Adriaanse, 1996). This was done for the water layer and for the sediment with a pesticide subject to sorption and to transformation. In the water layer constant flow was simulated. In the sediment downward seepage was simulated. The transport after a pulse input of the pesticide in the system was simulated. In both compartments the concentration profiles calculated by the model showed an excellent correspondence with analytical solutions.

9.1.3 Model use and testing

Adriaanse *et al.* (2013) applied TOXSWA for a ditch, modelled as a pond-type system with sloping walls and no flow. A procedure was designed that was suitable for estimating the degradation rate in water from mesocosm studies with limited datasets. The procedure was tested on a dataset for prosulfocarb in stagnant ditches. Ter Horst & Koelmans (2016) applied TOXSWA as part of a semi-global parameter estimation procedure for estimation of degradation rates in water and in sediment using artificial experimental datasets of water-sediment studies. A series of pesticides ranging in sorption and degradation properties were simulated. Diepens *et al.* (2016) applied TOXSWA for a pond with transient flow. Chlorpyrifos concentrations in sediment were simulated, and its exposure was combined with effect models. Adriaanse *et al.* (2017) applied TOXSWA for streams with transient flow, combined with runoff fluxes calculated by PRZM. Simulations were done with substances with varying sorption coefficients.

9.2 Ongoing developments

9.2.1 Introduction

In this section ongoing developments are discussed. At the moment we are working on the next version of the TOXSWA kernel (version 3.4). This version is not yet released, but used occasionally for research purposes only. Some of the items discussed in this Section 9.2 are already operational in TOXSWA 3.4. Other concepts are implemented but not yet fully tested and its implementation is not yet described.

The following two concepts are already operational in TOXSWA 3.3, but not described in the main parts of this report: a new hydrology concept, i.e. the so-called 'simple ditch' model (Section 9.2.2) and the concept for atmospheric deposition (Section 9.2.3). Reason for not describing these concepts in the main parts of the report is that we constrained the report to those concepts relevant for simulations with the Dutch scenarios (TOXSWA 1.2) and with the FOCUS Surface Water scenarios.

9.2.2 Hydrology

Opheusden *et al.* (2011) derived a model for gradually varied flow from the basic principles of conservation of mass and momentum. The effect of external inflow from fields adjacent to the watercourse is considered in the model as well. The only restriction for this model is that the principle of gradual varying flow must be maintained, which implies that the external flow density must not change too rapidly along the channel. This concept is not implemented in TOXSWA. Part of the study of Opheusden *et al.* (2011) was to test the model derived for different situations, both for very slowly, and more rapidly flowing watercourses. As result of the tests it was shown that the water level is almost horizontal for watercourses with slow-flowing water. A simplified version of the model for gradually varied flow was developed for slow-flowing watercourses; 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. The 'simple ditch' model was implemented in TOXSWA 3.3 in order to perform simulations with the Dutch scenario for downwards spraying of field crops developed by Tiktak *et al.* (2012). TOXSWA 3.3 is implemented within the GEM (Greenhouse Emission Model) software tool (Wipler *et al.*, 2015b). For calculating the hydrology in the watercourse of the Dutch greenhouse scenarios in GEM the 'simple ditch' model in TOXSWA is used in conjunction with an imposed time-varying external upstream water flux.

9.2.3 Atmospheric deposition

A concept for atmospheric deposition has been implemented in TOXSWA 3.3. It is based upon a first-tier approach developed by FOCUS (2008). This approach aims at estimating deposition of plant protection products on edge-of-field surface waters due to volatilisation after application on the adjacent field, if drift mitigation is required. In the approach it is assumed that the wind blows perpendicular to the direction of the ditch which is a worst-case assumption. Furthermore, in the approach implemented in TOXSWA it is assumed that the deposition event starts at the time of application and has a constant deposition rate during the next 24 hours. The concept implemented in TOXSWA is described in Tiktak *et al.* (2012; section 7.3). TOXSWA 3.3 was used to perform simulations with the Dutch scenario for downwards spraying of field crops developed by Tiktak *et al.* (2012). In these simulations atmospheric deposition was simulated as one of pesticide entry routes in the watercourse of the scenario.

9.2.4 Temperature

In the TOXSWA model the dissipation processes of transformation in water and in sediment and volatilization from water to the air are a function of the ambient temperature. In the version of TOXSWA described here (version 3.3) the water temperature is approximated using monthly averages of either measured water temperature or air temperatures. However, the temperature in small water bodies is strongly influenced by weather conditions that vary at time scales down to less than one hour. Therefore, Jacobs *et al.* (2010) developed a 1D-bulk model for simulation of the thermal behaviour of water bodies. This model considers basic physically processes that describe the influence of weather on the energy balance of natural water bodies. This new temperature model has been implemented in TOXSWA 3.4 and a report describing its implementation, some example calculations and some specifically designed tests of the new temperature module in TOXSWA is currently prepared (Beltman *et al.*, in prep).

9.2.5 Volatilisation

At present in TOXSWA the exchange flux of the pesticide between the water layer and the atmosphere (J_a) is described by the so-called stagnant film model of Liss and Slater (1974). A drawback of this

approach is that it does not describe the influence of weather and the hydrodynamic conditions in the water on the volatilization process. Jacobs and Adriaanse (2012) propose a new approach for calculating volatilization. The approach proposed corresponds well with the assumption of vertically well-mixed water bodies that used in the present version of TOXSWA. Jacobs and Adriaanse (2012) recommend casting the new approach in a micrometeorological framework, based upon two atmospheric resistances and on aqueous resistance against gas transport. The proposed approach will also fit smoothly in the envisaged new temperature module discussed in Section 9.2.4. Implementation of the proposed approach of Jacobs and Adriaanse (2012) is not yet foreseen, but can be done once the new temperature model is implemented in TOXSWA (Beltman *et al.*, in prep).

9.2.6 Bioturbation

Pesticides may accumulate in sediments and may pose a risk to benthic organisms. The vertical distribution of pesticide in the sediment determines to a large extent the relative importance of exposure routes via pore water and via ingestion. The vertical distribution is driven by diffusion in pore water, degradation, adsorption and bioturbation. Bioturbation is associated with considerable increase in the vertical transport due to bioactivity. Bioturbation was implemented as a particle dispersion process (Koelmans *et al.*, 2000) in TOXSWA 3.4. The implementation is not yet fully tested and documented. However, Wipfler *et al.* (2016) compared chlorpyrifos exposure profiles calculated with TOXSWA 3.4 simulating i) bioturbation and ii) no bioturbation. They showed that the profiles of pore water concentrations did not deviate much; however, organic matter bound concentrations were lower in the top 2 mm when bioturbation was considered.

9.2.7 Transformation

As explained in section 8.2 TOXSWA versions up to 3.3 simulate transformation in water as a lumped first-order transformation process, assuming one transformation rate for the total mass in the water layer. Transformation in water, however, may be split in at least three separate processes; hydrolysis, photolysis and biotic transformation (Deneer *et al.*, 2010). Simulation of these processes separately and in more detail is expected to improve the performance of TOXSWA as it accounts better for external environmental conditions related to specific pesticide properties. Deneer *et al.* (2010) provided suggestions for how these individual processes could be implemented in TOXSWA. Photolysis has been implemented in TOXSWA 3.4 and a description of its implementation, example calculations and some specifically designed tests are described in Beltman *et al.* (2015). Hydrolysis and biotic transformation are currently implemented in TOXSWA 3.4 and work on the description of its implementation, some example calculations and some specifically designed tests of these new processes in TOXSWA is currently ongoing (Ter Horst *et al.*, in prep).

9.3 Landscape scale modelling

The CASCADE-TOXSWA model has been developed to assess the fate of pesticides in an interconnected system of watercourses with different hydrological characteristics (Van den Berg *et al.*, 2011). It is based on TOXSWA, but CASCADE-TOXSWA only considers the water layer in the system of watercourses. The sediment compartment has not been implemented. The transport processes being considered are advection and dispersion. The transfer of the pesticide from one watercourse to a receiving watercourse depends on the water discharge at the end of the watercourse and the pesticide concentration in this water flow. Dispersion is not yet taken into account at junctions. Spray drift is the only entry route considered. Other processes are simulated as in TOXSWA. Focks *et al.* (2013) show that other watercourses discharging into the same receiving watercourse may dilute the pesticide concentration in the receiving watercourse or add to the mass entering this watercourse. Furthermore, Focks *et al.* (2013) show that the spatio-temporal explicit exposure patterns simulated with CASCADE-TOXSWA could be used directly as input for population effect modelling.

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Justification

This report describes the mathematical concepts of TOXSWA version 3.3 i.e. the TOXSWA kernel that is incorporated in the FOCUS_TOXSWA 4.4.3 software tool. This report is constrained to describing those concepts in TOXSWA 3.3 that are relevant for simulations with the Dutch (excluding the greenhouse scenarios) and FOCUS surface water scenarios. Mathematical concepts are described independent of specific scenario properties.

The TOXSWA model is currently used for different purposes, e.g. calculation of exposure concentrations in the water layer and in the sediment of surface waters at the EU (FOCUS-TOXSWA) and at the national level (TOXSWA 1.2) of the registration procedure of pesticides and the calculation of exposure concentrations in the water layer and in the sediment of surface waters as result of pesticide emissions from greenhouses (GEM).

The report was written by several members of the TOXSWA development team of Wageningen Environmental Research (Alterra). The project was supervised by Jennie van der Kolk (contact of WOT N&M, theme Agri-environment) and Anja van Gernerden (Ministry of Economic Affairs).

Annex 1 List of symbols and units

Symbol	Description ⁸	Units
β	arc tan ($1/s_1$)	rad
δ	Dirac delta function	d^{-1}
ε	volume fraction of pore water	-
Φ	lineic volume flux of water, that is lateral inflow originating from drainage or runoff including drainage subsurface flow from the adjacent field	$m^3 m^{-1} d^{-1}$
K_M	Manning's coefficient of channel roughness	$m^{1/2} d^{-1}$
$K_{M,1m}$	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)	-
$\xi(t)$	the release time function	1
ρ_b	bulk density of dry sediment, i.e. volumic mass of dry sediment material	$kg m^{-3}$
ω	average flow velocity of pore water	$m d^{-1}$
$\chi_{p,1}$	molar fraction of parent transformed to product 1	-
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_x	wetted cross sectional area of flow at location x	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 [$c_{e,ss}$]	$kg m^{-3}$
$c_{s,r}$	reference concentration in the liquid phase for sorption to sediment [$c_{e,wb}$]	$kg m^{-3}$
C_F	coefficient	-
c_l	equilibrium mass concentration of substance at the water-gas interface in the water phase	$kg m^{-3}$
$c_{l,s}$	mass concentration of substance in liquid phase in the sediment [c_b]	$kg m^{-3}$
c_s^*	mass concentration in the sediment [c_b^*]	$kg m^{-3}$
c_{spg}	mass concentration in seepage water	$kg m^{-3}$
c_{slb}	solubility of substance in water	$kg m^{-3}$
$c_{slb,r}$	solubility at reference temperature	$kg m^{-3}$
c_u^*	mass concentration in water discharging into the waterbody at the upstream end of the waterbody	$kg m^{-3}$
c_w^*	mass concentration of substance in water layer, excluding substance sorbed to suspended solids and to macrophytes	$kg m^{-3}$
c_w	mass concentration of substance in the water phase (excluding substance sorbed to suspended solids and to macrophytes) [c]	$kg m^{-3}$
$c_{w,F}$	concentration in water from lateral discharge, by drainage or runoff	$kg m^{-3}$
$D_{l,s}$	diffusion coefficient in pore water [D_b]	$m^2 d^{-1}$
D_w	diffusion coefficient in water	$m^2 d^{-1}$
E	areic volume flux from evaporation; the flux is negative in an upward direction	$m^3 m^{-2} d^{-1}$
$E_{l,s}$	dispersion coefficient in pore water [E_b]	$m^2 d^{-1}$
E_{phys}	longitudinal dispersion coefficient (in the direction of flow)	$m^2 d^{-1}$

⁸ When the symbol differs from the symbol given by Adriaanse (1996), the symbol used by Adriaanse is added to the description between square brackets.

Symbol	Description ⁸	Units
f_d	fraction of downward aeric volume flux of water at 1 m soil depth that is drained into the stream	-
f_T	factor for the effect of temperature on the rate coefficient	-
G	slope of the energy line, for uniform flow equal to the hydraulic gradient (difference in water surface level at two locations divided by their distance), which is for uniform flow also equal to the bottom slope	-
H	Heaviside function (p.26 Jury and Roth, 1990)	1
ΔH_d	molar enthalpy of dissolution in water	J mol ⁻¹
ΔH_t	molar enthalpy of transformation (Arrhenius coefficient)	J mol ⁻¹
ΔH_v	molar enthalpy of vaporization	J mol ⁻¹
h	water depth of the waterbody	m
h_{crest}	upstream water level over the weir crest, also called head	m
h_{uni}	uniform flow depth, i.e. water depth at uniform flow	m
h_w	depth defining perimeter for exchange between water and sediment	m
h_{weir}	water depth immediately in front of weir	m
J_a	aeric mass flux of substance across the water-air interface (kg m ⁻² d ⁻¹) [the flux is negative in upward direction] [J_{wa}]	kg m ⁻² d ⁻¹
J_{er}	mass flux of substance associated with eroded soil	kg m ⁻² d ⁻¹
$J_{l,s}$	aeric mass flux by advection, dispersion and diffusion in the liquid phase of the sediment [J_{lb}]	kg m ⁻² d ⁻¹
J_s	aeric mass flux of substance across the water-sediment interface [J_{wb}]	kg m ⁻² d ⁻¹
J_w	aeric mass flux of substance in water layer by advection and dispersion	kg m ⁻² d ⁻¹
$K_{F,s}$	Freundlich coefficient for sorption to sediment [$K_{F,wb}$]	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
$K_{om,s}$	coefficient of equilibrium sorption on organic matter in sediment [$K_{om,wb}$]	m ³ kg ⁻¹
$K_{om,ss}$	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
k_p	rate coefficient for transformation of the parent substance in water	d ⁻¹
k_s	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
$k_{1,ref}$	rate coefficient for transformation at reference conditions	d ⁻¹
L	length of the pond	m
L_{dis}	dispersion length	m
M_m	molar mass of substance m	kg mol ⁻¹
m	mass of substance [M]	kg
m_{drift}	spray drift mass deposited at the water layer	kg m ⁻²
m_L	lineic mass of substance [M_L]	kg m ⁻¹
m_{LT}	lineic mass of substance [M_{LT}]	kg m ⁻¹ d ⁻¹
m_T	mass of substance [M_T]	kg d ⁻¹
m_{mp}	dry weight of macrophytes per area of sediment [DW]	kg m ⁻²
$m_{om,s}$	mass fraction of organic matter in sediment [$m_{om,wb}$]	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 [ss]	kg m ⁻³
N_s	Freundlich exponent for sorption to sediment [n_{wb}]	-
N_{ss}	Freundlich exponent for sorption to suspended solids [n_{ss}]	-
P	length of perimeter	m
P_r	aeric volume flux from precipitation, i.e. volume of precipitation divided by an appropriate waterbody surface area and by time; the flux is positive in a downward direction	m ³ m ⁻² d ⁻¹
P_D	length of perimeter at lower boundary of sediment at depth $z = D$	m
P_{sat}	saturated vapour pressure of substance [P]	m
$P_{sat,r}$	saturated vapour pressure at reference temperature	Pa

Symbol	Description ⁸	Units
P_{wet}	length of wetted perimeter of the waterbody	Pa
p_{weir}	height of weir crest above waterbody bottom	m
P_z	length of perimeter at depth z from the water-sediment interface	m
$P_{\frac{1}{2}z_{mix}}$	length of wetted perimeter at $z = \frac{1}{2}z_{mix}$ in sediment	m
$P_{0,x}$	length of wetted perimeter at the water-sediment interface ($z = 0$ from the perspective of the sediment) at location x	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_{out}	discharge of water at the downstream end of the waterbody	$m^3 d^{-1}$
Q_u	total discharge or volume flux of water entering the waterbody at the upstream boundary	$m^3 d^{-1}$
Q_{weir}	discharge at the location of the weir	$m^3 d^{-1}$
Q_x	discharge, i.e. volume flux of water passing through a vertical cross-section of the waterbody at location x	$m^3 d^{-1}$
q_F	areic volume flux of excess water from the adjacent field	$m^3 m^{-2} d^{-1}$
$q_{F,down}$	areic volume flux of excess water at 1 m soil depth originating from the adjacent field	$m^3 m^{-2} d^{-1}$
$q_{F,r}$	areic volume flux of surface runoff excess water from the adjacent field	$m^3 m^{-2} d^{-1}$
$q_{F,s}$	areic volume flux from seepage flow from the adjacent field, expressed per surface area adjacent field	$m^3 m^{-2} d^{-1}$
R	universal gas constant	$J mol^{-1} K^{-1}$
$R_{f,p}$	rate of formation of parent substance in the water layer	$kg m^{-3} d^{-1}$
$R_{t,p,1}$	rate of formation of product 1 from the parent compound	$kg m^{-3} d^{-1}$
$R_{t,p}$	rate of transformation of substance in the water layer (i.e. in water phase, sorbed to suspended solids and sorbed to macrophytes)	$kg m^{-3} d^{-1}$
$R_{s,f,p}$	rate of formation of parent substance in the sediment	$kg m^{-3} d^{-1}$
$R_{s,t,p}$	rate of transformation of parent substance in the sediment	$kg m^{-3} d^{-1}$
$R_{t,1}$	rate of transformation of the product 1	$kg m^{-3} d^{-1}$
R_{wet}	hydraulic radius of the wetted cross-section	m
r	number of point type inputs	-
S	areic volume flux from seepage; the flux is positive in a downward direction	$m^3 m^{-2} d^{-1}$
$S_{c,d}$	distributed source with continuous input [b_d]	$kg m^{-3} d^{-1}$
$S_{c,p}$	point type source with continuous input [b_p]	$kg m^{-3} d^{-1}$
$S_{p,d}$	distributed pulse input [p_d]	$kg m^{-3} d^{-1}$
$S_{p,p}$	point type pulse input [p_p]	$kg m^{-3} d^{-1}$
s_0	number of pulse input at location x_0	-
s_{00}	number of pulse input at location x_{00}	-
s_1	side slope (horizontal/vertical)	-
T	temperature	K
$T_{a,m}$	monthly average of the air temperature at 2 m above the ground	K
T_m	temperature at which the saturated vapour pressure, the solubility and the exchange coefficients are defined	K
T_r	reference temperature	K
T_{wb}	temperature of the waterbody	K
t	time	d
t_{re}	time at which the continuous release at location x_{re} ends	d
t_{rs}	time at which the continuous release at location x_{rs} starts	d
t_s	time of pulse input	d
t_{s0}	time of input	d
u	flow velocity of the water	$m d^{-1}$
\bar{u}	average cross-sectional flow velocity	$m d^{-1}$
u^*	shear velocity	$m d^{-1}$
W	width of water surface	m
W_x	width of water surface at location x	m

Symbol	Description ⁸	Units
w_{er}	width of the adjacent field of which soil is eroded	m
w_F	width of the adjacent field (perpendicular to the waterbody) discharging drainage or runoff water into the waterbody [t]	m
X_{mp}	content of substance sorbed to macrophytes	kg kg ⁻¹
X_s	mass sorbed to sediment [X_b]	kg kg ⁻¹
X_{ss}	mass content sorbed to suspended solids	kg kg ⁻¹
x	distance in the direction of flow	m
x_{rs}	location at which the continuous release starts	m
x_{re}	location at which the continuous release ends	m
x_0	location of input	m
x_{00}	number of location x_{00}	-
z	depth in the sediment from the water-sediment interface to area concerned	m
z_{mix}	thickness of top layer of sediment, into which pesticide sorbed to eroded soil is distributed	m

Annex 2 Lateral entries in the waterbody

A2.1 Introduction

Lateral entries of pesticides into the waterbody are inputs that are included as options in the conservation equation. This Annex provides the mathematical concepts for all four types of lateral entries.

The mass conservation equation for the pesticide in the water layer is extended with four types of entries of pesticide is:

$$\frac{\partial(c_w^*A)}{\partial t} = - \frac{\partial(A \cdot J_w)}{\partial x} - R_{t,p}A + J_a W - J_s P_0 + S_{p,p}A + S_{p,d}A + S_{c,p}A + S_{c,d}A \quad (73)$$

with:

$S_{p,p}(t,x)$ = point type pulse input ($\text{kg m}^{-3} \text{d}^{-1}$)

$S_{p,d}(t,x)$ = distributed pulse input ($\text{kg m}^{-3} \text{d}^{-1}$)

$S_{c,p}(t,x)$ = point type source with continuous input ($\text{kg m}^{-3} \text{d}^{-1}$)

$S_{c,d}(t,x)$ = distributed source with continuous input ($\text{kg m}^{-3} \text{d}^{-1}$)

Pulse type inputs (point type and distributed) are released into the water layer in an infinitesimally small period of time, so a certain mass of substance is released into the water layer (e.g. point type: spillage; distributed: spray drift event). Sources with continuous input (point type and distributed) are released into the waterbody as flux, i.e. mass released during a time interval as a rate (e.g. point: single discharging drain; distributed: series of discharging drains in an agricultural field).

Each of the four types of lateral input is described in sections A2.2 – A2.5. However, not all four types are operational in TOXSWA. The point type pulse input and the point type source with continuous input are not implemented. The distributed pulse input and the distributed source with continuous input are implemented in TOXSWA. For those lateral input entries that are operational in TOXSWA the specific implementation for the corresponding entry route(s) is given in Chapter 5.

The mass conservation equation for the pesticide in the sediment is also extended with four types of entries of pesticide is:

$$P \frac{\partial c_s^*}{\partial t} = \frac{\partial(P \cdot J_{L,s})}{\partial z} - R_{s,t,p}P + S_{p,p}P + S_{p,d}P + S_{c,p}P + S_{c,d}P \quad (74)$$

with:

$S_{p,p}(t,z)$ = point type pulse input ($\text{kg m}^{-3} \text{d}^{-1}$)

$S_{p,d}(t,z)$ = distributed pulse input ($\text{kg m}^{-3} \text{d}^{-1}$)

$S_{c,p}(t,z)$ = point type source with continuous input ($\text{kg m}^{-3} \text{d}^{-1}$)

$S_{c,d}(t,z)$ = distributed source with continuous input ($\text{kg m}^{-3} \text{d}^{-1}$)

Considering the sediment the distributed source with continuous input has been implemented in TOXSWA. The specific implementation for the corresponding entry route (erosion) is given in Chapter 5.

A2.2 Point-type pulse input

Note that this type of input is currently not implemented in TOXSWA. Example of point-type pulse inputs are e.g. spillage of the substance or rinsing application equipment. The mass of substance, released in an infinitesimally short time, m (kg) is assumed to be in an infinitesimally thin, vertical slice of the waterbody. Such a pulse input, occurring repeatedly, can be described by:

$$S_{p,p}(t, x) = \sum_{s_0=1}^{m_0} \frac{m\delta(x - x_0) \delta(t - t_{s_0})}{A} \quad (75)$$

with:

- m = mass of substance (kg)
- s_0 = number of pulse input at location x_0
- m_0 = total number of inputs (-)
- x_0 = location of input (m)
- t_{s_0} = time of input (d)

In Eq. ((75) $\delta(x - x_0)$ is the Dirac delta function (m^{-1}) defined by (see *Figure 18*):

$$\delta(x - x_0) = 0 \quad \text{for } x \neq x_0 \quad \text{and} \quad \int_{-\infty}^{\infty} \delta(x - x_0) dx = 1 \quad (76)$$

In Eq. (75) $\delta(t - t_{s_0})$ is the Dirac delta function (d^{-1}) defined by (see *Figure 19*):

$$\delta(t - t_{s_0}) = 0 \quad \text{for } t \neq t_{s_0} \quad \text{and} \quad \int_{-\infty}^{\infty} \delta(t - t_{s_0}) dt = 1 \quad (77)$$

If such a pulse input occurs at a second location, the term $S_{p,p}(t, x)$ becomes as follows (for every subsequent location another term is added):

$$S_{p,p}(t, x) = \sum_{s_0=1}^{m_0} \frac{m\delta(x - x_0) \delta(t - t_{s_0})}{A} + \sum_{s_{00}=1}^{m_{00}} \frac{m\delta(x - x_{00}) \delta(t - t_{s_{00}})}{A} \quad (78)$$

with:

- x_{00} = location x_{00} (m)
- s_{00} = number of pulse input at location x_{00}
- m_{00} = total number of inputs at location x_{00}

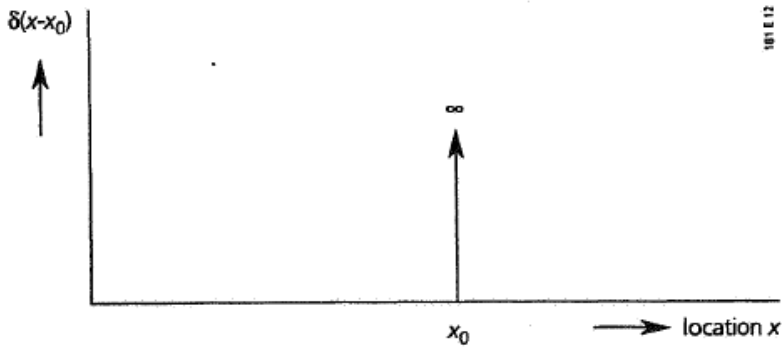


Figure 18 Dirac delta function for point type input

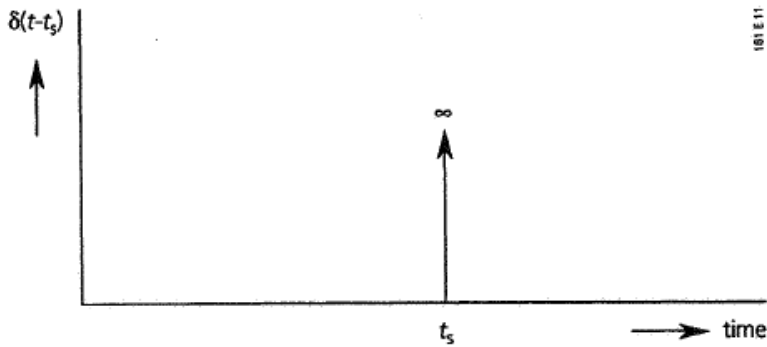


Figure 19 Dirac delta function for pulse input

A2.3 Point-type distributed input

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 in the water layer at the time of release. Such a pulse input, occurring repeatedly, can be described by:

$$S_{p,d}(t, x) = \sum_{s_0=1}^{m_0} \frac{m_L \delta(t - t_{s_0})}{A} \quad (79)$$

with

m_L = lineic mass of substance (kg m^{-1})

For simplicity reasons we consider a single event, hence Eq. (79) becomes

$$S_{p,d}(t, x) = \frac{m_L}{A} \delta(t - t_s) \quad (80)$$

with

δ = Dirac delta function (d^{-1})

t_s = time of pulse input (d)

The Dirac delta function (in Eq. (80)) can be defined as the derivative of the Heaviside function (p.26 Jury and Roth, 1990). The Heaviside function (dimension 1) is defined as

$$\begin{aligned} H(t - t_{s0}) &= 0 & \text{if } t < t_s \\ H(t - t_{s0}) &= 1 & \text{if } t > t_s \end{aligned} \quad (81)$$

and its derivative

$$\delta(t - t_s) = \frac{\partial H(t - t_s)}{\partial t} \quad (82)$$

Hence, replacing the Dirac delta function in Eq. (80) by the Heaviside function gives

$$S_{p,d}(t, x) = \frac{m_L}{A} \frac{\partial H(t - t_s)}{\partial t} \quad (83)$$

Substituting $S_{p,d}$ of Eq.(83) in Eq. (20) and Eq. (31) results in

$$\frac{\partial(c_w^* A)}{\partial t} = \frac{\partial(A \cdot J_w)}{\partial x} - R_{t,p}A + J_a W - J_s P_0 + m_L \frac{\partial H(t - t_s)}{\partial t} \quad (84)$$

Combining the time derivatives gives

$$\frac{\partial(c_w^* A) - m_L \partial H(t - t_s)}{\partial t} = \frac{\partial(A \cdot J_w)}{\partial x} - R_{t,p}A + J_a W - J_s P_0 \quad (85)$$

A2.4 Continuous point release

Note that this type of input is currently not implemented in TOXSWA. A discharging tributary and a release from a single discharging drain, adding water with a constant concentration of the substance are examples of continuous point releases. The mass of the substance released per unit of time is m_T (kg d^{-1}) and this is ideally mixed over the cross sectional area A .

$$S_{c,p}(t, x) = \sum_{r=1}^n \frac{m_T}{A} \xi(t) \delta(x - x_r) \quad (86)$$

with:

- m_T = mass of substance (kg d^{-1})
- r = number of point type inputs (total n inputs)

In Eq. (86) $\xi(t)$ is the release time function (dimension 1) defined by:

$$\begin{aligned} \xi(t) &= 0 \quad \text{for } t < t_{rs} \text{ or } t > t_{re} \\ \xi(t) &= 1 \quad \text{for } t_{rs} \leq t \leq t_{re} \end{aligned} \quad (87)$$

with

- t_{rs} = time at which the continuous release at location x_{rs} starts (d)
- t_{re} = time at which the continuous release at location x_{re} ends (d)

A2.5 Continuous distributed release

Releases via drainage and runoff are examples of continuous distributed releases into the water layer. Release via erosion is an example of a continuous distributed release into the sediment.

For the water layer the lineic mass of substance released per unit of time is m_{LT} ($\text{kg m}^{-1} \text{d}^{-1}$, e.g. calculated as release per unit of length in the flow direction).

$$S_{c,d}(t, x) = \sum_{r=1}^n \frac{m_{LT}}{A} \xi(t) \quad (88)$$

with:

m_{LT} = lineic mass of substance ($\text{kg m}^{-1} \text{d}^{-1}$)

For the sediment the lineic mass of substance released per unit of time is m_{LT} ($\text{kg m}^{-1} \text{d}^{-1}$, calculated as release per unit of length in the flow direction).

$$S_{c,d}(t, z) = \sum_{r=1}^n \frac{m_{LT}}{P_{1/2z_{mix}} z_{mix}} \xi(t) \quad (89)$$

with

$P_{1/2z_{mix}}$ = length of wetted perimeter at $z = 1/2z_{mix}$ in sediment (m)

z_{mix} = thickness of top layer of sediment, into which pesticide sorbed to eroded soil is distributed (m)

Annex 3 Iteration solution of the Freundlich sorption equation

In case of using the non-linear Freundlich sorption equation, the partitioning of the pesticide depends on the concentration in the liquid phase. Then the concentration in the liquid phase cannot be expressed in an explicit way as a function of the other quantities. The implicit equation has to be solved by iteration. This is needed for sorption to suspended solids in the water layer and for sorption to the solid phase in the sediment.

Sorption to suspended solids in the water layer

To approximate the fluxes of the substance in the right-hand term of the conservation equation for the water layer, Eq. (20), a value of the concentration in the liquid phase, c_w , have to be derived from known values of the total concentration c_w^* , which was given by:

The total pesticide concentration in the water layer, c_w^* , is given by Eq. (22). Combining Eqs. (22), (36) and (38) results in:

$$c_w^* = c_w + \frac{m_{mp} P_0}{A} K_{mp} c_w + m_{ss} K_{F,ss} c_{ss,r} \left(\frac{c_w}{c_{ss,r}} \right)^{N_{ss}} \quad (90)$$

with:

c_w^* = mass concentration of substance in water layer, including substance sorbed to suspended solids and to macrophytes (kg m^{-3})

c_w = mass concentration of substance in the water phase (kg m^{-3})

m_{mp} = dry weight of macrophytes per area of sediment (kg m^{-2})

P_0 = length of wetted perimeter at depth $z = 0$, via which exchange between water and sediment occurs (m)

A = wetted cross sectional area of flow (m^2)

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 ($\text{m}^3 \text{kg}^{-1}$)

m_{ss} = mass concentration of suspended solids in the water layer (kg m^{-3})

$K_{F,ss}$ = Freundlich coefficient for sorption to suspended solids ($\text{m}^3 \text{kg}^{-1}$)

$c_{ss,r}$ = reference concentration in the liquid phase for sorption to suspended solids (kg m^{-3})

N_{ss} = Freundlich exponent for sorption to suspended solids (1)

Eq. (90) shows that it is impossible to derive values of c_w from values of c_w^* in an explicit way. Rearranging Eq. (90) yields an implicit equation in c_w :

$$c_w = \frac{c_w^*}{1 + \frac{m_{mp} P_0}{A} K_{mp} + m_{ss} K_{F,ss} \left(\frac{c_w}{c_{ss,r}} \right)^{N_{ss}-1}} \quad (91)$$

In Step 1 of the iteration, the 'old' value of c_w is introduced at the right hand side of Eq. (91), and known values for the other variables of this right-hand term (including c_w^*). Then, a first estimate for c_w on the left hand side of the equation is obtained, the 'new' value of c_w . In Step 2, this 'new' value for c_w is filled in at the right hand side of Eq. (91) to replace the 'old' value of c_w . The iteration is continued until the difference between the 'new' and 'old' values of c_w becomes very small. The last c_w value calculated is the solution of the implicit Eq. (91).

Sorption to solid phase in sediment

To approximate the fluxes of the substance in the right-hand term of the conservation equation for the sediment, Eq. (26), a value of the concentration in the liquid phase, $c_{l,s}$, have to be derived from known values of the total concentration c_s^* , which was given by:

The total pesticide concentration in sediment, c_s^* , is given by Eq. (28). Combining Eq. (28) and (39) results in:

$$c_s^* = \varepsilon c_{l,s} + \rho_b K_{F,s} c_{s,r} \left(\frac{c_{l,s}}{c_{s,r}} \right)^{N_s} \quad (92)$$

with:

- c_s^* = mass concentration in the sediment (kg m^{-3})
- ε = volume fraction of pore water (1)
- $c_{l,s}$ = 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})
- $K_{F,s}$ = Freundlich coefficient for sorption to sediment ($\text{m}^3 \text{kg}^{-1}$)
- $c_{s,r}$ = reference concentration in the liquid phase for sorption to sediment (kg m^{-3})
- N_s = Freundlich exponent for sorption to sediment (-)

Eq. (92) shows that it is impossible to derive values of $c_{l,s}$ from values of c_s^* in an explicit way. Rearranging Eq. (92) yields an implicit equation in $c_{l,s}$:

$$c_{l,s} = \frac{c_s^*}{\varepsilon + \rho_b K_{F,s} \left(\frac{c_{l,s}}{c_{s,r}} \right)^{N_s - 1}} \quad (93)$$

To determine the concentration in the liquid phase, $c_{l,s}$, the iteration procedure described for suspended solids in the water layer is used with Eq. (93). The last $c_{l,s}$ value calculated is the solution of the implicit Eq. (93).

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