Katrijn Holvoet

MONITORING AND MODELLING
THE DYNAMIC FATE AND BEHAVIOUR OF PESTICIDES
IN RIVER SYSTEMS AT CATCHMENT SCALE

Thesis submitted in fulfillment of the requirements
For the degree of Doctor (PhD) in Applied Biological Sciences

Dutch translation of the title:

Meten en modelleren van het dynamisch gedrag en voorkomen van pesticiden in riviersystemen op bekkenschaal.

Please refer to this work as follows:

Holvoet K. (2006). Monitoring and modelling the dynamic fate and behaviour of pesticides in river systems at catchment scale. PhD thesis, Ghent University, Belgium, pp. 242.

ISBN-number: 9789059891401

What we know is a drop, what we don't know, an ocean.

Isaac Newton, English physicist (1643-1727).

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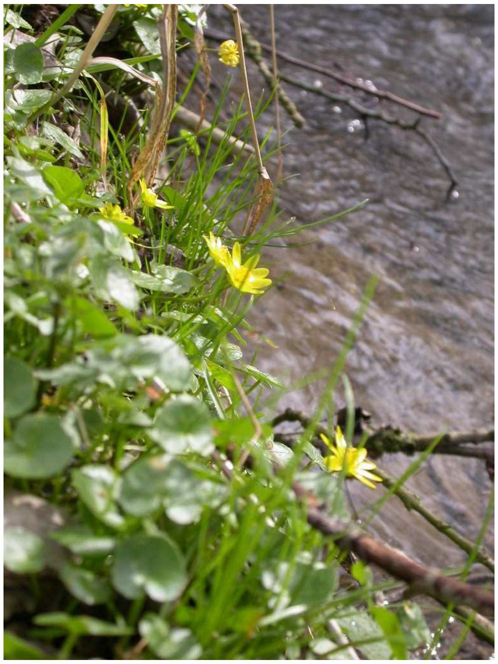
De Rivier



Ik voel me thuis in alle landen
Ik sta niet stil
Ik heb een grenzeloos gevoel
Ik heb mijn eigen weg gevonden
Ik draag het water naar de zee
Dat is mijn doel
Ik geboren als een zwerver
Ik ben maar even hier
Ik ben een rivier

En ik stroom door de eeuwen heen
Langs kastelen
Ik stroom door de eeuwen heen
Langs een stad
En aan het einde verlies ik mezelf in de zee
Ik stroom door de eeuwen heen

Fragment uit het lied "De rivier" (tekst Stef Bos).

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Chapter 3 Adapted from: Holvoet, K., Seuntjens, P., Mannaerts, R., De Schepper, V., Vanrolleghem, P.A. (2006). The water-sediment as a highly dynamic system: results of an intensive pesticide monitoring campaign. *Water Sci. Technol*. In press.

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Acknowledgement

Een doctoraat is eigenlijk het resultaat van werk van en de samenwerking met vele mensen. En niet alleen het werk zelf maar zeker ook alle nevenactiviteiten, de werksfeer en de collegialiteit zorgen ervoor of een persoon in 'goede doen' is en of een project al dan niet slaagt. Dit doctoraat is er 1 dat de eindstreep haalde, wat zeker te danken is aan alle voornoemde zaken! Zeer veel mensen hebben hiertoe bijgedragen en ik doe een poging om toch een deel van hen hiervoor persoonlijk te bedanken.

In de eerste plaats, en dit niet omdat het zo gaat in alle dankwoorden, gaat mijn oprechte dank uit naar mijn 2 promotoren: Prof. Peter Vanrolleghem en Prof. Piet Seuntjens. Samen hebben we de lijnen van dit doctoraat uitgezet, problemen en resultaten besproken en bediscussieerd en op het einde lange afstanden overbrugd via de ons bekende 'Skype' gesprekken. Ik heb jullie interesse voor mijn onderwerp en jullie onverminderd enthousiasme in die 4 jaar erg weten te appreciëren. Bovendien maakten de gemoedelijke sfeer en de humoristische opmerkingen het erg aangenaam om bij jullie ten rade te komen! Peter, bedankt voor al je enthousiasme en voor de tijd in Canada. Piet, bedankt voor al je steun en fijn reisgezelschap naar diverse industrieën en conferenties. Jullie waren 2 bijzondere reisgenoten!

Gedurende deze 4 jaar had ik ook geen gebrek aan collega's: Biomath en VITO mensen: bedankt! Een sociaal wezen als ikzelf bloeit dood in afwezigheid van wat genegenheid, humor en gekwebbel: maar zowel in Gent als in Mol was daar geen tekort aan. Daarnaast kon ik ook voor inhoudelijke vragen bij diverse mensen terecht. Hiervoor wil ik volgende mensen graag nog eens extra bedanken: Ann van Griensven, Veronique Vandenberghe, Lorenzo Benedetti, Frederik Verdonck, Gaspard Lequeux, Webbey De Keyser, Nele Desmet, Johan Patyn, Stijn Janssen, Ingeborg Joris: dank allemaal voor jullie inbreng/ondersteuning groot en klein! Daarnaast ook dank aan de laboranten van Biomath en VITO voor de grote hoeveelheden analytisch werk en de opzet van grootse meetcampagnes die we samen tot een goed einde brachten. Experimenteel werk loopt nooit helemaal van een leien dakje, maar het eindresultaat mag zeker gezien worden! Ook een extra woordje van dank voor mijn 2 excellente thesisstudenten Veerle De Schepper en Veerle Gevaert. Jullie werk vormt een belangrijk onderdeel van dit eindresultaat.

Een woord van dank ook aan Marnik Vanclooster en Agnieska Romanowicz voor het ter beschikking stellen van data en een gedetailleerde landgebruikskaart voor het Nil-bekken. De mensen van CODA wens ik te bedanken voor het doorgeven van erg waardevolle kennis en gegevens in verband met het pesticidengebruik in ditzelfde studiegebied. Ze vormden een onmisbare uitgangsbasis voor dit onderzoek.

The jury members are acknowledged for their comments and persistency when reading this manuscript.

En dan is er ook nog de achterhoede: de trouwe supporters aan de kant van de weg die hun 'coureur' op de lastigste stukken weer wat extra energie geven: familie en vrienden! Jullie zijn met zeer velen en wisten gedurende die 4 jaar van alles te verzinnen ter ontspanning. Wat kan ik hierop meer zeggen dan 'dankjewel' en 'laat ons dit nog maar vele jaren verder doen'!

Mam, pap en Fie, merci voor alle aanmoedigingen en vertrouwen: van in de kinderwieg tot nu, daar is eigenlijk al een boek voor nodig!!

Jan, jij komt als laatste in de rij … na al die jaren, weet je als geen ander hoe me te doen lachen en kleine zorgen te vergeten, je nam me mee op grootse tochten met rugzak, fiets en surfplank en wist me daardoor in perfecte balans te houden om dit doctoraat tot een goed einde te brengen. Bedankt voor alles!!

Katrijn Holvoet
15 september 2006

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List of abbreviations

AA-EQS	Environmental Quality Standard expressed as an Annual Average value
AGNPS	Agricultural NonPoint Source pollution model
AnnAGNPS	Annualised Agricultural NonPoint Source pollution model
AI	Active Ingredient
ARS	Agricultural Research Service
ASM	Activated Sludge wastewater treatment plant Models
AWC	Available Water Capacity
BOD	Biological Oxygen Demand
BMP	Best Management Practice
COD	Chemical Oxygen Demand
DEM	Digital Elevation Model
DO	Dissolved Oxygen
DWSM	Dynamic Watershed Simulation Model
EC_{50}	Effect Concentration at 50%: statistically derived concentration of a substance in an environmental medium expected to produce a certain effect in 50% of test organisms in a given population under a defined set of conditions (IUPAC, 1997)
EQS	Environmental Quality Standard
EXAMS	Exposure Analysis Modeling System
FOCUS	FOrum for the Coordination of pesticide fate models and their Use
GIS	Geographic Information System
GREAT-ER	Geo-referenced Regional Exposure Assessment Tool for European Rivers
HCp	Hazardous Concentration at p%
HGE	Hierarchical Graphical Editor
HSPF	Hydrological Simulation Program – Fortran
HRU	Hydrologic Response Unit
LC_{50}	Lethal Concentration at 50%: statistically derived concentration of a substance in an environmental medium expected to have a mortality of 50% of organisms in a given population under a defined set of conditions (IUPAC, 1997)

LH	Latin Hypercube
LOD	Limit of Detection: the lowest concentration of a given substance that can be detected in a given sample. In chromatographical practice it is primarily accepted as the threefold of the analytical “noise”.
LOQ	Limit Of Quantification. Below the LOQ no numerical results should be reported. Concentrations between the LOD and the LOQ are considered to be detected but not quantifiable.
MAC-EQS	Environmental Quality Standard expressed as an Maximum Allowable Concentration
MEC	Measured Environmental Concentration
NA	Not Available
NOEC	No Observed Effect Concentration
OAT	One-factor-At-a-Time
OED	Optimal Experimental Design
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
RBD	River Basin District
RBMP	River Basin Management Plan
RWQM1	River Water Quality Model N°1
RQ_m	Risk Quotient for mixtures of herbicides with a similar mode of action
SSD	Species Sensitivity Distribution
SWAT	Soil and Water Assessment Tool
TERRACE	Terrestrial Runoff Modelling for Risk Assessment of Chemical Exposure
TMDL	Total Maximum Daily Load
TOXSWA	TOXic substances in Surface Waters
UA	Uncertainty Analysis
VITO	Flemish Institute for Technological Research
VMM	Flemish Environment Agency
WASP	Water Quality Analysis Simulation Program
WFD	Water Framework Directive
WWTP	Waste Water Treatment Plant

List of symbols

Roman symbols

Symbol	Description	Dimension
A	Ganzelmeier regression coefficient	-
A_{bottom}	bottom surface	L²
A_{cros}	area of the cross section of a tank	L²
A_{ch}	cross-sectional area of flow in the channel	L²
$Area$	subbasin area	L²
AP_EF	pesticide application efficiency as a percentage	-
ap_{rate}	pesticide application rate	$M\ L^{-2}$
$area_{hru}$	area of the HRU	L²
$area_{river\_reach}$	area of the receiving river stretch	L²
b	width of the buffer strip	-
B	Ganzelmeier regression coefficient	-
C	concentration	$M\ L^{-3}$
C_{CH}	channel cover factor	-
$CFRG$	coarse fragment factor	-
CN	curve number for a given day	-
$conc_{sed}$	concentration of suspended solids in the water	$M\ L^{-3}$
$conc_{sed,ch,i}$	concentration of sediment in the reach at the beginning of the time step	$M\ L^{3}$
$conc_{sed,ch,mx}$	maximum concentration of sediment in the reach that can be transported by the water	$M\ L^{3}$
C_{runoff}	runoff coefficient	-
$c_{soilstr}$	soil structure class	-
c_{sp}	coefficient in sediment transport equation	-
c_{perm}	profile permeability class	-
C_{USLE}	USLE cover and management factor	-
d	depth	L

d_s	average particle diameter	L
$depth$	depth of the water in the channel	L
$direct\_loss_{drift}$	amount of pesticide lost during or immediately after application as a drift loss	M
$direct\_loss_{point}$	amount of pesticide lost during or immediately after application as a point loss	M
$diversions$	volume of water added or removed from the reach for the day through diversions	L^3
d_{max}	maximum thickness of a sediment layer	L
$\overline{Drift}$	mean percent drift loading across a water body	-
d_X	particle diameter	L
E_a	amount of evapotranspiration on a given day	L
E_{ch}	evaporation from the reach for the day	L^3
E_0	erodibility constant	$M\ L^{-2}\ T^{-1}$
f_c	friction factor	-
f_d	fraction of totally dissolved pesticides	-
F_d	fraction of total pesticide in the dissolved phase	-
f_{DOC}	fraction of sorbed pesticides on dissolved organic carbon	-
f_p	fraction of sorbed pesticides on particulate organic carbon	-
F_p	fraction of total pesticide in the particulate phase	-
f_{sed}	fraction of particles that settles	-
g	gravitational fall velocity	$L\ T^{-2}$
h	depth of the flow	L
i	rainfall intensity	$L\ T^{-1}$
I_a	initial abstractions which include surface storage, interception and infiltration prior to runoff	L
k_b	first order rate constant for biodegradation	T^{-1}
$k_{b,20}$	biodegradation constant at 20°C	T^{-1}
k_{burial}	first order rate constant for burial	T^{-1}
k_{res}	first order rate constant for resuspension	T^{-1}
k_{sed}	first order rate constant for sedimentation	T^{-1}

K	temperature constant	°C^{-1}
K_{CH}	channel erodibility factor	-
K_d	pesticide partition coefficient	L^3 M^{-1}
$K_{L,GC}$	diffusion mass transfer coefficient	L T^{-1}
K_{OC}	sorption coefficient	L^3 M^{-1}
K_{OW}	octanol-water partition coefficient	M L^{-1}
K_{sat}	saturated hydraulic conductivity for a soil layer	L T^{-1}
K_{USLE}	soil erodibility factor	
LS_{USLE}	USLE topographic factor	-
M	mass	M
m_c	percent clay content	-
M_{part}	particle-size parameter for estimation of USLE K factor	-
m_{silt}	percent silt content	-
m_{vfs}	percent very fine sand content	-
n	Manning's coefficient	-
$N_{f,s}$	particle fall number	-
OM	percent organic matter	-
$orgC$	percent organic carbon content of the soil layer	-
p	porosity	-
$pest$	actual amount of pesticide applied on the field	M L^{-2}
$pest2$	effective amount of pesticide applied on the field	M L^{-2}
prf	peak rate adjustment factor	-
pst_{bur}	amount of pesticide removed from the sediment via burial	M
$pst_{deg,sed}$	amount of pesticide removed from the sediment via degradation	M
$pst_{deg,wtr}$	amount of pesticide removed from the water via degradation	M
pst_{dif}	amount of pesticide transferred between the water and sediment through diffusion	M
pst_{in}	pesticide added to the rach segment via inflow	M
$pst_{rsp,wtr}$	amount of pesticide removed from the water via resuspension	M
pst'_{sol}	pesticide solubility	M L^{-1}
$pst_{sol,o}$	amount of dissolved pesticide removed via outflow	M

$pst_{stl,wtr}$	amount of pesticide removed from the water via settling	M
$pst_{sorb,o}$	amount of particulate pesticide removed via outflow	M
$pst_{vol,wtr}$	amount of pesticide removed from the water via volatilization	M
P_{USLE}	USLE support practice factor	-
Q	water flow	$L^3\ T^{-1}$
q_{ch}	rate of flow in the channel	$L^3\ T^{-1}$
$q_{ch,pk}$	peak flow rate in the channel	$L^3\ T^{-1}$
Q_{gw}	return flow to the main channel	$L^3\ T^{-1}$
q_{ov}	average overland flow rate	$L^3\ T^{-1}$
q_{peak}	peak runoff rate	$L^3\ T^{-1}$
Q_{surf}	amount of surface runoff on a given day	L
r	reaction rate for conversion processes	$M\ L^{-3}\ T^{-1}$
R_{ch}	hydraulic radius for a given depth of flow	L
R_{day}	amount of rainfall on a given day	L
s	slope of the buffer strip	$L\ L^{-1}$
S	concentration of dissolved component	$M\ L^{-3}$
S_{crop}	average distance between grass blades	L
sed	sediment yield on a given day	M
sed_{ch}	amount of suspended sediment in the reach segment	M
sed_{deg}	amount of sediment reentrained in the reach segment	M
sed_{dep}	amount of sediment deposited in the reach segment	M
sed_{out}	amount of sediment transported out of the reach	M
S_{GC}	pesticide concentration	$M\ L^{-3}$
slp	bottom slope of river stretch	-
slp_{ch}	slope along the channel length	$L\ L^{-1}$
$spexp$	exponent in sediment transport equation	-
S_S	retention parameter in SCS curve number equation	L
SW	amount of water in the soil profile	L
t	time	T
t_{conc}	time of concentration	T

t_{loss}	volume of water lost from the reach via transmission through the bed	L^3
$trap_{ef}$	fraction of the constituent loading trapped by the filter strip	-
$T_{r,s}$	trapping efficiency for the sediment fraction by the filter strip	-
T_W	mean water temperature	°C
V	volume	L^3
v_c	flow velocity	$L\ T^{-1}$
$v_{ch,pk}$	peak channel velocity	$L\ T^{-1}$
V_{ch}	volume of water in the reach segment	T^3
V_{in}	volume of water flowing in to the reach during the time step	T^3
v_m	average mean flow velocity between grass blades	$L\ T^{-1}$
V_{out}	volume of water flowing out of the reach during the time step	T^3
v_s	settling velocity based on Stoke's law	$L\ T^{-1}$
V_{bnk}	volume of water added to the reach via return flow from bank storage	L^3
V_{stored}	volume of water in the reach	L^3
W	channel width	L
W_{btm}	bottom width of the channel	L
$width_{filtstrip}$	width of the filter strip	L
w_{seep}	amount of percolation from the soil profile on a given day	L
X	concentration of particulate component	$M\ L^{-3}$
z	slope of the river bank	-
z_1	distance from the edge of the treated field to the closest edge of the river	L
z_2	distance from the edge of the treated field to the farthest edge of the river	L
z_{ch}	inverse of the channel slope	-

Greek symbols

Symbol	Description	Dimension
α	elemental mass fraction	-
α_{tc}	fraction of daily rainfall that occurs during time of concentration	-
Δpst_{rchsed}	change in pesticide mass in the sediment layer	M
Δpst_{rchwtr}	change in pesticide mass in the water layer	M
ϑ_H	hydraulic retention time	T^{-1}
μ	kinematic viscosity	$L^2\ T^{-1}$
ρ	density of particles	$M\ L^{-3}$
ρ_w	density of water	$M\ L^{-3}$
τ_b	bottom shear stress	$N\ L^{-2}$
$\tau_{crit,sed}$	critical bottom shear stress above which no sedimentation occurs	$N\ L^{-2}$
$\tau_{crit,res}$	critical bottom shear stress above which resuspension occurs	$N\ L^{-2}$

Mathematical and statistical symbols

Symbol	Description	Dimension
f	fraction by which a parameter Φ_i is changed	-
m	number of intervals in the Latin Hypercube method	-
p	number of parameters considered in the sensitivity analysis	-
$S_{i,j}$	partial effect for parameter Φ_I	-
SSE	sum of squared errors	-
Φ_I	parameter considered in the sensitivity analysis	-

Chapter 1

GENERAL INTRODUCTION

1.1 Problem statement

1.1.1 The pesticide market and environmental issues

Pesticides are useful to society because of their ability to exterminate disease-causing organisms and control insects, weeds and other pests. At the same time, most pesticides may be harmful to humans, animals and the environment because of their ecotoxicity, their potential bio-accumulating properties or their hormone disrupting effects. Pimentel and Greiner (1996) described and summarized the environmental and socio-economic costs of pesticide use as follows: pesticide use has an impact on national health and live stock, it results in less effective predators and higher costs due to pesticide resistance, it affects bees, birds, fish and other aquatic organisms and it contaminates ground and surface water reserved for drinking water purposes. Belgaqua, the Belgian federation for the water industry, estimates the economic impact in Belgium of pesticide residues to amount to 20 million Euros a year (Legros, personal communication 2004).

Pesticides are of concern for public authorities, as it seems that pesticide pollution is not a fleeting issue. World wide sales figures show that the agrochemical market has been relatively static for almost 20 years, increasing in line with inflation. In 2004, herbicides accounted for 45.4% of the agrochemical market, followed by insecticides 27.5%, fungicides 21.7% and other products 5.4%. The most noticeable trend is the increased share of herbicides and reduced share of insecticides (Dingham, 2005). In Flanders, i.e. the northern part of Belgium, a decreasing tendency in total use of pesticides can be observed from 7 million kg active ingredient (AI) in 1992 towards 5.5 million kg a.i. in 2002. Nevertheless, the contribution of herbicides seems to stagnate in recent years around 3 million kg AI.

When pesticides are applied on the field, only a certain percentage of the applied dose will reach the target crop. The remaining fraction will enter the soil, air, surface and groundwaters through different pathways. In the different compartments of the ecosystem, pesticides are then -to a smaller or larger extent- available for organisms. Depending on the exposure concentration and the mode of action, pesticides can be harmful to humans, animals and the ecosystem.

Therefore, public authorities and industry tried to minimise the negative consequences of pesticide use. The use of certain highly toxic pesticides has been banned and the use of triazine herbicides, organophophate and carbamate insecticide has been restricted. These groups of pesticides have been replaced by other classes of pesticides that have shorter half-lives or are applied in smaller amounts. Through monitoring and modelling, one can gain insight in the occurrence of pollutants in the different compartments of the ecosystem. Besides, models can be used as a decision tool in the selection of mitigation measures in order to reduce environmental contamination.

1.1.2 Occurrence of pesticides in surface waters in Belgium

In Belgian surface waters, different pesticides are frequently detected. An overview is given in Table 1 of the percentages of detection for the 20 most found pesticides in water samples during the years 2003 and 2004 (VMM, 2005). From this table it appears that glyphosate, diuron, MCPA, atrazine, isoproturon, linuron, carbendazim, chloridazon, simazine and bentazone are the 10 most frequently detected pesticides. In Figure 1, a map of Flanders is presented showing the number of pesticides found at different locations (VMM, 2005). From this figure it is clear that the Demer and the Ijzer catchment are exposed to the highest number of pesticides in Flanders.

Table 1. Percentages of detection of the 20 most found pesticides in water samples in 2004, compared to those detected in 2003 (VMM, 2005).

	Percentage of positive detections 2004*	Percentage of positive detections 2003*
AMPA**	88	75
Glyphosate	79	91
Diuron	67	82
MCPA	43	40
Atrazine	42	48
Isoproturon	41	50
Linuron	40	5
Carbendazim	37	45
Chloridazon	34	30
Simazine	33	34
Bentazone	31	28
MCPP	26	27
2-hydroxy-atrazine	26	23
Metolachlor	23	24
Dimetoaat	23	17
Endosulfan-sulfaat	21	22
24-DP (dichloorprop)	19	16
Chloortoluron	17	15
24-D	16	18
Lindane	16	26

* detections above the detection limit

** degradation product of glyphosate

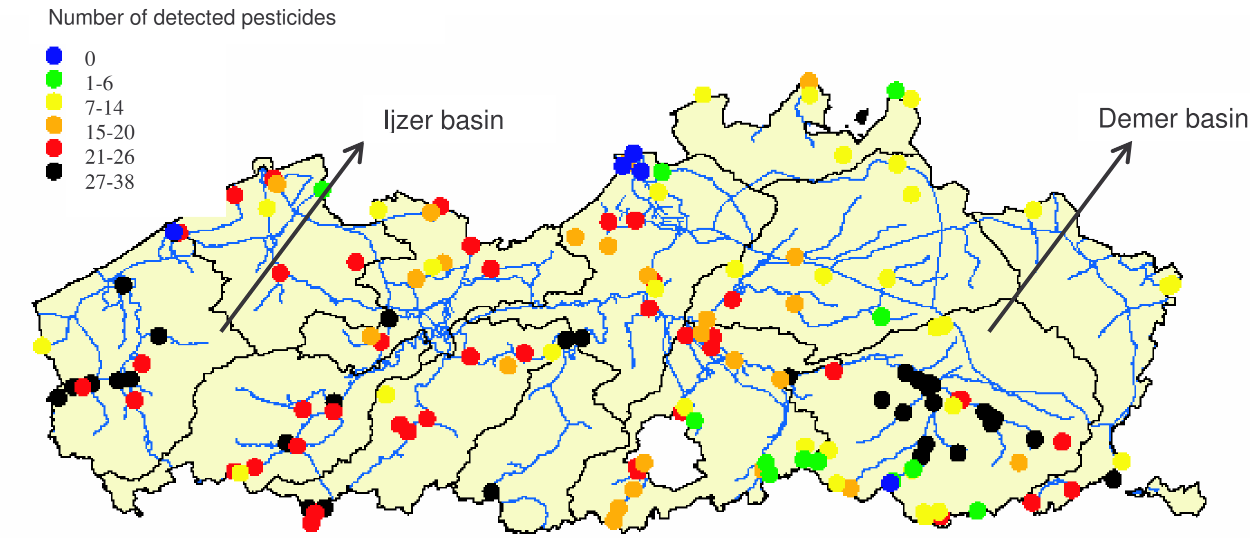


Figure 1. Number of pesticides found at different sampling locations in Flanders (Belgium) in 2004 (VMM, 2005).

1.2 Research objectives

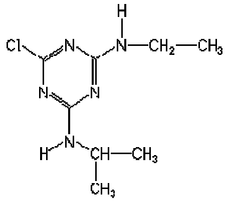
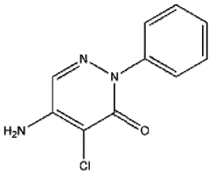
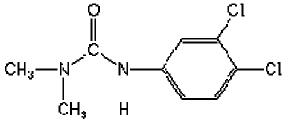
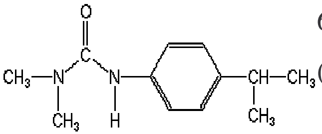
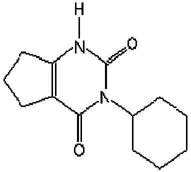
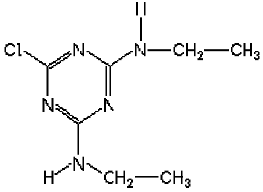
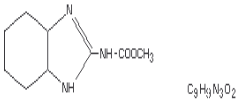
The research objectives of this dissertation were as follows:

- The study of the physical and chemical processes determining the dynamic fate and exposure of pesticides in surface water. Special attention is given to sub daily dynamics of pesticides in the water column and to the dynamics happening in the sediment. The high level of detail and the interaction with the sediment are innovative in this research field.
- The development or extension of a model predicting the distribution of pesticides in a river system. A state-of-the-art in modelling pesticide fate is given in Chapter 2 and shows that the development of a dynamic model for pesticides at catchments scale is desirable as no such tool is available.
- The developed model should be calibrated and evaluated on a concrete case study. If possible, this should be done for different catchment sizes.
- Performing a preliminary risk assessment. In a risk assessment, predicted and/or measured exposure concentrations are compared to predicted no effect concentrations. Such a comparison can show where the areas 'at risk' are in a catchment, but also learns what the difficulties and shortcomings are in current risk assessments for dynamic pesticide occurrences in river systems.

1.3 Selection of pesticides

First, a determination of the most frequently detected herbicides and fungicides in Belgium was made, based on historical data of the Flemish Environment Agency (VMM, 2005; see alsoTable 1) and on studies performed by the Belgian water association Belgaqua (Groenboek, 2002). The selection of 6 herbicides was then further based on the availability of data of a 4 year lasting project (1998-2001) in the Nil-catchment performed by the Veterinary and Agrochemical Research Centre (Beernaerts et al., 2002). In this project, 6 herbicides were measured daily during spring and farmers were intensively questionaired about pesticide use, dosis and application dates. Glyphosate and MCPA (4-chloro-2-methylphenoxy acetic acid) were not included in this study because no application information was available for these herbicides. The fungicide was selected as being the most detected one in Flanders, being of concern in orchard areas. The selected pesticides are presented together with their chemical properties in Table 2. The application period of the different pesticides under study was given by Beernaerts et al. (personal communication, 2003) and is schematically shown in Table 3.

Table 2. Chemical properties of the studied pesticides (Tomlin, 2003).

Pesticide	Formula	S_w (mg/l)	log K_{OW}	K_{OC} (ml/g)	DT_{50soil} (days)	$DT_{50water}$ (days)
Herbicides						
Atrazine		33 (pH 7, 22°C)	2.5 (25°C)	39-173	35-50	80
Chloridazon		340 (20°C)	1.19 (pH 7)	89-340	42-56	56
Diuron		36.4 (25°C)	2 .85± 0.03 (25°C)	538-902*	90-180	29
Isoproturon		65 (22°C)	2.5 (20°C)	NA	6-28	40
Lenacil		3 (25°C)	2.31	136-417	82-150	91
Simazine		6.2	2.1 (25°C)	103-277	70-110	46
Fungicide						
Carbendazim		8 (pH 7, 24°C)	1.51 (pH 7)	200-250	8-32	60-750

* Agritox database. Available at www.inra.fr/agritox/

** Footprint pesticide database. Available at www.herts.ac.uk/aeru/footprint/

NA = Not Available from the above mentioned sources.

Table 3. Application periods of the studied pesticides. (AI = active ingredient)

AI	culture	March		April		May		June		July	
Atrazine	corn				▨	▨	▨	▨			
Carbendazim	apple, pear					▨	▨	▨	▨		
Chloridazon	beets	▨	▨	▨	▨						
Diuron	non agriculture			▨	▨	▨	▨	▨	▨	▨	▨
Isoproturon	winter wheat		▨	▨							
	barley		▨	▨	▨	▨					
Lenacil	beets					▨	▨	▨	▨		
	flax				▨	▨	▨	▨			
Simazine	non agriculture			▨	▨	▨	▨	▨	▨	▨	▨
	green peas		▨	▨	▨						

In Belgium the 7 studied pesticides are registered but they are currently undergoing an EU review process based on recent priority programs. As this process is rather slow, only few pesticides yet got reviewed, the others are still in the queue. The periods of known permission at the moment of publication of the dissertation are given in Table 4.

Table 4. Permission period for active ingredients (www.fytoweb.fgov.be).

Pesticide	permission till	restricted use from	can be sold till	can be used till
Atrazine	10-09-2004		10-09-2004	10-09-2005
Carbendazim	depending on product formulation	15-09-2006		
Chloridazon	depending on product formulation			
Diuron	depending on product formulation	12-10-2002 (<1.6 kg/ha)		
Isoproturon	1-1-2012 *			
Lenacil	depending on product formulation			
Simazine	1-01-2007	10-09-2005	1-01-2007	restricted use till end 2007

* as defined in Annex I of Directive 91/414/EEC

1.4 Selection of study areas

Two study areas were selected based on the frequent occurrence of pesticides in surface water and sediments (Beernaerts et al., 2002; VMM Flemish Environmental Agency, 2005; see also Figure 1). The geographical location of these two basins in Belgium is presented in Figure 2. The average rainfall in Belgium amounts to 780 mm a year.

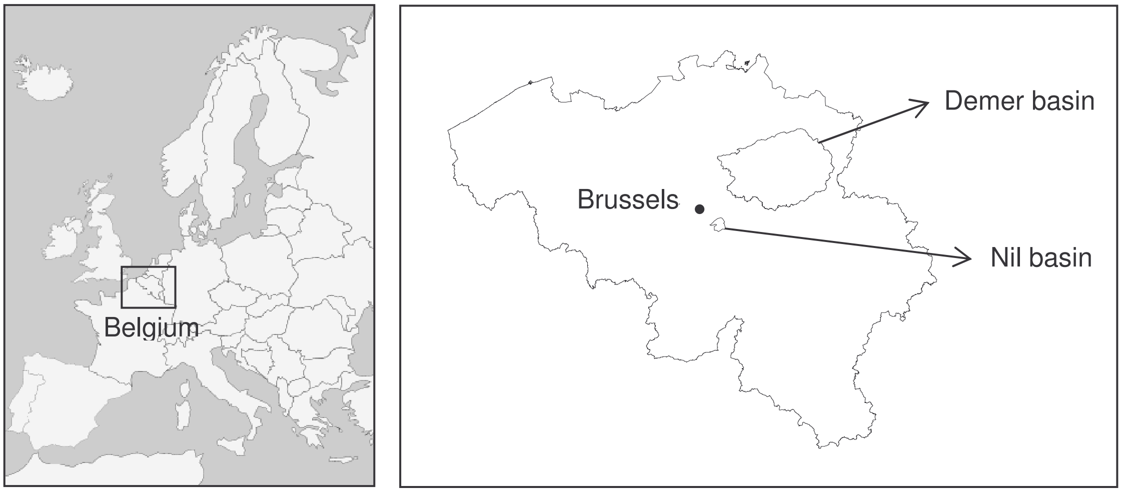


Figure 2. Geographical location of the Nil and the Demer basin.

1.4.1 The Nil catchment

The Nil basin was selected because it is a well documented basin, studied in detail in terms of pesticide application during the period 1998-2002 (Beernaerts et al., 2002). It is a small and hilly basin situated in the central part of Belgium, Southeast of the capital (Figure 2). The average elevation is 151 m a.s.l., with the highest top reaching 167 m a.s.l. and the watershed outlet lying at 110 m a.s.l. The Nil catchment drains an area of 32 km², is 14 km long and has a retention time of about 1 day. The average flow amounts to 0.148 m³/s, based on hourly data for the period 2000-2004 obtained from the DGRNE (Direction Génerale des Ressources Naturelle et de l'Environnement).. The predominant soil type is loam. Seven % of the area is inhabited and the main crops grown are winter wheat (22% of the catchment area), corn (15%) and sugar beet (10%) (Figure 3). There are no drainpipes and no wastewater treatment plants situated in the catchment.

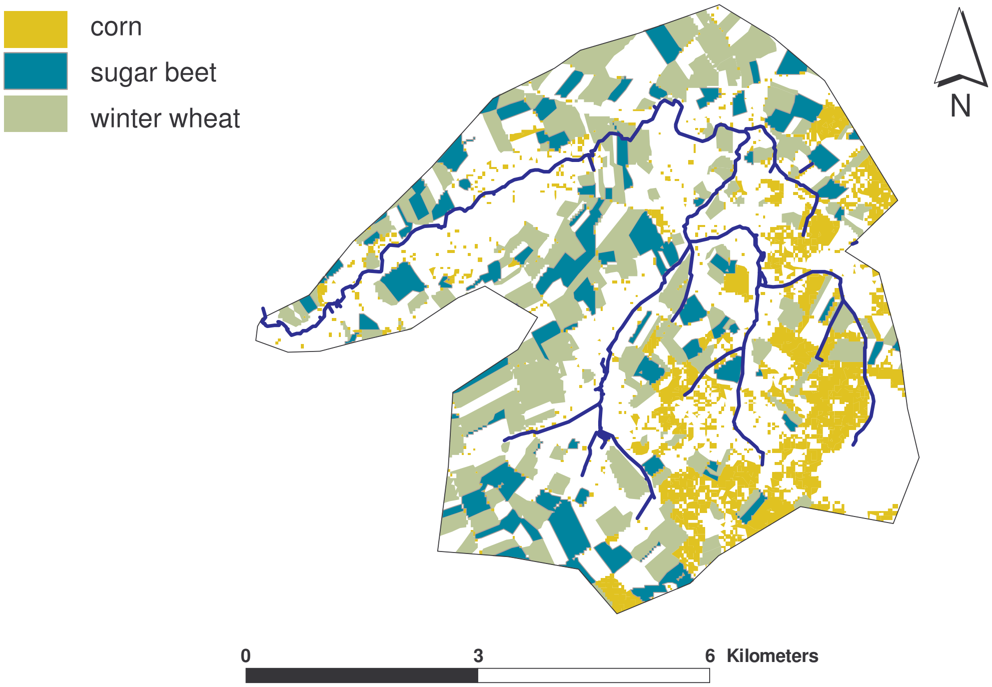


Figure 3. Landuse (1999) in the Nil catchment (adapted from: Romanowicz et al., 2003).

Further, the catchment is characterised by a low baseflow which results from its specific geological structure (Figure 4). Highly permeable Brusselian sands, showing hydraulic conductivities between 10^{-3} and 10^{-5} m/s, lay above a less permeable rock (Abdeslam, 1998). Hereby, an important part of the groundwater of the Nil-catchment is drained to the adjacent river 'Train'.

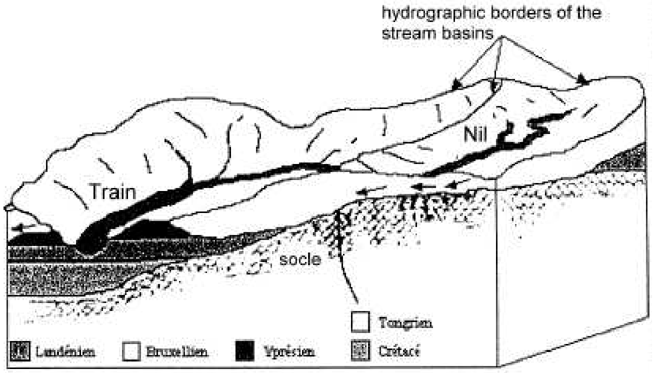


Figure 4. 3-D view of the geological structure of the Nil catchment.

1.4.2 The Demer catchment

The Demer basin was selected because it is known for its high pesticide concentrations both in the water column and in the sediment (VMM, 2005). A significant contribution of this pesticide pollution is attributed to an orchard region upstream. In this region, three important tributaries can be distinguished: the Herk, the Gete and the Velpe.

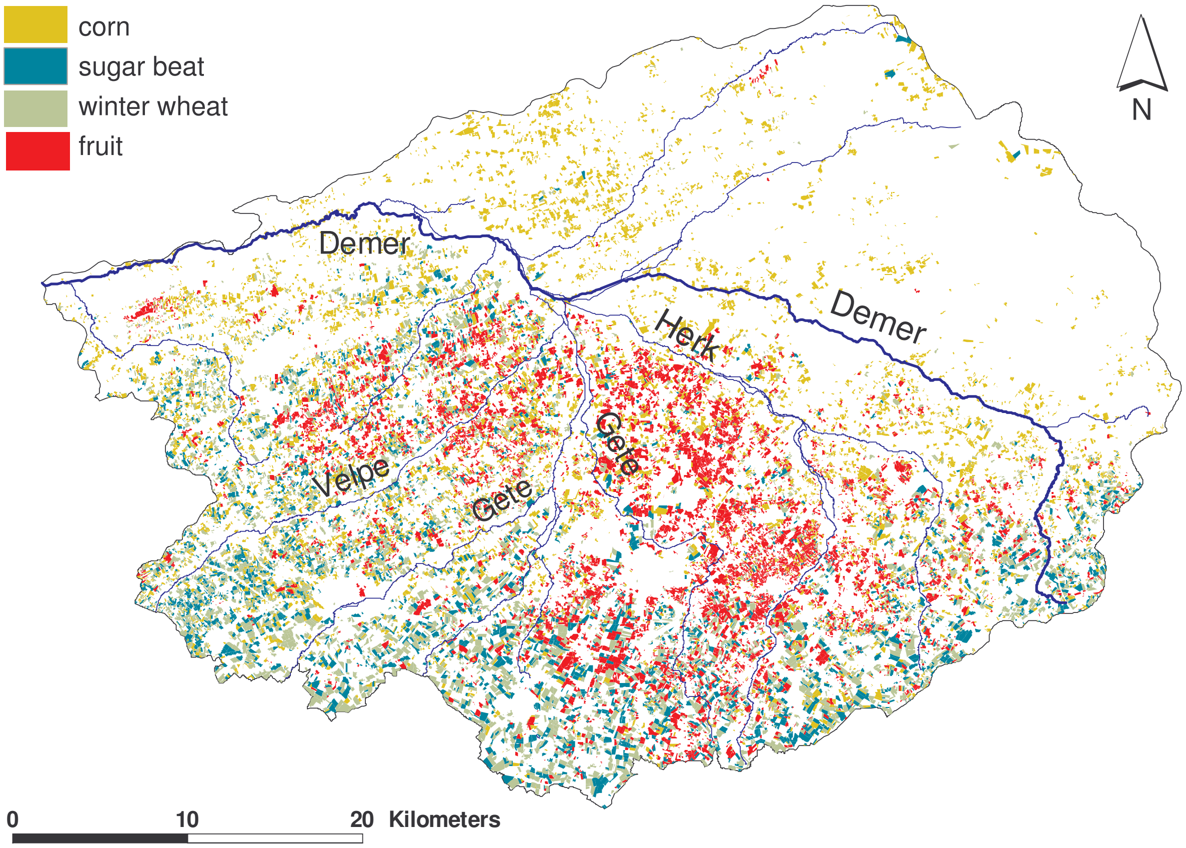


Figure 5. Landuse (2002) in the Demer catchment (adapted from: VLM, 2002).

The Demer forms a large river basin in the Northeast of Belgium. The highest top reaches 137 m a.s.l. and the watershed outlet lies at 11 m a.s.l. The Demer catchment drains an area of 2130 km², is 85 km long and has a retention time between the upstream tributaries and the mouth of about 13 hours. At the mouth, the river is about 16m wide and the average flow amounts to 18.7 m³/s. The average flows of the upstream tributaries the Velpe, the Herk and the Gete amount to respectively 0.75, 2 and 6.1 m³/s. These data are based on hourly data for the period 2000-2004 obtained from

HIC (Hydrological Information Center). Five percent of the catchment consists of pasture, 52% is agricultural land with fruit orchards (5%), corn(6%), sugar beet (4%) and winter wheat (6%) (Figure 5). South of the river Demer, the southern half of the area consists mainly of loamy soils. The other part close to the river Demer itself are sandy loamy soils. North of the river Demer there are sandy soils. In the catchment, 32 wastewater treatment plants are scattered over the area and several others are still under construction. A detailed map is given in Appendix A.

1.5 Outline of the dissertation

Whereas this introductory chapter only gives a rough problem statement, Chapter 2 reviews in detail the different aspects of the occurrence of pesticides in river systems. This chapter starts by sketching the legislative context relevant for pesticides in surface waters. Next, the different entry routes of pesticides towards surface water are described and possible mitigation measures are indicated. An overview is given of the processes that affect the fate of pesticides in surface waters and sediments. The ecotoxicological significance of this kind of water pollution is shortly discussed and current gaps in effect data are quoted. Finally, a state-of-the-art of available models describing the fate of pesticides is given: from simple screening tools towards more complex catchment models. Also a review is given of existing tools for risk assessment and the current approach used for modelling pesticides in their registration procedure is summarized.

In Chapter 3, the set up of 2 intensive monitoring campaigns during spring 2004 and 2005 is described in detail (see Holvoet et al., 2006). The processing and the method of analyses of the different fractions of the samples are given. Subsequently, the results of the sub-daily water samples and monthly taken sediment samples are discussed. Results are compared between the different monitoring points and measurement campaigns. Advise is given for future monitoring campaigns of pesticides in surface water. The objective of the monitoring campaigns was to gain insight in the dynamic processes occurring in the different compartments of a river system and in the interactions between those. Afterwards, these extensive data sets were used for model evaluations (see Chapter 4 and 5). Also a preliminary risk assessment was performed in order to determine if certain places in the studied catchments were at risk during certain periods.

Chapter 4 is rather extensive. In this chapter, an attempt was made to model pesticide fluxes towards the river. Important entry routes were considered and simulation results were compared with the obtained monitoring data (Chapter 3). Chapter 4 comprises the work performed with the SWAT model (Soil and Water Assessment Tool). In a first step, a hydrologic model was developed for the Nil catchment. To do this properly, a sensitivity analysis was performed in order to gain insight in the most influential parameters for hydrology. This was also done for the parameters determining pesticide fluxes towards the river (see Holvoet et al., 2005). Next, pesticide management data were added to the calibrated hydrological model and simulated pesticide concentrations were compared to measured ones. Some extensions were made to the original SWAT-code, including point losses and drift losses. Afterwards, the contribution of different entry routes to the pesticide load in the river could be assessed. A preliminary uncertainty analysis was then performed giving information concerning the anticipated order of uncertainty related to the simulation results. Finally, the SWAT model was used to compare different mitigation measures for the reduction of pesticide fluxes towards the river Nil.

In Chapter 5, the focus is on modelling processes occurring in a river system. The RWQM1 (River Water Quality Model N°1) was found to be more suitable for modelling in-stream processes compared to the SWAT model. The advantage of the RWQM1 model lies in the fact that it has closed elemental mass balances and that it explicitly considers microbial biomass as a state variable. A better accounting of biological activities will also affect the way the environmental conditions in the river change (e.g. pH, dissolved oxygen concentration) which may influence the fate of pesticides in the water column.. Compared to the SWAT model, RWQM1 allows to study different pesticides at the same time and to represent sedimentation and resuspension processes more accurately. In this dissertation, the processes of the herbicides chloridazon and diuron in a river system are modelled. To this end, the RWQM1 model was extended. The sorption/desorption and biodegradation processes are described in detail. The exchange of pesticides between the water column and the sediment is described by three transport processes: diffusion, sedimentation and resuspension. Burial of sediments is also included. Simulation results are compared to measured values resulting from the 4 month intensive monitoring campaign of bulk and pore water performed during spring 2004 (Chapter 3).

In Chapter 6 some overall conclusions are made. Besides, some recommendations for future monitoring campaigns and further research are given.

Chapter 2

PESTICIDES IN SURFACE WATERS: A REVIEW

Adapted from: Holvoet, K., Seuntjens, P., Vanrolleghem, P.A. (2006). Monitoring and modeling pesticide fate in surface waters at catchment scale: A Review. Submitted.

2.1 Legislative context

2.1.1 The Water Framework Directive

Early European water legislation began, in a "first wave", with standards for those rivers and lakes used for drinking water abstraction in 1975 (EU Surface Water Directive, 1975), and culminated in 1980 in setting binding quality targets for drinking water (EU Drinking Water Directive, 1980). It also included quality objective legislation on fish waters (EU Fresh Water Directive, 1978), shellfish waters (EU Shellfish Directive, 1979), bathing waters (EU Bathing Water Directive, 1976) and groundwaters (EU Groundwater Directive, 1980). Its main emission control element was the Dangerous Substances Directive (1967).

In 1988 the Frankfurt ministerial seminar on water reviewed the existing legislation and identified a number of improvements that could be made and gaps that could be filled. This resulted in the second phase of water legislation, the first results of this were, in 1991, the adoption of

- the Urban Waste Water Treatment Directive, providing for secondary (biological) wastewater treatment, and even more stringent treatment where necessary.
- the Nitrates Directive, addressing water pollution by nitrates from agriculture.

Other legislative results of these developments were Commission proposals for action on

- a new Drinking Water Directive, reviewing the quality standards and, where necessary, tightening them (adopted November 1998),
- a Directive for Integrated Pollution and Prevention Control (IPPC), adopted in 1996, addressing pollution from large industrial installations.

Nevertheless, the various water-related directives collectively represented a disparate approach to water management (Chave, 2001). Therefore, the Water Framework Directive (WFD) (2000) was formulated, addressing these weaknesses. The WFD signaled the arrival of a new integrated, participatory and spatial approach to water management in Europe. This Directive was adopted in October of 2000 and should have been transposed into national legislation by the 22nd of December 2003 (European Commission, 2006a). The directive aims at

- expanding the scope of water protection to all surface and groundwater and waters up to one nautical mile from the coast
- managing water resources at the river basin scale
- achieving ‘good status’ for most of Europe’s waters by 2015
- combining the emission limit values approach and the quality standards approach
- getting the prices right: charges for water and wastewater reflecting the true costs
- promoting citizen participation
- streamlining existing European water legislation

The WFD aims at a sustainable use of water, with a focus on a good water quality for each river basin. This requires the establishment of river basin districts (RBD), each of which must produce a river basin management plan (RBMP). The production of RBMPs represents a new approach to water resource management based not on political and administrative boundaries but on natural hydrological units. This requires an integrated and systematic approach with international co-operation for river basins crossing national borders.

For surface water in particular, the policy requires each EU member state to have a ‘good ecological’ and a ‘good chemical’ status by the year 2015. Concerning the good ecological status, controls are specified as allowing only a slight departure from the biological community which would be expected in conditions of minimal anthropogenic impact. A set of procedures for identifying that point for a given body of water, and establishing particular chemical or hydromorphological standards to achieve it, is provided. Good chemical status is defined in terms of compliance with all the quality standards established for chemical substances at European level. The Directive also provides a mechanism for renewing these standards and establishing new ones by means of a prioritisation mechanism for hazardous chemicals. This will ensure at least a minimum chemical quality, particularly in relation to very toxic substances, everywhere in the Community.

To implement the Directive, a continuous and transparent process is proposed. Different steps have to be taken by the different Member States (see Table 5) to achieve the required water quality by 2015. If a water body does not meet the required water quality level, Member States can petition for the deadline to be extended by 6 years twice. Even after an additional 12 years, a request for a third extension can be addressed to the European Commission.

Table 5. Overall time table of the Water Framework Directive (2000/60/EC).

Year	Issue	Reference
2000	Directive entered into force	Art. 25
2003	Transposition in national legislation	Art. 23
	Identification of River Basin Districts	Art. 3
2004	Characterisation of river basin: pressures, impacts and economic analysis	Art. 5
2006	Establishment of environmental monitoring programmes	Art. 8
	Start public consultation (at the latest)	Art. 14
2008	Present draft river basin management plan	Art. 13
2009	Finalise river basin management plan including programme of measures	Art. 13 & 11
2010	Introduce pricing policies	Art. 9
2012	Implement programme of measures	Art. 11
2015	Achieve environmental objectives specified in the first RBMP	Art. 4
up to 2027	Produce River Basin Management Plans every 6 years	Art. 4 & 13

In the Water Framework Directive, strategies are undertaken against chemical pollution of surface waters on two levels. First, on the Community level a selection of priority substances is made and Community-wide measures will be defined. The list of substances of concern contains substances that present a significant risk to or via the aquatic environment. The Commission is currently preparing Community-wide emission controls and quality standards for the priority substances. The aim is to establish measures to help reaching the quality status and other environmental objectives of the Water Framework Directive (article 4, Directive 2000/60/EC) - progressive reduction of emissions, losses and discharges of all priority substances - and in addition to achieve phase-out or cessation of emissions, losses and discharges of priority hazardous substances. Second, Member States should set quality standards for river basin specific pollutants and take measures at river basin level against relevant pollutants (European Commission, 2004). In Belgium, the determined maximum concentrations in surface water for the pesticides atrazine and simazine, for instance, amount respectively 2 µg/l and 1 µg/l (VMM, 2005).

Thirty three substances or groups of substances are on the list of priority substances including selected existing chemicals, pesticides, biocides, metals and other groups like Polyaromatic Hydrocarbons (PAH) that are mainly incineration by-products and Polybrominated Biphenylethers (PBDE) that are mainly used as flame retardants. The complete list is given in Appendix B. The pesticides atrazine, diuron, isoproturon and simazine are on the list and are/were frequently used in Belgium. Their occurrence in Belgian surface waters will be discussed further in this thesis. In July 2006, a proposal was written by the European Commission (2006d) containing Environmental Quality Standards (EQS) for priority substances and for other pollutants. They are expressed as annual average values (AA-EQS) and maximum allowable concentrations (MAC-EQS). The pesticides appearing in this proposal and their EQS are summarised in Table 6.

Table 6. Proposal for Environmental Quality Standards (EQS) for pesticides in surface waters (European Commission, 2006d).

Name of substance	CAS number	AA-EQS* (µg/l)	MAC-EQS** (µg/l)
Atrazine	1912-24-9	0.6	2.0
Diuron	330-54-1	0.2	1.8
Isoproturon	34123-59-6	0.3	1.0
Simazine	122-34-9	1	4

* Environmental Quality Standard expressed as an annual average value

** Environmental Quality Standard expressed as a maximum allowable concentration

2.1.2 The Drinking Water Directive

The Drinking Water Directive (98/83/EC) concerns the quality of water intended for human consumption. It sets standards for the most common substances (so-called parameters) that can be found in drinking water. A total of 48 microbiological and chemical parameters must be monitored and tested regularly. In principle, WHO guidelines for drinking water are used as a basis for the standards in the Drinking Water Directive (European Commission, 2006b). The Member States of the European Union have to translate the Directive in their own national legislation but they can include additional requirements, e.g. regulate additional substances that are relevant within their territory or set higher standards.

The Flemish regional legislation determines a limit of 0.1 µg active substance a litre for each pesticide. For the sum of concentrations of individual pesticides, a limit of 0.5µg a litre exists (VMM, 2005).

2.1.3 The Plant Protection Products Directive

In an ambitious work programme launched in 1991, the European Commission started a Community-wide review process for all active ingredients used in plant protection products within the European Union (The Plant Protection Products Directive (91/414/EEC)). From then on, in a review process based on scientific assessments, each applicant has to prove that a substance can be used safely regarding human health, the environment, ecotoxicology and residues in the food chain. It is a dual system where the Community evaluates active substances and Member States evaluate and authorise products containing them (European Commission, 2006c).

The main elements of the Directive are as follows:

- The harmonisation of the authorisation of plant protection products within the European Union. This is achieved by establishing agreed criteria for considering the safety of those products. Product authorisation remains the responsibility of individual Member States.
- The Directive establishes a positive list of active substances (Annex I), that have been shown to be without unacceptable risk to people or the environment.
- Active substances are added to Annex I of the Directive as existing active substances are reviewed (under the European Commission (EC) Review Programme) and new ones authorised.
- Member States can only authorise the marketing and use of plant protection products after an active substance is listed in Annex I, except where transitional arrangements apply.

Before an active substance can be considered for inclusion in Annex I of Directive 91/414/EEC, companies must submit a complete data package (dossier) on both the active substance and at least one plant protection product containing that active substance. The data required:

- identify an active substance and plant protection product;
- describe their physical and chemical properties;
- their effects on target pests, and;
- allow for a risk assessment to be made of any possible effects on workers, consumers, the environment and non-target plants and animals. In a risk assessment, a comparison is made between exposure to a certain substance and its effects on humans, health or the ecosystem.

In addition to the required experimental data, results from different model calculations should be considered in the registration procedure.

The Directive provided for a 12-year programme of evaluation of the 834 active substances already on the market at the time of its entry into force in July 1993 (“existing” active substances) and permitted their remaining on the market until July 2003 under certain conditions. Due to the long review process, the period of evaluation was finally extended until 2008. The Commission split the review programme for the “existing” substances into four phases (see Table 7). All other substances presented since July 1993 are considered as “new” substances. Both new and existing substances are evaluated in parallel.

Table 7. Different phases in the review programme of existing active substances (European Commission, 2006c).

Phase	N° of substances (market share in 1993)	N° of AI that will be withdrawn	Deadline
1	90 (30%)	16	July 2003
2	149 (40%)	89	
3	402 (25%)	235	
4	193 (5%)	27	2008
TOTAL	834 (100%)	367	2008

2.1.4 Link towards monitoring and modelling pesticides and other priority substances

Integration is the key concept underlying the Water Framework Directive (WFD). The implementation of the WFD requires integration of the management of all water resources at the river basin scale, using tools developed to incorporate a wide range of measures, involving stakeholders and civil society in decision-making and sometimes transnational water management. Challenges are to incorporate “soft” information (socio-economics) into water quality models and vice versa.

Integrated river basin water quality models enable a holistic analysis of water and pollution in a river basin and their usefulness in view of the WFD is readily apparent. Such models can assist in the development of pollution abatement plans to achieve the desired water quality standards and objectives. The models act as a surrogate to expensive water quality monitoring, where they can provide water quality variables whenever there are no or few data. Catchment models can be used in watershed management to quantify the pollutant sources to a receiving water. Once the model has been validated for a watershed’s existing conditions, it can then be used to predict impacts of alternative management plans to reduce pollutant loadings. However, the results of modelling studies require careful evaluation, and models need to be rigorously validated as part of this process.

In view of the Drinking Water Directive, integrated river basin water quality models can be useful when water is withdrawn from surface waters. By means of optimal experimental design (Dochain and Vanrolleghem, 2001), one can determine locations with high and low pollution potential and periods when the withdrawal of water should be avoided, in order to safeguard the excessive use of e.g. expensive carbon filters at the drinking water treatment plant.

The usefulness of modelling tools in pesticide registration lies in their ability to predict environmental concentrations in different compartments of a receiving ecosystem. As such, different scenarios and management plans can be easily compared. Model predictions can replace enormous monitoring and experimental efforts necessary to gain insight in the fate of a contaminant, which implies a serious cost reduction. Besides predicting environmental concentrations, certain models also make predictions on the effect side, resulting in models useful for risk assessment.

2.2 Pesticides in river systems

2.2.1 Occurrence and sources of pesticides in rivers

Pesticides can enter river systems as point sources, i.e. at certain locations along the river, or as diffuse sources which are inputs along the whole water course (Figure 6). Examples of point sources of pesticides are sewage treatment plants, sewer overflows and losses due to bad management practices of farmers. As diffuse input pathways runoff, drainflow, drift, deposition and a contribution through groundwater can be distinguished.

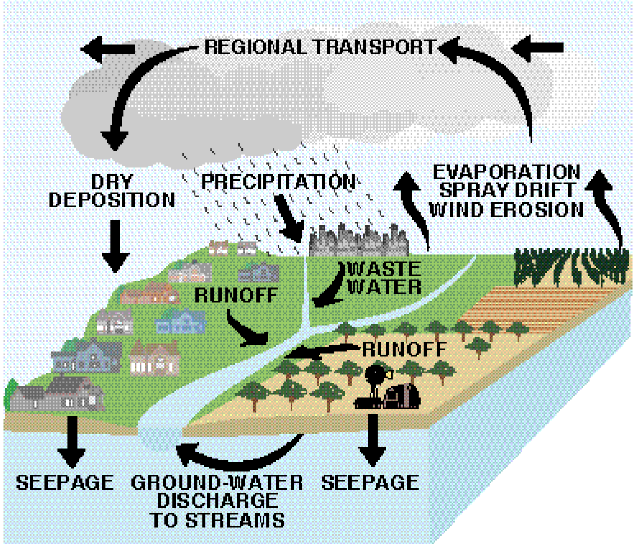


Figure 6. Pathways of pesticide movement in the hydrologic cycle.

From large-scale studies that monitored herbicide losses to surface water it can be concluded that, on average, less than 2% of the total mass applied within large catchments is ultimately lost to surface waters and that losses occur primarily during and right after the application period (Capel et al., 2001). Furthermore, such studies show that weather conditions, soil type, land use, intrinsic properties of the compound, as well as point sources are crucial factors influencing the overall herbicide loss from a watershed (Kreuger, 1998; Capel et al., 2001). Kreuger and Törnqvist (1998), Neumann et al. (2002) and Tesfamichael and Kaluarachchi (2006) found that the amount applied in the catchment region is more important than the K_{ow} value, in influencing the load of pesticides occurring in the river for all pesticide classes considered. The contribution increases with decreasing entry routes and with decreasing sorption or degradation.

Point sources and mitigation

The contribution of point sources to pesticide pollution in river systems was demonstrated to be very important in several catchments in Europe. In different catchments in Germany (Seel et al., 1994; Fischer et al., 1996a; Fischer et al., 1998a; Bach et al., 2001; Neumann et al., 2003) with varying catchments sizes between 7 and 1940 km², in Switzerland (Gerecke et al., 2002; Leu et al., 2004a), in Sweden (Kreuger, 1998), in the UK (Hankinson and Welland, 2001; Mason, 2003) and in Belgium (Beernaerts et al., 2002), it was shown that the load of pesticides in rivers could be attributed for 30 up to 90% to point sources. The spilling during the filling of the spraying equipment, the cleaning of the equipment and processing of spray waste on paved surfaces are the main causes of point sources (Fisher et al., 1998a, Kreuger, 1998; Beernaerts et al., 2002; Neumann et al., 2002). It seems that pesticide loads are higher when agriculture is extensive, small-scale and when older spraying equipment is used (Fischer et al., 1998a; Bach, personal communication, 2006). When pesticide applications are performed by agricultural contractors, the loads towards surface water are lower as compared to applications performed by farmers themselves, due to fewer alterations of different pesticides and thus fewer rinsing of their spraying equipment (Bach, personal communication, 2006).

The pesticide contamination of surface waters through point sources can be significantly reduced without relevant financial consequences for the agricultural sector, by only minimizing improper operations. Careful pesticide handling (Neumann et al., 2002) and the execution of as many operations as possible directly on the treated field (e.g. rinsing of spray tank with fresh water) are already highly effective strategies (Gerecke et al., 2002; Campbell et al., 2004). This can be supported by intense information campaigns (Fischer et al., 1996b; Fischer et al., 1998b; Kreuger and Nilsson, 2001; Beernaerts et al., 2002), action programmes (Saethre et al., 1999; Kreuger and Nilson, 2001) or sending a letter containing the most important points of 'good agricultural practice' for pesticide application (Gerecke et al., 2002). This sensitization of farmers should be repeated frequently and maintained in order to preserve low pesticide loads towards the river (Fischer et al., 1998b; Beernaerts et al., 2002). Kreuger and Nilsson (2001) found that farmers are more willing to accept information when given personally and adjusted to site specific conditions than when received through general letters and pamphlets. The different initiatives have proven their usefulness: pesticide load reductions from 20 up to more than 80% were achieved (Fischer et al., 1996b; Kreuger and Nilsson, 2001; Beernaerts et al., 2002; Gerecke et al., 2002). Besides, biobeds can be installed on the farm yard to collect and treat spillage during filling of the agricultural spraying equipment and during rinsing afterwards (Torstensson, 2000; Mason, 2003; Fogg, 2004; Vischetti et al., 2004; Spliid et al., 2006). A phytobac is a similar system, but it has an impervious bottom (Phytofar, 2006). A biofilter exists of different biobeds in series with drainage systems at their bottom. Especially for mobile pesticides, the efficiency of the biobed technique will be improved by having several passages (Phytofar, 2006).

Diffuse sources and mitigation

Concerning the diffuse sources of pesticides towards surface waters, the modelling work of Bach et al. (2001) showed that surface run-off is the major source of diffuse pesticide input in Germany. Non-point source input via tile drainage is far less important and spray-drift is only an issue in specific orchard regions (Bach et al., 2001; Ritter et al., 2001). From field measurements, Kreuger (1998) and Neumann et al. (2002) also found that inputs by drift, direct spraying or from the atmosphere in precipitation (Majewski et al., 2000; Rossi et al., 2003) or dry deposition (Foreman et al., 2000) are less important.

As **runoff** is considered to be the pathway that forms the most important source of diffuse pesticide pollution (Wauchope and Leonard, 1980; Huber et al., 1998; Neumann et al., 2002), its main contributing factors are reviewed here in detail. Surface runoff occurs whenever the rate of water application to the ground surface exceeds the rate of infiltration and the surface storage capacity is exceeded. The amount and rate of runoff depend on rainfall and watershed characteristics. Important rainfall characteristics include duration, intensity and areal distribution. Watershed characteristics that influence runoff include soil properties, land use, vegetation cover, moisture condition, size, shape, topography, orientation, geology, cultural practices and channel characteristics (Wolfe, 2001). The abrasive power of surface runoff and the impact of raindrops will detach soil particles and cause erosion. Some soils erode more easily than others even when all other factors are the same. Wischmeier and Smith (1978) noted that a soil type usually becomes less erodible with decrease in silt fraction, regardless of whether the corresponding increase is in the sand fraction or clay fraction. Runoff susceptibility and soil erodibility are enhanced by silting and crusting of the soil surface due to raindrop impact and splash during high-intensity rainfalls (Le Bissonais et al., 1995). The sediment delivery towards surface waters depends on the size and shape of the contributing area; the steepness, length and shape of contributing surfaces; sediment characteristics; buffer zones; storm characteristics and land use (Nearing et al., 2001).

Both pesticides in solution and pesticides bound to sediment particles can be transported during a runoff event. The partitioning of a pesticide between the solution and soil phases is defined by its sorption coefficient K_{OC} and by the organic carbon content of the soil. For most pesticides losses via runoff are considered far more important than losses via erosion, because the amount of eroded soil lost from a field is usually small compared with the runoff volume (Leonard, 1990). Only for strongly sorbing substances with a K_{OC} greater than ca. 1000 L kg^{-1}, erosion is considered to be the main loss pathway (Kenaga, 1980). The amount of pesticides lost towards the river through runoff depends on the amount of pesticide in the active zone at the soil surface at the time of runoff and is mainly determined by the period of time between application and the first rainfall event (Wauchope, 1978; Müller et al., 2003) and by the application dose (Müller et al., 2003). Martin and Owens (2003) came to the conclusion that the timing of rainfall and runoff relative to atrazine application can have a much greater effect on the yearly losses of the parent compound and its metabolites than the agronomic management practices investigated. Besides, also the slope (Dabrowski et al., 2002; Leu et al., 2004b), the width of buffer strips and the presence of erosion rills are important catchment variables determining runoff (Dabrowski et al., 2002). The sorption coefficient, water solubility and biodegradation rate are important pesticide characteristics determining pesticide losses through runoff.

If **drainage** channels are present, pesticide concentrations in the channels can rise to extremely high concentrations (Neumann et al., 2002). Consistent research findings have demonstrated that preferential flow phenomena are key contributors to the rapid transfer of pesticides to drainage systems (Kladivko et al., 1991; Novak et al, 2001). Pesticide transport by preferential flow to drains can cause high transient concentrations in agricultural ditches and small rivers (Williams et al., 1996; Fenelon and Moore, 1998; Brown et al., 2004; Leu et al., 2004b).

Spraydrift can occur during pesticide application by spraying. During the application, a part of the spray liquid may be carried out of the treated area by wind or the air stream of the sprayer and reach a nearby river system. Drifting spray is a complex problem in which equipment design and application parameters, spray physical properties and formulation, and meteorological conditions interact and influence pesticide loss (Gil and Sinfort, 2005). Its contribution to surface water pollution in European countries is thought to be rather small compared to the contribution due to runoff or point sources (Kreuger, 1998; Huber et al., 2000; Neumann et al., 2002; Röpke et al., 2004)

Leaching of pesticides into groundwater and a possible input of pesticides into surface waters by outflowing groundwater is assumed to be negligible as pesticides in groundwater resources in Belgium occur locally or in low concentrations (Groenboek, 2002). Moreover, slow groundwater movement and pesticide attenuation in the groundwater due to sorption and degradation further diminish the pesticide concentrations.

Further diffuse input pathways for pesticides into surface waters are atmospheric deposition after volatilization, and aeolian deposition of pesticide-loaded soil particles previously eroded by wind. For volatile pesticides downwind short-range transport can become important under certain weather conditions (Bedos et al., 2002; Siebers et al., 2003).

The contamination of surface waters through diffuse pesticide sources can be significantly reduced by i) a reduction in pesticide use, ii) the implementation of runoff and erosion control practices and by iii) drift reducing measures. A **reduction in pesticide use** is possible through guided pest control with a warning system that informs farmers when to use for example insecticides (targeted pest control) (Campbell et al., 2004; Baets et al., 2005), through biological control (van Lenteren, 2000; Corrales and Campos, 2004) or by means of an integrated approach which is a combination of different pest control methods (van Lenteren, 2000; Tantau and Lange, 2003; Mansingh et al., 2006).

Different **runoff and erosion control practices** exist which will reduce pesticide loads towards the river. Their effectiveness depends upon the amount of infiltration, the adsorption characteristics of the pesticide and the degree of fine-sediment transport reduction. Through conservation tillage practices, minimal cultivation systems leave crop residues near the surface. These crop residues directly protect soils from erosion and the high organic matter layer produced over time in the top few centimetres gives rise to a well-structured stable soil which reduces rainfall run-off by increasing the infiltration capacity of the soil and reduces the detachment effect of raindrop impact (Ritter, 2001). Other erosion control practices that will reduce pesticide loads are to grow green manure crops post harvest, to sow crops protective of vulnerable soils such as grass and cereals, to use crop residue mulches (Rice et al., 2006), to perform contour ploughing or contour strip cropping, to construct diversion terraces and to implement vegetated buffer strips (Campbell et al., 2004). Several studies investigated the benefits of vegetated buffer strips. They function through infiltration, which reduces the volume of runoff, and through adsorption/sedimentation, which reduces the concentration of pollutants in runoff (Dosskey, 2001; Connolly et al., 2002). The results of these studies show high removal efficiencies for pesticides and sediments (Klöppel et al., 1997; Syversen and Bechmann, 2004; Kronvang et al., 2005; Syversen, 2005; Syversen and Haarstad, 2005; Vianello et al., 2005), which are variable in time (Viaud et al., 2004). For example, in a study of Popov et al. (2006) the total load of atrazine could be reduced by 40-85%. In buffer strips, a relatively larger amount of the coarser fractions will be trapped compared to the clay fraction (Syversen and Bechmann, 2004). In order to capture more clay particles and as such more sorbed pesticides, the buffer width should be extended (Syversen, 2002). Several models were developed in order to derive an optimal buffer width, adapted to variable regional geographic factors (Lin et al., 2002; Watanabe and Grismer, 2003; Lin et al., 2004). Nevertheless, questions remain concerning the subsequent leaching of trapped pesticides (e.g. Delphin and Chapot, 2001). Pesticides in runoff can also be retained through wetlands (Kohler et al., 2004; Blankenberg et al., 2005) and grassed depressions or waterways (Campbell et al., 2004; Dabrowski et al., 2005; Dabrowski et al., 2006). Another simple and highly effective way to reduce pesticides in runoff is the time of application. Farmers should try to keep the time between application and the first rainfall event as long as possible.

Pesticide inputs into surface waters by **spraydrift can be mitigated** by the use of drift-reducing nozzles or anti-drift agents (Campbell et al., 2004), by vegetated buffer strips along field edges and water bodies (i.e., hedges and bank vegetation) (de Snoo and de Wit, 1996), or by simply keeping a sufficient distance to the nearest water body when spraying. In the current regulatory practice in Belgium, for each plant protection product there is a legally prescribed minimum spraying distance between 2 and 200 meters that must be kept by the farmer. These and other best management practices (BMP) have been published and summarized (Carter, 2000; Ritter and Shirmohammadi, 2001; Campbell et al., 2004).

2.2.2 Pesticide processes in river systems

Pesticides in river systems are subject to different reactions, depending on their physicochemical characteristics and the characteristics of the river system itself. Figure 7 schematically illustrates the pertinent processes.

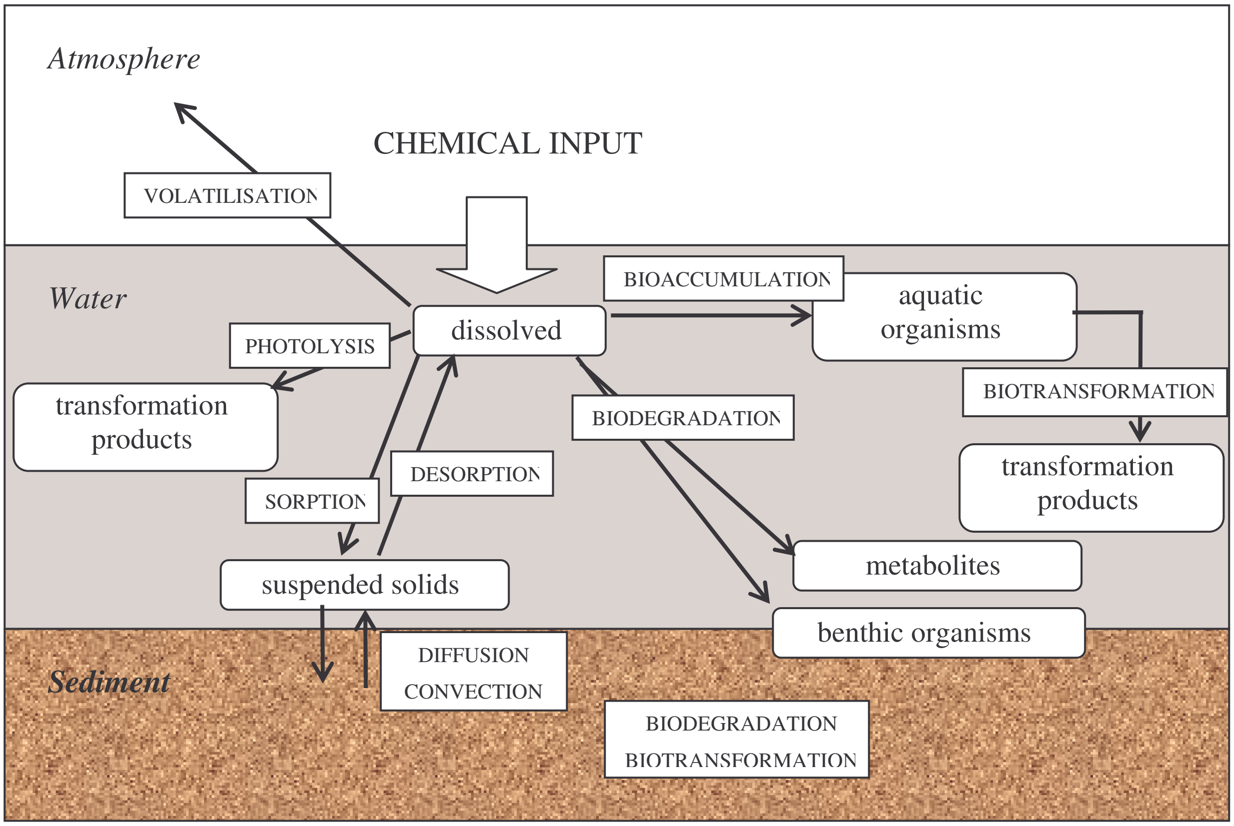


Figure 7. Fate processes of pesticides in water (Petit et al., 1995).

Biodegradation is a continuous process in nature, occurring both in aquatic and terrestrial environments (Pagga, 1997). Water is the most important transport and distribution medium for many substances, and hence an absolute prerequisite for biological processes. Consequently, surface waters are good environments for pesticide breakdown, especially when micro-organisms are able to attach on surfaces, such as the sediment-water interface, rocks and plants where they can form biofilms. Most of the microbial activity in an open ecosystem takes place in and around biofilms (Potera, 1996; Eberl et al., 2006). Several scientists (Ying and Williams, 2000; Smalling and Aelion, 2004) believe that the sorption of pesticides to suspended solids and to sediment organic carbon reduce the decay rates of pesticides in water systems. Many studies (Warren et al., 2003) have indeed demonstrated an inverse relationship between decay rates and the amount of organic matter. However, in some cases the opposite is observed, i.e. sorption accelerates degradation which is mainly the consequence of abiotic pathways (Ying and Williams, 2000). It should be realised that measured degradation rates are system dependent as they may be influenced by the dilution rate in the chemostat, the composition of the population of micro organisms, the test chemical and the composition of the medium (Rönnefahrt et al., 1997; Schrap et al., 2000). In natural systems, the pathways and rates of microbial degradation will depend on type of substrate, temperature, O_2 availability, nutrient supply, similarity of the compound to other food sources, previous exposure to the compound or similar ones and previous environmental conditions which will control the current population make-up (Warren et al., 2003). In the sediment, many types of compound will degrade more slowly below the oxic zone of bed-sediment and may therefore be persistent once buried (Warren et al., 2003).

Bioconcentration of toxicants is defined as the direct uptake of aqueous toxicants through the gills and epithelial tissues of aquatic organisms. This fate process is of interest because it helps to predict human exposure to the toxicant in food items, particularly fish (Bermúdez-Saldaña et al., 2005; Bossuyt and Janssen, 2005). Bioconcentration is part of the greater picture of bioaccumulation and biomagnification that includes food chain effects. Bioaccumulation refers to uptake of the toxicant by the fish from a number of different sources including bioconcentration from the water and bio uptake from various food items (prey) or sediment ingestion. Biomagnification refers to the process whereby bioaccumulation increases with each step on the trophic ladder (Schnoor, 1996).

Hydrolysis refers to reactions in which the bond of a molecule is cleaved and a new bond is formed with the hydrogen and the hydroxyl components of a water molecule. Hydrolytic reactions are catalyzed by acids or bases and, to a more limited extent, by water. These catalytic effects depend on the type of reaction the chemical structure of the compound. The pH and temperature of the solution have an influence on the rate of reaction (Chapra, 1997).

Chemical **oxidation reactions** occur in natural waters when a sufficient level of oxidant is present. Common types are dissolved oxygen, chlorine and ozone (Chapra, 1997). First-order reactions of pesticides have been reported in natural waters. However, these oxidations are often microbially mediated (Schnoor, 1996).

Redox reactions. Electron acceptors such as oxygen, nitrate and sulphate can be reduced in natural waters while oxidizing trace organic contaminants. Oxidation reactions of toxic organic chemicals are especially important in sediments and groundwater, where conditions may be anoxic or anaerobic (Schnoor, 1996).

Photolysis, a light-initiated transformation reaction, is a function of the incident energy on the molecule and the quantum yield of the chemical (Wolfe, 1976). It may be direct or indirect (sensitized) photolysis (Chapra, 1997) and usually results in an oxidation of the organic chemical. Inorganics, especially iron, play an important role in the photochemical cycle in natural waters (Zepp et al., 1992). Hydrogen peroxide, a common transient oxidant, is a natural source of hydroxyl radicals in rivers, oceans and atmospheric water droplets. These hydroxyl radicals are a highly reactive and important transient oxidant of a wide range of organic xenobiotics in solution (Schnoor, 1996).

The final destination of pesticides in rivers is strongly determined by their **sorption** behaviour. Besides the effect that sorption has on the physical transport, it can also influence directly or indirectly the degradation of the pesticide and its uptake by organisms. The chemical reactivity of a sorbed pesticide is significantly different from that in solution (Warren et al., 2003). Natural sorbents, like sediments, can indirectly control processes in the water phase by release or uptake of pesticides. Hence, natural sorbents form buffers that influence the reactivity of pesticides in a considerable way. For hydrophobic organic substances and for soils and sediments with a total organic carbon content higher than 0.1 %, it is proven that the content of natural organic carbon is the dominant sorbent (Karickhoff, 1984; Ying and Williams, 2000; Chefetz et al., 2004; Chen et al., 2004; Cooke et al., 2004). Hence, the sorption can be described by a constant normalized for the organic carbon content K_{OC} (Karickhoff, 1984; Warren et al., 2003). For sediments with a low organic carbon content (Karickhoff, 1984; Rae et al., 1998; Warren et al., 2003; Chen et al.,

2004) the sorption is proportional to the cation exchange capacity, to the sediment specific surface and to pH (Rae et al., 1998; Madsen et al., 2000; Ertli et al., 2004; Weber et al., 2004). The process of desorption of pesticides from sediment is commonly observed to be biphasic, involving a relatively fast initial release of sorbed pesticides followed by a prolonged and increasingly slower release as desorption proceeds (Gao et al., 1998). This suggests that the soil organic matter comprises two principal reactive domains: a highly amorphous, swollen domain and a condensed, tightly cross-linked domain (Chefetz et al., 2004; Chen et al., 2004; Cooke et al., 2004). It was shown that lipid content was the main factor to affect hysteresis phenomena (Chen et al., 2004). As the sorbent matrix is so important, it is practically impossible to find some generally applicable and accurate K_{OC} value (Chen et al., 2004; Cooke et al., 2004).

Volatilization is a transfer process of pollutants from water to air or from air to water. It does not result in the breakdown of a substance. The rate of volatilization is related to the size of the molecule, i.e. as measured by the molecular weight. Usually volatilisation is described as an equilibrium transfer between the gas phase and the water phase. The ratio of the chemical concentration in the gas phase and in the water phase is given by the Henry constant (Schnoor, 1996).

2.2.3 Ecotoxicological significance

Pesticides differ from most industrial organic compounds in being introduced into the environment with the explicit intention of exerting effects on one or more target organisms. Unfortunately, they do not exert their toxic action only where they are applied, but can, through persistence and transport, reach other compartments of the ecosystem and cause damage. The complexity of a natural ecosystem, and the interdependence of many species in the food web, means that the disruption of even small parts of a system, owing to the toxic effects of contaminants, can give rise to unpredictable effects (Warren et al., 2003).

The bioavailability of a compound determines the degree to which a contaminant in a potential source is free for uptake. It depends on the form of the compound (sorbed or in solution), on what and how organisms feed, on where the organisms live and what their physiology is (Warren et al. 2003). For macroscopic aquatic organisms, it has often been assumed that only compounds present in the solution phase will be available for uptake, so that bioavailability decreases as the extent of sorption increases (Landrum and Faust, 1994; Park and Erstfield, 1999). For some organisms however, particularly those which ingest sediment as a food source, the uptake of sorbed contaminants may contribute significantly to the total uptake of a compound. A number of the issues and difficulties relating to the assessment of the bioavailability of organic compounds in sediments and soils have recently been reviewed by Reid et al. (2000).

Many studies have been performed in laboratories to gain insight in the effect of different pesticides on a variety of species (Cuppen et al., 2000; Van den Brink et al., 2000; Hanson et al., 2002; Yamaguchi et al., 2003; Wendt-Rasch et al., 2004; Capkin et al., 2006). There have been few studies of the direct effects (in terms of toxic effects to particular species) or indirect effects (in terms of ecosystem disruption) of pesticides on fauna and flora in real freshwater environments (Warren et al., 2003). Also for sediments, ecotoxicological effects on the health of benthic invertebrates and bottom-feeding fish are not well known (Warren et al., 2003).

In order to define water quality criteria for pesticides in surface waters and to perform risk assessment, predicted no-effect concentrations (PNEC) were introduced. A PNEC is estimated based on several exposure studies. In each study, a no effect level for a certain species and an endpoint are determined. The conventional approach is then to take the lowest resulting level and apply a safety factor to account for various uncertainties, such as interspecies differences in sensitivity, acute-to-chronic ratios, and laboratory-to-field extrapolations (Chapman et al., 1998; Whitehouse, 2001). If the predicted environmental concentration (PEC) exceeds the PNEC, there is a potential for damaging effects to occur. More recently, species sensitivity distributions (SSD) are proposed (Wheeler et al., 2002). A SSD is a statistical function describing the variation in toxicity of a certain compound among a set of species. The underlying idea is to derive a concentration that protects 95% of the species (HC5). PNECs and HC5s are valid thresholds for chemicals that are continuously entering the ecosystem at a constant concentration.

For highly dynamic concentrations, such as observed for pesticides, the transient regime has to be taken into account. However, even these approaches do not take into account the frequency of exceedance of concentrations. This could be done by means of a concentration-duration-frequency curve (Dixon, 2002; Verdonck et al., 2003) which is a three-dimensional plots with on the three axes the concentration, the duration of an exceedance above a particular concentration and the frequency of an exceedance above a particular concentration with a particular duration. Concentration-duration-frequency effect assessment has already been done for general water quality variables such as NH_4 and dissolved oxygen (Verdonck et al., 2003). As there are no effect-duration-frequency data available for pesticides, this approach is not yet applied in risk assessment of pesticides. Also, the synergetic or antagonistic action of certain active ingredients is currently not taken into account.

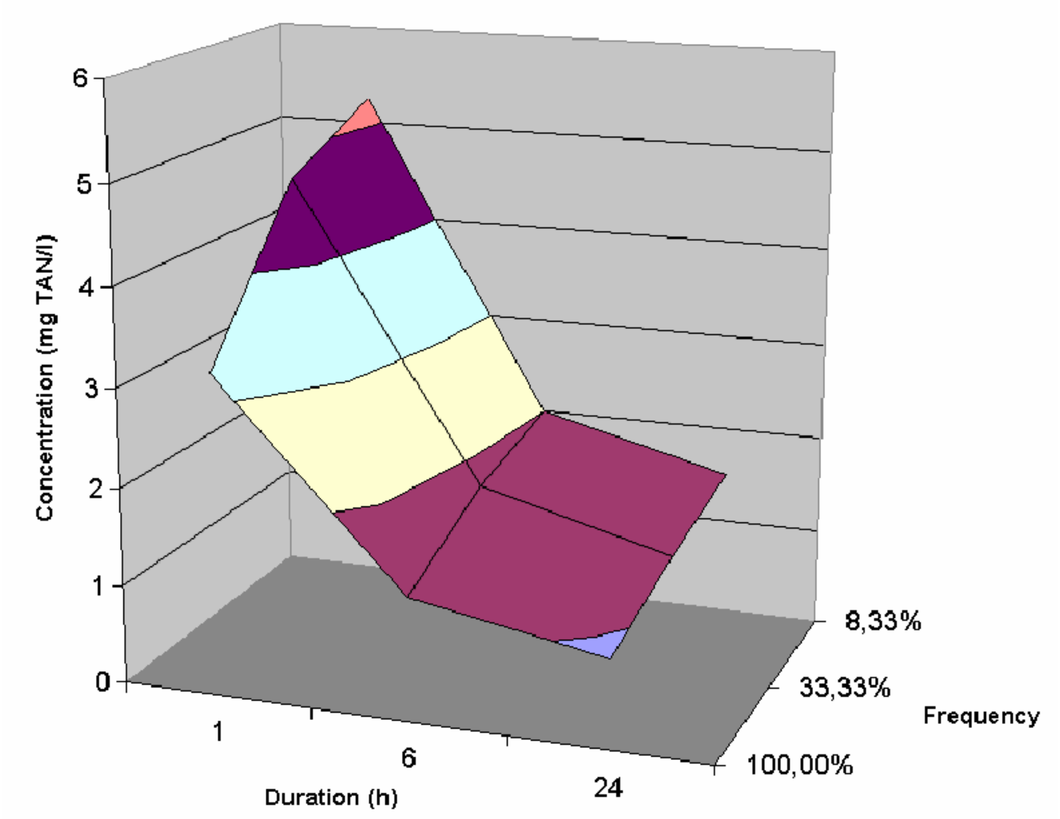


Figure 8. Effect concentration-duration-frequency surface of NH_4 for sustainable salmonid fishery (Verdonck et al., 2003).

2.3 Models for pesticides in surface water

2.3.1 Watershed modelling

Modelling for integrated water management

In view of the Water Framework Directive, the management of water resources should be integrated at the river basin scale. As air, soil and water constitute the environmental continuum and have complex interactions amongst them, a management change imposed on one component will have effects that propagate to the others. Some of these effects are unknown and cannot be quantified. Therefore, the environment needs to be managed and protected as a cohesive whole. In the past, this has rarely happened, as each compartment was managed by independent organisations having little interaction amongst them. Today, models can form useful instruments for integrated water management accomplished within a spatial unit, called watershed. The integrated water management can be viewed as a three or more dimensional process centred around the need for water, the policy to meet the needs and the management to implement the policy.

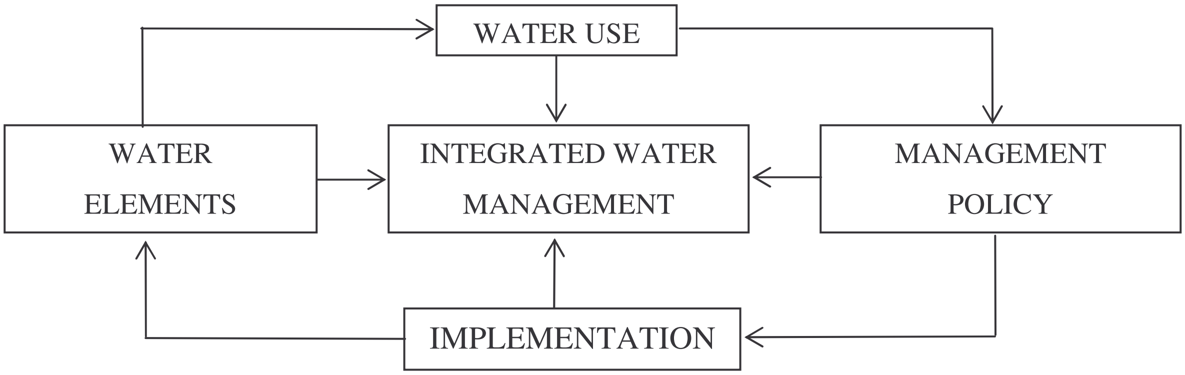


Figure 9. Integrated water management (Singh, 1995).

Classification of watershed models

Models are of different types and were developed for different purposes. Nevertheless, many of the models share structural similarities, because their underlying assumptions are the same, and some of the models are distinctly different. The watershed models can be classified according to their i) process description, ii) scale -both in space and time- and iii) technique of solution.

According to their process description, one can distinguish between conceptual or physically based, lumped or distributed, deterministic or stochastic or mixed models. While the parameters of conceptual models are necessarily defined through calibration, physically-based models describe the processes in such a way that the parameter values can be derived from physical data or by laboratory studies whereby it is often argumented that no calibration is required (van Griensven, 2002). Distributed models take explicitly account of spatial variability of process inputs, boundary conditions, and/or system characteristics. This is in contrast to lumped models that average their parameters over the area. The description of a process can be either deterministic, stochastic or mixed. In many cases, the models use combinations of above mentioned process descriptions. Extensive information concerning these classifications can be found elsewhere (Singh, 1995; van Griensven, 2002).

Calibration, validation and uncertainty

The process by which a set of parameters of a model is adjusted in order to simulate the behaviour of the study site is called model **calibration**. The parameter estimation is performed by means of a manual or an automatic calibration. The main weakness of manual calibration is that the absence of generally accepted objective measures of comparison makes it difficult to know when the process should be terminated. Because manual calibration involves a great deal of subjective judgement, different persons may obtain very different parameter values for the same watershed (Sorooshian and Gupta, 1995). A lot of automatic calibration methods exist (Sorooshian and Gupta, 1995; Chapra, 1997; van Griensven and Bauwens, 2003). For hydrologic models, there are only a few free parameters (Kuczera and Moroczkowski, 1998), whereas for physically distributed catchment models many more parameters are available. The main criticism against distributed modelling is therefore the inability to calibrate the many parameters during the calibration process. As such, there is a need for procedures to reduce the number of free parameters. One can perform a sensitivity analysis, in order to obtain the most sensitive parameters that need calibration (Chapra, 1997). If possible, parameter values or their physically acceptable intervals should be assessed from available field data (Refsgaard and Storm, 1996; Chapra, 1997; Henriksen et al., 2003).

Model **validation** is the process where a given site-specific model has to demonstrate its capability of making sufficiently accurate predictions with a new independent dataset or datasets (Chapra, 1997). A model's validity will always be limited in terms of space, time, boundary conditions and types of application (Refsgaard and Henriksen, 2004). However, it has been demonstrated that complex environmental models (like hypotheses in general) cannot be validated, but only tested and invalidated (Konikow and Bredehoeft, 1992; Oreskes et al., 1994). Nevertheless, confidence in a model can be established by "confirming observations", i.e. successful predictions of measured data. The greater the number and diversity of confirming observations, the higher the probability is that the model concept is not flawed (Oreskes et al., 1994).

Walker et al. (2003) describes **uncertainty** as manifesting itself at different locations in the model based water management process. These locations, or sources, may be characterised as follows:

- *Context*, i.e. at the boundaries of the system to be modelled. The model context is typically determined at the initial stage of the study where the problem is identified and the focus of the model study selected as a confined part of the overall problem. This includes, for example, the external economic, environmental, political, social and technological circumstances that form the context of problem.
- *Input uncertainty* in terms of external driving forces (within or outside the control of the water manager) and system data that drive the model such as land use maps, pollution sources and climate data.
- *Model structure uncertainty* is the conceptual uncertainty due to incomplete understanding and simplified descriptions of processes as compared to nature.
- *Parameter uncertainty*, i.e. the uncertainties related to parameter values.
- *Model technical uncertainty* is the uncertainty arising from computer implementation of the model, e.g. due to numerical approximations and bugs in the software.
- *Model output uncertainty*, i.e. the total uncertainty on the model simulations taken all the above sources into account, e.g. by uncertainty propagation.

All these problem areas are strongly interrelated (Beck, 1987). Different methods to determine the uncertainty of model results are given by Morgan and Henrion (1990), Chapra (1997), Melching (1997) and Cullen and Frey (1999). Disclosure of the sources and magnitude of the uncertainty is needed for the decision maker to understand how confident he or she can be about the decisions that are being made (Thienmann et al., 2000; van Griensven, 2002; Dubus et al., 2003).

2.3.2 Modelling pesticide fate in surface waters

A whole range of models predicting pesticide concentrations in river systems exist. They range from rather simple screening tools to complex catchment models. A brief overview is given here. An overview of existing drainflow and erosion/runoff models for pesticides is given elsewhere (Reichenberger, 2003) and falls beyond the scope of this dissertation.

Some more simple screening tools predicting pesticide concentrations in the different compartments of a river system assume **steady state conditions**, e.g. EXAMS (Burns, 2000), EUSES (2004), the Mackay Level III Model (Mackay, 2001) and principal component analysis (Gramatica and Di Guardo, 2002). They are based on the partitioning tendency of a certain pesticide. The advantage of such tools is that they require relatively few input data, but they can not reflect the dynamics - both in space and time - observed for pesticides in real river systems (Kreuger, 1998; Neumann et al., 2002; Leu et al., 2004). They are rather meant for worst case scenario analysis. As the occurrence of pesticides is highly dynamic and can pose acute toxicity to ecosystems, dynamic models are necessary to perform reliable risk assessments.

The European Surface Water FOCUS workgroup (FOrum for the Co-ordination of pesticide fate models and their USe) which is an initiative of the European Commission with the objective to harmonise the calculation of predicted environmental concentrations (PEC), advises to use the **dynamic model** TOXSWA (FOCUS, 2002; ter Horst, 2002). TOXSWA needs pesticide inputs calculated by other models via runoff and erosion (PRZM: Carsel et al. 1984; Carsel et al., 2003), drainage and spraydrift (MACRO: Jarvis, 1991; Jarvis, 2003). Limitations of this model exist in the fact that it is an edge-of-field model, neglecting sedimentation, resuspension and biomass growth. It was validated to a limited extent with field measurements (Adriaanse et al., 2006).

In Belgium, the SEPTWA model was developed (Beernaerts et al., 2005), taking into account both diffuse and point sources. It calculates average fortnight pesticide concentrations at the closing section of a river, based on detailed application data of the catchment and emission factors for the different input pathways of pesticides into surface waters. The model allows to make predictions of average pesticide loads leaving the system during a fortnight. It was validated with a data set based on daily grab samples.

In Germany, the DRIPS model was developed (Röpke et al., 2004), which is a GIS based model that simulates on a daily basis pesticide inputs via surface runoff, drainflow and spraydrift for pixels of 1 km×1 km size, based on spatially distributed input variables. Dispersion of the pesticide peak during transport in the river is accounted for in DRIPS by a convection-dispersion approach similar to the one proposed by Gustafson et al. (2004). Predicted concentrations at the closing section of the river underestimated measured concentrations due to the lack of point sources (Röpke et al., 2004).

In England, the TERRACE model (Terrestrial Runoff Modelling for Risk Assessment of Chemical Exposure) was developed (White et al., 2003), which is a coupling of the dynamic SWAT2000 model with the static GREAT-ER system (Boeije et al., 1997; Feijtel et al., 1998; Boeije et al., 2000). GREAT-ER uses a steady state, stochastic approach to allow risk assessment and is subsumed within a Geographic Information System (GIS). The TERRACE model provides statistical distributions of predicted levels of contamination.

Furthermore, there exist different in-stream water-quality models such as ISIS (HR Wallingford and Halcrow UK, 1998), MIKE11 (DHI, 1995) and RWQM1 (Reichert et al., 2001) (see Chapter 5 for a detailed description) that need the addition of several differential equations describing the fate of pesticides in order to predict pesticide concentrations along the river and in its different compartments. These in-stream water-quality models need as input pesticide fluxes towards the river coming from catchment models or from rough estimations. The disadvantage of ISIS lies in the fact that parameters are fixed throughout the model and as such no spatial variability in the parameters is possible (Cox, 2003).

There also exist **dynamic non-point source pollution models at catchment scale**. Some of them have single-event capabilities such as AGNPS (Young et al., 1987; Merritt, et al., 2003) and DWSM (Borah et al., 2002). Others are useful for analyzing long-term effects of hydrological changes and water management practices such as AnnAGNPS (Bingner and Theurer, 2001), HSPF (Donigian et al., 1995) and the Soil and Water Assessment Tool SWAT (Arnold et al., 1998). The latter are more interesting within the context of this dissertation. The disadvantage of AnnAGNPS is the lack of a transparent manual. According to Borah and Bera (2003), SWAT is a promising model for continuous simulations in predominantly agricultural watersheds and HSPF is promising for mixed agricultural and urban watersheds. Different studies comparing both models for flow reveal that they are equally well predicting hydrology (Im et al., 2003; Nasr et al., 2004; Singh et al., 2004). SWAT gives better predictions for pesticides (Nasr, personal communication, 2006) and is better documented and user friendly as compared to HSPF (Im et al., 2003). MIKE SHE (Refsgaard and Storm, 1995) is both a single-event and long-term continuous simulation model. It is a physically-based model using multi-dimensional flow-governing equations with numerical solution schemes, which makes the model computationally intensive and subject to numerical instabilities, inherent to the numerical solutions. MIKE SHE is therefore suitable for small areas or watersheds for detailed studies of hydrology and nonpoint-source pollution (Borah and Bera, 2003). Another complex 3D model is WASP (Wool et al., 2001). It is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. WASP allows the user to investigate 1, 2, and 3 dimensional systems, and a variety of pollutant types. WASP may become prohibitive for long-term continuous simulations in medium to large-sized watersheds. The new generation of models includes fully-coupled watershed models. Three fully-coupled numerical models are currently available, namely InHM (VanderKwaak, 1999; VanderKwaak and Loague, 2001; Loague et al., 2002; Loague et al., 2004; Loague et al., 2006), MOD-HMS (Panday and Huyakorn, 2004), and HydroGeoSphere (Sudicky et al., 2005; Colautti et al., 2005). The main distinguishing feature of these models is that they fully couple the surface and subsurface hydrologic domains by simultaneously solving one system of non-linear discrete equations describing flow and transport in both flow regimes. This is in contrast to the previous generation of watershed models, which solve separate equations for the different sub-systems, followed by iteration (or not) between the two solutions.

2.3.3 Modelling tools for chemical risk assessment

Models have also been developed that combine predictions of environmental concentrations and their effects resulting in tools for risk assessment. In EUSES (2004), different modules are coupled as represented in Figure 10. One module describes the steady-state distribution of a pollutant in the environment and distinguishes between two environmental scales, i.e. a regional scale which is determined by complete mixing and a continental scale in which inter-media transport is calculated for. In the exposure module, exposure levels for humans and predating birds and mammals are estimated. In the risk characterisation module, risks are derived by comparing exposure levels to suitable (no)-effect levels.

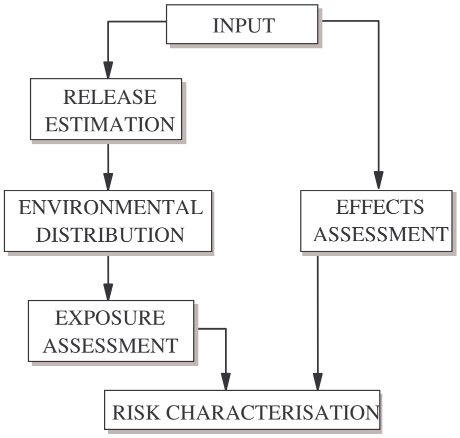


Figure 10. System structure of EUSES (EUSES, 2004).

The DREAM model (Karman, 2002) looks promising in modelling ecological risks and is an example of the application of mechanistic time-to-event models and is expected to generate a more realistic estimation of the environmental impact of produced water discharges coming from oil companies. Similar work in the pesticide field would be helpful for a more realistic risk assessment.

The PERPEST model (Van Nes and Van den Brink, 2003) predicts the effects of a given concentration of a pesticide based on the outcome of experiments using experimental ecosystems (Van den Brink et al., 2006). An exhaustive literature review resulted in an extensive database containing effects of herbicides and insecticides. The PERPEST model searches for analogous situations in the database based on relevant environmental fate characteristics of the compound, exposure concentration and type of ecosystem to be evaluated. A probability prediction is provided by using weighted averages of the effects reported in the most relevant literature references (Van den Brink et al., 2002; Van Nes and Van den Brink, 2003). For the moment, PERPEST can not handle mixtures of pesticides (Van den Brink et al., 2006).

Tefamichael and Kaluarachchi (2006) propose a method for regulator decision making to assess the risk of an existing pesticide and potential future substitutes. Analyses of standard data sets are required to validate such models and to identify the advantages and disadvantages of time-to-event analysis in risk assessment (Karman, 2002).

2.3.4 Modelling tools for pesticide registration

The EU registration procedure for pesticides, based on Directive (91/414/EEC) and it numerous amendments (see Section 2.1.3.), advises to use models in order to calculate predicted environmental concentrations (PEC). To organize the use of models within the EU countries and to help the user/regulator in using models a “Forum for the coordination of pesticide fate models and their use” (FOCUS) was established. The organisation is an initiative of the European Commission and is based on co-operation between scientists of regulatory agencies, academia and industry.

FOCUS started in 1993 via the FOCUS Leaching Modelling Workgroup and the installation of the FOCUS Steering Committee. Subsequently several other working groups were installed such as the FOCUS Surface Water Workgroup and the Landscape and Mitigation Workgroup.

The FOCUS Surface Water Workgroup, has defined the estimation of the Predicted Environmental Concentration in surface water as a stepwise approach dealing with 4 steps (Figure 11). If the result of a certain step indicates that use is not safe, then it is necessary to proceed to the next more refined step in the exposure assessment. The resulting concentrations in a predefined aquatic environment are calculated for the relevant time points as required in the risk assessment process related to EU Guideline 91/414/EEC.

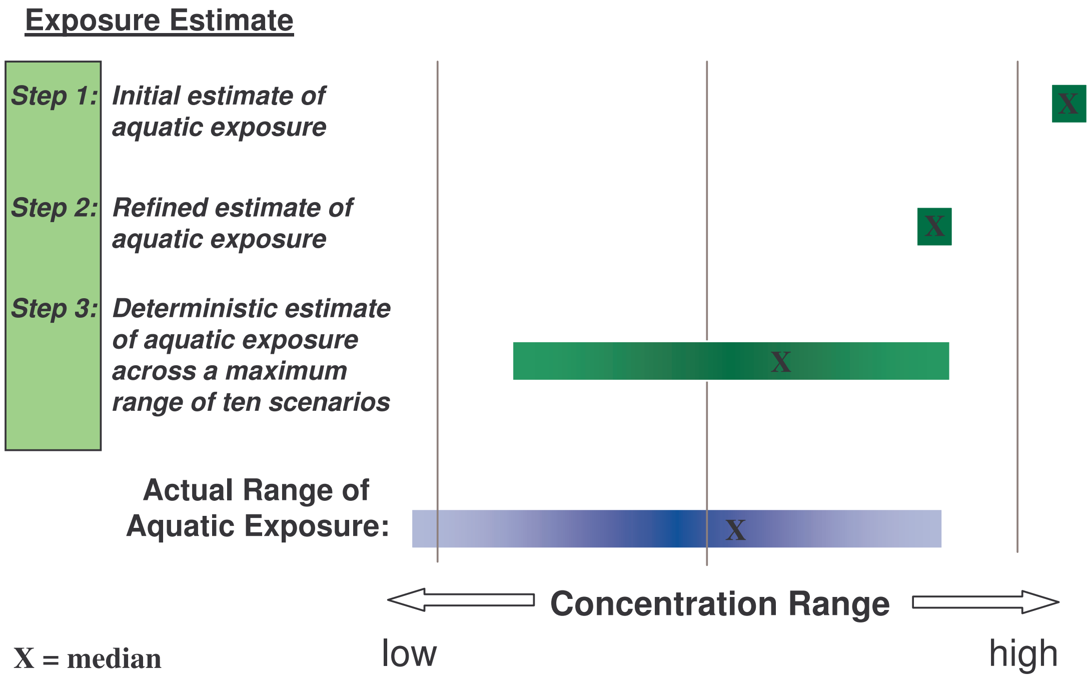


Figure 11. Conceptual relationship of FOCUS Steps 1, 2 and 3 (FOCUS, 2001).

Step 1 accounts for an ‘all at once’ worst-case loading without specific additional characteristics. It is a simple spreadsheet calculation intended to provide conservative aquatic concentration estimates (Figure 11). The estimated exposure may be compared to the relevant toxicity concentrations, the lethal or effect concentration, L(E)C50, or the No-effect concentration, NOEC, of the water organisms investigated. At Step 2, loadings are refined as a series of individual applications, each resulting in drift to the water body, followed by a run-off/erosion/drainage event occurring four days after the last application and based upon the region of use (Northern or Southern Europe), season of application, and the crop interception. Again the PECs - which in this step represent the high end of actual aquatic exposure - are calculated and may be compared to the same and/or different toxicity levels for aquatic organisms. As with Step 1, if the use is considered safe at this stage, no further risk assessment is required whereas an ‘unsafe’ assessment necessitates further work using a Step 3 calculation. Step 3 requires the use of deterministic models such as PRZM, MACRO and TOXSWA. They use a set of 10 scenarios defined and characterised by the working group and representing ‘realistic worst-case’ situations for surface water within Europe. Three different types of water bodies are defined: a pond, a ditch and a stream. Each of them has fixed dimensions and the contributing area for runoff and drainage is determined for each of them. An example of the FOCUS Stream scenario is given in Figure 12 (FOCUS, 2001).

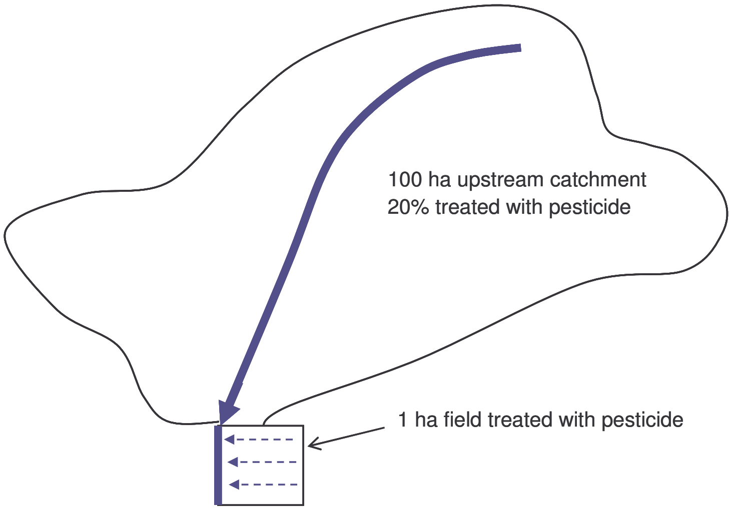


Figure 12. Schematic representation of the FOCUS stream scenario (FOCUS, 2001).

At this stage, the calculated PECs for each scenario are compared with relevant toxicity data and a decision made as to whether it is necessary to proceed to Step 4 exposure estimation. Risk assessments using Step 3 exposure estimation may incorporate higher-tier toxicity data generated from micro- or mesocosm studies. The final step of the FOCUS process is Step 4. This may include a variety of refinement options of different degrees of complexity covering risk mitigation measures, refinement of fate input parameters, or regional and landscape-level approaches. By its nature, Step 4 will be a 'case-by-case' process, depending on the properties of the compound, its use pattern, and the areas of potential concern identified in the lower tier assessments. As such, the FOCUS Surface Water Workgroup did not make specific recommendations for the Step 4 process. A Step 4 analysis is only considered necessary for those GAP applications that failed Step 3 and for which the applicant wants to continue the registration process. Some guidance on the types of approaches that may be applied has been developed (FOCUS, 2005). It is conceivable that Step 4 approaches would be used both for Annex I listing and for national registration purposes. For example, for certain compounds it may be possible to identify a range of acceptable uses across the EU when appropriate mitigation measures (e.g., buffer zones) are applied. For certain specific uses, Step 4 approaches could also be useful for identifying safe uses at Member State level, for example if certain local or regional considerations mean that the lower-tier, EU level assessments were overly conservative (FOCUS, 2001).

In June 2002, a new working group was established to review potential approaches to higher-tier (Step 4) surface water exposure assessments and mitigation measures: the FOCUS Landscape and Mitigation Workgroup. The remit of the group was to review the current state-of-the-art, where possible recommending approaches that could be implemented forthwith, and to also produce recommendations on where further work is needed. The working group considered approaches suitable for supporting listing on Annex I of Directive 91/414/EEC, but also those that could be applied in risk assessments to support national registration. Their conclusions and recommendations at that time (FOCUS, 2005) were that ecological risk assessment for the aquatic compartment should remain at the field scale as at catchment scale spatially-distributed tools are not fully developed, point sources should be included and multiple compounds and stressors should be taken into account. The working group made the following conclusions on the priorities for further work:

- improve landscape analysis, modelling and mitigation approaches
- evaluate the impact of mitigation measures
- develop ecological characteristics for use in higher-tier effects assessments
- develop complementary approaches for terrestrial systems

2.4 Conclusions

Pesticide concentrations in surface water are highly dynamic and are mainly due to point sources, runoff events and drainage losses. The importance of suddenly appearing high concentrations in the river due to point losses should be taken into account during the setup of monitoring campaigns: an integrated sampling should be preferred above grab sampling. Also in models, point sources are often neglected. As such, an important contributor of pesticides is missed.

Few monitoring studies performed in the past contained mixed water samples instead of grab samples. As far as we know, no studies were performed on both the dynamics of pesticides in the water column as in the sediment. There is a need for intensive monitoring campaigns based on sub-daily composite samples of the water column and frequent sediment sampling, in order to gain insight in the dynamics of pesticides in each of these compartments as well as between the compartments themselves.

Besides monitoring, models form an interesting tool for decision makers as they can reduce the high monitoring costs, they can help in gaining insight in the processes occurring in the different compartments of the ecosystem and show whether the sediment results in an important subsequent delivery, and they could be used for comparison of mitigation measures. For pesticides, there seems to be a lack of dynamic models taking into account point losses as entry route. Also models describing in-river processes based on closed mass balances usable at catchment scale are as far as we know not available. Moreover, few models are well validated with extensive monitoring data.

In their registration procedure pesticide industries need dynamic models for predicting pesticide concentrations. Recently, a tier 3 approach was suggested by the FOCUS Surface Water Workgroup. Nevertheless, by combining the PRZM, MACRO and TOXSWA models, the important contribution of point sources is neglected. In order to obtain more realistic predictions, a dynamic model should be developed at catchment scale, taking into account point sources and in-river processes. The developed model should be validated with extensive monitoring data.

Concerning risk assessment, still a lot is unknown at the effect side of pesticide use. The influence of mixtures of pesticides on species communities and on the ecosystem as a whole, the effect of successive pulse exposures of varying concentrations and the effect of existing resistance or adaptation against highly dynamic pesticide concentrations in surface water is only partly known yet.

Chapter 3

MONITORING CAMPAIGNS

Adapted from: Holvoet, K., Seuntjens, P., Mannaerts, R., De Schepper, V., Vanrolleghem, P.A. (2006). The water-sediment as a highly dynamic system: results of an intensive pesticide monitoring campaign. *Water Sci. Technol*. In press.
And: Holvoet, K., Mannaerts, R., Vanermen G., Seuntjens, P., Vanrolleghem, P.A. (2006). Sub-daily dynamics of pesticide pollution in small and large watersheds in Belgium and their risk assessment. Submitted.

3.1 Introduction

Different studies have shown that the presence of pesticides in river systems can be harmful to the local fauna and flora (Lytle and Lytle, 2002; Fleeger et al., 2003; Scott and Sloman, 2004; Wendt-Rasch et al., 2004; Lytle and Lytle, 2005). To date, very few studies looked at the short-term dynamics of pesticides in the river water (Neumann et al., 2002; Leu et al., 2004; Beernaerts et al., 2005). They found that pesticide concentrations can vary strongly in time and that the contribution of point sources to the pesticide load may be important.

Little is known about the interactions of pesticides with the sediment in real river systems (Warren et al., 2003) and how important the transfer from the sediment to the water column can be.

Besides the temporal variation of pesticide concentrations in river systems, there is also spatial variation. Upstream river stretches in agricultural areas are more likely to be exposed to higher pesticide concentrations (Leu et al., 2004; Claver et al., 2006; Konstantinou et al., 2006). From an ecological point of view, these upstream river stretches are highly valuable as they function as a mating, breeding and feeding place for different species (Meyer et al., 2001; Roni, 2002). Downstream river stretches in larger river basins are less prone to pesticide pollution as the loads are more diluted. This has important consequences for drinking water production from surface water in large catchments as water for this purpose is mainly withdrawn downstream.

Therefore, by monitoring the different compartments of river systems in several small and large catchments, insight in the dynamics and fate of pesticides can be gained. Moreover, monitoring catchments of various sizes allows to investigate whether a link exists between the magnitude of pesticide pollution in the receiving surface water and the scale of the watershed, as was found for watersheds in the US (Gustafson et al., 2004).

As high pesticide concentrations during shorter or longer periods in river systems can pose negative effects on the local ecosystem, the collected data sets of this study will be used for a preliminary risk assessment. In literature, acute and chronic toxicity data are available for a whole range of pesticides, but only for a limited number of species (Van den Brink et al., 2002; Agritox database). In Europe, predicted no-effect concentrations (PNECs) are often used as a water quality criterion for each pesticide in surface waters (Babut et al., 2003; Agritox database). This parameter is usually estimated based on several exposure studies, by taking the lowest resulting value and by applying a safety factor to account for various uncertainties, such as interspecies differences in sensitivity, acute-to-chronic ratios, and laboratory-to-field extrapolations. More recently, hazardous concentrations (HC) have been proposed instead of PNECs (Reiley et al., 2003). They are derived from the species sensitivity distribution (SSD), a statistical function describing the variation in toxicity of a certain compound among a set of species. A HC5 represents a concentration that protects 95% of the species. Chèvre et al. (2006) proposed a methodology to determine a risk quotient for mixtures of herbicides with similar modes of action. In this paper this method will be used in an attempt to determine the risk of the measured pesticide concentrations.

3.2 Materials and methods

3.2.1 Studied pesticides

We focused on 6 herbicides and 1 fungicide, that are (or were, in the near past) found in high concentrations in Belgian surface waters (Beernaerts et al., 2005; VMM, 2005). Their chemical and environmental properties are presented in Table 8.

Table 8. Chemical and environmental properties of the studied pesticides (Tomlin, 2003).

Pesticide	S_w (mg/l)	log K_{OW}	K_{OC} (ml/g)	$DT_{50,soil}$ (days)	$DT_{50,water}$ (days)
Herbicides					
Atrazine	33 (pH 7, 22°C)	2.5 (25°C)	39-173	35-50	80
Chloridazon	340 (20°C)	1.19 (pH 7)	89-340	42-56	56
Diuron	36.4 (25°C)	2 .85± 0.03 (25°C)	538-902 *	90-180	29
Isoproturon	65 (22°C)	2.5 (20°C)	NA	6-28	40
Lenacil	3 (25°C)	2.31	136-417	82-150	91
Simazine	6.2	2.1 (25°C)	103-277	70-110	46
Fungicide					
Carbendazim	8 (pH 7, 24°C)	1.51 (pH 7)	200-250	8-32	60-750

* Agritox database. Available at www.inra.fr/agritox/

** Footprint pesticide database. Available at www.herts.ac.uk/aeru/footprint/

NA = Not Available from the above mentioned sources.

3.2.2 Study areas

During spring 2004 and spring 2005, two different river basins were studied. During 2004 a monitoring campaign was set up in the river basin Nil, in 2005 the larger Demer basin was monitored. The geographical location of these two basins in Belgium is represented in Figure 2 (see Chapter 1).

River basin Nil

The Nil basin was selected because it is a well documented basin, studied in detail in terms of pesticide application during the period 1998-2002 (Beernaerts et al., 2005). It is a small and hilly basin situated in the central part of Belgium, Southeast of the capital (Figure 2, Chapter 1). The average elevation is 151 m a.s.l., with the highest top reaching 167 m a.s.l. and the watershed outlet lying at 110 m a.s.l. The Nil catchment drains an area of 32 km², is 14 km long and has a retention time of about 1 day. The upper 10 cm layer of the streambed sediment was examined for 3 sediment samples taken at the upstream sampling station (see Figure 13), which were supposed to be representative for the river stretch under study. It has a median clay content of 20%, a median loam content of 75% (particle size between 2-50 µm) and a median organic carbon content of about 4% (De Schepper, 2005). Seven percent of the area is inhabited and the main crops grown are winter wheat (22% of the catchment area), corn (15%) and sugar beet (10%) (Figure 13). Crop rotation occurs, but results only in minor switches on a local scale. The predominant soil type is loam.

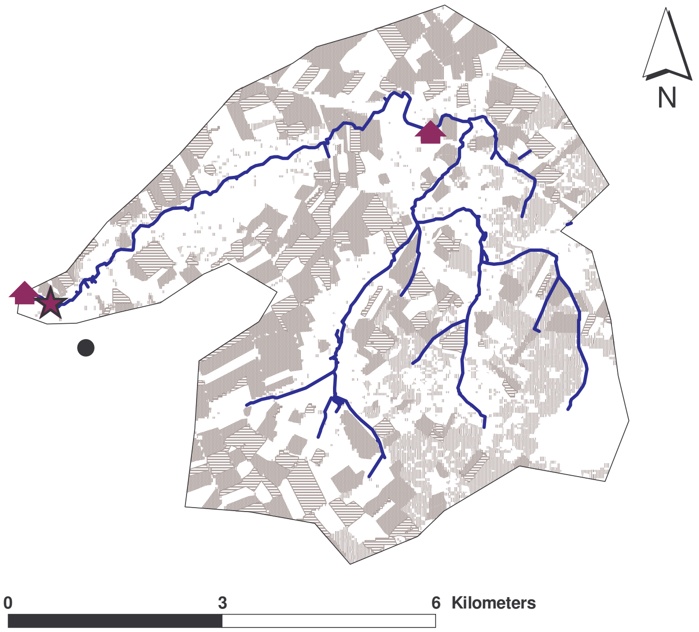


Figure 13. Land use in the Nil basin (1999), with ||||| = corn, ▤ = sugar beet and ▦ = winter wheat. The sampling stations are represented by ⬆, the Hydrolab DS3 probe by ★, the meteorological station Chastre-Blanmont by ●.

River basin Demer

The Demer basin was selected because it is known for its high pesticide concentrations both in the water column and in the sediment (VMM, 2005). A significant contribution of this pesticide pollution originates from an orchard region upstream. In this region, three important tributaries can be distinguished: the Herk, the Gete and the Velpe (Figure 14).

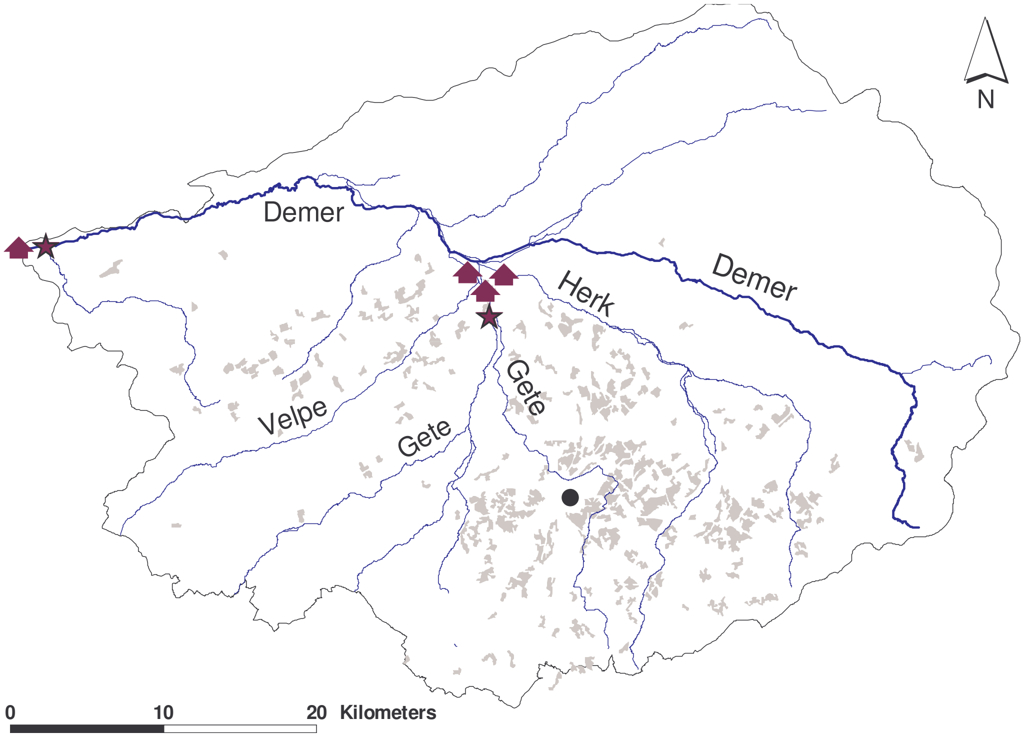


Figure 14. Orchards in the Demer basin (shaded area), with its 3 main tributaries Herk, Gete and Velpe (adapted from: VLM, 2002). The sampling stations are represented by ⌂, the Hydrolab DS3 probes by ★, the pluviograph of Sint-Truiden by ●.

The Demer forms a relatively large river basin in the Northeast of Belgium. The highest top reaches 137 m a.s.l. and the watershed outlet lies at 11 m a.s.l. The Demer catchment drains an area of 2130 km², is 85 km long and has a retention time between the confluence of the upstream tributaries and the mouth of about 13 hours. At the mouth, the river is about 16m wide. Five percent of the catchment consists of pasture, 52% is agricultural land with fruit orchards (5%), corn (6%), sugar beet (4%) and winter wheat (6%). South of the river Demer, the southern half of the area consists mainly of loamy soils. The other part close to the river Demer itself are sandy loamy soils. North of the river Demer there are sandy soils.

3.2.3 Monitoring campaign

In the Nil basin, an intensive monitoring campaign was run during spring 2004, i.e., the main application period of herbicides. The campaign started on March 15 and ended on June 15. Two refrigerated sampling stations taking water samples were placed along the river: one upstream and one at the mouth. Besides water and sediment samples that were taken at these two locations, also physicochemical variables (pH, water temperature, conductivity and oxygen concentration) were measured at the mouth of the river using a Hydrolab DS3 (HydroTech, Hutto, Texas, USA) multi parametric probe. Daily rainfall data for the meteorological station Chastre-Blanmont were obtained from the Royal Meteorological Institute (RMI) and hourly discharge data at the mouth of the river Nil were made available by DGRNE (Direction Génerale des Ressources Naturelle et de l'Environnement).

In the Demer basin, a similar campaign was set up in 2005 from May 15 till July 1st. On four locations in the Demer basin, sampling stations were placed. Three of them were located upstream at the mouth of the three important tributaries (Gete, Herk and Velpe) and one was placed at the mouth of the river Demer (represented by ⌂ in Figure 14). Hydrolab DS3 probes were installed at the mouth of the river Gete and at the mouth of the river Demer (represented by ★ in Figure 14). Hourly rainfall data for the meteorological station Sint-Truiden were obtained from the Royal Meteorological Institute (RMI) and hourly discharge data at the mouth of the tributaries were made available by HIC (Hydrological Information Centre).

Data collection

To collect the pesticide and other relevant data, automatic samplers were placed in the river basins as described before. Every 15 minutes, 50 ml of river water was taken by each sampler and collected in one glass bowl during 8 hours. This resulted in a composite sample every 8 hours. During rainfall events, the frequency was increased and each composite sample represented 6 hours of passing water. The automatic samplers were dark inside and were kept at a temperature of 4°C. Every 3 days, the samples were collected. They were then transferred into amber glass bottles capped with Teflon lined screw caps and transported in cold conditions. At the lab, the samples were stored in the dark at 4°C until analysis.

Except for carbendazim, storage stability experiments were performed for all studied pesticides in water samples of the Nil during 30 days. These stability experiments showed no loss of the analytes under storage conditions. Only for lenacil, the sensitivity of the analytical equipment was not that high.

Analyses of water samples were performed for at least one sample a day for each monitoring point. For the sampling stations upstream, the 2^{nd} sample of the day was always analysed. For the sampling stations downstream, the residence time was taken into account in order to follow the same plug of pollution. For the Nil basin for example, the residence time between the upstream and downstream sampling stations during average low flow conditions amounted about 16 hours. Therefore, at the mouth of the river every first sample of the day was analysed. The same rule was applied for the Demer basin. Once the results of the screening analyses were available, periods showing high peaks of pesticide concentrations were selected. For these periods, the 2 remaining samples per day were analysed as well, both upstream and downstream. Analyses were performed for the herbicides atrazine, chloridazon, diuron, isoproturon, lenacil and simazine. In the Demer basin, the fungicide carbendazim was analysed as well.

After rainfall events, suspended solids were separated in the lab and pesticide concentrations on the particles were determined.

Undisturbed sediment samples were taken upstream and downstream. This was done twice (mid May and mid June) by means of a macro-core. The samples were immediately frozen on the field with CO_2-ice. This way, the sediment samples could be easily transported avoiding any disturbance. Once in the lab, the samples were sliced and analysed for pesticides in pore water and on the sediment.

Analysis

Water samples.

Twenty ml of each water sample was filtered through a 0.45µm membrane filter. Ten ml of the filtered water was spiked with 10 µl of a 2,5 µg/ml 13C-atrazine (Dr. Ehrenstorfer) internal standard solution in methanol. The water samples of the 2004 campaign were extracted with an on-line SPE unit (Merck-Hitachi OSP-2A with C18 phase). Desorption was performed with a mobile phase. By means of an automated transfer system, the pesticides were then analysed by LC-MS/MS. The water samples of the 2005 campaign were extracted by SPE using a conditioned Chromabond EASY cartridge (Macherey Nagel, 6ml, 200mg). After washing and thoroughly drying, the analytes were desorbed from the SPE phase with 2 x 1 ml methanol. The extract was concentrated to 250 µl. To this final extract 750 µl of a 5mM solution of ammoniumacetate in water and 10 µl of a 2,5 µg/ml solution of trietazine in methanol were added. Twenty five µl of the extract were injected into a LC-MS/MS (Micromass Quattro 2). The pesticides were detected in multiple reaction monitoring mode (MRM) using positive ion electrospray. By doing so, fragments are created with specific masses for each of the pesticides. The ions monitored were: atrazine: 216>174, chloridazon: 222>104, diuron: 233>72, isopropturon: 207>72, lenacil: 235>153, simazine: 202>132, carbendazim: 192>160, 13C-atrazine: 219>177, trietazine: 230>202. The limits of quantification (LOQ) for atrazine, carbendazim, chloridazon, diuron, isoproturon, lenacil and simazine were on average respectively 50, 20, 50, 25, 15, 40 and 15 ng/l. They were determined as the sixfold of the analytical "noise". Recoveries varied between 85 to 110% for the samples of the 2004 campaign depending on the pesticide and between 60 to 95% for the samples of the 2005 campaign.

Soil samples.

First the sediment slices were weighed. Next, the pore water and the sediment were separated by applying vacuum over a 0.45 µm filter. The amount of extracted pore water was measured. The pore water could be further analysed as described for the water samples. The remaining sediment was weighed and then dried at 40°C. The dry sample was again weighed so that the amount of pesticides originating from not completely extracted pore water could be recalculated afterwards. Fifteen g of soil was mixed with Na_2SO_4 and extracted by sonication with acetone. The organic solvent was then evaporated. The residue was dissolved in 1 ml methanol and further diluted with 9 ml ultrapure water. Following this, the procedure was similar to that previously described for water samples.

Suspended solids.

Two hundred ml of homogenised water sample was filtered through a glass fibre filter. The filter was dried during 4 days in an oven at 40°C. After addition of 10 µl of a 2,5 µg/ml 13C-atrazine (Dr. Ehrenstorfer) solution in methanol the filter was extracted with 30 ml acetone during 30 minutes in an ultrasonic bath. The acetone was decanted and the extraction step was repeated twice with 20 ml acetone. The combined acetone fractions were dried with Na_2SO_4 and concentrated to nearly complete dryness. The residue was dissolved in 1 ml methanol and further diluted with 9 ml ultrapure water. Following this, the procedure was similar to that previously described for water samples.

3.2.4 Preliminary risk assessment

Chèvre et al. (2006) developed a methodology to determine a chronic risk quotient for mixtures of herbicides with a similar mode of action (RQ_m). This method was applied in this study. Here fore, the measured environmental concentration (MEC) for each herbicide is compared with its water quality criterion, i.e. the HC5-95%. This is the lower 95% confidence limit of the HC5 derived from the species sensitivity distribution that is based on no observed effect concentration (NOEC) data (SSD_{NOEC}). The mixture effect is predicted by the concept of concentration addition. The RQ_m must remain less than one to ensure that a mixture of chemicals presents an acceptable risk to the environment:

$$RQ_m = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{MEC_i}{HC5-95\%} < 1 \qquad \text{(eq. 3-1)}$$

In the aforementioned study, HC5-95% values for different herbicides with a similar mode of action were derived from the SSD curve of atrazine. For all herbicides, only toxicity data obtained with the active ingredient on algae and water plants were considered. The HC5-95% values hold for exposure times longer than 3 days (see Table 9). As such, a chronic risk is given if the risk ratio exceeds 1 for a period of more than 3 days.

A less conservative approach to calculate risks is proposed in the German guideline for monitoring programs (Pestemer et al., 2005). Assuming a purely additive effect, the total hazard of a mixture of active ingredients is calculated as follows:

$$\text{Total hazard} = \sum_{i=1}^{n} \frac{MEC_i}{EC_{50} \text{ or } LC_{50} \text{ or } NOEC} < 1 \qquad \text{(eq. 3-2)}$$

where EC_{50} and LC_{50} are statistically derived concentrations of a substance in an environmental medium expected to produce respectively a certain effect on 50% of the test organisms or a mortality of 50% of the test organisms in a given population under a defined set of conditions (IUPAC, 1997). The substance mixture may be toxic at values >1. For each substance, the values of EC_{50}, LC_{50} and NOEC for the most sensitive organism should be used.

Table 9. Ecotoxicological parameters of the studied pesticides (Footprint pesticide database: Available at http://www.herts.ac.uk/aeru/footprint/ and *: Chèvre et al., 2006).

Pesticide	Most sensitive group	EC_{50} (µg/l)	HC5-95% (µg/l) *	NOEC (µg/l) *
Herbicides				
Atrazine	Aquatic plants	19 *Lemna gibba*	1.8	3.0 *Mycrocystis aeruginosa*
Chloridazon	Algae	1900 *Chlorella fusca*	-	-
Diuron	Algae	2.7 *Scenedesmus quadricauda*	0.1	0.46 *Scenedesmus subspicatus*
Isoproturon	Algae	13 *Navicula pelliculosa*	0.3	3.2 *Scenedesmus subspicatus*
Lenacil	Algae	14 *unknown species*	-	-
Simazine	Algae	40 *Scenedesmus subspicatus*	2.8	5.0 *Scenedesmus quadricauda*
Fungicide				
Carbendazim	Aquatic invertebrates	130 *Daphnia magna*	-	-

3.3 Results and discussion

3.3.1 Hydrology of the different catchments during the monitoring campaigns

The obtained daily rainfall data and the hourly discharge data for the Nil and the Demer catchment are represented in respectively Figure 15 a and b.

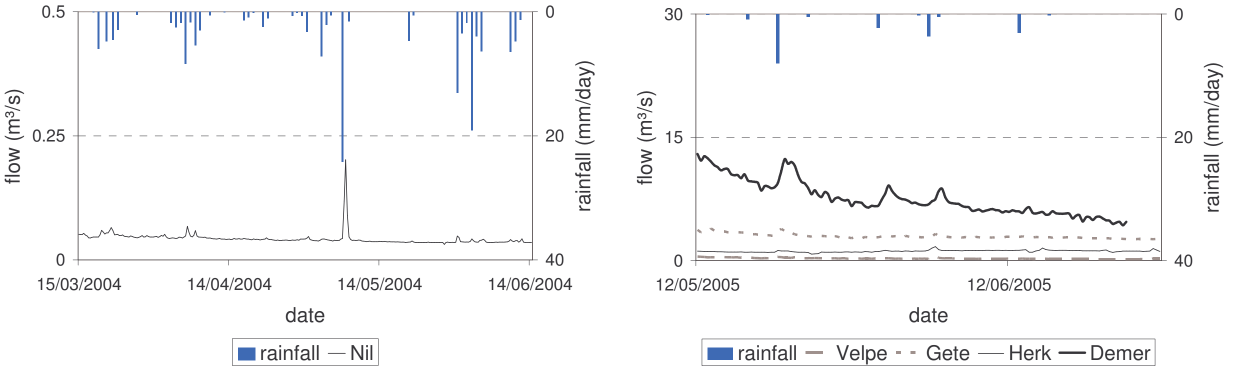


Figure 15. Daily rainfall and hourly runoff data for a) the Nil and b) the Demer catchment during their respective monitoring campaigns.

The monitoring period for the Nil catchment in 2004 started 2 months earlier and stopped 2 weeks earlier than that of the Demer catchment in 2005. If the number of rainfall events and the total rainfall amount between the 12th of May and the 15th of June are compared, one observes that the Demer catchment was subjected to fewer rainfall events in 2005. Moreover, the rainfall events that occurred in the Demer catchment were smaller compared to those observed during the monitoring campaign of the Nil in 2004. The total amount of rainfall measured during this period in the Nil catchment amounted to 66 mm, whereas for the Demer catchment this was only 19 mm. This difference in rainfall amounts will have consequences for measured pesticide concentrations in the rivers. Fewer and smaller rainfall events will reduce the contribution of runoff.

The Nil catchment is a small and hilly catchment with a residence time of about 1 day. As a consequence, a heavy rainfall event will result in a quick response in the river itself. A sharp flow peak will appear and only a limited tailing will occur. In contrast, when a rainfall event occurs in the Demer catchment it can be more spatially distributed. The travel time (time of concentration) for water from all over the catchment to reach the mouth of the river, will be more diverse and will result in a tailing of the discharge curve (see Figure 15b).

3.3.2 Dynamics in the water column

For the Nil basin, the dynamics of the six investigated pesticides in the water column are represented in Figure 16.

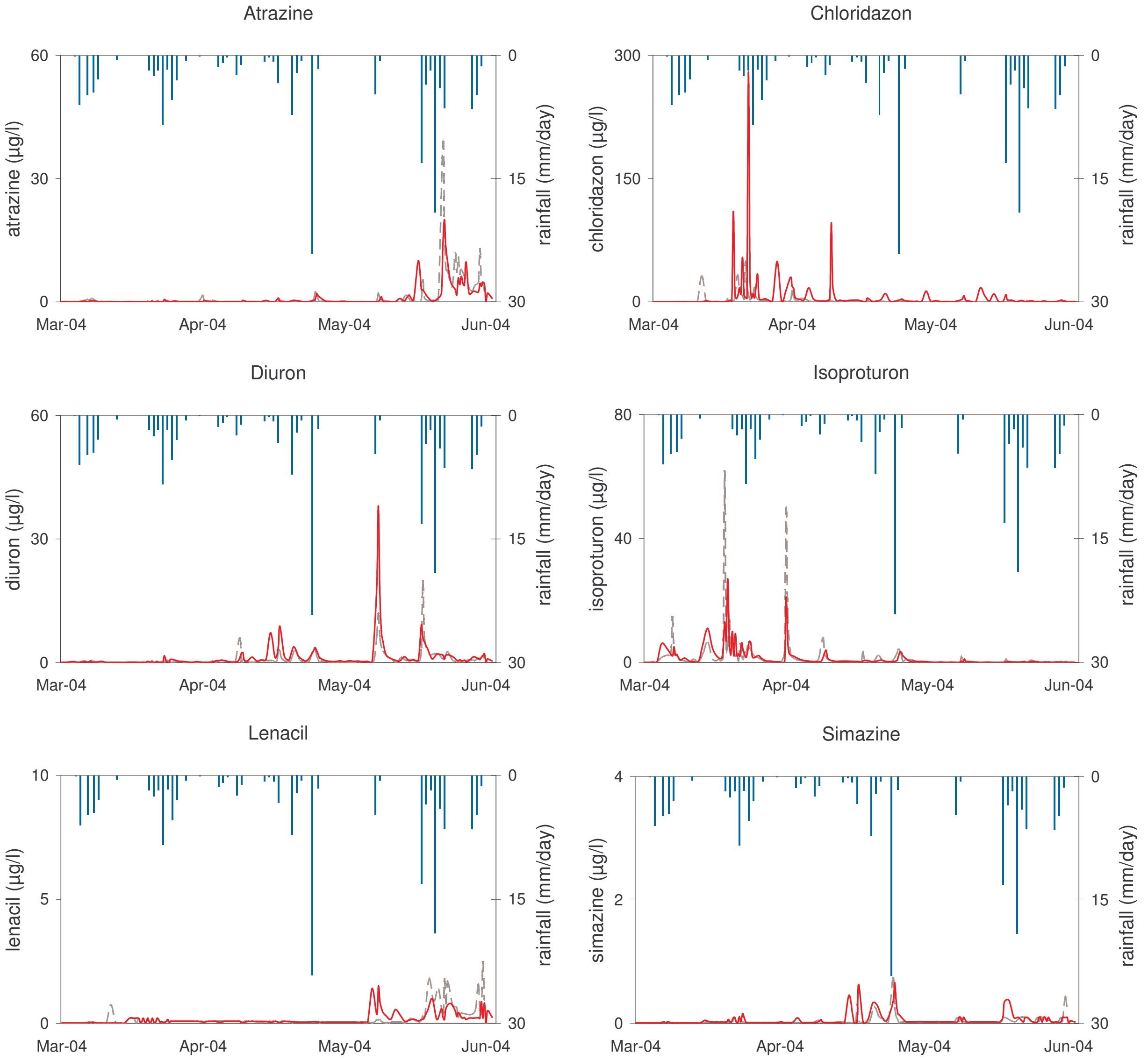


Figure 16. Measured herbicide concentrations at the mouth (full line) and upstream (dashed line) of the river Nil during spring 2004, together with the rainfall data (bars at the top).

Figure 16 shows that the pesticide concentrations in the Nil follow a time-varying course, frequently exceeding the Flemish standards for basic water quality (atrazine < 2µg/l, simazine < 1µg/l) (VMM, 2005). Lenacil and simazine were found in much lower concentrations than the other studied herbicides. Simazine never exceeded 1 µg/l, lenacil stayed below 3 µg/l. For chloridazon, a concentration of 280 µg/l was measured on the 4th of April, in an 8 hour composite sample taken during the evening. This high peak wasn't seen upstream and hence, the source of this peak should be located between the two monitoring points. Taking into account that all samples are composite samples, this means that one can assume that the real concentration that passed at a certain point in time during this sampling period probably must have been much higher than 280 µg/l.

High pesticide concentrations could be found in the river after rainfall events due to runoff. Even more important peaks were observed in the absence of rain immediately after application, e.g., through the clean-up of spray equipment, leaking tools, processing of spray waste and this on paved surfaces. On Figure 16 such an event can for instance be seen for chloridazon around the 15th of April: there is a period without rain but still high chloridazon concentrations were observed. In this study (Figure 17) and in a previous study performed by Beernaerts et al. (2005), it was shown that 30 to 95% of the total annual pesticide load passing in the river Nil could be attributed to these point losses. The total pesticide load in the river Nil was calculated by multiplying the measured concentrations with the corresponding mean flow data. Concentrations for samples that were not analysed were determined by interpolation. If the total amount of rainfall on a certain day was below 2mm, it was assumed that no runoff occurs (see Figure 15) and it was decided that the resulting loads could be attributed to point sources.

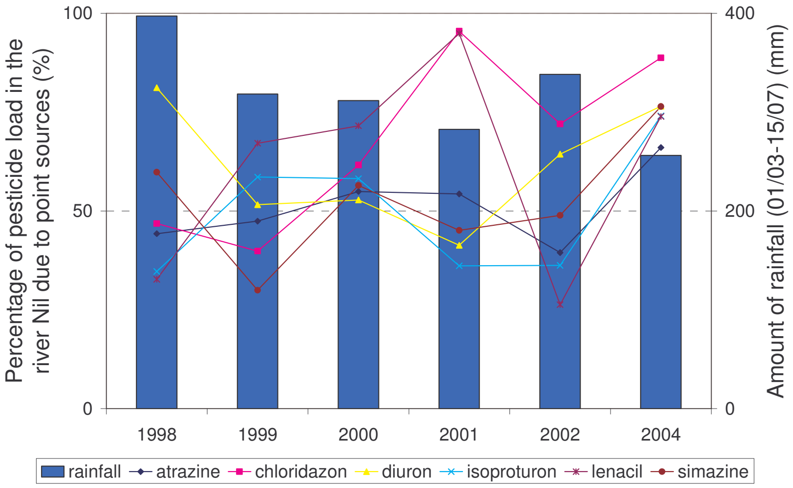


Figure 17. Percentage of the total pesticide load in the river Nil that can be attributed to point sources for the spring periods of 1998-2002 and 2004.

From Figure 17 it can be deduced that for most pesticides a decrease in the contribution of point sources occurs in 2000 and 2001 even though the total rainfall amount is smaller, which logically promotes the contribution of point sources. This decrease can be explained by the setup of a senstization campaign of the farmers during the years 2000-2001 (Figure 18).

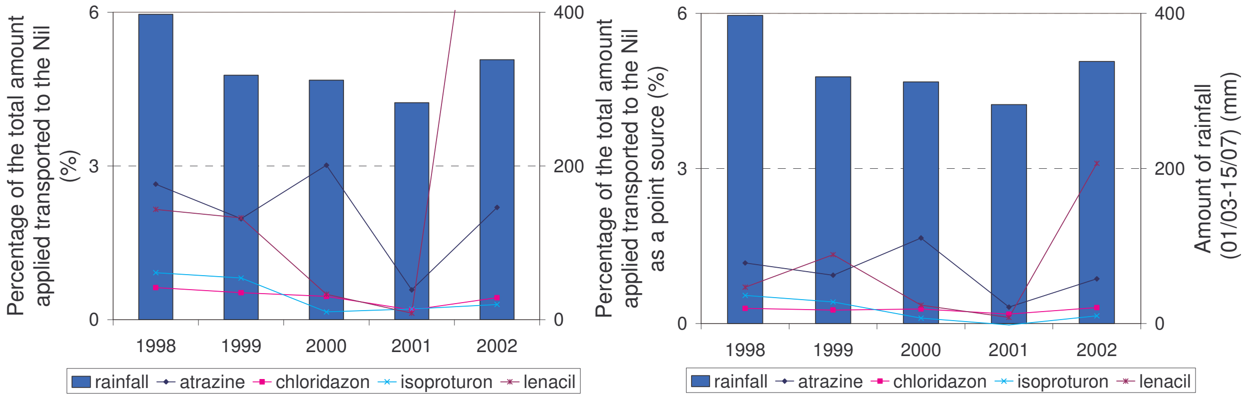


Figure 18. Percentage of the total amount of applied pesticides that is a) transported through the river Nil and b) that is transported through the river Nil and can be attributed to point sources.

Figure 18a shows that there is a decrease in total pesticide load in the river Nil during the period 2000-2001. In order to show that this decrease is not only due to fewer runoff events and less rain, Figure 18b demonstrates that there also occurred a decrease in the pesticide load originating from point losses during this period. When the sensitization campaign was finished in 2002, pesticide loads in the river immediately increased (Beernaerts et al., 2002) and the contribution of point sources also did (Figure 18). This proves the importance of direct losses, which were estimated to be 30 to 95 % of the total amount of pesticides found in the river 'Nil'.

Pesticide concentrations on suspended solids in the water samples were analysed during periods of rainfall events, as one can expect that the sediment concentrations in the water will reach a maximum then. As there occurred only one significant rainfall event in the whole monitoring period, the results of this event (24 mm/day) on the 7th of May 2004 are presented in Figure 19.

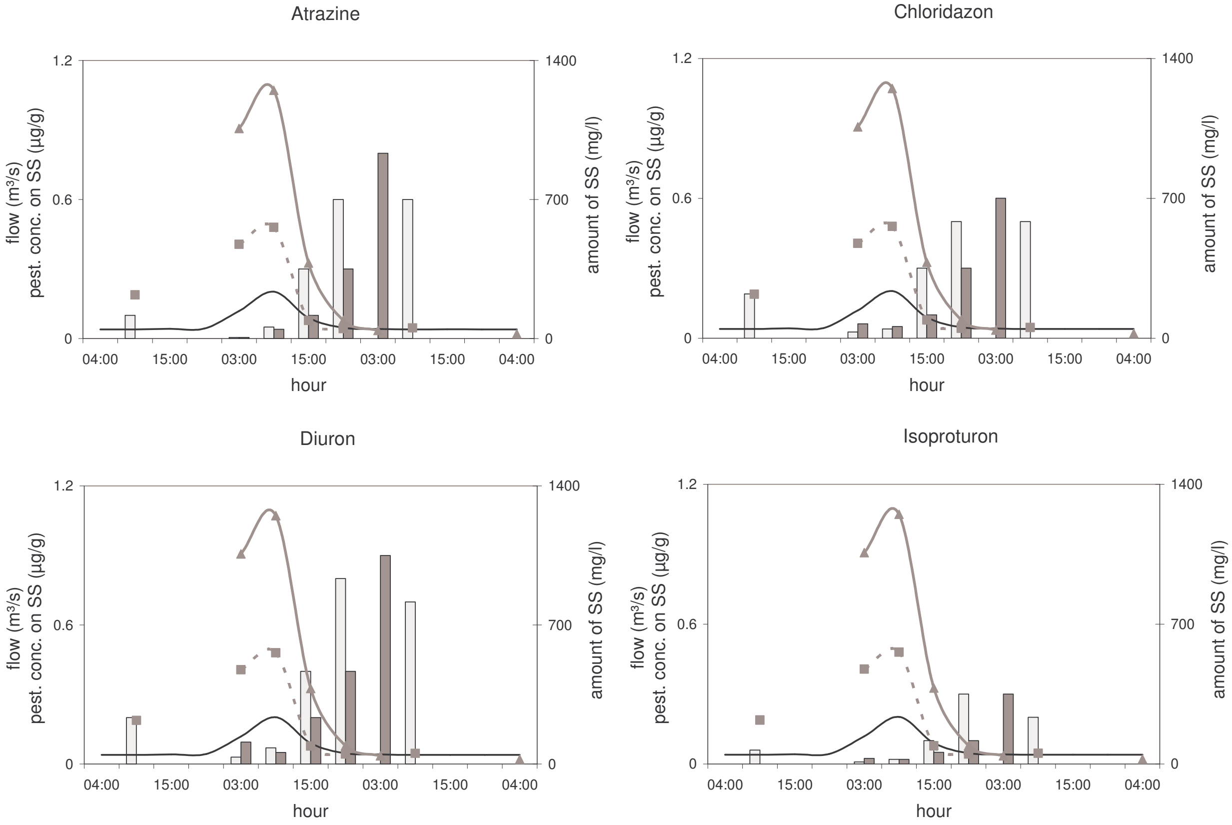


Figure 19. Measured flow (black line) (m³/s) and suspended solids (SS) concentrations (mg/l) upstream (dashed grey line) and downstream (full grey line) the river Nil during a rainfall event that started at 15 o'clock on the 7th of May 2004. The measured pesticide concentrations upstream are presented by white bars, those measured downstream by grey bars (µg/g).

In Figure 19 it can be seen that the amount of suspended solids (SS) during the peak event is twice as high downstream as compared to those measured upstream. This is due to the contributing area between the two measuring points: it is characterized by steeper slopes than the upstream area. Resuspension in the river itself will have contributed too. The maximum concentration of SS in the 6 hour composite samples comes at the same time as the flow peak but lasts longer. This was also seen in other studies (Heywood and Walling, 2003; Laignel et al., 2006). The highest pesticide concentrations on the suspended solids are observed at the end of the SS peak. A possible explanation is that in the Nil catchment, treated fields along the river are almost all situated upstream. After a period equal to the residence time, the concentrations on the

SS increase. For lower SS concentrations, the results become less reliable. If the figures for the different pesticides are compared the concentrations on the SS show the following order: isoproturon < chloridazon < atrazine ≈ diuron. This is in agreement with the application period of the different pesticides (see Figure 16), their K_{OC}-value and their half life in soil.

For the Demer basin, the dynamics of pesticide concentrations in the water column are represented in Figure 20.

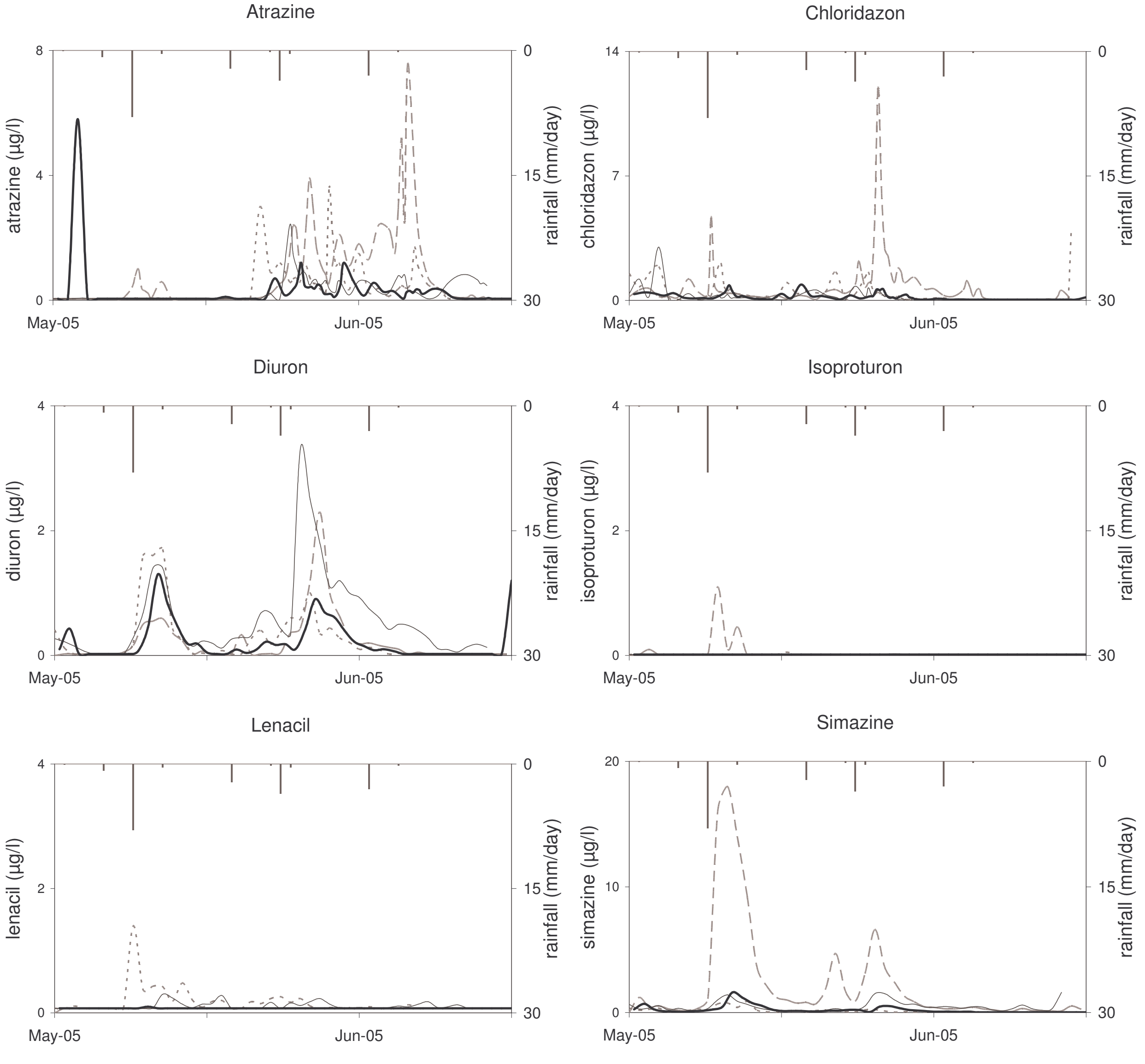


Figure 20. Measured herbicide concentrations at the mouth of the river Gete (dotted grey line), Herk (full fine black line) and Velpe (dashed grey line) and downstream the river Demer (full thick black line) together with the rainfall data (bars at the top).

As for the Nil basin, in the Demer basin too the pesticide concentrations show a highly variable course which is due to runoff events and point losses. Nevertheless, the maximum concentrations for all the observed pesticides at all monitoring stations in the Demer basin are lower than those measured in the Nil basin, except for simazine. The high simazine concentrations measured in the river Velpe may be caused by some local pea cultivation (145 ha) or by non agricultural use. The carbendazim concentrations in the upstream tributaries were never higher than 270 ng/l after a runoff event (results not shown). For chloridazon and isoproturon, the application period was almost finished during the monitoring campaign of the Demer basin, which explains their low concentrations.

The importance of point losses can be seen for pesticides which were still applied during this monitoring campaign i.e. atrazine, carbendazim, diuron, lenacil and simazine. High concentration peaks originating from point losses are clearly visible for atrazine around mid June during a period without rainfall.

Concentration peaks due to runoff events can be seen for all observed pesticides. The peaks can be expected to be highest shortly after application. For the smaller upstream tributaries, the concentration peaks are higher and more narrow compared to those seen downstream, which are more suppressed and spread out due to dilution and dispersion. The peaks at the mouth of the catchment also arrive somewhat later. The influence of a bigger upstream tributary (e.g. the Gete) on pesticide concentrations at the mouth of the river will be larger than for a smaller one (e.g. the Velpe).

Comparison of pesticide concentrations in rivers with different scales

In order to evaluate the scaling effects on measured herbicide concentrations on different watershed scales, the measured concentrations were adjusted for use intensity within the watershed. To this end, the maxima of the measured pesticide concentrations for each catchment were normalised to a use intensity of 1 kg/ha. This was done by dividing the concentrations by the total applied mass of a herbicide on a catchment, divided by the total area of that catchment. As we had only information on application doses for atrazine, chloridazon and isoproturon, only the results for these herbicides are given in Figure 21.

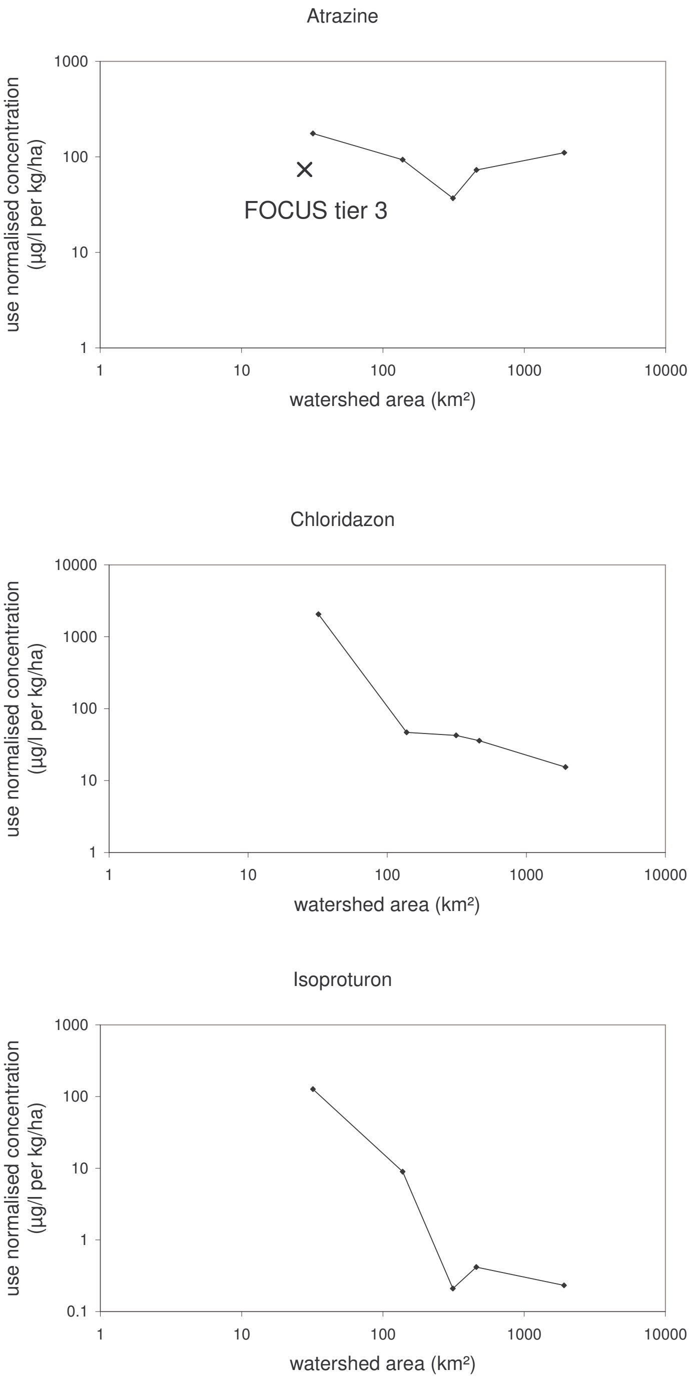


Figure 21. Use normalised maximum concentrations determined for the rivers Nil, Velpe, Herk, Gete and Demer during their respective monitoring campaigns.

From Figure 21, it seems that in general there is a scaling effect due to dilution and dispersion. Sharp peaks of short duration would be expected for small watersheds while broad peaks of longer duration would be expected for larger watersheds. This explains the slope in the concentration trajectories in Figure 21. As the watershed area decreases, the maximum daily concentration tends to increase, reflecting the sharper peak concentrations. This is in agreement with other studies (Müller et al., 2003; Gustafson et al., 2004).

The results for chloridazon and isoproturon are somewhat biased for the bigger watersheds. This is due to the shorter monitoring period (15th of May till the end of June) that occurred in the bigger watersheds during spring 2005. The highest concentration peaks for these herbicides may be expected during early spring and were as such missed. The use-normalised concentrations for chloridazon and isoproturon would be probably higher in the bigger watersheds if the monitoring period had been started earlier (early March). The slope of the line would be less steep then. For atrazine, the results can be compared with results of a similar study obtained by Gustafson et al. (2004) for watersheds in the US. The use normalised concentrations for Belgium seem to be higher than those measured in the US. Moreover, the edge of field estimate of the maximum daily atrazine concentration that was calculated there (Gustafson et al., 2004) with the PRZM model for a watershed of 30 km², is 2 times lower than the use normalised concentration that was found in the river Nil. It seems that the PRZM prediction underestimates the real situation in small rivers in agricultural areas. A possible cause can be the absence of point sources in PRZM. The FOCUS surface water scenario R1 for the spring period results in a predicted use-normalised surface water concentration of 82 µg/l (see Figure 21, top).

Advise for the setup of monitoring campaigns

Based on the experience obtained during the aforementioned monitoring campaigns, some advise can be given for the setup of future campaigns.

- In view of the EU Water Framework Directive, different countries and research institutes started in recent years to investigate the status of the current river water quality through the set up of monitoring campaigns. Many of those campaigns observed the overall trends by taking grab samples. The Flemish Environmental Protection Agency for example takes water samples at a large number of fixed locations once every two months (VMM, 2005). From our monitoring campaigns and from other studies (Neumann et al., 2002; Leu et al., 2004; Beernaerts et al., 2005) it is clear that the dynamics of pesticide concentrations can only be captured by continuous monitoring or by means of a time-integrated sampling e.g. by using diffusive samplers (Allan et al., 2006). An additional advantage of this kind of samplers is that they directly provide an estimate of the bio-available fraction of the pesticide in the surface water.

- Monitoring campaigns should preferably be set up during the application period of the observed pesticides.
- Special attention should be given to the smaller upstream rivers connected to rural areas where extreme concentrations are most likely to occur.
- Backtracking of peak events can reveal direct losses due to poor agricultural practices.
- To assist in the optimisation of sampling strategies, the combined use of monitoring data and models is advised (Dochain and Vanrolleghem, 2001; De Pauw and Vanrolleghem, 2006). By iterating between model runs and experiments cost-optimized sampling schemes for the next experimental stages can be designed.

3.3.3 Dynamics in the sediment

For the Nil basin, the dynamics of the pesticide concentrations in the pore water are presented in Figure 22. The dynamics on the sediment particles can be seen in Figure 23. The average porosity found in the upper 10 cm of the sediment samples amounted to 0.61 g/cm³ for the upstream samples and 0.55 g/cm³ for the downstream samples. Their average densities amounted to respectively 1.47 and 1.58 kg/l.

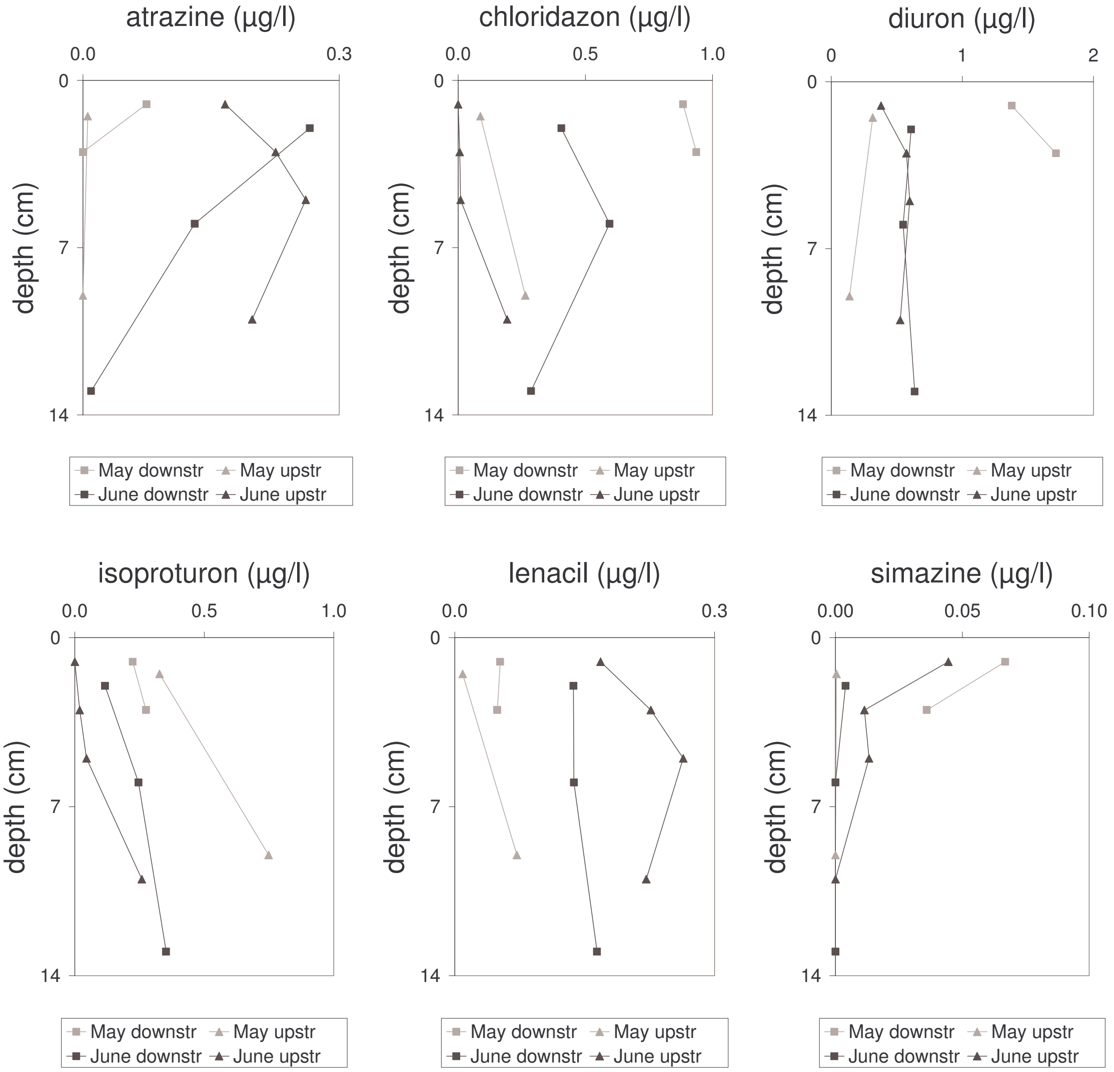


Figure 22. Depth distribution of measured pesticide concentrations in the pore water of the Nil at the sampling days in May and June.

Figure 22 shows that the pore water follows the dynamics of the application scheme of the pesticides. For example, the atrazine concentration in the pore water rises from May to June as this pesticide is applied during this period. Only for simazine there is an unexpected shift of the concentrations measured downstream.

In most cases, there is a decrease in concentration with depth, due to a combination of chemical reactions, biodegradation and diffusion. The downstream concentrations are higher than the upstream ones. This can be explained by the similar flow upstream and downstream, but higher loads passing downstream. The studied pesticides are mainly applied upstream (see Figure 5, Chapter 1).

Compared to the concentrations found in the water column, those found in the pore water are 1 or 2 orders of magnitude lower. This can be explained by a limited exchange between the water column and the pore water through diffusion.

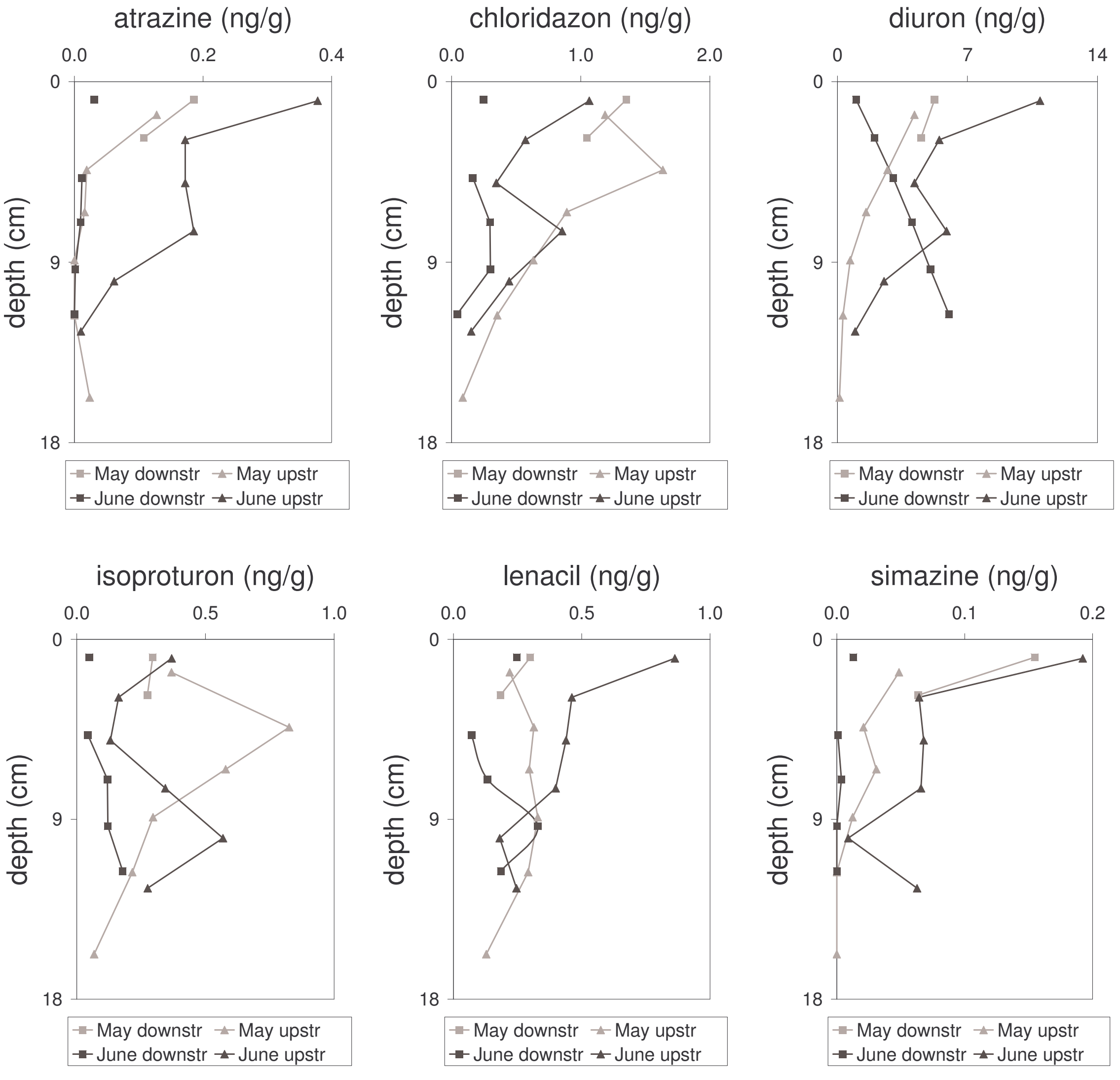


Figure 23. Depth distribution of measured pesticide concentrations on the sediment particles of the Nil at the sampling days in May and June.

For the concentrations of the studied pesticides on the sediment presented in Figure 23, the results should be interpreted with the necessary caution. In the samples taken downstream there were some stones, especially in the sample taken in June. The stones were removed during filtration, but the weight of the sub-samples was determined before, hence being too high to relate the pesticide amounts to. As a result, an underestimation of the real pesticide concentrations on the sediment in the downstream samples can be expected, especially for the one taken in June. This effect can be seen for atrazine, diuron, lenacil and simazine. To avoid this, in the monitoring campaign of the Demer basin during spring 2005 three replicates of each soil sample were taken and stones were removed before determination of the weight of a sub-sample.

Nevertheless, the concentrations in the pore water and on the sediment can be understand from the K_{OC} value of the pesticides. The concentrations of diuron in the pore water are almost twice those measured for chloridazon, whereas concentrations of chloridazon in the water column are higher as compared to diuron. Because of its high K_{OC} value, a higher sorption (factor 7) compared to chloridazon can be explained and higher pore water concentrations can be expected due to the chemical equilibrium.

For the Demer basin, the dynamics of the pesticide concentrations in the pore water are presented in Figure 24. Here, 3 replicates were taken of every sediment sample. Confidence intervals could therefore be calculated. During the sampling in May, no downstream sediment sample could be taken due to the high flow rate. The average porosity found in the upper 10 cm of the sediment samples taken in May amounted to 0.32 g/cm³ for the upstream samples, the average density was 1.66 kg/l. The lower average porosity compared to the value determined in June, could be attributed to the high flow rate occurring at the day of sampling, which probably removed the upper less dense part of the sediment layer (resuspension). For the samples taken in June, the average porosity amounted to 0.39 g/cm³ for the upstream samples and 0.36 g/cm³ for the downstream samples. Their average densities amounted to respectively 1.55 and 1.62 kg/l.

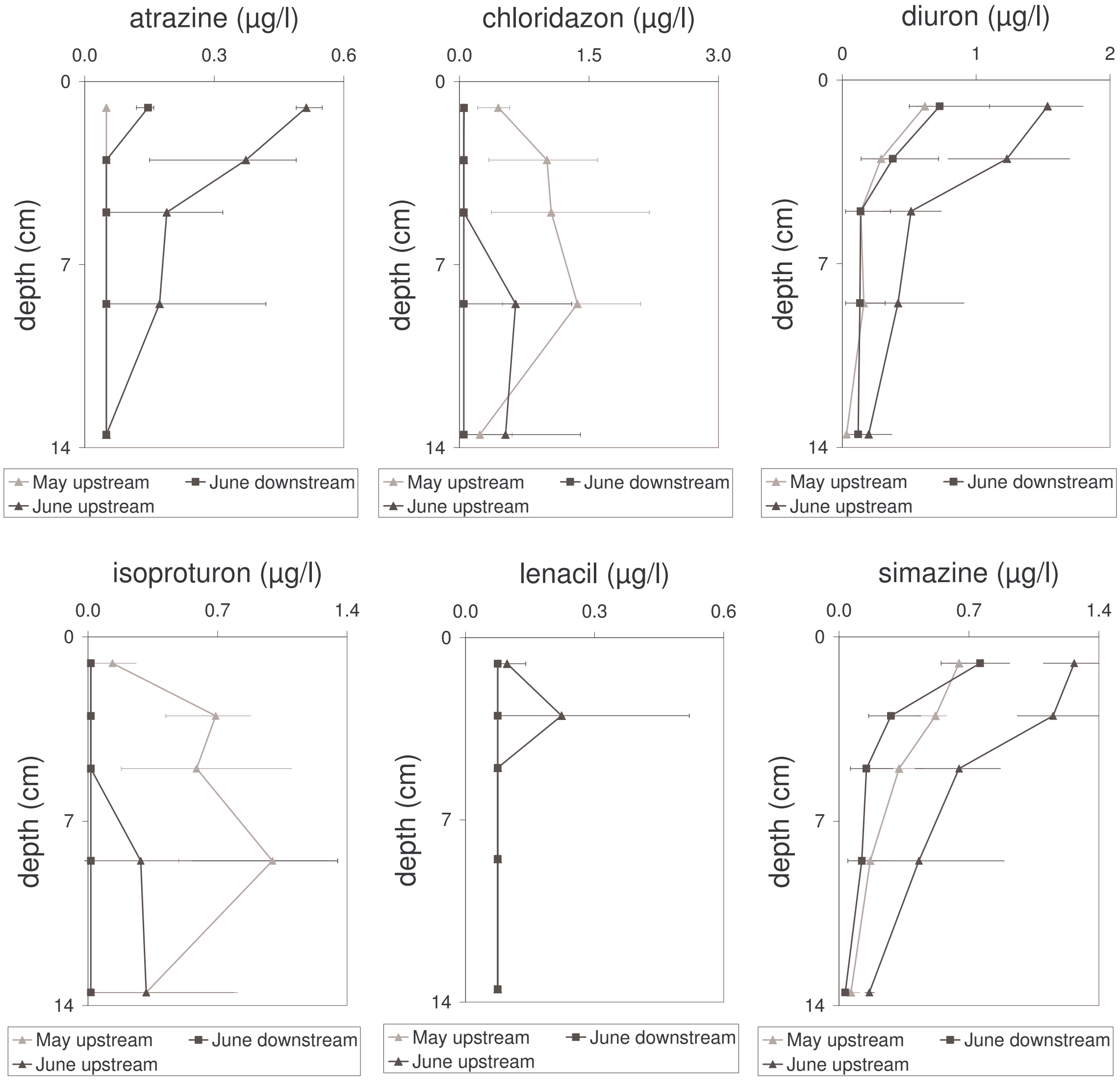


Figure 24. Depth distribution of measured pesticide concentrations in the pore water of the Demer at the sampling days in May and June.

As can be seen from Figure 24, all measured depth distributions of herbicide concentrations in the pore water show a logical shift from May to June in agreement with the application scheme. The concentrations were almost a factor 2 higher as compared to the pore water of the Nil sediment, which can be attributed to the higher loads passing in the Demer catchment. For simazine there was even a factor 10 of difference. For the Demer catchment, the upstream concentrations in the pore water were higher than the concentrations measured downstream. This can be attributed to lower flow conditions and to lower dilution upstream which results in a larger concentration gradient acting as a driving force.

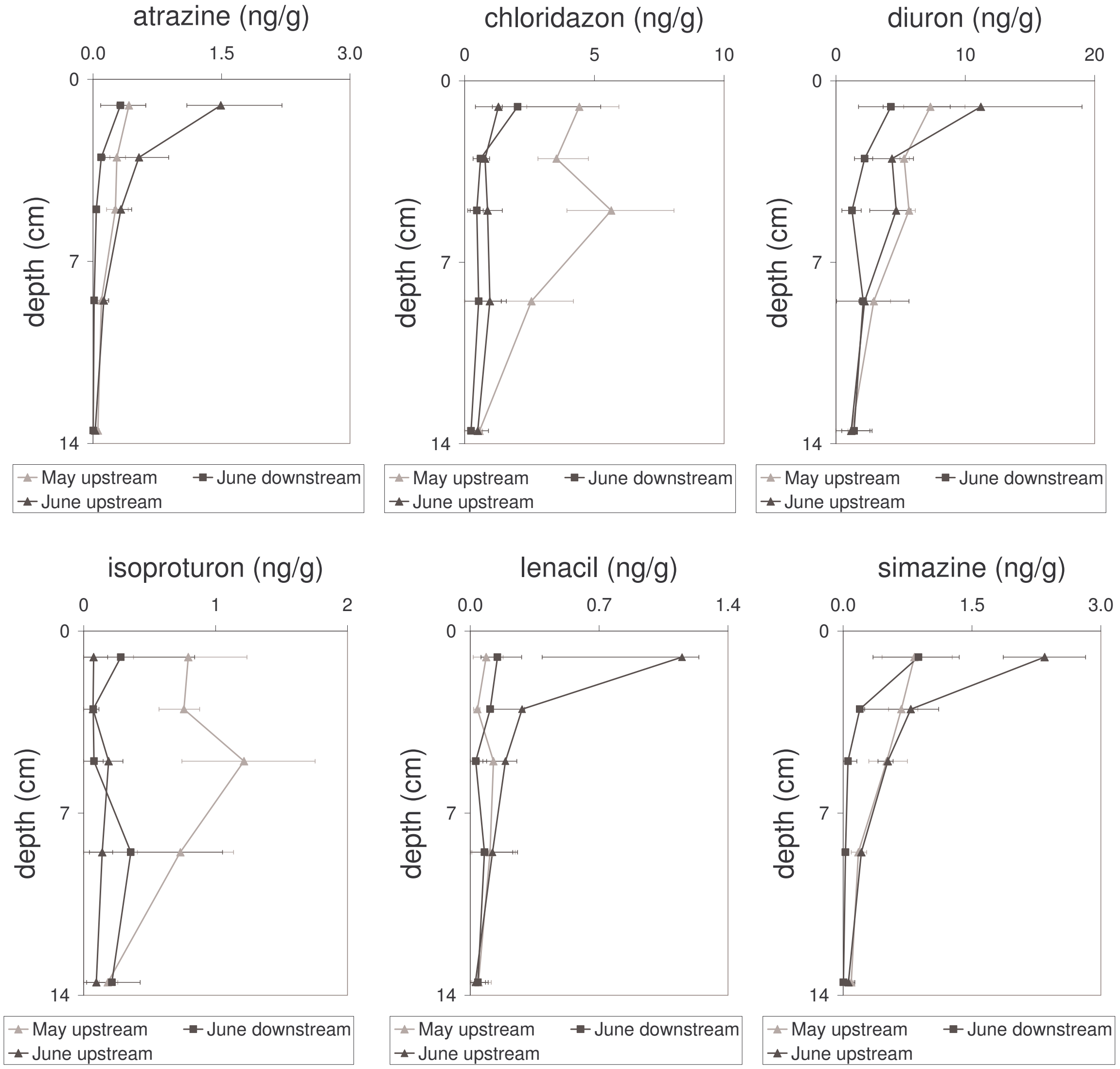


Figure 25. Depth distribution of measured pesticide concentrations on the sediment particles of the Demer at the sampling days in May and June.

The depth distribution of the pesticide concentrations on the sediment particles in the Demer catchment are presented in Figure 25. These results are much more reliable than those for the Nil catchment as stones were removed before weight determination of the sub-samples and because 3 replicates were taken.

The same dynamics can be seen on the sediment as in the pore water. The concentrations on the sediment are again much higher for the Demer catchment compared to the Nil catchment. For atrazine and chloridazon they were almost a factor 5 higher, for isoproturon a factor 2 and for simazine almost a factor 10. Only for diuron and lenacil the concentrations on the sediment were comparable for the Demer and the Nil catchment. The higher concentrations can be attributed to higher concentrations in the pore water rather than to a higher organic carbon content.

The results for diuron and isoproturon on sediment both for the Nil and the Demer catchment, were in the same order of magnitude as concentrations found by the Flemish Environmental Agency (VMM, 2005), but were much lower than concentrations found in a comparable Danish study (Kronvang et al., 2003). In the Danish study, the mean organic carbon content had a median value of 15.4%, which is a factor 4 larger than in the Nil basin and a factor 15 as compared to the Demer basin. This can explain the higher pesticide concentrations found on sediment particles in the Danish rivers.

The results for the carbendazim concentrations in the pore water and on the sediment particles are presented in Figure 26. For both compartments, an increase in concentrations can be seen during the monitoring campaign which is in agreement with the time of application. The high concentrations in the pore water (9.4 µg/l) and on the sediment can be explained by the high K_{oc} value of carbendazim and by the fact that one of the three replicates was strongly enriched in carbendazim. A possible explanation for that could be that this sample was taken on a location where considerable sedimentation ocurred. Carbendazim also has a low degradation rate in water (see Table 8).

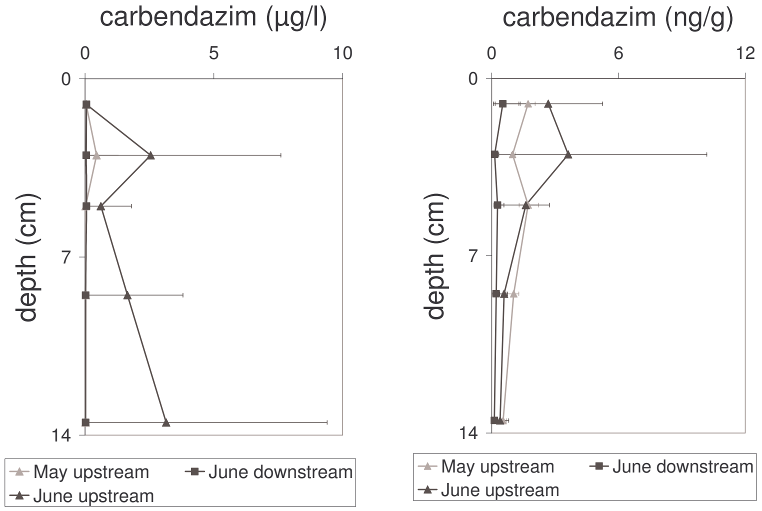


Figure 26. Depth distribution of measured carbendazim concentrations in the pore water and on the sediment particles of the Demer at the sampling days in May and June.

3.3.4 Preliminary risk assessment

Chronic risk assessment

In Figure 27, the risk factor RQ_m is presented for both the Nil and the Demer basin. RQ_m is calculated as the summation of the risk factors for atrazine, diuron, isoproturon and simazine. For the other measured pesticides, no HC5-95% values were determined by Chèvre et al. (2006).

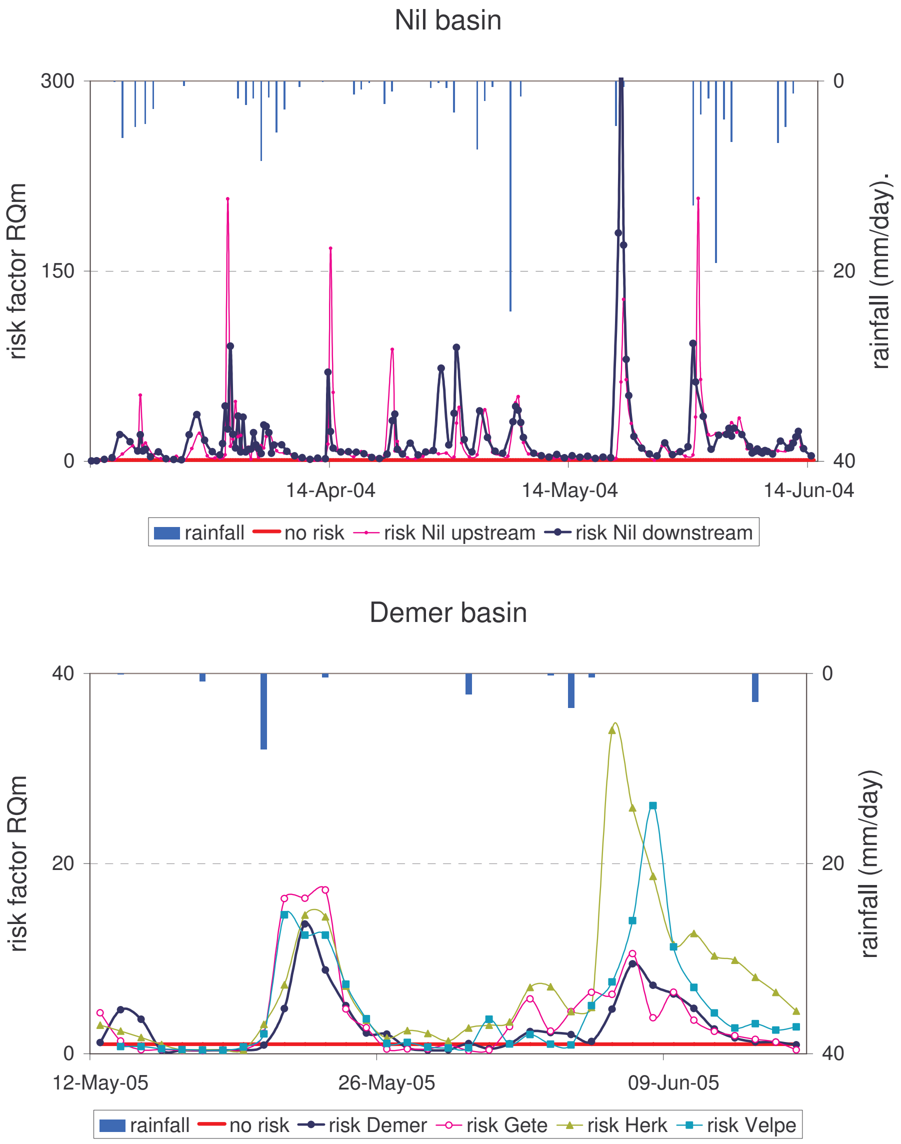


Figure 27. Summed risk factor for atrazine, diuron, isoproturon and simazine in the Nil and the Demer basin during the monitoring campaigns of spring 2004 and 2005. A chronic risk occurs if the risk ratio exceeds 1 for a period of more than 3 days.

As can be seen from Figure 27, the calculated risk factor frequently exceeds the ‘no risk’ value during more than 3 days. For the Nil basin the exceedance is almost permanent, both upstream and at the mouth of the river due to the high pesticide concentrations. For the period from the 15th of March 2004 till the end of April isoproturon forms the main contributor to the risk. From the end of April till the end of the monitoring campaign diuron becomes the main contributor. This means that from May on, based on the performed risk assessment, it is no longer agriculture which is contributing most to pesticide pollution, but it are the applications of diuron on paved surfaces by municipalities, farmers and households.

For the Demer basin, the risk factor is higher in the upstream tributaries compared to the risk at the mouth, which is analogous to the concentration profiles. It seems that for upstream rivers in agricultural areas, there is a high pressure on the ecosystem both after rainfall events and during application days. There are longer periods of no risk in the Demer basin compared to the Nil basin. Due to the shorter monitoring period and its timing, the main contributor to the risk is diuron.

Note that the HC5-95% is a rather conservative threshold for risk determination, as it protects 95% of the species with a 95% confidence limit. A less conservative approach will lower the calculated risk values. This is done in the next paragraph.

By using a less conservative approach as proposed in the German guideline for monitoring programs (Total hazard based on NOECs) (Pestemer et al., 2005), similar curves as in Figure 27 were obtained. Since the target values increased a lot according to this guideline, the curves decreased accordingly. For diuron the NOEC value is almost a factor 5 higher than its respective HC5-95%, for isoproturon there is a factor 10 of difference (see Table 9). As such, the periods of risk were smaller. An example is given in Figure 28 for the Nil catchment. As the NOEC value for isoproturon is almost a factor 10 larger than its respective HC5-95%-value, the curve of the total hazard (NOEC) decreased accordingly during the period from March till the end of April. This decrease was only half that strong during the period from May to June, because of a smaller increase of the target value for diuron.

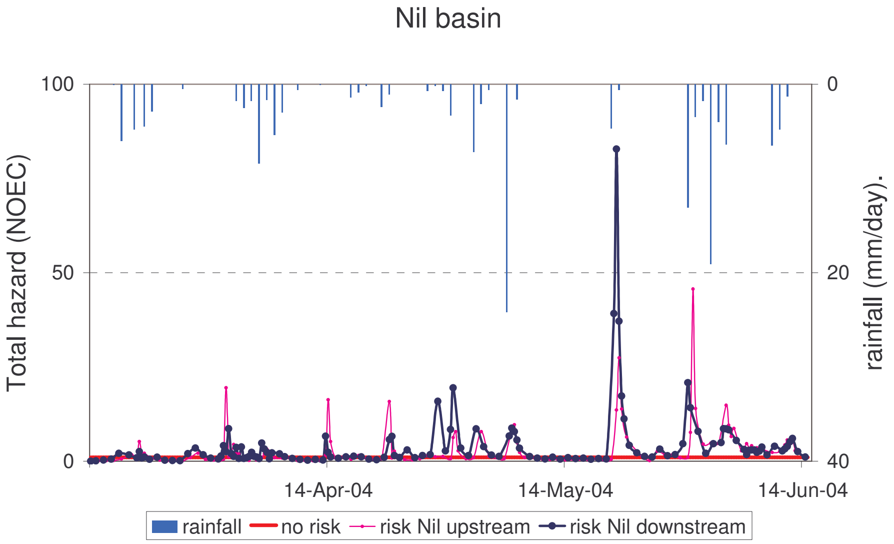


Figure 28. Total hazard calculated for the mixture of monitored pesticides in the Nil catchment during spring 2004, based on their NOEC values. A risk can be expected when the total hazard exceeds 1 frequently or during longer period.

Acute risk assessment

Similarly, a total hazard could be computed on the basis of the appropriate effect concentrations (EC_{50}). In this case an acute risk is determined. This is represented for the Nil in Figure 29.

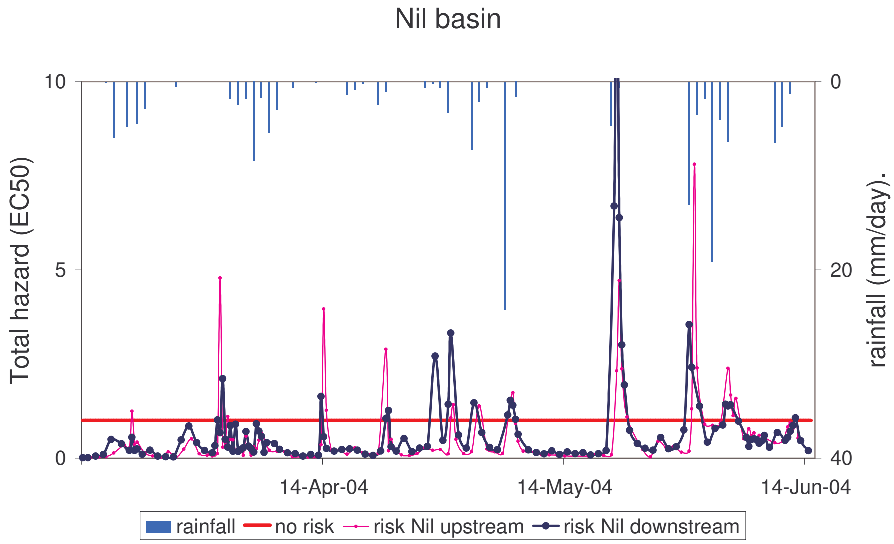


Figure 29. Total hazard calculated for the mixture of monitored pesticides in the Nil catchment during spring 2004, based on their EC_{50} values. A risk can be expected when the total hazard exceeds 1.

For the Demer basin (results not shown) only an acute risk was calculated for the Herk at the 6th of June and for the Velpe at the 8th of June. During the remaining period of the monitoring campaign there were no acute risks in the Demer basin according to the calculated total hazard based on EC_{50} values.

Nevertheless, it should be stressed that in this study the risk was only calculated as a summation of the studied pesticides. In reality, many more herbicides/fungicides/insecticides were present in the monitored rivers and one can thus expect an even higher risk.

Shortcomings

In this study, the frequency of exceedance of concentrations was not taken into account during the risk assessment. This could have been done by means of a concentration-duration-frequency curve (Dixon, 2002; Verdonck et al., 2003). However, as there are no analogue effect-duration-frequency data available, this approach can not be applied in risk assessment yet. Besides, also the synergetic or antagonistic action of certain active ingredients was not taken into account. In this respect, several models look promising in modelling ecological risks. The DREAM model (Karman, 2002) is an example of the application of mechanistic time-to-event models and is expected to generate a more realistic estimation of the environmental impact of produced water discharges coming from oil companies. Similar work in the pesticide field would be helpful for realistic risk assessment. The PERPEST model predicts the effects of a given concentration of a pesticide based on the outcome of already performed experiments using experimental ecosystems. It also quantifies uncertainty by taking a probabilistic approach and it provides uncertainty limits to the predicted values. For the moment, PERPEST can not handle mixtures of pesticides (Van den Brink et al., 2006). Analyses of standard data sets are required to validate such models and to identify the advantages and disadvantages of time-to-event analysis in risk assessment (Karman, 2002). Evidently, still a lot of work has to be done on the effect side of micro-pollutants in order to come to reliable risk assessments.

3.4 Conclusions

For the two monitoring campaigns performed during spring 2004 and 2005, the important contribution of runoff events and point losses to the pesticide load in the river system was identified. The high concentrations of the studied pesticides in the water column frequently exceeded the Flemish standards for basic water quality of surface waters. As the concentrations show a highly dynamic, time-varying course, continuous monitoring or the use of diffusive sampling systems during the application window are advisable. Moreover, upstream rivers in agricultural areas need special attention, as they can form important ecosystems which are not exposed to or experience litte influence from other sources of pollution such as households and industries and are therefore more vulnerable. A scaling effect with high pesticide concentrations in the small upstream river stretches and low concentrations downstream due to dilution, was confirmed here even though it was probably somewhat biased due to the shorter monitoring period in 2005.

The concentrations in the sediment followed the dynamics of the water column well, but the concentrations were much lower (2 orders of magnitude). The contribution of the sediment towards the water column is rather negligible. Pesticides on suspended solids showed a typical distance effect after rainfall events: in the beginning of the event herbicides located near the closing section of the river will leave the catchment, followed by pesticides coming from the more remote areas or fields.

Finally, the performed risk assessment revealed a frequent exceedance of the ‘no risk’ threshold in the water column. For the period from the 15th of March till the end of April isoproturon forms the main contributor to the risk. From the end of April till the end of June diuron occupies that place. This means that from May on, based on the performed risk assessment, it is no longer agriculture which is contributing most to pesticide pollution, but it are the applications of diuron on paved surfaces by municipalities, farmers and households. Upstream small rivers in agricultural areas seem to be at risk during longer periods as compared to downstream locations.

Chapter 4

THE SOIL AND WATER ASSESSMENT TOOL

Adapted from:

Holvoet, K., van Griensven, A., Seuntjens, P., Vanrolleghem, P.A., 2005. Sensitivity analysis for hydrology and pesticide supply towards the river in SWAT. *Phys. Chem. Earth*, **30**, 518–526.

Holvoet, K., van Griensven, A., V. Gevaert, V., Seuntjens, P., Vanrolleghem, P.A. (2006). Modifications to the SWAT code for modelling direct pesticide losses. Submitted.

Holvoet, K., Gevaert, V., van Griensven, A., Seuntjens, P., Vanrolleghem, P.A. (2006). Modelling the effectiveness of agricultural measures to reduce the amount of pesticides entering surface waters. Submitted.

4.1 Model choice for predicting pesticide fluxes towards the river

From the literature review (see Chapter 2), different models were selected that are suitable for simulating pesticide fluxes towards a river at catchment scale. Five continuous models were compared, in order to choose the most suitable tool for predicting pesticide fluxes towards the river: i.e. AnnAGNPS (Bingner and Theurer, 2001), SWAT (Arnold et al., 1998), HSPF (Donigian et al., 1995), MIKE SHE (Refsgaard and Storm, 1995) and WASP (Wool et al., 2001). In Table 10 the different decision criteria are shown on which the selection of the most suitable continuous simulation model was based. Information was found in the different model manuals and in the review articles of Borah and Bera (2003), Cox (2003) and Shoemaker et al. (2005). The model review performed by Shoemaker et al. (2005) is highly recommendable, as it compares 62 modelling tools at different levels: e.g. the TMDL (Total Maximum Daily Loads) endpoints that are supported, their general and special land and water features, and their applicability such as required experience and time, data needs, available support and cost.

Table 10. Summary of the different decision criteria taken into account during model selection.

Decision criterium	AnnAGNPS	HSPF	MIKE SHE	SWAT	WASP
Catchment scale, land and water features					
suitable for larger catchments	X	X		X	
agricultural management included	X	X	X	X	
river processes included		X	X	simplified	X
surface/groundwater interactions		medium	X	medium	
BMP evaluation for pesticides		X		X	
Use as decision support tool					
frequently used for decision support			X	X	
Applicability					
freely available	X	X		X	X
open source code	X	X		X	X
extensive manual		X	X	X	X
user friendly			X	X	
GIS interface	X		X	X	X
experience required	lim. tr.	prof.	prof.	mod. tr.	prof.

Key: BMP: Best Management Practice
lim. tr.: limited training required (assuming some familiarity with basic environmental models)
mod. tr.: moderate training required (assuming some experience with basic watershed and/or water quality models)
prof.: substantial training or modeling expertise required (generally requires professional experience with advanced watershed and/or hydrodynamic and water quality models)

Based on these criteria the SWAT model was selected to perform simulations of pesticide fluxes towards the river. The main reasons for this choice were its suitability for larger catchments, the possibility to compare different agricultural best management practices, the freely available open source code and the existence of an extensive manual.

4.2 Description of the SWAT model

4.2.1 Introduction

SWAT - the Soil and Water Assessment Tool- was developed by the USDA Agricultural Research Service (ARS) (Arnold et al., 1998) to predict the impact of land management practices on water, sediment and amount of chemicals originating from agriculture, in large complex river basins with varying soils, land use and management conditions over a long period of time. It is a partly physically-based and partly distributed, continuous model with a daily calculation time step. As such, the model is not designed to simulate detailed, single-event flood routing.

SWAT incorporates features of several ARS models and is a direct outgrowth of the SWRRB model (Simulator for Water Resources in Rural Basins) (Williams et al., 1985; Arnold et al., 1990). Specific models that contributed significantly to the development of SWAT were CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) (Knisel, 1980), GLEAMS (Groundwater Loading Effects on Agricultural (Erosion-Productivity Management Systems) (Leonard et al., 1987), and EPIC (Impact Calculator) (Williams et al., 1984).

We used the AVSWAT2000 version of the model, where the simulator is integrated in a GIS by an ArcView pre-processor (Di Luzio et al., 2002). It uses a gridded digital elevation model (DEM), polygon/grid coverages of soils and land use, and point coverages of weather stations as basic input to the model (Figure 30). In July 2006, SWAT2005 and the analogue AVSWAT-X versions were made publicly available (Neitsch et al., 2005).

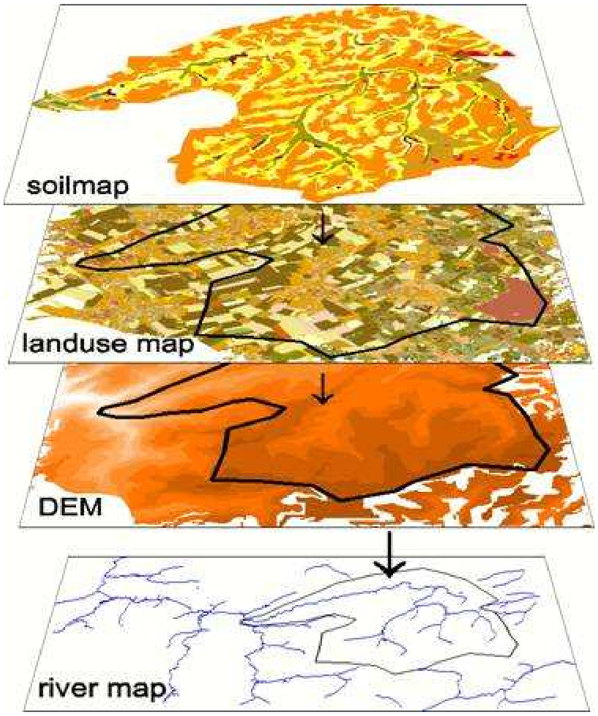


Figure 30. Overlay of different information layers connected to the SWAT-model.

4.2.2 Watershed configuration

The first step in setting up a watershed simulation is to partition the watershed into subunits. SWAT allows several different subunits or objects to be defined within a watershed (Neitsch et al., 2002a):

- Subbasins
  - unlimited number of hydrologic response units (HRUs) (1 per subbasin required)
  - one pond (optional) (1 per subbasin)
  - one wetland (optional) (1 per subbasin)
- Reach/main channel segments (1 per subbasin)
- Impoundments on main channel network (optional)
- Point sources (optional)

The first level of subdivision is the subbasin. Subbasins possess a geographic position in the watershed and are spatially related to one another, e.g. the outflow from subbasin 5 enters subbasin 7 (Figure 31). They are based on the threshold area which defines the minimum drainage area required to form the origin of a stream. A subbasin will contain at least one HRU, a tributary channel and a main channel or reach. Two types of impoundments, a pond and/or wetland, may also be defined in a subbasin.

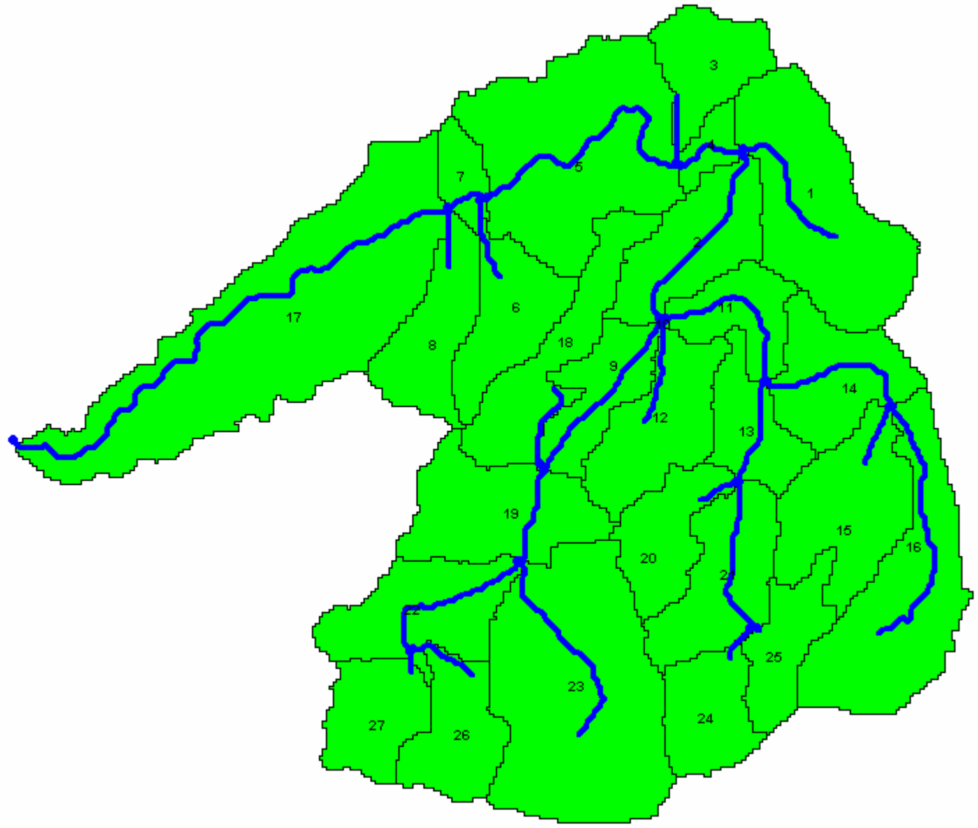


Figure 31. Subbasin delineation of the Nil catchment.

Within the subbasins, hydrologic response units (HRU's) are defined. An HRU is not synonymous to a field. Rather it is the total area in the subbasin with a particular combination of land use, management and soil. While individual fields with a specific land use, management and soil may be scattered throughout a subbasin, these areas are lumped together to form one HRU. Implicit in the concept of the HRU is the assumption that there is no interaction between HRU's in one subbasin. Loadings (runoff with sediment, nutrients, etc. transported by the runoff) from each HRU are calculated separately and then summed together to determine the total loadings from the subbasin. If the interaction of one land use area with another is important, rather than defining those land use areas as HRU's they should be defined as subbasins. It is only at the subbasin level that spatial relationships can be specified. As a general rule, a given subbasin should have 1-10 HRU's. For those wishing to incorporate more complexity into a dataset, it is recommended to define a larger number of subbasins in the watershed rather than many HRU's within a few subbasins.

4.2.3 The land phase of the hydrologic cycle

The water quantity processes simulated by SWAT include precipitation, evapotranspiration, surface run-off, lateral subsurface flow, groundwater flow and river flow. The land phase of the hydrologic cycle is based on the following water balance equation:

$$SW_t = SW_0 + \sum_{i=1}^{t} (R_{day} - Q_{surf} - E_a - w_{seep} - Q_{gw}) \qquad \text{(eq. 4-1)}$$

where, t is the time (days), SW_t is the final soil water content (mm H_2O), SW_0 is the initial soil water content (mm H_2O), R_{day}, Q_{surf}, E_a, w_{seep} and Q_{gw} are respectively the daily amounts of precipitation, runoff, evapotranspiration, percolation and return flow (mm H_2O). The most important processes involved in the fate of pesticides are briefly described in the following sections. More detailed descriptions of all processes can be found in the SWAT manual (Neitsch et al., 2002a).

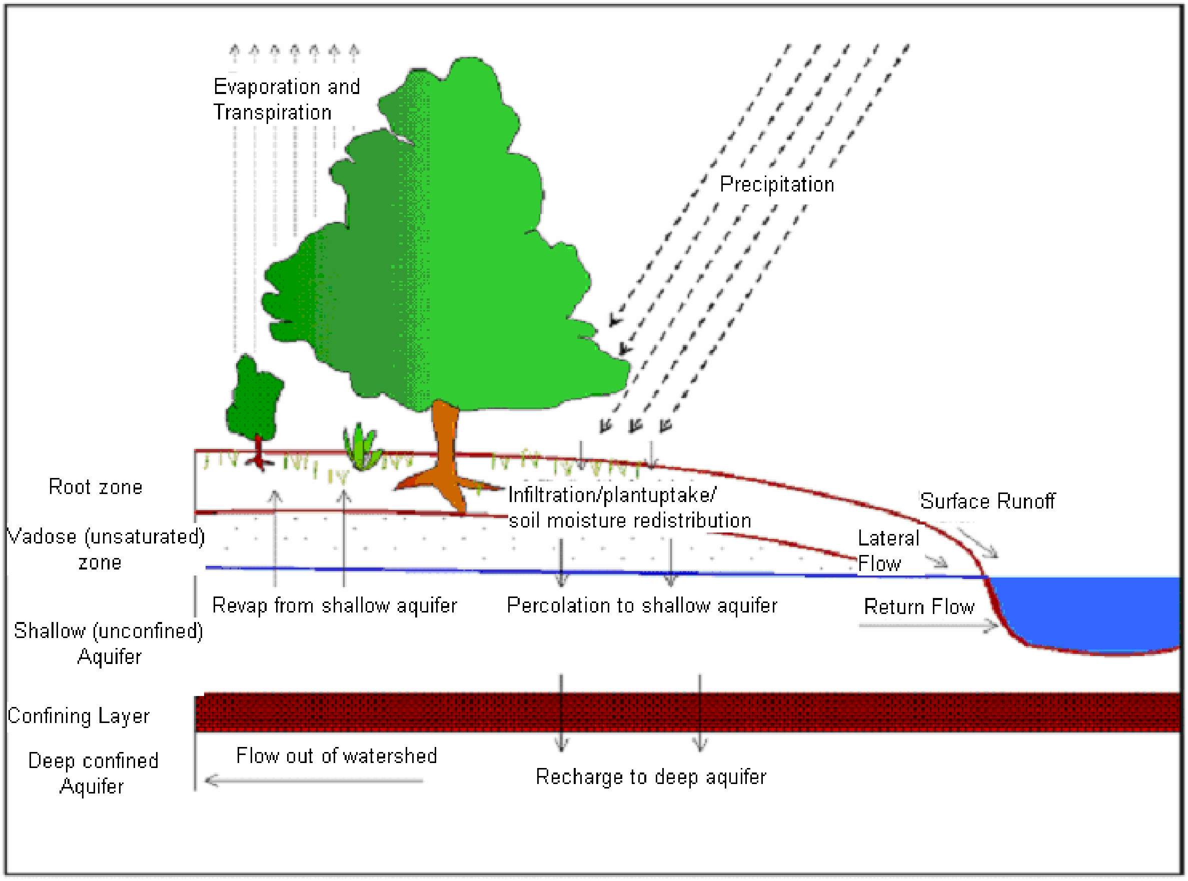


Figure 32. Schematic representation of the hydrologic cycle in SWAT (Neitsch et al., 2002a).

The soil horizon is represented by soil layers with a determined horizon thickness, certain basic soil properties such as percentage of sand, clay and silt, their texture class, percentage of carbon, their hydraulic conductivity (K_{sat}) and their available water capacity (AWC).

Weather generator

SWAT requires daily values of precipitation, maximum and minimum temperature, solar radiation, relative humidity and wind speed. The user may choose to read these inputs from a file or generate the values using monthly average data summarized over a number of years. SWAT includes the WXGEN weather generator model (Sharpley and Williams, 1990) to generate climatic data or to fill in gaps in measured records. The model generates a set of weather data for each subbasin. This weather generator was developed for the whole U.S. If the user prefers a different weather generator, daily input values for the different weather parameters may be generated with an alternative model and formatted for input to SWAT.

Canopy storage

Canopy storage is the water intercepted by vegetative surfaces (the canopy) where it is held and made available for evaporation.

Evapotranspiration

Evapotranspiration is a collective term that includes all processes by which water at the earth’s surface is converted to water vapor. It includes evaporation from the plant canopy, transpiration, sublimation and evaporation from the soil. The model computes evaporation from soils and plants separately as described by Ritchie (1972). Potential evapotranspiration is the rate at which evapotranspiration would occur from a large area completely and uniformly covered with growing vegetation which has access to an unlimited supply of soil water. The model offers three options for estimating potential evapotranspiration: Hargreaves (Hargreaves et al., 1985), Priestley-Taylor (Priestley and Taylor, 1972), and Penman-Monteith (Monteith, 1965). Actual soil water evaporation is estimated by using exponential functions of soil depth and water content. Plant transpiration is simulated as a linear function of potential evapotranspiration and leaf area index.

Surface runoff and infiltration

SWAT provides two methods for estimating surface runoff: the SCS curve number procedure (SCS, 1972) and the Green & Ampt (1911) infiltration method. The Green & Ampt method requires sub-daily precipitation data and is due to data limitations not further discussed in this dissertation. The SCS runoff equation is an empirical model that came into common use in the 1950s. It was the product of more than 20 years of studies involving rainfall-runoff relationships from small rural watersheds across the U.S. The SCS curve number equation is (SCS, 1972):

$$Q_{surf} = \frac{(R_{day} - I_a)^2}{R_{day} - I_a + S_S} \qquad \text{(eq. 4-2)}$$

where Q_{surf} is the accumulated runoff or rainfall excess, R_{day} is the rainfall depth for the day, I_a is the initial abstractions which include surface storage, interception and infiltration prior to runoff. S_S is the retention parameter which varies spatially due to changes in soils, land use, management and slope and temporally due to changes in soil water content. All units are mm H_2O. The retention parameter is defined as:

$$S_S = 25.4(\frac{1000}{CN} - 100) \qquad \text{(eq. 4-3)}$$

where CN is the curve number for the day. Runoff will occur only when $R_{day} > I_a$.

For peak runoff rate predictions, SWAT uses a modification of the rational method. The peak runoff rate is used to predict sediment losses and is based on the assumption that if a rainfall of intensity i begins instantaneously and continues indefinitely, the rate of runoff will increase until the time of concentration, $t = t_{conc}$, when the entire subbasin area is contributing to the flow at the outlet. The rational formula is:

$$q_{peak} = \frac{C_{runoff} \times i \times Area}{3.6} \qquad \text{(eq. 4-4)}$$

where q_{peak} is the peak runoff rate ($m^3\ s^{-1}$), C_{runoff} is the runoff coefficient, i is the rainfall intensity (mm/hr), $Area$ is the subbasin area (km^2) and 3.6 is a unit conversion factor. The runoff coefficient is the ratio of the inflow rate, $Area \times i$, to the peak discharge rate, q_{peak}. The coefficient will vary from storm to storm and is calculated with the equation:

$$C_{runoff} = \frac{Q_{surf}}{R_{day}} \qquad \text{(eq. 4-5)}$$

where Q_{surf} is the surface runoff (mm H_2O) and R_{day} is the rainfall for the day (mm H_2O).

In the modified rational formula, the peak runoff rate is a function of the proportion of daily precipitation that falls during the subbasin t_{conc}, the daily surface runoff volume and the subbasin time of concentration. The proportion of rainfall occurring during the subbasin t_{conc} is estimated as a function of total daily rainfall using a stochastic technique. The subbasin time of concentration is estimated using Manning's formula considering both overland and channel flow. The modified rational formula used by SWAT to estimate peak flow rate is:

$$q_{peak} = \frac{\alpha_{tc} \times Q_{surf} \times Area}{3.6 \times t_{conc}} \qquad \text{(eq. 4-6)}$$

where α_{tc} is the fraction of daily rainfall that occurs during the time of concentration, t_{conc} is the time of concentration of the subbasin (hr) and 3.6 is a unit conversion factor.

Redistribution

Redistribution refers to the continued movement of water through a soil profile after the input of water (via precipitation or irrigation) has ceased at the soil surface. The redistribution component of SWAT uses a storage routing technique to predict flow through each soil layer in the root zone. Downward flow, or percolation, occurs when field capacity of a soil layer is exceeded and the layer below is not saturated. The flow rate is governed by the saturated conductivity of the soil layer. Redistribution is affected by soil temperature. If the temperature in a particular layer is 0°C or below, no redistribution is allowed from that layer.

Lateral subsurface flow

Lateral subsurface flow, or interflow, is stream flow contribution which originates below the surface but above the zone saturated with water. Lateral subsurface flow in the soil profile (0-2m) is calculated simultaneously with redistribution. A kinematic storage model (Sloan et al., 1983) is used to predict lateral flow in each soil layer. The model accounts for variation in conductivity, slope and soil water content.

Return flow

Return flow, or base flow, is the volume of stream flow originating from groundwater. SWAT partitions groundwater into two aquifer systems: a shallow, unconfined aquifer which contributes return flow to streams within the watershed and a deep, confined aquifer which contributes return flow to streams outside the watershed (Arnold et al., 1993). The latter can be seen as a loss of the watershed system. Water percolating past the bottom of the root zone is partitioned into two fractions—each fraction becomes recharge for one of the aquifers. In addition to return flow, water stored in the shallow aquifer may replenish moisture in the soil profile in very dry conditions or be directly removed by plant. Water in the shallow or deep aquifer may be removed by pumping.

Land cover and plant growth

SWAT utilizes a single plant growth model to simulate all types of land covers. The model is able to differentiate between annual and perennial plants. Annual plants grow from the planting date to the harvest date or until the accumulated heat units equal the potential heat units for the plant. Perennial plants maintain their root systems throughout the year, becoming dormant in the winter months. They resume growth when the average daily air temperature exceeds the minimum, or base, temperature required. The plant growth model is used to assess removal of water and nutrients from the root zone, transpiration, and biomass/yield production.

Erosion

Erosion and sediment yield are estimated for each HRU with the Modified Universal Soil Loss Equation (MUSLE) (Williams, 1975). While the USLE uses rainfall as an indicator of erosive energy, MUSLE uses the amount of runoff to simulate erosion and sediment yield. The substitution results in a number of benefits: the prediction accuracy of the model is increased, the need for a delivery ratio is eliminated, and single storm estimates of sediment yields can be calculated. The modified universal soil loss equation (Williams, 1995) is:

$$sed = 11.8 \times (Q_{surf} \times q_{peak} \times area_{hru})^{0.56} \times K_{USLE} \times C_{USLE} \times P_{USLE} \times LS_{USLE} \times CFRG$$

(eq. 4-7)

where sed is the sediment yield on a given day (metric tons), Q_{surf} is the surface runoff volume (mm H_2O), q_{peak} is the peak runoff rate (m³/s), $area_{hru}$ is the area of the HRU (ha), K_{USLE} is the soil erodibility factor, C_{USLE} is the USLE cover and management factor, P_{USLE} is the USLE support practice factor, LS_{USLE} is the USLE topographic factor and *CFRG* is the coarse fragment factor. The hydrology model supplies estimates of runoff volume Q_{surf} and peak runoff rate q_{peak} which, with the subbasin area, are used to calculate the runoff erosive energy variable.

Some soils erode more easily than others even when all other factors are the same. This difference is termed soil erodibility and is caused by the properties of the soil itself. Direct measurement of the erodibility factor K_{USLE} is time consuming and costly. Wischmeier et al. (1971) developed a general equation to calculate the soil erodibility factor when the silt and very fine sand content make up less than 70% of the soil particle size distribution.

$$K_{USLE} = \frac{0.00021 \times M_{part}^{\;1.14} \times (12 - OM) + 3.25 \times (c_{soilstr} - 2) + 2.5 \times (c_{perm} - 3)}{100} \qquad \text{(eq. 4-8)}$$

where K_{USLE} is the soil erodibility factor, M_{part} is the particle-size parameter, *OM* is the percent organic matter (%), $c_{soilstr}$ is the soil structure code used in soil classification and c_{perm} is the profile permeability class. The particle-size parameter, M_{part}, is calculated as follows:

$$M_{part} = (m_{silt} + m_{vfs}) \times (100 - m_c) \qquad \text{(eq. 4-9)}$$

where m_{silt} is the percent silt content (0.002-0.05 mm diameter particles), m_{vfs} is the percent very fine sand content (0.05-0.10 mm diameter particles), and m_c is the percent clay content (< 0.002 mm diameter particles). The percent organic matter content, *OM*, of a layer can be calculated:

$$OM = 1.72 \times orgC \qquad \text{(eq. 4-10)}$$

where *orgC* is the percent organic carbon content of the layer (%).

The crop management factor C_{USLE} is defined as the ratio of soil loss from land cropped under specified conditions to the corresponding loss from clean-tilled, continuous fallow (Wischmeier and Smith, 1978). The plant canopy affects erosion by reducing the effective rainfall energy of intercepted raindrops. Because plant cover varies during the growth cycle of the plant, SWAT updates C_{USLE} daily. Equations can be found in the SWAT manual (Neitsch et al., 2003).

The support practice factor, P_{USLE}, is defined as the ratio of soil loss with a specific support practice to the corresponding loss with up-and-down slope culture. Support practices include contour tillage, strip cropping on the contour and terrace systems. Values for P_{USLE} for the different practices are listed in the SWAT manual (Neitsch et al., 2003).

The topographic factor, LS_{USLE}, is the expected ratio of soil loss per unit area from a field slope to that of a standard field with a length of 22.1 metres and a uniform slope of 9 percent under otherwise identical conditions. The topographic factor can be calculated by means of a formula of Wischmeier and Smith (1978) and can be found in the SWAT manual (Neitsch et al., 2003).

Pesticides

Although SWAT does not simulate stress on the growth of a plant due to the presence of weeds, damaging insects, and other pests, pesticides may be applied to an HRU to study the movement of the chemical in the watershed. SWAT simulates pesticide movement into the stream network via surface runoff (in solution and sorbed to sediment transported by the runoff), and into the soil profile and aquifer by percolation (in solution). The equations used to model the movement of pesticide in the land phase of the hydrologic cycle were adopted from GLEAMS (Leonard et al., 1987). The movement of the pesticide is controlled by its solubility, degradation half-life, and soil organic carbon adsorption coefficient. Pesticide on plant foliage and in the soil degrade exponentially according to the appropriate half-life. Pesticide transport by water and sediment is calculated for each runoff event and pesticide leaching is estimated for each soil layer when percolation occurs.

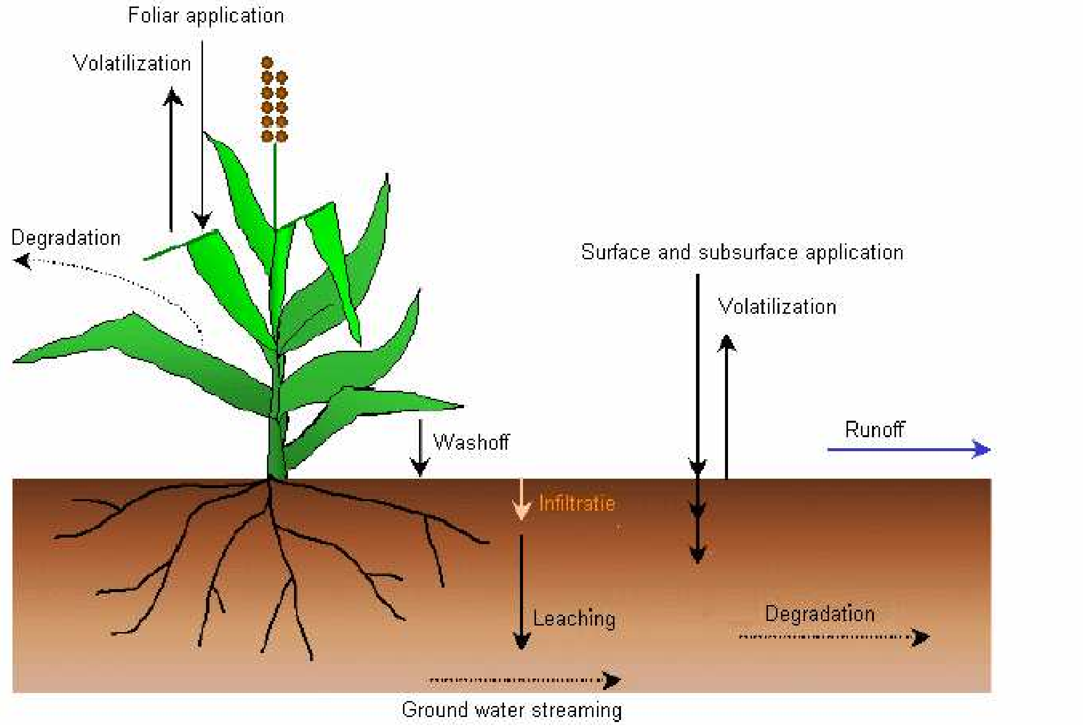


Figure 33. Pesticide fate and transport in the land phase of SWAT (Neitsch et al., 2003).

Management

SWAT allows the user to define management practices taking place in every HRU. The user may define the beginning and the ending of the growing season, specify timing and amounts of fertilizer, pesticide and irrigation applications as well as timing of tillage operations. At the end of the growing season, the biomass may be removed from the HRU as yield or placed on the surface as residue. In addition to these basic management practices, operations such as grazing, automated fertilizer and water applications, and incorporation of every conceivable management option for water use are available. Also routines to calculate sediment and nutrient loadings from urban areas are included.

4.2.4 The routing phase of the hydrologic cycle

Once SWAT determines the loadings of water, sediment, nutrients and pesticides to the main channel, the loadings are routed through the stream network of the watershed using a command structure similar to that of HYMO (Williams and Hann, 1973). In addition to keeping track of mass flow in the channel, SWAT models the transformation of chemicals in the stream and streambed. Figure 34 illustrates the different in-stream processes modeled by SWAT.

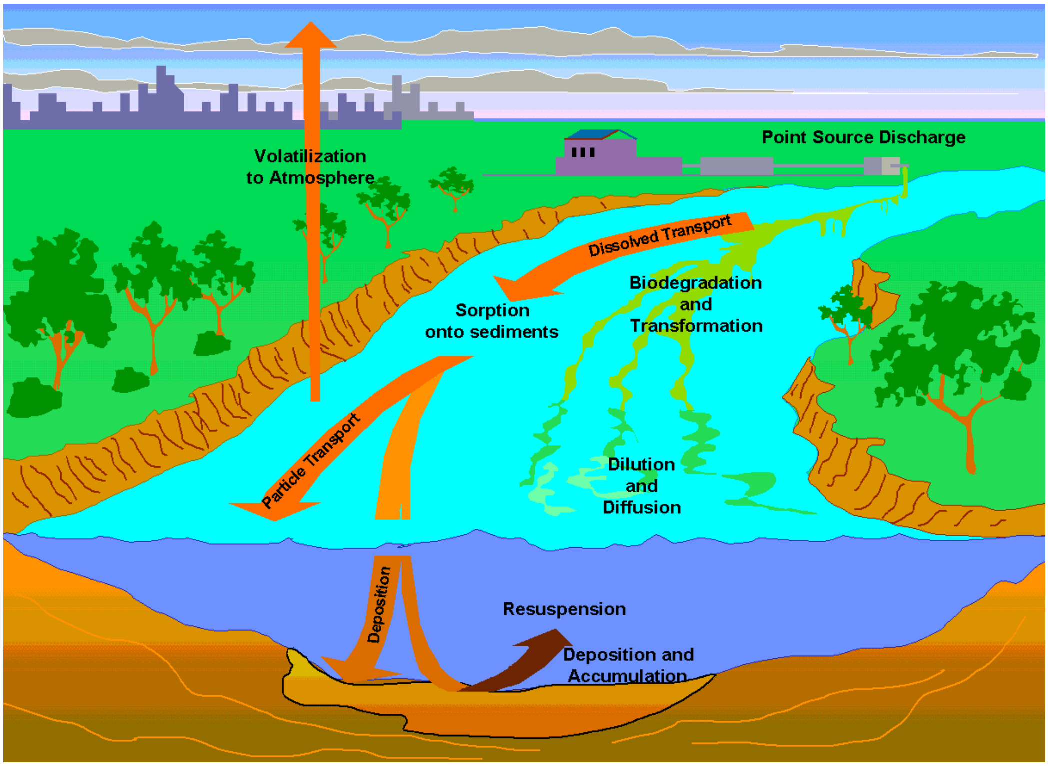


Figure 34. In-stream processes modelled by SWAT (Neitsch et al., 2003).

Water routing

As water flows downstream, a portion may be lost due to evaporation and transmission through the bed of the channel. Another potential loss is removal of water from the channel for agricultural or human use. Flow may be supplemented by the fall of rain directly on the channel and/or addition of water from point source discharges. Flow is routed through the channel using a variable storage coefficient method developed by Williams (1969) or the Muskingum routing method. Manning's equation for uniform flow in a channel is used to calculate the rate and velocity of flow in a reach segment for a given time step:

$$q_{ch} = \frac{A_{ch} \times R_{ch}^{2/3} \times slp_{ch}^{1/2}}{n} \qquad \text{(eq. 4-11)}$$

$$v_c = \frac{R_{ch}^{2/3} \times slp_{ch}^{1/2}}{n} \qquad \text{(eq. 4-12)}$$

where q_{ch} is the rate of flow in the channel (m^3/s), A_{ch} is the cross-sectional area of flow in the channel (m^2), R_{ch} is the hydraulic radius for a given depth of flow (m), slp_{ch} is the slope along the channel length (m/m), n is Manning's "n" coefficient for the channel and v_c is the flow velocity (m/s). The cross-sectional area of flow is calculated:

$$A_{ch} = (W_{btm} + z_{ch} \times depth) \times depth \qquad \text{(eq. 4-13)}$$

where W_{btm} is the bottom width of the channel (m), z_{ch} is the inverse of the channel slope and *depth* is the depth of water in the channel (m).

Water storage in the reach at the end of the time step is calculated:

$$V_{stored,2} = V_{stored,1} + V_{in} - V_{out} - tloss - E_{ch} + diversions + V_{bnk} \qquad \text{(eq. 4-14)}$$

where $V_{stored,2}$ is the volume of water in the reach at the end of the time step, $V_{stored,1}$ is the volume of water in the reach at the beginning of the time step, V_{in} is the volume of water flowing into the reach during the time step, V_{out} is the volume of water flowing out of the reach during the time step, *tloss* is the volume of water lost from the reach via transmission through the bed, E_{ch} is the evaporation from the reach for the day, *diversions* is the volume of water added to the reach by rainfall or point source discharges or removed from the reach for agricultural or human use and V_{bnk} is the volume of water added to the reach via return flow from bank storage. All units are m^3 H_2O.

During periods when a stream receives no groundwater contributions, it is possible for water to be lost from the channel via transmission through the side and bottom of the channel. Transmission losses are estimated with the equation:

$$tloss = K_{ch} \cdot TT \cdot P_{ch} \cdot L_{ch} \qquad \text{(eq. 4-15)}$$

where *tloss* accounts for the channel transmission losses (m^3 H_2O), K_{ch} is the effective hydraulic conducti-vity of the channel alluvium (mm/hr), TT is the flow travel time in the reach (hr), P_{ch} is the wetted perimeter (m), and L_{ch} is the channel length (km). Transmission losses from the main channel are assumed to enter bank storage or the deep aquifer. Travel time is computed by dividing the volume of water in the channel by the flow rate:

$$TT = V_{stored}/q_{out} \qquad \text{(eq. 4-16)}$$

where TT is the travel time (s), V_{stored} is the storage volume (m³ H_2O) and q_{out} is the discharge rate (m³/s). Evaporation losses from the reach are calculated as follows:

$$E_{ch} = coef_{ev} \cdot E_o \cdot L_{ch} \cdot W \cdot TT/24 \qquad \text{(eq. 4-17)}$$

where E_{ch} is the evaporation from the reach for the day (m³ H2O), $coef_{ev}$ is an evaporation coefficient, E_o is potential evaporation (mm H2O), L_{ch} is the channel length (km), W is the channel width at water level (m), and TT is the traveling time (hr).

Sediment routing

In SWAT the maximum amount of sediment that can be transported from a reach segment is a function of the peak channel velocity. Available stream power is used to reentrain loose and deposited material until all of the material is removed. Excess stream power causes bed degradation. Bed degradation is adjusted for stream bed erodibility and cover.

The peak channel velocity, $v_{ch,pk}$, is calculated as follows:

$$v_{ch,pk} = \frac{q_{ch,pk}}{A_{ch}} \qquad \text{(eq. 4-18)}$$

where $q_{ch,pk}$ is the peak flow rate (m³/s) and A_{ch} is the cross-sectional area of flow in the channel (m²). The peak flow rate is defined as:

$$q_{ch,pk} = prf \times q_{ch} \qquad \text{(eq. 4-19)}$$

where prf is the peak rate adjustment factor and q_{ch} is the average rate of flow (m³/s). Calculations of the average rate of flow, q_{ch}, and the cross-sectional area, A_{ch}, are given in equations 4-11 and 4-13. Because SWAT can not directly calculate the sub-daily hydrograph, the *prf* variable was incorporated to allow adjustment for the effect of the peak flow rate on sediment routing. This variable impacts channel degradation. If no value for *prf* is entered, the model will set *prf* = 1.0 (Srinivasan, personnal communication 2006).

The maximum amount of sediment that can be transported from a reach segment is calculated:

$$conc_{sed,ch,mx} = c_{sp} \times v_{ch,pk}{}^{sp\exp} \qquad \text{(eq. 4-20)}$$

where $conc_{sed,ch,mx}$ is the maximum concentration of sediment that can be transported by the water (ton/m³ or kg/L), c_{sp} is a coefficient defined by the user, $v_{ch,pk}$ is the peak channel velocity (m/s) and *spexp* is an exponent defined by the user. The exponent, *spexp*, normally varies between 1.0 and 2.0 and was set at 1.5 as in the original Bagnold stream power equation (1977) (Arnold et al., 1995).

The maximum concentration of sediment calculated with equation 4-17 is compared to the concentration of sediment in the reach at the beginning of the time step, $conc_{sed,ch,i}$.

If $conc_{sed,ch,i} > conc_{sed,ch,mx}$, deposition is the dominant process in the reach segment and the net amount of sediment deposited is calculated:

$$sed_{dep} = (conc_{sed,ch,i} - conc_{sed,ch,mx}) \times V_{ch} \qquad \text{(eq. 4-21)}$$

where sed_{dep} is the amount of sediment deposited in the reach segment (metric tons), $conc_{sed,ch,i}$ is the initial sediment concentration in the reach (ton/m³ or kg/L), $conc_{sed,ch,mx}$ is the maximum concentration of sediment that can be transported by the water (ton/m³ or kg/L) and V_{ch} is the volume of water in the reach segment (m³ H_2O).

If $conc_{sed,ch,i} < conc_{sed,ch,mx}$, degradation is the dominant process in the reach segment and the net amount of sediment reentrained is calculated:

$$sed_{\deg} = (conc_{sed,ch,mx} - conc_{sed,ch,i}) \times V_{ch} \times K_{CH} \times C_{CH} \qquad \text{(eq. 4-22)}$$

where sed_{deg} is the amount of sediment reentrained in the reach segment (metric tons), K_{CH} is the channel erodibility factor (cm/hr/Pa) and C_{CH} is the channel cover factor. The channel erodibility factor, K_{CH}, is conceptually similar to the soil erodibility factor used in the USLE equation. Channel erodibility is a function of properties of the bed or bank materials. Channel erodibility can be measured with a submerged vertical jet device (see SWAT manual: Neitsch et al., 2003). In general, values for channel erodibility are an order of magnitude smaller than values for soil erodibility. The channel cover factor, C_{CH}, is defined as the ratio of degradation from a channel with a specified vegetative cover to the corresponding degradation from a channel with no vegetative cover. The vegetation affects degradation by reducing the stream velocity, and consequently its erosive power, near the bed surface. C_{CH} is set to a value between 0.0 and 1.0. A value of 0.0 indicates that the channel is completely protected from degradation by cover while a value of 1.0 indicates there is no vegetative cover on the channel.

Once the amount of deposition and degradation has been calculated, the final amount of sediment in the reach is determined:

$$sed_{ch,i+1} = sed_{ch,i} - sed_{dep} + sed_{\mathrm{deg}} \qquad \text{(eq. 4-23)}$$

where $sed_{ch,\ i+1}$ is the amount of suspended sediment in the reach (metric tons) and $sed_{ch,i}$ is the amount of suspended sediment in the reach at the beginning of the time period (metric tons). The amount of sediment transported out of the reach is calculated:

$$sed_{out} = sed_{ch} \times \frac{V_{out}}{V_{ch}} \qquad \text{(eq. 4-24)}$$

where sed_{out} is the amount of sediment transported out of the reach (metric tons) and V_{out} is the volume of outflow during the time step (m³ H_2O).

Pesticide routing

While an unlimited number of pesticides may be applied to the HRUs, only one pesticide may be routed through the channel network of the watershed due to the complexity of the processes simulated. As for the nutrients, the total pesticide load in the channel is partitioned into dissolved and sediment-attached components. While the dissolved pesticide is transported with water, the pesticide attached to sediment is affected by sediment transport and deposition processes. Pesticide transformations in the dissolved and sorbed phases are governed by first-order decay relationships. The major in-stream processes simulated by the model are settling, burial, resuspension, volatilization, diffusion and transformation.

This can be written into mass balance equations for the well-mixed reach segment and the well-mixed sediment layer:

$$\Delta pst_{rchwtr} = pst_{in} - (pst_{sol,o} + pst_{sorb,o}) - pst_{\deg,wtr} - pst_{vol,wtr} - pst_{stl,wtr} + pst_{rsp,wtr} \pm pst_{dif} \quad \text{(eq. 4-25)}$$

$$\Delta pst_{rchsed} = -pst_{\deg,sed} + pst_{stl,wtr} - pst_{rsp,wtr} - pst_{bur} \pm pst_{dif} \quad \text{(eq. 4-26)}$$

where Δpst_{rchwtr} is the change in pesticide mass in the water layer; Δpst_{rchsed} is the change in pesticide mass in the sediment layer; pst_{in} is the pesticide added to the reach segment via inflow; $pst_{sol,o}$ and $pst_{sorb,o}$ are the amounts of respectively dissolved and particulate pesticide removed via outflow; $pst_{deg,wtr}$, $pst_{vol,wtr}$, $pst_{stl,wtr}$, $pst_{rsp,wtr}$ are the amounts of pesticide removed from the water via respectively degradation, volatilization, settling and resuspension; pst_{dif} is the amount of pesticide transferred between the water and sediment by diffusion; $pst_{deg,sed}$ and pst_{bur} are the amounts of pesticide removed from the sediment respectively via degradation and via burial. All units are mg pesticide.

Pesticides will partition into particulate and dissolved forms. The fraction of pesticide in each phase is a function of the pesticide's partition coefficient and the reach segment's suspended solid concentration:

$$F_d = \frac{1}{1 + K_d \times conc_{sed}} \quad \text{(eq. 4-27)}$$

$$F_p = \frac{K_d \times conc_{sed}}{1 + K_d \times conc_{sed}} = 1 - F_d \quad \text{(eq. 4-28)}$$

where F_d and F_p are respectively the fraction of total pesticide in the dissolved and in the particulate phase, K_d is the pesticide partition coefficient (m³/g) and $conc_{sed}$ is the concentration of suspended solids in the water (g/m³). The pesticide partition coefficient can be estimated from the octanol-water partition coefficient K_{ow} (Chapra, 1997):

$$K_d = 3.085 \times 10^{-8} \times K_{ow} \qquad \text{(eq. 4-29)}$$

Values for K_{ow} have been published for many chemicals. If a published value cannot be found, it can be estimated from solubility data (Chapra, 1997):

$$\log(K_{ow}) = 5.00 - 0.67 \times \log(pst'_{sol}) \qquad \text{(eq. 4-30)}$$

where pst'_{sol} is the pesticide solubility (µmoles/L).

The degradation, volatilisation, settling, diffusion, resuspension and burial processes are all written as first order reactions and are described in detail in the SWAT manual (Neitsch et al., 2003).

4.2.5 Conclusions

The SWAT model is able to simulate different processes both in the land phase and in the routing phase of the hydrologic cycle influencing the fate of pesticides. Disadvantages of the model are the lack of point losses towards the river on the day of application and the lack of closed mass balances. Given the importance of point sources, this source of pollution should be added to the source code of the SWAT model. Mass balances need to be checked.

4.3 Sensitivity analysis for hydrology and pesticide supply

4.3.1 Introduction

Dynamic models form suitable instruments for risk assessment of toxic components in natural river systems (Deksissa and Vanrolleghem, 2004). By using exposure models under time-varying conditions, risks can be determined more realistically as compared to a steady state or a static approach (Verdonck et al., 2002). Advantages consist in better predictions of impacts of accidental discharges, of effects of specific climatological or seasonal variations and of evolutions in water quality. A prominent example is the dynamic modelling of pesticides.

The first step in the development of a dynamic exposure model for pesticides is to build a reliable hydrological model (Novotny and Olem, 1994). The hydrology of a river catchment will determine to a great extent the transport of solutes, suspended sediments and colloids in the water system. SWAT was found to be a suitable tool for modelling non-point source pollution on catchment scale. A SWAT model not only allows hydrological predictions but also predictions of pesticide loads at different locations along the river as function of time.

Pesticide modelling is much more complex than hydrologic modelling. As mentioned by Rickert (1993) and Ongley (1996), the modelling of pesticides is situated on a high level of scientific complexity and a lot of processes are not yet completely understood (Warren et al., 2003). They require a lot of additional input data that are often unavailable, incomplete or uncertain. Nevertheless, they are of great importance for a correct representation of the pesticide fate (Neitsch et al., 2002b). Examples are the application rates and dates of a particular pesticide, which depend on the farmer and vary from year to year (Beernaerts et al., 2002). Correct and detailed information is generally not available and lumped assessments for the entire catchment do not give reliable results, especially when spatial and temporal dynamics at small scales are of interest.

The objectives of this study are twofold: first, to determine the most influential model parameters, which results in a reduced set of parameters for model calibration and second, to gain insight into the important processes determining the fate of pesticides. Moreover, knowledge of the most important sources of uncertainty for the modelling of pesticide fate is useful in anticipation of oriented data collection for future pesticide modelling.

4.3.2 Methods

4.3.2.1 Catchment area

In this study we focus on the Nil basin, which was described in detail in Chapter 3. The Nil catchment was selected because it is a well documented basin, studied in detail in terms of pesticide application (Beernaerts et al., 2002).

4.3.2.2 Model adaptations

This paragraph focuses on the pesticide atrazine. Since the monitoring of in-stream atrazine concentrations showed clear peaks during non-rainy periods and even non-windy days, it was concluded that significant direct losses occur during the pesticides application dates (e.g. through the clean up of spray equipment, leaking tools, processing of spray waste etc.) (Beernaerts et al., 2002; see Section 3.3.2). Therefore, the SWAT codes were slightly modified in order to consider these direct losses by changing the meaning of the parameter 'AP_EF' (application efficiency coefficient) from indicating the process whereby a fraction of the applied rate is lost from the system towards the process by which a fraction of the applied pesticide is diverted directly to the river system. This modification is allowed in this case, in which pesticides are not applied by airplanes but directly on the fields by spray equipments and where losses outside the system are not expected to be significant. The direct losses are considered to be lower than 5% of the applied amount (see Figure 18), but their impact is nevertheless significant since these losses are directly ending up in the river system.

4.3.2.3 Input data

For the Nil-catchment, weather data from 1998 to 2002 were obtained from the Belgian Royal Meteorological Institute for the stations of Chastre and Ernage. These data include daily precipitation and daily maximum and minimum temperatures.

Because the quality of the performed calculations will strongly be influenced by the detail of the maps used, special attention was given to utilise high resolution maps. A 30 m resolution DEM created by local government authorities was added to the AVSWAT model-interface (Figure 35).

The 1999 land use map with a spatial resolution of 30 m, was obtained from Romanowicz et al. (2003). They combined Landsat TM satellite images with the SIGEC data set. The SIGEC data set includes information of crop distribution over a catchment area and is based on the claims of farmers for EU subsidies. A standard classification resulted in 50 classes, which was reduced to 23 land use classes which can be handled by the SWAT model (Figure 35). Crop rotation occurs, but results only in minor switches on a local scale. As the SWAT model is lumping areas and crop rotations will occur within the same subbasin area, the assumption of using the same land use map for different simulation years is justified.

A detailed soil map was created by digitizing the required parts of the maps 117E, 130E and 130W; all at scale 1:25.000 (IRSIA, 1961) (Figure 35). The basic soil properties (percentage of sand, clay and silt, the texture class, the percentage of carbon and the horizon thickness) were obtained from the analytical database AARDEWERK (Van Orshoven and Vandenbroucke, 1993). In order to calculate the hydraulic conductivity (Ksat), pedotransfer functions from the HYPRES database were used (Wösten et al., 1999). The available water capacity (AWC) was estimated from water contents at pF 4.2 and 2.5 using the RETC-program (van Genuchten et al., 1991).

Pesticide data were collected by CODA (2003). To this end, inquiries were conducted during springs of 1998 until 2002. The farmers were asked to give as detailed information as possible concerning the amount of pesticide they applied, the application dates, the kinds of pesticides they utilised for their different crops and the treated surface. 42% of the farmers could give detailed information. In this study, we focus on the use of atrazine on corn during the growth season of 1999, when the application rate amounted to 0.783 kg ha^{-1}. All applications occurred in the month May.

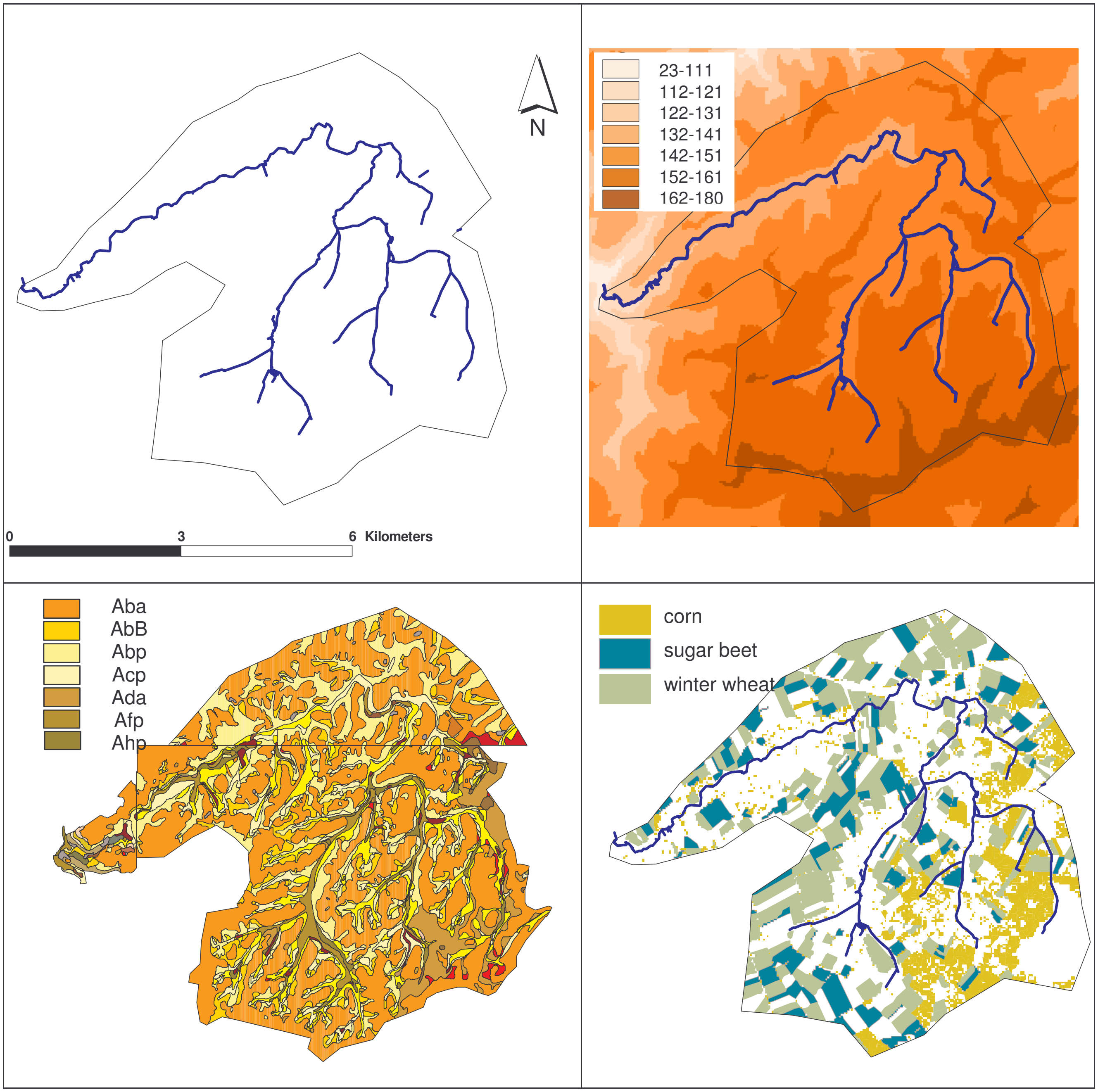


Figure 35. The different data layers used in the SWAT model: the location of the river Nil, the digital elevation model (m), the digitized soil map and the land use map (Romanowicz et al., 2003) of the Nil catchment.

For the simulation, the Nil was divided into 27 sub-basins and reaches. The sub-basins are further divided into 227 HRU's, as defined by land use and soil type.

4.3.2.4 Sensitivity analysis for the model parameters

Sensitivity analysis and parameter reduction

A complex hydrologic model is generally characterised by a multitude of parameters. Due to spatial variability, measurement error, incompleteness in description of both the elements and processes present in the system, etc., the values of many of these parameters will not be exactly known. Therefore, to achieve a good fit between simulated and measured data, models need to be conditioned to match reality by optimising their internal parameters. This model calibration procedure can be either manual or automated. In both cases, it is advisable to be supported by techniques such as sensitivity analysis. A parameter sensitivity analysis provides insights on which parameters contribute most to the output variance due to input variability. Based on this information, a calibration can be performed for a limited number of influential parameters. The performance of the calibration may then be evaluated by performance criteria such as e.g. the Nash-Sutcliffe coefficient of efficiency (Nash and Sutcliffe, 1970).

The LH-OAT sensitivity analysis

In this study, we performed an LH-OAT sensitivity analysis. The LH-OAT method combines the One-factor-At-a-Time (OAT) design and Latin Hypercube (LH) sampling by taking the Latin Hypercube samples as initial points for an OAT-design (Figure 36) (van Griensven et al., 2006a).

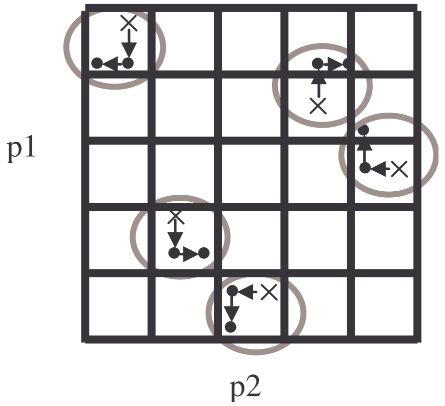


Figure 36. Illustration of LH-OAT sampling of values for a two parameters model where × represent the Monte-Carlo points and • the OAT points (van Griensven et al., 2006a).

Latin-Hypercube sampling (McKay, 1988) is a sophisticated way to perform random sampling such as Monte-Carlo sampling, resulting in a robust analysis requiring not too many runs (Saltelli et al., 2002). It subdivides the distribution of each parameter into *m* ranges, each with a probability of occurrence equal to 1/*m*. Random values of the parameters are generated, such that each range is sampled only once. For each of the *m* random combinations of the parameters an OAT loop is performed.

In the OAT design (Morris, 1991), only one input parameter is modified between two successive runs of the model. Therefore, the change in model output (e.g. SSE of the surface runoff) can then be unambiguously attributed to such a parameter modification by means of an elementary partial effect Si,j defined by equation 4-28.

$$S_{i,j} = \left[\frac{SSE(\Phi_1,...,\Phi_i * (1+f),...,\Phi_p) - SSE(\Phi_1,...,\Phi_i,...,\Phi_p)}{f} \right] \qquad \text{(eq. 4-31)}$$

where $S_{i,j}$ is a partial effect for parameter Φ_i around an LH point j, f is the fraction by which the parameter Φ_i is changed (a predefined constant) and SSE is the sum of squared errors. In equation 4-28, the parameter is randomly increased or decreased with the fraction f . Considering *p* parameters, one loop involves performing *p*+1 model runs to obtain one partial effect for each parameter. As the influence of a parameter may depend on the values chosen for the remaining parameters, the experiment is repeated for all the *m* LH samples. The final effect will then be calculated as the average of a set of the *m* partial effects.

As a result, the LH-OAT sensitivity analysis method is a robust and efficient method: for *m* intervals in the LH-method, a total of *m*×(*p*+1) runs is required. The LH-OAT provides ranking of parameter sensitivity based on the final effects. Using the LH and One-factor-At-a-Time techniques in unison means that the sensitivity of model output to a given parameter is assessed across the entire feasible range for that parameter and across a number of different values for other parameters in the model, thus incorporating a limited amount of parameter interaction.

Parameter sensitivity for hydrology

The sensitivity analysis was performed for 27 parameters that may have a potential to influence river flow (Table 11). The ranges of variation of these parameters are based on a listing provided in the SWAT manual (Neitsch et al., 2002a) and are sampled by considering a uniform distribution. The distributed parameters are changed in a lumped way by sampling a relative change (in percentage), whereby they are restricted to their physical range. The analysis was carried out using simulations for hydrology at the mouth of the river, for the period between 1998 and 2001.

Table 11. Parameters and parameter ranges used in the sensitivity analysis + sensitivity ranking (with Gw. = groundwater, Evap. = evaporation, Geom. = Geomorphology)

Name	min	max	Definition	Process
ALPHA_BF	0	1	Baseflow alpha factor (days)	Gw.
BIOMIX	0	1	Biological mixing efficiency	Soil
blai	-50	50	Leaf area index for crop *	Crop
canmx	0	10	Maximum canopy index	Runoff
CH_K2	0	150	Effective hydraulic conductivity in main channel alluvium (mm/hr)	Channel
ch_n	-20	20	Manning coefficient for channel	Channel
CN2	-50	50	SCS runoff curve number for moisture condition II *	Runoff
epco	-50	50	Plant evaporation compensation factor *	Evap.
ESCO	0	1	Plant evaporation compensation factor	Evap.
GW_DELAY	0	100	Groundwater delay (days)	Gw.
GW_REVAP	0.02	0.2	Groundwater “revap” coefficient	Gw.
GWQMN	0	1000	Threshold depth of water in the shallow aquifer required for return flow to occur (mm)	Soil
rchrg_dp	0	1	Groundwater recharge to deep aquifer (fract)	
REVAPMN	0	500	Threshold depth of water in the shallow aquifer for “revap” to occur (mm)	Gw.
SFTMP	-2	2	Snowfall temperature (°C)	Snow
SLOPE	-50	50	Average slope steepness (m/m) *	Geom.
SLSUBBSN	-50	50	Average slope length (m/m) *	Geom.
SMFMN	0	10	Min. melt rate for snow (mm/°C/day)	Snow
SMFMX	0	10	Maximum melt rate for snow (mm/°C/day)	Snow
SMTMP	-2	2	Snow melt base temperature (°C)	Snow
sol_alb	0	1	Moist soil albedo	Soil
SOL_AWC	-50	50	Available water capacity (mm/mm soil)	Soil
sol_k	-50	50	Soil conductivity (mm/hr) *	Soil
sol_z	-50	50	Soil depth *	Soil
surlag	0	10	Surface runoff lag coefficient	Runoff
TIMP	0.01	1	Snow pack temperature lag factor	Snow
TLAPS	-50	50	Temperature laps rate (°C/km) *	Geom.

* relative percent change

Grey background: parameters that were optimised in the manual calibration

Parameter sensitivity for atrazine modelling

In addition to the hydrological parameters of Table 11, the pesticide parameters of Table 12 were also included in the sensitivity analysis. The ranges of variation are defined based on the extensive literature review for atrazine that was performed by Liu et al. (1998). Only for the parameter ‘wofp_pest’ (wash off fraction), no information was found, and an arbitrary range of +/- 20% was taken. The parameter sensitivities for the pesticide sub-model focus on the variation of the daily average pesticide concentrations and the daily average pesticide loads for the period 1998-2001 at the mouth of the river.

Table 12. Pesticide parameters and parameter ranges used in the sensitivity analysis + sensitivity ranking

Name	default	min	max	Definition	Process
AP_EF	-	0.95	1	Application efficiency when considering direct losses	Pesticide
hlff_pest	5	4	7	Degradation half-life of the chemical on the foliage (days)	Pesticide
hlfs_pest	60	8	170	Degradation half-life of the chemical in the soil (days)	Pesticide
Koc_pest	100	64	135	Soil adsorption coefficient	Pesticide
pwsol_pest	33	28	70	Solubility of the chemical in water (mg/l)	Pesticide
wofp_pest	0.45	0.36	0.54	Wash-off fraction	Pesticide

* relative percent change

4.3.2.5 Sensitivity analysis for the model inputs

Compared to water quantity modelling, pesticide modelling is confronted with many more uncertainties related to the model inputs. This may even cause a parameter calibration to be impossible. For instance, correct information on the amount and date of pesticide application does often not exist while it is expected that such information is crucial for a correct modelling (Neitsch et al., 2002b). A proper calibration then requires some inverse modelling techniques to tackle this problem. A sensitivity analysis of these model inputs can help to get insights in what the major input factors are that affect the model output and that hence need special attention.

To perform a sensitivity analysis, the model inputs cannot be dealt with in the same way as the model parameters since they cannot be represented by a single value: for each run, a series of error values needs to be sampled to consider the spatial or temporal variation of the system. It is, for instance, not likely that the error in rainfall input is the same for each rain gauge or for each day. It is neither likely that all farmers apply pesticides on the same day or that the error on application rate is the same within the entire catchment. Therefore, another procedure must be used to evaluate the sensitivity of model outputs to uncertainties that are inherent to the model inputs.

A new module “CANOPI” (Confidence ANalysis Of Physical Inputs) was developed within the SWAT codes that allows for a random variation on model inputs for each day (for the climate data) or for each HRU within the model (for both the pesticide application data) according to a uniform or normal distribution. For each input factor, N runs are performed whereby that particular input factor is randomly varied in time and/or space according to the provided error range. The average and variation of a model output are calculated for each input. The corresponding coefficient of variation provides insights in the relative importance of the uncertainty of these input factors.

Both the influence of climatic inputs (such as daily rainfall and temperature data) and atrazine application data (such as atrazine application rate and dates) are analysed. For both, a uniform distribution is considered over the ranges of variation that are listed in Table 13.

Table 13. Ranges of variation for the input data.

Type of input data	Range	Variability
rainfall	+/- 10 %	Temporal: daily
temperature	+/- 1 °C	Temporal: daily
atrazine application rate	+/- 20 %	Spatial: for each HRU with CORN
dates	+/- 20 days (from May 15)	Spatial: for each HRU with CORN

4.3.3 Results and discussion

4.3.3.1 Parameter sensitivity for hydrology

Figure 37 summarizes the sensitivity ranking for the performance for flow, which is determined by calculating the sum of squared errors (SSE) between daily simulated flows and daily flow observations. When we focus on the spring periods (March-June), the same parameters appear to be important.

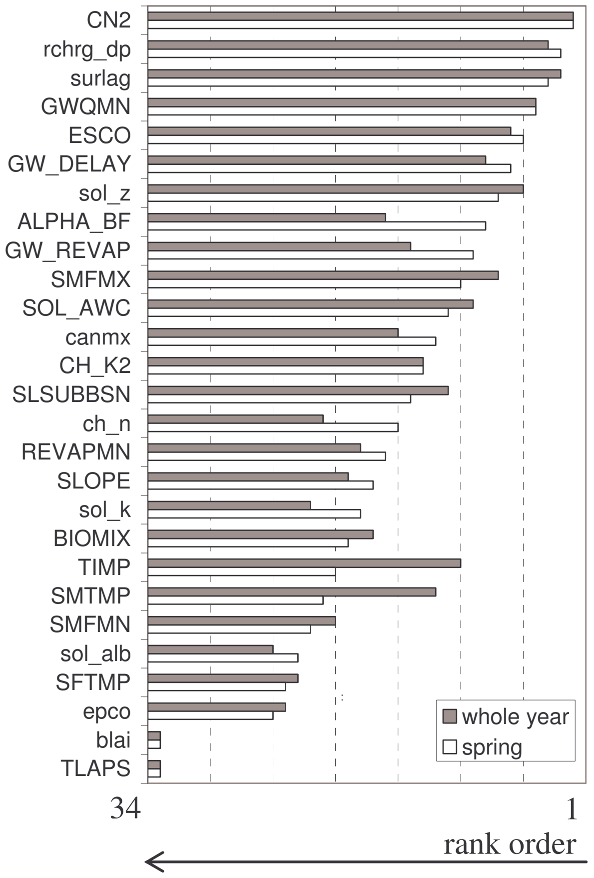


Figure 37. Graphical representation of the sensitivity ranking for hydrology over the whole year and during spring, for a subset of parameters. The definition of the different parameters can be found in Table 11.

In both cases the curve number (CN2) is the most important parameter, followed by the parameters surlag, rchrg_dp and GWQMN. The importance of the curve number can be attributed to the runoff driven hydrology of the small Nil catchment. The importance of the groundwater parameters is not surprising, due to the fact that drainage to deeper groundwater is high which has its origin in the geological structure of the catchment. Through the permeable Brusselian sands, groundwater of the Nil-catchment passes towards the adjacent river ‘Train’ (Abdeslam, 1998).

The importance of the curve number is consistent with results determined in other studies (e.g. Cryer and Heavens, 1996; Lenhart et al., 2002; van Griensven et al., 2006b).

4.3.3.2 Calibration of the hydrological parameters

In the manual calibration, parameters influencing baseflow and surface flow are optimised. To reduce the number of parameters that will be calibrated, the above-mentioned ranking of influential parameters is used. Only the most influential parameters are eligible for calibration. As the parameters SOL_AWC and sol_z are supposed to be determined precisely, no optimisation was performed for them. The parameters that are given priority in the manual calibration are indicated with a grey background in Table 11.

The results of the manual calibration are given in Figure 38a. By way of comparison, cold simulation results are presented in Figure 38a. Cold simulation results are produced by the model before any calibration is performed.

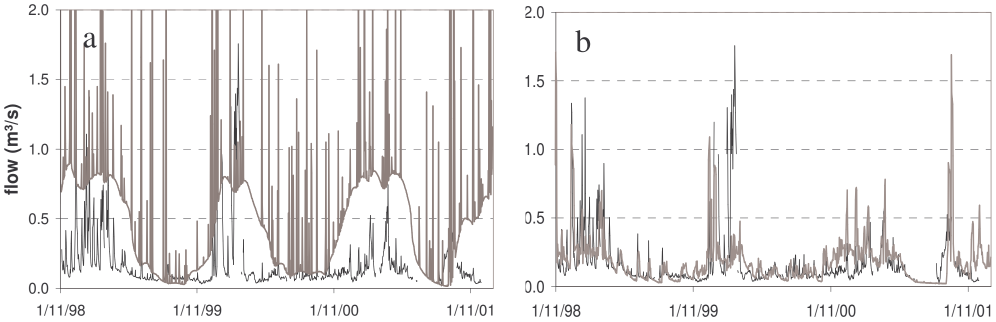


Figure 38. a) Comparison of measured (—) and cold simulation (—) flow data.
b) Comparison of measured (—) and manually calibrated (—) flow data.

As shown in Figure 38b, a reasonable fit was obtained for the manually calibrated flows. Nevertheless, better calibration is possible if seasonally dependent parameters could be adjusted throughout the year. For example, different values for the ESCO parameter during winter and summer would permit more realistic simulations of water evaporation during both seasons and thereby increase model efficiency. As herbicides are applied during the spring period from begin March to the end of June, we focused on good prediction performance in that period and we optimised the selected parameters specific for spring. As shown in Figure 39, a good fit is obtained between measured and simulated flows during spring. The Nash-Sutcliffe coefficient improved from an initial value of -22.4 for the cold simulation, to +0.53 after calibration specific for spring.

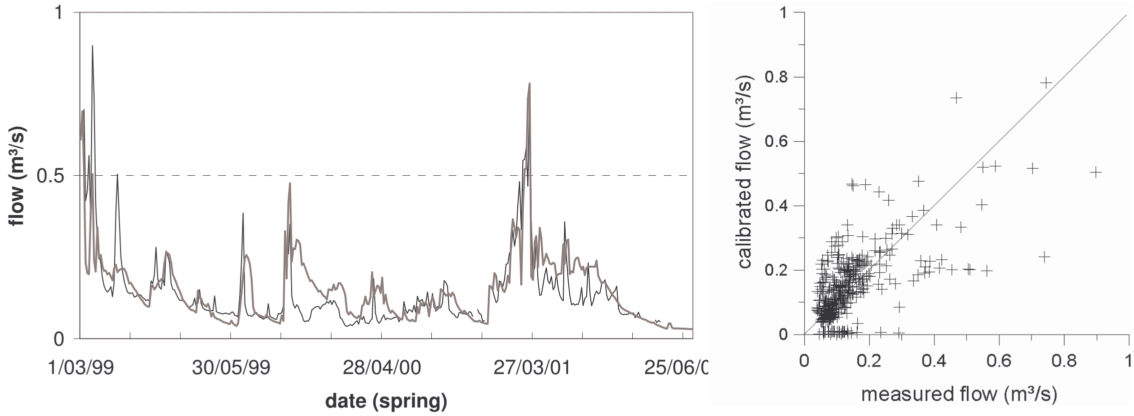


Figure 39. Comparison of measured (—) and manually calibrated (—) flow data for the spring periods shown sequentially from 1999 up to 2001.

4.3.3.3 Parameter sensitivity for atrazine modelling

As presented in Figure 40, the main parameter that is in competition with the hydrological parameters is ‘AP_EF’. In this case, this parameter controls the direct losses to the river system (see above). The importance of direct losses in the Nil-catchment was already mentioned by Beernaerts et al. (2002) and was also found to be important in certain catchments in Germany (Neumann et al., 2002) and Greece (Albanis et al., 1998). Also the halflife of pesticides on soil (hlfs_pest) seems to be rather important.

In summary, for making reliable predictions of atrazine towards the river, it is highly important that the hydrology, especially the curve number, is well calibrated while a correct estimation of the direct losses is of importance as well.

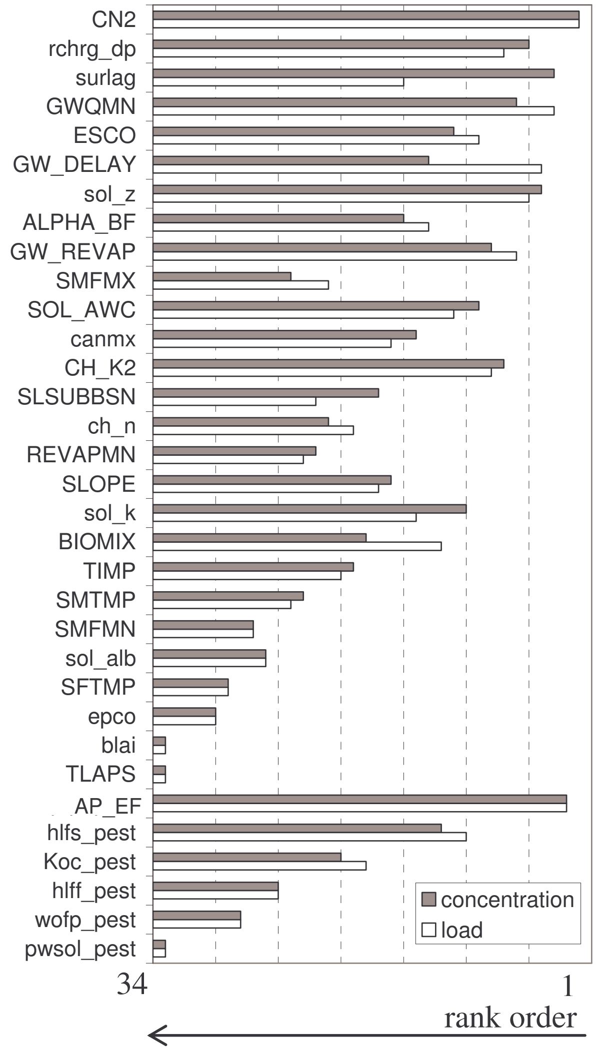


Figure 40. Graphical representation of the sensitivity ranking for atrazine modelling for a subset of parameters. The definition of the different parameters can be found in Table 11 and Table 12.

4.3.3.4 Input sensitivity for atrazine modelling

This sensitivity analysis is performed with the previously described manually calibrated model, but a recalibration might be needed when pesticides are also considered. However, since this may require better assessments for the model inputs, it is first aimed to define the most important input factors.

For each input factor, 100 runs were performed. The results for the average concentrations and average loads (Table 14) show that the date of application is much more important than errors that may occur in the application rate or rainfall errors. Errors in temperatures are the least important. The importance of the application date can be explained twofold: first, the contribution of direct losses (through the clean up of spray equipment, leaking tools, processing of spray waste etc.) to the total amount of atrazine found in the river is estimated to be 40 to 70% in the studied catchment. Consequently, errors in application date will result in significant errors in predictions of the direct losses in this catchment. Secondly, the percentage of pesticides that eventually will reach the river through surface run-off depends highly on the period between the application and the next rain event. In Belgium, a randomly defined application date may easily coincide with a rainy day. In reality, farmers will not apply pesticides on rainy days. Therefore, it is important to consider the weather pattern while setting up the management files for pesticide applications. If we would consider this also in the sensitivity analysis, we may expect a somewhat smaller influence of the application date on the losses originating from surface runoff.

Table 14. Coefficient of Variation for the CANOPI results.

Type of input data	Average atrazine concentration	Average atrazine load
rainfall	0.0434	0.0512
temperature	0.0029	0.0031
atrazine application rate	0.0321	0.0324
dates	0.3024	0.3233

4.3.4 Conclusions

A methodology to obtain information about the sensitivity towards parameters and model inputs for hydrology and pesticide supply in SWAT, was presented. First, an intensive data collection, the digitisation of soil maps and the calculation of related soil parameters was performed for the Nil catchment.

An LH-OAT sensitivity analysis for hydrology allowed for the screening of the large set of input parameters. The selected subset of parameters was then used for model calibration. The manual calibration resulted in good fits to the observed flows. Better results would be possible if seasonally dependent parameters could be adjusted to the current season.

By including pesticide parameters in the sensitivity analysis, it appears that besides a good calibration of the hydrology also a correct estimation of the direct losses is important. The importance of these direct losses for this catchment was already proven by an experiment during the years 1998-2002. Measurements of pesticide concentrations at the mouth of the river Nil (1998-1999) showed high peaks even during non-rainy wind still days. Consequently, these high peaks can only originate from direct losses due to the clean up of spray equipment, leaking tools, etc. During the years 2000-2001, sensitization of farmers regarding this issue resulted in a significant decrease of pesticide loads in the river. When this sensitization campaign was finished in 2002, pesticide loads in the river immediately increased (Beernaerts et al., 2002). This proves the importance of direct losses, which were estimated to be 30 to 90 % of the total amount of pesticides found in the river 'Nil' depending on pesticide.

Finally, the sensitivity analysis for the input factors reveals that the date of application is much more important than errors that may occur in the application rate or rainfall errors. Consequently, the application date can be an important source of uncertainty and needs special attention for data collection. As the management files were not adapted to the weather pattern, we can expect that such a sensitivity analysis will result in a smaller influence of the application date on the losses originating from surface runoff .

The importance of hydrology and of the reduction of uncertainties in inputs for modelling pesticide fate were also mentioned by Dubus et al. (2003).

4.4 Extending the SWAT model for point sources

4.4.1 Introduction

Pesticides are useful to society thanks to their ability to increase crop yields by destroying disease-causing organisms and controlling insects, weeds and other pests. At the same time, most pesticides may be harmful to humans, animals and the environment because of their ecotoxicity, their potential bio-accumulating properties or their hormone disrupting effects (Cuppen et al., 2000; Van den Brink et al., 2000; Hanson et al., 2002; Yamaguchi et al., 2003; Wendt-Rasch et al., 2004; Capkin et al., 2006).

Pesticides can enter river systems both immediately after application, i.e. as a direct loss, or with some time delay due to runoff or leaching. We define a direct loss as the sum of point losses and drift losses on an application day that will reach the river the same day. Point losses are due to the clean-up of spray equipment, leaking tools, wastewater treatment plants etc. Different studies demonstrated the importance of direct losses (Leu et al., 2004a; Beernaerts et al., 2002; Gerecke et al., 2002; Neumann et al., 2002; Bach et al., 2001). An intensive monitoring campaign in the river Nil in Belgium during the years 1998-2002 revealed high herbicide concentrations at the mouth of the river, even during dry and wind-still days. Consequently, these high peaks could only originate from point losses (e.g. through the clean-up of spray equipment, leaking tools, etc.). This was further confirmed in the authors' own monitoring campaign in which the dynamics of the water-sediment system were followed intensively during spring 2004 (see Chapter 3). The contribution of these point losses can be decreased by sensitizing farmers as was proven during the years 2000-2001. When this sensitization campaign was stopped in 2002, pesticide loads in the river immediately increased (Beernaerts et al., 2002) (Figure 18). This proves the importance of direct losses, which were estimated to be 30 to 90 % of the total amount of pesticides found in the river 'Nil' depending on pesticide. As the Nil was also studied in detail for pesticide applications and management practices during the period 1998-2002, we chose it as a test case for analysing the processes underlying the direct and diffuse sources through modelling and monitoring.

Some deterministic models exist that describe long-term effects of hydrological changes and water management practices on a watershed scale, such as AnnAGNPS (Bingner and Theurer, 2001), HSPF (Donigian et al., 1993) and SWAT (Arnold et al., 1996). As far as we know, none of them implemented the aforementioned direct losses. To account for direct losses of pesticides to surface water, adaptations to the original SWAT model were needed. In a first step, the original SWAT model results were compared to the results of the intensive monitoring campaign performed during the years 1998-2002. Hereby, some hiatus and inaccuracies in the source code were highlighted. With the modelling objective in mind, adaptations were done on the source codes in order to get a model that adequately describes the diffuse and point source pollution while respecting the mass balance.

4.4.2 Case study

In this study we focus on the Nil basin, which was described in detail in Chapter 3. The Nil catchment was selected because it is a well documented basin, studied in detail in terms of pesticide application (Beernaerts et al., 2002).

A hydrologic model for the Nil catchment was developed, calibrated and is described in Section 4.3.

Pesticide data were collected by CODA (2003) by taking daily grab samples of river water. Furthermore, inquiries were conducted during the spring seasons of 1998 until 2002. The farmers were asked to give as detailed information as possible concerning the amount of pesticide they applied, the application dates, the kinds of pesticides they used for their different crops and the treated surface. Forty two percent of the farmers could give detailed information. In this study, we focus on the use of atrazine on corn during the growth season of 1998, when the application rate amounted to 0.741 kg ha^{-1}. The validation of the model for predicting pesticide fluxes is performed for the period 1999 till 2002.

4.4.3 Model improvements for pesticide fluxes

Different steps were taken to model both indirect losses (i.e. through runoff) and direct losses (i.e. through drift, leaking equipment, the cleaning of spraying tools). They will be discussed one by one.

Original source code

By adding pesticide characteristics and management to the SWAT-model, the movement of the chemical in the watershed could be predicted. A comparison of simulated and measured pesticide concentrations in solution at the mouth of the river showed that runoff related pesticide peaks could be modelled but needed further calibration. Most importantly, the SWAT2000 model could not represent pesticide peaks during dry periods, a clear model deficiency. This is represented for the year 1998 in Figure 41. The figure shows that pesticide peaks originating from direct losses are missed.

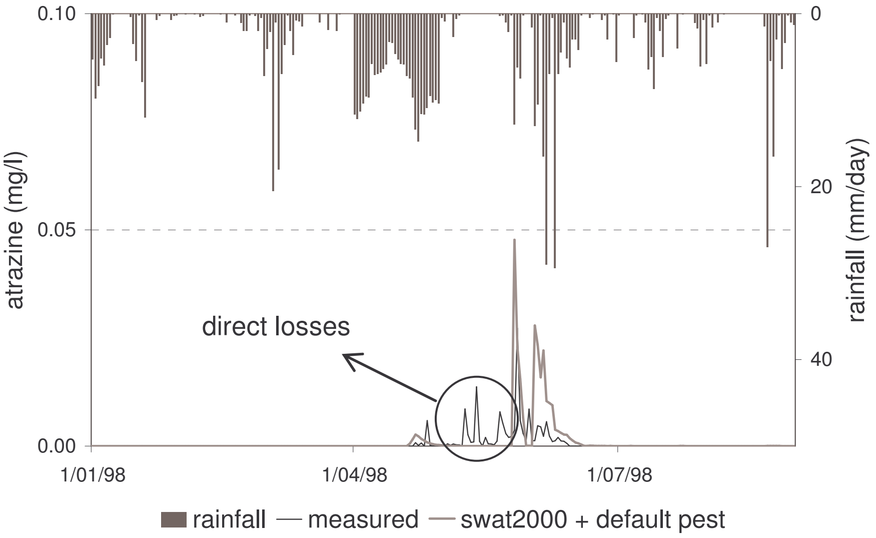


Figure 41. Measured and predicted atrazine concentrations in the Nil (1998), with missing direct losses.

Implementing direct losses

To enable the SWAT code to account for direct losses, the codes were slightly modified by changing the parameter ‘AP_EF’ (application efficiency coefficient). Originally, the parameter indicates the process whereby a fraction of the applied rate is lost from the system. In the adapted code, the parameter is changed to the process by which a fraction of the applied pesticide is diverted directly to the river system, i.e., a direct loss. The adaptation of the source code existed in a modification in the module for pesticide application, which can be written as:

$$direct\_loss_{point} = ap_{rate} \times (1 - AP\_EF) \times area_{hru} \times 1e8 \qquad \text{(eq. 4-32)}$$

where $direct\_loss_{point}$ is the amount of pesticide lost during or immediately after application as a point loss (mg); ap_{rate} is the pesticide application rate (kg /ha); AP_EF is the pesticide application efficiency; $area_{hru}$ is the area of the HRU (km²) and $1e8$ is a unit conversion factor. The effective amount of pesticide applied on the field then becomes:

$$pest2 = pest \times AP\_EF \qquad \text{(eq. 4-33)}$$

where $pest2$ is the effective amount of pesticide applied (kg/ha) and $pest$ is the actual amount of pesticide applied (kg/ha).

The direct losses are summed to the outputs of the land phase section in SWAT and are in that way directly diverted to the river. These modifications are allowed in this case, in which pesticides are not applied by airplanes but directly on the fields by spray equipment and where losses outside the system are not expected to be significant. The direct losses are considered to be lower than 2 % (see Figure 18), but their impact is nevertheless significant since these losses are directly ending up in the river system.

The result of the implementation of direct losses can be seen in Figure 42. Direct losses are simulated, but the simulation results clearly overpredict the pesticide concentrations with an estimated order of magnitude of 2.

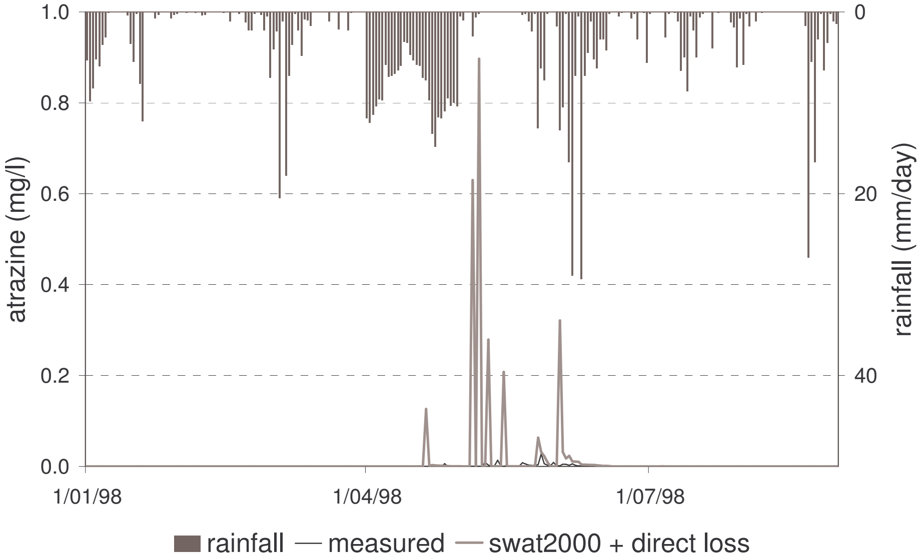


Figure 42. Measured and predicted atrazine concentrations at the mouth of the river Nil (1998), with contribution of direct losses.

Setting the mass balances right

After applying the above mentioned change, mass balances could be checked. If the application efficiency AP_EF was set to 0, all applied pesticides should reach the river by direct loss and only a little fraction is expected to be lost during transport in the reach. To assess this, a closer look was given to Subbasin 25 with atrazine application. It seemed that the applied dose reached the river, but during transport through the river almost half of the applied pesticide dose disappeared. The relevant mass balances are presented in Table 15. In a first attempt to elucidate the origin of the problem, the in-stream pesticide processes were deactivated, such as adsorption/desorption to sediments. This change did not affect the errors in the mass balance.

Apparently, SWAT only considers chemicals when flows equal at least 0.01 m^3/s. Since point source pollution typically happens during low flow periods, and because the model was subdivided into hundreds of sub-units (HRU's), this threshold was not always reached. Therefore, this threshold was reduced in several routines of the code to the value of 0.000001.

Table 15. Simulated amounts of pesticides in solution leaving different locations in the Nil during the year 1998 with an application efficiency AP_EF set to 0, for different versions of the SWAT2000 source code. Strange values are represented in bold.

		subbasin 25	reach 25	at the mouth
Area of corn (ha)		37.5		569.7
Applied dose (kg/ha)		0.741		0.741
expected load (kg)	= Area × dose	27.78	27.78	422
without modifications (kg)	= initial model	0	0	0
modification 1 (kg)	= implementation direct losses	27.75	**0.11**	**214.98**
modification 2 (kg)	= correction of flow threshold	27.75	27.75	**419.29**
modification 3 (kg)	= correct. mass losses/creation	27.75	27.75	421.47

The mass balances represented in Table 15 show that the abovementioned modifications result in more realistic values for pesticides in solution, both at reach-level and at the mouth of the river. At the mouth of the river, there is still a small amount of pesticides missing. Concerning pesticides sorbed on suspended solids, no sorbed pesticides could be found when the application efficiency AP_EF was set to 0, as in the source code direct losses were sent to the river as solubles and all river processes (including sorption) were de-activated. If the application efficiency AP_EF was given a value different from 0, by lowering the threshold value of flow for chemical routing sorbed pesticides were simulated too (results not shown).

Corrections for losses or mass creation

A closer look at the losses from and inputs towards the river revealed that there were some miscalculations in the original source code (van Griensven et al., 2006c). Therefore, the following modifications were performed:

1) The losses in the river were originally based on the basis of the residence time calculation, while the integration time step should be used.

   In order to get stable calculations in the SWAT routing, both the Muskingum method and the Variable Storage method (see Section 4.2.4) were not applied in a correct way. In both methods, the hydrological state variables such as river flow, depth, wetted perimeter, cross section area and flow velocities are based on the summation of the water volume in the reach and the inflow instead of taking only the volume:

$$A_{ch} = \frac{\left(V_{in} + V_{stor}\right)}{L_{ch} \cdot 1000.} \qquad \text{(eq. 4-34)}$$

where A_{ch} is the cross-sectional area of flow in the channel (m²) and L_{ch} is the length of the channel (km). This gave stable calculations also for small reaches because the inflow acts as a kind of a buffer for the storage in the reach, but the stability has wrong underlying calculations. In case the residence time is an hour, 24 times of the volume is added to the reach volume and the resulting calculated traveling time *TT* (see eq. 4-16) is a strong underestimation of an order of 24, while the river *depth* calculation (see eq.4-13) is strongly overestimated. When the Muskingum and Variable Storage routing would be implemented in the proper way, unstable river volume and hence river depth and velocities would be obtained in situations with short residence times. Therefore, a new routing module was developed in which the relation between velocity and flow is calculated by solving of the Manning equations in an iterative way till an A_{ch} is found (and corresponding R_{ch}) that corresponds to the inflow q_{ch}:

$$q_{ch} = \frac{A_{ch} \cdot R_{ch}^{2/3} \cdot slp_{ch}^{2/3}}{n} \qquad \text{(eq. 4-35)}$$

where q_{ch} is the flow rate in the channel (m³/s), A_{ch} is the cross-sectional area of flow in the channel (m²), R_{ch} is the hydraulic radius for a given depth of flow (m), slp_{ch} is the slope along the channel length (m/m) and *n* is Manning's "n" coefficient for the channel. A corresponding reach volume $V_{manning}$ can be calculated:

$$V_{manning} = 1000 \cdot L_{ch} \cdot A_{ch} \qquad \text{(eq. 4-36)}$$

The key solution to get stable calculations for both situations where the residence time is smaller or bigger than the calculation time step, is to use distinct equations for these situations. In case the residence time γ (days) is smaller than the calculation time step Δt (days), the reach volume at the end of the time step $V_{stored,2}$ (m^3) will be equal to $V_{manning}$ (m^3):

$$V_{stored,2} = V_{manning} \qquad \text{(eq. 4-37)}$$

However, when γ is larger than the time step, only part of $V_{stored,1}$ (m^3) will be replaced by $V_{manning}$:

$$V_{stored,2} = V_{stored,1} - \frac{\Delta t}{\gamma}(V_{stored,1} - V_{manning}) \qquad \text{(eq. 4-38)}$$

The routing component needed a final correction: the calculation of the transitional losses (infiltration or evaporation) and the river bank contributions are based on the calculation time step instead of the residence time. Note that they are also heavily influenced by the previous routing corrections as they depend on the wetted perimeter too.

2) For the routing of water the addition of bank flow is included. This water is added to the river outflow, but the concentrations of the chemicals were in the meantime kept constant whereas a dilution factor should be applied. This resulted in a creation of pesticide mass. This was corrected by calculating chemical concentrations based on the total amount of water leaving the reach.

3) Finally, in the original source code the losses in the river bed were abstracted from the available water, but the concentrations were kept constant. This resulted in a loss of chemicals/pollutions. This approach was kept for the solutes, as they leave the system with the infiltrating or evaporating water. It was programmed that the solids remain in the river during the evaporation/infiltration, resulting in an increase in their concentrations.

The mass balance results of these modifications are presented in Table 15 and show that reliable mass balances are now achieved. If all applied pesticides are assumed to be direct losses (AP_EF = 0), the simulated load of atrazine at the mouth of the river in the year 1998 amounts 421.47 kg in case all processes and losses are ignored. This is in good agreement with the applied dose of 422 kg.

Implementing an estimator for drift

During the application of plant protection products, a part of the spray liquid may be carried out of the treated area by wind or the air stream of the sprayer and reach a nearby river system. Therefore, an estimator for drift was added to the source code, in order to estimate the contribution of drift to the direct losses.

The calculation of spray drift deposition was based on the German drift database (Ganzelmeier et al., 1995). These data were generated from a series of studies (at a number of locations and with a variety of crops) whose objective was to determine the absolute level of drift in practice under a variety of conditions. However, even this extensive database only partly reflects environmental, crop and application factors prevailing in Germany, but still, it is recommended by the FOCUS Surface Water workgroup because it is currently the most comprehensive, widely available data set. The use of this database also has a significant precedent in the EU evaluation process (FOCUS, 2001). The database is useful for plant protection products that are applied in compliance with the principles of Good Agricultural Practice. This comprises the application during low wind velocities only, the use of approved equipment as well as the application under favourable climatic conditions only. If these rules are not followed, it must be expected that larger amounts of plant protection products will be drifted than specified by the basic drift values. Ganzelmeier drift data are the 90th percentile worst case drift values obtained for wind directions perpendicular to the receiving water bodies and at wind velocities at the upper end of the conditions compliant with good agricultural practice. As such, they have to be considered as conservative.

The mean (integrated) drift deposition into surface water bodies can be calculated from the following equation:

$$\overline{Drift} = \left[A * \int_{z_1}^{z_2} (z^B) dz \right] * \frac{1}{z_2 - z_1} \qquad \text{(eq. 4-39)}$$

where $\overline{Drift}$ is the mean percent drift loading across a water body that extends from a distance of z_1 to z_2 from the edge of the treated field (%); A and B are previously defined regression parameters (Ganzelmeier et al., 1995); z_1 is the distance from the edge of the treated field to the closest edge of the water body (m); and z_2 is the distance from the edge of the treated field to the farthest edge of the water body (m). Here it is possible to take into account the effect of buffer zones on the reduction of drift towards a river. In this case, the values for z_1 and z_2 will be increased with the width w of the buffer strip.

The integrated form of this equation is as follows:

$$\overline{Drift} = \frac{A}{(z_2 - z_1) * (B+1)} * [z_2^{B+1} - z_1^{B+1}] \qquad \text{(eq. 4-40)}$$

The values for A and B were extracted from the database of Ganzelmeier et al. (1995). As the focus is on the application of atrazine on corn fields, values for ‘arable crops’ with ‘3 applications’ were looked for. The values found for A and B are respectively 2.0244 and -0.9956.

To calculate the drift loading towards the receiving surface water, the following formula was implemented:

$$direct\_loss_{drift} = ap_{rate} \times AP\_EF \times area_{river\_reach} \times \overline{Drift} \qquad \text{(eq. 4-41)}$$

where $direct\_loss_{drift}$ is the amount of pesticide lost during application as a drift loss (mg); ap_{rate} is the pesticide application rate (kg/ha); AP_EF is the pesticide application efficiency; and $area_{river\_reach}$ is the area of the receiving water (m²); $\overline{Drift}$ is the mean percent drift loading across a water body that extends from a distance of z_1 to z_2 from the edge of the treated field (%). The area of the receiving water is calculated as follows:

$$area_{river\_reach} = \sqrt{area_{hru}} \times W \times 1000 \qquad \text{(eq. 4-42)}$$

where W is the channel width (m) and 1000 is a unit conversion factor. The length of the channel along an HRU was set equal to the root square of the HRU area. As in SWAT the HRUs are lumped areas, no information about the position of the original fields is available. Therefore, as it is not known whether a field borders the stream according to its length or to its width, the assumption that HRUs have a square shape forms an intermediate solution.

The effective amount of pesticide applied on the field can then be calculated by subtracting point losses, drift losses to the river and the amount of drifted pesticide that is captured in the buffer zone, from the initial application dose.

In cases where data concerning wind direction, wind velocity, air temperature and humidity, as well as nozzle type, spraying pressure and tractor driving speed are missing, the Ganzelmeier approach forms a 90th percentile worst case drift estimator. If more detailed information concerning the application conditions is available, more detailed drift descriptions could be used for simulation (Cox et al., 2000; Gil and Sinfort, 2005; Tsai et al., 2005).

4.4.4 Results and discussion

After the model was improved for direct losses, a calibration of the most influential parameters (see Section 4.3) was performed for the year 1998, followed by a validation for the years 1999-2002. In Figure 43, measurement and simulation results for atrazine concentrations are presented for the spring periods (1st of March till the end of July) during the years 1998-2002. As can be seen from Figure 43, a good approximation between measured and simulated atrazine concentrations at the mouth of the river could be achieved. For the year 1998, the Nash-Sutcliff improved from a value of -2.63 to 0.66.

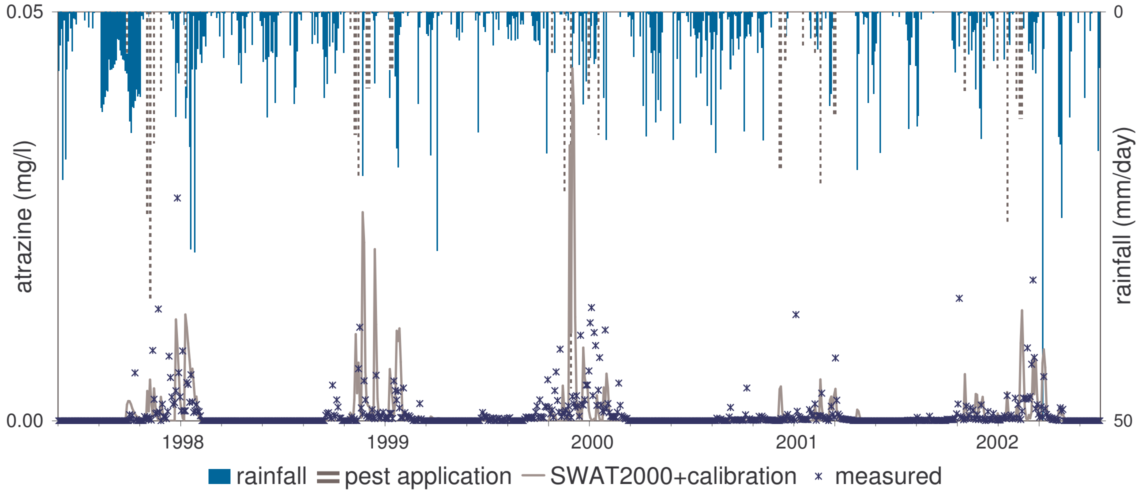


Figure 43. Measured and predicted atrazine concentrations at the mouth of the river Nil after calibration (spring periods of 1998-2002).

If application data of pesticides are missing or incorrect (e.g. april-may 1999 and 2001), good simulations of direct losses are obviously impossible. Moreover, predicted values of direct losses will always be rough estimates, as currently the application efficiency AP_EF has a constant value during simulation. In reality, the efficiency will be highly variable over the different applications, due to variability in farmers, in farmers working methods and in daily differences. Nevertheless, this approximation is much more correct than ignoring direct losses and results in more realistic mass fluxes. For the period 1998-2002, a value of 99.8% for the application efficiency AP_EF was found to result in a good average agreement between measured and predicted pesticide concentrations.

During the years 2000-2001, sensitization of farmers resulted in a significant decrease of pesticide loads in the river. For atrazine, only during 2001 a reduction took place (Beernaerts et al., 2002; see Figure 18). This reduction could also be seen during calibration: a higher value for the application efficiency AP_EF of 99.9% resulted in a better fit during 2001, whereas a lower value could better predict direct losses during the remaining years.

In Table 16 a comparison is made between percentages of applied pesticides reaching the river obtained through modelling and measurements (Figure 18). This comparison reveals that there is a good agreement for the total percentage of applied pesticides that will leave the river. However, the fraction reaching the river that can be attributed to direct losses, i. e. 1-AP_EF, seems to be underestimated compared to the results obtained from the monitoring campaigns. This can be attributed to some underpredictions of flow at days of application, which will result in high pesticide concentrations and as such will influence the calibration process. During calibration, measured and simulated pesticide concentrations at the mouth of the river were compared. This resulted in an overestimation of the application efficiency AP_EF. As such, special attention should be paid to the simulation of hydrology, as concentrations of direct losses are based on the mass of water passing the system. If flows are underestimated, pesticide concentrations will be over predicted and vice versa.

Table 16. Comparison between simulated and measured percentages of applied atrazine amounts reaching the river Nil as a total loss or as a direct loss.

	1998	1999	2000	2001	2002	2004
Percentage of the applied atrazine amount reaching the river (total loss)						
simulated (%)	1.9	2.2	1.5	0.3	2.2	
measured (%)	2.6	2.0	3.0	0.6	2.2	
Percentage of the applied amount reaching the river through direct losses						
simulated (%)	0.2	0.2	0.2	0.1	0.2	
measured (%)	1.2	0.9	1.7	0.3	0.9	
Percentage of the river load of atrazine that can be attributed to direct losses						
simulated (%)	11	9	13	38	9	
measured (%)	44	47	55	54	39	66

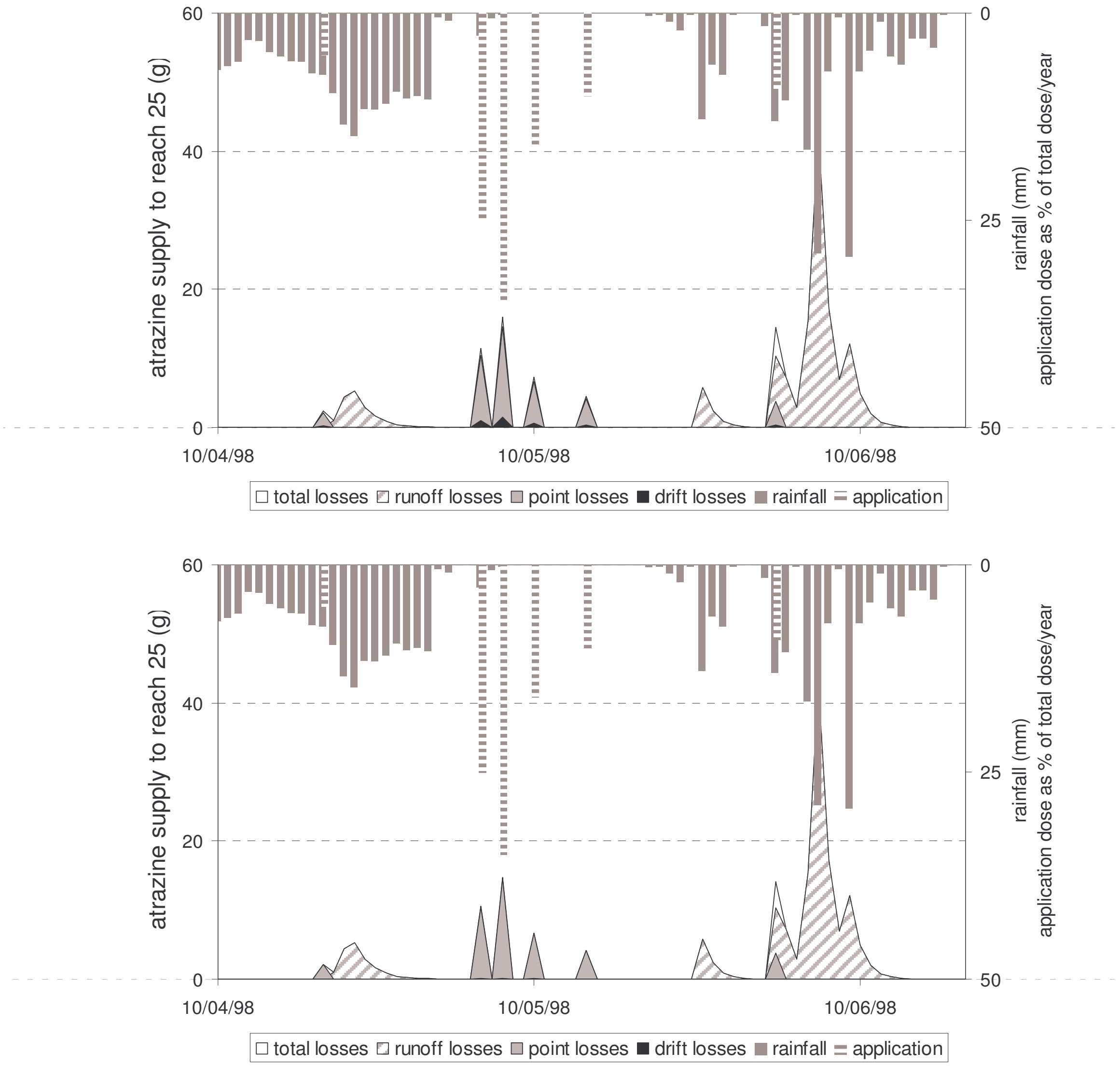


Figure 44. Predicted atrazine loads coming from subbasin 25 a) in the absence of a buffer strip and b) with a buffer strip of 1m between field border and river.

In Figure 44, the contribution of drift to the total losses is represented for the load coming from subbasin 25 towards reach 25. Subbasin 25 consists of many corn fields on which atrazine is applied. In Figure 44a no buffer zone was considered, whereas in Figure 44b a ‘no spray zone’ of 1 meter was introduced which matches the Good Agricultural Practise in Belgium. From these figures, it can be deduced that even a small ‘no spray zone’ has a positive effect on pesticide mass fluxes towards a river system. The drift losses could be reduced by 87%. On application days, the fraction of drift towards the river was reduced from 13% of the application dose per unit area to 1.6%, with respectively standard deviations of 0.057 and 0.007. The latter fraction is in agreement with values found in literature, stating that current drift losses towards an adjacent river in West-Europe amount between 1 and 2% of the dosage per unit area (de Snoo and de Wit, 1998; Siebers et al., 2003). Nevertheless, the contribution of drift losses to the total pesticide load in the river system is almost negligible. Bach et al. (2001) also found that the input in arable farming by spraydrift is very low. On the other hand, in fruit culture these contributions may be significant.

On the other hand, point losses are very important. On a yearly basis, point losses contributed for 30 up to 90% of the pesticide loss during the period 1998-2002 depending on pesticide and therefore warrant special attention in pesticide reduction strategies. This is especially true because point losses occur during low flow conditions, which can result in severe impacts on water ecosystems. Most severe impacts can be expected in upstream, small rivers, where different amphibians, fishes, etc. brood and have their habitat.

As mentioned before by different authors (Dabrowski et al., 2003; Leu et al., 2004), the importance of runoff as a transport route of pesticides towards the river was also demonstrated in this modelling study. Different management strategies can reduce these fluxes (Mostaghimi et al., 2001; Schreiber et al., 2001; Santhi, 2006). A comparison of different management strategies is performed in Section 4.6.

4.4.5 Conclusions

In this Section, an attempt was made to include the description of direct pesticide losses in the source code of the SWAT model. Different steps were taken to improve model predictions for direct losses. If application data for pesticides are available and reliable, reasonable predictions can be made. Nevertheless, as the occurrence of point losses is subject to a large variability, only average estimates can be expected. It would be useful to describe application data as probability distributions, in order to reflect the uncertainty related to these parameter.

It was shown that the lower atrazine load leaving the river Nil during the year 2001, could to a large extent be attributed to a higher engagement of the farmers: a higher application efficiency

AP_EF during 2001 could describe the decrease of direct losses. Sensitization of farmers seems to play an import role in reducing direct losses. During the year 2001, the percentage of applied pesticide leaving with the river decreased from 2% in 1998 to 0.3% in the year 2001.

The application efficiency AP_EF seems to be overestimated compared to the results obtained from the monitoring campaigns. As such, 1-AP_EF or the contribution of direct losses is underpredicted. This can be attributed to some underpredictions of flow at days of application, which will result in high pesticide concentrations and as such influence the calibration process. In reality, the contribution of point losses is higher than predicted by the model.

By means of a drift estimator, the contribution of drift in direct losses could be estimated. It was found that the contribution of drift losses to the total pesticide losses is of minor importance compared to point losses and losses coming from runoff. The latter need special attention in pesticide management strategies.

Former pesticide studies performed with the SWAT2000 model (Neitsch et al., 2002b; Winchell et al., 2005; Santhi et al., 2006) should be examined with caution, as errors were detected in the source code by checking mass balances. The errors were resolved.

The modified SWAT code can be used for quantification of pesticide reductions through different measures. Hereby, ranking of different measures based on effectiveness will be possible (see Section 4.6). Besides, realistic risk assessments can be performed, taking into account spatial and temporal variability of pesticide applications on catchment scale.

4.5 Preliminary uncertainty analysis

4.5.1 Introduction

In the field of environmental modelling and assessment, uncertainty analysis (UA) is a necessary tool to provide, next to the simulation results, also a quantitative expression of the reliability of those results. In this study, we only consider parameter and input uncertainty that can be minimised by gathering additional data. Model uncertainty and mathematical uncertainty are not taken into consideration. The study was performed for the Nil catchment, where the model has been calibrated for hydrology and pesticide supply (see Section 4.3) and which was extended for direct losses (see Section 4.4).

4.5.2 Methods

By means of a sensitivity analysis performed in Section 4.3, the most influential parameters for predicting pesticide fluxes towards the river were determined. Based on this knowledge, the uncertainty related to the 9 main contributing parameters was estimated. The ranges of variation of these parameters were based on literature values (Tomlin, 2003; Footprint pesticide database), expected ranges or on a twenty percent change of the calibrated values. They are presented in Table 17.

Table 17. Parameters and parameter ranges used in the uncertainty analysis. All parameters have a uniform distribution.

Name	min	max	Definition	Process
AP_EF	0.9975	0.9985	Application efficiency when considering direct losses	Pesticide
CN2	-20	20	SCS runoff curve number for moisture condition II *	Runoff
GWQMN	0.536	0.804	Threshold depth of water in the shallow aquifer required for return flow to occur (mm)	Soil
GW_DELAY	24.8	37.2	Groundwater delay (days)	Ground Water
GW_REVAP	0.0704	0.0106	Groundwater “revap” coefficient	Ground Water
hlfs_pest	7	60	Degradation half-life of the chemical in the soil (days)	Pesticide
Koc_pest	40	200	Soil adsorption coefficient	Pesticide
rchrg_dp	0.624	0.936	Groundwater recharge to deep aquifer (fract)	Ground Water
surlag	0.8	1.2	Surface runoff lag coefficient	Runoff

* relative percent change

Besides parameter uncertainty, also input uncertainty was taken into account. The day of application was expected to vary over 1 day, i.e. the application can occur one day earlier or one day later. The range of variation for the application doses was based on a 20 percent change. By means of Monte Carlo sampling with the UNCSAM software (Janssen et al., 1992), the parameters and input data were uniformly sampled between the uncertainty bounds described above.

The Monte Carlo principle is illustrated in Figure 45. The method has been extensively described in literature (Hammersley and Morton, 1964; Vose, 1996; Cullen and Frey, 1999). For each model input that is considered to be a random variable, a probability distribution is specified. One random sample from each input distribution is selected, and the set of samples is entered into the SWAT model. The model is then solved, as it would be for any deterministic analysis. The model results are stored and the process is repeated until the specified number of model iterations (called here shots) is completed. Using Monte Carlo techniques, it is therefore possible to represent uncertainty in the output of a model by generating sample values for the model inputs, and running the model repetitively. Instead of obtaining a discrete number for model outputs as in a deterministic simulation, a set of output samples is obtained (Cullen & Frey, 1999).

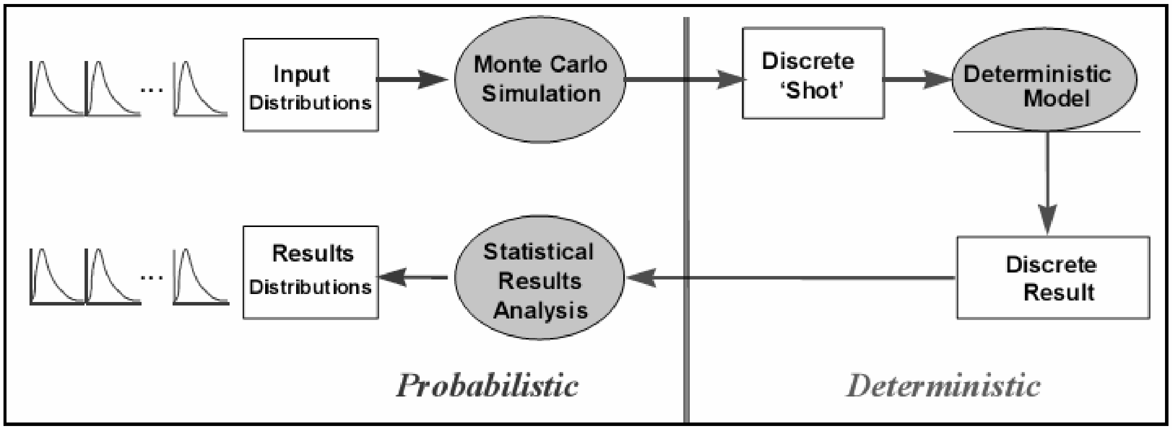


Figure 45. Principle of Monte Carlo simulation (Verdonck, 2003).

A script was written in the Perl language (Kuhn, 2001) in order to adapt the input files needed by the SWAT model (see Appendix C). The analysis was carried out for the period between 1998 and 2002 for 100 runs.

4.5.3 Results and discussion

The parameter uncertainty bands (i.e. the 5% and 95% percentiles) were calculated for the results of the time series at the mouth of the river Nil. Figure 46a shows the propagation in time of the parameter uncertainty for atrazine in the river Nil during the period 1998-2002. In Figure 46b this was done for the summation of parameter and input uncertainty.

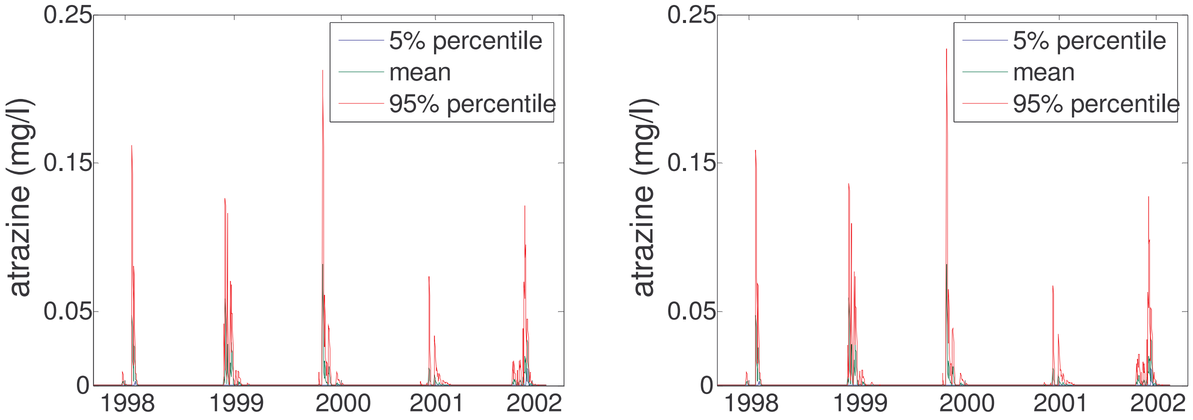


Figure 46. Simulation of atrazine with confidence intervals related to a) parameter uncertainty and b) to parameter and input uncertainty for the river Nil (1998-2002).

From Figure 46 it can be deduced that the effect of parameter uncertainty becomes important at certain moments, i.e. during the application window of the considered pesticide. The uncertainty is high for the largest pesticide peaks. However, the difference between the parameter uncertainty and the combined parameter and input uncertainty is rather small. The parameter and input uncertainty bands (Figure 46b) are somewhat higher and wider compared to those for parameter uncertainty (Figure 46a). This can be better seen in Figure 47 which is an enlargement of Figure 46 for spring 2002.

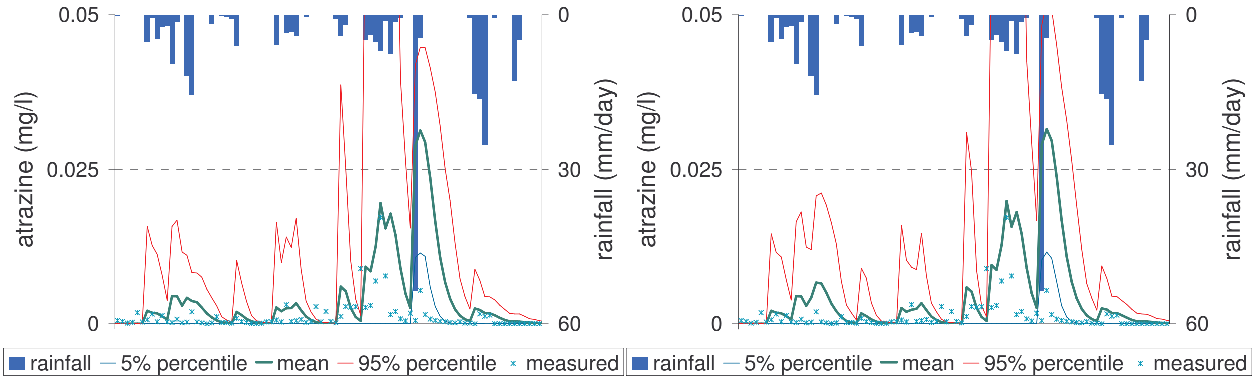


Figure 47. Simulation of atrazine concentrations for the river Nil during spring 2002. The mean and the confidence are given for a) parameter uncertainty and b) parameter and input uncertainty.

By linking the obtained results with rainfall data, it seems that the uncertainty is propagated both in wet and dry periods.

4.5.4 Conclusions

The uncertainty on pesticide predictions can mainly be attributed to parameter uncertainty and is highest for the higher pesticide peaks. It is therefore advisable to put some effort in determining the parameters well. The uncertainty is propagated both in wet and dry periods.

4.6 Determining the effectiveness of different mitigation measures using SWAT

4.6.1 Introduction

It is known that pesticide pollution may pose a serious problem in upstream agricultural areas (Leu et al., 2004; Claver et al., 2006; Konstantinou et al., 2006). In order to reduce the negative impact on the receiving ecosystem, pesticide fluxes towards the river system can be diminished by means of various measures. For pesticide pollution, a distinction can be made between point sources and diffuse sources. As point sources can contribute for 30 to 90% of the pesticide load in river systems (Leu et al., 2004; Beernaerts et al., 2005; Chapter 3) it is important also to consider measures diminishing these losses.

In view of the Water Framework Directive, tools should be tested that integrate the management of all water resources at the river basin scale. By using catchment models, the impact of measures on hydrology, sediment transport, nutrients and pesticide loads can be assessed. Catchment models integrate landscape features, climatology and management, such that they are suitable for ranking mitigation measures according to their effectiveness. This can support decision makers.

4.6.2 Materials and methods

Case study

In this study, we focus on the use of the herbicide atrazine for the cultivation of corn in the Nil catchment (Figure 48).

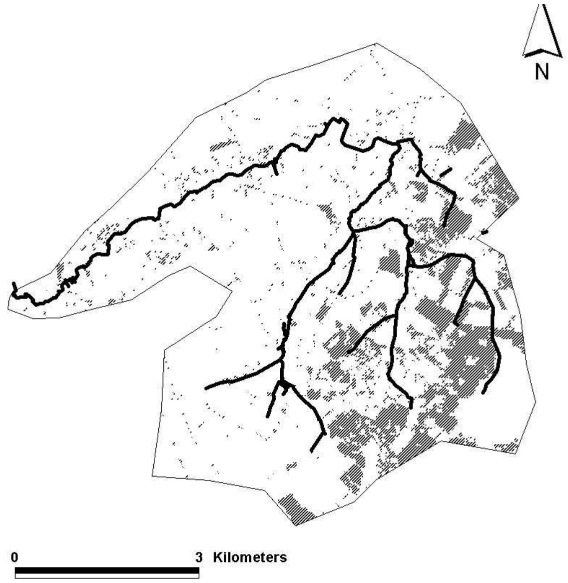


Figure 48. The cultivation of corn (grey area) in the Nil catchment.

The adapted SWAT model

The SWAT model (Arnold et al., 1998) is chosen for modelling catchment-scale pesticide fluxes to the river. It is a well-documented model with open source code, able to manage hydrology, sediments, nutrients and pesticides. Once calibrated, it can be used for optimising agricultural management (see Sections 4.3 and 4.4).

Measures to reduce point pollution

As different studies have shown that point sources contribute significantly to the pesticide fluxes into surface waters (Neumann et al., 2002; Leu et al., 2004; see Chapter 3 and Section 4.3), an important measure to investigate is the reduction of point losses. Point losses are caused by the cleaning of spray equipment on paved surfaces, the leakage of tools, spills, etc. As shown by Beernaerts et al. (2002), sensitization of farmers regarding this issue can result in an important reduction of point losses. Unfortunately, when the sensitization campaign was stopped, the contribution of point sources rose immediately.

In the adapted SWAT model described in Section 4.4, the parameter 'AP_EF' (application efficiency coefficient) is the fraction of the applied pesticide which is deposited on the treated field. The remainder is diverted directly to the river system, i.e. as a direct loss (point loss + drift loss). By increasing its value, one can simulate the effect of reduced direct losses. Point losses can be reduced due to an increased awareness of farmers or to the presence of a biobed, biofilter or phytobac system on the farm. A reduction of drift losses is possible through the use of field shields, through the use of adapted spraying equipment which reduces the amount of small, driftable droplets in the spray pattern (nozzle type), etc.

During the simulations, it was assumed that the application efficiency has a constant value over the simulation period. However, in reality there will exist variability in time in the fraction of applied pesticides lost as a point loss due to day-to-day variations and farmers customs.

Measures to reduce diffuse pollution

Several best management practices (BMPs) can result in a reduction of pesticide fluxes towards the river. For Belgium, the following BMPs were worthwhile considering: residue management, sowing cover crops, contour farming, strip cropping and buffer strips.

- <u>Residue management</u>: In cropland, leaving adequate residue on the ground after harvest and prior to tillage for planting will reduce sheet and rill erosion. However, farmers often plough the land after harvest and turn-around the soil, which brings less organic soil to the top which is more sensitive to erosion. By means of residue management, at least 30% of the crop residues or of the green manuring stays in the top layer of the soil. One can achieve this by different ploughing practices which are compared here.

The farmers in the Nil catchment plough their corn fields twice: once at the beginning of the winter period with a disk plough and once before seeding with a roller harrow. The different scenarios studied as ploughing alternatives are represented in Table 18. By means of a mouldboard plough only 5 up to 10% of the crop residues remain in the upper soil layer. On the other hand, with a chisel plough this value becomes 70%.

Table 18. Model parameters/management inputs used to represent the different BMPs

BMP		Changed parameters/management inputs
Residue management	mouldboard plough	instead of disk plough
	chisel plough	instead of disk plough
	only seedbed preparation	no ploughing before winter
	direct seeding	bed preparation during seeding
Sowing cover crops	mouldboard plough	instead of disk plough + rye
	chisel plough	instead of disk plough + rye
	only seedbed preparation	no ploughing before winter + rye
	direct seeding	bed preparation during seeding + rye
Contour farming		USLE_P: 0.6; CN2: -3
Strip cropping		USLE_P: 0.3; CN2: - 6
Buffer strips		see detailed description

- Sowing cover crops: To reduce erosion, it is recommended to cover the soil during the winter period with a crop. As corn is only harvested late, the possibilities for cover crops are limited to rye and grass. However, grass is not resistant against the herbicide atrazine. Therefore, we focus on rye as a cover crop. In the studied scenarios, rye is sown after corn harvest at the end of October. It is a hardy annual. To protect the soil from drying out before corn seeding, the rye is harvested or killed three weeks before, somewhere mid April.

- Contour farming: Crops grown in the sloping lands cause sheet and rill erosion and transport of sediments, nutrients and pesticides. With contour farming farmers plough and sow perpendicular to the contour lines, which strongly reduces the losses. The SWAT manual (Neitsch et al., 2002) advises to change the value of the parameter USLE_P. This parameter is defined as the ratio of soil loss with a specific support practice to the corresponding loss with up-and-down slope culture. Support practices include contour tillage, strip cropping on the contour and terrace systems. Besides the parameter USLE_P, the SWAT manual also suggests to change the value for the curve number CN2.

- Strip cropping: Strip cropping has the same properties as contour farming, but in this case crops with different plant spacing are alternated. A dense crop is alternated with a less dense crop. As written before, the parameters USLE_P and CN2 should be adapted.

- Buffer strips: Buffer strips have different filtering capacities through sedimentation and infiltration processes. In the original SWAT code, the filter strip trapping efficiency for sediments, nutrients and pesticides is calculated as follows:

$$trap_{ef} = 0.367(width_{filtstrip})^{0.2967} \qquad \text{(eq. 4-43)}$$

where $trap_{ef}$ is the fraction of the constituent loading trapped by the filter strip and $width_{filtstrip}$ is the width of the filter strip (m). This formula has the following limitations:

- The maximum width of the filter strip that can be chosen is 30m. Wider strips result in a trapping efficiency that equals 1: everything is retained by the buffer strip. In reality, this will not be valid under all circumstances and under all rainfall intensities.
- For each compound, a same fraction is retained in the buffer strip. In reality, there will be a difference between coarse and small particles and between dissolved and sorbed fractions. The coarser particles will sediment faster and pesticides for example are mainly bound to the small clay particles.
- The model does not take into account hydrologic variations in runoff scenarios. In reality, the trap efficiency will be different for storm events and normal rainfall events, i.e. the rain intensity will play a role.
- The model considers a buffer strip for a whole hydrologic response unit (HRU) (which is a lumped area with a unique combination of land use and soil in a subbasin) and not only for the fields that are situated truly along the river.
- The formula was derived from US empirical data on buffer strip efficiency (Bärlund et al., 2006).

Therefore, the source code was adapted by extending the processes in the infiltration part and by adding a part describing sedimentation in the buffer strip. In this study, the exercise was made for 2 adjacent fields: one corn field and a buffer strip. The results were then extrapolated for all corn fields in the catchment situated along the river. A schematic respresentation is given in Figure 49.

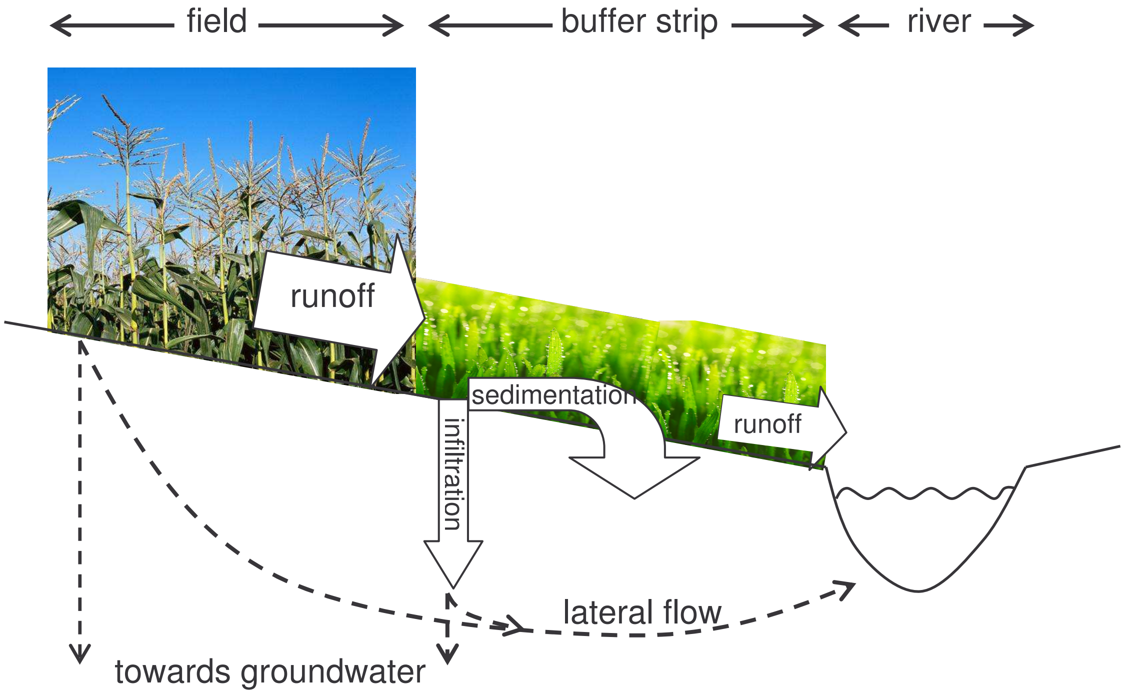


Figure 49. Schematic representation of processes occurring in a buffer strip that are added or extended in the SWAT source code.

The extension of the infiltration part in the buffer strip, consisted of the addition of runoff from the corn field to the rainfall in the adjacent buffer strip. The considered amount of water can then infiltrate together with the dissolved nutrients and pesticides.

The sedimentation process was implemented in the source code as described below. Deletic (2001) found a correlation between the trapping efficiency for the sediment fraction *s* (particles of diameter d_s), $T_{r,s}$ (-), and the particle fall number $N_{f,s}$:

$$T_{r,s} = \frac{N_{f,s}^{0.69}}{N_{f,s}^{0.69} + 4.95} \qquad N_{f,s} = \frac{b \times v_s}{h \times v_m} \qquad \text{(eq. 4-44)}$$

where *b* is the width of the buffer strip (m); v_s the Stokes settling velocity of the particle d_s (m/s); *h* the depth of the flow (m); and v_m the average mean flow velocity between grass blades (m/s). The average mean overland flow velocity v_m is calculated in SWAT as follows:

$$v_m = \frac{q_{ov}^{\ 0.4} \times s^{0.3}}{n^{0.6}} \qquad \text{(eq. 4-45)}$$

where q_{ov} is the average overland flow rate considering a strip 1 meter wide down the sloping surface (m³/s); s is the slope of the buffer strip (estimated to be 0.1%) (m m^{-1}) and n is Manning's roughness coefficient (Neitsch et al., 2002). The parameter q_{ov} was calculated by means of the peak flow q_{peak} divided by the width of the buffer strip. The peak flow q_{peak} was used instead of the 24 hour runoff average, as the latter would overestimate the real trapping efficiency. In SWAT q_{peak} is calculated as described in equation 4-6 (see Section 4.2).

In order to determine the depth of flow h used in equation 4-44, the formula of Tollner et al. (1977) is implemented:

$$h = \frac{1.5 \times q_{ov} \times n}{R^{2/3} \times S_{crop}^{\ 1/2}} \qquad \text{(eq. 4-46)}$$

The two unknowns in equation 4-38 are the hydraulic radius R (m) and the distance S_{crop} between the grass blades (m). The hydraulic radius equals $R = \frac{S_{crop} \times h}{2 \times h + S}$ (Tollner et al., 1977). S_{crop} is estimated to amount 4.5 mm (Gharabaghi et al., 2000).

The above mentioned equations are based on the assumptions that no resuspension occurs and that the water flow over the buffer strip is superficial. The inflowing sediment load in the buffer strip is divided into its three main fractions sand, silt and clay by analogy with the soil profile. Their respective average particle diameters (d_s) are 975, 24 and 1 µm.

4.6.3 Results and discussion

Measures to reduce point pollution

Different scenarios were compared, where each time the value of the application efficiency parameter AP_EF was slightly increased, corresponding to reduced point losses. The initial value for AP_EF reached after calibration was 0.998 (see Section 4.4). The results of the simulations for the year 1998 are presented in Table 19.

Table 19. Simulated load of atrazine in the river Nil during the year 1998 for different values of the application efficiency parameter, together with the percentage of increase or decrease compared to the initial atrazine load.

Application efficiency	0.998	0.9985	0.999
load of atrazine in solution (kg)	2.58	2.38	2.12
increase (+)/ decrease (-) in load (%)	0	-8.8	-19.4

Table 19 illustrates that diminishing the point losses with 50% during the year 1998 results in a decrease of the total atrazine load in the river with almost 20%. A reduction in point losses with 25% is estimated to result in almost 10% of load reduction in the river Nil during the year 1998. However, as mentioned in Section 4.4.4, 1-AP_EF (direct losses) was probably underestimated. As such, a reduction of point losses with 50% will in reality result in a higher decrease of the total atrazine load in the river than predicted by the model. From the monitoring campaigns (Chapter 3), it seems that lowering the point losses with 50% will reduce the atrazine load in the river with 20 to 35%.

Measures to reduce diffuse pollution

The simulation results for the studied best management practices (BMPs) for corn cultivation in the Nil basin are presented in Table 20 for the year 1998. They allow ranking of BMPs for atrazine mitigation.

Table 20. Results of BMPs for the reduction of atrazine loads (g) in the river Nil for the year 1998.

BMP		Increase(+) /decrease(-) atrazine load (%)	% change dissolved atrazine	% change sorbed atrazine
Residue management	mouldboard plough	+0.9	-0.15	+19.90
	chisel plough	-1.0	+0.33	-23.26
	only seedbed preparation	-1.2	+0.57	-32.78
	direct seeding	-1.4	+1.02	-43.84
Sowing cover crops	mouldboard plough	-31.4	-32.12	-33.97
	chisel plough	-32.1	-32.12	-47.16
	only seedbed preparation	-32.3	-32.08	-51.51
	direct seeding	-32.7	-32.04	-58.43
Contour farming		-26.9	-25.93	-56.50
Strip cropping		-38.7	-37.27	-80.79
Buffer strips	5m width	-11.4	-11.64	-12.07

Before making any conclusions, it should be stressed that the change of the parameter values CN2 and USLE_P is based on literature. It is known that model predictions are rather sensitive to the curve number CN2 (Section 4.3). As a consequence, the performed study should be considered to provide a ranking in effectiveness of different measures rather than a quantitative assessment. To achieve the latter, field data would be necessary in order to be able to better parameterise the model for BMPs.

From Table 20 it is clear that strip cropping is the most successful practice for atrazine reduction in the Nil basin, both for the dissolved and sorbed atrazine fractions. It is followed by sowing cover crops and contour farming. The latter has its largest impact on the sorbed atrazine fraction. The construction of buffer strips results in a smaller decrease in atrazine load. Hereby, it should be noticed that this measure was not applied on all corn fields as was done with the other measures, but only on corn fields situated along the river. Moreover, the model does not take into account runoff water coming from the fields situated above. This can result in underpredicting the amount of runoff water entering the buffer strip and in underestimating the overland flow velocity. Also, the buffering capacity is only calculated if a real grassed buffer strip is present. Modifications of ploughing practices seems the least efficient measure in this study.

4.6.4 Conclusions and recommendations

From this study, a ranking in effectiveness of measures for atrazine load reduction could be obtained: strip cropping seems to be more efficient than the sowing of cover crops, the construction of buffer strips, a 25% reduction of point losses and finally plough management, in that order. As indicated by Santhi et al. (2006), extensive monitoring data and intensive observation of BMPs are essential for assessing the effects of BMPs in a watershed. As for the moment there is no adequate literature available showing the quantitative benefits of BMPs, a modelling approach is very useful.

Chapter 5

THE RIVER WATER QUALITY MODEL N°1

Parts of this chapter are adapted from: De Schepper, V.C.J., Holvoet, K.M.A., Benedetti, L., Seuntjens, P., Vanrolleghem, P.A. (2006). Extension of the River Water Quality Model N°1 with the fate of pesticides. Submitted.

5.1 Model choice for in-stream water quality

Several types of river water quality models for conventional pollutants (e.g. organic and inorganic nutrients) are available. The complexity and number of state variables of these models increase from the simplest Streeter-Phelps (Streeter and Phelps, 1925) to more extended models. In 1925, Streeter and Phelps derived the classic equations for simulating DO (dissolved oxygen) and BOD (biological oxygen demand) in rivers. These equations have formed the basis for many water quality models that have been developed around the world since that time. In the last twenty years, with the increased use of computers in the field of hydrology, there have been a number of significant developments in the field of water quality modelling and these have resulted in a variety of models including SIMCAT, TOMCAT, QUAL2E, MIKE-11 and ISIS. SIMCAT (SIMulation of CATchments) and TOMCAT (Temporal/Overall Model for CATchments) are stochastic models making use of Monte Carlo analysis techniques (Cox, 2003). QUAL2E simulates dissolved oxygen and the many associated water quality parameters of the C, N and P cycle in rivers and streams under conditions of steady stream flow and pollutant discharge. Currently, QUAL2E is the most widely available stream water quality model (Cox, 2003). Many water quality simulators are following similar modelling approaches like MIKE11 (DHI, 1992), ISIS (Wallingford Software, 1994) and DUFLOW (Aalderink et al., 1995).

However, the QUAL2E type model were indicated to have some limitations. One of the major limitations is the continued reliance on BOD (Biological Oxygen Demand) as the primary state variable, despite the fact that BOD does not include all biodegradable matter. Besides, there is only a poor representation of benthic flux terms. As a result of these limitations, it is impossible to completely close mass balances in most existing models (Rauch et al., 1998).

An integrated water quality modelling approach also requires a river water quality model that can be connected easily to, and is compatible with, typical Activated Sludge wastewater treatment plant Models (ASMs) (Reichert et al., 2001). In contrast to QUAL2E type models, ASMs are based on Chemical Oxygen Demand (COD) as a measure of carbonaceous organic matter, and also explicitly consider microbial biomass as state variable. Accordingly, the IWA Task Group on River Water Quality Modelling proposed the River Water Quality Model number 1 (RWQM1) (Reichert et al., 2001). This model considers microbial biomass as state variables, and it is also based on COD. It is thus compatible with the existing IWA Activated Sludge Models: ASM1 (Henze et al., 1987), ASM2 (Henze et al., 1995) and ASM3 (Gujer et al., 1999).

The advantage of using RWQM1 instead of SWAT for modelling pesticide processes in the river lies in the fact that it has closed elemental mass balances and that it explicitly considers microbial biomass as a state variable. Explicitly accounting for the presence of more or less biomass will affect the degradation of pesticides, will affect the concentration of particulate material to which pesticides can sorb and settle. A better accounting of biological activities will also affect the way the environmental conditions in the river change (e.g. pH, dissolved oxygen concentration) which may influence the fate of the pesticide in the water column. Another big advantage of RWQM1 lies in its possibility to study the fate and behaviour of different pesticides at the same time while the SWAT model can only route one pesticide at a time. Within the SWAT model, the partitioning of pesticides in the river between water and particles is based on K_d instead of a K_{OC}. The sedimentation and resuspension processes are described by means of rather empirical equations that are based on empirical parameters (see eq. 4-18 up to 4-20). A more realistic approach based on K_{OC} values and dissolved organic carbon (DOC) and particulate organic carbon (POC) as carriers for pesticides, allows RWQM1 to represent the sedimentation, resuspension and burial processes in a more realistic way. Hereby, the simulations will form a closer approach to reality and extrapolations become more reliable, e.g. when performing scenario analysis of management options. With the RWQM1 model very small time steps can be used (e.g. minutes) compared to the SWAT model which uses daily or hourly (ESWAT) time steps. For modeling sedimentation and resuspension processes, this an important advantage.

5.2 Description of the RWQM1 model

The equations of the conversions or biochemical model are based on three assumptions:

- First, it is assumed that for each model application the elemental composition of all compounds and organisms, as well as the stoichiometry of all processes is constant in time.
- No adaptation of specific organisms takes place and changes in the composition within organism classes are neglected.
- Finally, it is assumed that oxygen and/or nitrate is always available. If anaerobic processes in the water column or the river sediment are of importance for the turnover of the compounds considered in the model, the model must be extended to account for these processes.

In the RWQM1 model, 24 processes and 23 state variables are considered. The interactions between the different system components can be represented in matrix form (Table 21). The first line and column of this matrix represent the state variables and the processes respectively. Soluble components are represented by means of an S, insoluble components by means of an X. Subscripts are used to represent state variables. A description of the components and processes is given in Section 5.2.1 and 5.2.2 respectively.

Table 21. Qualitative stoichiometric matrix of the complete River Water Quality Model N°1 (Reichert et al., 2001).

Component → *i*		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)
j	Proces ↓	S_S	S_I	S_{NH4}	S_{NH3}	S_{NO2}	S_{NO3}	S_{HPO4}	S_{H2PO4}	S_{O2}	S_{CO2}	S_{HCO3}	S_{CO3}	S_H	S_{OH}	S_{Ca}	X_H	X_{N1}	X_{N2}	X_{ALG}	N_{CON}	X_S	X_I	X_P	X_{II}
(1a)	Aerobic Growth of Heterotrophs with NH_4	-		?				?		-	+			?			1								
(1b)	Aerobic Growth of Heterotrophs with NO_3	-					-	?		-	+			?			1								
(2)	Aerobic Respiration of Heterotrophs			+				+		-	+			-			-1						+		
(3a)	Anoxic Growth of Heterotrophs with NO_3	-				+	-	?			+			?			1								
(3b)	Anoxic Growth of Heterotrophs with NO_2	-				-		?			+			?			1								
(4)	Anoxic Respiration of Heterotrophs			+			-	+			+			-			-1						+		
(5)	Growth of 1st-stage Nitrifiers			-		+		-		-	-			+				1							
(6)	Aerobic respiration of 1st-stage Nitrifiers			+				+		-	+			-				-1					+		
(7)	Growth of 2nd-stage Nitrifiers					-	+	-		-	-								1						
(8)	Aerobic respiration of 2nd-stage Nitrifiers			+				+		-	+			-					-1				+		
(9a)	Growth of Algae with NH4			-				-		+	-			-						1					
(9b)	Growth of Algae with NO3						-	-		+	-			-						1					
(10)	Aerobic Respiration of Algae			+				+		-	+			-						-1			+		
(11)	Death of Algae			(+)				(+)		(+)	?			?						-1		+	+		
(12a)	Growth of Consumers on XALG			(+)				(+)		-	?			?						-	1	+			
(12b)	Growth of Consumers on XS			(+)				(+)		-	?			?							1	-			
(12c)	Growth of Consumers on XH			(+)				(+)		-	?			?			-				1				
(12d)	Growth of Consumers on XN1			(+)				(+)		-	?			?				-			1				
(12e)	Growth of Consumers on XN2			(+)				(+)		-	?			?					-		1				
(13)	Aerobic Respiration of Consumers			+				+		-	+			-							-1		+		
(14)	Death of Consumers			(+)				(+)		(+)	?			?							-1	+	+		
(15)	Hydrolysis	+		(+)				(+)		(+)	?			?								-1			
(16)	Equilibrium CO2 <-> HCO3										-1	1		+											
(17)	Equilibrium HCO3 <-> CO3											-1	1	+											
(18)	Equilibrium H2O <-> H+OH													1	1										
(19)	Equilibrium NH4 <-> NH3			-1	1									+											
(20)	Equilibrium H2PO4 <-> HPO4							1	-1					+											
(21)	Equilibrium Ca <-> CO3												+			1									
(22)	Adsorption of Phosphate							-1																1	
(23)	Desorption of Phosphate							1																-1	

In Table 21, the signs of all non-zero stoichiometric coefficients are given: '+' indicates a positive stoichiometric coefficient, '-' a negative coefficient, '?' indicates a coefficient the sign of which depends on the composition of the organic substances involved in the process and on the stoichiometric parameters, and '(+)' is the same as '?', but in this case, the composition of compounds and the stoichiometric parameters should be chosen in a way that guarantees that this coefficient is non-negative (because there is no limiting factor to the corresponding compound in the process rate). Stoichiometry and kinetics of processes are briefly discussed in the following paragraph.

The composition of organic matter is approximated by mass fractions of the elements C, H, O, N and P and the 'compound' X that summarises all other elements. For this reason, the composition of organic substances can uniquely be described by the mass fractions α_C, α_H, α_O, α_N, α_P en α_X. These mass fractions fulfil the constraint

$$\alpha_C + \alpha_H + \alpha_O + \alpha_N + \alpha_P + \alpha_X = 1 \qquad \text{(eq. 5-1)}$$

The key process leading to conversion formulas between the elemental approach and the conceptual COD (chemical oxygen demand) approach is the mineralization process of organic compounds:

$$COD = 32 \times \left(\frac{\alpha_C}{12} + \frac{\alpha_H}{4} - \frac{\alpha_O}{32} - \frac{3\alpha_N}{56} + \frac{5\alpha_P}{124} \right) \times OM \qquad \text{(eq. 5-2)}$$

where *OM* is the dry mass of organic material.

5.2.1 Model components

The different model components are presented in Table 22. Their concentrations will change in time as they are subject to different processes (see Section 5.2.2)

Table 22. State variables in the River Water Quality Model N°1.

State variables	Description
S_S	Dissolved organic substances, available for rapid biodegradation by heterotrophic organisms
S_I	Inert dissolved organic substances, not biodegradable within the time frame of relevance
S_{NH4}	Ammonium nitrogen: NH_4^+-N
S_{NH3}	Ammonia nitrogen: NH_3-N
S_{NO2}	Nitrite nitrogen: NO_2^--N
S_{NO3}	Nitrate nitrogen: NO_3^--N
S_{HPO4}	Part of inorganic dissolved phosphorus: HPO_4^{2-}-P
S_{H2PO4}	Part of inorganic dissolved phosphorus: H_2PO_4-P
S_{O2}	Dissolved oxygen: O_2
S_{CO2}	Sum of dissolved carbon dioxide and H_2CO_3: CO_2-C + H_2CO_3-C
S_{HCO3}	Bicarbonate: HCO_3^-
S_{CO3}	Dissolved carbonate: CO_3^{2-}
S_H	Hydrogen ions: H^+
S_{OH}	Hydroxyl ions: OH^-
S_{Ca}	Dissolved calcium ions: Ca^{2+}
X_H	Heterotrophic organisms growing aerobically as well as anoxically
X_{N1}	Organisms oxidising ammonia to nitrite, first step nitrifiers
X_{N2}	Organisms oxidising nitrite to nitrate, second step nitrifiers
X_{ALG}	Algae and macrophytes
X_{CON}	Consumers
X_S	Particulate organic material, available for biodegradation and hydrolysis
X_I	Inert particulate organic material, not biodegradable within the time frame of relevance
X_P	Phosphate adsorbed to particles
X_{II}	Particulate inorganic material

5.2.2 Model processes

The following processes are considered in the model (numbers correspond to the rows in Table 21 and Table 23).

(1) Aerobic Growth of Heterotrophs: Growth of heterotrophic organisms using dissolved organic substrate, dissolved oxygen and nutrients. If the organic substrate contains enough phosphorus, no phosphate uptake from the surrounding water is necessary and the limiting term with respect to phosphate can be neglected. If there is not enough nitrogen in the substrate, ammonia is consumed by process (1a). The ammonia limitation term in process

(1a) and the whole process (1b) can be omitted if there is enough nitrogen in the substrate. In this case, the excess nitrogen is released as ammonia by process (1a).

(2, 6, 8, 10, 13). Aerobic endogenous Respiration: Loss of biomass by aerobic endogenous respiration.

(3) Anoxic Growth of Heterotrophs: Growth of heterotrophic organisms with oxygen gained by reducing nitrate tot nitrite or nitrite to molecular nitrogen. This process is inhibited by the presence of dissolved oxygen.

(4) Anoxic Endogenous Respiration of Heterotrophic Organisms: Loss of heterotrophic biomass in the absence of dissolved oxygen by endogenous respiration with nitrate.

(5) Growth of 1st Stage Nitrifiers: Growth of organisms that oxidise ammonia to nitrite.

(7) Growth of 2nd Stage Nitrifiers: Growth of organisms that oxidise nitrite to nitrate.

(9) Growth of Algae: Growth of algae by primary production (photosynthesis).

(11, 14) Death of Algae or Consumers: Conversion of algae or consumers to slowly degradable and inert organic mater by death, lysis, etc.

(12) Growth of Consumers: Growth of consumers by grazing on algae, on particulate organic matter and on heterotrophic and autotrophic organisms (subprocesses 12a to 12e respectively) with production of faecal pellets in the form of slowly biodegradable particulate organic matter.

(15) Hydrolysis: Dissolution of slowly biodegradable particulate organic matter to dissolved organic matter catalysed by heterotrophic biomass.

(16-21) Chemical Equilibria. Chemical Equilibria between CO_2 and HCO_3^-, between HCO_3^- and CO_3^{2-}, between H_2O and H^+ and OH^-, between NH_4^+ and NH_3, between $H_2PO_4^-$ and HPO_4^{2-}, and between Ca^{2+} and CO_3^{2-} and $CaCO_3$ (s).

(22) Adsorption of Phosphate: Any type of binding of phosphate on particulate matter.

(23) Desorption of Phosphate: Release of phosphate previously bound on particulate matter.

Table 23. Process rates in RWQM1 (terms in square brackets are omitted under certain circumstances) (Reichert, 2001).

Nr.	Process	Rate
(1a)	Aerobic Growth of Heterotrophs with NH4	$k_{gro,H,aer,To} e^{\beta_H (T-T_o)} \frac{S_s}{K_{s,H,aer} + S_s} \frac{S_{02}}{K_{02,H,aer} + S_{O2}} \left[\frac{S_{NH4} + S_{NH3}}{K_{N,H,aer} + S_{NH4} + S_{NH3}} \right] \left[\frac{S_{HPO4} + S_{H2PO4}}{K_{HPO4,H,aer} + S_{HPO4} + S_{H2PO4}} \right] X_H$
(1b)	Aerobic Growth of Heterotrophs with NO3	$k_{gro,H,aer,To} e^{\beta_H (T-T_o)} \frac{S_s}{K_{s,H,aer} + S_s} \frac{S_{02}}{K_{02,H,aer} + S_{O2}} \frac{K_{N,H,aer}}{K_{N,H,aer} + S_{NH4} + S_{NH3}} \frac{S_{NO3}}{K_{N,H,aer} + S_{NO3}} \left[\frac{S_{HPO4} + S_{H2PO4}}{K_{HPO4,H,aer} + S_{HPO4} + S_{H2PO4}} \right] X_H$
(2)	Aerobic Respiration of Heterotrophs	$k_{resp,H,aer,To} e^{\beta_H (T-T_o)} \frac{S_{O2}}{K_{O2,H} + S_{O2}} X_H$
(3a)	Anoxic Growth of Heterotrophs with NO3	$k_{gro,H,an,To} e^{\beta_H (T-T_o)} \frac{S_s}{K_{s,H,an} + S_s} \frac{K_{02,H,aer}}{K_{02,H,aer} + S_{O2}} \frac{S_{NO3}}{K_{NO3,H,an} + S_{NO3}} \left[\frac{S_{HPO4} + S_{H2PO4}}{K_{HPO4,H,an} + S_{HPO4} + S_{H2PO4}} \right] X_H$
(3b)	Anoxic Growth of Heterotrophs with NO2	$k_{gro,H,an,To} e^{\beta_H (T-T_o)} \frac{S_s}{K_{s,H,an} + S_s} \frac{K_{02,H,aer}}{K_{02,H,aer} + S_{O2}} \frac{S_{NO2}}{K_{NO2,H,an} + S_{NO2}} \left[\frac{S_{HPO4} + S_{H2PO4}}{K_{HPO4,H,an} + S_{HPO4} + S_{H2PO4}} \right] X_H$
(4)	Anoxic Respiration of Heterotrophs	$k_{resp,H,an,To} e^{\beta_H (T-T_o)} \frac{K_{02,H,aer}}{K_{02,H,aer} + S_{O2}} \frac{S_{NO3}}{K_{NO3,H,an} + S_{NO3}} X_H$
(5)	Growth of 1st-stage Nitrifiers	$k_{gro,NI,To} e^{\beta_H (T-T_o)} \frac{S_{O2}}{K_{O2,NI} + S_{O2}} \frac{S_{NH4} + S_{NH3}}{K_{NH4,NI} + S_{NH4} + S_{NH3}} \left[\frac{S_{HPO4} + S_{H2PO4}}{K_{HPO4,H,N1} + S_{HPO4} + S_{H2PO4}} \right] X_{NI}$
(6)	Aerobic respiration of 1st-stage Nitrifiers	$k_{resp,NI,To} e^{\beta_H (T-T_o)} \frac{S_{O2}}{K_{O2,NI} + S_{O2}} X_{NI}$
(7)	Growth of 2nd-stage Nitrifiers	$k_{gro,N2,To} e^{\beta_H (T-T_o)} \frac{S_{O2}}{K_{O2,N2} + S_{O2}} \frac{S_{NO2}}{K_{NO2,N2} + S_{NO2}} \left[\frac{S_{HPO4} + S_{H2PO4}}{K_{HPO4,N2} + S_{HPO4} + S_{H2PO4}} \right] X_{N2}$
(8)	Aerobic respiration of 2nd-stage Nitrifiers	$k_{resp,N2,To} e^{\beta_H (T-T_o)} \frac{S_{O2}}{K_{O2,N2} + S_{O2}} X_{N2}$
(9a)	Growth of Algae with NH4	$k_{gro,ALG,To} e^{\beta_{ALG} (T-T_o)} \frac{S_{NH4} + S_{NH3} + S_{NO3}}{K_{N,ALG} + S_{NH4} + S_{NH3} + S_{NO3s}} \frac{S_{NH4} + S_{NH3}}{K_{N,ALG} + S_{NH4} + S_{NH3}} \left[\frac{S_{HOP4} + S_{H2PO4}}{K_{HPO4,ALG} + S_{HOP4} + S_{H2PO4}} \right] \left[\frac{1}{K_1} \exp \right] \left[1 - \frac{1}{K_I} \right] X_{ALG}$
(9b)	Growth of Algae with NO3	$k_{gro,ALG,To} e^{\beta_{ALG} (T-T_o)} \frac{S_{NH4} + S_{NH3} + S_{NO3}}{K_{N,ALG} + S_{NH4} + S_{NH3} + S_{NO3s}} \frac{S_{NH4,ALG},}{K_{NH4,ALG} + S_{NH4} + S_{NH3}} \left[\frac{S_{HOP4} + S_{H2PO4}}{K_{HPO4,ALG} + S_{HOP4} + S_{H2PO4}} \right] \left[\frac{1}{K_1} \exp \right] \left[1 - \frac{1}{K_I} \right] X_{ALG}$
(10)	Aerobic Respiration of Algae	$k_{resp,ALG,To} e^{\beta_{ALG} (T-T_o)} \frac{S_{O2}}{K_{O2,ALG} + S_{O2}} X_{ALG}$

Table 21. Process rates in RWQM1 (terms in square brackets are omitted under certain circumstances) (continued)

(11)	Death of Algae	$k_{dood,ALG,To}e^{\beta_{ALG}(T-T_o)}X_{ALG}$	
(12a-e)	Growth of Consumers on X_I	$k_{grà,CON,To}e^{\beta_{CON}(T-T_o)}\dfrac{S_{O2}}{K_{O2,CON}+S_{O2}}X_i\,X_{con}$	i = ALG,S, H, N1, N2
(13)	Aerobic Respiration of Consumers	$k_{resp,CON,To}e^{\beta_{CON}(T-T_o)}\dfrac{S_{O2}}{K_{O2,CON}+S_{O2}}X_{con}$	
(14)	Death of Consumers	$k_{dood,CON,To}e^{\beta_{CON}(T-T_o)}X_{con}$	
(15)	Hydrolysis	$k_{hyd,To}e^{\beta_{hyd}(T-T_o)}X_s$	
(16)	Equilibrium CO2 <-> HCO3	$k_{eq,1}\left(S_{CO2}-S_H S_{HCO3}\big/K_{eq,1}\right)$	
(17)	Equilibrium HCO3 <-> CO3	$k_{eq,w}\left(1-S_H S_{HO}\big/K_{eq,w}\right)$	
(18)	Equilibrium H2O <-> H+OH	$k_{eq,2}\left(S_{HCO3}-S_H S_{HCO3}\big/K_{eq,2}\right)$	
(19)	Equilibrium NH4 <-> NH3	$k_{eq,N}\left(S_{NH4}-S_H S_{NH3}\big/K_{eq,N}\right)$	
(20)	Equilibrium H2PO4 <-> HPO4	$k_{eq,P}\left(S_{H2PO4}-S_H S_{HPO4}\big/K_{eq,P}\right)$	
(21)	Equilibrium Ca <-> CO3	$k_{eq,s0}\left(1-S_{Ca}S_{CO3}\big/K_{eq,s0}\right)$	
(22)	Adsorption of Phosphate	$k_{ads}S_{HPO4}$	
(23)	Desorption of Phosphate	$k_{des}X_P$	

5.3 The simulation software WEST

In this chapter, the World Wide Engine for Simulation, Training and Automation (WEST) is used as simulation software for modelling river water quality. WEST® provides the modeller with a user-friendly platform to use existing models or to implement and test new models. Basically, WEST® is a modelling and simulation environment for any kind of process that can be described as a structured collection of Differential Algebraic Equations (DAE systems). Currently, the WEST® simulator is mainly used to model wastewater systems (Vanhooren et al., 2003). However, it can be readily applied to river water quality systems by extending the open model base (Deksissa et al., 2004).

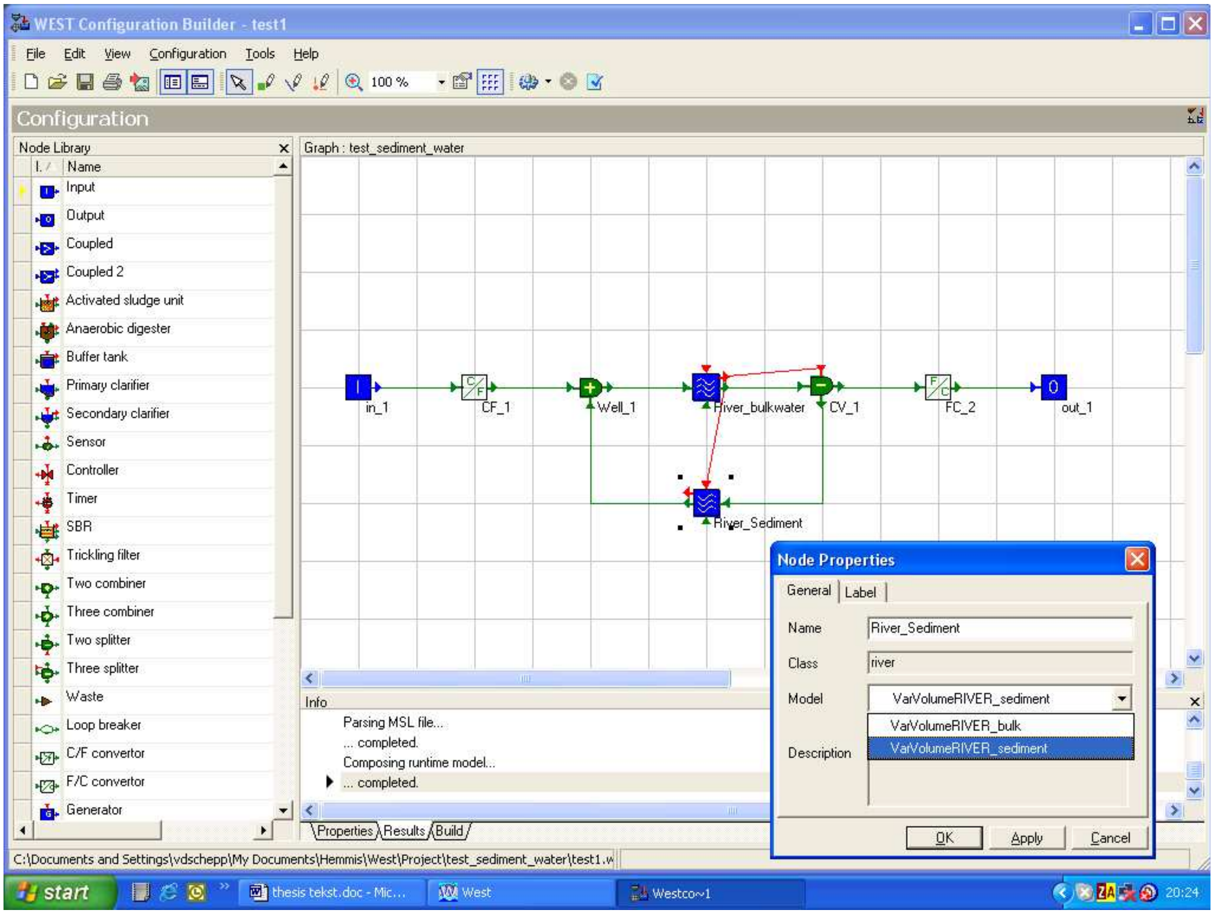
WEST® was developed at BIOMATH, the Department of Applied Mathematics, Biometrics and Process Control of Ghent University in collaboration with Hemmis NV (Kortrijk, Belgium) since 1991. It resulted in the software package WEST 1.0 which was first commercialized in 1993 by HEMMIS. In this dissertation WEST® 3.7 is used.

The general architecture of WEST® exists of two environments and a model base:

- a modelling environment, also called the configuration builder
- an experimentation environment
- and model base: MSL-USER.

One of the central components of WEST® is the model base. In this model base, models are described in MSL-USER (MSL stands for Model Specification Language), a high level object-oriented modelling language (Vanhooren et al., 2003). The model base is aimed at maximal re-use of existing knowledge and is therefore structured hierarchically. All re-usable knowledge, such as mass balances, physical units, default parameter values and applicable ranges, is defined centrally and can be used to build new models. In this way, WEST® has an open structure which allows the user to change existing models and define new ones as needed.

When the modelling environment (configuration builder) is started, the model base is loaded and all relevant information for the modeller is extracted from it. Using the symbolic information in the model base, the 'atomic' models available in the model base are linked to a graphical representation, i.e. graphical building blocks. A hierarchical graphical editor (HGE) allows for the interactive composition of complex configurations from these basic graphical building blocks. Also the input-output structures (terminals) of the models are extracted from the model base so as to decide whether or not two models can be linked together in the HGE. For instance, a model for the activated sludge process can not directly be coupled to a river water quality model, since the set of components used in these models to describe the substrates is not the same. In case such coupling needs to be done, an explicit component converter needs to be used. Next, the parameter set of the different models is loaded so that parameters of different submodels can be linked. As such, a representation of the studied system can be performed. An illustration of the configuration builder is shown in Figure 50.



Parsing MSL file...
... completed.
Composing runtime model...
... completed.

Name: River_Sediment
Class: river
Model: VarVolumeRIVER_sediment

Figure 50. View of the configuration builder for a simple river system.

When a configuration has been put together, the configuration builder starts from the information extracted from the model base and creates and outputs a ‘coupled model’ in MSL-USER, which is automatically added to the model base for further use in new modelling exercises. Additional information about the structure of the model base and the MSL-USER language can be found in Vanhooren et al. (2003) and Deksissa (2004).

In a next step, a model compiler is used to generate low-level MSL-EXEC (C++) code from the MSL-USER model and the atomic model representations in the modelbase. After compilation of this MSL-EXEC code, a model library is formed which can be used for execution in the experimentation environment.

In the experimentation environment the compiled model is loaded and symbolic information is retrieved from the library. Examples of such symbolic information are the model structure and listings of parameters and variables. These listings contain the units, descriptions, default values, initial values and lower and upper bounds for the parameters and variables. After initial values and case-specific parameter values have been seet, the solvers within the experimentation environment generate simulation data which can be used for plotting, model calibration, process optimization, output to files, etc. (Vanhooren et al., 2003).

In Deksissa (2004), the building of the river water quality model base is described in detail.

5.4 Extension of the River Water Quality Model N°1 with the fate of pesticides

5.4.1 Introduction

Pesticides are of concern to water quality managers and environmental risk regulators to maintain and achieve a good water quality status. From this perspective, dynamic models can form suitable instruments for risk assessment and can help to gain insight in the most important processes determining the fate of pesticides. When pesticides enter an aquatic environment, they are exposed to different physical, chemical and microbial processes. Two processes which have a major impact on the fate of pesticides are the sorption-desorption processes and biodegradation. They are described in detail in Chapter 2 (see Section 2.2.2). Both are strongly influenced by the presence of a sediment layer (Warren et al., 2003).

The strength of the River Water Quality Model N°1 (Reichert et al., 2001) lies in the dynamics it can handle, in its ability to guarantee closed elemental mass balances and in the fact that it also takes into account the growth and decay of biomass. Therefore, in this study the existing model (which focuses on nutrients and organic pollutants in bulk water) was extended with the most important processes describing the fate of pesticides in the bulk water and the sediment.

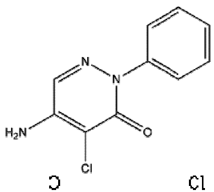
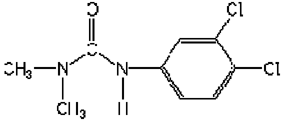
5.4.2 Case study

Study site and pesticides

This study focuses on the Nil, a small, hilly basin described comprehensively in Chapter 1. The Nil catchment was selected because it is a well documented basin, studied in detail in terms of pesticide application (Beernaerts et al., 2002).

Two pesticides with clearly different characteristics were selected to be studied in more detail, diuron and chloridazon. Diuron belongs to the phenyl urea herbicides group and it is rather hydrophobic, while chloridazon contains a pyridazinone compound and is rather hydrophilic (see Table 24). Due to their differences, the fate of the two pesticides in the river is expected to be different.

Table 24. Chemical properties of chloridazon and diuron (Tomlin, 2003).

Pesticide	Formula	S_w (mg/l)	log K_{OW}	K_{OC} (ml/g)	DT_{50soil} (days)	$DT_{50water}$ (days)
Herbicides						
Chloridazon		340 (20°C)	1.19 (pH 7)	89-340	42-56	56**
Diuron		36.4 (25°C)	2 .85± 0.03 (25°C)	538-902*	90-180	29**

* Agritox database. Available at www.inra.fr/agritox/

** Footprint pesticide database. Available at http://www.herts.ac.uk/aeru/footprint/

Monitoring campaign

An intensive monitoring campaign was run during spring 2004, i.e. the main application period of herbicides. The campaign started on March 15 and ended on July 15. Besides water and sediment samples, physiochemical variables (pH, water temperature, conductivity and oxygen concentration) were measured at the mouth of the river using a Hydrolab DS3 (HydroTech, Hutto, Texas, USA) multi-parametric probe. Two automatic samplers were placed in the river basin, one at the closing section and one upstream (see Figure 1). Every 15 minutes, 50 ml of river water was taken by each sampler and collected in one glass bowl during 8 hours. This resulted in one composite sample every 8 hours. During rainfall events, the frequency was increased to have 6-hour composite samples. Undisturbed sediment samples were taken twice (17th of May, 29th of June) by means of a macro-core and were immediately frozen on the field with CO_2-ice. This way, the sediment samples could be easily transported avoiding any disturbance. Once in the laboratory, the samples were sliced and analysed for pesticides in pore water and in the sediment. A detailed description of the data collection, sample handling and analysis of the different samples and fractions is given in Section 3.2.3.

5.4.3 Model development

The model developed in this section comprises a hydraulic model and a model describing the biochemical conversions, which is called the River Model No. 1 with Generic Chemical (RM1GC). This model finds its origin in the model CHETOX1 developed by Deksissa et al. (2004), which in itself is a development of the RWQM1 model (Reichert et al., 2001). Implementation of the model and the simulations were performed with the WEST® software (Hemmis nv, Kortrijk, Belgium).

Hydraulics

The hydraulic model consists of a cascade of continuously stirred tank reactors in series (CSTRS) (Figure 52) with variable volume (Beck and Reda, 1994; Deksissa et al., 2004), and it is based on the following water mass balance:

$$\frac{dV(t)}{dt} = Q_{in}(t) + Q_d(t) - Q_{out}(t) \qquad \text{(eq. 5-3)}$$

with V the volume of water in the tank at time t (m³); Q_{in} the inflow from upstream at time t and equal to the outflow of the previous tank (except for the first tank) (m³ d^{-1}); Q_d the flow from tributaries, groundwater and run off (m³ d^{-1}); and Q_{out} the outflow of the tank at time t (m³ d^{-1}).

The hydraulic parameters were defined in accordance with the parameters and calculations resulting from the Soil and Water Assessment Tool (SWAT) (Arnold et al., 1998). The SWAT model was used to create input data such as runoff and groundwater flow (see Section 4.3).

The considered tanks have a prismatic shape with a trapezoidal cross section (Deksissa et al., 2004).

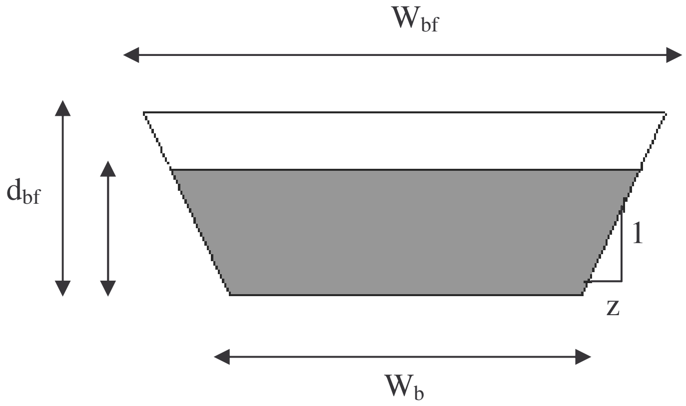


Figure 51. Cross section of a river tank.

In the developed hydraulic model the outflow is calculated with Manning's equation:

$$q(t) = \frac{A_{cros}(t)R(t)slp^{1/2}}{n} \tag{eq. 5-4}$$

where A_{cros} is the area of the cross section of the tank (m²), R is the hydraulic radius (m), *slp* is the slope along the channel length (m/m) and n is Manning's coefficient.

The depth of the surface water is calculated as follows:

$$d(t) = \sqrt{\frac{A_{cros}(t)}{z} + \left(\frac{W_{btm}(t)}{2\,z}\right)^2} - \frac{W_{btm}(t)}{2\,z} \tag{eq. 5-5}$$

where d is the depth of the surface water (m), W_{btm} is the bottom width (m), A_{cros} is the area of the cross section of the tank (m²) and z is the slope of the bank (-).

The velocity $v(t)$ (m d^{-1}) in the tank is function of the outflow:

$$v(t) = \frac{Q_{out}(t)}{A_{cros}(t)} \tag{eq. 5-6}$$

Biochemical conversions

The developed RM1GC model describes the fate of pesticides in both bulk water and sediment. The RM1GC model is an extension and at the same time a simplification of the RWQM1 model (Reichert et al., 2001). The RWQM1 model is extended with a sediment compartment and with the fate of chemicals (in this case two pesticides), while the activity of algae and protozoa is neglected. The model is based on and has improved the previously developed model CHETOX1 (Deksissa et al., 2004).

Basic Water Quality Model: In the sediment and in the bulk water compartment the same biochemical conversion processes are described. The conversion processes represent how biological, chemical and physical processes influence the different substances. In the following mass balance equation all conversion processes are described by the use of a volumetric reaction rate, r:

$$\frac{d(V\,C)}{dt} = Q_{in}(t)\,C_{in}(t) + Q_d(t)\,C_d(t) - Q_{out}(t)\,C(t) + r(t)\,V(t) \qquad \text{(eq. 5-7)}$$

with C the outflow concentration and the concentration in the tank, assuming a completely mixed solution (mg L^{-1}); C_{in} the inflow concentration (mg L^{-1}); and r the reaction rate for the conversion processes (mg L^{-1} d^{-1}) (Figure 52).

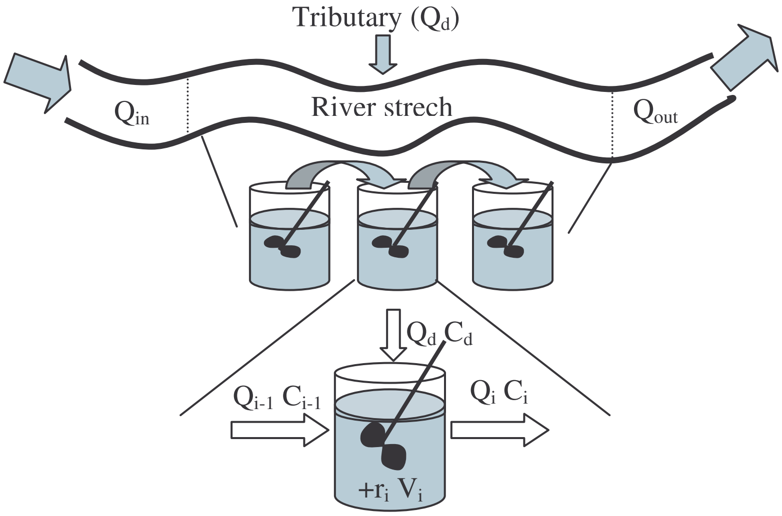


Figure 52. Schematic representation of continuously stirred tank reactors in series with their conversion reaction rate *r*.

The RWQM1 was developed to be a standard river water quality model for conventional pollution problems such as nutrients, suspended solids and algal blooms. The conversion processes of these substances are formulated on the basis of Monod kinetics and the stoichiometric coefficients are calculated by taking into account both elemental and charge balances. The RWQM1 is a comprehensive eutrophication model with many model parameters and state variables, so its simplification is highly recommended for practical/specific applications. In this paper the model simplification of Deksissa et al. (2004) was used. The state variables and the Petersen matrix of the simplified model are shown in Table 25 and Table 26.

Table 25. State variables in the RM1GC model

	State Variables	Description
1	S_{GC}	Dissolved and sorbed generic compound (pesticide)
2	S_S	Readily biodegradable COD
3	S_I	Inert soluble COD
4	S_{NH}	Ammonia nitrogen (NH_3)
5	S_{NO2}	Nitrite nitrogen
6	S_{NO3}	Nitrate nitrogen
7	S_{PO}	Phosphate phosphorus (H_2PO_4 and HPO_4)
8	S_{O2}	Dissolved oxygen
9	X_H	Heterotrophic biomass
10	X_{N1}	Nitrifying biomass (first step)
11	X_{N2}	Nitrifying biomass (second step)
12	X_S	Particulate biodegradable organic matter
13	X_I	Particulate inert COD
14	X_P	Phosphorus adsorbed to particles

Table 26. Petersen matrix for the RM1GC model

Component → *i*		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
j	Process ↓	S_{GC}	S_S	S_I	S_{NH}	S_{NO2}	S_{NO3}	S_{PO}	S_{O2}	X_H	X_{N1}	X_{N2}	X_S	X_I	X_P
(1a)	Aerobic Growth of Heterotrophs with NH_4		-		?			?	-	1					
(1b)	Aerobic Growth of Heterotrophs with NO_3		-				-	?	-	1					
(2)	Aerobic Respiration of Heterotrophs				+			+	-	-1				+	
(3)	Anoxic Growth of Heterotrophs with NO_3		-			+	-	?		1					
(4)	Anoxic Growth of Heterotrophs with NO_2		-			-		?		1					
(5)	Anoxic Respiration of Heterotrophs				+		-	+		-1				+	
(6)	Growth of 1^{st}-stage Nitrifiers				-	+		-	-		1				
(7)	Aerobic respiration of 1^{st}-stage Nitrifiers				+			+	-		-1			+	
(8)	Growth of 2^{nd}-stage Nitrifiers					-	+	-	-			1			
(9)	Aerobic respiration of 2^{nd}-stage Nitrifiers				+			+	-			-1			
(10)	Hydrolysis		(+)		(+)			(+)	(+)				-1		
(11)	Adsorption of Phosphorus							-1							1
(12)	Desorption of Phosphorus							1							-1
(13)	Aeration								1						
(14)	Aerobic Degradation of GC by Heterotrophs	-1							-	+					
(15)	Anaerobic Degradation of GC by Heterotrophs	-1								+					

Pesticide fate model: The simplified RWQM1 was subsequently extended with two generic pesticide components, i.e. the state variable S_{GC1} and S_{GC2}. For simplicity, in the description of the model only one variable (S_{GC}) is mentioned as there are no assumed interactions between the two chemicals.

The studied pesticides, diuron and chloridazon, are subject to aerobic biodegradation and sorption processes both in the bulk water and in the sediment. The considered transport processes between the two compartments are sedimentation, resuspension and diffusion. In the sediment compartment a burial process occurs as well (Figure 53).

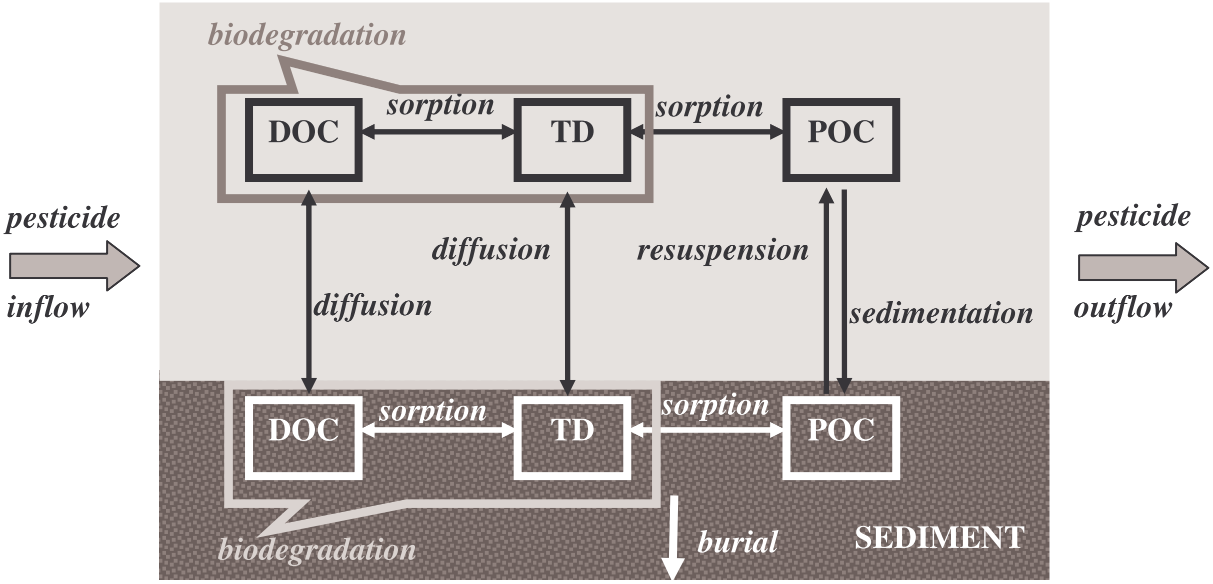


Figure 53. Schematic representation of processes which determine the fate of pesticides in rivers according to the RM1GC model (Deksissa et al., 2004).

The model has two compartments: the bulk water and the sediment. The pesticides can be present in three different forms: totally dissolved in water (TD), sorbed to dissolved organic carbon (DOC) and sorbed to particulate organic carbon (POC). Pesticide concentrations are calculated by means of mass balances which include some assumptions concerning the pesticide:

- Only the dissolved fraction of the pesticide ($f_d + f_{DOC}$) is subject to diffusion and biodegradation, the sorbed phase (f_p) can settle and resuspend, but is not biodegradable.
- There is a difference between the concentration in the pore water ($S_{GC,pore}$) and the concentration in the overall bed compartment ($S_{GC,bed}$). The relationship between the two concentrations is given by the porosity (p) and the dissolved fraction:

$$S_{GC,pore} = (1\text{-}f_p)\frac{\mathrm{S_{GC,bed}}}{p}.$$

- Only biodegradation, sorption, sedimentation, resuspension and burial are considered in the degradation and transport processes of the pesticides. This approximation is acceptable for the pesticides diuron and chloridazon, as their volatilization is negligible since their Henry coefficient or water-air partition is low (Tomlin, 2003). The chemical hydrolysis process is also neglected. Data have shown that chloridazon and diuron are stable (Tomlin, 2003; Agritox database).

- Furthermore, it is assumed that the sorption equilibrium is reached very quickly, hence the use of a partition coefficient is acceptable.
- The model keeps the porosity of each sediment layer constant, which implies that the thickness of the sediment is variable. With this approach, the advective transport between sediment and bulk water is neglected.

The mass balances for the pesticide concentrations are as follows:

Bulk water

$$\begin{aligned}\frac{d(V\,S_{GC})}{dt} = & \underbrace{Q_{in}(t)\,S_{GC,in}(t)+Q_d(t)\,S_{GC,d}(t)-Q_{out}(t)\,S_{GC}(t)}_{\text{hydraulics}}-\underbrace{k_b\left(1-f_p(t)\right)S_{GC}(t)\,V(t)}_{\text{biodegradation}} \\ & -\underbrace{k_{sed}\,f_p(t)\,S_{GC}(t)\,V(t)}_{\text{sedimentation}}+\underbrace{k_{res}\,f_{p,bed}(t)\,S_{GC,bed}(t)\,V_{bed}(t)}_{\text{resuspension}} \\ & +\underbrace{K_{L,GC}\left[\left(1-f_{p,bed}(t)\right)\frac{S_{GC}(t)}{p}-\left(1-f_p(t)\right)S_{GC}(t)\right]A_{bottom}}_{\text{diffusion}}\end{aligned} \qquad \text{(eq. 5-8)}$$

Sediment

$$\begin{aligned}\frac{d(V_{bed}\,S_{GC,bed})}{dt} = & -\underbrace{k_b\left(1-f_{p,bed}(t)\right)S_{GC,bed}(t)\,V_{bed}(t)}_{\text{biodegradation}}+\underbrace{k_{sed}\,f_p(t)\,S_{GC}(t)\,V(t)}_{\text{sedimentation}} \\ & -\underbrace{k_{burial}\,S_{GC,bed}(t)\,\mathrm{V}_{\mathrm{bed}}(t)}_{\text{burial}}-\underbrace{k_{res}\,f_{p,bed}(t)\,S_{GC,bed}(t)\,V_{bed}(t)}_{\text{resuspension}} \\ & -\underbrace{K_{L,GC}\left[\left(1-f_{p,bed}(t)\right)\frac{S_{GC}(t)}{p}-\left(1-f_p(t)\right)S_{GC}(t)\right]A_{bottom}}_{\text{diffusion}}\end{aligned} \qquad \text{(eq. 5-9)}$$

where S_{GC} and $S_{GC,bed}$ are the total – dissolved and sorbed – pesticide concentration in respectively the bulk water and the sediment (mg L^{-1}); k_b, k_{sed}, k_{res} and k_{burial} are the first order rate constants for respectively biodegradation, sedimentation, resuspension and burial (d^{-1}); f_p and $f_{p,bed}$ are the pesticide fractions sorbed on respectively suspended and benthic POC (-); $K_{L,GC}$ is the mass transfer coefficient which describes the diffusion of the pesticide from bulk water to sediment (m d^{-1}); p is the porosity (-); V and V_{bed} are the volumes of respectively the bulk water and sediment compartment (m³); and A_{bottom} is the bottom surface of the reach (m²).

Besides the mass balances for the pesticides, there are also mass balances formulated for the other state variables used in the simplified RWQM1 (Deksissa et al., 2004), such as COD, biomass, oxygen, nitrogen, … Those variables are subject to the biochemical conversion processes already described for the basic water quality model (see Section 5.2.2). Since RWQM1 only defines the first term in the components' mass balance, the processes which affect the dissolved components (S_i) (mg/l) have to be extended with a diffusion process, while processes influencing the particulate components (X_i) (mg/l) have to be extended with sedimentation and resuspension processes.

Bulk water

$$\frac{d(V\,S_i)}{dt} = Q_{in}(t)\,S_{i,in}(t) + Q_d(t)\,S_{i,d}(t) - Q_{out}(t)\,S_i(t) - r\,V(t) + K_{L,S_i}\left(\frac{S_{i,bed}(t)}{p} - S_i(t)\right)A_{bottom} \tag{eq. 5-10}$$

$$\frac{d(V\,X_i)}{dt} = Q_{in}(t)\,X_{i,in}(t) + Q_d(t)\,X_{i,d}(t) - Q_{out}(t)\,X_i(t) - r\,V(t) - k_{sed}\,X_i(t)\,V(t) + k_{res}\,X_i(t)\,V_{bed}(t) \tag{eq. 5-11}$$

Sediment

$$\frac{d(V_{bed}\,S_{i,bed})}{dt} = -r\,V_{bed}(t) - K_{L,S_i}\left(\frac{S_{i,bed}(t)}{p} - S_i(t)\right)A_{bottom} - k_{burial}\,S_{i,bed}(t)\,V_{bed}(t) \tag{eq. 5-12}$$

$$\frac{d(V_{bed}\,X_{i,bed})}{dt} = -r\,V_{bed}(t) + k_{sed}\,X_i(t)\,V(t) - k_{res}\,X_i(t)\,V_{bed}(t) - k_{burial}\,X_{i,bed}(t)\,V_{bed}(t) \tag{eq. 5-13}$$

To solve the model a large number of model parameters need to be provided. For the ***sorption*** process the most important parameter is the partition coefficient K_{OC} (m³ g^{-1}). The use of this coefficient presumes that sorption is proportional to the organic carbon content (Karickhoff, 1984; Warren et al., 2003). This assumption is reasonable for hydrophobic pesticides (Chefetz et al., 2004; Chen et al., 2004), such as diuron, and less valid for chloridazon which is rather hydrophilic. When K_{OC} is known, the state variables f_d, f_{DOC} and f_p can be calculated in each compartment (c) as follows (Deksissa et al., 2004):

$$f_{p,c}(t) = \frac{K_{OC} S_{POC,i}(t)}{1 + K_{OC}\left(S_{POC,i}(t) + S_{DOC,i}(t)\right)} \qquad \text{(eq. 5-14)}$$

$$f_{DOC,c}(t) = \frac{K_{OC} S_{DOC,i}(t)}{1 + K_{OC}\left(S_{POC,i}(t) + S_{DOC,i}(t)\right)} \qquad \text{(eq. 5-15)}$$

$$f_{d,c}(t) = 1 - f_{DOC,i}(t) - f_{p,i}(t) \qquad \text{(eq. 5-16)}$$

where $S_{DOC,i}$ and $S_{POC,i}$ are derived from the state variables in accordance with the carbon fraction (α_C) of the different components:

$$S_{DOC,i}(t) = \alpha_C\ S_{S,c}(t) + \alpha_C\ S_{I,c}(t) \qquad \text{(eq. 5-17)}$$

$$S_{POC,i}(t) = \alpha_C\ \mathrm{X}_{S,c}(t) + \alpha_C\ \mathrm{X}_{I,c}(t) + \alpha_C\ \mathrm{X}_{H,c}(t) + \alpha_C\ \mathrm{X}_{N,c}(t) \qquad \text{(eq. 5-18)}$$

The ***biodegradation*** process for pesticides is typically described according to first order kinetics (Hamaker, 1972; Wu and Nofziger, 1999) with temperature dependent rates:

$$k_b = k_{b,20}\ e^{K(T_w - 20)} \qquad \text{(eq. 5-19)}$$

The exponential term in the above equation corrects the biodegradation constant at 20°C, $k_{b,20}$ (d^{-1}), with the mean measured temperature in the compartment, T_W. K is a temperature constant and has a typical value of 0,069 (°C^{-1}) (Warren et al., 2003). The pesticides sorbed on POC are considered as not biodegradable.

The ***sedimentation*** process is responsible for the transport of particles from the bulk water to the sediment. The sedimentation rate constant, k_{sed} (d^{-1}), is function of the settling velocity of the particles and the shear stress on the bottom (Blom and Aalderink, 1998; Liu et al., 2002; Lumborg, 2005; Perianez, 2005). To keep the model simple, the mass of particles that settles, is calculated on the basis of the outflowing flux of bulk water.

$$k_{sed}(t) = \frac{f_{sed}(t)\left(1 - \dfrac{\tau_b(t)}{\tau_{crit,sed}}\right)}{\theta_H(t)} \qquad \left(\text{if } \ \tau_\mathrm{b} \le \tau_{crit,sed}\right) \qquad \text{(eq. 5-20)}$$

$$k_{sed}(t) = 0 \qquad \left(\text{if } \tau_{\text{b}} > \tau_{crit,sed}\right) \qquad \text{(eq. 5-21)}$$

with
$$\tau_{\text{b}}(t) = 0{,}5\, \rho_w\, f_c\, v^2(t) \qquad \text{(eq. 5-22)}$$

$$f_{sed}(t) = \frac{v_s\ \theta_H(t)}{d(t)} \qquad \text{(eq. 5-23)}$$

$$\theta_H(t) = \frac{V(t)}{Q_{out}(t)} \qquad \text{(eq. 5-24)}$$

$$v_s = \frac{\rho - \rho_w}{\rho_w} \frac{g\, d_X^2}{18\, \mu} \qquad \text{(eq. 5-25)}$$

where f_{sed} is the fraction of particles that can settle on the basis of their hydraulic retention time and their sedimentation velocity (-); τ_b is the shear stress at the bottom of the river (N m^{-2}); $\tau_{crit,sed}$ is the critical shear stress above which no sedimentation can occur because of turbulence (N m^{-2}); θ_H is the hydraulic retention time of the bulk water compartment (d^{-1}); ρ_w and ρ are respectively the density of water and of the particles (kg m^{-3}), f_c is the friction factor (-), v is the velocity in the bulk water compartment (m s^{-1}), v_s the sedimentation velocity based on Stoke's law (m d-^{1}), d is the depth of the water column (m), g is the gravitational fall acceleration (m s^{-2}), d_X is the diameter of the particles (m) and μ the kinematic viscosity at mean water temperature (m² s^{-1}). As shown in equations 5-20 and 5-21, sedimentation is only possible when the bottom shear stress is smaller than the critical value. The sedimentation constant, k_{sed}, has in the numerator the fraction of particles that disappear from the bulk water during the retention time, while the denominator contains the time frame in which the particles are leaving, namely the retention time.

The ***resuspension process*** is responsible for particles flowing from the sediment to the bulk water. The calculation of the resuspension rate constant, k_{res} (d^{-1}), is based on an experimentally determined erodibility constant (Blom and Aalderink, 1998; Liu et al., 2002; Lumborg, 2005; Perianez, 2005). It is assumed that resuspension only occurs when the turbulence is higher than a certain value.

$$k_{res}(t) = E_0 \left(\frac{\tau_b(t)}{\tau_{crit,res}} - 1\right) \frac{A}{\left(M_{POC,bed}(t)\right)} \qquad \left(\text{if } \tau_{\text{b}} > \tau_{crit,res}\right) \qquad \text{(eq. 5-26)}$$

$$k_{res}(t) = 0 \qquad \left(\text{if } \tau_{\mathrm{b}} \le \tau_{crit,res}\right) \qquad \text{(eq. 5-27)}$$

with E_0 the erodibility constant (g m^{-2} d^{-1}); $\tau_{crit,res}$ the critical shear stress above which resuspension occurs (N m^{-2}); $M_{POC,bed}$ the mass of particles which are in the sediment compartment at a certain time and which is calculated as $S_{POC,bed}\,V_{bed}$ (g).

The ***burial*** process is introduced to create a gradient in the sediment layer. When settled material accumulates on the river bottom, the sediment-water interface is advecting upward and the active layer also moves accordingly. Although the deep sediments under the active layer do not actually move, their distance from the sediment-water interface increases. It is reasonable to conceptualize this process to be a burial process, namely the interface is static and the deeper inactive layers are moving downward (Wang et al., 2003). In the developed model, the sediment consists of three sediment layers, the first two have a maximum thickness and the last one, the deepest layer, is a sink layer with unlimited thickness. The burial rate constant, k_{burial} (d^{-1}), is set proportional to the settling velocity:

$$k_{burial}(t) = \frac{v_s\, A}{V_{bed}} \qquad \text{if } (d > d_{\max}) \qquad \text{(eq. 5-28)}$$

$$k_{burial}(t) = 0 \qquad \text{if } (d \le d_{\max}) \qquad \text{(eq. 5-29)}$$

where d is the thickness of the layer and d_{max} is the maximum thickness of the layer. Between the different sediment layers there is only exchange of material by diffusion and burial.

Boundary conditions

Different boundary conditions were imposed on the model. For the hydraulics, inputs of water through runoff and groundwater could be calculated by means of the calibrated SWAT model for the Nil catchment (see Section 4.3). These water inputs were predicted for the upstream monitoring point and for the tributaries. For the pesticide concentrations, the results of the monitoring campaign could be used for the upstream input. As there was no data available concerning application doses or dates for spring 2004, the pesticide inputs coming from the tributaries could not be predicted with the SWAT model. Therefore, pesticide inputs from the tributaries were estimated. Based on the pesticide loads passing at the upstream and downstream monitoring point, an estimation of the incoming pesticide mass between these 2 points could be made. This mass was then spatially distributed based on the landuse map.

5.4.4 Model implementation in WEST

The proposed model was implemented in the WEST® modeling and simulation software. Figure 54 shows the WEST® configuration of the tank-in-series model for the Nil River case study.

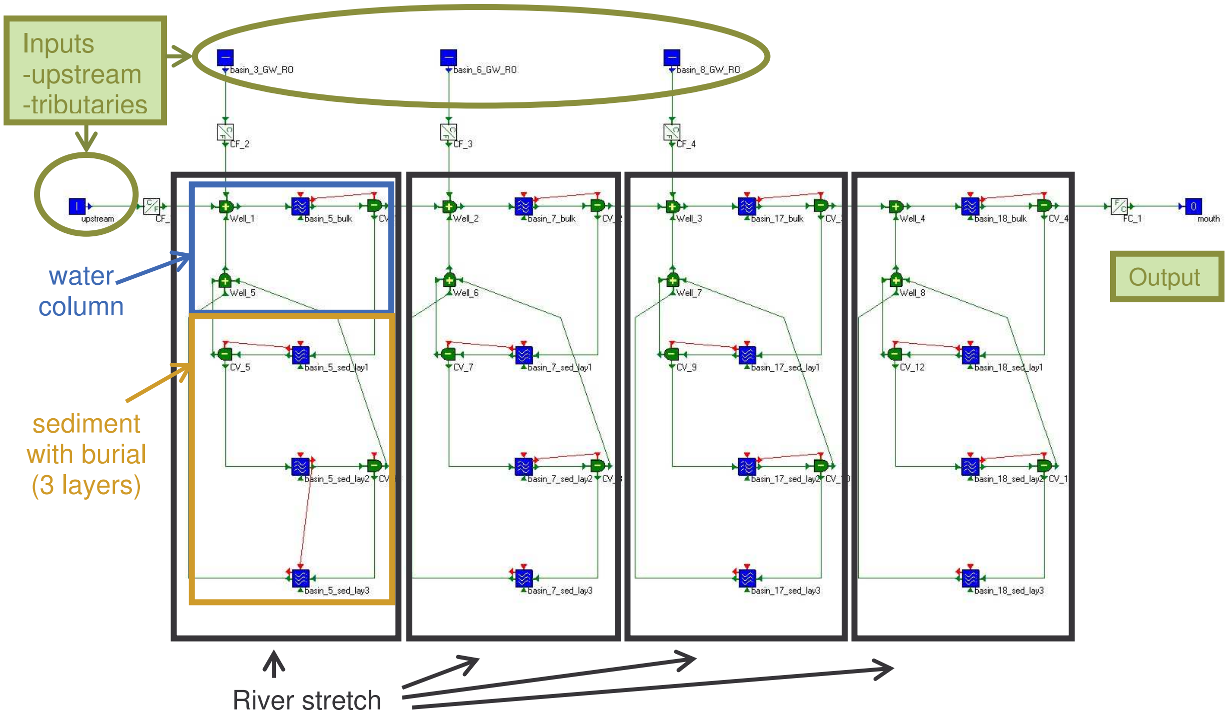


Figure 54. Model configuration in WEST of the RM1GC model for the stream 'the Nil'

Figure 54 points out that each bulk water compartment consists of one river tank and a sediment compartment of three tanks for each of the three sediment layers. In the configuration the full and dotted arrows represent respectively physical and data transfers. The physical transfers refer to mass fluxes, while the data transfer refers to information exchange. How the different transport processes are implemented in WEST® is shown in Figure 55. The mass of each component, which is transported from the bulk water to the sediment by sedimentation and diffusion, is calculated in a special 'splitter'. In contrast the mass that will leave the sediment layer through resuspension, diffusion or burial, is calculated in the sediment compartment itself. The resuspended sediment particles are added to the inflowing bulk water. To get the overall exchange between bulk and sediment, the equilibrium of diffusion from the bulk water to the sediment and the diffusion in the opposite direction, namely from the sediment to the bulk water, is calculated.

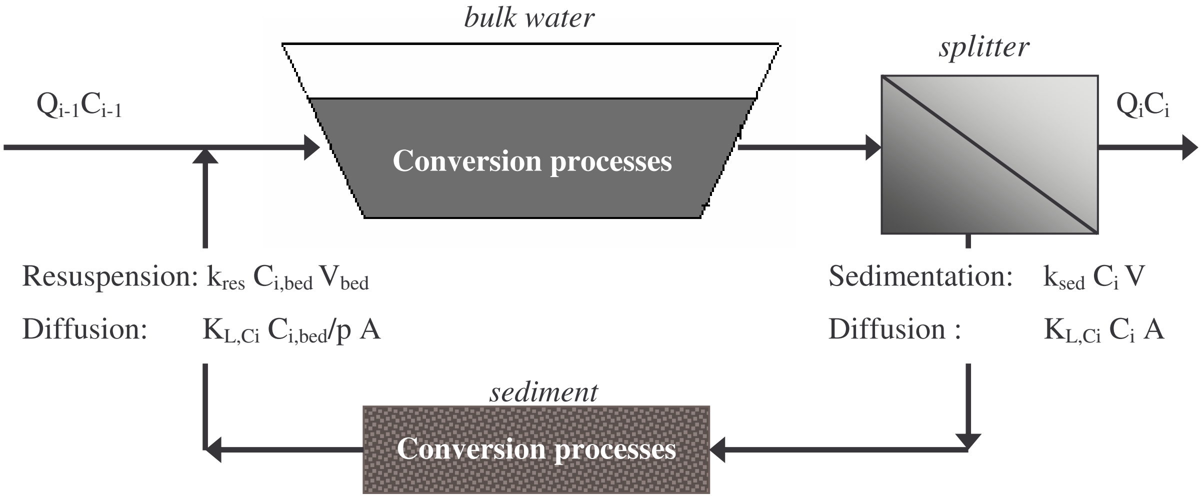


Figure 55. Schematic representation of the model implementation in WEST.

5.4.5 Uncertainty analysis

In order to gain insight in the parameter sensitivity of the developed model, a sensitivity analysis was performed with the WEST® software. In this way, model parameters that have a significant influence on the modelling results can be identified. Uncertainty in influential parameters propagates to uncertainty in the output results while non-influential parameters are of minor importance in this aspect. This information is useful for model users as it tells which parameters should be investigated with the most accuracy.

In this study, the relative sensitivity *S* of a variable *R* to a parameter *P* is defined as follows:

$$S = \frac{|\Delta R/R|}{|\Delta P/P|} \qquad \text{(eq. 5-30)}$$

Note that as *R* is a dynamic variable, also the sensitivity is function of time. In this study, the average values of *S* over time were calculated. The sensitivity analysis was performed for 13 parameters that may have influence on the fate of pesticides in a river system (see Table 27). Each parameter has a certain range of variation, as the exact value is in most cases not known or is not determined on the field. The range of variation of each of the parameters in this study is based on literature and on values observed in the study area (Arnold et al., 1998; Tomlin, 2003; Blom and Aalderink, 1998; Liu et al., 2002; Lumborg, 2005; Perianez, 2005). The outputs studied were the pesticide concentrations in the bulk water, the pore water and on the sediment particles.

Table 27. Parameters and parameter ranges used in the sensitivity analysis. All parameters have a uniform distribution, except d_X, n, slp, and $\tau_{crit,sed}$ which have a triangular distribution.

Name	min	median	max	Definition	Process
d_X	1	45	60	Particle size diameter (µm)	Sedimentation
E_0	207	-	311	Erodibility constant (g m^{-2} d^{-1})	Resuspension
f_c	0.0032	-	0.0048	Friction coefficient (-)	Sedimentation
$k_{b,GC1}$	0.02	-	0.028	Biodegradation constant for pesticide 1 (d^{-1})	Biodegradation
$k_{b,GC2}$	0.0105	-	0.02	Biodegradation constant for pesticide 2 (d^{-1})	Biodegradation
$K_{L,GC1}$	0.00432	-	0.00648	Diffusion coefficient for pesticide 1 (m d^{-1})	Diffusion
$K_{L,GC2}$	0.00432	-	0.00648	Diffusion coefficient for pesticide 2 (m d^{-1})	Diffusion
$K_{OC,GC1}$	89	-	340	Sorption coefficient pesticide 1 (ml water g^{-1}POC)	Sorption
$K_{OC,GC2}$	453	-	1058	Sorption coefficient pesticide 2 (ml water g^{-1}POC)	Sorption
n	0.02	0.04	0.07	Manning coefficient (-)	Hydraulics
slp	0.01	0.015	0.02	Slope of the bottom of the river stretch (m m^{-1})	Hydraulics
$\tau_{crit,res}$	0.09	-	0.11	Critical shear stress above which resuspension occurs (N m^{-2})	Resuspension
$\tau_{crit,sed}$	0.045	0.05	0.055	Critical shear stress below which sedimentation occurs (N m^{-2})	Sedimentation

5.4.6 Results and discussion

Comparison of simulated and measured values

This section verifies whether the simulation results approximate the measured pesticide concentrations. The parameter values in the model were taken from literature. Hence, no calibration was performed to reach the results presented in Figure 56, Figure 57 and Table 28.

The measured pesticide concentrations in the bulk water at the closing section are compared with the simulated values in Figure 56. At two times there was a major overshoot of the measured pesticide concentration.

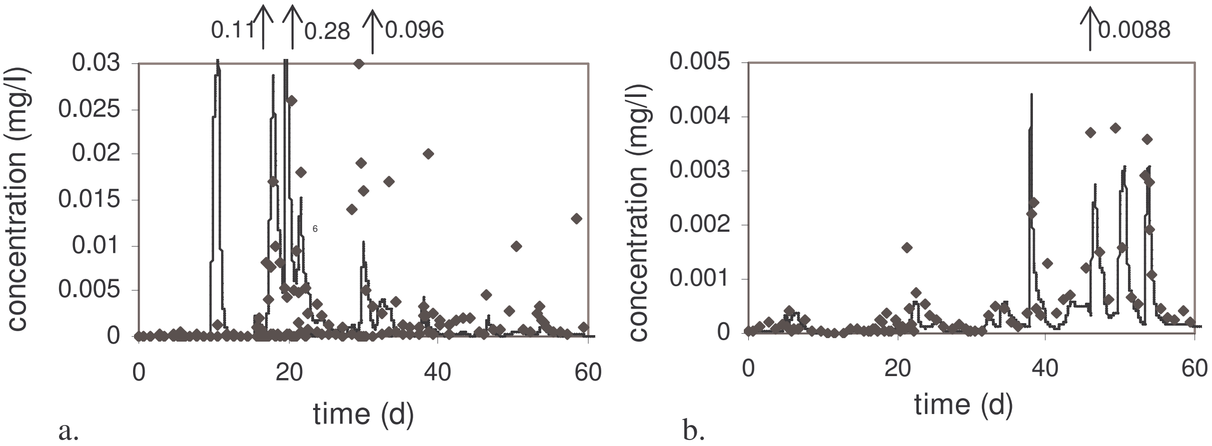


Figure 56. Simulated (full lines) and measured (dots) concentrations of chloridazon (a) and diuron (b) at the closing section of the river Nil.

It appears from that the simulated concentrations approximate the measured concentrations satisfactorily. However, in most of the cases the simulated concentrations are underestimated. This underestimation might be attributed to incomplete input data rather than to bad estimation of the model parameters. Indeed, the input data take into account the contribution of pesticide fluxes coming from tributaries, groundwater flow and runoff. Those contributions were estimated by an existing SWAT model (see Section 4.3). This SWAT model only provides daily estimations of runoff and groundwater fluxes, while the real pesticide fluxes are fluctuating with hourly timescale as the experimental data showed. Consequently, the estimated pesticide input in the input data is not as dynamic as the real and measured concentrations and will be more smooth than in reality. Figure 57, which is a representation of the measured values upstream and at the closing section, shows that the pesticide concentrations at certain times are much higher downstream than upstream. This phenomenon is mainly caused by runoff (rain) and point losses (in periods without rain) in the considered river section (see Chapter 3). For periods without rain and still higher concentrations downstream, a rough estimation of input data coming from point losses could be made based on mass balances, but resulted in an underestimation of the concentrations.

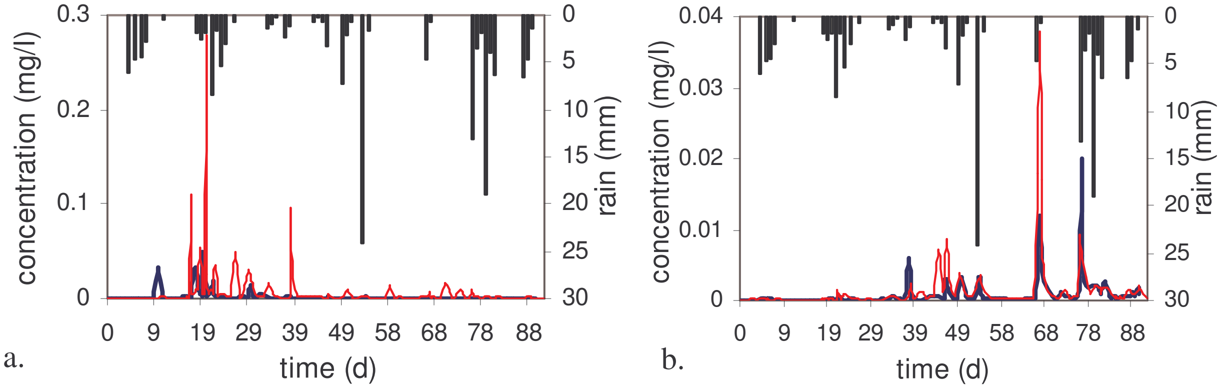


Figure 57. Measured chloridazon (a) and diuron (b) concentrations downstream (thick line) and upstream (thin line) of the river Nil, with measured rainfall (black bars).

In Table 28 the measured sediment concentrations observed on May 17th, are compared with the simulated values. Measurements were available of pesticide concentrations in the pore water and of the amount of pesticides sorbed on the sediment particles.

Table 28. Measured and simulated values of pesticide concentrations in pore water and the amount of sorbed pesticides on the sediment particles at two locations in the river

compartment	pesticide	mouth measured	simulated
pore water (ng/l)	chloridazon	940	594
	diuron	1540	73.5
sediment particles (ng/g)	chloridazon	1.2	2.5
	diuron	4.9	13.4

From Table 28 it can be seen that the measured pore water concentration for chloridazon on May 17th is in the same order of magnitude as the predicted concentration. However, for diuron the simulated pore water concentration downstream is much lower than the real measured concentration on this sampling day. They differ with a factor 20. Again this is probably caused by point losses which occurred between the two sampling points (Figure 57) around the 28th of April, day 45 in the simulation window. Moreover, for the pesticides sorbed on the sediment particles, the model overestimates compared to the measured value on the 17th of May. It should be mentioned that in the performed analyses stones were not removed from the sediment. This caused an overestimation of the sediment weight and consequently the measured pesticide concentration per weight of sediment is underestimated. It is also possible that the parameters from literature, such as the sorption constant and biodegradation constant, are not representative for the considered sediment. If the sorption constant would be calibrated, it is clear that a lower value would generate lower diuron concentrations on the sediment and higher concentrations in the pore water.

Model-based analysis of pesticide fate in the Nil catchment

The developed model gives the opportunity to study the distribution of pesticides between bulk water and sediment in time and space. Such a distribution is shown in Figure 58, showing pesticide concentration in the bulk water and in the pore water at the closing section of the river.

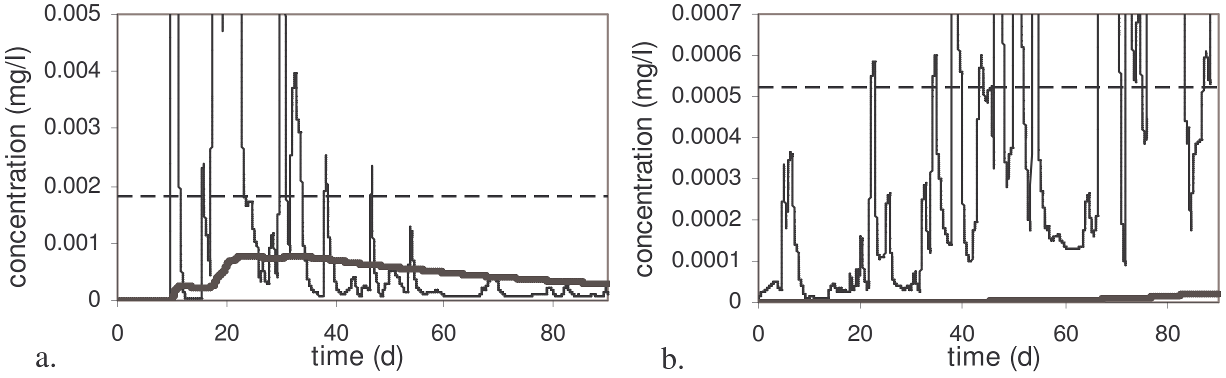


Figure 58. Simulated concentrations for chloridazon (a) and diuron (b) in the bulk (thin line) and pore water (thick line) at the closing section of the river Nil, together with their PNEC value (dashed line).

From Figure 58 it is clear that in absolute value the chloridazon concentration is much higher than the diuron concentration. A possible cause is the lower usage of diuron during the simulated period. The application period of chloridazon lasts from March till April, so it is almost at its end during the monitoring period, while for diuron the application period has just started, as it is mainly used from April till July. Another cause may be the sorption properties of diuron, which sorbs much easier to particles than chloridazon, and, hence, a smaller amount runs off the land into the river. Also, in the river itself diuron will be immobilized faster and a lower concentration will therefore be detected in the river water.

From the profile in Figure 58 it is clear that the concentrations in the pore water are much lower than the concentrations in the bulk water. Also the shape of the profile is quite different. In the bulk water the pesticide concentrations vary rapidly from very high to very low values. On the other hand, the concentration profile in pore water shows a tailed behaviour, i.e. the concentrations do not vary as much as in the bulk water and maintain elevated levels much longer. For chloridazon this results at the end of the simulation period in a higher concentration in the pore water compared to that in the bulk water (Figure 58a). At that moment desorption processes take place in the sediment and the pesticides, which were attached to the sediment particles in a previous period, are gradually released to the pore water.

The time profile of the pesticide distribution has ecological consequences. Values for predicted no effect concentrations (PNECs) can be found in literature. They are based on ecotoxicity tests performed on different species and with different test durations. The value found for the most sensitive species is then multiplied with a safety factor to account for various uncertainties, such as interspecies differences in sensitivity, acute-to-chronic ratios, and laboratory-to-field extrapolations. Table 29 gives the PNEC-values for diuron and chloridazon found in literature (Agritox database, 2006).

Table 29. PNEC values found in literature for chloridazon and diuron (Agritox database, 2006).

Pesticide	PNEC-value (µg/l)	Most sensitive species	test duration (h)
Chloridazon	1.8	*Daphnia magna*	48
Diuron	0.52	algae	96

In Figure 58 the pesticide concentrations in the bulk and pore water are plotted together with PNEC-values that were determined for species living in bulk water (see Table 29). As such, only the bulk water concentrations should be compared to the PNEC values. As can be seen from Figure 58, the concentrations of chloridazon and diuron in the bulk water frequently exceed the PNEC value to a large extent, albeit for short periods. Hence, the organisms in the bulk water are likely to suffer from toxic effects. For benthic organisms, one should compare environmental concentrations with PNEC values determined for benthic invertebrates, e.g. chironomids. However, these PNEC values were not available.

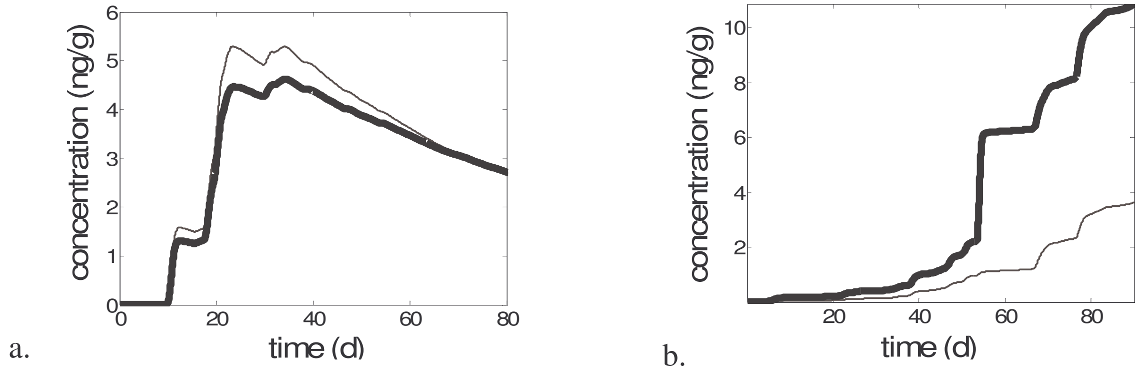


Figure 59. Simulated amount of chloridazon (a) and diuron (b) sorbed on the sediment particles upstream (thin line) and downstream (thick line) in the river Nil.

The profile of the amount of pesticides sorbed on the sediment particles is shown in Figure 59. From this profile it seems that the amount of chloridazon sorbed to the sediment particles is almost the same for up- and downstream river stretches. For diuron there is a sharp increase in the sorbed amount in the sediment downstream on May 9th (day 54). The increase is caused by an intense rainfall on May 8th which increased the river flow considerably and caused resuspension in the central reach of the river. At the closing section sedimentation occurs because of the small slope in that part of the river. For chloridazon the effect of sedimentation is much less pronounced due to its lower sorption constant (Figure 59a). It should also be mentioned that the amount of diuron sorbed to the sediment particles is higher than the amount of sorbed chloridazon, while in the bulk and pore water the chloridazon concentration is higher than the diuron concentration.

Uncertainty analysis

In Figure 60 the 5th, 50th and 95th percentiles of the simulated concentrations for chloridazon and diuron in the bulk water at the closing section of the river Nil are represented. From this figure, it can be seen that pesticide predictions in the bulk water are not sensitive to the studied parameters (Table 27) as their uncertainty hardly propagates into the model predictions. It seems that concentrations in the bulk water are mainly determined by input data rather than by processes in the river system. This is due to the fact that the processes are slow compared to the residence time.

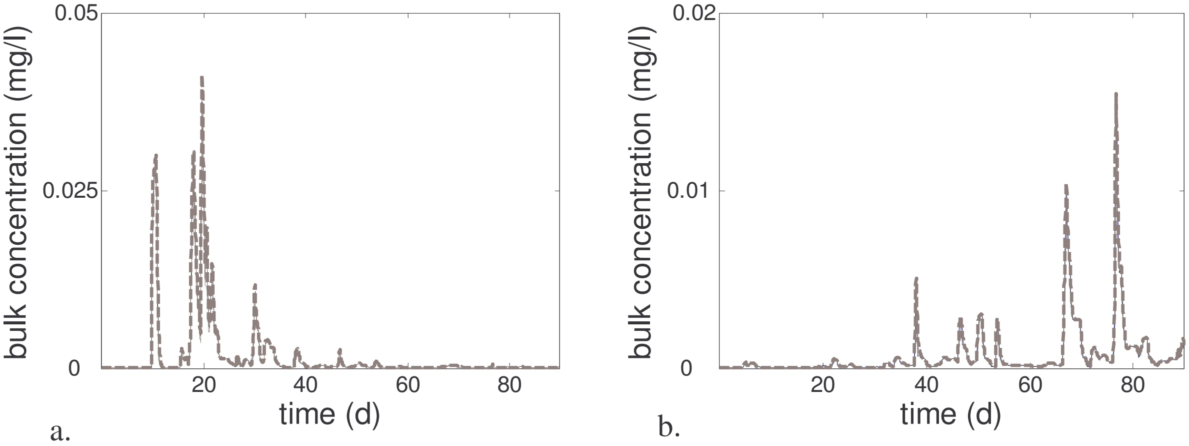


Figure 60. 50th percentile of the simulated concentrations of chloridazon (a) and diuron (b) in the bulk water at the closing section of the river Nil (black line) with 5th and 95th percentiles (grey lines). The interval lines overlay on the 50^{th} percentile.

For diuron at the closing section of the river, the uncertainty in the model results for the pore water and particle concentrations is illustrated in Figure 61. As can be seen, these concentrations are much more influenced by the studied parameters than the concentrations in the bulk water do. The results for diuron and chloridazon upstream were similar (not shown).

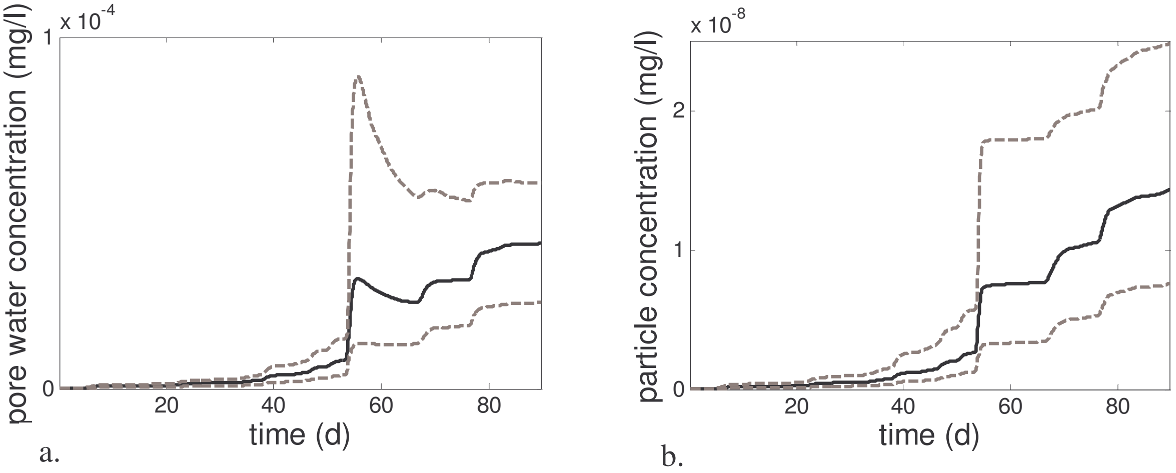


Figure 61. 50^{th} percentile of the simulated concentrations of diuron in the pore water (a) and on the particles (b) at the closing section (black line) with 5^{th} and 95^{th} percentiles (stripped grey lines).

In Figure 62 the sensitivity S of the three output variables to the seven most influential parameters P is visualized. From this figure, it is clear that the diffusion coefficient $K_{L,GC}$ is by far the most influential parameter for the bulk water concentrations. But even this parameter has almost no influence on the predicted bulk water concentrations, as could be derived from Figure 60.

For the concentrations on the sediment particles, the K_{OC} is the most influential parameter for diuron, whereas for chloridazon it is the diffusion coefficient $K_{L,GC}$ closely followed by the K_{OC}. As the model predictions for concentrations on particles are sensitive to these parameters, it means that the value for these parameters should be assessed with sufficient accuracy to reduce the degree of uncertainty in the results. The importance of a good estimation of the K_{OC} parameter was expected, as it determines to a great extent the sorption of pesticides on particles. For the concentrations in the pore water, the parameters that are most influential for diuron are the particle size diameter (d_x) and the slope of the river stretch. For chloridazon it is the K_{OC} and the $K_{L,GC}$.

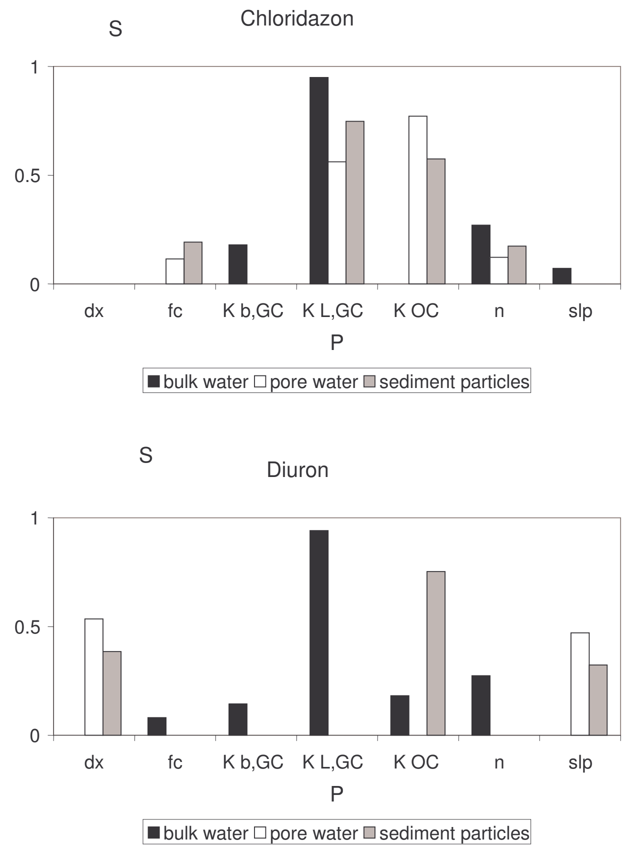


Figure 62. Graphical representation of the sensitivity *S* of three output variables of the RM1GC model to the seven most influential parameters *P*. The definition of the different parameters can be found in Table 27.

5.4.7 Conclusions

An extension of the RWQM1 model with the fate of pesticides was presented. Comparison between measured and simulated concentrations in the water column showed good prediction results. For the sediment compartment, more samples would be desirable for model evaluation. The model can be used to gain insight in the importance of different processes occurring in a river. It was found that it is important to feed the model with reliable pesticide input data. By means of a sensitivity analysis, it was further shown that special attention should be given to the determination of the sorption coefficient K_{OC} and the diffusion coefficient $K_{L,GC}$. A reliable estimation of both parameters will reduce the uncertainty in the model results for the pore water and particle concentrations. From this modelling study, one can learn that for small rivers pesticide concentrations in the bulk water seem to be mainly determined by input sources, rather than by river processes. Further research should show whether river processes become important in larger catchments with longer residence times. The dataset of the Demer catchment would be better for model verification than the Nil data.

Chapter 6

GENERAL DISCUSSION, CONCLUSIONS & PERSPECTIVES

6.1 General conclusions

6.1.1 Monitoring pesticides

The literature review reveals that few monitoring campaigns were performed in the past which disclosed the real dynamics of pesticides in a river system. In many cases, grab samples were taken and no attention was given to the dynamics and interactions with the sediment. The two monitoring campaigns that were performed as part of this dissertation, show that pesticide concentrations in the water column can vary significantly on an hourly basis, especially in small upstream agricultural areas. The maximum concentrations measured for atrazine, chloridazon, diuron, isoproturon, lenacil and simazine in the Nil catchment amounted respectively 45, 280, 40, 62, 3 and 1 µg/l and frequently exceeded the Flemish standards for basic water quality of surface waters. In the Demer catchment, lower concentrations were measured, due to dilution and the shorter monitoring period which was somewhat after the most intensive spraying period for most of the herbicides. A scaling effect, showing higher concentrations upstream and lower concentrations downstream, could be seen. This scaling effect was however not pronounced due to the later and shorter monitoring period in the Demer catchment. Also, the climatological conditions were different in the two monitoring campaigns, as they were performed in different years. During the campaign in the Nil catchment, there were more and more intense rainfall events than during the monitoring campaign in the Demer catchment. The latter resulted in smaller runoff events.

High pesticide concentration peaks were observed during runoff events and after applications, i.e. as point losses. The highest pesticide loads passing at the closing section of rivers can be found in the dissolved phase. Pesticides on suspended solids showed a typical distance effect after rainfall events: in the beginning of the event herbicides located near the closing section of the river will leave the catchment, followed by pesticides coming from the more remote areas or fields.

The concentrations in the sediment followed the dynamics of the water column well, but the concentrations were much lower (2 orders of magnitude). The contribution of the sediment towards the water column is rather negligible.

Despite the fact that it is difficult to estimate the effects of mixtures of pesticides on a local ecosystem, it can be expected for the two studied catchments that the ‘no risk’ threshold for the water column is frequently exceeded. This exceedance is worse in the smaller upstream agricultural areas as compared to the larger downstream river areas. From March till the end of April isoproturon forms the main contributor to the risk. From May till the end of June diuron occupies that place. This means that from May on, based on the performed risk assessment, it is no longer agriculture which is contributing most to pesticide pollution, but it are the applications of diuron on paved surfaces by municipalities, farmers and households. Nevertheless, it should be emphasized that the ‘no risk’ threshold is based on relatively simple laboratory experiments that are only intended to flag up the potential for risk. Although the concentrations in pore water were much lower compared to those found in the bulk water, also benthic organisms can still experience negative effects. Some of them feed on sediment particles, which are highly loaded with pesticides and other hydrophobic components.

As the upstream river areas are highly valuable from an ecological point of view (mating, breeding and feeding place for many species) special attention should be given to safeguard these areas from severe pollution. However, an acute risk to pesticide exposure especially holds for these upper catchments, typically characterized by more sensitive ecosystems that can develop there thanks to the absence or minimal impact of other pollution pressures from households and industries. Policy makers should pay enough attention to these sensitive areas and take necessary and effective measures to prevent the loss of important ecological systems.

6.1.2 Advice for the setup of monitoring campaigns for pesticides

Different lessons were learned from the monitoring work which could be useful for future monitoring campaigns:

- Monitoring campaigns should preferably be performed during relevant periods: it is advisable to use the application schemes when planning a pesticide monitoring campaign. In case background concentrations or contributions of groundwater can be expected fewer samplings will be sufficient as the dynamics are considerably slower.
- The water system is a highly dynamic system characterized by direct spills and runoff events. As a consequence, continuous monitoring within the application window is preferable. Grab sampling is in this case not suitable at all. If the focus is on runoff events only, flow related sampling is advisable. In case intense rainfall events occur during weekends, one should also be prepared to collect those samples. Such a monitoring strategy implies revisions in the current sampling practices and in the employment of mobile sampling teams.
- Passive sampling may be a suitable alternative, as it integrates the loads passing during a certain time interval. Most passive sampling systems were already extensively tested in the laboratory, but need further investigation in the field (Allan et al., 2006).
- Monitoring of herbicides should preferably take place in smaller upstream rivers connected to rural areas where high concentrations are most likely to occur.
- To assist in the optimisation of sampling strategies, the combined use of monitoring data and models is advised (Vanrolleghem et al., 1999; Dochain and Vanrolleghem, 2001; De Pauw and Vanrolleghem, 2006). By iterating between model runs and experiments cost-optimized sampling schemes for the next experimental stages can be designed. This can be useful information for environmental agencies and drinking water industries. Performing optimal experimental design (OED) in practice involves a series of steps summarized in Figure 63 (Dochain and Vanrolleghem, 2001). A first and essential requirement of the experimental design procedure is the availability of a preliminary model. Once a preliminary model is available, the experimental degrees of freedom and constraints which define the boundaries for the experimental design procedure can be defined. Also an objective has to be defined. The iterative procedure can then be started.

By means of optimal experimental design, one can determine the optimal period of the campaign, the sampling frequency, the sampling interval, etc.

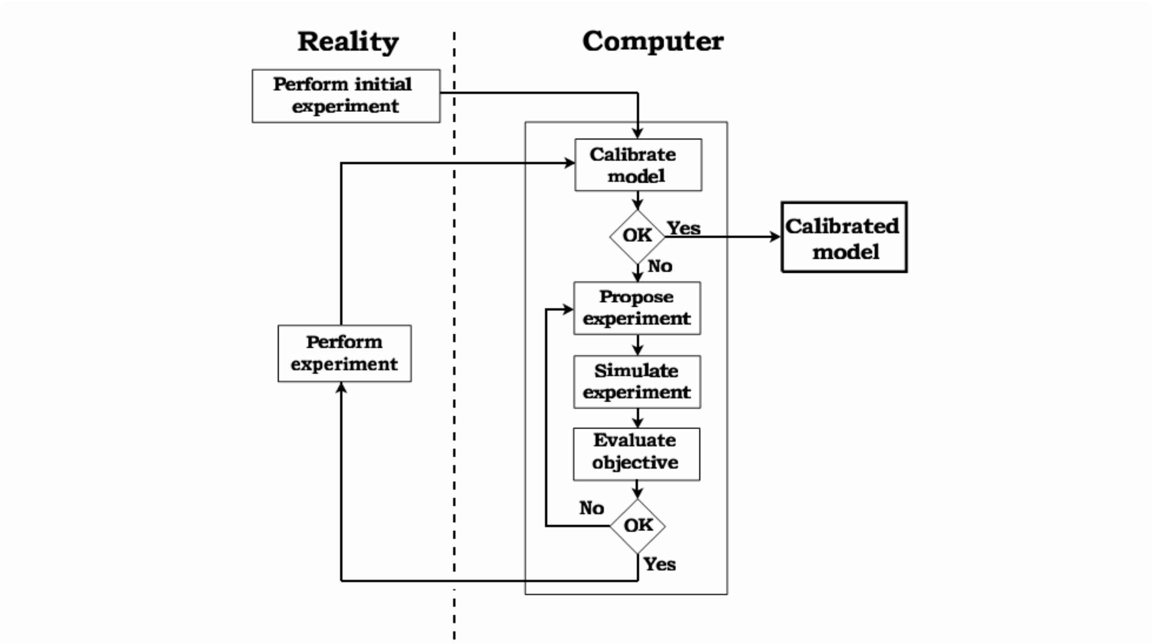


Figure 63. Schematic representation of the optimal experimental design procedure (Dochain and Vanrolleghem, 2001).

6.1.3 Modelling pesticides

In this dissertation, two different models were used: the SWAT model was used for predicting pesticide fluxes towards the river whereas the RWQM1 model was extended in order to describe in-river processes for pesticides. Both models were evaluated with extensive monitoring data.

SWAT

The SWAT model finds its origin in a hydrological model. Later on, it was reviewed and extended for simulating sediments, nutrients and pesticides. As such, it was only occasionally used for pesticides. In this dissertation, we used SWAT to model pesticide fluxes towards the river Nil.

After collecting all necessary input data, an LH-OAT sensitivity analysis was performed on the SWAT model in order to gain insight in the most important parameters determining hydrology and pesticide supply towards the river Nil. The resulting subset of parameters could then be used for calibration. For hydrology, it was shown that the curve number and some parameters related to groundwater were very influential. The importance of the groundwater related parameters could be attributed to the specific geology of the studied catchment. For a good simulation of pesticide supply, it appears that besides a good calibration of the hydrology also a correct estimation of the direct losses is important. To this end, detailed enquiries of local farmers form necessary information. A sensitivity analysis of the input factors revealed that the date of application is much more important than errors that may occur in the application rate or rainfall errors. Consequently, the application date can be an important source of uncertainty and needs special attention for data collection.

Because point sources form an important contribution to the pesticide loads found in a river, in the dissertation the SWAT model was extended for direct losses, which were defined as the summation of drift losses and point losses occurring at the day of application. For this purpose, a drift estimator was implemented and a fraction of the applied dose was sent immediately to the river reach. This resulted in more realistic mass fluxes in the river. The modified SWAT model could then be used to compare the contribution of runoff events, point losses and drift losses to the pesticide load. It was found that the contribution of runoff events and point losses are important and that the contribution of drift is rather negligible. This is in agreement with the literature. For fruit orchards, the contribution of spray drift will be more important.

In the dissertation, the SWAT model was also extended with processes occurring in a buffer strip. As such, different measures for pesticide reduction could be compared. In the performed modelling study, a ranking in effectiveness of measures for atrazine load reduction could be obtained: strip cropping seems to be more efficient than the sowing of cover crops, the construction of buffer strips, a 25% reduction of point losses and finally plough management. Nevertheless, extensive monitoring data and intensive observation of best management practices are essential for assessing their effects in a watershed. As for the moment there is no adequate literature available showing the quantitative benefits of best management practices, a modelling approach is very useful. In addition to this, the economic costs and/or benefits of different management practices should be taken into account. This was out of the scope of this dissertation.

By extending the SWAT source codes and checking the mass balances, it was found that there were some inaccuracies in the routing of pesticides in the reaches. Therefore, former pesticide studies performed with the SWAT2000 model should be examined with caution, as the source code contained some mass balance errors.

As all models also the SWAT model has some limitations. The most important limitations that were encountered during this dissertation are listed here:

- The SWAT model is a useful tool for studies at catchment scale, looking at a longer time scale. For studying one rainfall or runoff-event in detail, the SWAT model is not suitable as it uses a daily time step. In this case, one should use the ESWAT model (van Griensven and Bauwens, 2005) based on an hourly time step or one of the event models described in the literature review (see Section 2.3.2). The daily time step has some consequences if one wants to extend the source code for modelling processes occurring in a buffer strip (see Section 4.6). Those processes are strongly influenced by runoff and infiltration and as such need a sub-daily approach in order to be represented realistically.

- In the SWAT model, drainage to deep groundwater lead to a mass loss from the system. Also nutrients and pesticides in solution in deep drainage are lost. This leads to unclosed mass balances. In the study of the Nil catchment, this did not affect the results for hydrology, as also in reality, the deep ground water is lost to the adjacent river 'Le Train'. In some catchments, this can however result in inconsistencies.
- The SWAT model comprises over 100 parameters. The model requires training for inexperienced users. In order to calibrate the model, it is therefore advisable to first perform a sensitivity analysis. This allows to identify which parameters are most influential on the model results.
- Certain processes are described in a very simplified manner in SWAT. The question is whether these simplifications are always justified. An example concerns the different measures that can be taken to reduce runoff and erosion in a catchment. Many of the equations use not well-founded parameters, e.g. the parameters prf (eq. 4-16) , K_{CH} and C_{CH} (eq. 4-19). Consequently, it should be validated with field experiments whether model results for best management practices are in agreement with the observations.
- Point sources form an important contribution to the pesticide load passing in river systems. Therefore, the source code was extended to account for this source of pollution. By doing so, some inaccuracies were detected which were replaced and are described in detail in Section 4.4.
- As it was found that the day of application is highly important for predicting dynamic pesticide concentrations in rivers, a method should be foreseen that allows to take uncertainty concerning the application dates into account. Statistical approaches should therefore be implemented in the source code.

RWQM1

The RWQM1 model was extended (called the RM1GC model) in order to describe the in-stream processes of the herbicides diuron and chloridazon. The main advantage of using RWQM1 instead of SWAT, lies in its ability to use closed elemental mass balances and in the fact that it explicitly considers microbial biomass as a state variable. Besides, RWQM1 can easily be coupled to the existing IWA Activated Sludge Models, which makes an integration with wastewater treatment plants (WWTPs) connected to rivers possible. Moreover, the RWQM1 model allows the investigation of different pesticides at the same time and makes it possible to describe the sedimentation, resuspension and burial processes in a more realistic way.

Promising similarities were observed between measured and simulated concentrations in the water column. For the sediment, more data points are needed to perform an evaluation. It should be stressed, that the model needs high quality input data of pesticide concentrations in water coming from upstream, runoff, groundwater and tributaries, as the concentrations in the water column are mainly determined by input concentrations rather than by in-stream processes. This input can be delivered by the SWAT model. For pesticide predictions in the pore water and on the sediment, a good approximation of the sorption coefficient K_{OC} and the diffusion coefficient $K_{L,GC}$ is necessary. This will reduce model uncertainty.

In this dissertation, an evaluation of the RM1GC model was performed for the Nil catchment for a river stretch of 8km. Over such a short distance, in-stream processes seemed not important as compared to the input data and the question therefore remains on how good these processes were modelled. Unfortunately, due to time constraints, the RM1GC model could not be validated for the Demer catchment. Here, a much longer distance of 30km exists between the measuring points. It would have been interesting to see whether model predictions and measurements would still be that satisfying.

The currently developed RM1GC model can easily be extended with processes that could be of importance for other pesticides such as volatilisation and hydrolysis. To this end, differential equations should be added to the hierarchically developed model in the modelbase included in the WEST modelling software.

Advantages of modelling and of the coupling between SWAT and RWQM1

The advantage of modelling a system consists of, among others, the reduction of monitoring costs and gaining insight in processes that are sometimes difficult to measure. The advantages of modelling the occurrence of pesticides in river systems are:

- The simulation results can be used for risk assessment and product registration. Questions such as ‘what are the expected concentrations in a river when one applies a new compound, with a certain dosage on certain fields’ can be more easily answered.
- By means of optimal experimental design (OED) environmental agencies and drinking water companies can gain insight concerning the periods in which they have to monitor, at which locations, at what frequency, etc.
- One can model the effects of different measures that could be taken to reduce pesticide pollution in surface waters. Based on the model results a ranking can be made showing the effectiveness of different mitigation measures. This can help decision makers.
- In-stream processes can be visualised and the importance of each process can be determined.

The developed tool, which is a combination of the extended SWAT and RWQM1 models, forms a suitable tool for industries, drinking water companies and environmental agencies that are interested in modelling pesticide fate in river systems or that need to answer certain questions. The developed tool can easily be adapted for other micro-pollutants. It is a dynamic tool, able to perform simulations at catchment scale and therefore interesting in view of the EU Water Framework Directive. Besides, it contains a spatial component and can be used for comparison of mitigation measures.

6.2 Recommendations for further research

In this section, certain gaps that were encountered during the study in the current knowledge or in current monitoring techniques for the determination of the occurrence of pesticides in surface waters and their effects are summarized here.

- In order to improve time integrated sampling of pesticides in surface waters, passive sampling systems should be further investigated on the field, preferably in parallel with a continuous monitoring campaign. These integrated sampling results also give an idea about the bio available fraction of pesticides present in the water column.
- Environmental agencies should consider to perform optimal experimental design prior to the setup of their monitoring campaigns. Also the cost-efficiency of OED should then be elaborated.
- The implementation of buffer strips into the SWAT model should be improved.
- Different tools such as sensitivity and uncertainty analysis should be integrated within SWAT.
- The SWAT code should contain statistical approaches in order to be able to simulate the uncertainty on, for example, the days of application. This would also be helpful, in cases where no enquiries of farmers were performed and dates of application could only be estimated roughly. Also, rainfall events will influence the behaviour of farmers as farmers normally will not spray shortly before an expected rain event. This could also be integrated in the statistical approach.
- The developers of SWAT should try to bring together all currently developed SWAT versions and extensions.
- SWAT has proven to be a valuable tool for pesticide fate modelling in small catchments. The use of SWAT for large-scale “standard” catchments should be investigated, with the focus on use in tier 4 registration calculations. Databases and maps at pan-EU scale are available on river basins, topography, soils, etc.
- The developed RM1GC model should be further tested on bigger catchments, e.g. on the Demer catchment, where all the necessary data are currently available.
- The developed RM1GC model should be further tested with more biodegradable pesticides.

- Further research should be performed studying the effect of pesticides on their own biodegradation and on other biological activities in the river, such as algae growth (herbicides), etc.
- A real connection or coupling between SWAT and WEST should be developed as now all interaction happens through files.
- The effectiveness of different management practices on the reduction of pesticide supply towards the river, should be tested with real field experiments. Model results should then be compared to the real data. Only then models can gain confidence and is it justified to use them as instruments for decision support.
- Besides a ranking of different management practices through modelling, a parallel economic study should be performed indicating costs and benefits of different practices.
- Modelling the fate and behaviour of mixtures of pesticides and other pollutants would be a challenge.
- At the effect side, the effect of a pesticide on communities of species is not yet known, the synergetic or antagonistic action of certain active ingredients is currently not well understood, the effect of repeated pulse exposures of different concentration still has to be further investigated, the effect of mixtures of pesticides is unknown, etc. This information will improve current risk assessment.

6.3 Concluding thought

The monitoring and modelling of a highly dynamic system under natural conditions, with varying and sometimes unpredictable boundary conditions, will always remain a big challenge. In order to safeguard the environment and future generations of pernicious effects of pesticides, environmental agencies, researchers and industries should continue their exploratory expedition that will finally result in more reliable risk assessments.

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Summary

Pesticides are useful to society thanks to their ability to exterminate disease-causing organisms and control insects, weeds and other pests. At the same time, most pesticides may be harmful to humans, animals and the environment because of their ecotoxicity, their potential bio-accumulating properties or their hormone disrupting effects. In order to gain insight in the processes determining the fate of pesticides in river systems, monitoring and modelling are complementary tools.

From several studies it has become clear that pesticides in surface waters show a time-varying course which can not be monitored by grab sampling. Few monitoring studies performed in the past contained composite water samples instead of grab samples. As far as we know, no studies were performed on both the dynamics of pesticides in the water column and in the sediment. Therefore, it was decided to set up intensive monitoring campaigns taking into account both the water compartment and the sediment. Besides monitoring, models form useful tools for decision makers. For pesticides, there seems to be a lack of dynamic models taking into account point losses as entry route. Also models describing in-river processes based on closed mass balances usable at catchment scale are as far as we know not available. Moreover, few models are well validated with extensive monitoring data. The objective of this thesis was to fill these modelling gaps and to perform a validation by means of the collected monitoring data.

During spring 2004 and 2005, two continuous monitoring campaigns (sampling interval of 8 hours, for 3 months) were set up in river basins of varying sizes in Belgium. Both in the water column and in the sediment the following pesticides were investigated in detail: atrazine, carbendazim, chloridazon, diuron, isoproturon, lenacil and simazine. The water compartment showed hourly variations in pesticide peak concentrations, regularly exceeding the Flemish standards for basic water quality of surface waters (for instance 2 µg/l for atrazine and 1µg/l for simazine). The maximum measured concentrations were respectively 45, 0.25, 280, 40, 62, 3 and 18 µg/l. The concentration of pesticides in pore water, measured on a monthly basis, followed the

trends of the water compartment remarkably well, but with concentrations that were 1 or 2 orders of magnitude lower. A comparison between river basins of different scales demonstrates that a scaling effect exists: the highest concentrations occur in the smaller upstream areas, whereas the concentrations downstream are more diluted and dispersed. A risk assessment was performed based on the bulk water concentrations of diuron and isoproturon and their respective HC5-95% values. A HC5 represents a concentration that protects 95% of the species. A HC5-95% is the lower 95% confidence limit of the HC5 derived from the species sensitivity distribution that is based on no observed effect concentration (NOEC) data (SSD_{NOEC}). These HC5-95% values are rather rigorous thresholds. Longer periods of severe exceedance of the threshold occur in smaller catchments as compared to the bigger catchments where dilution and dispersion diminish the risk for local fauna and flora. Hence, an acute risk to pesticide exposure especially holds for upper catchments, that are, moreover, typically characterized by more sensitive ecosystems due to the absence or minimal impact of other pollution pressures from households and industries.

In order to model pesticide fate in river systems at catchment scale, 2 different models were used. The SWAT model was used for predicting pesticide fluxes towards the river whereas the RWQM1 model was extended in order to describe in-river processes for pesticides. The advantage of the RWQM1 model lies in the fact that it has closed elemental mass balances and that it explicitly considers microbial biomass as a state variable.

By means of an LH-OAT sensitivity analysis, the most influential parameters for hydrology and pesticide supply towards the river were determined for the Nil catchment. The LH-OAT method combines the One-factor-At-a-Time (OAT) sensitivity analysis and Latin Hypercube (LH) sampling by taking Latin Hypercube samples as initial points for the OAT-sensitivity analysis. It was shown that the curve number and some parameters related to groundwater were very influential. The importance of the groundwater related parameters could be attributed to the specific geology of the studied catchment. Besides a well calibrated hydrology, a correct estimation of the point losses is necessary for reliable pesticide predictions. To this end, the SWAT model was extended for direct losses, which were defined as the summation of drift losses and point losses occurring at the day of application. It was then found that the contribution of runoff events and point losses is much more important than the contribution attributable to drift.

Besides, the SWAT source code was extended with processes occurring in a buffer strip. Different management scenarios were simulated and compared to the initial situation. The results revealed that strip cropping seems to be more efficient than the implementation of cover crops, than buffer strips, than a 25% reduction of point losses and plough management, in that order. The study showed that modelling can be used to estimate the impacts of water quality management programs in river basins. Such an approach allows to rank different mitigation measures for pesticide fluxes towards surface waters.

The RWQM1 was extended and modified with processes determining the fate of non-volatile pesticides. The exchange of pesticides between the water column and the sediment is described by three transport processes: diffusion, sedimentation and resuspension. Burial of sediments is also included. The modified model was implemented in WEST (World Wide Engine for Simulation, Training and Automation, Hemmis NV, Kortrijk, Belgium) and used to predict the concentrations of diuron and chloridazon in the river Nil. Simulated pesticide concentrations were compared with measured values resulting from the intensive monitoring campaign performed during spring 2004. The comparison showed good agreement between model predictions and observed concentrations, even without calibration. The simulation results showed that pesticide concentrations in the bulk water were not sensitive to the selected biochemical model parameters along the 8-km long river stretch, but they were mainly determined by the imposed upstream concentrations. This is probably due to the short retention time in the considered stretch. The high concentrations in the bulk water were not observed in the sediment pore water due to a limited exchange between the water column and the sediment that is determined by diffusion and sorption. The concentrations on the sediment varied in time due to sorption, sedimentation and resuspension. Furthermore, the sensitivity of the model output to changes in the model parameters was tested. The concentrations in the pore water and on the sediment particles were highly sensitive to the diffusion and the sorption coefficient. Model users should determine these parameters with accuracy in order to reduce the degree of uncertainty in the results.

Some final conclusions and recommendations for further research are summarized at the end of the dissertation.

Samenvatting

Pesticiden zijn enerzijds erg nuttig voor de maatschappij: ze bieden de mogelijkheid om insecten, onkruid, schimmels en ziekten te bestrijden en zo de gewasopbrengsten aanzienlijk te verhogen. Anderzijds kunnen veel pesticiden erg schadelijk zijn voor mens, dier en natuur omwille van hun ecotoxiciteit, hun mogelijk bio-accumulerende eigenschappen en/of hun hormoonverstorende effecten. Om inzicht te verwerven in de processen die het gedrag van pesticiden in riviersystemen bepalen, vormen meetgegevens en modellen elkaar aanvullende instrumenten.

Uit verschillende studies blijkt dat pesticidenconcentraties in oppervlaktewater een grillig verloop in de tijd kennen, hetgeen niet kan gevolgd worden door het nemen van schepstalen. In het verleden werden slechts enkele meetcampagnes gebaseerd op mengstalen in plaats van schepstalen. Voor zover wij weten, werden er tot nu toe geen studies uitgevoerd waarbij zowel de dynamiek van pesticiden in de waterkolom als in het sediment bestudeerd werden. Daarom werd beslist om in deze doctoraatsstudie intensieve meetcampagnes op te zetten die zowel het watercompartiment als het sediment beschouwen. Naast meetgegevens vormen modellen nutige instrumenten voor beleidsmakers. Voor pesticiden blijkt er echter een gebrek te zijn aan modellen die puntverliezen als aanvoerroute beschouwen. Ook blijken er geen modellen beschikbaar te zijn die de processen in de rivier beschrijven op bekkenschaal en die gebaseerd zijn op gesloten massa balansen. Bovendien blijken weinig modellen gevalideerd te zijn met uitgebreide meetgegevens. Het doel van deze thesis bestond er dan ook in om deze leemten in het modelleren van pesticiden in rivierbekkens op te vullen en een validatie uit te voeren aan de hand van de verzamelde meetgegevens.

Tijdens de lenteperiodes van 2004 en 2005 werden 2 continue meetcampagnes (met een meetinterval van 8 uur, gedurende 3 maand) opgezet in een aantal rivierbekkens van verschillende grootte in België. Zowel in de waterkolom als in het sediment werden de volgende pesticiden in detail bestudeerd: atrazine, carbendazim, chloridazon, diuron, isoproturon, lenacil en simazine. Het water compartiment vertoonde uurlijkse variaties in pesticidenconcentraties die geregeld de Vlaamse normen voor basiswaterkwaliteit voor oppervlaktewater overschreden (bijvoorbeeld, 2 µg/l atrazine, 1 µg/l simazine). De concentraties van pesticiden in het poriewater werden op maandelijkse basis gemeten. Zij volgden de trend van het water compartiment opvallende goed, maar met concentraties die 1 tot 2 grootteordes lager gelegen waren. De massa van de bestudeerde pesticiden die aan de monding van de rivieren passeerde, bevond zich voornamelijk in de waterfase. Een vergelijking tussen rivierbekkens van verschillende grootte toont aan dat er een schaaleffect optreedt: de hoogste pesticidenconcentraties worden teruggevonden in de kleinere bovenlopen gelegen in landbouwgebied terwijl lagere concentraties worden waargenomen in de grotere benedenlopen door verdunning en dispersie. Een risicobepaling werd uitgevoerd gebaseerd op de waargenomen concentraties aan chloridazon en diuron in het water compartiment. Deze werden vergeleken met hun overeenkomstige HC5-95% waarden. Een HC5 geeft de concentratie weer die 95% van alle soorten moet beschermen. Een HC5-95% is het 95% betrouwbaarheidsinterval van de HC5 die afgeleid wordt van een soorten-gevoeligheids-verdeling die gebaseerd is op gegevens van concentraties die geen effect hebben op een soort (NOEC). Deze HC5-95% waarde is een vrij strenge drempelwaarde. Hierbij werden langere periodes van ernstige overschrijding van de risico-norm vastgesteld in de kleinere bovenlopen in vergelijking met de grotere benedenlopen waar het risico voor de lokale fauna en flora verkleint door verdunning. Bijgevolg zal een acuut risico op pesticidenblootstelling meer waarschijnlijk zijn in bovenlopen gelegen in agrarisch gebied, die bovendien typisch gekenmerkt worden door de afwezigheid of beperkte impact van andere vervuilingsbronnen zoals huishoudens en industrie.

Om het gedrag van pesticiden in rivieren op bekkenschaal te modelleren, werden 2 modellen gebruikt. Enerzijds werd het SWAT model geselecteerd om de aanvoer van pesticiden naar de rivier te voorspellen. Daarnaast werd het RWQM1 model uitgebreid om processen in de rivier te beschrijven. De voordelen van het RWQM1 model bestaan in zijn gesloten elementen massa balansen en in het feit dat het expliciet microbiële biomassa als een toestandsvariabele beschouwt.

Door middel van een LH-OAT gevoeligheidsanalyse werden voor het Nil bekken de belangrijkste parameters voor hydrologie en pesticidenaanvoer naar de rivier bepaald. De LH-OAT methode combineert een One-factor-At-a-Time (OAT) gevoeligheidsanalyse met een Latin Hypercube (LH) steekproef waarbij de Latin Hypercube steekproeven als initiële punten voor de

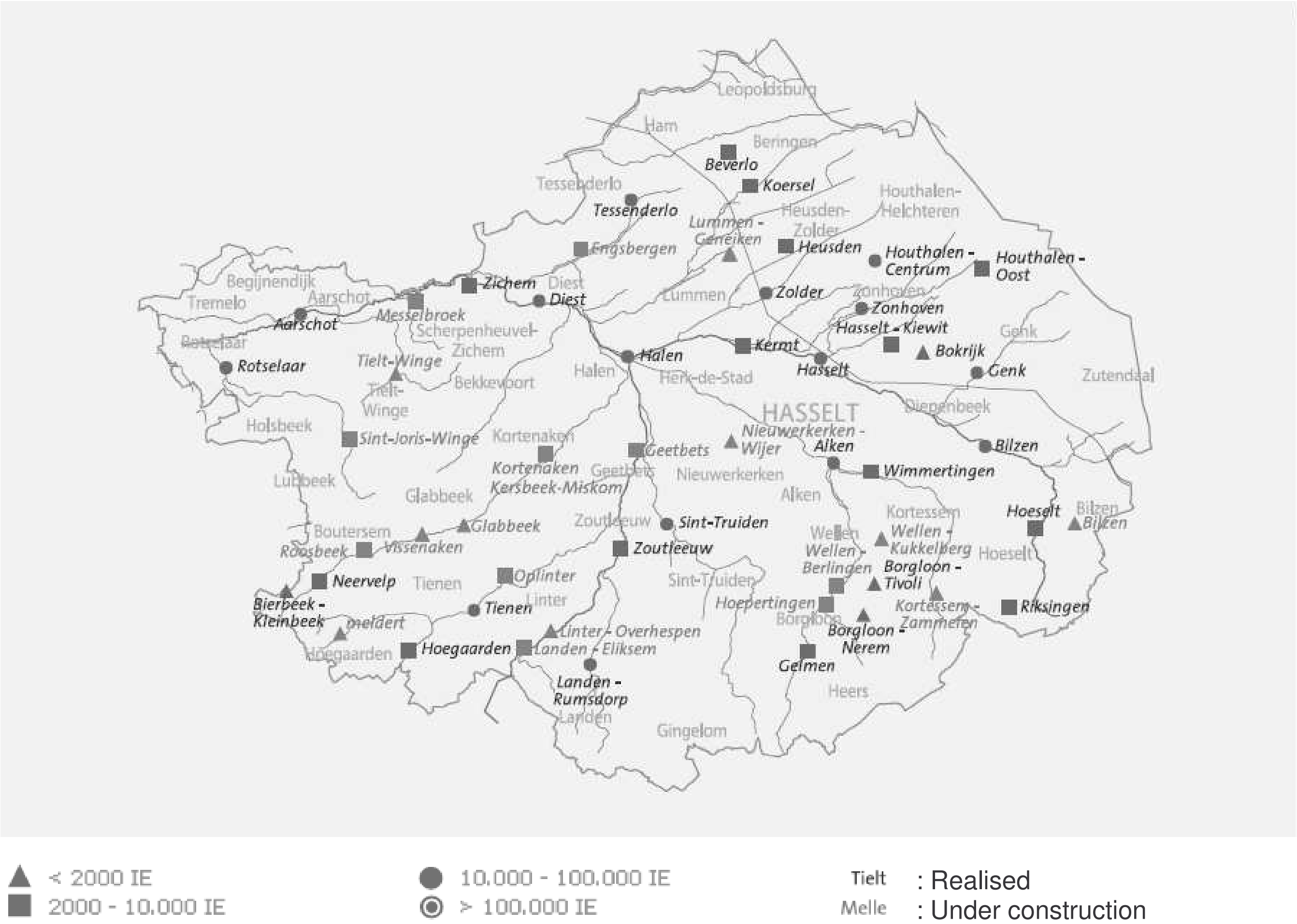
OAT-analyse worden gebruikt. Er werd aangetoond dat de afspoelingsfactor (‘curve number’) en enkele parameters gerelateerd met het grondwater erg sterk de modelresultaten beïnvloeden. Het belang van de parameters gerelateerd met grondwater kan toegeschreven worden aan de specifieke geologische structuur van het bestudeerde bekken. Naast een goed gecalibreerde hydrologie is een correcte inschatting van puntverliezen noodzakelijk om tot betrouwbare modelvoorspellingen te komen. Daarom werd het SWAT model uitgebreid voor directe verliezen, die gedefinieerd werden als zijnde de som van drift- en puntverliezen die op de dag van toediening plaatsgrijpen. Hiermee kon worden aangetoond dat de bijdrage van runoff en puntverliezen aan de pesticidenvracht in een rivier veel belangrijker is dan de bijdrage die kan toegeschreven worden aan drift. De model code werd ook uitgebreid met processen die plaatsvinden in een bufferstrook. Vervolgens konden verschillende management scenario’s gesimuleerd worden dewelke vergeleken werden met de initiële situatie. De model resultaten toonden aan dat strokenbouw efficiënter is dan de volgende praktijken die in aflopende volgorde worden opgesomd: het implementeren van grondbedekkers, de aanleg van bufferstroken, een reductie van de puntverliezen met 25% en management van de ploegpraktijk. De uitgevoerde studie toonde aan dat een modelleerbenadering gebruikt kan worden voor het inschatten van impacten van waterkwaliteitsmanagement programma’s op bekkenschaal. Een dergelijke benadering laat toe om verschillende reductiemaatregelen die de aanvoer van pesticiden naar de rivier beperken onderling te rangschikken.

Het RWQM1 model werd uitgebreid en aangepast voor processen die het gedrag van niet-volatiele pesticiden bepalen. De uitwisseling van pesticiden tussen de waterkolom en het sediment wordt hierin beschreven door drie transportprocessen: diffusie, sedimentatie en resuspensie. Begraving van sedimenten werd ook toegevoegd. Het aangepaste model werd geïmplementeerd in WEST (World Wide Engine for Simulation, Training and Automation, Hemmis NV, Kortrijk, België) en gebruikt om concentraties van chloridazon en diuron te voorspellen in de rivier de Nil. De gesimuleerde pesticidenconcentraties werden vergeleken met meetwaarden bekomen tijdens de intensieve meetcampagne van de lente in 2004. Deze vergelijking resulteerde in een goede overeenkomst tussen modelvoorspellingen en geobserveerde concentraties, zelfs zonder voorafgaande calibratie. De simulatieresultaten toonden aan dat de pesticidenconcentraties in het bulk water over een afstand van 8 km niet beïnvloed werden door de biochemische model parameters, maar voornamelijk bepaald werden door de inkomende concentraties van de bovenloop en de zijrivieren. Dit is vermoedelijk te wijten aan de korte verblijftijd in het beschouwde rivierdeel. De hoge concentraties in het bulkwater werden niet teruggevonden in het poriewater wat kan toegeschreven worden aan een beperkte uitwisseling tussen de waterkolom en de waterbodem. Deze uitwisseling wordt bepaald door diffusie en sorptie. De concentraties op de sedimentdeeltjes in de waterbodem varieerden in de tijd door sorptie, sedimentatie en resuspensie. Daarnaast werd ook de sensitiviteit van de modelresultaten aan veranderingen in de modelparameters getest. Hieruit bleek dat de concentraties in het poriewater en op de sedimentdeeltjes sterk beïnvloed worden door de diffusie en de sorptiecoëfficiënt. Modelgebruikers dienen bijgevolg deze parameters nauwkeurig te bepalen om zo de graad van onzekerheid in de modelresultaten te beperken.

Ten slotte worden enkele finale conclusies en aanbevelingen voor verder onderzoek geformuleerd.

Appendix A

Overview of the 32 wastewater treatment plants that are scattered over the Demer catchment. Several others are still under construction.



Available at: http://www.aquafin.be/nl/indexb.php?n=8&e=34&bekken=09

Appendix B

List of priority substances in the field of water policy (2000/60/EC)

	CAS number	EU number	Name of priority substance	priority substance
(1)	15972-60-8	240-110-8	Alachlor	
(2)	120-12-7	204-371-1	Anthracene	(X)***
(3)	1912-24-9	217-617-8	Atrazine	(X)***
(4)	71-43-2	200-753-7	Benzene	
(5)	n.a.	n.a.	Brominated diphenylethers (**)	X****
(6)	7440-43-9	231-152-8	Cadmium and its compounds	X
(7)	85535-84-8	287-476-5	C_{10-13}-chloroalkanes (**)	X
(8)	470-90-6	207-432-0	Chlorfenvinphos	
(9)	2921-88-2	220-864-4	Chlorpyrifos	(X)***
(10)	107-06-2	203-458-1	1,2-Dichloroethane	
(11)	75-09-2	200-838-9	Dichloromethane	
(12)	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	(X)***
(13)	330-54-1	206-354-4	Diuron	(X)***
(14)	115-29-7	204-079-4	Endosulfan	(X)***
	959-98-8	n.a.	(alpha-endosulfan)	
(15)	206-44-0	205-912-4	Fluoranthene (*****)	
(16)	118-74-1	204-273-9	Hexachlorobenzene	X
(17)	87-68-3	201-765-5	Hexachlorobutadiene	X
(18)	608-73-1	210-158-9	Hexachlorocyclohexane	X
	58-89-9	200-401-2	(gamma-isomer, Lindane)	
(19)	34123-59-6	251-835-4	Isoproturon	(X)***
(20)	7439-92-1	231-100-4	Lead and its compounds	(X)***
(21)	7439-97-6	231-106-7	Mercury and its compounds	X
(22)	91-20-3	202-049-5	Naphthalene	(X)***
(23)	7440-02-0	231-111-4	Nickel and its compounds	
(24)	25154-52-3	246-672-0	Nonylphenols	X
	104-40-5	203-199-4	(4-(para)-nonylphenol)	
(25)	1806-26-4	217-302-5	Octylphenols	(X)***

	140-66-9	n.a.	(para-tert-octylphenol)	
(26)	608-93-5	210-172-5	Pentachlorobenzene	X
(27)	87-86-5	201-778-6	Pentachlorophenol	(X)***
(28)	n.a.	n.a.	Polyaromatic hydrocarbons	X
	50-32-8	200-028-5	(Benzo(a)pyrene),	
	205-99-2	205-911-9	(Benzo(b)fluoroanthene),	
	191-24-2	205-883-8	(Benzo(g,h,i)perylene),	
	207-08-9	205-916-6	(Benzo(k)fluoroanthene),	
	193-39-5	205-893-2	(Indeno(1,2,3-cd)pyrene)	
(29)	122-34-9	204-535-2	Simazine	(X)***
(30)	688-73-3	211-704-4	Tributyltin compounds	X
	36643-28-4	n.a.	(Tributyltin-cation)	
(31)	12002-48-1	234-413-4	Trichlorobenzenes	(X)***
	120-82-1	204-428-0	(1,2,4-Trichlorobenzene)	
(32)	67-66-3	200-663-8	Trichloromethane (Chloroform)	
(33)	1582-09-8	216-428-8	Trifluralin	(X)***

* Where groups of substances have been selected, typical individual representatives are listed as indicative parameters (in brackets and without number). The establishment of controls will be targeted to these individual substances, without prejudicing the inclusion of other individual representatives, where appropriate.

** These groups of substances normally include a considerable number of individual compounds. At present, appropriate indicative parameters cannot be given.

*** This priority substance is subject to a review for identification as possible "priority hazardous substance" The Commission will make a proposal to the European Parliament and Council for its final classification not later than 12 months after adoption of this list. The timetable laid down in Article 16 of Directive 2000/60/EC for the Commission's proposals of controls is not affected by this review.

**** Only Pentabromobiphenylether (CAS number 32534-81-9)

***** Fluoranthene is on the list as an indicator of other, more dangerous Polyaromatic Hydrocarbons

Appendix C

This appendix contains the Perl script that was written to adapt the input files needed by the SWAT model in the preliminary uncertainty analysis.

The ‘mod01$number3.mod’, ‘mod02$number3.mod’ and ‘toe01$number3.toe’ files are files containing parameter input data for the SWAT model that were created by Monte Carlo sampling with the UNCSAM software (Janssen et al., 1992). The parameters and input data were uniformly sampled between the uncertainty bounds as described in Section 4.5. Next, the input files are adapted and the SWAT model is run 100 times (= number of files). The output is stored in the ‘output$number3.out’ files, which can then be further processed.

```
print ("Give number of files \n");
$num = <STDIN>;
chomp $num;
print ("number of files is $num \n");
for ($ii = 1; $ii<=$num; $ii++){
        my $number3 = sprintf("%0.3d",$ii);
        open (READ2, "d:\\uncsam\\nil\\mod01$number3.mod");
        close(READ2);
        system ("copy d:\\uncsam\\nil\\mod01$number3.mod d:\\uncsam\\pest\\model.in");
        open (READ3, "d:\\uncsam\\nil\\mod02$number3.mod");
        system ("copy d:\\uncsam\\nil\\mod02$number3.mod d:\\uncsam\\pest\\pest.dat");
        close(READ3);
        system ("d:\\uncsam\\pest\\programbatch.bat");
        open (READ1, "d:\\uncsam\\nil\\toe01$number3.toe");
        while (<READ1>) {
                ($jj,$k)=split " ", $_;
        }
        if ($jj <200) {
                $j = -1;
        }
        elsif (($jj >=200) and ($jj <300)) {
                $j = 0;
        }
        else {
                $j = 1;
        }
        my @mgtfiles = ("000010001", "000010002", "000120005", "000120006", "000130005",
                "000140006", "000140007", "000140008", "000150001", "000160001",
                "000160002", "000200005", "000200006", "000210006", "000210007",
                "000210008", "000230009", "000240003", "000240004", "000240005",
```

```
        "000250003", "000250004", "000140009", "000150002", "000160003",
        "000200007", "000230010", "000230011");
foreach my $item (@mgtfiles) {
        open (FIN, "< d:\\uncsam\\pest\\$item.mgt");
        open (FOUT, "> d:\\uncsam\\nil\\outpest$number3.out");
        while (<FIN>) {
                my $line = $_;
                my @splitline = split " ", $line;
                if      ((scalar(@splitline)==5) and ($splitline[3]==3)){
                        $splitline[1] = $splitline[1]+$j;
                        $splitline[4] = $splitline[4]+($splitline[4]*$k)/100;
                        if ($splitline[1]==0) {
                                $splitline[0] = $splitline[0]-1;
                                $splitline[1] = 30;
                        }
                        printf FOUT "%4d%4d       %4d      %4d%6.3f\n", @splitline;
                } else {
                        print FOUT $line;
                }
        }
        close(FIN);
        close(FOUT);
        system ("copy d:\\uncsam\\nil\\outpest$number3.out
        d:\\uncsam\\pest\\$item.mgt");
}
system ("d:\\uncsam\\pest\\swat2000.exe");
system ("copy d:\\uncsam\\pest\\watout.dat d:\\uncsam\\nil\\output$number3.out");
my @mgtfiles = ("000010001", "000010002", "000120005", "000120006", "000130005",
               "000140006", "000140007", "000140008", "000150001", "000160001",
               "000160002", "000200005", "000200006", "000210006", "000210007",
               "000210008", "000230009", "000240003", "000240004", "000240005",
               "000250003", "000250004", "000140009", "000150002", "000160003",
               "000200007", "000230010", "000230011");
foreach my $item (@mgtfiles) {
        system ("copy d:\\uncsam\\pest\\backup\\$item.mgt d:\\uncsam\\pest\\$item.mgt");
        }
```

Curriculum vitae

Personal information

Holvoet Katrijn	° 24/05/1979 (Gent, Belgium)
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Education

2002-2005	PhD training in Applied Biological Sciences (Ghent University)
1997-2002	Bio-engineer in Environmental Technology (K.U.Leuven)
thesis	*Participative development of irrigation charts for a sustainable water use in the Highveld region (Zimbabwe)* (Prof. D. Raes)
1991-1997	Mathematics-Sciences (Lyceum Hemelsdaele, Brugge)

Career

Nov 2002-	PhD, VITO – Ghent University, Department of Applied Mathematics, Biometrics and Process Control
Oct 2002	Teacher in mathematics (Sint Jan Berghmanscollege, Brussels)

Obtained prices

- 2006: Best platform presentation: Conference: Pesticide behaviour in soils, water and air, Warwick university, UK, March 27-29 2006
  Best poster presentation: Scaldit Final Event, Mechelen, October 24 2006
- 2005: Best poster presentation: B-IWA, Brusssels, March 22 2005
- 2004: Best poster presentation: 2nd IWA Young Research Conference, Wageningen, the Netherlands, May 3-4 2004

Publications and participations to symposia

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Participation at International Conferences: active

- 9th PhD Symposium on Applied Biological Sciences, Leuven, Belgium, 16 October 2003.
  Poster: Development and evaluation of a dynamic exposure model for surface waters: an outline.
- SETAC Europe, 14th annual meeting, Prague, Czech republic, 18-22 April 2004.
  Platform: Harmonising chemical fate and basic water quality modelling at the catchment scale.
  Poster: Predicting the time-varying release of pesticides in surface waters using SWAT.
- European Geosciences Union, 1st General Assembly, Nice, France, 25-30 April 2004.
  Platform: Dynamic modelling of pesticide fluxes to surface waters using SWAT.
- IWA 2nd Young Research Conference, Wageningen, the Netherlands, 3-4 May 2004.

Platform: Hydrodynamic modelling with the non-point source pollution model SWAT for dynamic modelling of pesticides.

Poster: Preliminary study on the partitioning on pesticides in surface waters.

- Symposium on Liquid Chromatography - Mass Spectrometry, Montreux, Switzerland, 11-12 November 2004.

  Poster: Monitoring of pesticides in surface water using on-line SPE-LC-MS/MS.

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  Platform: Determination of the sorption coefficient of pesticides for implementing pesticide behaviour into the River Water Quality model N°1.

  Poster: Dynamic modeling of pesticide fluxes towards surface waters using SWAT.

- 57th International Symposium on Crop Protection, Gent, Belgium, 10 May 2005.

  Platform: The water-sediment as a highly dynamic system: results of an intensive pesticide monitoring campaign.

- 3rd International SWAT Conference, Zurich, Switserland, 11-15 July 2005.

  Platform: Dynamic modeling of pesticide fluxes to surface waters using SWAT.

- IWA 9th Specialist Conference on Diffuse Pollution, Johannesburg, South Africa, 9-12 August 2005.

  Platform: The water sediment as a highly dynamic system: results of an intensive pesticide monitoring campaign.

  Poster: Dynamic modeling of pesticide fluxes to surface waters using SWAT.

- IWA 10th International Specialised Conference on Watershed and Riverbasin Management, Calgary, Canada, 13-15 September 2005.

  Platform: Sensitivity Analysis as a Tool for River Basin Management.

- Pesticide behaviour in soils, water and air, Warwick university, UK, 27-29 March 2006.

  Platform: Modelling the fate of pesticides in a highly dynamic water-sediment system.

- Harmoni-CA 3rd Conference, Osnabrück, Germany, 5-7 April 2006.

  Poster: Intensive monitoring of pesticides in river systems: lessons learned.

- EGU 3rd General Assembly, Vienna, Austria, 2-7 April 2006.

Platform: The importance of a measuring campaign for model development: modifications to SWAT for pesticides.

- SETAC Europe 16th annual meeting, Den Hague, the Netherlands, 7-11 May 2006.

  Platform: Enhancements in modelling pesticides fate: a comparison between intensive monitoring and dynamic modelling results.

  Poster: Results of an intensive pesticide monitoring campaign and its ecotoxicological impact.

Participation at International Conferences: passive

- Ecological informatics applications in water management, Gent, Belgium, 5-6 November 2002.
- Waterforum watersysteemkennis VIWC, Brussels, Belgium, 31 January 2003.
- SETAC Europe 13th annual meeting, Hamburg, Germany, 27 April - 1 May 2003.
- 6th Agro Conference: fate, exposure and regulatory issues. Behaviour of Pesticides in Air, Soils and Water, Cologne, Germany, 8-9 July 2004.