Higher tier approaches for linking environmental exposure to bioaccumulation in regulatory context: MERLIN-Expo Tool estimations versus Monitoring data

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Background

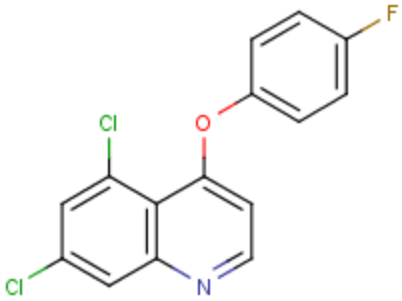
- The bioaccumulation of active substances of PPPs in non-target organisms represents an area of high concern.
- Within the Environmental Risk Assessment (ERA) the potential of a substance for bioaccumulation and biomagnification through the trophic web is investigated.
- Current harmonized approach involves only highly conservative and generic assumptions.
- Few higher-tier options are available to refine the scenario description or to implement mitigation measures within the exposure modelling.

Objectives

- To investigate the possibilities given by MERLIN-Expo as higher-tier refinement tool to assess Quinoxyfen fate in the environment and its bioaccumulation in aquatic species;
  - link Quinoxyfen environmental exposure estimation, after its application on grapes, to its accumulation in the aquatic food web of a surface water body located next to the vineyards;
  - to asses the performance of the tool by comparing the estimated results with monitoring available data;

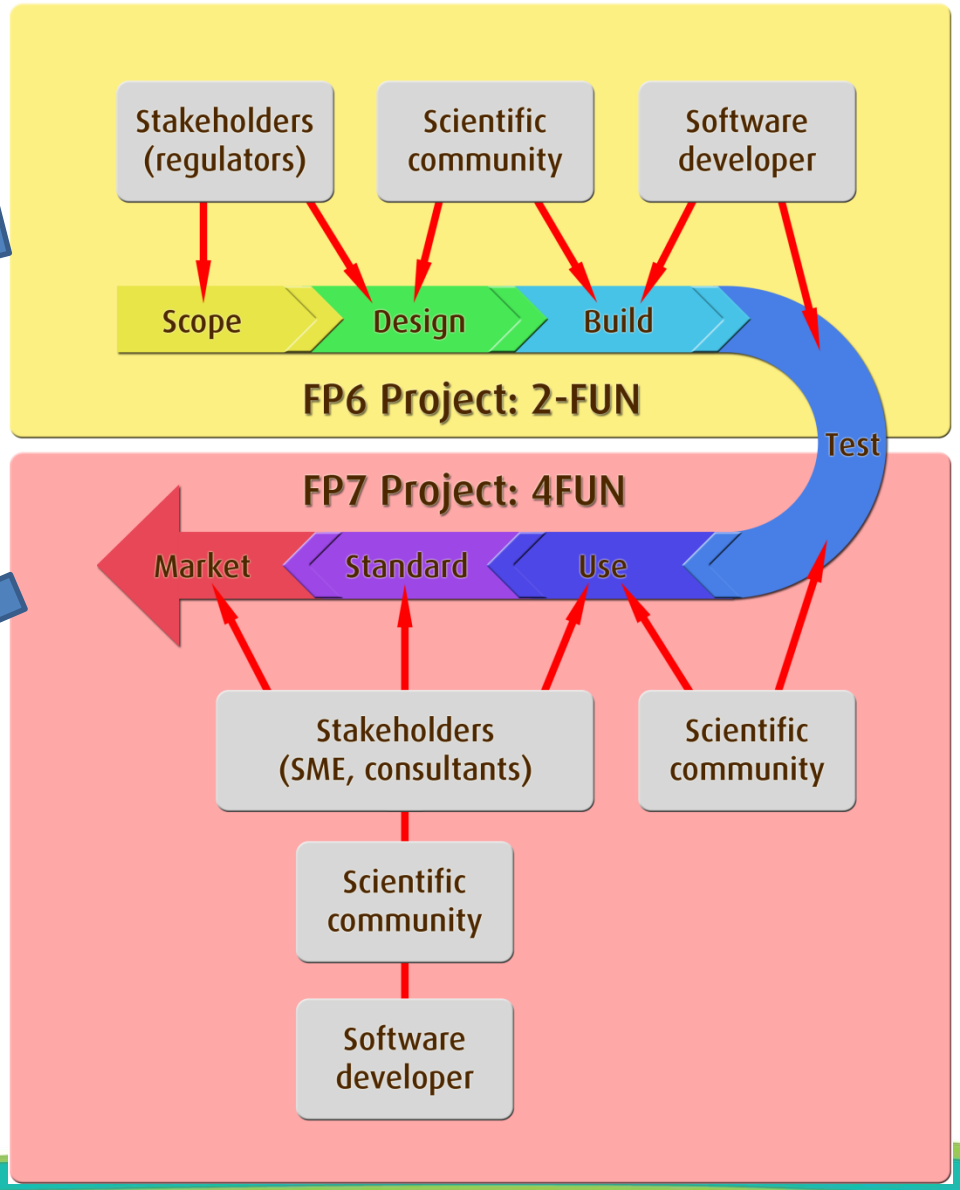
The Fungicide Quinoxifen

- Status under Reg.(EC) No 1107/2009: candidate for substitution (exp: 30/08/2018)
- Chemical class: phenoxyquinolines
- IUPAC name: 5,7-dichloro-4(p fluorophenoxy)quinoline
- Formula: $C_{15}H_8Cl_2FNO$
- Molecular weight: 308.1 g/mole
- Vapour pressure: 1.2 x 10^{-5} Pa (20°C)
- Log Kow: 4.66 (20°C, pH 6.6)
- Solubility (water): 0.116 mg/L (20°C, pH 6.45)
- Koc: 18339-28897 mL/g (mean 22929 mL/g)
- Soil DT50 (lab): 224-508 days (mean 374 days, 20°C, four soils)
- BCF (fish, *Oncorhynchus mykiss* normalized to 5% lipid): **7 450 L/kg**



Introduction -*The 2FUN and 4FUN EU projects*

The life cycle of a software development



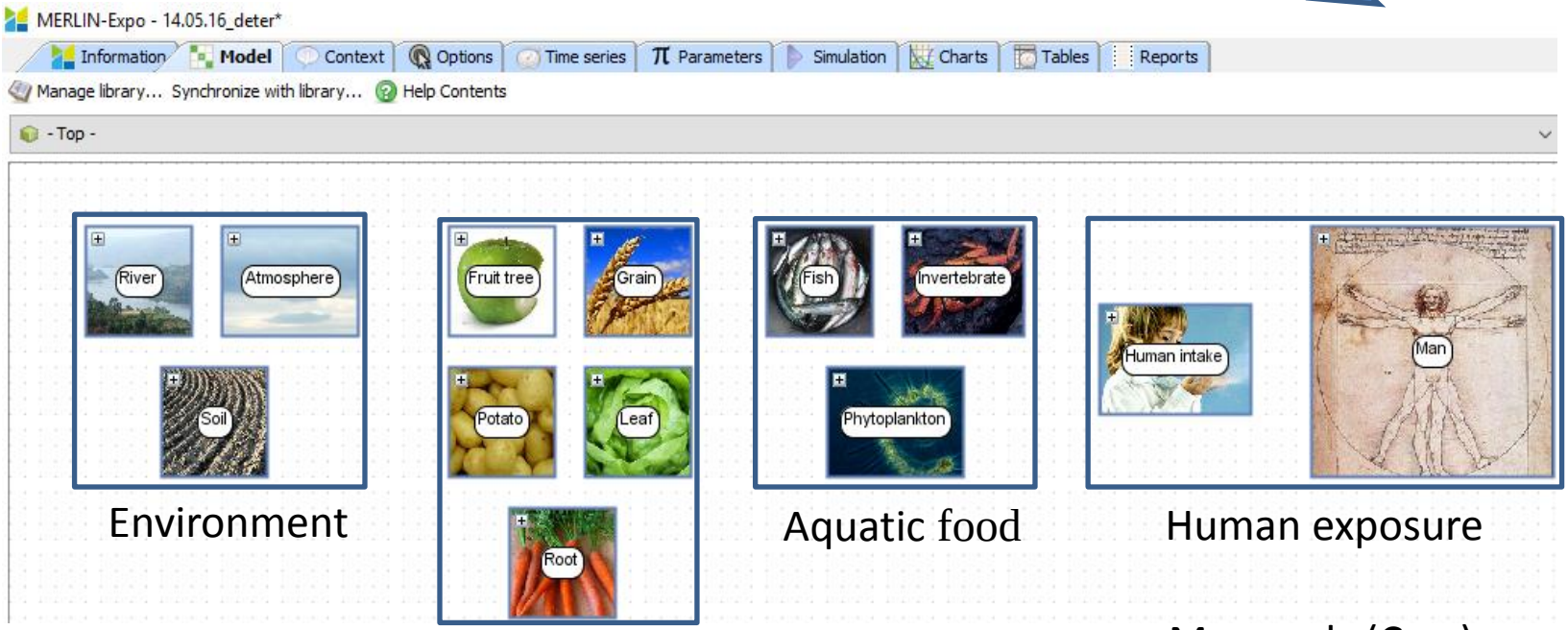
To provide all documentation, validation and demonstration elements for a standard tool

Introduction - *MERLIN-Expo*

Robust and regulatory-relevant tool for environmental fate and exposure assessments

Modelling **E**xposure to chemicals (organic and inorganic) for **R**isk assessment: a comprehensive **L**ibrary of multimedia and PBPK models for **I**ntegration, Prediction, u**N**certainty and Sensitivity analysis.

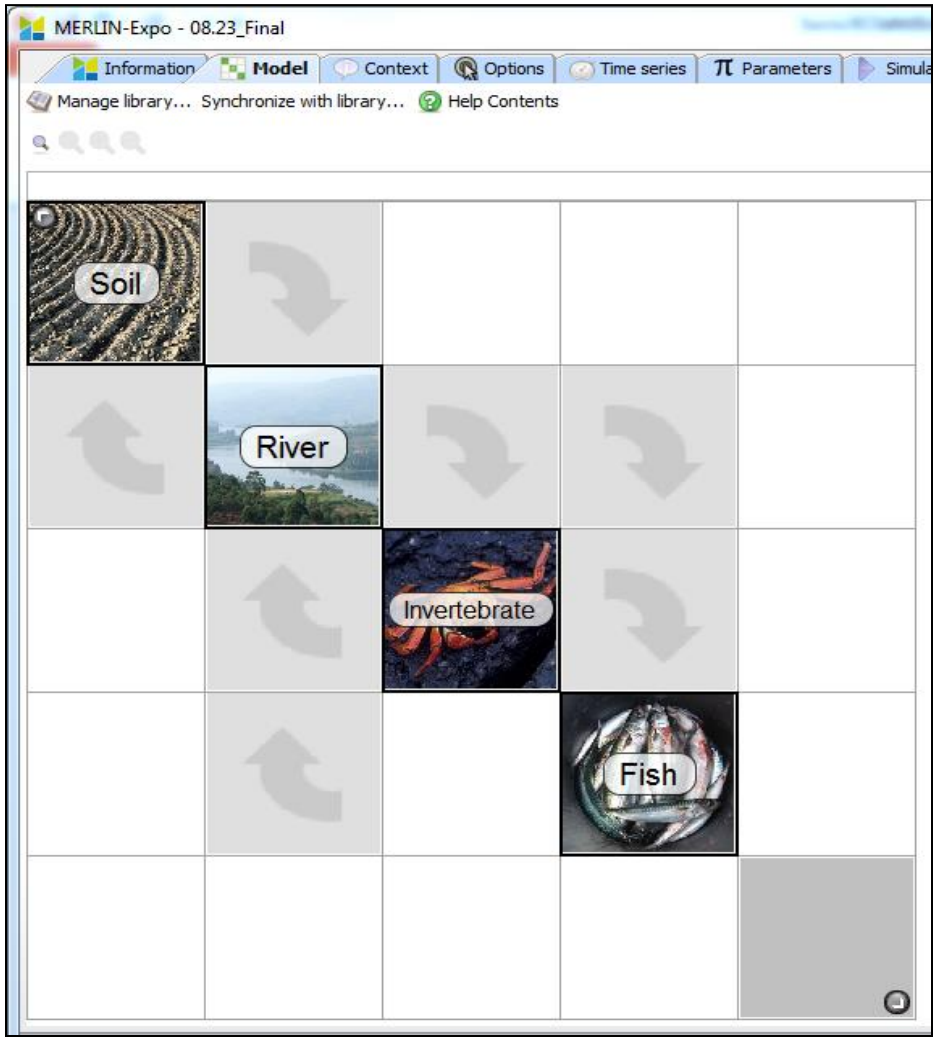
(http://merlin-expo.eu/)



+ Mammals (Cow)
Available soon

6

Scenario development



Matrices: soil, water, invertebrates, fish

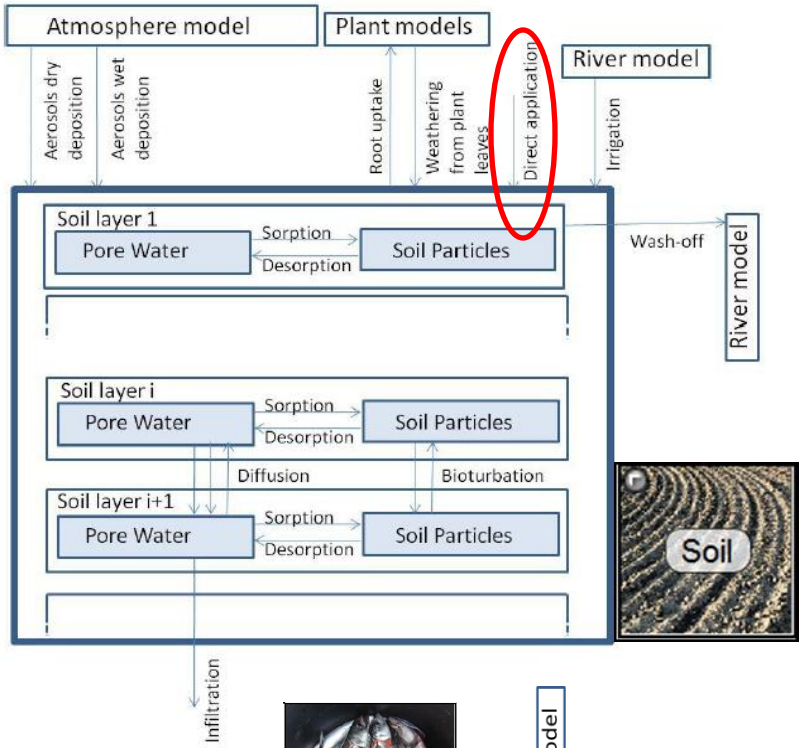
INPUT Quinoxifen:

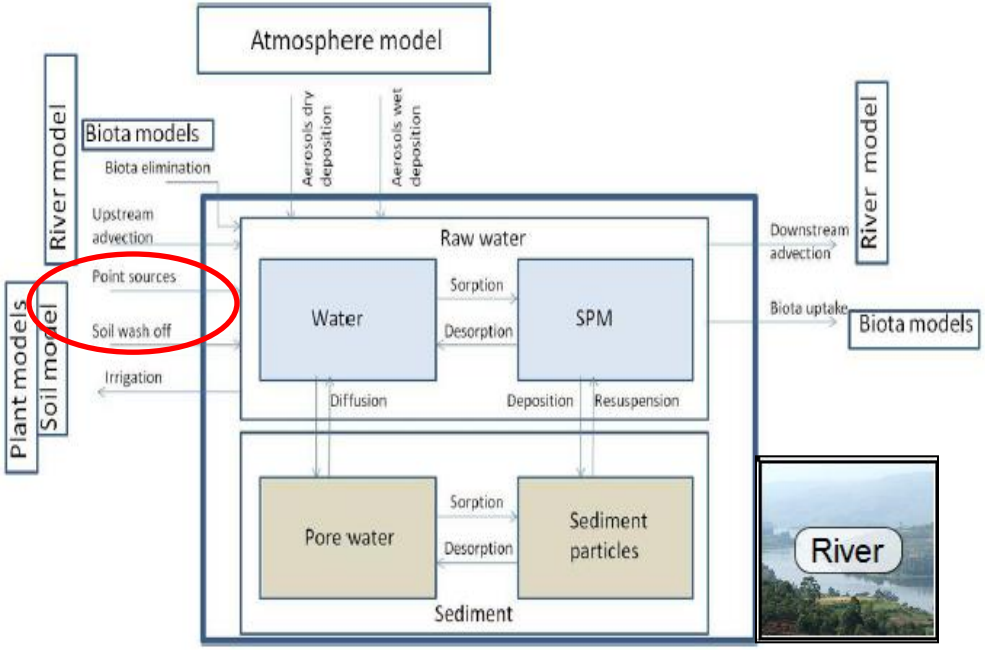
- **Soil:** Fungicide application considering the crop interception ($mg/m^2/d$)
- **Water:**
  1) Spray Drift (mg/d)
  2) Wash-off
- **Invertebrates:** concentration in sediments (scavengers); concentration in scavengers (predators)
- **Fish**: concentrations in sediment and invertebrates

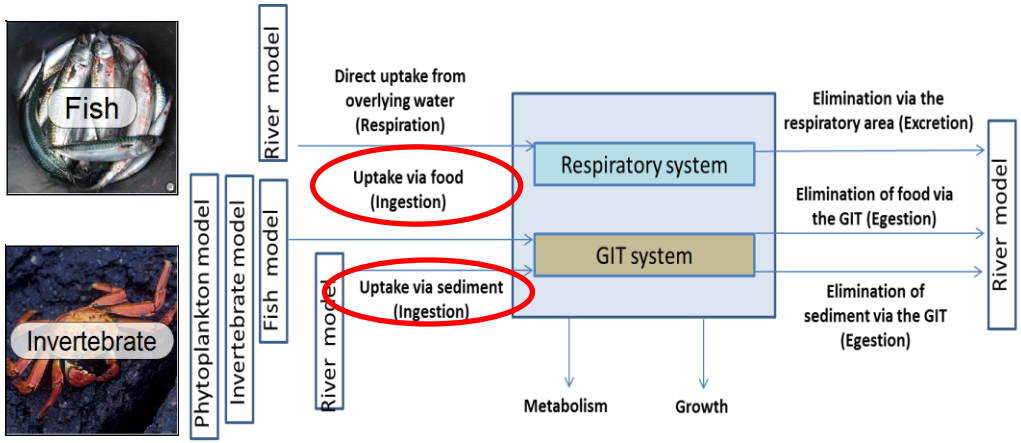
- **Crop interception**: 60% (EFSA, 2014)
- **Spray drift** – estimated with the drift calculator included in the SWASH tool (FOCUS, 2001; BBA, 2000)

Monitoring data from: **Capri E and Merli A (2008) - Pesticide risk assessment in vineyard ecosystems, La Goliardica Pavese, ISBN 8878304948, Italy**

Selected MERLIN-Expo models







Input data required by MERLIN-Expo models

"parameters" - constant over each simulation: chemical related parameters (e.g., physico-chemical properties of Quinoxyfen), site specific parameters (field dimensions and water body characteristics) and biota related parameters (e.g., diet preferences, physiological parameters of selected species);

"time series" - time-dependent environmental data (e.g. application scheme and rate of Quinoxyfen, water temperature, ***precipitation, wind speed and solar radiation - data from FOCUS, 2001 scenario Bologna - MARS Project (Vossen e Meyer-Roux, 1995)***)

Quinoxyfen specific parameters		Value	Reference
Henry's law constant (Pa m3 mol-1)		0.0319	Review Report Quinoxyfen E.C. 2003
Molar mass of the contaminant (g mol-1)		308.14	Review Report Quinoxyfen E.C. 2003
Log K_{OW} (m^3m^{-3})		4.66	Review Report Quinoxyfen E.C. 2003
Water-organic carbon partition coefficient (log_{10} of L/kg)		4.26	Review Report Quinoxyfen E.C. 2003
BCF (L $kg.fw^{-1}$)		3.7	Review Report Quinoxyfen E.C. 2003
Matabolic half-life of chemicals	d	2.7	Review Report Quinoxyfen E.C. 2003
Global degradation rate (ln2/DT50)	sediment	0.003	Review Report Quinoxyfen E.C. 2003
	water	0.099	Review Report Quinoxyfen E.C. 2003
	soil	0.0018	Review Report Quinoxyfen E.C. 2003

Input data - Site specific parameters

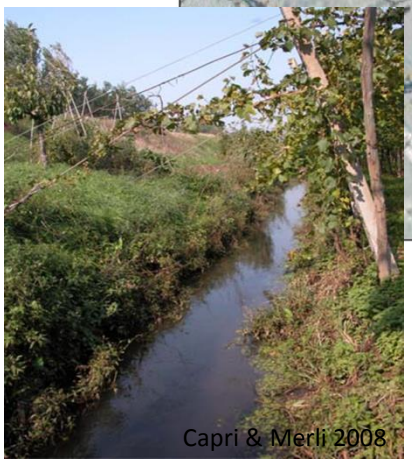
Parameters	Terrossa	Reference
River		
Depth of the river (m)	0.6	Capri & Merli 2008
Dry bulk density of sediment (kg/m3)	800	FOCUS R3
Fraction of organic matter in sediments	0.0526	Capri & Merli 2008
Initial sediment thickness (m)	0.05	FOCUS R3
Fraction of organic matter in SPM	0.1	Capri & Merli 2008
Lenght of the river (m)	173	Capri & Merli 2008
Width of the river (m)	1.5	Capri & Merli 2008
Soil		
Depth of the root zone (m)	1.6	FOCUS R3
Dry density of soil (kg/m3)	1460	FOCUS R3
Fraction of organic matter in soil	0.0312	Capri & Merli 2008
Depth of the soil layers (cm)	10	User decision
Soil surface (m2)	15000	Capri & Merli 2008
Soil water content at field capacity in the root zone	0.37	FOCUS R3
Soil water content at wilting point in the root zone	0.22	FOCUS R3
Theta 0	0.28	User decision

Characteristics of Field 2: Terrossa vineyard

- Surface: 1.5 ha
- Cultivation: wine grape cv "*Garganega*", "a pergola veronese" (planting space)

No other information is available on the cultivating techniques at this site.

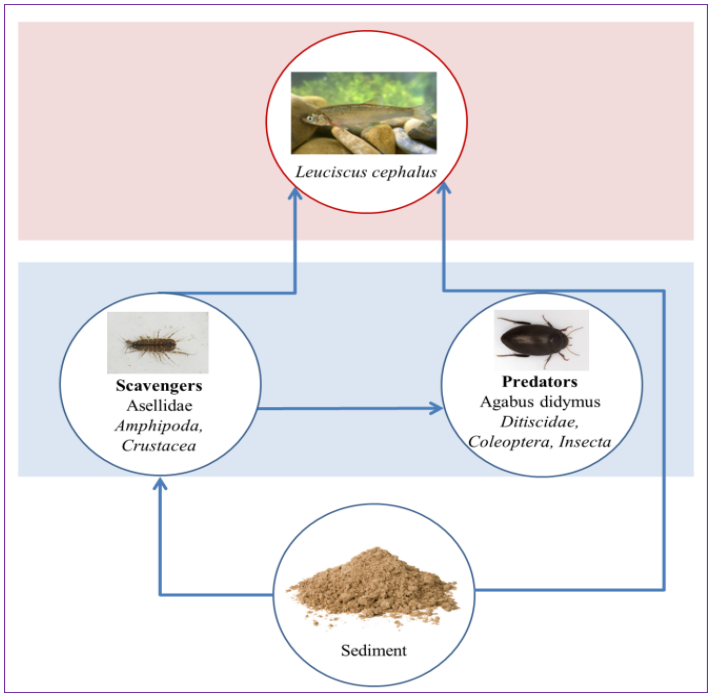
Figure 3.2.1.2 Aerial view of Terrossa site (arrow indicates the ditch)



Capri & Merli 2008

Input data – Real aquatic food web

FISH MODEL Parameters	*Leuciscus cephalus*	
	Value	Reference
Food transport coefficient (kg/kg/d) γ	0.03	MERLIN-Expo default data
Fraction of assimilated food	0.73	MERLIN-Expo default data
Lipid Fraction	0.05	MERLIN-Expo default data
Age at maturity (d)	1460	http://www.fishbase.se/summary/Squalius-cephalus.html
Lenght at maturity (cm)	30	http://www.fishbase.se/summary/Squalius-cephalus.html
Intercept of weight-length relationship	0.0087	http://www.fishbase.se/popdyn/LWRelationshipList.php?ID=4482&GenusName=Squalius&SpeciesName=cephalus&fc=122
Slope of weight-length relationship	3.12	http://www.fishbase.se/popdyn/LWRelationshipList.php?ID=4482&GenusName=Squalius&SpeciesName=cephalus&fc=122



INVERTEBRATE MODEL Parameters	Scavengers		Predators	
	Asellidae (Amphipoda, Crustacea)		*Agabus didymus* (Ditiscidae, Coleoptera, Insecta)	
	Value	Reference	Value	Reference
Food transport coefficient (kg/kg/d) γ	0.03	Default data for blue mussel	0.03	Default MERLIN-Expo for blue mussel
Fraction of assimilated food (-)	0.73	Default data for blue mussel	0.73	Default MERLIN-Expo for blue mussel
Lipid Fraction (-)	0.014	Giubilato et al. 2016	0.05	Giubilato et al. 2016
Age at maturity (d)	35	User decision	35	User decision
Weight at maturity (kg)	3.97E-05	Kangur K. Tuvikene L 1998	3.97E-05	Kangur K. Tuvikene L 1998

Inputs from Monitoring study

Quinoxyfen Applications				
n° Applications	Date of application	Julian day	Application rate (g/ha)	*Drift loading onto water body (mg/m^2)
1	12/06/2005	163	104	0.1629
2	20/06/2005	171	104	0.1629
3	23/05/2006	508	100	0.1570
4	12/06/2006	528	100	0.1570
5	20/07/2006	566	100	0.1570

* estimated with the drift calculator included in the SWASH tool

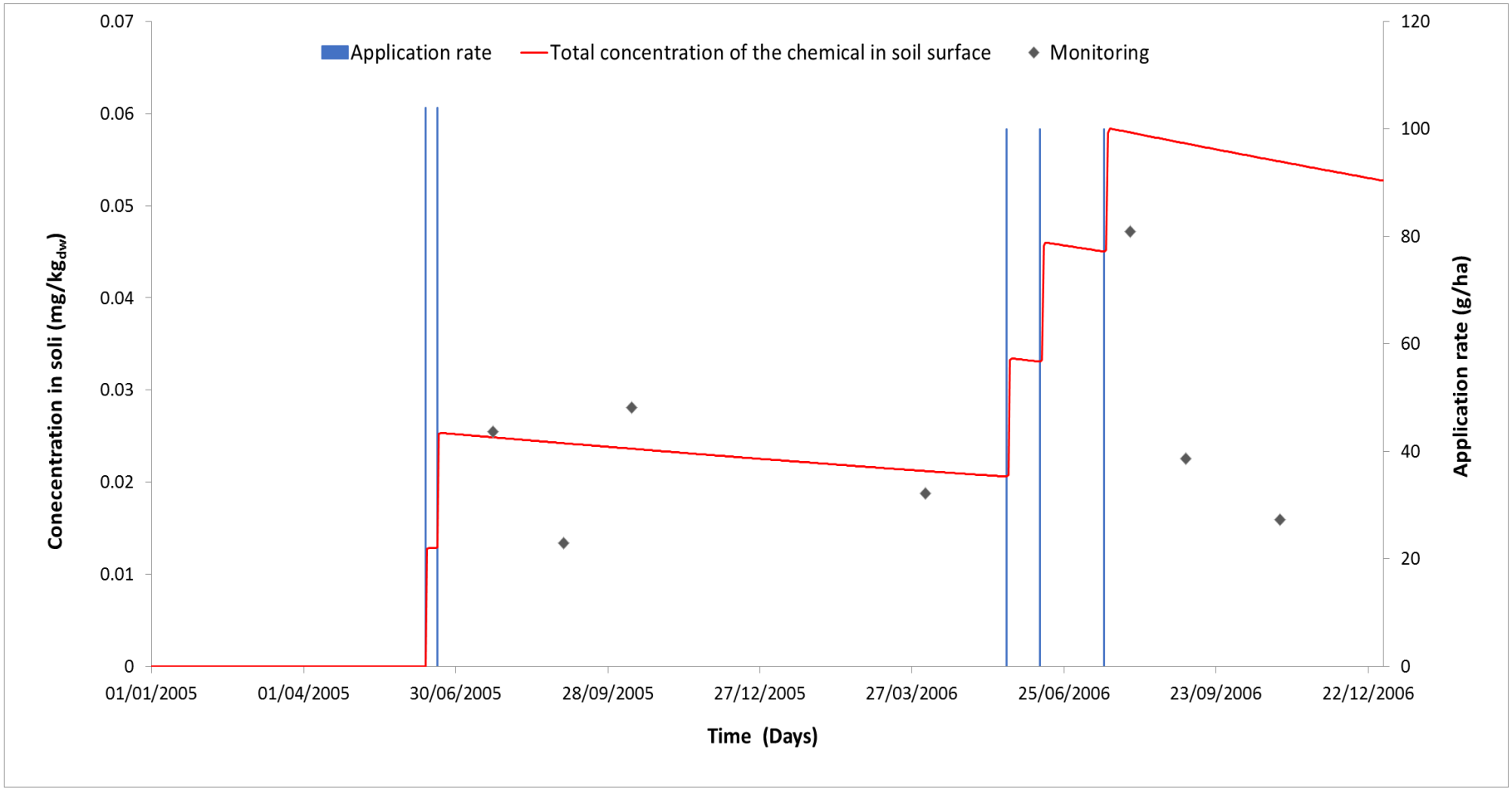
Application scheme

Monitoring data

Exposure monitoring	2005	08/06/2005
		22/07/2005
		02/09/2005
		12/10/2005
	2006	04/04/2006
		03/08/2006
		05/09/2006
		31/10/2006
Biota monitoring	2005	October
	2006	April, October

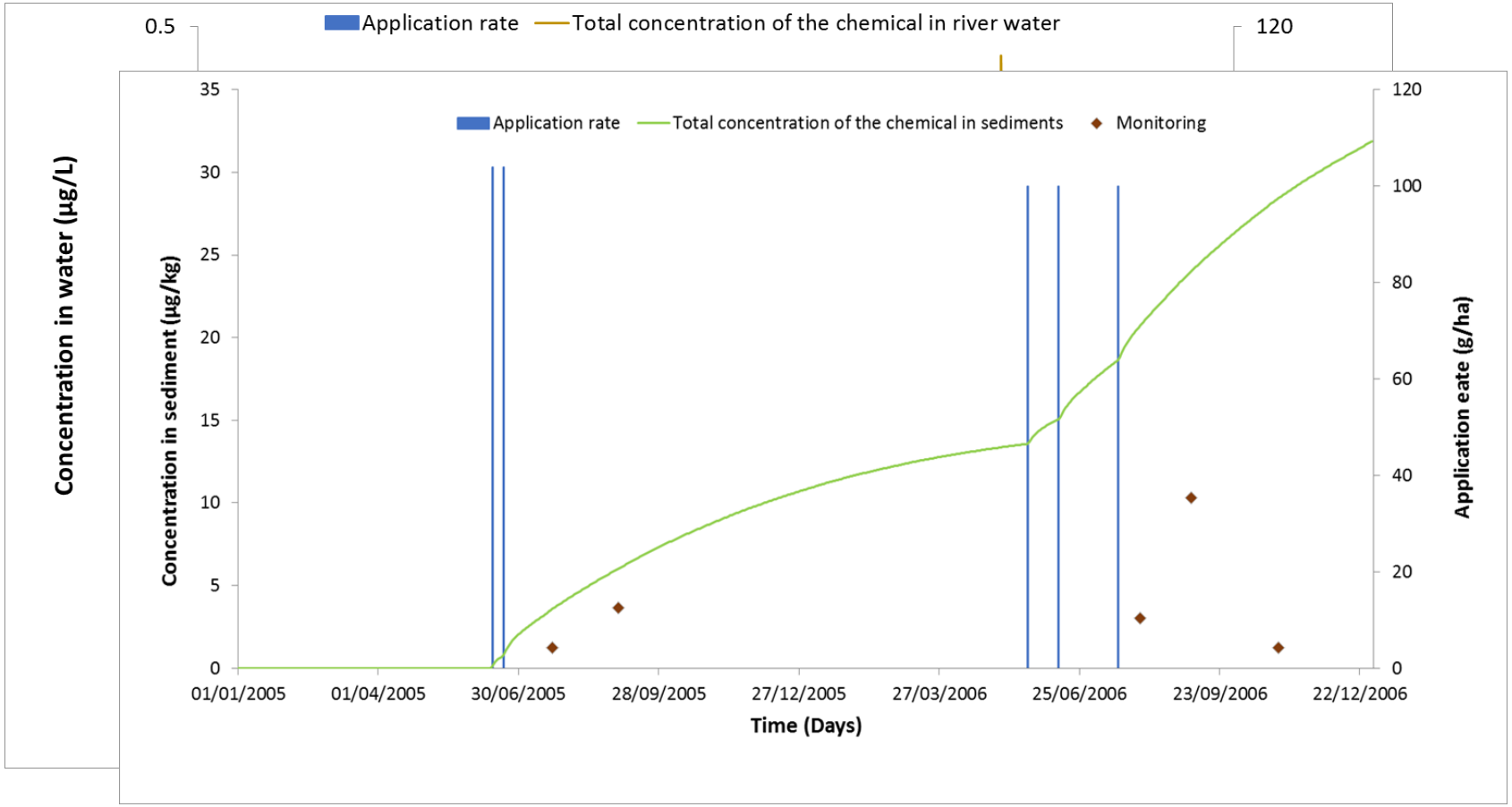
Quinoxyfen in soil -Modelling Vs Monitoring

- Deterministic simulation, 2 years period



Quinoxyfen in the water system-Modelling Vs Monitoring

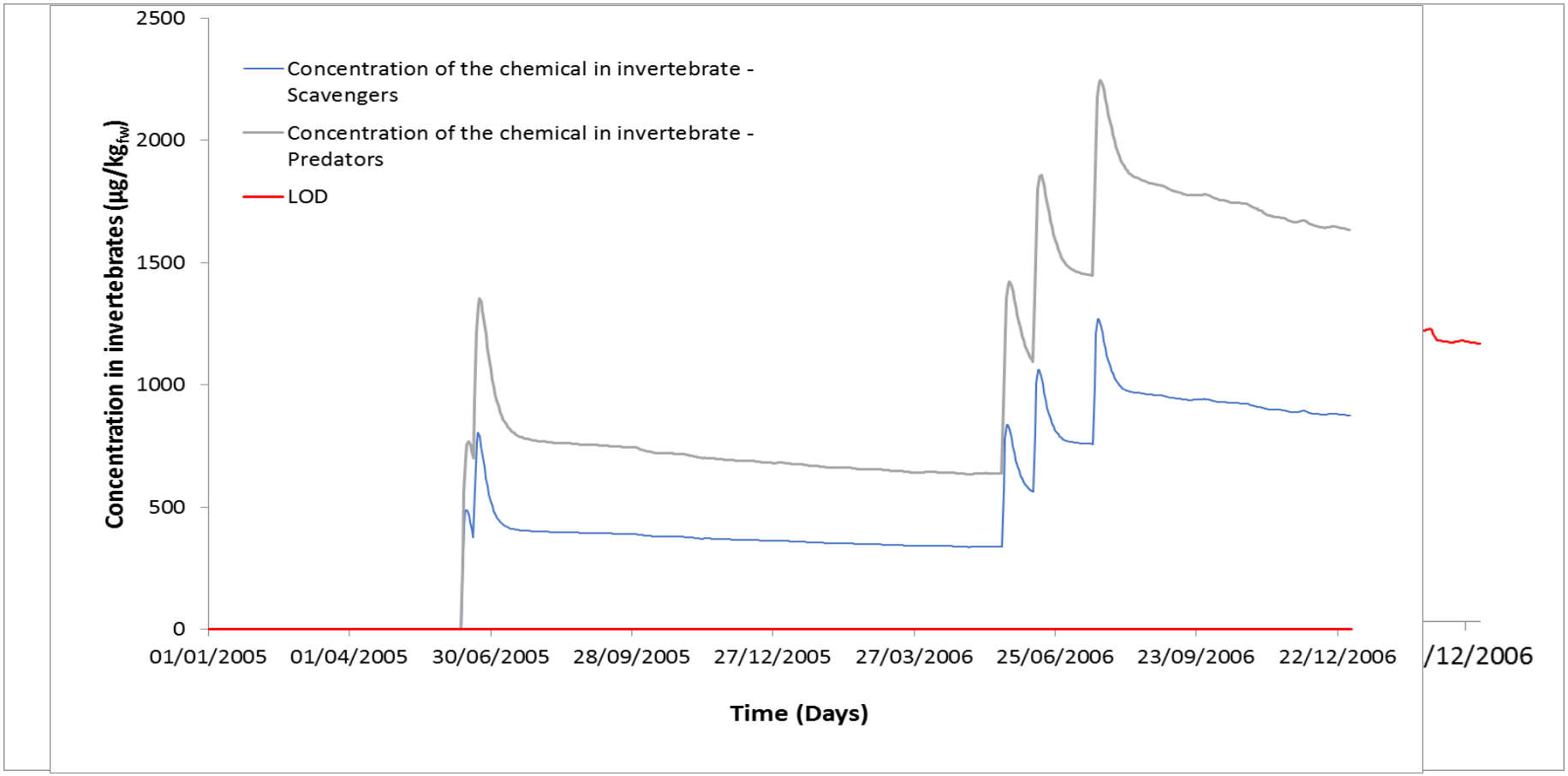
- Deterministic simulation, 2 years period



Quinoxyfen in the aquatic organisms – Modelling Vs Monitoring

Monitoring data – values below the LOD

LOD of 0.54 µg/kg



Invertebrate starting its life at the beginning of the simulation.
Fish starting its life at the beginning of the simulation.

Conclusions

- Based on preliminary results, MERLIN-Expo may be adapted to be used for the exposure assessment of aquatic organisms to PPPs, by linking soil, water and aquatic organism models in the tool.

- Merlin-Expo was able to simulate the concentration of Quinoxifen in soil and sediment, near to the monitoring data values, using indications from the regulatory framework of pesticides (FOCUS R3 Scenario and SWASH model).

- The model overestimates the concentrations of Quinoxyfen in fish and invertebrates if compered with monitoring data; several variables influenced the comparison;

- Additionally probabilistic simulations and sensitivity analysis are required to refine the results and to effectively test the tool applicability for the regulatory framework of PPPs, including the implementation of mitigation measures.

References:

- Model documentation and training materials available on:

http://merlin-expo.eu/

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Elisa Giubilato [a], Artur Radomyski [a], Andrea Critto [a], Philippe Ciffroy [b], Céline Brochot [c], Lisa Pizzol [a], Antonio Marcomini [a,*]

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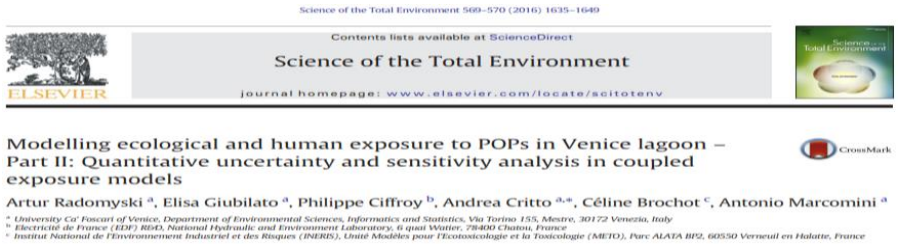

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Potential for MERLIN-Expo, an advanced tool for higher tier exposure assessment, within the EU chemical legislative frameworks

Nicoleta Suciu [a,*], Alice Tediosi [b], Philippe Ciffroy [c], Annette Altenpohl [d], Céline Brochot [e], Frederik Verdonck [f], Federico Ferrari [b], Elisa Giubilato [g], Ettore Capri [a], Gabriella Fait [h]

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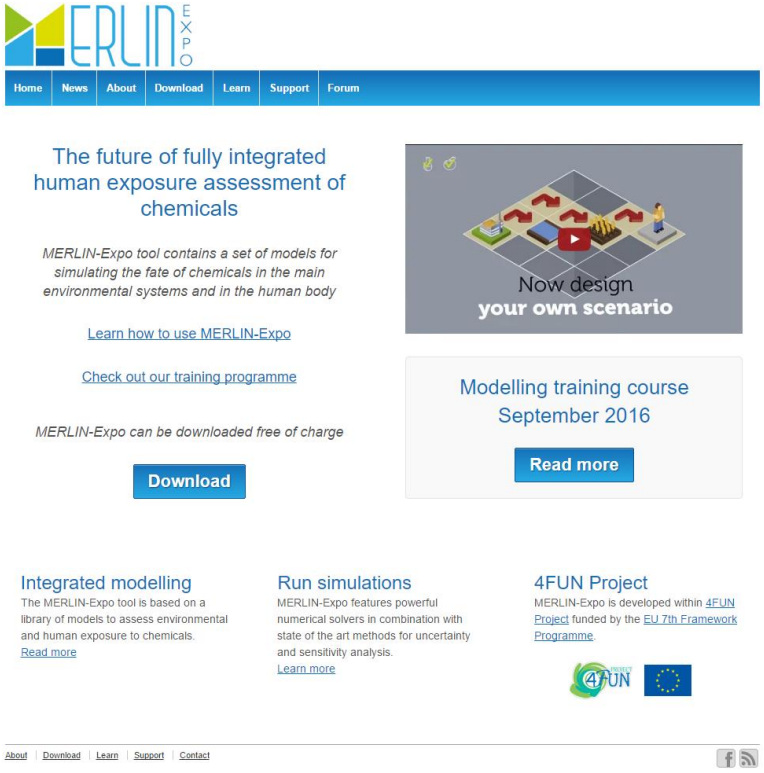

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