...In practice...
How to calculate PEC?
A case of study

Case study presentation: Cosazole

Phyisical-Chemical features

Parameter	Value	Unit
Molar mass	153	g/mol
Water solubility	256	mg/L
Saturated vapour press.	9.5 e-06	Pa

Application details

Parameter	Value	Unit
Application per year	3	#
Time between application	12	Days
Application rate	0.8	kg/ha
Crops	Sunflower	
BBCH	22-25	

Crop interception

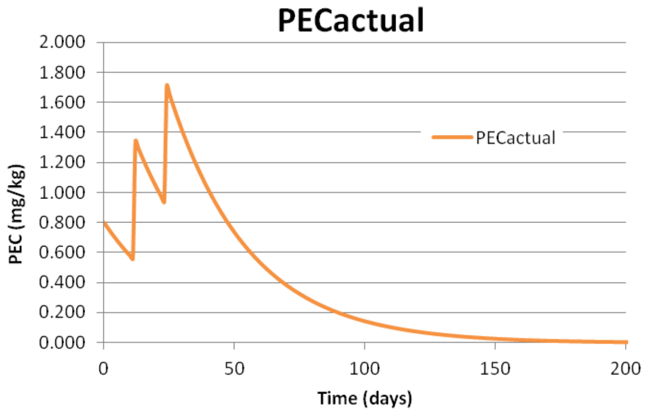
Table 1.5: Interception by other crops dependent on growth stage

Crop	Bare – emergence	Leaf development	Stem elongation		Flowering		Senescence Ripening
	BBCH#						
	0– 09	10–19	20–39		40–89		90–99
Beans (field + vegetable)	0	25	40		70		80
Cabbage	0	25	40		70		90
Carrots	0	25	60		80		80
Cotton	0	30	60		75		90
Grass##	0	40	60		90		90
Linseed	0	30	60		70		90
Maize	0	25	50		75		90
Oil seed rape (summer)	0	40	80		80		90
Oil seed rape (winter)	0	40	80		80		90
Onions	0	10	25		40		60
Peas	0	35	55		85		85
Potatoes	0	15	60		85		50
Soybean	0	35	55		85		65
Spring cereals	0	0	BBCH 20–29*	BBCH 30–39*	BBCH 40–69	BBCH 70–89	80–
			20	80	90	80	
Strawberries	0	30	50		60		60
Sugar beets	0	20	70 (rosette)		90		90
Sunflower	0	20	50		75		90
Tobacco	0	50	70		90		90
Tomatoes	0	50	70		80		50
Winter cereals	0	0	BBCH 20–29*	BBCH 30–39*	BBCH 40–69	BBCH 70–89	80
			20	80	90	80	

#The BBCH code is indicative (Meier, 2001).
##A value of 90 is used for applications to established turf.
*BBCH code of 20–29 for tillering and 30–39 for elongation.

PECsoil Cosazole

3 applns 800 g/ha, 12 days interval
Plant intercp 50% for all applns
DT_{50} = 21.3 days



Solution will appear here

n day 24

$PEC_{plateau}$ = 0 mg/kg

Metabolite

PECs will be calculated by considering a fake direct application of the metabolite

$$AppRate_{met} = AppRate_{par} \cdot MaxObserved(\%)_{met} \cdot \frac{MolWeight_{met}}{MolWeight_{par}}$$

Using Formation fraction instead of MaxObserved will result in a further overestimation of the initial PEC.

Calculate!

Solution will appear here

PEC groundwater calculation

Case study

Cosazolo		
Parameter	***Value***	***Unit***
Physical-Chemical features		
Molar mass	153	g/mol
Water Solubility	256	mg/L
Henry constant	3.00E-02	Pa m^3/mol
Saturated vapour pressure	9.50E-06	Pa
Koc	347	mL/g
Freundlich exponent	0.897	Adim.
DT_{50} soil	9	Days
Application features		
Application per year	3	#
Time between application	12	Days
Application rate	0.8	kg/ha
Crops	Winter cereals/Sunflower	
BBCH	12-16/22-25	

Metabolite		
Parameter	***Value***	***Unit***
Physical-Chemical features		
Molar mass	112	g/mol
Water Solubility	347	mg/L
Saturated vapour pressure	6.70E-05	Pa
Koc	476	mL/g
Freundlich exponent	0.987	Adim.
DT50soil	8	Days
DT50wat	0.5	Days
DT50sed	2	Days
Formation from parent in s	13	%

Case study

1) Sunflowers → just Piacenza and Sevilla

2) Dates of application: *what to look*?
   - BBCH, HARVEST DATE – PHI
   - Use of FOCUSgw appendix for harvest/emergence dates of all crops given for each scenario

Crop	C	H	J	K	N	P	O	S	T
apples	+	+	+	+	+	+	+	+	+
grass (+ alfalfa)	+	+	+	+	+	+	+	+	+
potatoes	+	+	+	+	+	+	+	+	+
sugar beets	+	+	+	+	+	+	+	+	+
winter cereals	+	+	+	+	+	+	+	+	+
beans (field)		+		+	+				
beans (vegetables)							+		+
bush berries			+						
cabbage	+	+	+	+			+	+	+
carrots	+	+	+	+			+		+
citrus						+	+	+	+
cotton								+	+
linseed					+				
maize	+	+		+	+	+	+	+	+
oilseed rape (summer)			+		+		+		
oilseed rape (winter)	+	+		+	+	+	+		
onions	+	+	+	+			+		+
peas (animals)	+	+	+		+				
soybean						+			
spring cereals	+	+	+	+	+		+		
strawberries		+	+	+				+	
sunflower						+		+	
tobacco						+			+
tomatoes	+					+	+	+	+
vines	+	+		+		+	+	+	+

C Châteaudun, H Hamburg, J Jokioinen, K Kremsmünster, N Okehampton, P Piacenza, O Porto, S Sevilla, T Thiva.

3. DEFINITION OF THE FOCUS SCENARIOS

3.1 Châteaudun

Table 3-1. Crop parameters for Châteaudun.

Crop	Growth Stage				Max. LAI		Root Depth (m)
	Planting (dd/mm)	Emergence (dd/mm)	Senescence (dd/mm)	Harvest (dd/mm)	($m^2 m^{-2}$)	(dd/mm)	
apples	perennial	01/04[@]	01/09	01/10[#]	4	31/05	1.0
grass + alfalfa	perennial[$]	01/04 16/05 01/07 16/08	NA	15/05 30/06 15/08 30/09	5 5 5 5	15/05 30/06 15/08 30/09	0.5 0.5 0.5 0.5
potatoes	15/04	30/04	02/08	01/09	4	15/06	0.6
sugar beets	25/03	16/04	05/09	15/10	5	15/07	1.0
winter cereals	20/10	26/10[*]	20/06	15/07	7.5	31/05	0.8
cabbage		20/04[&] 31/07[&]	20/06 30/09	15/07 15/10	3 3	31/05 05/09	0.6 0.6
carrots	28/02 30/06	10/03 10/07	01/05 21/08	31/05 20/09	3 3	20/04 10/08	0.8 0.8
maize	20/04	01/05	01/09	01/10	4.5	15/08	0.8
oil seed rape (win)	30/08	07/09[**]	10/06	10/07	4	20/04	1.0
onions	15/04	25/04	18/07	01/09	3	30/06	0.6
peas (animals)	25/03	05/04	31/07	15/08	4	07/06	0.6
spring cereals	20/02	10/03	30/06	20/07	5	10/06	0.6
tomatoes		10/05[&]	26/07	25/08	6	30/06	0.8
vines	perennial	01/04	13/08	01/11	6	31/07	1.0

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth

Case study

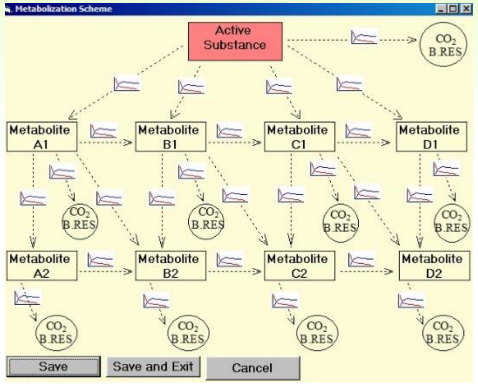
Sunflowers: **BBCH 22-25 is approximately between LEAF and SHOOT DEVELOPMENT stages (cfr. BBCH monograph)**
Dates of application chosen (with the support of AppDate):

Piacenza: 10.5 [130], 22.5 [142], 03.06 [154] *12 d of interval!*
Sevilla : 30.3 [339], 11.4 [101], 23.4 [113]

BBCH 22-25 corresponds to 50% crop interception

Case study – PELMO vers. 5.5.3

1) Create/modify pesticide file
2) New file
3) Input name, mol mass
4) Click on edit leaching locations
5) Select interested locations (e.g. all for Winter cereals, Piacenza-Sevilla for sunflowers) and add all
6) Choose mode of application (in this case every year – otherwise it may be every other year or every third year)
7) Choose number of application per year (here n. 3)
8) Select interested locations from the dropdown list in "absolute application dates" window, and insert all relevant application dates and application rates (A.R.)
9) !! In order to consider crop interception, input the relative A.R. – crop interception (in this case: 0.6 kg/ha for winter cereals, 0.4 kg/ha for sunflowers)



Case study – PELMO vers. 5.5.3

10) Leave default value for plant uptake factor, unless user can adjusted it to measured values, if substance specific uptake factors have been determined in appropriate experiments;

11) Insert henry constant, Koc value, Freundlich exponent

12) Click on *Done*

13) Now we need to calculate the transformation rates for each metabolite given (here only 1) and for CO_2 production (both for parent compound and for each metabolite considered), using the following expression:

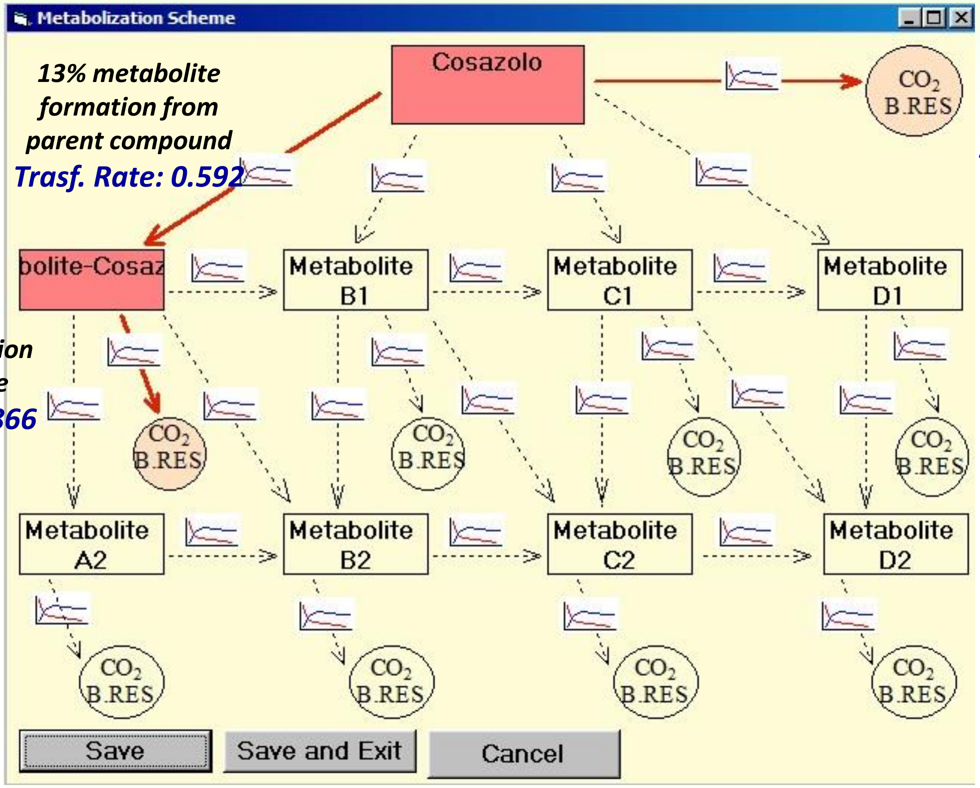
$$\frac{\ln 2}{DT50_{parent} \times (\%metabolite \text{ or } CO2/100)}$$

Case study – PELMO vers. 5.5.3

13% metabolite formation from parent compound
Trasf. Rate: 0.592

87% CO2 formation from parent compound
Trasf. Rate: 0.0885

100% CO2 formation from metabolite
Trasf. Rate: 0.0866



Case study – PELMO vers. 5.5.3

14) Save and exit

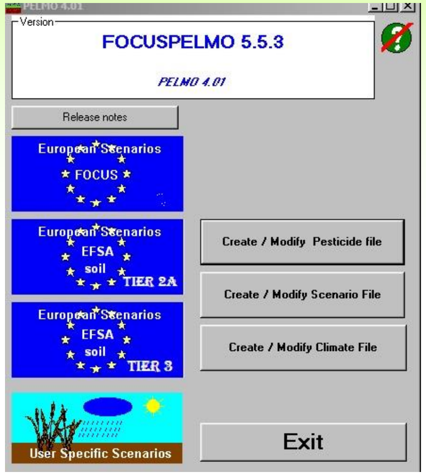
15) Enter on European scenarios FOCUS

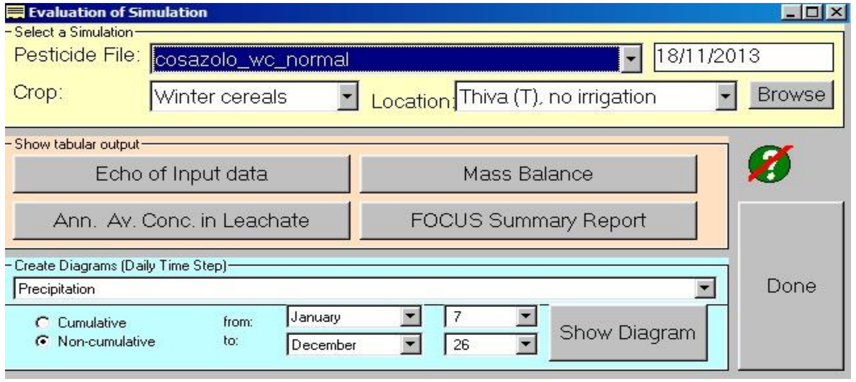
16) Select the crop, select your pesticide file, mark all locations interested for batch

17) Start Batch

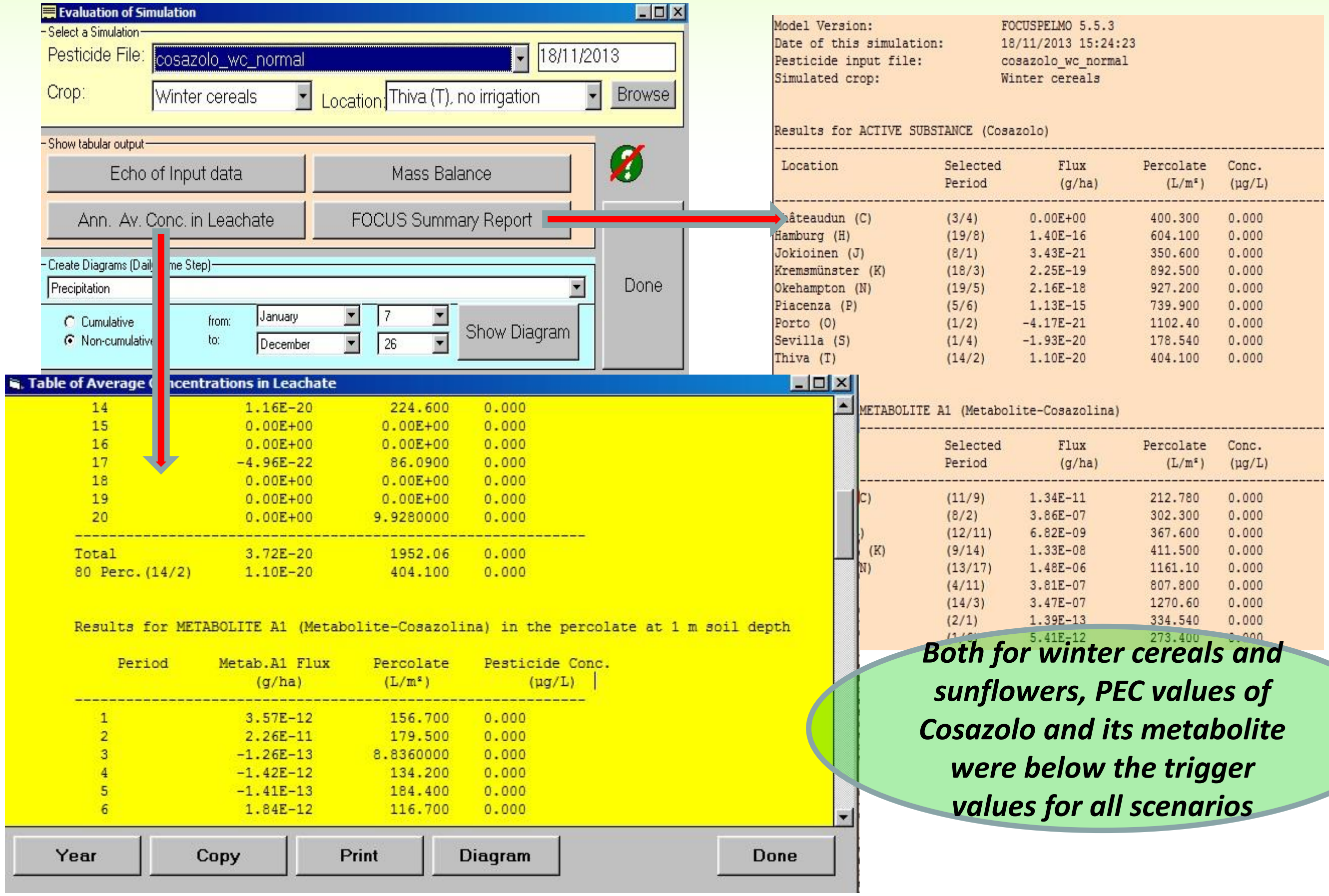
18) Evaluation

17) Input values and output reports are now available





Case study – PELMO vers. 5.5.3



Both for winter cereals and sunflowers, PEC values of Cosazolo and its metabolite were below the trigger values for all scenarios

Particular cases

1) **In case Koc values are pH-dependent**, PELMO requires both the pKa value and the reference pH at which the Koc was obtained in order to adjust the sorption for pH in the profile. **CLICK ON pH-dependent sorption to input values.**

2) **In case a correlation between sorption (Kf/Kd) and soil clay content** can be observed, **horizon-specific Kf-values sho** ... t values (tex ... ables of FO(

Table 3-3. Soil parameters for Châteaudun.

Horizon	Depth (cm)	Classification	pH-H_2O*	pH-KCl†	Texture (μm) <2	Texture (μm) 2-50	Texture (μm) >50	om (%)	oc (%)	Bulk Density (g cm^{-3})	Depth Factor@
Ap	0-25	silty clay loam	8.0	7.3	30	67	3	2.4	1.39	1.3	1.0
B1	25-50	silty clay loam	8.1	7.4	31	67	2	1.6	0.93	1.41	0.5
B2	50-60	silt loam	8.2	7.5	25	67	8	1.2	0.7	1.41	0.5
II C1	60-100	limestone#	8.5	7.8	26	44	30	0.5	0.3	1.37	0.3
II C1	100-120	limestone#	8.5	7.8	26	44	30	0.5	0.3	1.37	0
II C2	120-190	limestone#	8.5	7.8	24	38	38	0.46	0.27	1.41	0
M	190-260	limestone#	8.3	7.6	31	61	8	0.36	0.21	1.49	0

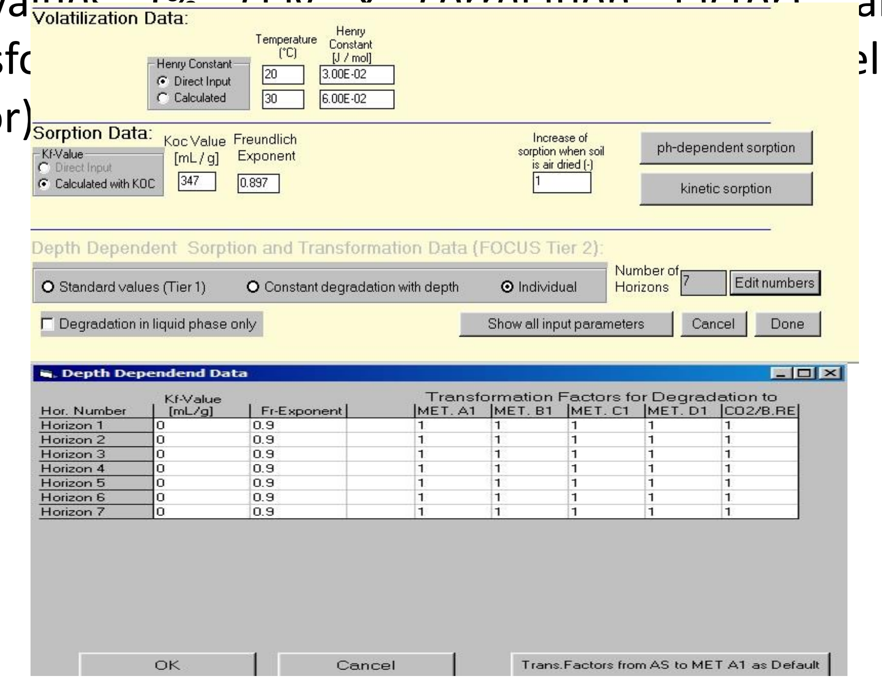
The limestone is cryoturbated in the C-horizons and powdery in the M-horizon.

* Measured at a soil solution ratio of 1:5

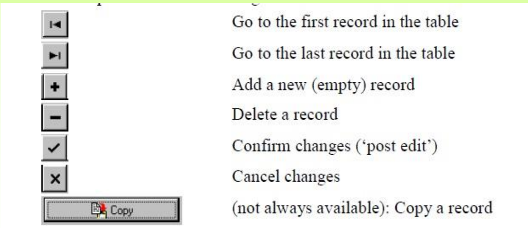
† These values are estimated from the measured water values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

Particular cases

2) …select "individual" and insert the relative number of horizons for each scenario; then, edit number for insertion of Kf values (% clay x correlation factor) and relative transf… …elative depth factor)



Case study - PEARL 4.4.4



1) Edit → substance → click on "+", as insert record
2) Input all values reported below inside each record-sheet, and leave default values for other parameters. In Freundlich sorption, for our example case, use "Kom, pH-independent".
3) ... click on optimum moisture ... e ... n

Cosazolo		
Parameter	**Value**	**Unit**
Physical-Chemical features		
Molar mass	153	g/mol
Water Solubility	256	mg/L
Henry constant	3.00E-02	Pa m^3/mol
Saturated vapour pressure	9.50E-06	Pa
Koc	347	mL/g
Freundlich exponent	0.897	Adim.
DT_{50} soil	9	Days
Application features		
Application per year	3	#
Time between application	12	Days
Application rate	0.8	kg/ha
Crops	Winter cereals/Sunflower	
BBCH	12-16/22-25	

Metabolite		
Parameter	**Value**	**Unit**
Physical-Chemical features		
Molar mass	112	g/mol
Water Solubility	347	mg/L
Saturated vapour pressure	6.70E-05	Pa
Koc	476	mL/g
Freundlich exponent	0.987	Adim.
DT50soil	8	Days
DT50wat	0.5	Days
DT50sed	2	Days
Formation from parent in s	13	%

Case study - PEARL 4.4.4

6) Click again on the row created before for the parent compound, and press on "Transformation Scheme" in order to open the relative window

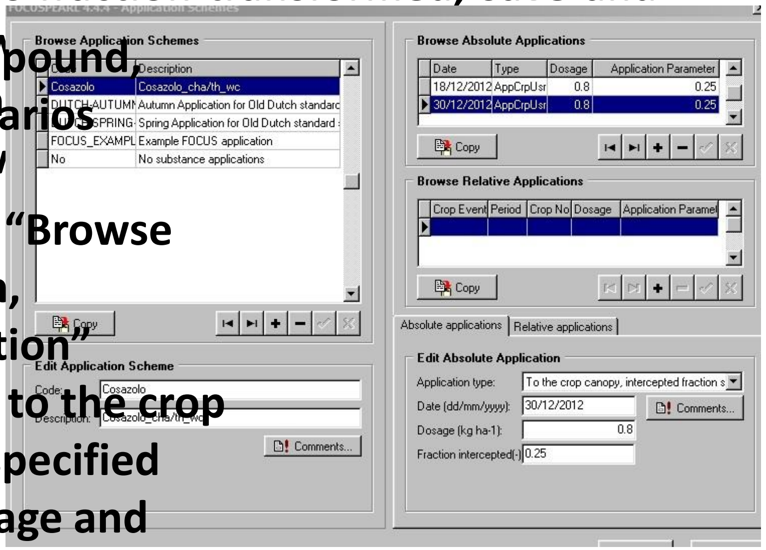
7) Now click on "+", and select your metabolite from the dropdown list of "Edit metabolite".

8) Then, insert the metabolite's fraction transformed, save and close the substance window

9) Edit → we are going to in… the "application scheme" w…

10) Insert name of parent compound, fill the description of the scenarios in use, and save.

11) Then, edit a new record in "Browse Absolute Applications" section, and fill "Edit Absolute Application" with type of appl. (in this case to the crop canopy, interception fraction specified by the user), date of appl, dosage and fraction intercepted.



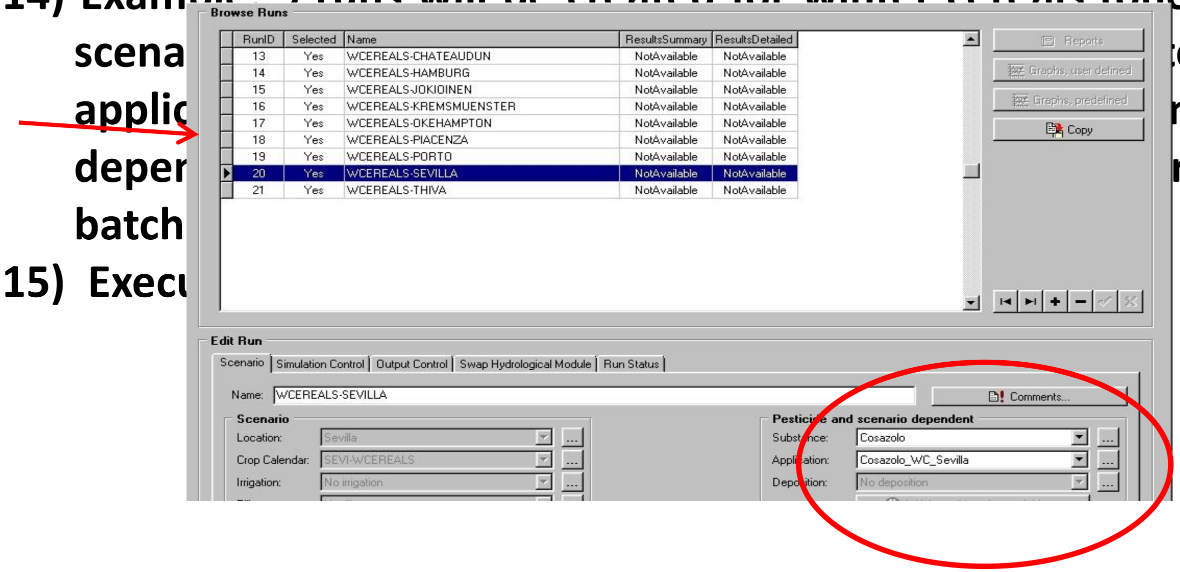
Case study - PEARL 4.4.4

12) Then, click on “Focus wizard”, select the crop in use, and all its available scenarios

13) Select your substance and one application scheme from the dropdown list, give a name to your project, and press “Finish”

14) Example: 9 runs will be created for winter cereals (one per scena ... e its applic ... nario deper ... re, a batch

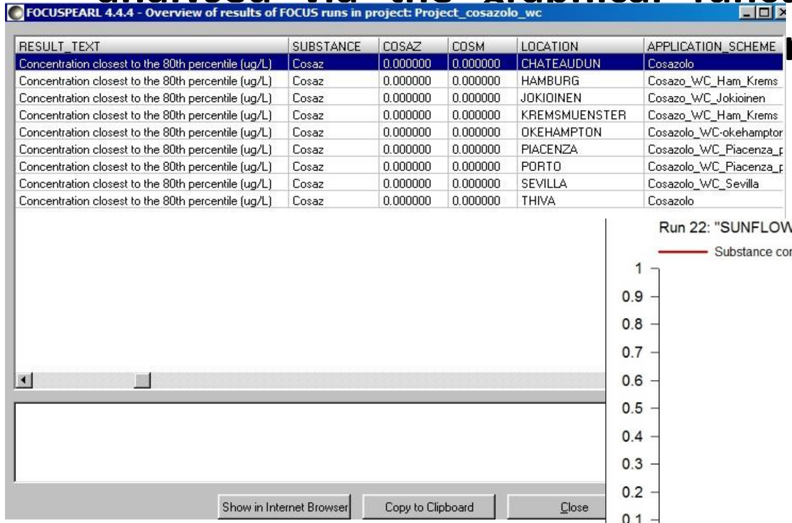
15) Execu



Case study - PEARL 4.4.4

16) Click on "Report" for obtaining the results' overview, both for parent compound and metabolite.

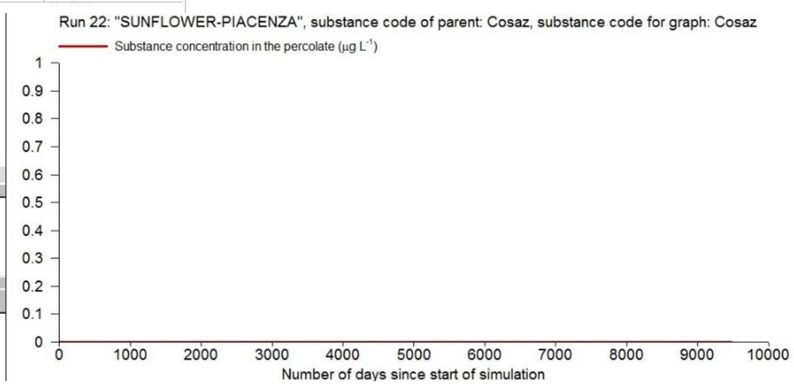
17) After a model run has been completed, the output can be analysed via the graphical function with the PEARL model ... r own graphs.



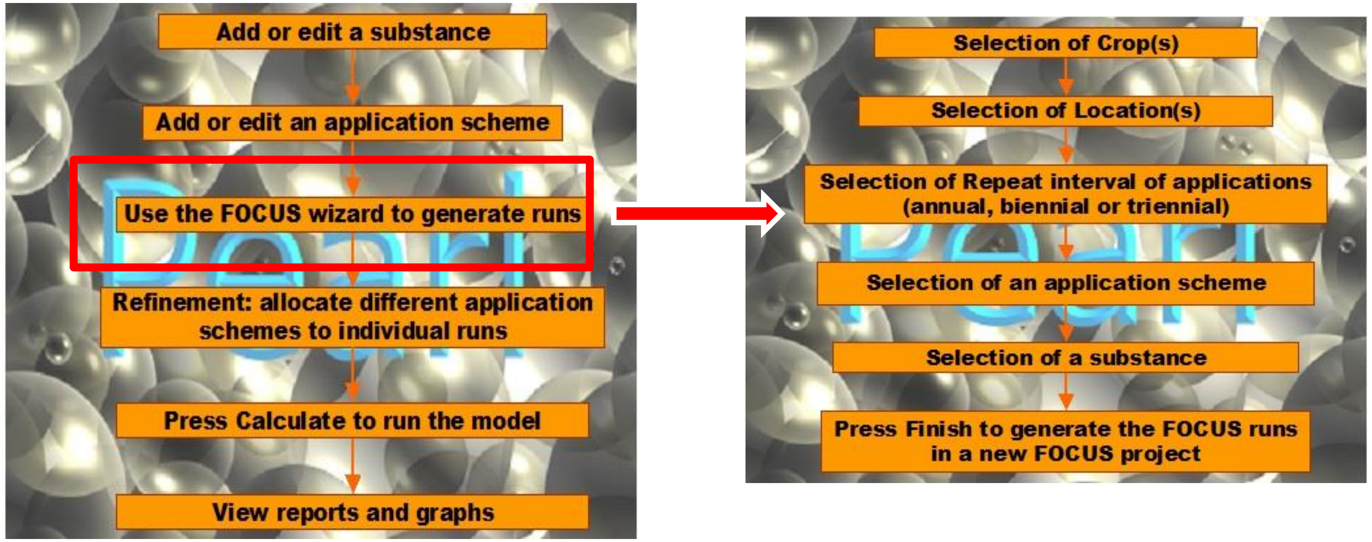
FOCUSPEARL 4.4.4 - Overview of results of FOCUS runs in project: Project_cosazolo_wc

RESULT_TEXT	SUBSTANCE	COSAZ	COSM	LOCATION	APPLICATION_SCHEME
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	CHATEAUDUN	Cosazolo
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	HAMBURG	Cosazo_WC_Ham_Krems
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	JOKIOINEN	Cosazo_WC_Jokioinen
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	KREMSMUENSTER	Cosazo_WC_Ham_Krems
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	OKEHAMPTON	Cosazolo_WC-okehamptor
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	PIACENZA	Cosazolo_WC_Piacenza_p
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	PORTO	Cosazolo_WC_Piacenza_p
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	SEVILLA	Cosazolo_WC_Sevilla
Concentration closest to the 80th percentile (ug/L)	Cosaz	0.000000	0.000000	THIVA	Cosazolo

Show in Internet Browser | Copy to Clipboard | Close



To sum up - PEARL 4.4.4



Particular cases

1) **In case Koc values are pH-dependent, PEARL requires both the pKa value and the two extreme Kom values (one at very low pH and one at very high pH).**
   Open substance window → select "Kom, pH-dependent" in the folder of Freundlich sorption and insert pKa, the two Kom values, and the pH correction (if available).

2) In cases that the sorption of pesticides is dependent on other soil properties than the organic matter content, the Freundlich coefficient measured in the top soil can be introduced directly, setting the "Kf, user defined".

If there is a pH-dependent sorption and degradation, but values reported above are not available, a worst-case simulation for the compound should be performed with FOCUS-PEARL.

PEC surface water calculation

Case study: Cosazole – Step 3

Chemical input

Parameter	Value	Unit
Molar mass	153	g/mol
Water solubility	256	mg/L
Saturated vapour press.	9.5 e-06	Pa
Solubility in water	256	mg/L
Koc	347	L/kg
Freundlich exponent	0.897	-
DT_{50} soil	9	days
DT_{50} water	26	days
DT_{50} sediment	17	days

Case study: Cosazole – Step 3

Application pattern input

Parameter	Value	Unit
Application per year	3	#
Time between application	12	Days
Application rate	0.8	kg/ha
Crops	Sunflower	
BBCH	22-25	
Scenarios	All relevant scenarios for sunflower	
CAM (only for R scen)	2 – Appln foliar	
Application dates	Consistent with BBCH and any scenario	

Calculate PECsw/sed!

Case study: Cosazole – Step 3

Results – Sunflower

Scenario	PECsw (µg/L)	PECsed (µg/kg)
D5 POND	0.27	0.7095
D5 STREAM	2.75	0.2052
R1 POND	1.543	3.48
R1 STREAM	17.73	5.752
R3 STREAM	28.72	14.01
R4 STREAM	**28.85**	11.60

Tier 1 Risk Assessment

W.C. Step 3 PECsw = 28.85 µg/L

Acute endpoints

Species	LC50 (µg/L)	AF	RAC (µg/L)	
Oncorhynchus mykiss	1467	100	14.67	✗
Daphnia magna	2130	100	21.3	✗

Chronic endpoints

Refinement needed!

Oncorhynchus mykiss	172	10	17.2	✗
Daphnia magna	432	10	43.2	✓
Scenedesmus subspicatus	3000	10	300	✓
Lemna gibba	2500	10	250	✓

Step 4 calculations

- Highest PEC_{sw} were found for R scenarios, so drift and runoff are the most relevant entry routes.
- Vegetated buffer strips have the potential to mitigate both entry routes
  - Drift is reduced according to Ganzelmeier calculations
  - Runoff, both water volume and eroded mass, are reduced according to % defined in the FOCUS document on mitigation measures
- Due to crop management constraints, vegetated buffer strips cannot be more than 10 m wide.

Runoff mitigation

Buffer width (m)	10-12	18-20
Reduction in volume of runoff water (%)	60	80
Reduction in mass of pesticide transported in aqueous phase (%)	60	80
n (for aqueous phase)	*36*	*30*
Reduction in mass of eroded sediment (%)	85	95
Reduction in mass of pesticide transported in sediment phase (%)	85	95
n (for sediment phase)	*19*	*11*

Case study: Cosazole – Step 4

Results – Sunflower (10 m of vegetated buffer strip)

Scenario	PECsw (µg/L)	PECsed (µg/kg)
D5 POND	0.1805	0.5058
D5 STREAM	0.6018	0.1710
R1 POND	0.6549	1.566
R1 STREAM	8.032	2.56
R3 STREAM	13.05	6.033
R4 STREAM	12.98	5.154