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Study Report

Predicted Environmental Concentrations in Groundwater of Cyanamide and Calcium cyanamide after fertilization with PERLKA® (DT50 AC) using FOCUSPEARL

Simulations in apples

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Statement of compliance

This study "*Predicted Environmental Concentrations in Groundwater of Cyanamide and Calcium cyanamide after fertilization with PERLKA® (DT50 AC) using FOCUSPEARL-Simulations in apples*" was conducted according to the procedures described herein. This report is a true and accurate record of the results obtained. There were no circumstances that may have adversely impacted the quality or integrity of the study.
The GLP-regulation is not applicable. However, the study was performed in accordance with the Codex of "Good Modelling Practices" (Görlitz 1993 und Travis 1995)

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1. Simulation model

The simulation model FOCUS-PEARL 4.4.4 was used for the calculation of the predicted environmental concentrations in groundwater (PECgw) of cyanamide and calcium cyanamide after application of PERLKA. Solute transport was calculated with the Convection-Dispersion-Equation (CDE). Non-linear sorption was implemented using a Freundlich isotherm. Depth-dependent sorption and transformation parameters were considered according to the common approach in FOCUS (2000) and FOCUS (2009).

2. Scenarios

Soil and climate scenarios of the FOCUS simulation models

The soil and climate scenarios defined by FOCUS 2000 were selected to represent a vulnerability approximating the 90th percentile for each scenario (realistic worst-case). Soils were selected by expert judgment whereas the weather data sets were obtained from the MARS meteorological database (MARS = Monitoring Agricultural ResourceS). The nine locations cover all climatic regions of agricultural relevance in Europe (Figure 1) and are briefly characterized in Table 1. For all scenarios, daily weather data are available for a period of 20 years.

Figure 1: Locations of the nine FOCUS groundwater scenarios

Table 1: Characteristics of the nine weather and soil scenarios created by FOCUS

Location	Soil type (USDA)	Organic Matter [%]	Annual average air temperature [°C]	Annual sum of precipitation [mm]
Châteaudun	silty clay loam	2.4	11.3	648+ I*
Hamburg	sandy loam	2.6	9.0	786
Jokioinen	loamy sand	7.0	4.1	638
Kremsmünster	loam/silt loam	3.6	8.6	900
Okehampton	loam	3.8	10.2	1038
Piacenza	loam	2.2	13.2	857 + I*
Porto	loam	2.5	14.8	1150
Sevilla	silt loam	1.6	17.9	493 + I*
Thiva	loam	1.3	16.2	500 + I*

*irrigation

Crop scenarios

For the simulations a single variation (continuous cropping of apples) over a period of 26 years is taken into account according to the recommendations of FOCUS [FOCUS 2000].

3. Physico-chemical and Degradation Data

PERLKA

The maximum concentration of calcium cyanamide in PERLKA is about 45%. In order to adequately simulate the slow release of cyanamide from PERLKA granules to soil, cyanamide was defined as a metabolite. According to experimental data the half-life of PERLKA (Ca CN2) in soil was found to be between 0.60 days and 1.80 days. The experimental values were normalised to 20 °C using a Q10 factor of 2.2 as recommended by FOCUS (2000). The experimental half-lives were also normalised to pF 2 (field capacity, see appendix A) using an exponent of 0.7 as the model requires degradation at optimised moisture conditions. Also the moisture correction was done according to FOCUS (2000). The geometric mean of all normalised half-lives was found to be 0.721 days. This value was considered for the modelling.

PERLKA granules cannot be dissolved in water without being transformed to cyanamide. In order to simulate the fate of PERLKA realistically the sorption constant in soil KOC was set to an artificial, high number (172400 L/kg). This should guarantee that within the model the granules remain at the applied location in soil and are only transformed to cyanamide without leaching to deeper soil layers. This can be considered a worst case selection of the formation of cyanamide.

Cyanamide

According to experimental data cyanamide is further transformed to urea. Also for cyanamide the experimental half-lives were normalised to 20 °C using a Q10-Factor of 2.2 as given by FOCUS (2000). However, for cyanamide no soil moisture normalisation was done since according to the experimental results the degradation of cyanamide does not increase with soil moisture (Klein 2019). Consequently, the soil moisture correction in the model FOCUS PEARL model is not suitable and the moisture correction was switched off. For the modelling a half-life of 0.78 days was used. The value represents the geometric mean of all experimental data after normalisation to 20 °C but without soil moisture normalisation (see Klein 2019).

For cyanamide an average (geometric mean) sorption constant of 4 L/kg was considered which was based on experimental sorption studies (EFSA 2010).

Cyanamide has a Henry's law constant of 2.68 10^{-5} J/mol. However this value cannot be entered directly into FOCUS PEARL but will be internally calculated based on water solubility, vapour pressure and molecular mass.

Plant uptake was not considered since the granules are usually applied before emergence of the crop.

Calcium cyanamide

Molecular Mass:	80.11 g/mol
Vapour pressure:	0
Water solubility:	800 000 mg/L at 20 °C (value of cyanamide)
Adsorption	172400 L/kg (Koc) (artificial, to reflect immobility of granulated PERLKA) 100 000 L/kg (Kom)
Freundlich Exponent.	1 (worst case)
Diffusion coefficient in water:	4.3 10-5 m² d-1 (FOCUS default)
Diffusion coefficient in air:	0.43 m² d-1 (FOCUS default)
Degradation:	DT50: 0.721 d at 20 °C Temperature correction: Reference temperature T0: 20 °C (FOCUS, 2000) Activation energy: 54 kJ mol-1 (FOCUS, 2009) Moisture correction: Moisture exponent: 0.7 (FOCUS, 2000) Reference soil moisture: 100 % FC
Application date:	14 days before the leaf emergence of the apples
Application mode:	annual application
Application rate:	Scenario 1: Apple, 300 kg/ha at the soil surface Scenario 2: Apple, 500 kg/ ha, uniform incorporation over 10 cm Scenario 3: Apple, 700 kg/ha at the soil surface
Plant uptake factor:	0.0 (worst case)

Cyanamide

Molecular Mass:	42.04 g/mol
Vapour pressure:	0.51 Pa
	Water solubility: 800 000 mg/L at 20 °C
Adsorption	4 L/kg (Koc)
	2.32 L/kg (Kom)
Freundlich Exponent.	1 (worst case)
Diffusion coefficient in water:	4.3 10-5 m² d-1 (FOCUS default)
Diffusion coefficient in air:	0.43 m² d-1 (FOCUS default)
Degradation:	DT50: 0.78 d at 20 °C
	Temperature correction:
	Reference temperature T0: 20 °C (FOCUS, 2000)
	Activation energy: 54 kJ mol-1 (FOCUS, 2009)
	Moisture correction:
	Moisture exponent: 0 (no correction)
	Reference soil moisture: not applicable
Formation fraction:	45%
Plant uptake factor:	0.0 (worst case)

4. Results

The global maximum concentrations are summarised in the following tables. Three simulation for apple using different application patterns are performed:

- Scenario 1: Apple, 300 kg/ha at the soil surface
- Scenario 2: Apple, 500 kg/ ha, uniform incorp. 10 cm
- Scenario 3: Apple, 700 kg/ha at the soil surface

The highest concentrations of cyanamide in leachate in all scenarios are obtained in Jokioinen. The increase of application amount (scenario 1 versus 3) leads to approximately 2.3 times higher concentrations of cyanamide in leachate. The higher concentrations at Jokioinen could be caused by low degradation due to cold temperature conditions in Finland.

Table 2: 80th percentile of annual leaching concentration for PERLKA and cyanamide of scenario 1

Scenario 1	Apple, 300 kg/ha at surface	
Location	80th percentile of concentration in leachate (µg Ca CN2/L)	80th percentile of concentration in leachate (µg cyanamide/L)
CHATEAUDUN	0	0.000636
HAMBURG	0	2.285091
JOKIOINEN	0	23.839136
KREMSMUENSTER	0	0.029789
OKEHAMPTON	0	0.27783
PIACENZA	0	0.40049
PORTO	0	0.307336
SEVILLA	0	0.002777
THIVA	0	0.000697

Table 3: 80th percentile of annual leaching concentration for PERLKA and cyanamide of scenario 2

Scenario 2	Apple, 500 kg/ ha, uniform incorp. 10 cm	
Location	80th percentile of concentration in leachate (µg Ca CN2/L)	80th percentile of concentration in leachate (µg cyanamide/L)
CHATEAUDUN	0	0.002931
HAMBURG	0	7.635438
JOKIOINEN	0	73.368748
KREMSMUENSTER	0	0.118402
OKEHAMPTON	0	0.821958
PIACENZA	0	0.796303
PORTO	0	0.970017
SEVILLA	0	0.012994
THIVA	0	0.003159

Table 4: 80th percentile of annual leaching concentration for PERLKA and cyanamide of scenario 3

Scenario	Apple, 700 kg/ha at surface	
Location	80th percentile of concentration in leachate (µg Ca CN2/L)	80th percentile of concentration in leachate (µg cyanamide/L)
CHATEAUDUN	0	0.001485
HAMBURG	0	5.331892
JOKIOINEN	0	55.624652
KREMSMUENSTER	0	0.069508
OKEHAMPTON	0	0.648269
PIACENZA	0	0.934477
PORTO	0	0.717117
SEVILLA	0	0.006479
THIVA	0	0.001627

5. Conclusion

Three different scenarios are considered to calculate the concentration of calcium cyanamide as well as of the metabolite cyanamide in the leachate. It should be noted that the formulated PERLKA as such cannot leach to groundwater because the granules are immobile. In the model, this is reflected by the artificially high adsorption coefficient (KOC) of 172,400 L/kg, invariably resulting in groundwater concentrations of 0 µg/L for the product PERLKA. Instead, the key metabolite cyanamide, which is formed rapidly upon contact water/moisture, and in turn shows rapid biological degradation, may nevertheless reach groundwater by leaching (Table 2, Table 3 and Table 4).

6. References

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7. Appendix: PEARL FOCUS Summary Output file

Apple, 300 kg/ha at surface

RUN_ID	RESULT_TEXT	SUBSTANCE	PRLKA	CN2	LOCATION	APPLICATION_SCHEME	CROP_CALENDAR	SOIL_TYPE	METEO_STATION	IRRIGATION_SCHEME
34	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.000636	CHATEAUDUN	PERLKA_Apple_300	CHAT-APPLES	CHAT-S_Soil	CHAT-M	FOCUS
35	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	2.285091	HAMBURG	PERLKA_Apple_300	HAMB-APPLES	HAMB-S_Soil	HAMB-M	No
36	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	23.839136	JOKIOINEN	PERLKA_Apple_300	JOKI-APPLES	JOKI-S_Soil	JOKI-M	No
37	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.029789	KREMSMUENSTER	PERLKA_Apple_300	KREM-APPLES	KREM-S_Soil	KREM-M	No
38	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.27783	OKEHAMPTON	PERLKA_Apple_300	OKEH-APPLES	OKEH-S_Soil	OKEH-M	No
39	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.40049	PIACENZA	PERLKA_Apple_300	PIAC-APPLES	PIAC-S_Soil	PIAC-M	FOCUS
40	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.307336	PORTO	PERLKA_Apple_300	PORT-APPLES	PORT-S_Soil	PORT-M	FOCUS
41	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.002777	SEVILLA	PERLKA_Apple_300	SEVI-APPLES	SEVI-S_Soil	SEVI-M	FOCUS
42	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.000697	THIVA	PERLKA_Apple_300	THIV-APPLES	THIV-S_Soil	THIV-M	FOCUS

Apple, 500 kg/ ha, uniform incorp. 10 cm

RUN_ID	RESULT_TEXT	SUBSTANCE	PRLKA	CN2	LOCATION	APPLICATION_SCHEME	CROP_CALENDAR	SOIL_TYPE	METEO_STATION	IRRIGATION_SCHEME
43	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.002931	CHATEAUDUN	PERLKA_Apple_500	CHAT-APPLES	CHAT-S_Soil	CHAT-M	FOCUS
44	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	7.635438	HAMBURG	PERLKA_Apple_500	HAMB-APPLES	HAMB-S_Soil	HAMB-M	No
45	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	73.368748	JOKIOINEN	PERLKA_Apple_500	JOKI-APPLES	JOKI-S_Soil	JOKI-M	No
46	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.118402	KREMSMUENSTER	PERLKA_Apple_500	KREM-APPLES	KREM-S_Soil	KREM-M	No
47	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.821958	OKEHAMPTON	PERLKA_Apple_500	OKEH-APPLES	OKEH-S_Soil	OKEH-M	No
48	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.796303	PIACENZA	PERLKA_Apple_500	PIAC-APPLES	PIAC-S_Soil	PIAC-M	FOCUS
49	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.970017	PORTO	PERLKA_Apple_500	PORT-APPLES	PORT-S_Soil	PORT-M	FOCUS
50	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.012994	SEVILLA	PERLKA_Apple_500	SEVI-APPLES	SEVI-S_Soil	SEVI-M	FOCUS
51	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.003159	THIVA	PERLKA_Apple_500	THIV-APPLES	THIV-S_Soil	THIV-M	FOCUS

Apple, 700 kg/ha at surface

RUN_ID	RESULT_TEXT	SUBSTANCE	PRLKA	CN2	LOCATION	APPLICATION_SCHEME	CROP_CALENDAR	SOIL_TYPE	METEO_STATION	IRRIGATION_SCHEME
52	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.001485	CHATEAUDUN	PERLKA_Apple_700	CHAT-APPLES	CHAT-S_Soil	CHAT-M	FOCUS
53	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	5.331892	HAMBURG	PERLKA_Apple_700	HAMB-APPLES	HAMB-S_Soil	HAMB-M	No
54	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	55.624652	JOKIOINEN	PERLKA_Apple_700	JOKI-APPLES	JOKI-S_Soil	JOKI-M	No
55	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.069508	KREMSMUENSTER	PERLKA_Apple_700	KREM-APPLES	KREM-S_Soil	KREM-M	No
56	Concentration closest to the 80th	PRLKA	0	0.648269	OKEHAMPTON	PERLKA_Apple_700	OKEH-APPLES	OKEH-S_Soil	OKEH-M	No

	percentile (ug/L)									
57	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.934477	PIACENZA	PERLKA_Apple_700	PIAC-APPLES	PIAC-S_Soil	PIAC-M	FOCUS
58	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.717117	PORTO	PERLKA_Apple_700	PORT-APPLES	PORT-S_Soil	PORT-M	FOCUS
59	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.006479	SEVILLA	PERLKA_Apple_700	SEVI-APPLES	SEVI-S_Soil	SEVI-M	FOCUS
60	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.001627	THIVA	PERLKA_Apple_700	THIV-APPLES	THIV-S_Soil	THIV-M	FOCUS