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Study Report

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

_______________________________________ __October 30, 2019______

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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 EFSA the half-life of PERLKA (Ca CN2) in soil was set to 1.45 days at 12°C (ECHA 2019, table 47).

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. According to EFSA a half-live in soil of 2.9 days at 12°C is used for cyanamide.

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

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: 1.45 d at 12 °C (EFSA in ECHA 2019, table 47)
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: 2.9 d at 12 °C (EFSA in ECHA 2019, table 47)
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	0.09872
HAMBURG	0	28.615236
JOKIOINEN	0	50.820806
KREMSMUENSTER	0	0.943201
OKEHAMPTON	0	9.69697
PIACENZA	0	7.223495
PORTO	0	11.482939
SEVILLA	0	0.123981
THIVA	0	0.108706

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	0.358304
HAMBURG	0	72.539544
JOKIOINEN	0	178.290595
KREMSMUENSTER	0	2.488344
OKEHAMPTON	0	22.52629
PIACENZA	0	17.394956
PORTO	0	28.026104
SEVILLA	0	0.285735
THIVA	0	0.355204

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	0.230349
HAMBURG	0	66.768905
JOKIOINEN	0	118.58196
KREMSMUENSTER	0	2.200805
OKEHAMPTON	0	22.626217
PIACENZA	0	16.854828
PORTO	0	26.793526
SEVILLA	0	0.289304
THIVA	0	0.25365

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

FOCUS (2000). FOCUS groundwater scenarios in the EU plant protection product review process. Report of the FOCUS Groundwater Scenario Workgroup, EC Document Reference Sanco/321/2000.

FOCUS (2009): Technical advice on the Q10, agreed by the Commission Standing Committee on the Food Chain and Animal Health (provided by EFSA), available at FOCUS home page (http://viso.ei.jrc.it/focus/docs/Technical%20advice%20on%20the%20Q10.doc)

Görlitz G. (1993): Verfahrensregeln zur korrekten Durchführung und Auswertung von Modellrechnungen zur Simulation des Umweltverhaltens von Pflanzenschutzmitteln.

Travis K.Z. (1995): Recommendations for the correct use of models and reporting of modelling results.- in: ‘Leaching Models and EU registration’. Final report of the FOCUS Group. Doc. 4952/VI/95

ECHA (2019): Annex XV restriction report. Proposal for a restriction. Substance name: Calcium cyanamide. Version number: 1.0. Date: 19 July 2019. Helsinki.

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
61	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.09872	CHATEAUDUN	PERLKA_Apple_300	CHAT-APPLES	CHAT-S_Soil	CHAT-M	FOCUS
62	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	28.615236	HAMBURG	PERLKA_Apple_300	HAMB-APPLES	HAMB-S_Soil	HAMB-M	No
63	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	50.820806	JOKIOINEN	PERLKA_Apple_300	JOKI-APPLES	JOKI-S_Soil	JOKI-M	No
64	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.943201	KREMSMUENSTER	PERLKA_Apple_300	KREM-APPLES	KREM-S_Soil	KREM-M	No
65	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	9.69697	OKEHAMPTON	PERLKA_Apple_300	OKEH-APPLES	OKEH-S_Soil	OKEH-M	No
66	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	7.223495	PIACENZA	PERLKA_Apple_300	PIAC-APPLES	PIAC-S_Soil	PIAC-M	FOCUS
67	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	11.482939	PORTO	PERLKA_Apple_300	PORT-APPLES	PORT-S_Soil	PORT-M	FOCUS
68	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.123981	SEVILLA	PERLKA_Apple_300	SEVI-APPLES	SEVI-S_Soil	SEVI-M	FOCUS
69	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.108706	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
70	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.358304	CHATEAUDUN	PERLKA_Apple_500	CHAT-APPLES	CHAT-S_Soil	CHAT-M	FOCUS
71	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	72.539544	HAMBURG	PERLKA_Apple_500	HAMB-APPLES	HAMB-S_Soil	HAMB-M	No
72	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	178.290595	JOKIOINEN	PERLKA_Apple_500	JOKI-APPLES	JOKI-S_Soil	JOKI-M	No
73	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	2.488344	KREMSMUENSTER	PERLKA_Apple_500	KREM-APPLES	KREM-S_Soil	KREM-M	No
74	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	22.52629	OKEHAMPTON	PERLKA_Apple_500	OKEH-APPLES	OKEH-S_Soil	OKEH-M	No
75	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	17.394956	PIACENZA	PERLKA_Apple_500	PIAC-APPLES	PIAC-S_Soil	PIAC-M	FOCUS
76	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	28.026104	PORTO	PERLKA_Apple_500	PORT-APPLES	PORT-S_Soil	PORT-M	FOCUS
77	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.285735	SEVILLA	PERLKA_Apple_500	SEVI-APPLES	SEVI-S_Soil	SEVI-M	FOCUS
78	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.355204	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
79	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.230349	CHATEAUDUN	PERLKA_Apple_700	CHAT-APPLES	CHAT-S_Soil	CHAT-M	FOCUS
80	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	66.768905	HAMBURG	PERLKA_Apple_700	HAMB-APPLES	HAMB-S_Soil	HAMB-M	No
81	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	118.58196	JOKIOINEN	PERLKA_Apple_700	JOKI-APPLES	JOKI-S_Soil	JOKI-M	No
82	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	2.200805	KREMSMUENSTER	PERLKA_Apple_700	KREM-APPLES	KREM-S_Soil	KREM-M	No
83	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	22.626217	OKEHAMPTON	PERLKA_Apple_700	OKEH-APPLES	OKEH-S_Soil	OKEH-M	No
84	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	16.854828	PIACENZA	PERLKA_Apple_700	PIAC-APPLES	PIAC-S_Soil	PIAC-M	FOCUS
85	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	26.793526	PORTO	PERLKA_Apple_700	PORT-APPLES	PORT-S_Soil	PORT-M	FOCUS
86	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.289304	SEVILLA	PERLKA_Apple_700	SEVI-APPLES	SEVI-S_Soil	SEVI-M	FOCUS
87	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.25365	THIVA	PERLKA_Apple_700	THIV-APPLES	THIV-S_Soil	THIV-M	FOCUS