Fraunhofer IME

Study Report

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

Simulations in cabbage and potatoes

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GLP-compliance

This study "*Predicted Environmental Concentrations in Groundwater of Cyanamide and Calcium cyanamide after fertilization with PERLKA® using FOCUSPEARL- Simulations in cabbage and potatoes*" 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 study does not describe an experimental study, so 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 2, 2018

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Contents **page**

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

2.1 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

2.2 Crop scenarios

For the simulations a single variation (continuous cropping of cabbage or potatoes) 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 0.506 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.

<u>Cyanamide</u>

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. 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 0.766 days was used. The value represents the geometric mean of all experimental data after normalisation to 20 °C but without soil moisture normalisation [see appendix A].

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: 0.546 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 emergence to guarantee that the application is done before sowing
Application mode:	annual application
Application rate:	500 kg/ha (cabbage), 400 kg/ha (potatoes)
Incorporation depth:	15 cm
Plant uptake factor:	0.0 (worst case)

<u>Cyanamide</u>

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: 0.766 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. According to the results no concentrations above 0.1 µg/L in the groundwater is expected for both application pattern.

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

Computer model	FOCUS PEARL	
Scenario	Cabbage, 500 kg/ha, 15 cm uniform incorp.	
Location	80^{th} percentile of concentration in leachate (µg Ca CN2/L)	80^{th} percentile of concentration in leachate (µg cyanamide/L)
CHATEAUDUN	0	0
HAMBURG	0	0.000001
JOKIOINEN	0	0.000031
KREMSMUENSTER	0	0.000079
PORTO	0	0.08148
SEVILLA	0	0
THIVA	0	0

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

Computer model	FOCUS PEARL	
Scenario	Potatoes, 400 kg/ha,15 cm uniform incorp.	
Location	80^{th} percentile of concentration in leachate (µg Ca CN2/L	80^{th} percentile of concentration in leachate (µg cyanamide/L)
CHATEAUDUN	0	0
HAMBURG	0	0.000002
JOKIOINEN	0	0.00004
KREMSMUENSTER	0	0.000104
OKEHAMPTON	0	0.001687
PIACENZA	0	0.00006
PORTO	0	0.001587
SEVILLA	0	0.001058
THIVA	0	0.00001

5. Conclusion

As worst cases, the two highest application rates of 500 kg/ha Perlka in cabbage and 400 kg/ha Perlka in potatoes were used to calculate the concentration of calcium cyanamide as well as of the metabolite cyanamide in the leachate; all nine locations (see table 1) were covered by these two types of crops. 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, as reflected by noticeable yet very low concentrations (
Table 2, **Fehler! Verweisquelle konnte nicht gefunden werden.**).

The results show that for both crops (application rates) the 80th percentile of the concentration in the leachate is well below 0.1 µg cyanamide/L in all FOCUS scenarios, and thus below the 0.1 µg/L threshold for pesticides as laid down in Council Directive 98/83/EC – Part B (chemical parameters).

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

7. Appendix A: Moisture correction

Laboratory degradation are undertaken at various moisture contents often between of 40-50% MWHC. Additional data provided in study reports may include the actual moisture content of the soil during the study as volumetric (% volume/volume), or as gravimetric (% mass/mass). Other studies may define the reference soil moisture in terms of; % field capacity (FC), or as matric potential values such as pF, kPa or Bar. According to FOCUS (2000) a special procedure called “normalisation” has to be performed before an average value can be calculated.

For the normalisation following equation is used:

$$DT50_{pF2} = DT50_{exp} \cdot \left(\frac{\Theta_{exp}}{\Theta_{pF2}} \right)^{0.7}$$

$DT50_{pf2}$: DT50 value at moisture content pF2 (normalised condition)

$DT50_{exp}$: DT50 value at experimental conditions

Θ_{exp}: experimental soil moisture

Θ_{pF2}: normalised soil moisture (pF 2)

In the following table the resulting normalised values are presented for the transformation of Ca CN2 to cyanamide:

Table A1: Soil moisture normalisation of DT50 values of Ca CN2 to reference conditions (pF 2)

Soil	Soil type (USDA)	Moisture at pF2 (%)*	Moisture in the experiment (%)	normalisation factor	DT50 (at exp. soil moisture) in days	Dt50 at pF 2 in days
Refesol 01-A	Loamy sand	12	10	0.880	0.585	0.515
Refesol 01-A	Loamy sand	12	5	0.542	0.958	0.519
Refesol 02-A	Silt loam	26	21	0.861	0.463	0.399
Refesol 02-A	Silt loam	26	10.4	0.527	0.867	0.457
Refesol 01-A	Loamy sand	12	10	0.880	0.6	0.528
Refesol 01-A	Loamy sand	12	5	0.542	1.21	0.656
				Geometric mean	0.546	**0.506**

* These are default values taken from FOCUS (2000)

For cyanamide no soil moisture normalisation was done since according to the experimental results the degradation of cyanamide does not increase with soil moisture (see the following table). Consequently, the soil moisture correction in the model FOCUS PEARL model is not suitable and the moisture correction was switched off in the simulation. For the modelling a half-life of 0.766 days was used. The value represents the geometric mean of all experimental data after normalisation to 20 °C but without soil moisture normalisation.

Studies on degradation (hydrolysis) of Ca CN2 to cyanamide

Table A1: DT50 values of cyanamide under different conditions

Study	Soil	Temperature (°C)e	exp. soil moisture	DT50 after normalisation to 20 °C (days)
Güthner	Refesol 01-A	12	10%	1.171
	Refesol 01-A	12	5%	0.692
Weinfurtner	Refesol 02-A	12	21%	0.506
	Refesol 02-A,	12	10.4%	0.420
Weinfurtner.	Refesol 01-A	20	10%	0.820
	Refesol 01-A	20	5%	0.770
	Sandy Loam (Ashland, USA)	20		0.700
	Loamy sand (SP 257)	20		0.960
	Loamy sand (SP 357)	20		1.240
	Geometric mean (only temperature normalisation)			**0.766**

8. Appendix B: PEARL FOCUS Summary Output file

RUN_ID	RESULT_TEXT	SUBSTANCE	PRLKA	CN2	LOCATION	APPLICATION_SCHEME	SOIL_TYPE	METEO_STATION	IRRIGATION_SCHEME
2	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0	CHATEAUDUN	PERLKA_Cabbage	CHAT-CABBAGE	CHAT-S_Soil	CHAT-M
3	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.000001	HAMBURG	PERLKA_Cabbage	HAMB-CABBAGE	HAMB-S_Soil	HAMB-M
4	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.000031	JOKIOINEN	PERLKA_Cabbage	JOKI-CABBAGE	JOKI-S_Soil	JOKI-M
5	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.000079	KREMSMUENSTER	PERLKA_Cabbage	KREM-CABBAGE	KREM-S_Soil	KREM-M
6	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.07922	PORTO	PERLKA_Cabbage	PORT-CABBAGE	PORT-S_Soil	PORT-M
7	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0	SEVILLA	PERLKA_Cabbage	SEVI-CABBAGE	SEVI-S_Soil	SEVI-M
8	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0	THIVA	PERLKA_Cabbage	THIV-CABBAGE	THIV-S_Soil	THIV-M

16	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0	CHATEAUDUN	PERLKA_Potatoes	CHAT-SPOTATOES	CHAT-S_Soil	CHAT-M
17	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.000002	HAMBURG	PERLKA_Potatoes	HAMB-SPOTATOES	HAMB-S_Soil	HAMB-M
18	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.00004	JOKIOINEN	PERLKA_Potatoes	JOKI-SPOTATOES	JOKI-S_Soil	JOKI-M
19	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.000104	KREMSMUENSTER	PERLKA_Potatoes	KREM-SPOTATOES	KREM-S_Soil	KREM-M
20	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.001687	OKEHAMPTON	PERLKA_Potatoes	OKEH-SPOTATOES	OKEH-S_Soil	OKEH-M
21	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.00006	PIACENZA	PERLKA_Potatoes	PIAC-SPOTATOES	PIAC-S_Soil	PIAC-M
22	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.001587	PORTO	PERLKA_Potatoes	PORT-SPOTATOES	PORT-S_Soil	PORT-M
23	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.001058	SEVILLA	PERLKA_Potatoes	SEVI-SPOTATOES	SEVI-S_Soil	SEVI-M

24	Concentration closest to the 80th percentile (ug/L)	PRLKA	0	0.00001	THIVA	PERLKA_Potatoes	THIV-SPOTATOES	THIV-S_Soil	THIV-M