

Study Report

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

Simulations in cabbage, potatoes and sugar beet

Sponsor

AlzChem Trostberg GmbH Dr.-Albert-Frank-Str. 32 83308 Trostberg Germany

Institute

Fraunhofer Institute for Molecular Biology and Applied Ecology IME Auf dem Aberg 1 57392 Schmallenberg Germany

Head of Applied Ecology

Prof. Dr. Christoph Schäfers

Author Dr. Michael Klein Dr. Judith Klein

May 21, 2018



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Statement of-compliance

This study "Predicted Environmental Concentrations in Groundwater of Cyanamide and Calcium cyanamide after fertilization with PERLKA[®] using FOCUSPEARL- Simulations in cabbage, potatoes and sugar beets" 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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May 21, 2019 Date

Dr. Michael Klein Exposure Modelling Fraunhofer Institute IME Auf dem Aberg 1 57392 Schmallenberg

Tel +49 2972 302 256 Fax +49 2972 302 319 judith.klein@ime.fraunhofer.de



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1. <u>Simulation model</u>

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. <u>Scenarios</u>

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.



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Figure 1: Locations of the nine FOCUS groundwater scenarios

| 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* |
| * [*] • • • • • • | | | | |

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

*irrigation



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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].



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3. <u>Physico-chemical and Degradation Data</u>

PERLKA

The maximum concentration of calcium cyanamide in PERLKA is about 45%. This was considered in the simulation by assuming a formation fraction of 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 2.51 days (Klein 2019). 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 (Klein 2019) 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 transformation in soil.

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). That should guarantee that the granules remain at the applied location in soil and are only transformed to cyanamide without leaching to deeper soil layers.



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Cyanamide

According to experimental data cyanamide is further transformed to urea (Vilsmeier et Amberger 1978). 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 models FOCUS MACRO and PRZM are 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.



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Calcium cyanamide

| Molecular Mass: | 80.11 g/mol |
|---------------------------------|--|
| Water solubility: | 800,000 mg/L at 20 °C (value of cyanamide) |
| Adsorption | 172400 L/kg (Koc) (artificial to reflect immobility of granulated |
| | PERIKA) |
| | 100 000 L/kg (Kom) |
| Freundlich Exponent. | 1 (worst case) |
| Diffusion coefficient in water: | 4.3 10-5 m ² d-1 (FOCUS default) |
| Diffusion coefficient in air: | 0.43 m ² 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 emergence to guarantee that the application is done |
| | before sowing |
| Application mode: | annual application |
| Application pattern: | 500 kg PERLKA/ha in cabbage incorporated over 15 cm |
| | 400 kg PERLKA/ha in potatoes incorporated over 15 cm |
| | 200 kg PERLKA/ha in sugar beet deep placement at 10 cm |
| Plant uptake factor: | 0.0 (worst case) |



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Cyanamide

| Molecular Mass: | 42.04 g/mol | | | | | |
|---------------------------------|---|--|--|--|--|--|
| Vapour pressure: | 0.51 Pa (EFSA 2010) | | | | | |
| | Water solubility: 800 000 mg/L at 20 °C | | | | | |
| Adsorption | 4 L/kg (Koc, EFSA 2010) | | | | | |
| | 2.32 L/kg (Kom, calc. using Koc) | | | | | |
| Freundlich Exponent. | 1 (worst case) | | | | | |
| Diffusion coefficient in water: | 4.3 10-5 m ² 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, 2000) | | | | | |
| | Moisture correction: | | | | | |
| | Moisture exponent: 0 (no correction) | | | | | |
| | Reference soil moisture: not applicable | | | | | |
| Formation fraction: | 45% | | | | | |
| Plant uptake factor: | 0.0 (worst case) | | | | | |



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4. <u>Results</u>

The global maximum concentrations are summarised in the following tables. According to the results the maximum concentration was found to be 0.1 μ g/L cyanamide (application in cabbage, scenario Porto). All other simulations were well below the trigger of 0.1 μ g/L

| Computer model | FOCUS PEARL | | | | | |
|----------------|--|--|--|--|--|--|
| Scenario | m uniform incorp. | | | | | |
| Location | 80 th percentile of concentration in leachate | 80 th percentile of concentration in leachate | | | | |
| | (µg CaCN₂/L) | (µg cyanamide/L) | | | | |
| CHATEAUDUN | 0 | 0 | | | | |
| HAMBURG | 0 | 0.00002 | | | | |
| JOKIOINEN | 0 | 0.000066 | | | | |
| KREMSMUENSTER | 0 | 0.000065 | | | | |
| PORTO | 0 | 0.102289 | | | | |
| SEVILLA | 0 | 0 | | | | |
| THIVA | 0 | 0 | | | | |

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



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| Computer model | FOCUS PEARL | | | | |
|----------------|--|--|--|--|--|
| Scenario | Potatoes, 400 kg/ha,15 cm uniform incorp. | | | | |
| Location | 80 th percentile of concentration in leachate | 80 th percentile of concentration in leachate (μg cyanamide/L) | | | |
| | (μg CaCN₂/L | | | | |
| CHATEAUDUN | 0 | 0 | | | |
| HAMBURG | 0 | 0.000002 | | | |
| JOKIOINEN | 0 | 0.000111 | | | |
| KREMSMUENSTER | 0 | 0.000099 | | | |
| OKEHAMPTON | 0 | 0.002186 | | | |
| PIACENZA | 0 | 0.000064 | | | |
| PORTO | 0 | 0.002696 | | | |
| SEVILLA | | | | | |
| | 0 | 0.00124 | | | |
| THIVA | 0 | 0.00008 | | | |

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



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| Computer model | FOCUS PEARL | | | | |
|----------------|--|--|--|--|--|
| Scenario | Sugar beet, 200 kg PERLKA/ha, deep placement at 10 | | | | |
| Location | 80 th percentile of concentration in leachate | 80 th percentile of concentration in leachate | | | |
| | (µg CaCN2/L | (µg cyanamide/L) | | | |
| CHATEAUDUN | 0 | 0 | | | |
| HAMBURG | 0 | 0.000002 | | | |
| JOKIOINEN | 0 | 0.000137 | | | |
| KREMSMUENSTER | 0 | 0.000082 | | | |
| OKEHAMPTON | 0 | 0.000197 | | | |
| PIACENZA | 0 | 0.001698 | | | |
| PORTO | 0 | 0.001503 | | | |
| SEVILLA | | | | | |
| | 0 | 0.00036 | | | |
| THIVA | 0 | 0 | | | |

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



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5. <u>Conclusion</u>

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 172400 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, Table 3).

The results show that for the potato application (400 kg/ha PERLKA) the 80th percentile of the concentration in the leachate is well below 0.1 μ g cyanamide/L in all FOCUS scenarios and thus below the 0.1 μ g/L threshold for pesticides as laid down in Council Directive 98/83/EC – Part B (chemical parameters).

The results in cabbage (500 kg/ha PERLKA) reaches 0.1 in a single scenario (Porto) where for the other 6 scenarios the concentrations were below practically 0 (below 0.0001 μ g/L).



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6. <u>References</u>

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7. Appendix: PEARL FOCUS Summary Output file

| RUN_ | | SUBSTA | PRLK | | | APPLICATION_SC | CROP_CALEN | SOIL_TYP | METEO_STA |
|------|-----------------------------------|--------|------|--------|-----------|-----------------|--------------|----------|-----------|
| ID | RESULT_TEXT | NCE | Α | CN2 | LOCATION | HEME | DAR | E | TION |
| | Concentration closest to the 80th | | | | CHATEAUDU | | CHAT- | CHAT- | |
| 2 | percentile (ug/L) | PRLKA | 0 | 0 | Ν | PERLKA_Cabbage | CABBAGE | S_Soil | CHAT-M |
| | Concentration closest to the 80th | | | 0.0000 | | | HAMB- | HAMB- | |
| 3 | percentile (ug/L) | PRLKA | 0 | 02 | HAMBURG | PERLKA_Cabbage | CABBAGE | S_Soil | HAMB-M |
| | Concentration closest to the 80th | | | 0.0000 | | | | JOKI- | |
| 4 | percentile (ug/L) | PRLKA | 0 | 66 | JOKIOINEN | PERLKA_Cabbage | JOKI-CABBAGE | S_Soil | JOKI-M |
| | Concentration closest to the 80th | | | 0.0000 | KREMSMUEN | | KREM- | KREM- | |
| 5 | percentile (ug/L) | PRLKA | 0 | 65 | STER | PERLKA_Cabbage | CABBAGE | S_Soil | KREM-M |
| | Concentration closest to the 80th | | | 0.1022 | | | PORT- | PORT- | |
| 6 | percentile (ug/L) | PRLKA | 0 | 89 | PORTO | PERLKA_Cabbage | CABBAGE | S_Soil | PORT-M |
| | Concentration closest to the 80th | | | | | | | SEVI- | |
| 7 | percentile (ug/L) | PRLKA | 0 | 0 | SEVILLA | PERLKA_Cabbage | SEVI-CABBAGE | S_Soil | SEVI-M |
| | Concentration closest to the 80th | | | | | | THIV- | THIV- | |
| 8 | percentile (ug/L) | PRLKA | 0 | 0 | THIVA | PERLKA_Cabbage | CABBAGE | S_Soil | THIV-M |
| | Concentration closest to the 80th | | | | CHATEAUDU | | CHAT- | CHAT- | |
| 16 | percentile (ug/L) | PRLKA | 0 | 0 | Ν | PERLKA_Potatoes | SPOTATOES | S_Soil | CHAT-M |
| | Concentration closest to the 80th | | | 0.0000 | | | HAMB- | HAMB- | |
| 17 | percentile (ug/L) | PRLKA | 0 | 02 | HAMBURG | PERLKA_Potatoes | SPOTATOES | S_Soil | HAMB-M |
| | Concentration closest to the 80th | | | 0.0001 | | | JOKI- | JOKI- | |
| 18 | percentile (ug/L) | PRLKA | 0 | 11 | JOKIOINEN | PERLKA_Potatoes | SPOTATOES | S_Soil | JOKI-M |



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| RUN | | SUBSTA | PRLK | | | APPLICATION SC | CROP CALEN | SOIL TYP | METEO STA |
|-----|-----------------------------------|--------|------|--------|-----------|-----------------|------------|----------|-----------|
| ID | RESULT_TEXT | NCE | Α | CN2 | LOCATION | HEME | DAR | E | TION |
| | Concentration closest to the 80th | | | 0.0000 | KREMSMUEN | | KREM- | KREM- | |
| 19 | percentile (ug/L) | PRLKA | 0 | 99 | STER | PERLKA_Potatoes | SPOTATOES | S_Soil | KREM-M |
| | Concentration closest to the 80th | | | 0.0021 | OKEHAMPTO | | OKEH- | OKEH- | |
| 20 | percentile (ug/L) | PRLKA | 0 | 86 | Ν | PERLKA_Potatoes | SPOTATOES | S_Soil | OKEH-M |
| | Concentration closest to the 80th | | | 0.0000 | | | PIAC- | PIAC- | |
| 21 | percentile (ug/L) | PRLKA | 0 | 64 | PIACENZA | PERLKA_Potatoes | SPOTATOES | S_Soil | PIAC-M |
| | Concentration closest to the 80th | | | 0.0026 | | | PORT- | PORT- | |
| 22 | percentile (ug/L) | PRLKA | 0 | 96 | PORTO | PERLKA_Potatoes | SPOTATOES | S_Soil | PORT-M |
| | Concentration closest to the 80th | | | 0.0012 | | | SEVI- | SEVI- | |
| 23 | percentile (ug/L) | PRLKA | 0 | 4 | SEVILLA | PERLKA_Potatoes | SPOTATOES | S_Soil | SEVI-M |
| | Concentration closest to the 80th | | | 0.0000 | | | THIV- | THIV- | |
| 24 | percentile (ug/L) | PRLKA | 0 | 08 | THIVA | PERLKA_Potatoes | SPOTATOES | S_Soil | THIV-M |
| | Concentration closest to the 80th | | | | CHATEAUDU | PERLKA_Sugarbee | CHAT- | CHAT- | |
| 25 | percentile (ug/L) | PRLKA | 0 | 0 | N | t | SUGARBEET | S_Soil | CHAT-M |
| | Concentration closest to the 80th | | | 0.0000 | | PERLKA_Sugarbee | HAMB- | HAMB- | |
| 26 | percentile (ug/L) | PRLKA | 0 | 02 | HAMBURG | t | SUGARBEET | S_Soil | HAMB-M |
| | Concentration closest to the 80th | | | 0.0001 | | PERLKA_Sugarbee | JOKI- | JOKI- | |
| 27 | percentile (ug/L) | PRLKA | 0 | 37 | JOKIOINEN | t | SUGARBEET | S_Soil | JOKI-M |
| | Concentration closest to the 80th | | | 0.0000 | KREMSMUEN | PERLKA_Sugarbee | KREM- | KREM- | |
| 28 | percentile (ug/L) | PRLKA | 0 | 82 | STER | t | SUGARBEET | S_Soil | KREM-M |
| | Concentration closest to the 80th | | | 0.0001 | OKEHAMPTO | PERLKA_Sugarbee | OKEH- | OKEH- | |
| 29 | percentile (ug/L) | PRLKA | 0 | 97 | Ν | t | SUGARBEET | S_Soil | OKEH-M |



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| RUN | | SUBSTA | PRLK | | | APPLICATION SC | CROP CALEN | SOIL TYP | METEO STA |
|-----|-----------------------------------|--------|------|--------|----------|-----------------|------------|----------|-----------|
| ID | RESULT_TEXT | NCE | Α | CN2 | LOCATION | HEME | DAR | E | TION |
| | Concentration closest to the 80th | | | 0.0016 | | PERLKA_Sugarbee | PIAC- | PIAC- | |
| 30 | percentile (ug/L) | PRLKA | 0 | 98 | PIACENZA | t | SUGARBEET | S_Soil | PIAC-M |
| | Concentration closest to the 80th | | | 0.0015 | | PERLKA_Sugarbee | PORT- | PORT- | |
| 31 | percentile (ug/L) | PRLKA | 0 | 03 | PORTO | t | SUGARBEET | S_Soil | PORT-M |
| | Concentration closest to the 80th | | | 0.0003 | | PERLKA_Sugarbee | SEVI- | SEVI- | |
| 32 | percentile (ug/L) | PRLKA | 0 | 6 | SEVILLA | t | SUGARBEET | S_Soil | SEVI-M |
| | Concentration closest to the 80th | | | | | PERLKA_Sugarbee | THIV- | THIV- | |
| 33 | percentile (ug/L) | PRLKA | 0 | 0 | THIVA | t | SUGARBEET | S_Soil | THIV-M |