**Study Report**

Predicted Environmental Concentrations in Groundwater

of Cyanamide and Calcium cyanamide after fertilization with PERLKA® using FOCUSPEARL

*Simulations in apples*

**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

October 1, 2019

This page was intentionally left blank for statements of the sponsor or submitter.

Statement of 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 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 1, 2019\_\_\_\_\_\_

Dr. Judith Klein Date

Modelling and Statistics

Fraunhofer Institute IME

Auf dem Aberg 1

57392 Schmallenberg

Tel +49 2972 302 256

Fax +49 2972 302 319

judith.klein@ime.fraunhofer.de

**Contents page**

[GLP-compliance 3](#_Toc20900557)

[1. Simulation model 5](#_Toc20900558)

[2. Scenarios 5](#_Toc20900559)

[Soil and climate scenarios of the FOCUS simulation models 5](#_Toc20900560)

[Crop scenarios 7](#_Toc20900561)

[3. Physico-chemical and Degradation Data 8](#_Toc20900562)

[4. Results 12](#_Toc20900563)

[5. Conclusion 14](#_Toc20900564)

[6. References 14](#_Toc20900565)

[7. Appendix A: Moisture correction 15](#_Toc20900566)

[8. Appendix B: PEARL FOCUS Summary Output file 18](#_Toc20900567)

[ Apple, 300 kg/ha at surface 18](#_Toc20900568)

[ Apple, 500 kg/ ha, uniform incorp. 10 cm 19](#_Toc20900569)

[ Apple, 700 kg/ha at surface 20](#_Toc20900570)

# 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).

# 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]** |
| --- | --- | --- | --- | --- |
| audun | silty clay loam | 2.4 | 11.3 | 648 + I\* |
| 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 cabbage or potatoes) over a period of 26 years is taken into account according to the recommendations of FOCUS [FOCUS 2000].

# 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.

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. 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 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: 0.766 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)

# 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 Jokionen. 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 Jokioninen 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 | 80th percentile of concentration in leachate |
| (µg Ca CN2/L) | (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 | 80th percentile of concentration in leachate |
| (µg Ca CN2/L) | (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 | 80th percentile of concentration in leachate |
| (µg Ca CN2/L) | (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 |

# 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).

# 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

# 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:



DT50pf2: DT50 value at moisture content pF2 (normalised condition)

DT50exp: DT50 value at experimental conditions

Θexp: experimental soil moisture

ΘpF2: 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** |

# Appendix B: 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 percentile (ug/L) | PRLKA | 0 | 0.648269 | OKEHAMPTON | PERLKA\_Apple\_700 | OKEH-APPLES | OKEH-S\_Soil | OKEH-M | No |
| 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 |