Supporting Information

Impacts of (nano)formulations on the fate of an insecticide in soil and consequences for environmental exposure assessment

Melanie Kah*, Anne-Kathrin Weniger, Thilo Hofmann*

University of Vienna, Department of Environmental Geosciences and Environmental Science Research Network, Althanstrasse 14, UZA2, 1090 Vienna, Austria
melanie.kah@univie.ac.at, thilo.hofmann@univie.ac.at
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Table S1. Approximate composition and key properties of the four formulations of bifenthrin considered in this study, as presented in the material safety data sheets or provided by the supplier for the nanoformulations (indicated with *). NFA, NFB and NFC are the three polymer-based nanoformulations, CF is the commercial formulation (all % are on a weight base)

	NFA	NFB	NFC	CF
Bifenthrin loading (%)*	19.6	21.8	19.4	17.2
Water (%)	40-70	40-70	40-70	-
Polymer nanoparticles (%)[a]	3-7	3-7	3-7	-
Ionic wetting agent (%)	-	1-5	-	-
Sulfonate dispersant (%)	1-5	-	1-5	-
Non-ionic dispersant (%)	1-5	-	-	-
Polymeric ionic dispersant (%)	-	1-5	-	-
Propane-1,2-diol (%)	5-10	5-10	5-10	5-10
Other inert ingredients (%)	1-30	1-30	1-30	72-77
Viscosity (cP) *	180	186	14.3	22.7
Density (g/mL) *	1.088	1.085	1.079	1.052
pH value*	4.2	5.4	5.2	6.8
Size in CIPAC D standard water[b] (nm)*	526.6	343.3	427.0	-

[a] NFA and NFB contain polymer nanoparticles derived from a 75:25 copolymer consisting of poly(methacrylic acid-*ran*-butylmethacrylate). NFC contains polymer nanoparticles derived from a 90:10 copolymer consisting of poly(methacrylic acid-*ran*-ethylacrylate).[b]by dynamic light scattering; CIPAC: Collaborative International Pesticides Analytical Council

Soil properties and characterisation

Table S2. Main properties of the two soils studied.

Texture (USDA)	Clay %	Sand %	Organic carbon (%)	pH	CEC[a] (meq/100 g)	MWHC[b] (g/100 g)
Loam	26.2 ± 1.9	33.2 ± 1.8	2.21 ± 0.46	7.2 ± 0.2	32.2 ± 4.4	43.8 ± 1.3
Sand	2.8 ± 1.0	86.7 ± 1.3	0.66 ± 0.10	5.2 ± 0.3	4.1 ± 0.6	30.8 ± 1.9

[a]Cation exchange capacity [b]Maximum water holding capacity

Methods for soil characterisation

The soil organic carbon content was calculated as the difference in carbon content (determined by heat-conductivity detector after combustion at 950°C) before and after combustion of the soil samples at 425 °C. The maximum water holding capacity corresponds to the residual water remaining in saturated soil samples, left to drain for 2 h onto a saturated sand bath [1]. Soil pH was measured in soil suspensions made of 10 g of soil in 25 mL 0.01 M $CaCl_2$ background solution.

Soil microbial bioactivity was evaluated during soil incubation by regularly measuring the dehydrogenase activity, an enzyme that is only active in living organisms [2, 3]. Soil samples (2.5 - 5.0 g) were incubated at 30 °C with 5 mL of colourless TTC solution (0.5 % by weight, 2,3,5-triphenyl2H-tetrazolium chloride, 98 %, Avocado, Research Chemicals Limited) in 0.1 M Tris buffer adjusted to pH 7.6 with HCl [tris(hydroxymethyl)aminomethane, general purpose grade, Merck Science]. TTC is reduced by dehydrogenase enzymes to red water-insoluble triphenylformazane (TPF), which was extracted with 25 mL of methanol after 24 h of incubation. The samples were shaken for 1 h (side-to-side shaker, 150 rpm) and centrifuged at 2500 g for 10 min. The intensity of the red colour of the supernatant was measured by spectrophotometry at 485 nm and converted to bioactivity (mg TPF/kg) based on a set of TPF standards (1,3,5-triphenylformazane, Sigma-Aldrich Co. Ltd.).

Attempts to measure the release rate

None of the approaches tested and briefly described below, appeared suitable to directly measure the release rates of bifenthrin from the nanocarriers. Bifenthrin is a compound particularly difficult to handle, due to its physico-chemical characteristics (i.e. very high sorption, relatively low volatility).

Filtration

Anodisc, alumina matrix, 0.02 µm pore diameter, 13 mm diameter (Whatman, UK). The filtration of an aqueous solution of pure bifenthrin (0.8 µg/L) resulted in large losses (73-74 %), much likely due to sorption to the filter.

In-tube extraction coupled to GC-MS (ITEX)

Due to the relatively low volatility of bifenthrin, enrichment on the trap (filled with polydimethylsiloxane) was low, leading to high limits of quantification of bifenthrin in aqueous solution. Heating the samples to increase partitioning into the gas phase was considered inadequate due to the possible impact of temperature on release rates.

Dialysis

A dialysis tube was filled with 50 mL bifenthrin aqueous solution (0.5 mg/L), placed into a beaker filled with ultrapure water (450 mL), and stirred for 24 h. Samples from the outside of the tube were taken regularly, extracted with hexane and analysed by GC-MS (following the methods described in the material and method section). Bifenthrin concentrations outside of the dialysis tube remain below the limit of detection, most likely due to the sorption of bifenthrin to the dialysis tube.

Passive sampling with solid phase microextraction (SPME)-fibre

Three SPME-fibres (polydimethylsiloxane, 1.5 cm long) were added to 15 mL sample of aqueous solution of bifenthrin (15 mg/L in 0.01 M $CaCl_2$). After 2 h shaking, the fibres were removed, dried and extracted with 100 µL hexane for 1 h. Extracts were analysed by GC-MS (see description in the material and method section). Coefficients of variations for triplicates ranged between 2 and 60 %, and tended to increase with concentration, preventing the use of the technique to quantify aqueous concentration of release bifenthrin.

Centrifugation

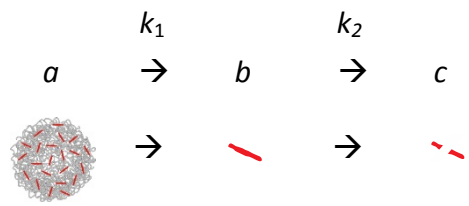
The difference in density between polymer particles and water is generally very small (i.e., between 0.051 and 0.078 g/mL) and a complete sedimentation of the polymer particles using classical centrifuge requires excessive time. For instance, particles with a diameter of 200 nm would take between 12 and 19 hours of continuous centrifugation at 2000 *g* to travel the 10 cm length of the centrifugation tubes.

Ultracentrifugation

The tubes used for ultracentrifugation are made of polypropylene, a material to which bifenthrin sorbs to a great extent [4].

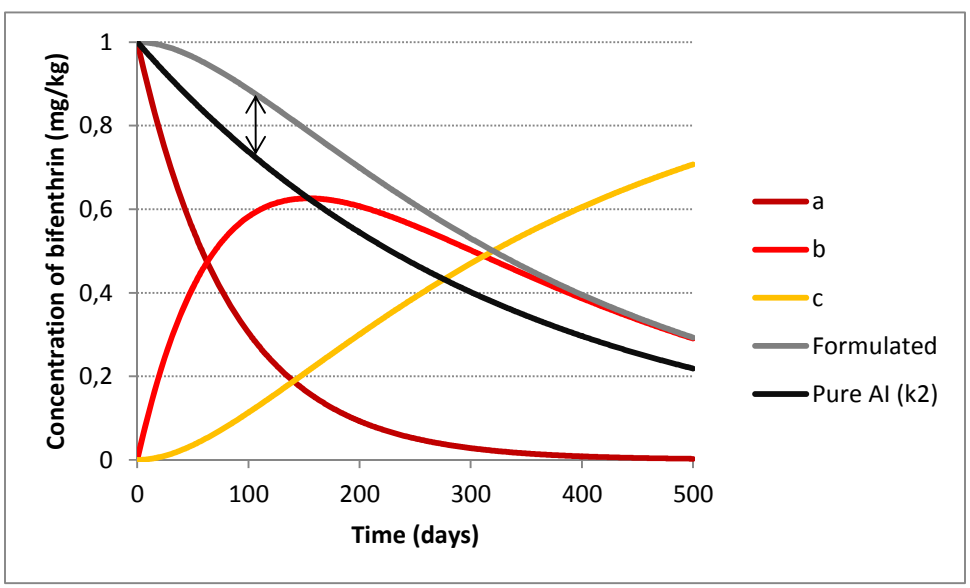
Indirect measurement of release rate

The approach, previously described in Ford et al. [5], consists in considering that only that portion of bifenthrin that was released from the nanocarriers was available for degradation. Hence, the slower degradation observed for the formulated bifenthrin (difference between the black and grey curves on Figure S1) can be ascribed to the release process. Assuming that both release [6] and degradation processes (verified in the present study) follow first order kinetics, the system can be described using a sequential first order model (similar to that describing e.g. radioactive decay,[7]:



where *a* is the concentration of bifenthrin associated with the nanocarriers, *b*, the concentration of bifenthrin released from the nanocarriers, *c*, the concentration of bifenthrin transformed; k_1 is the release rate, and k_2 is the degradation rate of the released bifenthrin.

Figure S1. Evolution of the concentration of bifenthrin associated with the nanocarriers (a), released (b) and transformed (c) over time (k_1 and k_2 are those derived for NFA in the loam).



$$\frac{da}{dt} = -k_1\, a \qquad (1)$$

$$\frac{db}{dt} = k_1\, a - k_2\, b \quad (2)$$

$$\frac{dc}{dt} = k_2\, c \quad (3)$$

In addition, let's assume that at t = 0, all bifenthrin was associated with the nanocarriers ($a = a_0$), and thus, at all time, $a + b + c = a_0$. Integrating equations (1), (2) and (3) gives:

$$a = a_0 e^{-k_1 t} \quad (4)$$

$$b = a_0 \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (5)$$

$$c = a_0(1 + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} + \frac{k_2 e^{-k_1 t}}{k_2 - k_1}) \quad (6)$$

The degradation rate, k_2, was derived from the experiments with the pure bifenthrin (black curves on Figure S1). The release rate, k_1, was derived by fitting the degradation curve generated for the formulated bifenthrin (grey curve in Figure S1) and which represent the evolution of ($a + b$) or ($a_0 - c$), over time. R_{50} values were then calculated from k_1, as the time required for half the bifenthrin to be released from the nanocarriers.

Table S3. Sorption coefficients (Kd, L/kg) of bifenthrin either spiked as nanoformulations (NFA, NFB, NFC), commercial formulation (CF) or pure bifenthrin (AI). Letters illustrate statistical differences within a column (i.e. among formulations for a given type of soil; Sidak's multiple comparisons test).

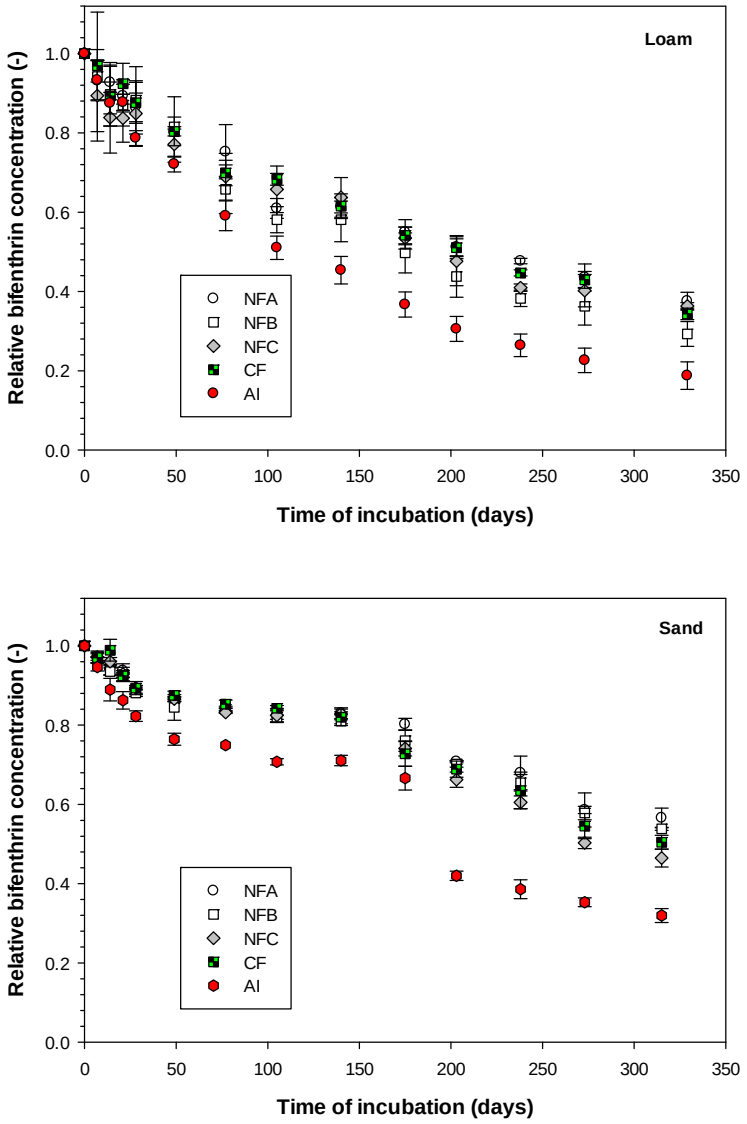
K_{OC} (L/kg) are the coefficients normalized for the soil organic carbon content ± standard deviation (n=3)

	K_d (L/kg)		**K_{OC} (10^3 L/Kg)**	
	Loam	**Sand**	**Loam**	**Sand**
NFA	6613 ± 772 bc	995 ± 123 ab	334 ± 39	149 ± 18
NFB	7395 ± 888 c	636 ± 54 a	373 ± 45	95 ± 8
NFC	4068 ± 522 a	281 ± 48 a	205 ± 26	42 ± 7
CF	5689 ± 808 b	1885 ± 40 b	287 ± 41	281 ± 6
AI	5557 ± 79 b	2692 ± 316 b	281 ± 4	402 ± 47

Note: preliminary kinetics experiments were carried out to determine an adequate time for equilibration. Sorption was measured in triplicates after 7, 24 and 48h equilibration time and following the protocol described in the paper. There was no significant difference between values measured after 24 and 48h ($p > 0.05$). An equilibration time of 24h was thus applied in the following experiments.

Figure S2. Concentration of bifenthrin decreasing over time in two soils, either spiked with nanoformulations (NFA, NFB, NFC), a commercial formulation (CF) or pure bifenthrin (AI).

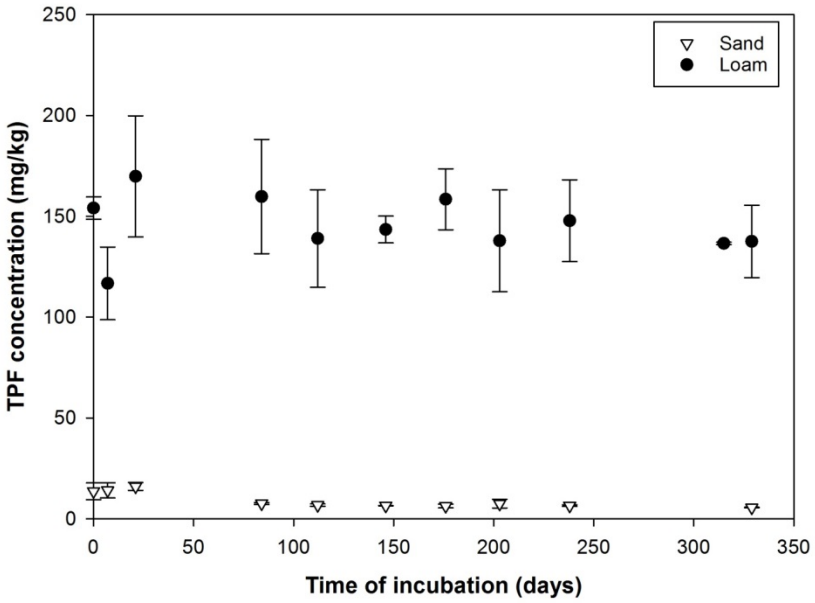
Error bars show the standard deviation of independent triplicates.



Discrepancies between measured and first order kinetics in the sand mainly arise from a slowdown of degradation in the period 77-175 days. The slower degradation is consistent with the decline in the soil microbiological activity observed after 77 days (see Figure S3). Jars containing the samples for the two soils were randomly distributed in the same incubator. Hence, the slowdown of degradation cannot not be attributed to changes in the conditions of incubation. This slower degradation period affected all formulations and should thus have no impact on the comparisons made.

Figure S3. Soil microbial activity over the course of incubation, estimated from concentrations of 2,3,5-triphenyltetrazolium chloride (TPF). Error bars are the standard deviation (n=4).

No significant variations occurred over time for the loam, while for the sand TPF concentrations became smaller at t > 21 days ($p < 0.05$).



Note: microbial activity was regularly evaluated on randomly selected samples undergoing incubation. There was not significant difference in the bioactivity measured in samples spiked with the different bifenthrin formulations and data were thus combined in the figure above.

Predicted concentration in soil: PEC_{soil} and $PEC_{soil\ plateau}$

The concentration of relatively persistent pesticides that are repetitively applied may build-up in soil and reach a plateau. Once the plateau has been reached concentrations fluctuate between a maximum when an application has just been made ($PEC_{soil\ plateau\ infinity}$) and a minimum just before the next application [8]. The plateau may take many years to be reached and the build-up concentrations after 6 consecutive years of application were also calculated ($PEC_{soil\ plateau\ 6\ years}$).
In both soils, all formulations tended to increase persistence of bifenthrin. The longest DT_{50} was observed for NFA, and was used to simulate worst-case scenarios for build-up of bifenthrin in soil. Based on our experimental data, dissipation of residues were considered to follow first order kinetics. Application occurred once per year, leading to $PEC_{initial}$ the first year, at 0.01 and 0.05 kg/ha (corresponding to rates for winter cereals and pome fruits, [9]). We considered a crop interception of 0, a soil bulk density of 1.5 g/cm^3 and soil incorporation of 5 cm.

Table S4. Prediction of PEC_{soil} and $PEC_{soil\ plateau}$

Application once per year at **0.01 kg/ha** (winter cereals)

	Loam			Sand		
	AI	**NF**	**Increase / AI**	**AI**	**NF**	**Increase /AI**
DT_{50} (d)	125	228	-	266	442	-
$PEC_{initial}$ (mg/kg)	0.013	0.013	1	0.013	0.013	1
$PEC_{soil\ plateau\ 6\ years}$	0.015	0.020	1.3	0.022	0.030	1.4
$PEC_{soil\ plateau\ infinity}$	0.015	0.020	1.3	0.022	0.031	1.4

Application once per year at **0.05 kg/ha** (pome fruits)

	Loam			Sand		
	AI	**NF**	**Increase / AI**	**AI**	**NF**	**Increase /AI**
DT_{50} (d)	125	228	-	266	442	-
$PEC_{initial}$ (mg/kg)	0.066	0.066	1	0.066	0.066	1
$PEC_{soil\ plateau\ 6\ years}$	0.077	0.099	1.3	0.108	0.148	1.4
$PEC_{soil\ plateau\ infinity}$	0.077	0.099	1.3	0.109	0.153	1.4

Comments:

- $PEC_{soil\ initial}$ only depends on the application rate and is thus the same for all formulations and soils for a given application scenario.
- Longer DT_{50} lead to larger $PEC_{soil\ plateau}$.
- According to the soil type and differences in the measured DT_{50}, the $PEC_{soil\ plateau}$ for formulated bifenthrin could be a maximum of 1.3-1.4-fold greater than that of the pure AI.

Modelling with PEARL 4.4.4. [10]: Predicted Environmental Concentrations in ground water (PEC_{GW})

Exposure assessment of plant protection products in the EU considers nine groundwater scenarios that collectively represent realistic worst-case scenarios for European agricultural conditions, by combining soil and weather location, long term application schedule and agronomic parameters (detailed description is available in FOCUS [11]). Simulations were undertaken over 20 years for the nine standard scenarios. The average annual concentration of bifenthrin in leachate at 1 m depth was calculated for each year and the 80th percentile recorded. Two crops were considered (winter cereals and apples), application occurred once a year at 0.01 and 0.05 kg/ha respectively [9]. Notes on input parameters: K_{OC} values were converted to K_{OM} using 1.72 conversion factor; Bifenthrin physico-chemical properties were the following: molecular weight: 422.88 g/mole; saturated vapour pressure: $2.4*10^{-5}$ Pa; solubility in water: 0.00376 mg/L. All other parameters were left as default values.

Direct Approach: direct input of the measured fate parameters.

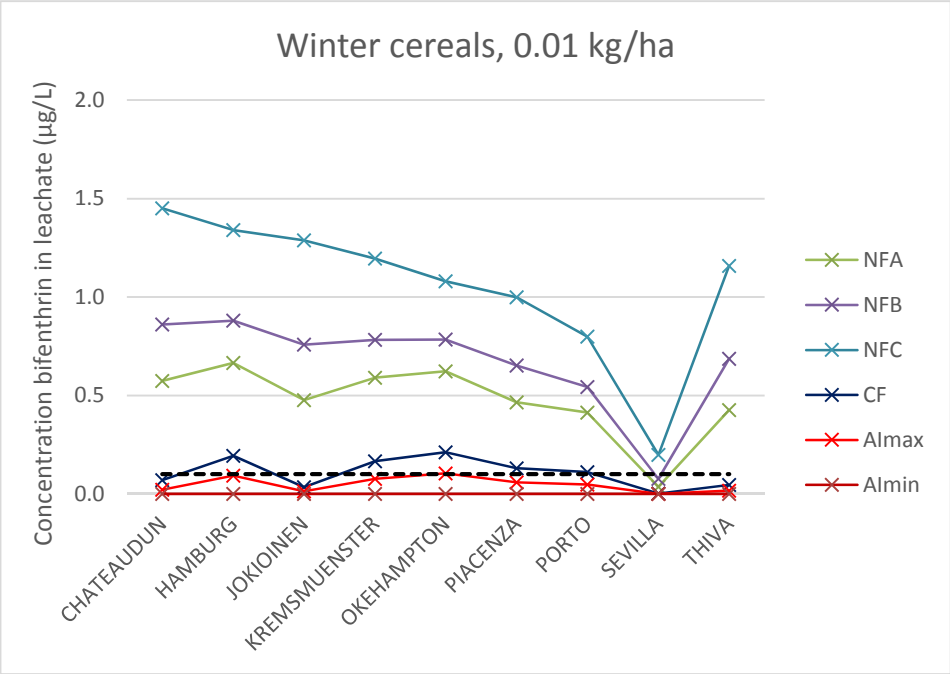
The fate of formulated bifenthrin was simulated by considering the parameters representing worst-case combinations for leaching (i.e. the lowest Kd and longest DT_{50} measured were selected for each formulation). For the pure AI, two cases were simulated: AI_{max} (i.e. lowest Kd and longest DT_{50}) and AI_{min} (i.e. highest Kd and shortest DT_{50}). Input parameters are detailed in Table S4, together with a summary of the model outputs.

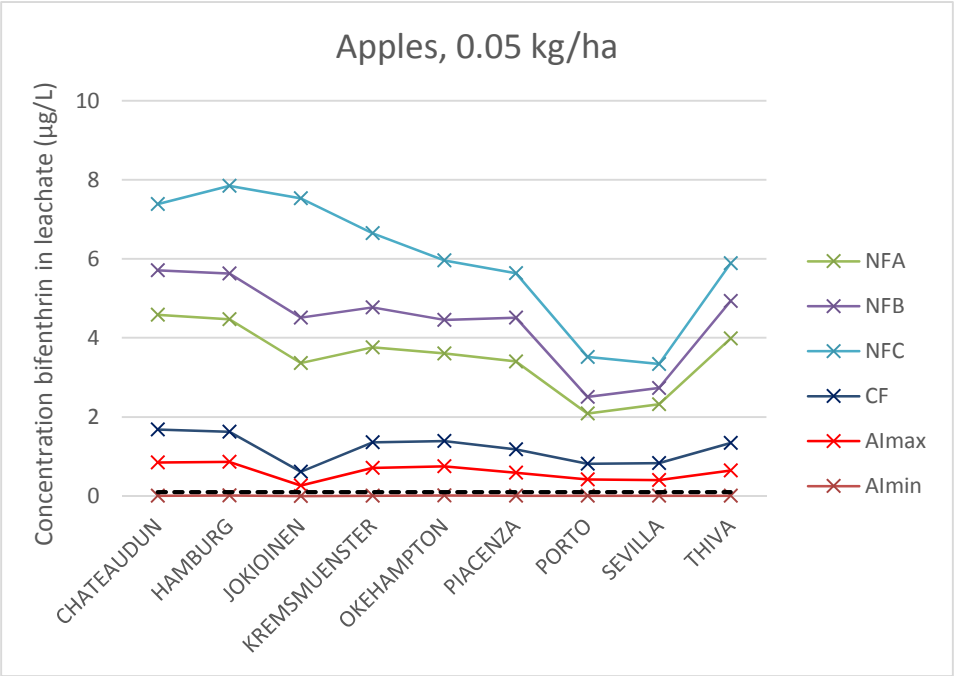
Table S5. Prediction of leaching using measured fate parameters as inputs (Direct Approach)

	Inputs		0.01 kg/ha winter cereals		0.05 kg/ha apples	
	K_{OM}	DT_{50}	Average PEC_{GW} (9 scenarios)	Increase relative to AI_{max}	Average PEC_{GW} (9 scenarios)	Increase relative to AI_{max}
	(L/kg)	(d)	(µg/L)	Min-Max (Average)	(µg/L)	Min-Max (Average)
NFA	86.63	442	0.475	7 - 92 (24)	3.509	5 - 13 (6)
NFB	55.23	382	0.669	7 - 193 (43)	4.418	6 - 17 (8)
NFC	24.42	319	1.057	10 - 505 (91)	5.973	8 - 29 (11)
CF	163.37	370	0.108	2 - 4 (3)	1.204	2 - 2 (2)
AI_{max}	163.37	266	0.048	-	0.611	-
AI_{min}	233.72	125	0.0002	-	0.006	-

Figure S4. Predicted concentration in groundwater using the parameters measured for each formulation (Direct Approach)

80th percentile of the average annual concentration of bifenthrin in leachate at 1 m depth over 20 years simulation for 9 European scenarios with the pesticide fate model PEARL 4.4.4. The dashed line represents the regulatory threshold of 0.1 µg/L. Lines only aim at easing comparisons.





Slow Release Approach: immobile or mobile nanocarriers

Nanocarriers were conceptualised as parent compounds that are "transformed" into bifenthrin according to a first-order rate reaction. As a first approximation, very high and very low "sorption" coefficients were used as input for the nanocarriers, with the aim to simulate immobile and mobile particles through a soil profile. In all cases, the vapour pressure of the nanocarriers was set to 1E-10 Pa.

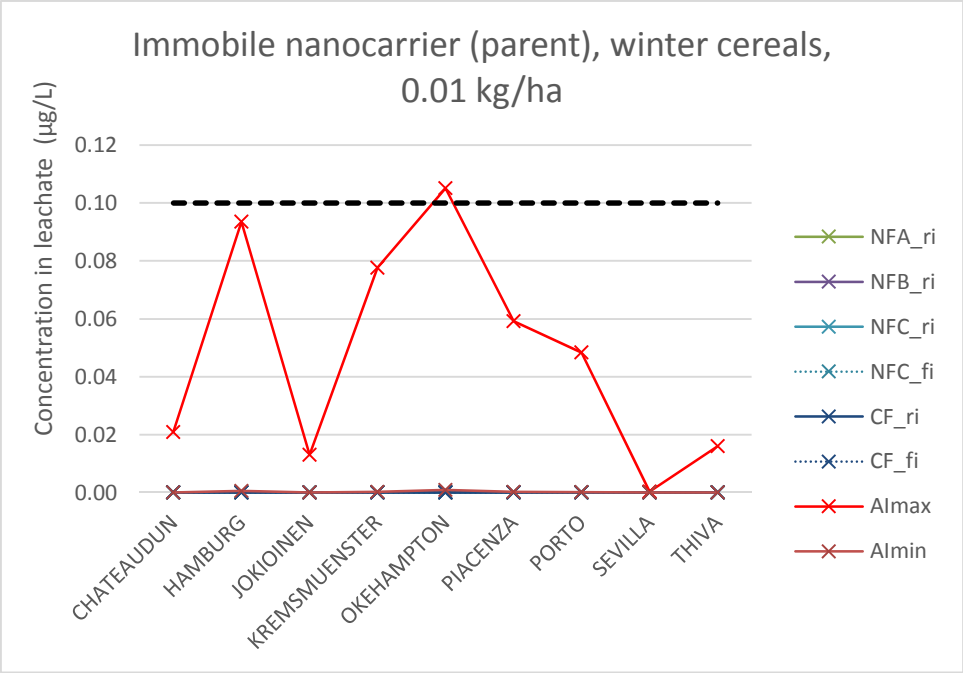
The first-order "transformation" rate of nanocarriers into bifenthrin ("metabolite") were set to the release half-life derived from our degradation experiments (R_{50}, Table 3). For each formulation, the slowest release rates was used, except for NFC_f and CF_f, for which the fastest was input. The "metabolite" (released bifenthrin) was given the parameters measured for the pure AI (worst-case for leaching). All parameters are used in Table S5 below.

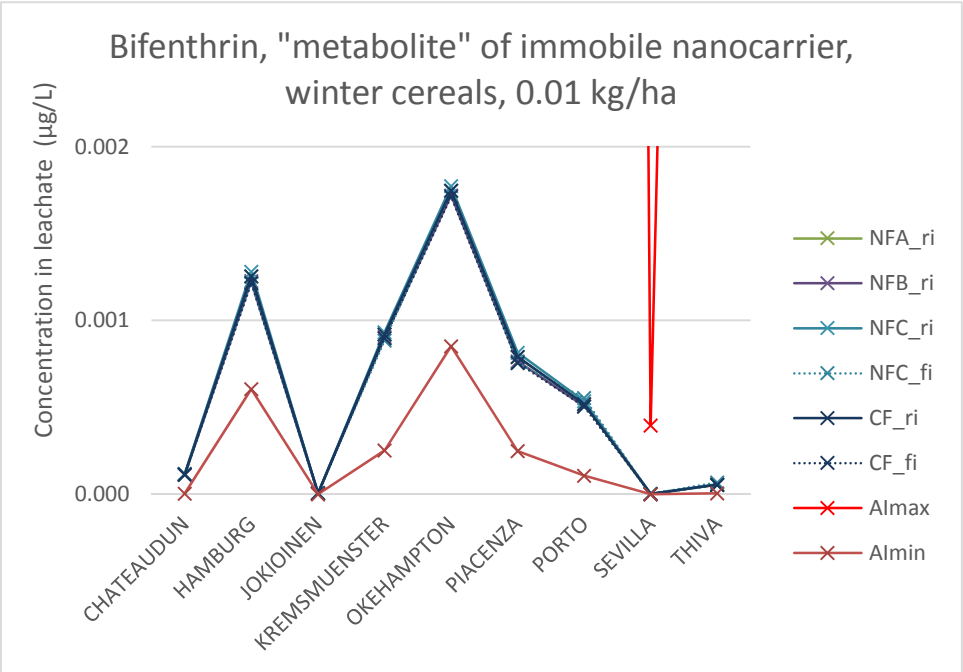
Table S6. Prediction of leaching with the Slow Release Approach with immobile nanocarriers

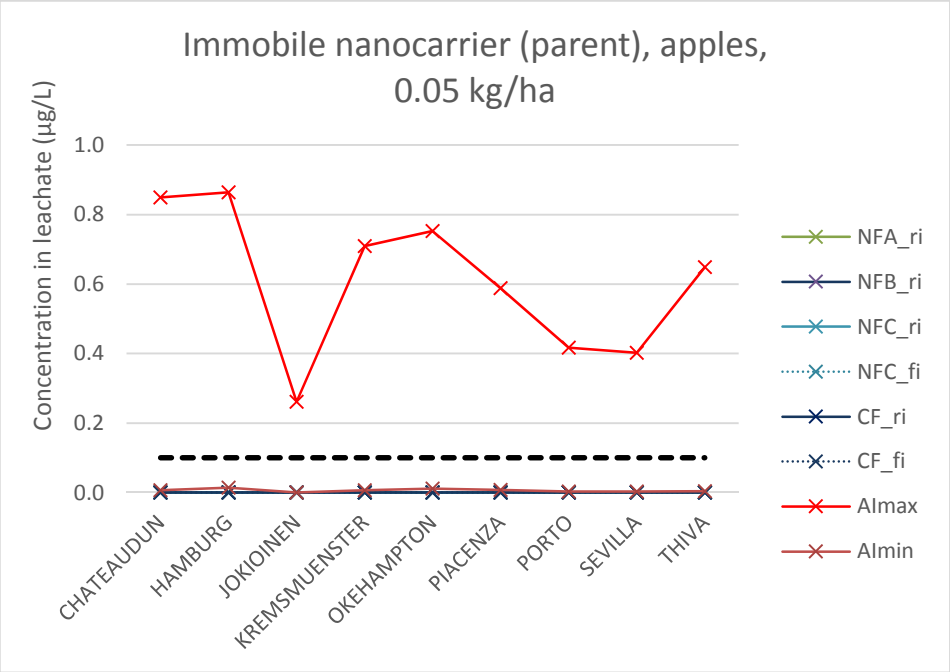
	Inputs parameters				**0.01 kg/ha winter cereals**		**0.05 kg/ha apples**	
	Parent (nanocarrier)		**Metabolite (AI_{max})**		**Average PEC_{GW} (9 scenarios)**	**Average increase / AI_{max}**	**Average PEC_{GW} (9 scenarios)**	**Average increase / AI_{max}**
	K_{OM} (L/kg)	DT_{50} (d)	K_{OM} (L/kg)	DT_{50} (d)	(µg/L)	-	(µg/L)	-
NFA_ri	1000.00	58.3	163.37	266	0.0006	0.009	0.0108	0.017
NFB_ri	1000.00	42.9	163.37	266	0.0007	0.010	0.0105	0.016
NFC_ri	1000.00	73.7	163.37	266	0.0006	0.009	0.0110	0.017
NFC_fi	1000.00	11.1	163.37	266	0.0006	0.009	0.0100	0.016
CF_ri	1000.00	59.0	163.37	266	0.0006	0.009	0.0108	0.017
CF_fi	1000.00	36.6	163.37	266	0.0006	0.008	0.0104	0.016
AI_{max}	-	-	163.37	266	0.0482	-	0.6116	-
AI_{min}	-	-	233.72	125	0.0002	-	0.0060	-

Figure S5. Predicted concentrations in groundwater with the Slow Release Approach with immobile nanocarriers

80th percentile of the average annual concentration in leachate at 1 m depth over 20 years simulation for 9 European scenarios with the pesticide fate model PEARL 4.4.4. Lines only aim at easing comparisons. Concentration calculated for the nanocarriers were 0.000000 µg/L.






Immobile nanocarrier (parent), apples, 0.05 kg/ha
Concentration in leachate (µg/L)
1.0
0.8
0.6
0.4
0.2
0.0
CHATEAUDUN
HAMBURG
JOKIOINEN
KREMSMUENSTER
OKEHAMPTON
PIACENZA
PORTO
SEVILLA
THIVA
NFA_ri
NFB_ri
NFC_ri
NFC_fi
CF_ri
CF_fi
AImax
AImin

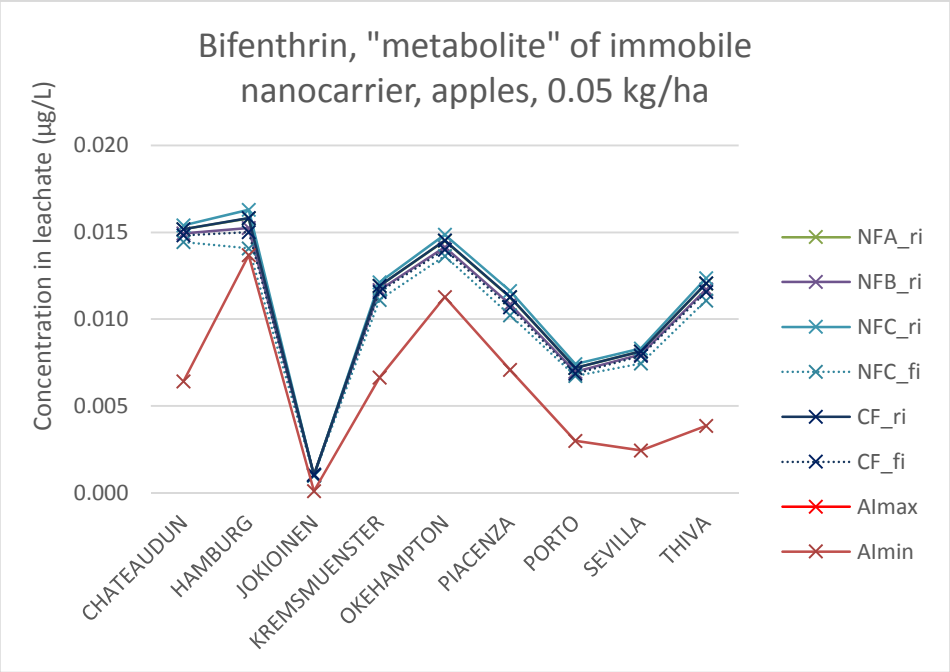
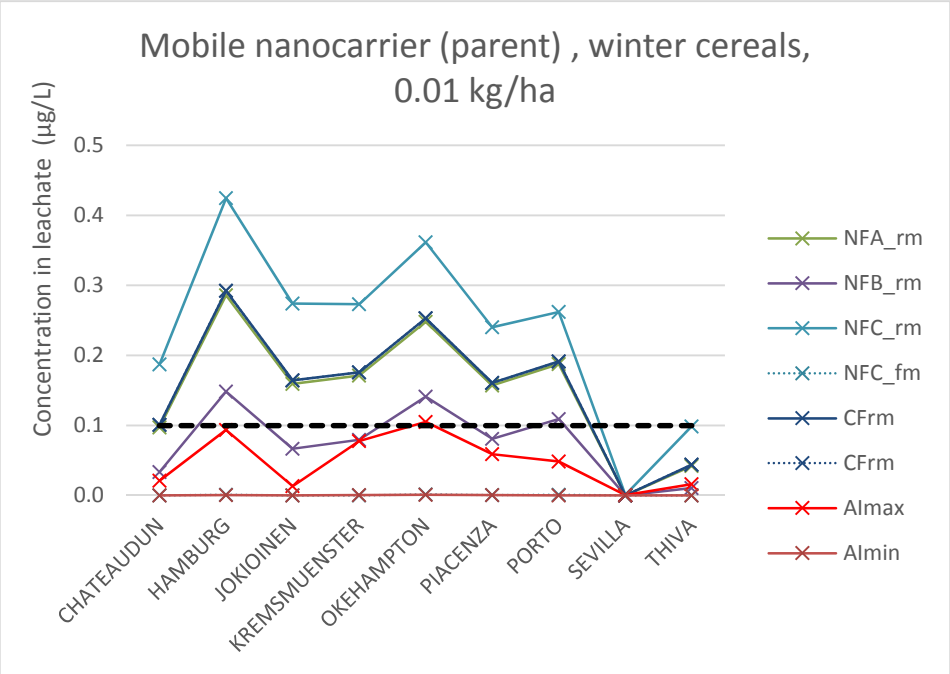

Bifenthrin, "metabolite" of immobile nanocarrier, apples, 0.05 kg/ha
Concentration in leachate (µg/L)
0.020
0.015
0.010
0.005
0.000
CHATEAUDUN
HAMBURG
JOKIOINEN
KREMSMUENSTER
OKEHAMPTON
PIACENZA
PORTO
SEVILLA
THIVA
NFA_ri
NFB_ri
NFC_ri
NFC_fi
CF_ri
CF_fi
AImax
AImin

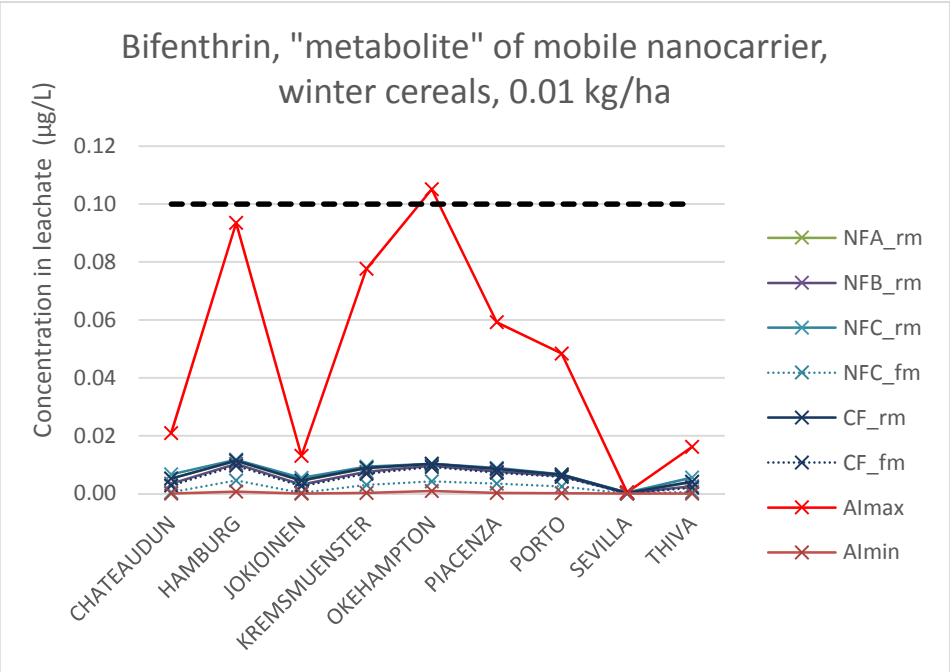
Table S7. Prediction of leaching of bifenthrin with the Slow Release Approach with mobile nanocarriers

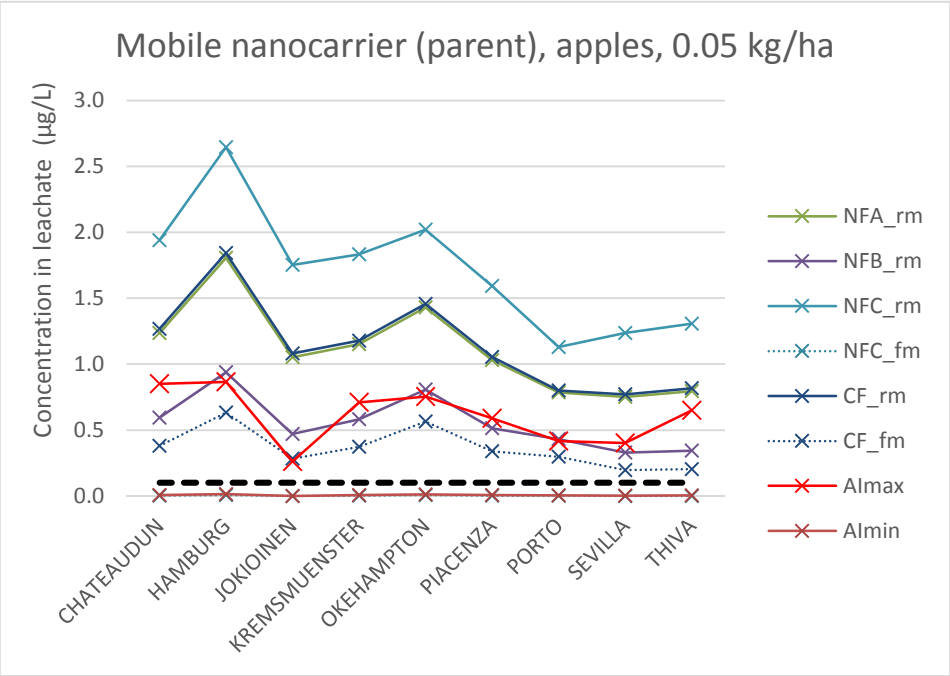
	Inputs parameters				0.01 kg/ha winter cereals		0.05 kg/ha apples	
	Parent (nanocarrier)		Metabolite (AI_{max})		Average PEC_{GW} (9 scenarios)	Average increase / AI_{max}	Average PEC_{GW} (9 scenarios)	Average increase / AI_{max}
	K_{OM} (L/kg)	DT_{50} (d)	K_{OM} (L/kg)	DT_{50} (d)	(µg/L)	-	(µg/L)	-
NFA_rm	25.00	58.3	163.37	266	0.0065	0.219	0.0553	0.094
NFB_rm	25.00	42.9	163.37	266	0.0056	0.160	0.0499	0.083
NFC_rm	25.00	73.7	163.37	266	0.0071	0.277	0.0573	0.098
NFC_fm	25.00	11.1	163.37	266	0.0021	0.041	0.0243	0.039
CF_rm	25.00	59.0	163.37	266	0.0066	0.221	0.0554	0.094
CF_fm	25.00	36.6	163.37	266	0.0051	0.137	0.0461	0.076
AI_{max}	-	-	163.37	266	0.0482	-	0.6116	-
AI_{min}	-	-	233.72	125	0.0002	-	0.0060	-

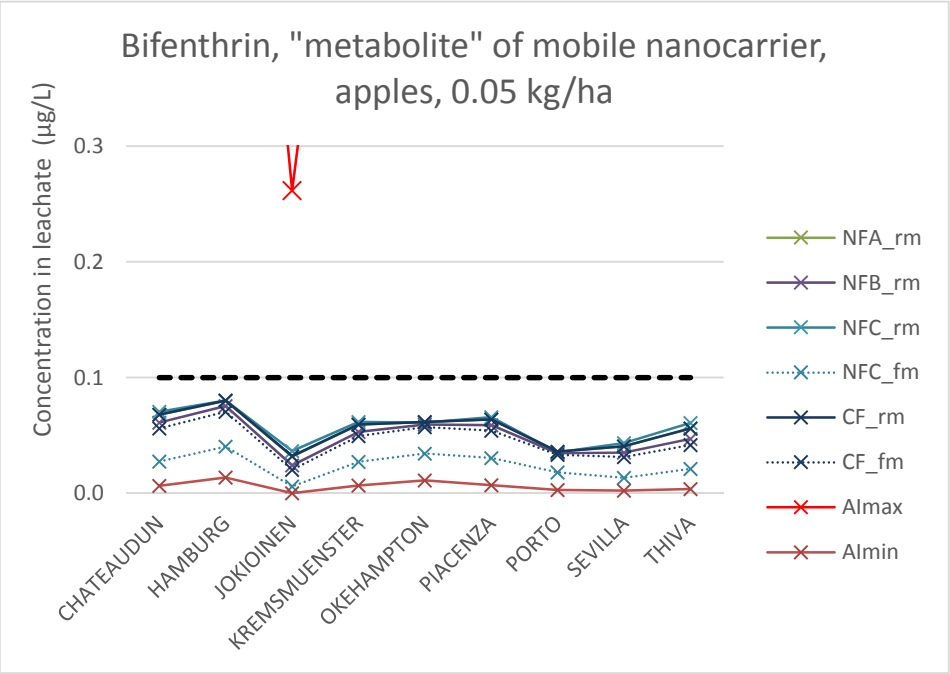
Figure S6. Predicted concentrations in groundwater with the Slow Release Approach with mobile nanocarriers

80th percentile of the average annual concentration of nanocarriers releasing bifenthrin in leachate at 1 m depth over 20 years simulation for 9 European scenarios with the pesticide fate model PEARL 4.4.4. Lines only aim at easing comparisons.






Mobile nanocarrier (parent), apples, 0.05 kg/ha
Concentration in leachate (µg/L)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
CHATEAUDUN
HAMBURG
JOKIOINEN
KREMSMUENSTER
OKEHAMPTON
PIACENZA
PORTO
SEVILLA
THIVA
NFA_rm
NFB_rm
NFC_rm
NFC_fm
CF_rm
CF_fm
AImax
AImin


Bifenthrin, "metabolite" of mobile nanocarrier, apples, 0.05 kg/ha
Concentration in leachate (µg/L)
0.3
0.2
0.1
0.0
CHATEAUDUN
HAMBURG
JOKIOINEN
KREMSMUENSTER
OKEHAMPTON
PIACENZA
PORTO
SEVILLA
THIVA
NFA_rm
NFB_rm
NFC_rm
NFC_fm
CF_rm
CF_fm
AImax
AImin

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