# Ground-Water Leaching Potential of Penflufen

Introduction:
Penflufen, N-[2-(l,3-dimethylbutyl)phenyl]-5-fluoro-l,3-dimethyl-lH-pyrazole-4-carboxamide, is a fungicide that is newly developed to control seed-borne and soil-borne diseases in crop plants (e.g., *Fusarium*, *Rhizoctonia*, and *Pythium* spp.). The compound belongs to the chemical class of carboxamides. It inactivates the succinate dehydrogenase system of the mitochondrial respiration chain as mode of action. The compound is labeled for seed or seed piece treatment on some crops (e.g., cereal grains, potatoes, legume vegetables, and oilseeds) including in-furrow spray application at planting, improving root health and crop productivity through the effective root disease control. The trade name of this compound is Evergol™ (developed by Bayer CropScience). Seven fungicides containing penflufen with different chemical substances are currently registered for end use products. The compound receives a toxicity class rating of III or IV (i.e., slight or least toxic) from US EPA with respect to acute human health effects, and raises some concerns due to its high toxicity to fish and detection probability in surface water and groundwater systems. It has been added to the list of US EPA's Pesticide Fact Sheets (CAS number: 494793-67-8) since May 2012.

Selected Physical/Chemical Properties of Penflufen:
    Chemical structure:
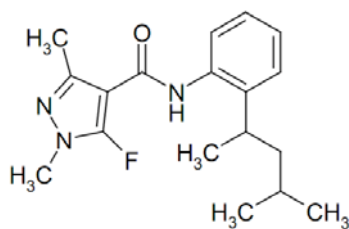
    Literature data

Chemical formula:	$C_{18}H_{24}FN_3O$
Molecular mass:	317.41 g/mole
Physical state:	Off-white colored powder
Water solubility (at pH 7, 20°C):	10.9 mg/L
Log P_{ow} (at pH 7, 20°C):	3.3
(at pH 4, 7, and 9, 25°C):	Ditto (registrant)
Vapor pressure (at 25°C):	4.1×10^{-04} mPa
Henry law constant (at 25°C):	1.05×10^{-05} Pa·m^3/mol[*]
(at 20°C):	4.90×10^{-9} dimensionless
K_{oc}:	209.6–409.5 (typical 279.9) mL/g
	Ditto (registrant) mL/g
Soil degradation half-life (lab):	115–458 (typical 192) days
	117–459 days (registrant)
Freundlich coefficients (K_f):	2.71–6.10 (typical 4.78)
Freundlich coefficient (1/n):	0.875–0.974 (typical 0.920)
GUS index:	3.55 (High leachability)
SCI-GROW index (ppb) for 1 kg/ha dose:	7.10×10^{-01} µg/L
Potential for particle bound transport index:	Medium

Environmental Fate Data:

Hydrolysis

The stability of [phenyl-UL-^{13}C$_6$/^{14}C]-labeled compound was studied in sterile aqueous solutions at three pH values: 4, 7, and 9. The experiment was conducted in the dark at 50°C. The concentration of the compound in solution was 1 mg/L. The samples were taken at selected time intervals for 7 days: 0, 2.5, 6, 24, 48, 120, and 168 hours. Buffers used to provide solutions at different pHs were 0.01 M acetate buffer (for pH 4), 0.01 M TRIS buffer (for pH 7), and 0.01 M borate buffer (for pH 9). The compound was found to be stable for all tested conditions, indicating that hydrolytic process was not responsible for degradation of this compound in the environment. The expected half-life of the compound at 25°C was > 1 year as the compound did not show more than 10% of the reaction for 5 days. Only negligible amounts of degradation products (up to 0.8%) were detected at the end of the experiment for pH 9.

Photodegradation in Natural Water

The phototransformation of [phenyl-UL-^{13}C$_6$/^{14}C]- and [pyrazole-3-^{14}C]-labeled compounds was investigated by the registrant in sterile natural water (collected from Rhine River, Germany) using artificial sunlight, a xenon lamp with a UV cutoff filter ($\lambda < 290$ nm). The test samples were continuously irradiated at 25°C for 70 hours, and were analyzed at selected time intervals– 0, 7, 24, 30, 48, 56, and 70 hours. CO_2 and organic volatiles were collected through traps connected to the test vessels. Photolysis experiments showed that no major degradates were observed using the phenyl-labeled compound, whereas the irradiated samples using the pyrazole-labeled compound detected two metabolites. The registrant reported BYF 14182-pyrazole-4-carboxamide and BYF14182-fluoro acid as the two photoproducts, which accounted for 6.8% and 9.8% of applied radioactivity, respectively. However, negligible amounts of CO_2 and volatiles (< 0.1% of applied radioactivity) were trapped using both labels of the compound. No degradation products were observed in the dark samples stored inside the cabinet at a constant temperature of 25°C for 70 hours. Through the single first order model, the experimental half-life values estimated for phenyl- and pyrazole-labeled compound were 4.46 and 3.50 days, respectively. And those under natural conditions (in Tokyo, Japan) are expected to be 41.4 and 32.7 days, respectively. Accordingly, photodegradation appeared to be partially responsible for dissipation of the compound in the aqueous environment.

Photodegradation in Aqueous Buffer

The registrant also studied the aqueous phototransformation of [phenyl-UL-^{13}C$_6$/^{14}C]- and [pyrazole-3-^{14}C]-labeled compounds in sterile buffer (0.01 M phosphate buffer at pH 7) with the exact same artificial sunlight, as mentioned above. The test samples were continuously irradiated at 25°C for 137.5 hours–the equivalent of 28 solar days (in Phoenix, AZ, USA) and 43 solar days (in Athens, Greece). The samples were taken at selected time intervals, 0, 24, 48, 72, 96, 120, and 137.5 hours. Both CO_2 and organic volatiles were collected through traps attached to the test vessels. The registrant reported that no major degradates were found using both labels of the compound, although various minor metabolites (< 5% of applied radioactivity) were detected

throughout the study. Only the irradiated samples using the pyrazole-labeled compound detected one largest metabolite recording 4.5% of applied radioactivity. As discussed above, small amounts of CO_2 and volatiles (< 3% of applied radioactivity) were observed using both labels of the compound and no degradation products were observed in the dark samples. By applying the single first order kinetic to the combined irradiated samples, the experimental half-life calculated was 17.3 days for the parent compound. Also, the predicted half-life values under natural conditions were expected to be 84.5 (in Phoenix, AZ, USA) and 130.9 days (in Athens, Greece). As stated above, photodegradation partially contributed to degradation of the compound in the aqueous environment.

Direct Photolysis in Aqueous Solutions
The direct photodegradation study of the compound was also carried out in aqueous solution (of approximately 4%) for an irradiation period of 500 minutes. The quantum yield of the compound under direct photolysis was determined using polychromatic light (> 295 nm) suggested by the ECETOC method. The average quantum yield Φ, estimated by UV absorption data (for wavelengths of 297.5 to 490 nm) and the degradation kinetics (for 500 minutes) from the replicates, was 0.00037. Environmental half-lives were calculated by two arithmetic models, the approaches of Zepp & Cline (without influence of clouds) and Frank & Kloepffer (with influence of clouds). The models required the quantum yield and the molar extinction coefficients as input parameters. Both methods yielded quite similar results: environmental half-lives estimated for 50th degree of latitude ranged from 210 to 293 days (for the method of Zepp & Cline) and from 210 to 270 days (for the method of Frank & Kloepffer) during spring-summer period. From these results, the compound appeared to be rarely degraded by direct phototransformation.

Phototransformation in Air
The phototransformation of the compound was estimated by the registrant using the computer program– Atmospheric Oxidation Program for Microsoft Windows (AOPWIN, version 1.91) released by US EPA as one of modules in EPI Suite™. This is because an experimental protocol to determine the reaction rate with the hydroxyl radical (k_{OH}) is laborious and difficult for chemicals with low vapor pressure. The AOPWIN adopted quantitative structure-activity relationship (QSAR) methods to estimate the rate constants, which determined half-lives of organic compounds in air from the chemical structure and atmospheric concentrations of the reaction partners such as hydroxyl radicals and ozone. The parent compound was degraded quickly by reactions with hydroxyl radicals, whereas reactions with ozone did not contribute to the degradation of the compound in air significantly. The atmospheric half-life of the compound estimated ranged 0.19 (for short term scenario) to 0.28 days (for long term scenario) depending on the average atmospheric concentrations of hydroxyl radicals. The compound was not expected to show significant emission at the soil surface because of its low Henry's law constant as well as to be long-lasting or accumulate in air due to rapid generation of secondary oxidation products.

Aerobic Degradation Studies in Water
Metabolism of radiolabeled compounds under aerobic aquatic conditions was studied using two water and sediment systems (Anglerweiher and Hoenniger Weiher in Germany). Two different labels, [phenyl-UL-^{14}C]- and [pyrazole-3-^{14}C]-labeled compounds, were used in the experiment and the applied dose was 500 g a.i./ha (corresponding to 50 µg/L in water). The water to

sediment ratio was 3:1 (v:v) and the test vessels were incubated in the dark at 20°C for 120 days. The sediment samples were initially extracted with acetonitrile-water mixed solvents (80:20, v:v) three times at room temperature. Then, they were extracted with the same solvent at 70°C using a microwave. From the experiments, the registrant suggested that the parent compound was removed from the water body mainly though translocation into the sediment. The estimated half-life values for the supernatant water were 93 (in Anglerweiher) and 3.9 days (in Hoenniger Weiher). In addition, the parent compound was degraded slowly in the entire water and sediment systems with a half-life of 333 (in Anglerweiher) and 301 days (in Hoenniger Weiher). Its metabolite BYF 14182-3-hydroxybutyl accounted for less than 13 (for both lables in Anglerweiher) and 3% of the applied radioactivity (in Hoenniger Weiher) in 4 months.

Anaerobic Degradation Studies in Water
The registrant also investigated the anaerobic aquatic transformation of [phenyl-UL-^{14}C]- and [pyrazole-3-^{14}C]-labeled compounds in sediment and pond water mixture. The test matrix, sediment and water, were collected from Lawrence, Kansas. The applied dose of radiolabeled compounds was 75 µg a.i./L. The water to sediment ratio was 3:1 (v:v), and the test systems were incubated in the dark at 20°C for 120 days. Extraction of sediment samples was conducted using ambient and accelerated solvent extractions with acetonitrile/water mixture (80:20, v:v). The experiment results showed that the parent compound degraded from the water with a half-life of 10 days. However, the parent compound was not degraded significantly in the entire water and sediment systems and its expected half-life was greater than 1 year. Any significant metabolite was not identified during the study. Bound residues explained 9% of the applied radioactivity upon termination of study.

Aerobic Degradation Studies in Soil
Aerobic soil metabolism study of phenyl- and pyrazole-labeled compounds was conducted using two US soils, one from Springfield, Nebraska and the other from Porterville, California. The soils from Springfield and Porterville were classified as a silt loam soil (with pH 6.5 in 0.01M $CaCl_2$ and 1.8% organic carbon) and a sandy loam soil (with pH 7.7 in 0.01M $CaCl_2$ and 0.6% organic carbon), respectively. Based on the nominal use rate, 0.11 mg a.i./kg of the labeled compounds was applied to the soils. The treated soil samples were incubated in the dark at room temperature of 25°C for 365 days. The soil moisture content was maintained at 1/3 bar during the experiment. CO_2 and volatile compounds were collected through traps connected to 300 mL cylindrical flasks. The soil samples, taken at selected time intervals, were extracted using acetonitrile-water mixtures (4:1, v/v) by shaking at room temperature three times. Accelerated solvent extraction at 100°C was additionally used, if the extractability conducted at room temperature fell below 90%.

It was found that metabolism of radiolabeled compounds was slow under aerobic conditions. In silt loam soil, phenyl- and pyrazole-labeled compounds decreased from 106.2 (at 0 day) to 43.2% (at 365 days) and from 102.8 (at 0 day) to 40.3% (at 365 days), respectively. Also, the compounds with the phenyl and pyrazole labels declined from 99.2 (at 0 day) to 54.3% (at 365 days) and from 98.0 (at 0 day) to 55.9% (at 365 days) in sandy loam soil, respectively. The combined half-life values, estimated from both labels using the simple first order kinetics, were 249 days (for silt loam soil) and 432 days (for sandy loam soil). The radiolabeled compounds mainly degraded to BYF 14182-3-hydroxybutyl in both soils, and BYF 14182-3-hydroxybutyl

was further degraded to Acetyl-BYF 14182 (i.e., AE 2300037) in silt loam soil. Unidentified metabolites accounted for less than 4% of the total radioactivity for phenyl- and pyrazole-labeled studies in both soils. CO_2 and bound residues explained less than 10 and 30% of the applied radioactivity in the two soils. No significant volatiles were observed in both soils under aerobic conditions. Figure 1a shows the proposed pathway of degradation of the parent compound under aerobic conditions.
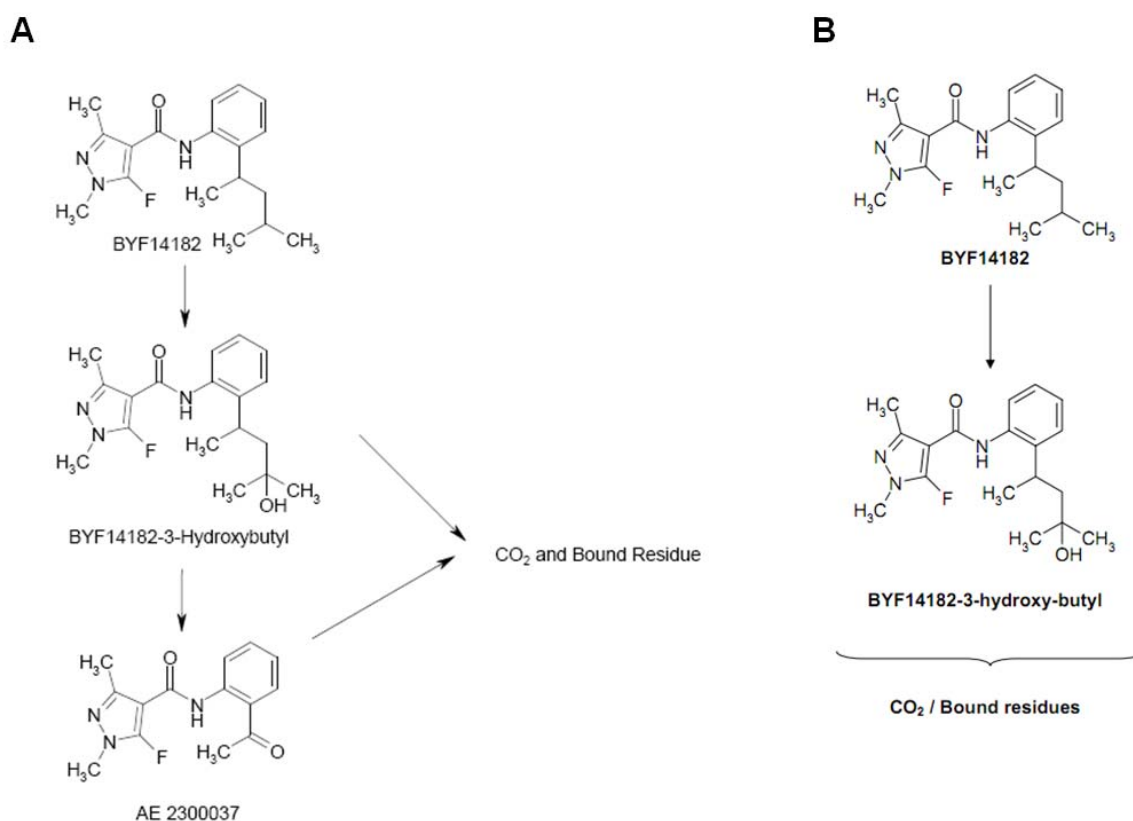

Figure 1. Proposed degradation pathway of penflufen (BYF 14182) (a) in two US soils and (b) in four European soils under aerobic condition. Note that according to the registrant's report, AE 2300037 appears to have several equivalent code names such as BYF 14182-pyrazolyl-AAP, BCS-AF73126, and Penflufen-pyrazolyl-AAP.

The registrant also performed aerobic soil metabolism studies of [phenyl-UL-^{14}C]-labeled compound using four European soils. The pH values and organic carbon content for the four European soils ranged from 5.4 to 6.7 and from 1.12 to 1.79%, respectively. Standard test conditions, similar to those of US soils mentioned above, were followed. The only difference between the experiments was that the soil samples were incubated in the dark at 20°C for 120 days under the 54% of the maximum water holding capacity for this experiment. The estimated half-life values for the test item were 117, 129, 193, and 459 days for the four European soils and their geometric mean was 191 days. BYF 14182-3-hydroxybutyl was identified as the major transformation product which represented 7.0 – 14.9% of the applied radioactivity in the four soils (see Figure 1b). Unidentified metabolites accounted for less than 6% of the total

radioactivity in the four soils. CO_2 and bound residues explained less than 7 and 20% of the applied radioactivity at the end of the study. Again, any significant volatiles were not observed in the soils under aerobic conditions.

Anaerobic Degradation Studies in Soil
Two test items, [phenyl-UL-^{14}C]- and [pyrazole-3-^{14}C]-labeled compounds, were applied at a rate of 250g a.i./ha to a silt loam soil (Hoefchen am Hohens eh, Burscheid, Germany). The test system was initially maintained for 30 days under aerobic conditions and was then shifted to anaerobic conditions by flushing with oxygen-free nitrogen gas. The test system was incubated in the dark at 20°C under both aerobic and anaerobic conditions. The samples were taken at various time intervals during the 184 days of anaerobic incubation. Then, they were analyzed for the parent compound and its metabolites. The parent compound was slowly degraded under anaerobic conditions. The applied radioactivity decreased to 69.9 (for pyrazole-labeled compound) and 73.7% (for phenyl-labeled compound) after a 184-day incubation period. The estimated half-life of the parent compound under anaerobic conditions was greater than 1 year. BYF 14182-3-hydroxybutyl was the major metabolite detected during the initial 30 days of aerobic incubation, accounting for a maximum of 6 and 6.3% of the applied radioactivity for pyrazole- and phenyl-labeled compounds, respectively. However, no significant change was observed in the level of metabolite under anaerobic conditions. Negligible amount of $^{14}CO_2$ (less than 1% of AR) was only detected under aerobic incubation. The radioactivity of non-extractable residues increased from 6.8% at the aerobic phase to 15% at the end of study.

Adsorption and Desorption to Soil
The registrant studied the adsorption and desorption behavior of [phenyl-UL-$^{13}C_6$/^{14}C]-labeled compound using batch equilibrium experiments. The experiments were conducted with soils from different origin (i.e., three European soils and two US soils) to investigate different soil properties could affect sorption processes. Table 1 shows characteristics of the five soils used in this study. As shown in the table, pH, organic carbon content, and the clay content for the selected soils range from 5.5 to 6.3, from 1.2 to 2.3%, and from 5 to 31%, respectively. For the adsorption study, the soils were air-dried and pre-equilibrated in 0.01 M $CaCl_2$ solution for at least one day. Then, the soil samples were spiked with five different concentrations of the parent compound (i.e., 0.01, 0.03, 0.1, 0.3, and 1 mg/L) in 0.01 M aqueous $CaCl_2$ solution at a soil to solution ratio of 1:10. For the desorption study, the decanted solution was replaced by fresh $CaCl_2$ solution without the test item. The soil samples were allowed to shake for 24 hours in the dark at 20°C during the adsorption and the first desorption cycle. Two additional desorption tests were conducted with the samples only treated at the highest concentration. In the tests, 0.01 M of the fresh stock solution was added again, and then shaken for 24 hours, each. The supernatant after each step was centrifuged at 9,000 rpm and was analyzed by liquid scintillation counting.

The Freundlich isotherm model was used to fit the experimental data (see Table 2). In the adsorption study, the calculated K_d values varied between 2.71 and 6.10 mL/g for the five soils, and their K_{oc} values estimated based on the organic carbon content varied between 209.6 and 409.5 mL/g. The Freundlich exponent ($1/n$) ranged from 0.88 to 0.98, indicating that the adsorption behavior was affected by the concentration of the parent compound. Also, the K_d and K_{oc} values estimated from the desorption isotherm were significantly higher than those of the adsorption isotherm, indicating that the compound once bound to the soils was not easily

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detached. No significant correlation was found between pH and adsorption. It should be noted that in the registrant another report that studied time-dependent sorption of the parent compound, the description constant K_{oc} further increased by a factor of 2.5 after aged in soils for 120 days.

Table 1. The key characteristics of the five test soils.

Soil origin	Soil type[1]	pH[2]	Organic carbon	Sand	Silt	Clay
	–	–	%	%	%	%
Laacher Hof AXXa, Germany	Sandy loam	6.1	1.7	69	21	10
Hoefchen am Hohenseh, Germany	Silt loam	6.3	2.3	19	63	18
Laacher Hof Wurmwiese, Germany	Loam	5.3	1.2	47	35	18
Pikeville, USA	Loamy sand	5.2	1.3	76	19	5
Stanley, USA	Clay loam	5.9	2.3	37	32	31

[1] Soil textural classes were determined according to the USDA classification.
[2] The pH was measured in calcium chloride ($CaCl_2$).

Table 2. Sorption and desorption data of the parent compound for the five selected soils.

Soil type	Adsorption				Desorption			
	K_d	$1/n$	R^2	K_{oc}	K_d	$1/n$	R^2	K_{oc}
	mL/g	–	–	mL/g	mL/g	–	–	mL/g
Laacher Hof AXXa, Germany	4.929	0.8945	0.9983	289.9	8.613	0.9377	0.9980	506.7
Hoefchen am Hohenseh, Germany	4.822	0.9077	0.9991	209.6	7.757	0.9226	0.9974	337.3
Laacher Hof Wurmwiese, Germany	2.705	0.9736	0.9958	225.4	6.942	1.0997	0.9790	578.5
Pikeville, USA	5.323	0.9483	0.9985	409.5	9.479	0.9842	0.9979	729.2
Stanley, USA	6.099	0.8749	0.9983	265.2	8.972	0.8892	0.9974	390.1
Mean	4.776	0.9198	0.9980	279.9	8.353	0.9667	0.9939	508.3

The registrant also carried out adsorption/desorption study for its metabolite BYF 14182-3-hydroxybutyl, [pyrazole-3-^{14}C]-labeled degradate (BCS-AA10006). Three European soils and two US soils, similar to the study on the parent compound, were used in the batch experiment. However, there is a slight difference between these two experiments in terms of basic soil properties and locations for collecting the soil samples. Standard test conditions were generally followed. 1:20 and 1:40 soil to solution ratios were used depending on the soil samples. The following are data for the Freundlich parameters of BYF 14182-3-hydroxybutyl:

Table 3. Sorption and desorption data of its metabolite BYF 14182-3-hydroxybutyl for the five selected soils.

Soil type	Adsorption				Desorption			
	K_d	$1/n$	R^2	K_{oc}	K_d	$1/n$	R^2	K_{oc}
	mL/g	–	–	mL/g	mL/g	–	–	mL/g
Pikeville, USA	0.4526	0.8994	0.9989	50.3	0.6504	0.9011	0.9985	72.3
Wurmwiese, Germany	0.6377	0.9497	0.9999	33.6	0.8113	0.9556	0.9998	42.7
Stanley, USA	1.3007	0.9559	0.9997	61.9	1.5550	0.9626	0.9998	74.0
Laacher Hoh AXXa, Germany	0.6254	0.9409	0.9997	26.1	0.7948	0.9462	0.9999	33.1
Hoefchen am Hohenseh, Germany	0.9281	0.9226	0.9998	32.0	1.1943	0.9374	0.9996	41.2
Mean	0.7889	0.9337	0.9996	40.8	1.0012	0.9406	0.9995	52.7

Both K_d and K_{oc} values of BYF 14182-3-hydroxybutyl, estimated from the adsorption and desorption isotherms, were significantly lower than those of the parent compound. These results indicated that the metabolite was more mobile than the parent compound. Also, the K_d and K_{oc} values estimated from the desorption isotherm were higher than those of the adsorption isotherm, suggesting that the metabolite once bound to the soils was not readily detached.

The same experimental methods described directly above were also followed in the another adsorption/desorption study for its metabolite BCS-AF73126, [pyrazole-3-^{14}C]-labelled degradate (BYF 14182-pyrazolyl-AAP). The following are the details of sorption and desorption parameters for BYF 14182-pyrazolyl-AAP:

Table 4. Sorption and desorption data of its metabolite BYF 14182-pyrazolyl-AAP for the five selected soils.

Soil type	Adsorption				Desorption			
	K_d	$1/n$	R^2	K_{oc}	K_d	$1/n$	R^2	K_{oc}
	mL/g	–	–	mL/g	mL/g	–	–	mL/g
Laacher Hof AXXa, Germany	14.674	0.7449	0.9986	863.2	20.556	0.7561	0.9979	1209.2
Hoefchen am Hohenseh, Germany	24.680	0.7560	0.9957	881.4	30.325	0.7495	0.9925	1083.0
Frankenforst, Germany	19.059	0.7900	0.9983	1058.8	23.747	0.7776	0.9727	1319.3
Pikeville, USA	10.999	0.6954	0.9963	1222.1	20.081	0.7267	0.9807	2231.2
Stanley, USA	126.701	0.8730	0.9974	6033.4	136.493	0.8698	0.9962	6499.7
Mean	39.222	0.7719	0.9973	2011.8	46.240	0.7759	0.9880	2468.5

Both K_d and K_{oc} values of BYF 14182-3-hydroxybutyl, estimated from the adsorption and desorption isotherms, were significantly higher than those of the parent compound and its metabolite BYF 14182-3-hydroxybutyl. These results indicated that the metabolite was immobile. Also, the K_d and K_{oc} values estimated from the desorption isotherm were higher than those of the adsorption isotherm, suggesting again that the metabolite once bound to the soils was rarely detached.

Field Dissipation Studies
The registrant individually examined terrestrial field dissipation of the compound on bare ground in three US locations: one in Minidoka County, Idaho (Ecoregion 10.1), another in Fresno County, California (Ecoregion 11.1), and the other in Tift County, Georgia (Ecoregion 8.3). The compound was applied on four replicate plots at one time through a broadcast spray application in a target rate of 275 g a.i./ha to Idaho soil, 55 g a.i./ha to California soil, and 55 g a.i./ha to Georgia soil. Based on soil depth, three soils were texturally classified as in the following: 1) loam (0–18 inches) and silt loam (18–48 inches) for Idaho soil, 2) sandy loam (0–48 inches) for California soil, and 3) sand (0–12 inches), loamy sand (12–18 inches), sandy loam (18–30 inches), and sandy clay loam (30–48 inches) for Georgia soil. The total amount of water added during the experimental period was higher than the 30-year average precipitation, corresponding to the 416 (in Idaho), 593 (in California), and 146 % of the historical average (in Georgia). Soil samples were collected to a depth of 48 inches in the predetermined sampling intervals (i.e., a total of 13 intervals) for 532 (for Idaho soil), 547 (for California soil), and 540 days (for Georgia soil). The soil samples were analyzed for the parent compound (BYF 14182) and its metabolites (BYF 14182-3-hydrolxy-butyl and BYF 14182-pyrazolyl-AAP) by every 6 inches to the depth of soil cores using acetonitrile-water mixtures (4:1, v/v).

From the experiment, registrant reported that in Idaho soil, the residues of the parent compound (BYF 14182) and the metabolite BYF 14182-3-hydrolxy-butyl were not detected below a depth of 24 and 6 inches, respectively. The metabolite BYF 14182-pyrazolyl-AAP was not observed in soil segments above the limit of quantitation (LOQ). For California soil, the residue of the parent compound (BYF 14182) was mainly found in the top 6 inches, including in a depth of 6–12 inches at the level below the LOQ. Two metabolites BYF 14182-3-hydrolxy-butyl and BYF 14182-pyrazolyl-AAP were found in the top 6 inches of the soil at the level below the LOQ. Again, the parent compound (BYF 14182) was observed in the top 6 inches in Georgia soil with minor residue detected under the LOQ up to a depth of 24 inches. Registrant reported that two metabolites BYF 14182-3-hydrolxy-butyl and BYF 14182-pyrazolyl-AAP were detected in the top 6 inches. However, the degradate BYF 14182-3-hydrolxy-butyl was not found in any soil segment at the level below the LOQ. From these results, the leaching potential of the parent compound and its degradates is expected to be low through soil profile. When the dissipation of the parent compound was assessed by the simple first order kinetics for three soils, the estimated half-life values of the parent compound were shown to highly vary between soils. The half-lives calculated were 382 (for Idaho soil), 3.2 (for California soil), and 33.7 days (for Georgia soil). With aerobic soil metabolism studies of radiolabeled compounds, the registrant confirmed that non-extractable residue and CO_2 (after mineralization) were the major route of dissipation of the parent compound in soils, which accounted for up to 28 and 10% of the applied amount after one year, respectively. Tables 5, 6, and 7 describe the degradation pathway of the parent compound in three US soils suggested by the registrant.

Table 5. Dissipation routes for BYF 14182 in Idaho soil.

Routes of dissipation	Percent of applied amount
Accumulation of BYF 14182 in soil at 532 days	**39.8%** - Average soil residue of BYF 14182
Max transformation products during the study	**2.2%** - BYF 14182 3-hydroxybutyl
	0.8% - BYF 14182-pyrazolyl-AAP
Max mineralization to CO_2 at 365 days	**10%** - Radiolabeled soil metabolism studies[1]
Max non-extractable residue at 365 days	**28%** - Radiolabeled soil metabolism studies[1]
Leaching, if measured	0.0% - No leaching beyond sampling cores.
Volatilization, if measured	0.0% - Non-volatile product
Plant uptake, if measured	0.0% - Not measured
Run off, if measured	0.0% - Not measured

[1] Mislankar, S.G., Dallstream, K.A. [Phenyl-UL-14C] BYF 14182 and [Pyrazole-3-14C] BYF 14182: Aerobic soil metabolism in two US soils. Bayer CropScience LP, Stilwell, KS, USA. Report No. MEELP001, September 15, 2009.

Table 6. Dissipation routes for BYF 14182 in California soil.

Routes of dissipation	Percent of applied amount
Accumulation of BYF 14182 in soil at 365 days	**7%** - Average soil residue of BYF 14182
Max transformation products during the study	**1.8%** - BYF 14182 3-hydroxybutyl
	2.5% - BYF 14182-pyrazolyl-AAP
Max mineralization to CO_2 at 365 days	**10%** - Radiolabeled soil metabolism studies[1]
Max non-extractable residue at 365 days	**28%** - Radiolabeled soil metabolism studies[1]
Leaching, if measured	0.0% - No leaching beyond sampling cores.
Volatilization, if measured	0.0% - Non-volatile product
Plant uptake, if measured	0.0% - Not measured
Run off, if measured	0.0% - Not measured

[1] Mislankar, S.G., Dallstream, K.A. [Phenyl-UL-14C] BYF 14182 and [Pyrazole-3-14C] BYF 14182: Aerobic soil metabolism in two US soils. Bayer CropScience LP, Stilwell, KS, USA. Report No. MEELP001, September 15, 2009.

Table 7. Dissipation routes for BYF 14182 in Georgia soil.

Routes of dissipation	Percent of applied amount
Accumulation of BYF 14182 in soil at 269 days	**19.7%** - Average soil residue of BYF 14182
Max transformation products during the study	**1.1%** - BYF 14182 3-hydroxybutyl
	2.0% - BYF 14182-pyrazolyl-AAP
Max mineralization to CO_2 at 365 days	**10%** - Radiolabeled soil metabolism studies[1]
Max non-extractable residue at 365 days	**28%** - Radiolabeled soil metabolism studies[1]
Leaching, if measured	0.0% - No leaching beyond sampling cores.
Volatilization, if measured	0.0% - Non-volatile product
Plant uptake, if measured	0.0% - Not measured
Run off, if measured	0.0% - Not measured

[1] Mislankar, S.G., Dallstream, K.A. [Phenyl-UL-14C] BYF 14182 and [Pyrazole-3-14C] BYF 14182: Aerobic soil metabolism in two US soils. Bayer CropScience LP, Stilwell, KS, USA. Report No. MEELP001, September 15, 2009.

The registrant also conducted terrestrial field dissipation of the compound on bare ground in three locations in Canada: one in Rockwood, Ontario (Ecoregion 8.1), another in Windthorst, Saskatchewan (Ecoregion 9.2), and the other in Hunter River, Prince Edward Island (Ecoregion 8.1). Standard test conditions were followed. The compound was applied on four replicate plots at one time through a broadcast spray application in a target rate of 240 g a.i./L to the soils. The three soils were texturally classified as sandy loam. The estimated half-life values were 24.2 (for Ontario soil), 305 (for Saskatchewan soil), and 15 days (for Prince Edward Island soil). Tables 8, 9, 10 provided the details of dissipation routes for BYF 14182 in three Canadian soils:

Table 8. Dissipation routes for BYF 14182 in Rockwood, Ontario, Canada.

Routes of dissipation	Percent of applied amount
Accumulation of BYF 14182 in soil at 168 days	**14.1%** - Average soil residue of BYF 14182
Max transformation products during the study	**1.7%** - BYF 14182 3-hydroxybutyl
	2.7% - BYF 14182-pyrazolyl-AAP
Max mineralization to CO_2 at 365 days	**10%** - Radiolabeled soil metabolism studies[1]
Max non-extractable residue at 365 days	**28%** - Radiolabeled soil metabolism studies[1]
Leaching, if measured	0.0% - No leaching beyond sampling cores.
Volatilization, if measured	0.0% - Non-volatile product
Plant uptake, if measured	0.0% - Not measured
Run off, if measured	0.0% - Not measured

[1] Mislankar, S.G., Dallstream, K.A. [Phenyl-UL-14C] BYF 14182 and [Pyrazole-3-14C] BYF 14182: Aerobic soil metabolism in two US soils. Bayer CropScience LP, Stilwell, KS, USA. Report No. MEELP001, September 15, 2009.

Table 9. Dissipation routes for BYF 14182 in Windthorst, Saskatchewan, Canada.

Routes of dissipation	Percent of applied amount
Accumulation of BYF 14182 in soil at 509 days	**25.3%** - Average soil residue of BYF 14182
Max transformation products during the study	**4.1%** - BYF 14182 3-hydroxybutyl
	2.1% - BYF 14182-pyrazolyl-AAP
Max mineralization to CO_2 at 365 days	**10%** - Radiolabeled soil metabolism studies[1]
Max non-extractable residue at 365 days	**28%** - Radiolabeled soil metabolism studies[1]
Leaching, if measured	0.0% - No leaching beyond sampling cores.
Volatilization, if measured	0.0% - Non-volatile product
Plant uptake, if measured	0.0% - Not measured
Run off, if measured	0.0% - Not measured

[1] Mislankar, S.G., Dallstream, K.A. [Phenyl-UL-14C] BYF 14182 and [Pyrazole-3-14C] BYF 14182: Aerobic soil metabolism in two US soils. Bayer CropScience LP, Stilwell, KS, USA. Report No. MEELP001, September 15, 2009.

Table 9. Dissipation routes for BYF 14182 in Hunter River, Prince Edward Island, Canada.

Routes of dissipation	Percent of applied amount
Accumulation of BYF 14182 in soil at 538 days	**22.8%** - Average soil residue of BYF 14182
Max transformation products during the study	**2.1%** - BYF 14182 3-hydroxybutyl
	2.0% - BYF 14182-pyrazolyl-AAP
Max mineralization to CO_2 at 365 days	**10%** - Radiolabeled soil metabolism studies[1]
Max non-extractable residue at 365 days	**28%** - Radiolabeled soil metabolism studies[1]
Leaching, if measured	0.0% - No leaching beyond sampling cores.
Volatilization, if measured	0.0% - Non-volatile product
Plant uptake, if measured	0.0% - Not measured
Run off, if measured	0.0% - Not measured

[1] Mislankar, S.G., Dallstream, K.A. [Phenyl-UL-14C] BYF 14182 and [Pyrazole-3-14C] BYF 14182: Aerobic soil metabolism in two US soils. Bayer CropScience LP, Stilwell, KS, USA. Report No. MEELP001, September 15, 2009.

Evaluation of Leaching Potential to Ground Water for Penflufen

Leaching potential of the parent compound was examined in soils (*n*=2,789) on the Oahu Island, Hawaii. Since there is a slight difference between literature and registrant's recommended values for half-life, we have run the CLERS model twice to assess leaching potential of the parent compound. The mean and standard deviation for K_{oc}, provided by both literature and the registrant, were 0.280 and 0.141 m^3/kg, respectively. The mean and standard deviation for half-life obtained from literature were 192 and 242.5 days. And those provided by the registrant were 192.5 and 168.1 days, respectively. Here, the standard deviation of half-life in literature was estimated from the two extremes in the given range, whereas the mean and standard deviation of half-life for the registrant was computed from both laboratory and field values.
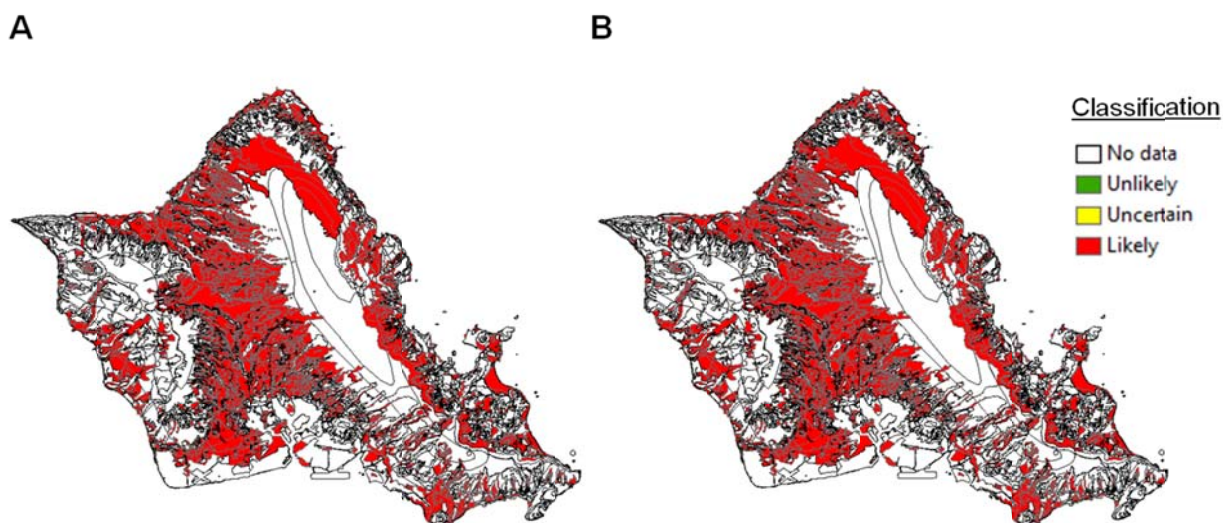

Figure 2. Leaching potential of the parent compound (on the Oahu Island, Hawaii) using (a) literature and (b) registrant's recommended values in CLERS model.

Figure 2 shows a leaching potential of the parent compound on the Oahu Island in Hawaii determined by literature and registrant's recommended values in the CLERS model. As shown in the figure, 1) there is no difference in the leaching potential of the parent compound using

literature values and registrant's recommended values and 2) most areas are prone to contamination by the parent compound. Table 6 also represents a descriptive statistics of the main evaluation criteria in the CLERS model. From the table, it is determined that there is no difference in revised attenuation (AFR) and retardation factors (RF) using both literature and registrant's recommended values in the CLERS model. Different half-life values obtained from literature and the registrant only slightly affect the uncertainty bands of the revised attenuation factor (compare both CVAFR values in the table). In addition, volatilization of the compound does not likely occur in soils due to a low Henry's law constant. Based on these results, it can be suggested that the compound is considered as a potential leacher in Hawaii. Thus, the compound should be used in appropriate use plan.

Table 6. Summary statistics of the main evaluation criteria in the CLERS model (*n*=2,789) [1].

	Literature				Registrant			
	AFR	CVAFR	RF	CVRF	AFR	CVAFR	RF	CVRF
Mean	4.31	0.21	20.87	0.30	4.31	0.16	20.87	0.30
SD	1.26	0.15	8.51	0.13	1.26	0.10	8.51	0.13

[1] Abbreviation: AFR– revised attenuation factor; CV– coefficient of variance, i.e., uncertainty band; RF– retardation factor; SD– standard deviation; *n*– the total number of soil polygons, where bulk density is greater than 0.

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Appendix A. Additional CLERS model runs for the remaining islands in Hawaii.
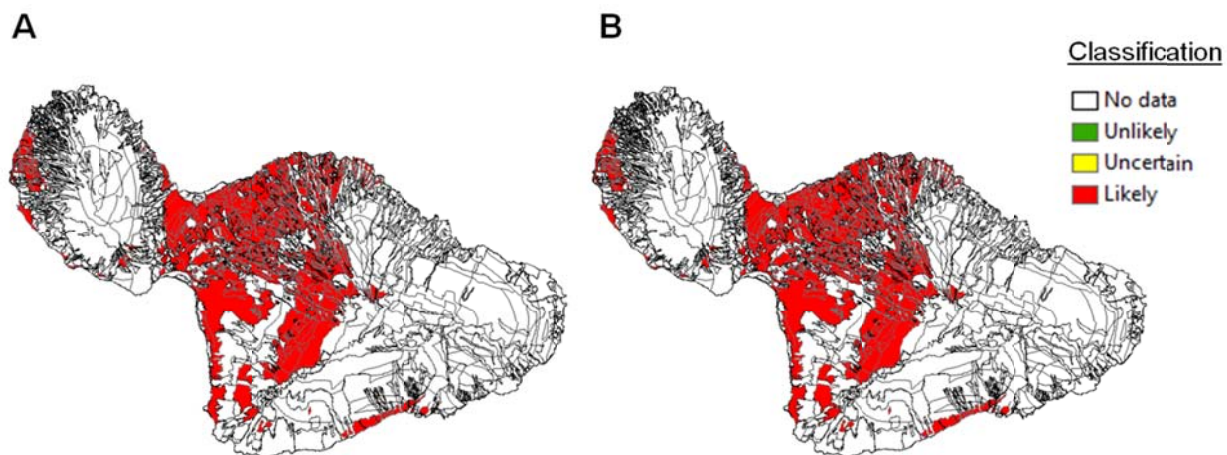
A1. Maui Island, Hawaii

Figure A1. Leaching potential of the parent compound (on the Maui Island, Hawaii) using (a) literature and (b) registrant's recommended values in the CLERS model.
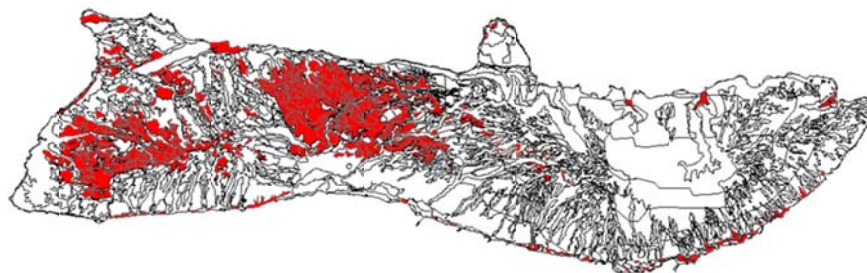
Table A1. Summary statistics of main evaluation criteria in the CLERS model for Maui Island, Hawaii (*n*=1,095) [1].

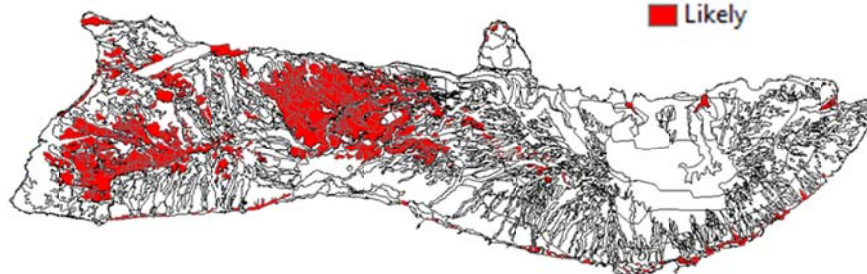|	Literature				Registrant			
	AFR	CVAFR	RF	CVRF	AFR	CVAFR	RF	CVRF
Mean	4.43	0.18	27.38	0.26	4.43	0.14	27.38	0.26
SD	0.80	0.13	13.27	0.13	0.80	0.08	13.27	0.13

[1] Abbreviation: AFR– revised attenuation factor; CV– coefficient of variance, i.e., uncertainty band; RF– retardation factor; SD– standard deviation; *n*– the total number of soil polygons, where bulk density is greater than 0.

A2. Molokai Island, Hawaii

Figure A2. Leaching potential of the parent compound (on the Molokai Island, Hawaii) using (a) literature and (b) registrant's recommended values in the CLERS model.

Table A2. Summary statistics of the main evaluation criteria in the CLERS model for Maui Island, Hawaii (*n*=515) [1].

| | Literature | | | | Registrant | | | |
	AFR	CVAFR	RF	CVRF	AFR	CVAFR	RF	CVRF
Mean	4.65	0.15	20.09	0.28	4.65	0.12	20.09	0.28
SD	0.47	0.11	13.44	0.11	0.47	0.07	13.44	0.11

[1] Abbreviation: AFR– revised attenuation factor; CV– coefficient of variance, i.e., uncertainty band; RF– retardation factor; SD– standard deviation; *n*– the total number of soil polygons, where bulk density is greater than 0.
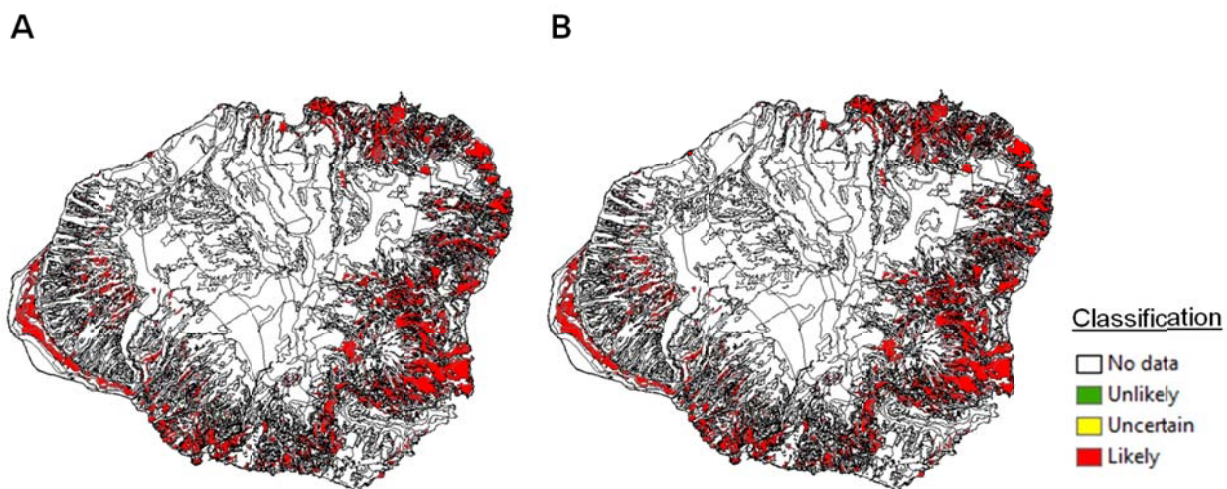
A3. Kauai Island, Hawaii

Figure A3. Leaching potential of the parent compound (on the Kauai Island, Hawaii) using (a) literature and (b) registrant's recommended values in the CLERS model.

Table A3. Summary statistics of the main evaluation criteria in the CLERS model for Kauai Island, Hawaii (*n*=1,236) [1].

| | Literature | | | | Registrant | | | |
	AFR	CVAFR	RF	CVRF	AFR	CVAFR	RF	CVRF
Mean	5.05	0.09	27.65	0.22	5.05	0.07	27.65	0.22
SD	0.92	0.09	10.90	0.10	0.92	0.06	10.90	0.10

[1] Abbreviation: AFR– revised attenuation factor; CV– coefficient of variance, i.e., uncertainty band; RF– retardation factor; SD– standard deviation; *n*– the total number of soil polygons, where bulk density is greater than 0.
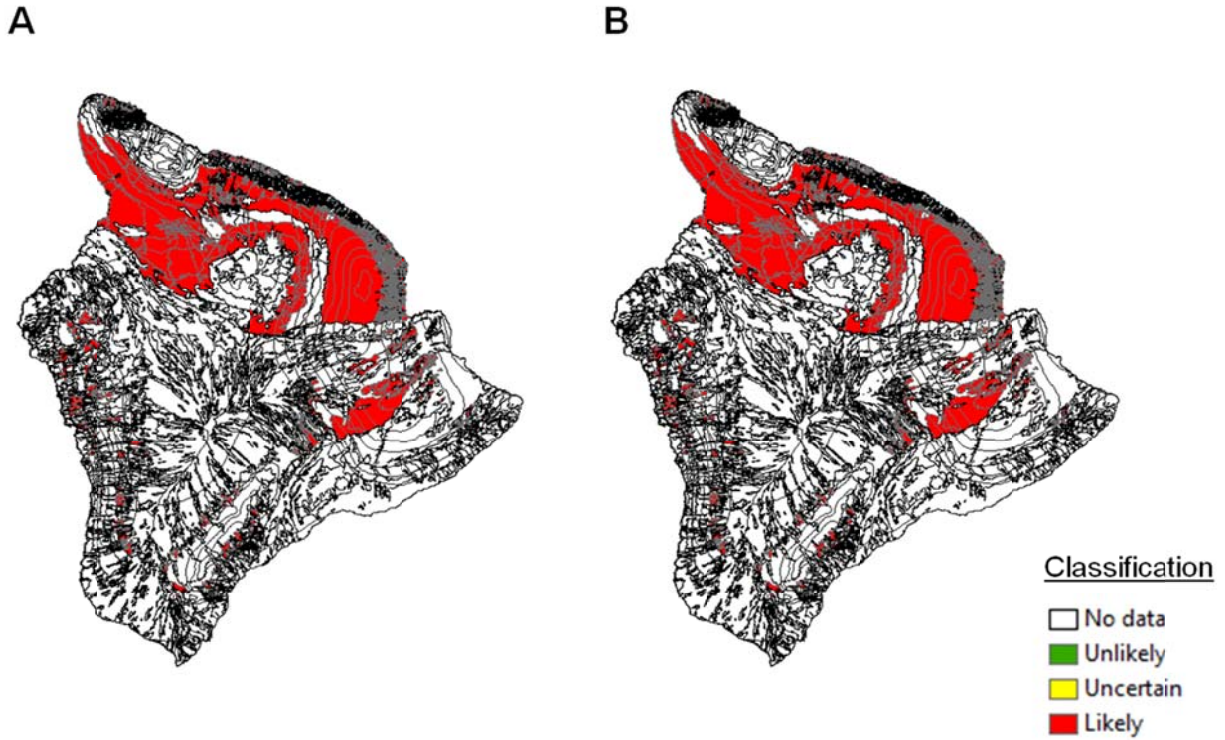
A4. Hawaii Island, Hawaii

Figure A4. Leaching potential of the parent compound (on the Hawaii Island, Hawaii) using (a) literature and (b) registrant's recommended values in the CLERS model.

Table A4. Summary statistics of the main evaluation criteria in the CLERS model for Hawaii Island, Hawaii (*n*=2,101) [1].

	Literature				Registrant			
	AFR	CVAFR	RF	CVRF	AFR	CVAFR	RF	CVRF
Mean	3.48	0.35	29.15	0.39	3.48	0.28	29.15	0.39
SD	1.54	0.25	11.34	0.15	1.54	0.18	11.34	0.15

[1] Abbreviation: AFR– revised attenuation factor; CV– coefficient of variance, i.e., uncertainty band; RF– retardation factor; SD– standard deviation; *n*– the total number of soil polygons, where bulk density is greater than 0.