

Supporting Information

Dual-Element Isotope Analysis of Desphenylchloridazon to Investigate its Environmental Fate in a Systematic Field Study - A Long-Term Lysimeter Experiment

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I. Formation and Transformation of Desphenylchloridazon

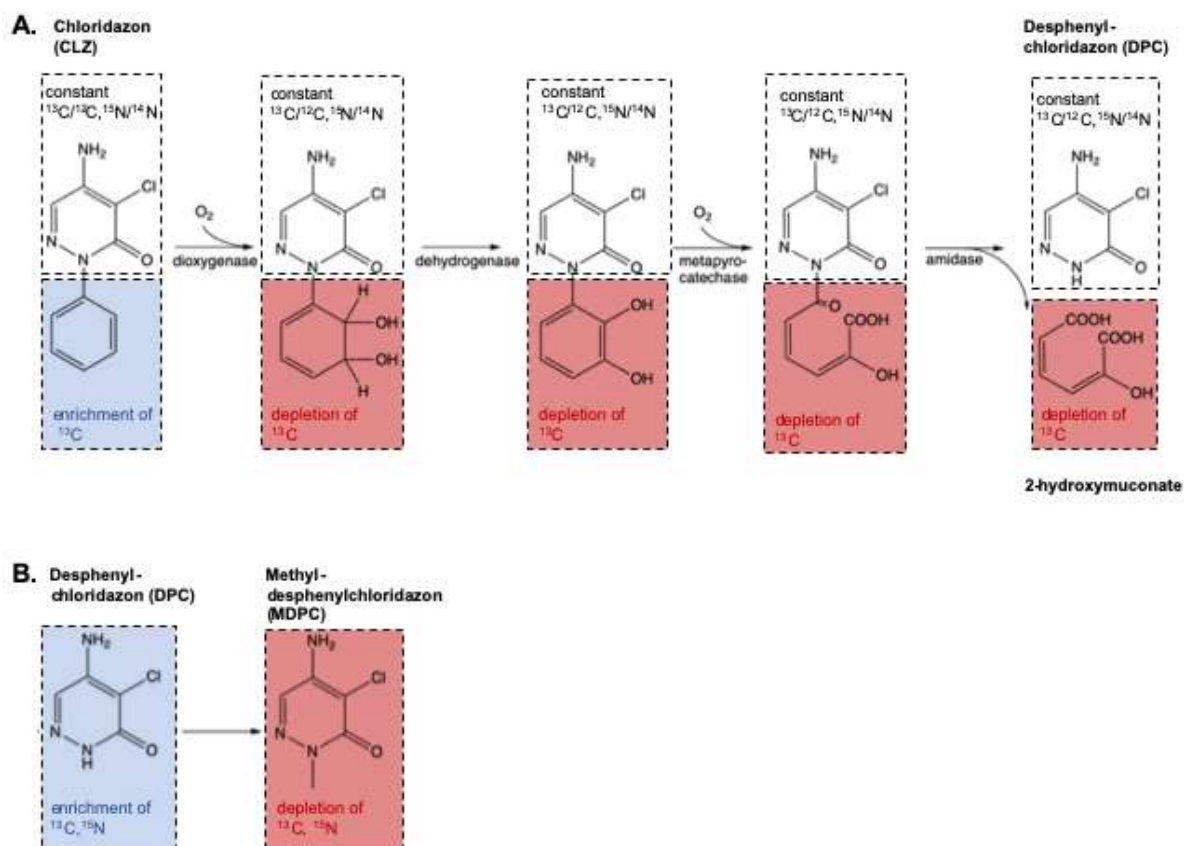


Figure S1: A. Formation of DPC, where the newly formed DPC is expected to contain equally or lower $^{13}\text{C}/^{12}\text{C}$ isotope ratio than its precursor CLZ; B. Transformation of DPC, where carbon and nitrogen isotope effects are expected (primary isotope effect); Reactive groups in CLZ and DPC for which isotope enrichment is expected compared to their initial isotope value are indicated in blue, while isotope depletion (which is expected for the formed MDPC and for 2-hydroxymuconate formed from the phenyl ring of CLZ) is indicated by red boxes; adapted from Lingens et al.¹ and Roberts et al.²

II. Materials and Methods

II.1. Chemicals

For experiments and isotope analysis, CLZ (5-Amino-4-chloro-2-phenylpyridazin-3(2H)-one, CAS no. 1698-60-8) was purchased from Cfm Oskar Tropitzsch GmbH (purity n.a., Marktredwitz, Germany), DPC (5-Amino-4-chloro-3-pyridazinone, CAS no.: 6339-19-1) was kindly provided from BASF (99.8%, Limburgerhof, Germany) and MDPC (5-amino-4-chloro-2-methyl-3(2H)-pyridazinone, CAS no.: 17254-80-7) was supplied by LGC Standards GmbH (Wesel, Germany). (Trimethylsilyl)diazomethane, 2.0 M dissolved in diethyl ether (CAS no.: 18107-18-1, acute toxicity and health hazardous), sodium persulfate ($\geq 99.9\%$, CAS no.: 7775-27-1) and phosphoric acid ($\geq 85\%$, CAS no.: 7664-38-2) were obtained from Sigma Aldrich (Merck KGaA, Darmstadt, Germany), while methanol ($\geq 99.9\%$, CAS no.: 67-56-1) and acetone ($\geq 99.9\%$, CAS no.: 67-64-1) were received from Roth (Karlsruhe, Germany). Ethyl acetate ($\geq 99.9\%$, CAS no.: 141-78-6) was supplied by Honeywell (Burdick & Jackson, Muskegon, USA). Ultrapure water was derived from a Millipore DirectQ apparatus (Millipore, Bedford, MA, USA). Empty polyethylene cartridges (6 mL and 60 mL) and matching polyethylene frits (20- μm pore size) were obtained from Grace (Columbia, SC, USA). Bakerbond SDB-1 sorbent was supplied by J.T. Baker (Phillipsburg, NJ, USA), whereas the Septra ZT sorbent was received from Phenomenex (Torrance, CA, USA). For concentration analysis, Pestanal-quality CLZ and terbuthylazine (CAS no.: 5915-41-3) standards were purchased from Sigma-Aldrich (Seelze, Germany). Certified standards of DPC, M-DPC and chloridazon- d_5 (CAS no.: 1346818-99-4) were purchased from Dr. Ehrenstorfer GmbH (Wesel, Germany).

II.2. Lysimeter Facility Set-Up

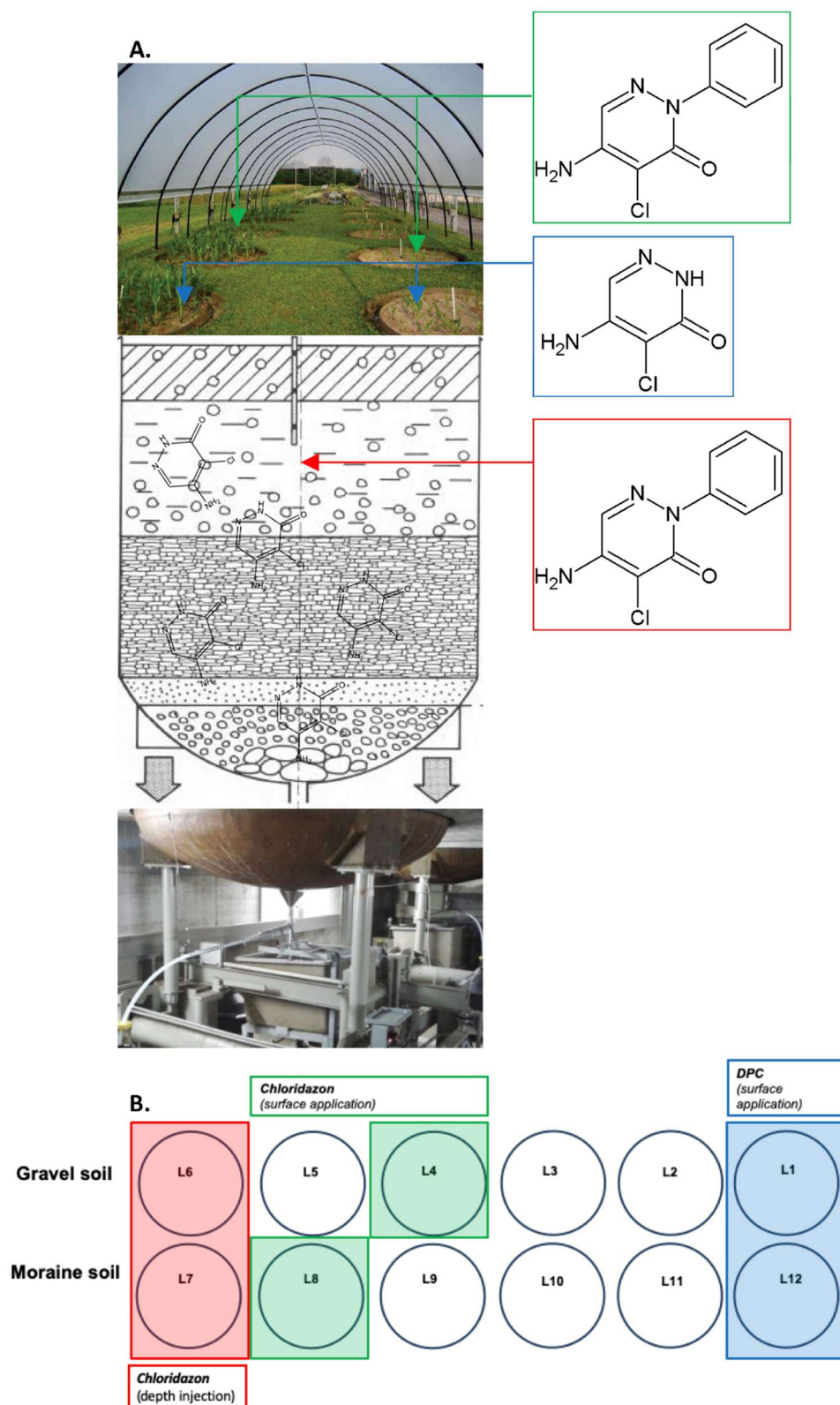


Figure S2: A. Facility and B. lysimeter set-up used for the lysimeter field study provided by Agroscope, pictures adapted from Reckenholtz^{3, 4}

Table S1: Main properties of the two lysimeter soils as described by Torrentó et al.⁵

Soil Horizon	Depth [cm]	Organic Matter [%]	Size Distribution of Mineral Particles [%]		
			Clay	Silt	Sand
Gravel Soil					
A _p	0 - 50	1.7	20	23	57
B ₁	50 - 60	0.9	27	20	64
B ₂	60 - 70	1.1	19	24	57
B ₃	70 - 100		20	24	57
B ₄	110 - 120		19	21	60
C	120 - 135		17	18	65
C	Sandy alluvial deposits				
Moraine Soil					
A _p	0 - 50	2.1	22	34	44
B ₁	50 - 70	1.5	23	35	43
B ₂	70 - 90	0.4	22	38	40
B ₃	90 - 110		20	40	40
B ₄	110 - 140		21	42	37
C	140 - 160		20	41	38
C	Loamy moraine deposits				

II.3. Application Details of Chloridazon and Desphenylchloridazon

Table S2: DPC and CLZ and tracers application to the lysimeters (L) and heavy irrigation events (30-50 mm at 1 mm/min) during the period of monitoring. Although not shown here, regular low-intensity irrigation events (5-20 mm once a week at 0.2 mm/min) were also applied. Sowing and harvest dates are also shown. The following winter covers were used: stubbles (2014), bare fallow (2015) and stubbles (2016 and 2017)

Date	DPC / CLZ Application	Heavy Irrigation [mm]
12-05-2014 Corn sowing		
14-05-2014	-	30 mm
12-06-2014	CLZ depth injection (L6, L7): 2.0 g per lysimeter + uranine (0.41 g per lysimeter)	40-55 mm
28-07-2014	-	40 mm
31-07-2014	-	30-35 mm
10-09-2014 Corn harvesting		
10-09-2014	-	40 mm
15-09-2014	-	40 mm
24-02-2015	-	30 mm
25-03-2015 Sugar beet sowing		
06-05-2015	CLZ surface application (L4, L8): 3.0 kg/ha + uranine (1.3 kg/ha) DPC surface application (L1, L12): 3.2 kg/ha + uranine (1.3 kg/ha) and NaBr (500 kg/ha)	50 mm
21-05-2015	-	55 mm
03-08-2015	-	30 mm
10-08-2015	-	45 mm
07-10-2015	-	40 mm
12-10-2015	-	40 mm
13-11-2015 Sugar beet harvesting		
12-05-2016 Corn sowing		
28-06-2016	-	50 mm
04-07-2016	-	50 mm
14-09-2016 Corn harvesting		
31-10-2016	-	50 mm
07-11-2016	-	50 mm
07-03-2017	-	30 mm
09-03-2017	-	40 mm
18-04-2017 Broccoli (L1,L4,L6) and Chinese cabbage (L12,L8,L7) planting		
20-06-2017 Broccoli and Chinese cabbage harvesting		
10-07-2017	-	40 mm
11-07-2017 Lettuce (L1,L4,L6) and leek Allium (L12,L8,L7) planting		
22-08-2017 Lettuce harvesting		
23-08-2017 Lettuce (L1,L4,L6) planting		
02-09-2017	-	40 mm
30-10-2017 Lettuce harvesting		
09-11-2017 Leek harvesting		

II.4. UHPLC-MS/MS Parameters

Table S3: Optimized compound dependent MS/MS parameters. Other source and collision cell parameters were set as follows: ion spray (IS) voltage +5.5 kV, gas temperature (TEM) 500 °C, nebulizing gas (GS1) 60 psi, drying gas (GS2) 40 psi, curtain gas (CUR) 15 psi

Compound	Retention time [min]	Precursor [m/z]	Fragment [m/z]	DP [V]	EP [V]	CE [V]	CXP [V]	Dwell time [ms]
CLZ (Q)	5.99	222.1	104.0	96	10	33	6	75
CLZ (q)	5.99	222.1	77.0	96	10	53	4	75
DPC (Q)	1.12	146.0	117.0	76	10	37	8	75
DPC (q)	1.12	146.0	66.0	81	10	55	4	75
M-DPC (Q)	1.96	160.0	117.0	81	10	33	8	75
M-DPC (q)	1.96	160.0	88.0	86	10	45	6	75
CLZ-d ₅ (Q)	5.97	227.0	108.0	96	10	39	6	75
CLZ-d ₅ (q)	5.97	227.0	81.0	91	10	55	4	75

Q: quantification ion; q: qualification ion; DP: declustering potential; EP: entrance potential; CE: collision energy; CXP: collision cell exit potential

II.5. UHPLC-QTOF-MS method

An Acquity UPLC™ system was coupled with a Synapt G2 QTOF-MS (Waters). A guard column (5 mm × 2.1 mm, 1.7 µm) and Acquity UPLC BEH C18 column (50 mm × 2.1 mm, 1.7 µm, Waters) were used at a flow rate of 0.4 mL/min in gradient mode. The mobile phase consisted of water (incl. formic acid 0.05 %) and acetonitrile (ACN) containing 0.05 % formic acid. The gradient method started at 2 % ACN/formic acid and was increased linearly to 65 % within 4.5 min. Subsequently, the gradient was increased to 100 % within 1 min, held for 1 min and re-set to 2 % for re-equilibration. The analytes were quantified based on peak area ratios using terbuthylazine as an internal standard. The quantifier ions for CLZ, DPC and MDPC were 222.039, 146.012 and 160.028, respectively.

II.6. Large Volume Solid-Phase Extraction According to Torrentó et al.⁶

For isotope analysis, all lysimeter samples were filtered through 0.7 µm glass fiber filters and were concentrated by SPE using the method described in Torrentó et al.⁶. Shortly, hand-filled 60 mL polyethylene cartridges packed with 8 g of Bakerbond SDB-1 sorbent and 8 g of Septra ZT sorbent were rinsed with 60 mL ethyl acetate (EtAc), conditioned with 60 mL methanol and 60 mL ultrapure water. Subsequently, sample volumes between 1 and 11 L were extracted at a flow rate of 5 mL/min. Each cartridge was then washed with 60 mL ultrapure

water. To remove residual water, all cartridges were dried under vacuum overnight. The analytes were then eluted with 120 mL EtAc and the extracts were finally evaporated until dryness using a CentriVap Benchtop vacuum concentrator (Labconco, Kansas City, MO, USA). Each dry extract was reconstituted in several steps. The final reconstitution volume and solvent varied depending on the isotope analysis method. For carbon isotope analysis, samples were reconstituted in 0.1 to 2.5 mL ultrapure water, while in preparation for nitrogen isotope analysis, each sample was reconstituted in 1 mL methanol.

II.7. Preparative HPLC

As already described by Melsbach et al.⁷, SPE extracts were reconstituted in 800 µL ultrapure water/ACN (90/10 v/v) and manually injected into a Shimadzu UHPLC-DAD (Nexera XR, LC-20AD XR) equipped with a Synergi 4 µm Hydro-RP 80 Å (100 mm x 4.6 µm; Phenomenex, Aschaffenburg, Deutschland). The oven was set to a temperature of 35 °C. A 0.5 mM KH₂PO₄ buffer at pH 7 and ACN were used as mobile phases. At a flow rate of 1.0 mL/min, a gradient method was used for peak separation. The proportion of ACN was 1 % for 2 min, was linearly increased to 10 % within 4 min (held for 0 min) was again linearly increased to 50 % within 3 min (held for 2 min) before a finally linear increase to 75 % within 9 min (held for 2 min). At the end of the run, the proportion of ACN was decreased to 1 % again (held for 5 min). The absorbance of the detector was set to 210 nm. DPC-containing fractions were collected from 1.8 min to 7.0 min and MDPC-containing fractions from 7.0 min to 11.0 min. Subsequently, the fractions were evaporated until dryness by freeze-drying. Afterwards, the fraction containing MDPC was reconstituted in 50 µL acetone, while the DPC fraction was prepared for derivatization by reconstituting the sample in 1 mL methanol.

II.8. Elemental-Analyzer Isotope Ratios used for Correction Procedure

Table S4: Isotope ratios of ¹³C and ¹⁵N of selected compounds used for isotope correction determined by EA-IRMS; measurement uncertainty is shown as standard deviation (SD) of n=5 measurements

Standard	$\delta^{13}\text{C} \pm \text{SD} [\text{‰}]$	$\delta^{15}\text{N} \pm \text{SD} [\text{‰}]$
Desphenylchloridazon	-17.84 ± 0.05	-3.81 ± 0.04
Methyldesphenylchloridazon	-21.17 ± 0.06	+0.99 ± 0.12

II.9. Calculation of Analyte Recovery from the Lysimeter Drainage Water

The balance between the applied/injected mass and the total recovered mass $\%Re_{total}$ (i.e. sum of the recovered masses of the applied/injected compound and its metabolite(s)) is based on the cumulative recovery $\%Re_{Compound}$ of CLZ, DPC and DPC from the drainage water according to equations S1 and S2:

$$\%Re_{Compound} = \frac{\sum_0^n c_{detected} \times V_{drainage\ water}}{m_{analyte\ applied}} \times 100 \quad (S1)$$

$$\%Re_{total} = \sum \%Re_{CLZ} + \%Re_{DPC} + \%Re_{MDPC} \quad (S2)$$

where n is the time of monitoring (days), $c_{detected}$ is the analyte concentration measured in the drainage water of the particular date, $V_{drainage\ water}$ is the corresponding volume of the drainage water eluting from the lysimeter and $m_{analyte\ applied}$ is the mass of the analyte (DPC or CLZ) applied/injected on the lysimeter.” The mass balance was considered incomplete when $\%Re_{total}$ differs from 100%. When possible, analyte mass retained in the first layer of the soil was also considered for the mass balance. To this end, the percentage of retained analyte was calculated from concentration measurements in soil samples assuming (i) homogenous areal distribution of the analytes, and (ii) that the first 10 cm soil layer corresponds to 408 kg of soil (using a bulk density of approximately 1.3 g/cm³ for the topsoil).

III. Results

III.1. Water balance

Table S5: Average monthly sums (in mm) of the water-balance components from the two soil types during 2014, 2015, 2016 and 2017: irrigation (I), drainage (D), change in soil water storage (Δ SWS), and evapotranspiration (ET).

	2014								2016							
	Gravel				Moraine				Gravel				Moraine			
	I	D	Δ SWS	ET	I	D	Δ SWS	ET	I	D	Δ SWS	ET	I	D	Δ SWS	ET
Jan	60	70	-1	0	60	68	-4	0	33	20	2	10	32	12	7	13
Feb	74	62	12	1	74	60	15	4	26	9	0	17	27	6	3	17
Mar	7	39	-60	29	8	37	-66	36	50	14	6	30	50	9	6	35
Apr	86	12	10	65	89	12	5	72	54	22	-7	39	53	17	-9	45
May	111	13	14	84	97	2	23	72	18	12	-19	26	18	10	-19	27
Jun	167	117	-51	102	187	126	-40	101	88	15	18	56	88	7	22	59
Jul	86	11	-3	78	89	9	0	80	115	41	-92	166	112	36	-103	178
Aug	91	19	-34	106	94	15	-27	105	60	4	-73	128	59	1	-83	141
Sep	123	14	49	60	126	18	51	58	27	1	-8	34	28	0	-16	43
Oct	32	8	9	16	32	11	7	15	73	0	56	16	73	0	53	19
Nov	30	4	13	13	30	7	7	15	160	21	125	13	158	5	134	18
Dec	68	39	4	24	65	45	1	19	0	15	-23	8	0	2	-14	12
Total	936	407	-38	577	950	409	-27	578	704	175	-15	544	697	108	-18	607

	2015								2017							
	Gravel				Moraine				Gravel				Moraine			
	I	D	Δ SWS	ET	I	D	Δ SWS	ET	I	D	Δ SWS	ET	I	D	Δ SWS	ET
Jan	27	14	-2	16	29	11	1	17	0	4	-5	3	0	2	-3	3
Feb	60	23	18	19	63	28	16	20	16	2	5	9	16	1	3	12
Mar	49	30	-12	31	52	30	-10	32	60	36	1	24	64	24	15	26
Apr	52	12	-3	43	52	9	-3	46	26	7	6	12	22	8	5	10
May	172	109	-8	71	164	104	-6	66	31	15	-34	50	31	12	-39	58
Jun	28	13	-80	95	27	10	-88	104	56	7	-40	88	62	3	-1	59
Jul	74	5	-38	108	73	2	-45	116	95	5	73	18	95	15	60	20
Aug	107	12	7	88	111	12	6	92	50	14	-17	53	42	36	-44	51
Sep	114	16	42	57	112	12	33	67	87	64	26	2	87	31	20	36
Oct	112	24	58	30	112	9	59	45	19	15	-3	7	16	5	-30	41
Nov	29	10	2	17	26	4	6	15	69	51	31	0	73	6	66	1
Dec	36	20	6	11	35	8	15	12	71	107	6	0	80	122	10	0
Total	861	287	-11	585	855	240	-18	633	581	327	48	266	588	266	61	315

III.2. Vegetation cover

No attempts were made to estimate the percentage of each lysimeter area covered by vegetation since no significant differences in the evolution with time of the plants development between the two soil types or between the two pesticide application methods were observed. In the lysimeters with DPC application (L1 and L12), most of the sugar beet plants died and thus the vegetation cover was much lower in these two lysimeters compared to the lysimeters with CLZ application. Figure S3 shows pictures of the evolution of the vegetation cover on selected lysimeters and dates. The effect of vegetation cover on DPC leaching and isotope fractionation was thus not assessed.

Lysimeters with CLZ application		Lysimeters with CLZ injection		Lysimeters with DPC application	
Gravel soil (L4)	Moraine soil (L8)	Gravel soil (L6)	Moraine soil (L7)	Gravel soil (L1)	Moraine soil (L12)
					
327 days before CLZ application (13.06.2014)	327 days before CLZ application (13.06.2014)	1 day after CLZ injection (13.06.2014)	1 day after CLZ injection (13.06.2014)	327 days before DPC application (13.06.2014)	327 days before DPC application (13.06.2014)
					
292 days before CLZ application (18.07.2014)	292 days before CLZ application (18.07.2014)	36 days after CLZ injection (18.07.2014)	36 days after CLZ injection (18.07.2014)	292 days before DPC application (18.07.2014)	292 days before DPC application (18.07.2014)

					
238 days before CLZ application (10.09.2014)	238 days before CLZ application (10.09.2014)	90 days after CLZ injection (10.09.2014)	90 days after CLZ injection (10.09.2014)	238 days before DPC application (10.09.2014)	238 days before DPC application (10.09.2014)
					
Corn harvesting, 238 days before CLZ application (10.09.2014)	Corn harvesting, 238 days before CLZ application (10.09.2014)	Corn harvesting, 90 days after CLZ injection (10.09.2014)	Corn harvesting, 90 days after CLZ injection (10.09.2014)	Corn harvesting, 238 days before DPC application (10.09.2014)	Corn harvesting, 238 days before DPC application (10.09.2014)
					
6 days before CLZ application (30.04.2015)	6 days before CLZ application (30.04.2015)	322 days after CLZ injection (30.04.2015)	322 days after CLZ injection (30.04.2015)	6 days before DPC application (30.04.2015)	6 days before DPC application (30.04.2015)
					
9 days after CLZ application (15.05.2015)	9 days after CLZ application (15.05.2015)	337 days after CLZ injection (15.05.2015)	337 days after CLZ injection (15.05.2015)	9 days after DPC application (15.05.2015)	9 days after DPC application (15.05.2015)



Figure S3: Changes with time in the vegetation cover of the lysimeters with CLZ application (left panels), the lysimeters with CLZ injection (middle panels) and the lysimeters with DPC application (right panels)

III.3. Analytes breakthrough and recovery

Table S6: Observed breakthrough parameters and recoveries for chloridazon (CLZ), desphenylchloridazon (DPC), bromide (BR), and uranine (UR) in the six lysimeters used in this study. Time and cumulative drainage values correspond to days passed and millimeters accumulated since application or injection, respectively. Maximum concentrations are shown as the absolute and normalized by the applied or injected mass (C/M_{applied}) values. Details about the calculation of analyte recovery can be found on section II.9. Note that bromide was only applied in lysimeters with DPC application. DPC data are also shown for lysimeters with CLZ application or injection for comparison (in grey). *: incomplete series, bql: below quantification limit (0.05 µg/L for UR and 10 µg/L for BR). Details about analytical methods for determining tracer concentrations can be found in Torrentó et al.⁵

DPC surface application	gravel soil (L1)			moraine soil (L12)		
	DPC	BR	UR	DPC	BR	UR
time of first arrival (d)	137	0.2	bql	15	0.4	0.4
time of peak concentration (d)	566	180	bql	425	354	0.4
maximum concentration (µg/L)	97	118020	bql	8.3	57400	bql
maximum concentration, C/M _{applied}	9.7E-05	9.7E-01	-	8.2E-06	4.7E-01	-
cumulative drainage at peak concentration (mm)	458	260	-	303	269	-
time of total recovery (d)	930	352*	566	939	354*	425
total recovery (%)	5.9	47.3*	0.001	0.3	10.5*	0.002
	No early breakthrough			No early breakthrough		
CLZ surface application	gravel soil (L4)			moraine soil (L8)		
	CLZ	DPC	UR	CLZ	DPC	UR
time of first arrival (d)	595	427	bql	425	425	0.1
time of peak concentration (d)	595	847	bql	425	889	0.1
maximum concentration (µg/L)	0.09	17.2	bql	0.23	5.64	3.55
maximum concentration, C/M _{applied}	9.6E-08	-	-	2.4E-07	-	8.7E-06
cumulative drainage at peak concentration (mm)	327	414	-	169	331	4
time of total recovery (d)	931	931	568	940	940	440
total recovery (%)	0.001	0.5	0.000	0.004	0.1	0.121
	No early breakthrough			Early breakthrough: UR		
CLZ depth injection	gravel soil (L6)			moraine soil (L7)		
	CLZ	DPC	UR	CLZ	DPC	UR
time of first arrival (d)	0.2	1.1	0.2	0.2	6.1	0.2
time of peak concentration (d)	270	495	11	266	756	0.2
maximum concentration (µg/L)	232.9	469.7	22.07	97.0	485.1	39.88
maximum concentration, C/M _{applied}	1.2E-04	-	5.4E-05	4.8E-05	-	9.8E-05
cumulative drainage at peak concentration (mm)	166	325	53	183	474	8
time of total recovery (d)	1259	1259	320*	1217	1217	320*
total recovery (%)	3.4	19.8	0.8*	2.0	21.2	1.2*
	Early breakthrough: CLZ, DPC, UR			Early breakthrough: CLZ, UR		

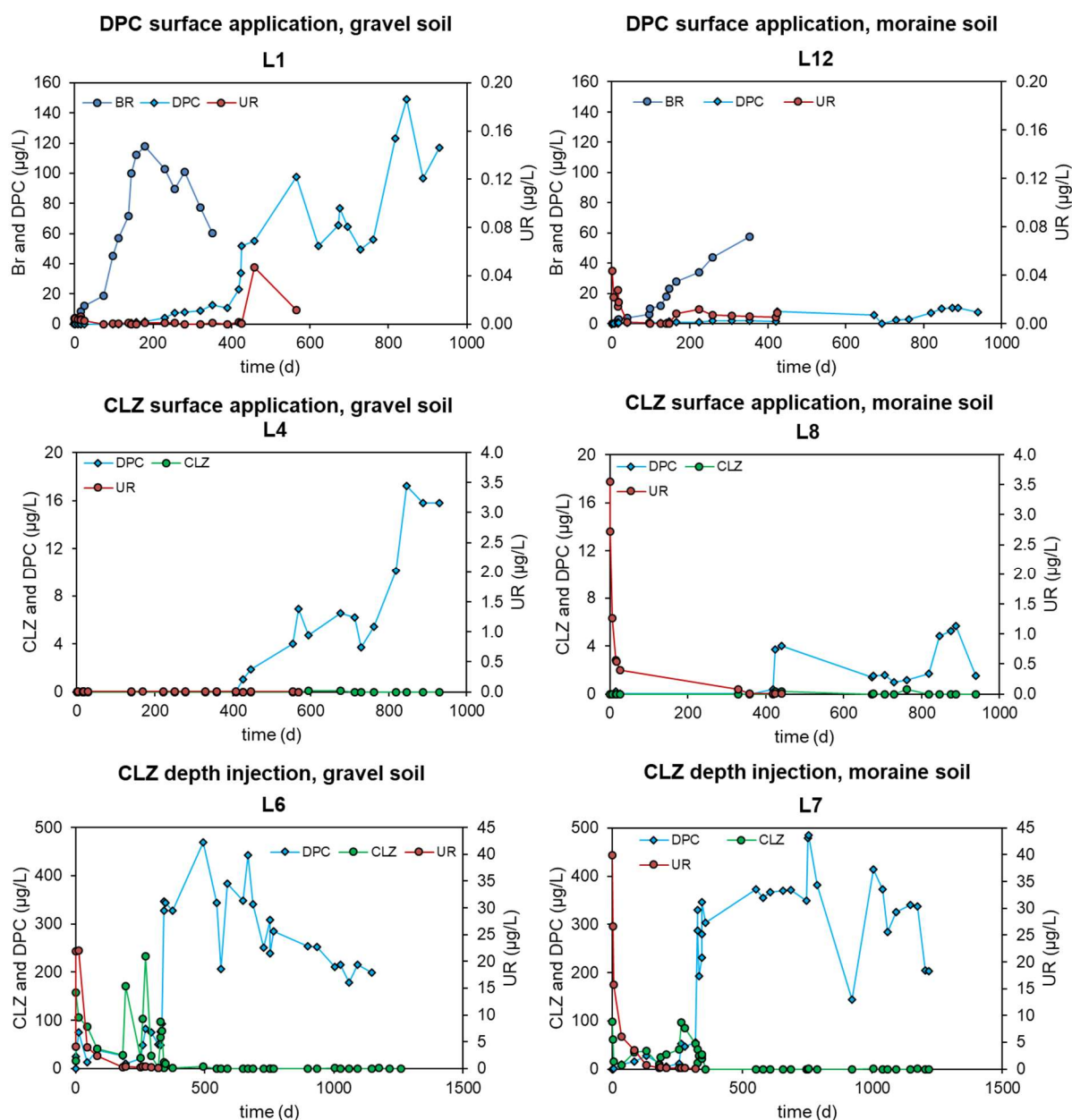


Figure S4: Breakthrough curves for chloridazon (CLZ), desphenylchloridazon (DPC), bromide (BR) and uranine (UR) in the six lysimeters used in this study.

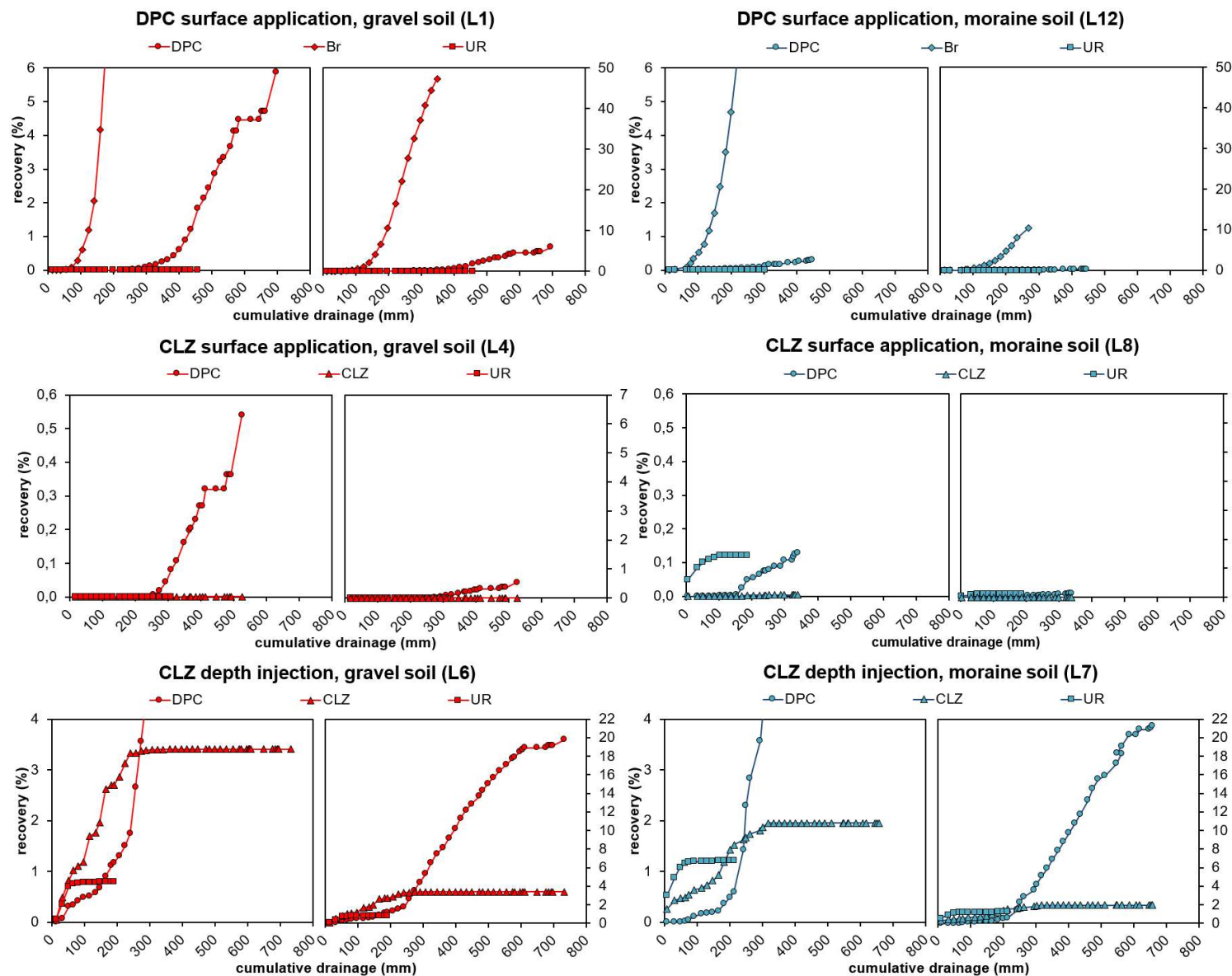


Figure S5. DPC, CLZ, bromide (Br), uranine (UR) recoveries against cumulative drainage for the six combinations of application method and soil type. Note that each lysimeter is shown in two different plots with different scales, as recoveries were in general much higher for bromide than for DPC, CLZ and uranine

III.4. Soil Analysis

Table S7: Concentration measurements of chloridazon and desphenylchloridazon residues within the first soil layers; the limit of quantification (LOQ) was 0.05 mg/kg for CLZ and DPC; measurement uncertainty is shown as 95 % confidence interval (95 % CI)

Lysimeter	CLZ [mg/kg $\pm$ 95 % CI]	DPC [mg/kg $\pm$ 95 % CI]
L1	na	0.082 $\pm$ 0.041
L12	na	0.18 $\pm$ 0.09
L6	<LOQ	<LOQ
L7	<LOQ	<LOQ
L4	<LOQ	0.081 $\pm$ 0.041
L8	<LOQ	0.12 $\pm$ 0.06

III.5. Elemental-Analyzer Isotope Ratios

Table S8: Isotope ratios of ^{13}C and ^{15}N of chloridazon and desphenylchloridazon applied to the lysimeters determined by EA-IRMS; measurement uncertainty is shown as standard deviation (SD) of n=5 measurements

Compound	$\delta^{13}\text{C} \pm \text{SD} [\text{‰}]$	$\delta^{15}\text{N} \pm \text{SD} [\text{‰}]$
Desphenylchloridazon	-17.84 $\pm$ 0.05	-3.81 $\pm$ 0.04
Chloridazon	-27.43 $\pm$ 0.02	-5.70 $\pm$ 0.03

III.6. Chloridazon Depth Injection

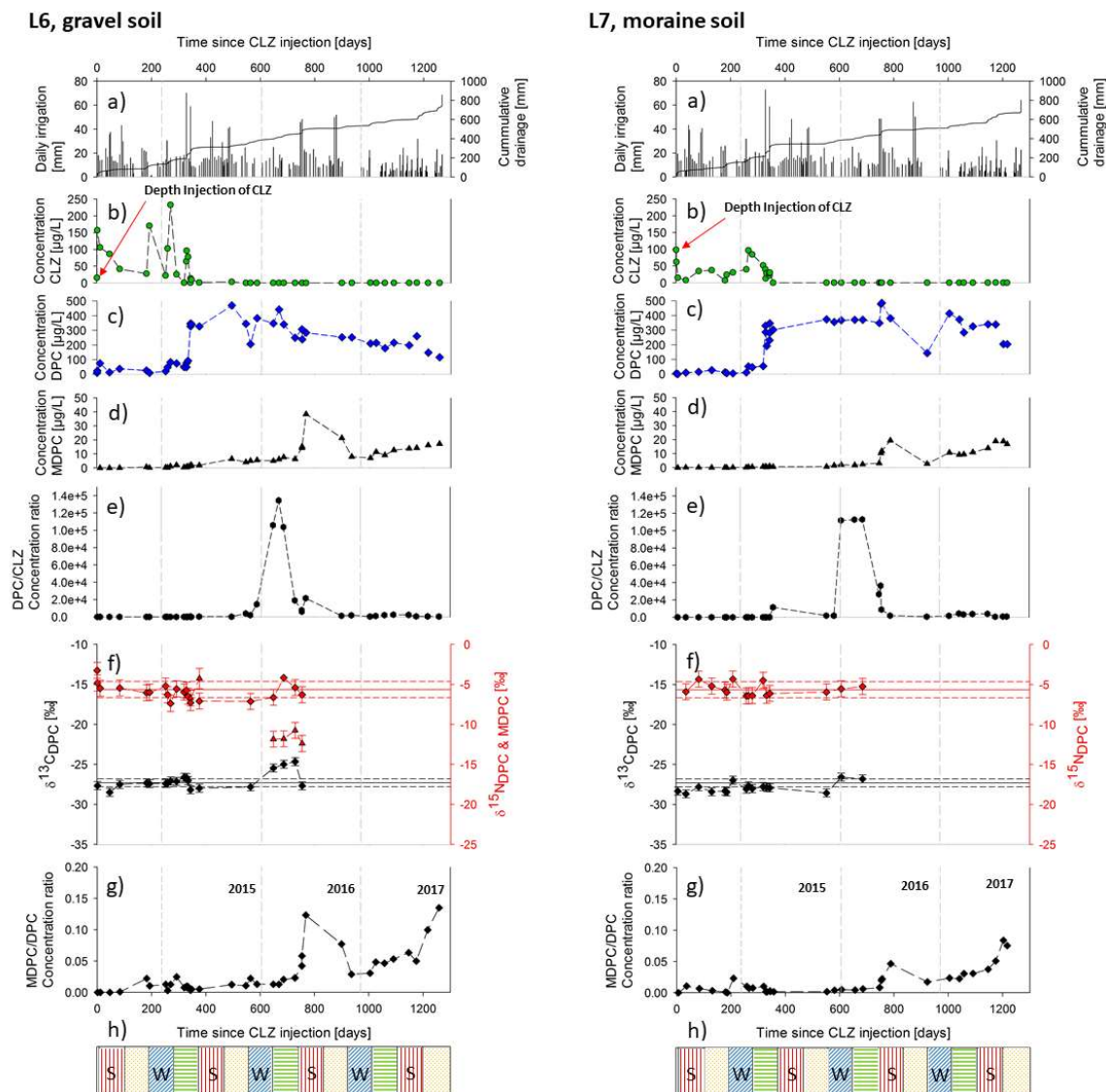


Figure S6: Lysimeters with CLZ injection in depth (a single injection in June 2014 at a depth of 40 cm): L6 in gravel soil (left panels) and L7 in moraine soil (right panels). a) Daily irrigation (black bars) and cumulative drainage (grey line), b-d) Concentration of CLZ (green circles), DPC (blue diamonds) and MDPC (black triangles), e) metabolite-to-parent compound molar ratio of DPC/CLZ (black hexagon), f) Carbon (black diamonds) and nitrogen (red diamonds) isotope ratios of DPC, and nitrogen isotope values of MDPC (red triangles), error bars show the associated uncertainties ($\pm 0.5\%$ for carbon, $\pm 1.0\%$ for nitrogen isotope analysis; or when exceeding this uncertainty, standard deviations of triplicate measurements are given, EA isotope values of the injected CLZ is shown as a line within the accepted standard deviation $\pm \sigma$ shown as a dashed line in the corresponding color; g) metabolite-to-parent compound molar ratio of MDPC/DPC (black diamonds), h) season corresponding to the time since injection – spring (green horizontal lines), summer (red vertical lines), autumn (yellow dots), winter (blue diagonal lines); the grey dashed lines repeated in each sub-figure represent the start of a new year.

III.7. Nitrogen Isotope Ratios of DPC and MDPC

Table S9: Nitrogen isotope ratio of DPC and their corresponding MDPC isotope values of lysimeter L1; measurement uncertainty is shown as standard deviation (SD) of triplicate measurements

Sample Date	$\delta^{15}\text{N}$ DPC $\pm$ SD [‰]	$\delta^{15}\text{N}$ MDPC $\pm$ SD [‰]	$\Delta\delta^{15}\text{N}$ [‰]
23/11/16	-0.9 ± 0.5	-5.3 ± 0.3	-4.4
09/03/17	-1.2 ± 0.2	-4.9 ± 1.0	-3.7
05/05/17	-1.0 ± 0.1	-5.2 ± 0.9	-4.2

Table S10: Nitrogen isotope ratio of DPC and their corresponding MDPC isotope values of lysimeter L12; measurement uncertainty is shown as standard deviation (SD) of triplicate measurements

Sample Date	$\delta^{15}\text{N}$ DPC $\pm$ SD [‰]	$\delta^{15}\text{N}$ MDPC $\pm$ SD [‰]	$\Delta\delta^{15}\text{N}$ [‰]
05/07/2016	-1.2 ± 0.3	-8.5 ± 0.7	-7.3
09/03/2017	-2.7 ± 0.1	-8.0 ± 1.4	-5.3

Table S11: Nitrogen isotope ratio of DPC and their corresponding MDPC isotope values of lysimeter L6; ; measurement uncertainty is shown as standard deviation (SD) of triplicate measurements; for one sample only a single measurement was possible, indicated by a missing standard deviation

Sample Date	$\delta^{15}\text{N}$ DPC $\pm$ SD [‰]	$\delta^{15}\text{N}$ MDPC $\pm$ SD [‰]	$\Delta\delta^{15}\text{N}$ [‰]
21/05/15	-7.3 ± 0.4	-6.7 ± 0.8	-1.1
23/06/15	-7.1 ± 0.4	-4.3 ± 1.3	-1.0
21/03/16	-6.6 ± 0.5	-11.9 ± 0.5	-5.8
28/04/16	-4.2	-11.8 ± 0.1	-6.6
09/06/16	-5.4 ± 0.8	-10.8 ± 0.4	-4.5
05/07/16	-6.3 ± 0.4	-12.4 ± 0.3	-6.8

IV. References

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