Supporting Information

Leaching of the Neonicotinoids Thiamethoxam and Imidacloprid from Sugar Beet Seed Dressings to Subsurface Tile Drains

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1 Physical and chemical soil properties

Table S1. *Selected physical and chemical properties of the soil at the experimental test site.*

Depth (cm)	Soil horizon	Particle size distribution (% by weight)[a]			pH [b]	C_{org} [c]	Bulk density
		Sand	Silt	Clay	($CaCl_2$)	(%)	(g/cm^3)
0−29	Ahp	35	37	28	7.0	1.89	1.23
29−42	Bg	35	32	33	7.2	1.71	1.63
42−80	Bgg	36	39	25	7.2	0.77	1.63
80−100	BCgg	32	50	18	7.7	0.23	1.36
>100	Cgg	21	66	13	7.8	0.06	1.37

[a] Pipette method (sand 64 µm−2 mm, silt 2−64 µm, clay < 2 µm). Soil was oven-dried and sieved to 2 mm prior to analysis;
[b] pH was measured in a suspension of soil (1 g) and 0.01 M $CaCl_2$ solution (5 mL);
[c] Total organic carbon content, C_{org}, was calculated from the organic matter content divided by 1.72. The organic matter content was determined via potentiometric titration of humic substances in aqueous medium.

2 Drainage-relevant area

An artificial irrigation experiment was performed on four 25 m × 25 m bare sub-plots in the upper part of the cropped area in the late summer of 2012 (Figure S1) to test the functionality of the tile drains and assess the surface area cropped with sugar beets that contributed to drainage flow. The sub-plots were irrigated individually with an intended irrigation flux density of 5−6 mm/h during 4 to 6 hours to establish a steady-state drainage flow rate.

No drainage at all was observed from the sub-plots on both edges. For the other two sub-plots, under the assumption that evaporation was negligible, 31 and 52% of the applied irrigation volume at steady state was recorded. Additionally, 15 and 2% of the applied irrigation volume at steady state were recorded by another sampler (lower sampler in Figure S1), which did not participate in the current pesticide transport experiment. For the two sub-plots in the middle with a total surface area of 50 m × 25 m, 41.5% of the irrigation water was recorded by the upper sampler and 8.5% was recorded by the lower sampler, while 50% of the irrigated water was not detected. This is in line with the findings of Kohler et al.[1] for a similar region. The missing volume most likely bypassed the drainage collection tubes, either as groundwater flow or as lateral flow over the dense B-horizon (Table S1), owing to the rather high irrigation flux

densities of 5−6 mm/h during several hours. This flux density was at the higher end for the measured hourly rain intensities during the growing season of the sugar beets, with 1% (40 values) ≥ 3 mm/h. Only during 15 individual hours the rain intensity was > 5.5 mm/h (maximum 15.9 mm/h).

For the calculation of the drainage-relevant area, it is essential to assign the 50% of the irrigated water that was not detected by the samplers. Under the assumptions that this amount was completely assigned to either the lower (2 × 25 m × 25 m × 0.415) or the upper sampler (2 × 25 m × 25 m × (0.415 + 0.5), a range of possible areas (520−1140 m^2) can be estimated. Since we consider it as most likely that the missing water contributed to the drainage area of both samplers proportional to their water recoveries (2 × 25 m × 25 m × (0.415 + 0.415)), we used a drainage-relevant area of 1040 m^2 for further calculations.

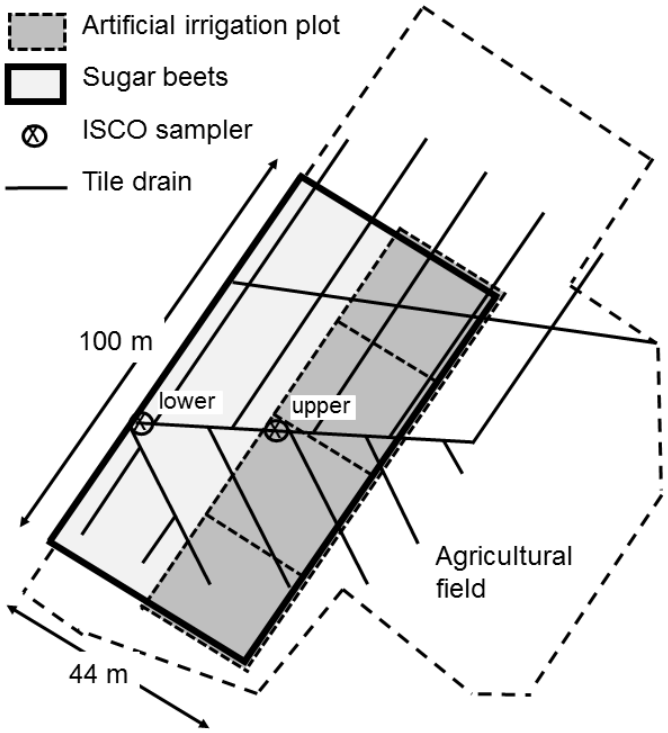

Figure S1. *Scheme of the experimental field site.*

The tile drains partly exceeded the cropped area. Uncontaminated water from outside the cropped area diluted the concentrations of the target substances. An estimation of the contribution of the uphill site to the drainage volume can be made based on simple water balance calculations. A total drainage volume of 461 m^3 was collected in our field study between seeding and harvest of the sugar beets. We assumed that an equal volume was not detected by the sampler based on the irrigation

experiment (V_{total} = 922 m^3). For the period of concern, the precipitation amounted to 700 mm and the potential crop evapotranspiration estimated using the FAO-recommended Penman-Monteith combination equation[2] amounted to 485 and 354 mm for the test site cropped with sugar beets and for the uphill site cropped with winter wheat and spring oat, respectively (see below). Net infiltration is at most 700 mm (no evapotranspiration) and at least 215 and 346 mm (maximum evapotranspiration) for the test site and the uphill site, respectively. Under the assumptions that water storage in the soil profile did not change and the areal contribution to groundwater recharge is constant over time, the range of the drainage area for the uphill site varied from 280 to 2020 m^2 for no and maximum evapotranspiration, respectively. Since the artificial irrigation experiment revealed a drainage-relevant area of 1040 m^2 for cropped area, the uncontaminated drainage water from the uphill site caused a dilution of the concentrations in the tile drains by a factor between 1.3 and 3.

However, maximal dilution will be less, since the maximum (or potential) evapotranspiration rate might be restricted by the soil hydraulic properties, which cannot sustain the required flux under dry soil conditions (e.g. from June 15−22). Equal increases in net infiltration for the test site and the uphill site of 50, 100, and 150 mm, as a consequence, will reduce the drainage-relevant area for the uphill site to 1630, 1330, and 1090 m^2, respectively. The water balance, including the net infiltration, can be better assessed by a numerical model for unsaturated flow in soil.

3 Potential crop evapotranspiration

Crop coefficients, K_c (-), were estimated based on the agricultural management of the site. The test site was fallow prior to the seeding of sugar beets on March 19, 2014 (emergence April 7). The sugar beets were harvested on October 29. For the uphill site, winter wheat was sown on November 15, 2013 (emergence December 1), was harvested on July 29, and succeeded by spring oat, which was sown on August 21 (emergence September 4). Typical values for the crop coefficients were assigned to the initial stage, the mid-season stage, and harvest, with linear interpolations in between.[3] We used a crop coefficient of 0.4 for fallow (ploughed) land (Figure S2ab).

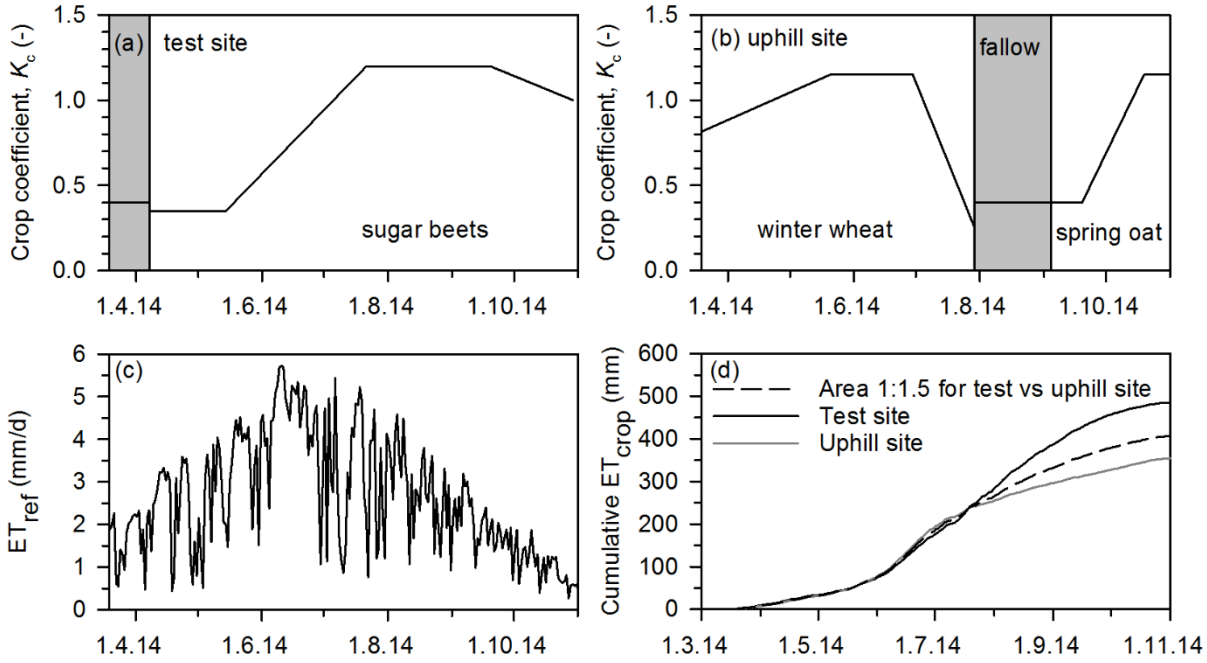

Figure S2. *Temporal dynamics of the crop coefficients, K_c, for (a) the test site cropped with sugar beets and for (b) the uphill site, (c) the reference potential evapotranspiration, ET_{ref}, and (d) the cumulative amount of the potential crop evapotranspiration, ET_{crop}.*

The reference potential evaporation, ET_{ref} (mm/d), was calculated for a well-watered, short grass cover with an albedo of 0.23 using the Penman-Monteith combination equation (Figure S2c). The evapotranspiration for a crop under standard conditions, ET_{crop} (mm/d), is calculated as $\boldsymbol{K}_c ET_{ref}$, amounting to 485 and 354 mm for the test site (sugar beets) and the uphill site, respectively (Figure S2d). The drainage water sampler sampled water from both the test site cropped with the sugar beets and the uphill site. Figure S2d also shows the cumulative reference evapotranspiration for the

case that the drainage-relevant area of the uphill site is by a factor of 1.5 larger than the drainage-relevant area for the test site (total drainage area 2600 m^2).

4 Pesticide application procedure

The pesticide application strategy during the sugar beet growing season in 2014 is given in Table S2. None of the target substances were detected (<LOD) in drainage water samples just before seeding of the sugar beets. The treated and pilled sugar beet seeds of the varieties Ribera (Syngenta, Dielsdorf, Switzerland) and Amalia (KWS Einbeck, Germany) were sown at 2 cm depth in alternating rows (50 cm rows, 18 cm interplant distance) on March 19, 2014. The Ribera and Amalia seeds were treated with the neonicotinoids thiamethoxam and imidacloprid, respectively. In addition, all sugar beet pills also contained the fungicides thiram and hymexazol. The Ribera seeds were also treated with the insecticide tefluthrin. S-metolachlor was sprayed as a pre-emergence herbicide on March 21. The herbicides metamitron, ethofumesate, phenmedipham and desmedipham were applied on April 15 and June 3 for weed control. The fungicides kresoxim-methyl, epoxiconazole and fenpropimorph were applied on July 17.

Table S2. *Pesticide application procedure during the cultivation of the sugar beets.*

Name [a]	Class[b]	Mode of application[c]	Date of application in 2014	Applied amount [g ha^{-1}]	Analyzed (drainage/plant)
Imidacloprid	I	SD	March 19	50	yes/yes
Thiamethoxam	I	SD	March 19	33.4	yes/yes
Thiram	F	SD	March 19	45	no/no
Hymexazol	F	SD	March 19	200	no/no
Tefluthrin	I	SD	March 19	45	no/no
S-metolachlor	H	S	March 21	450	yes/no
Metamitron	H	S	April 15, June 3	1050/1050	no/no
Ethofumesate	H	S	April 15, June 3	172.5/172.5	no/no
Phenmedipham	H	S	April 15, June 3	125.5/125.5	no/no
Desmedipham	H	S	April 15, June 3	22.5/22.5	no/no
Kresoxim-methyl	F	S	July 17	125	yes/no
Fenpropimorph	F	S	July 17	3000	no/no
Epoxiconazole	F	S	July 17	225	yes/no

[a] Bold: target substances analyzed in the drainage water samples;
[b] I = insecticide; F = fungicide; H = herbicide;
[c] S = spraying; SD = seed dressing;

5 Analysis of the drainage water samples

5.1 Chemicals

Ammonium acetate (LC-MS ultra grade), formic acid (LC-MS ultra grade) and neonicotinoid standards (clothianidin, D_3-clothianidin, imidacloprid, D_4-imidacloprid, thiamethoxam, D_3-thiamethoxam) were purchased from Sigma-Aldrich (Buchs, Switzerland). Metolachlor and D_6-tebuconazole were obtained from Dr. Ehrenstorfer (Augsburg, Germany). $^{13}C_6$-metolachlor was purchased from Cambridge Isotope Laboratories (Tewksbury, USA). Kresoxim-methyl acid was purchased from Toronto Research Chemicals (TRC, Toronto, Canada). Epoxiconazole and dimoxystrobin were obtained from BASF (Basel, Switzerland). Potassium bromide (99%) was delivered from Alfa Aesar (Heysham, United Kingdom). Methanol, acetonitrile and ethyl acetate were HPLC grade from Scharlau (Sentmenat, Spain). Water was purified before use with a Milli-Q Gradient A10 apparatus from Millipore (Molsheim, France).

5.2 Analysis of bromide

Bromide was analysed by ion chromatography with a limit of detection (LOD) of 0.014 mg/L and a limit of quantification (LOQ) of 0.027 mg/L.

5.3 Analysis of neonicotinoids

The drainage water samples (400 mL) were filtered over glass fiber filters MN 85/90 BF 55mm (Macherey-Nagel, Oensingen, Switzerland), weighed and poured into a 1 L conical shoulder bottle. After addition of deuterated internal standards (50 µL) containing D3-clothianidin, D4-imidacloprid, and D3-thiamethoxam (concentration of each substance, 0.8 mg/L), the bottle was swivelled gently. Bond Elut Plexa solid phase extraction cartridges (200 mg, 6 mL; Agilent, Santa Clara, CA) were preconditioned with 4 mL methanol, 4 mL water/methanol 50:50 (v:v) and 4 mL water, consecutively. After percolating the sample over the cartridge (total percolation time, 2 h), the solid phase was washed with 5 mL water and the remaining water was removed by the aid of vacuum for 5 minutes. The analytes were eluted with 4 mL ethyl acetate, which at the beginning had to be forced into the resin with a slight overpressure, collected in a conical reaction vial (Supelco, Bellefonte, PA) and reduced to dryness under a gentle stream of compressed air at 45°C. After addition of 400 µL water/methanol 80:20 (v:v) into the reaction vial and vortexing (15 secs), the extract was transferred into an autosampler vial and ready to analyze.

Analytical separation of the extracted analytes was performed by high performance liquid chromatography on a ProStar HPLC system (Varian, Walnut Creek, CA) using a Ultra Aromax column (50 x 2.1 mm, 3 µm, Restek, Bellefonte, PA) with eluents A: water / methanol 95:5 (v:v) and B: water / methanol 5:95 (v:v). Both eluents contained 3 mM ammonium acetate and 3 mM formic acid. Over a stainless steel loop 20 µL extract was injected by a constant flow rate of 0.2 mL/min with the following gradient: 0 min 35% B, 1.5 min 35 % B, 9 min 80% B, 9.25 min 100% B, 11.75 min 100% B, 12.00 min 35% B, 15.0 min 35% B. Detection of the analytes was made on a Varian 1200L mass spectrometer (Walnut Creek, CA) in electrospray positive ion mode by multiple reaction monitoring. Instrument settings and mass transitions for analytes and deuterated internal standards are listed in Table S3.

Table S3: *Settings of the Varian 1200L mass spectrometer.*

Mass spectrometer		
Main gas	5.8 bar	
Drying gas	1.24 bar, 200°C	
Nebulizing gas	3.0 bar	
ESI needle	4000 V	
Detector	1500 V	
Analytes	**Mass transition (collision energy)**	
Clothianidin	249.9 → 131.9 (-12eV)	Qualifier
	249.9 → 168.9 (-9eV)	Quantifier
D_3-Clothianidin	253.0 → 131.8 (-12eV)	Qualifier
	253.0 → 172.0 (-9eV)	Quantifier
Thiamethoxam	292.0 → 131.8 (-18eV)	Qualifier
	292.0 → 213.9 (-9eV)	Quantifier
D_3-Thiamethoxam	295.0 → 131.8 (-18eV)	Qualifier
	295.0 → 213.9 (-9eV)	Quantifier
Imidacloprid	256.0 → 175.0 (-15eV)	Qualifier
	256.0 → 209.0 (-12eV)	Quantifier
D_4-Imidacloprid	260.0 → 178.9 (-15eV)	Qualifier
	260.0 → 213.0 (-12eV)	Quantifier

Detector response was linear from 1 to 500 ng/L. Results from recovery experiments with spiked (analyte and internal standard) drainage water samples are listed in Table S4.

Table S4: *Quality control parameters for method and instrument.*

	Unit	Clothianidin	Thiamethoxam	Imidacloprid
Ion suppression [a]	%	26	24	19
Absolute recovery [b]	%	97	95	97
Relative recovery [c]	%	102	103	102
Method precision (n=5) [d]	%	3 – 8	2 – 4	3 – 7
Instrument precision (n=5) [e]	%	2 – 3	3	3 – 4
Breakthrough SPE analyte [f]	%	0.5 – 2.8	0.7 – 2.9	0
Breakthrough SPE internal standard [f]	%	0.7 – 2.7	1.5 – 3.9	0
Limit of detection (ng/L)	ng/L	0.4	0.2	0.1
Limit of quantification (ng/L)	ng/L	1.4	0.7	0.5

[a] Ion suppression: Ratio of the slopes of the respective calibration curves with matrix matched standard and standard in purified water;
[b] Absolute recovery: Ratio of the slopes of the respective calibration curves of analyte spiked before solid phase extraction (SPE) and matrix matched standard;
[c] Relative recovery: Ratio of the slopes of the respective calibration curves of the analyte and internal standard spiked before SPE and the curve matrix matched standard (analyte and internal standard);
[d] Method precision (relative standard deviation for multiple extraction and analysis of the same sample), given a range with highest and lowest precision for measurements at 25 ng/L, 250 ng/L, and 500 ng/L. The evaluation included the internal standard;
[e] Instrument precision (relative standard deviation for multiple analyses of the same extract, low: 25 ng/L, medium: 250 ng/L, high: 500 ng/L). The evaluation included the internal standard;
[f] Breakthrough SPE: extraction of samples from 400 to 1000 ng/L over two SPE cartridges stacked one on top of the other and with subsequent elution and quantification of each single cartridge. Breakthrough values were obtained as recovery values of the analyte in the second cartridge;
[g] Limit of detection: signal to noise is 3 to 1;
[h] Limit of quantification: signal to noise is 10 to 1 in mass transition used for quantification.

The stability of the analytes in drainage water samples was tested in ISCO plastic bottles (1L) and in green glass bottles (1 L) at refrigerator temperatures (4°C) and field conditions (5 up to 55°C). Slow degradation and/or sorption (imidacloprid: 5%, thiamethoxam: 11%) or production (clothianidin: 2%) were observed in the plastic bottles after storage of 14 days under field conditions, whereas the analytes remained stable in glass bottles at 4°C for at least 21 days. Based on these results, drainage samples were decanted at the field site into glass bottles usually within three days after collection. They were stored at 4°C and were processed within two weeks.

5.4 Analysis of S-metolachlor and fungicides

To analyze S-metolachlor, kresoxim-methyl, kresoxim-methyl acid and epoxiconazole, filtered drainage water samples (9 mL) were transferred to 10-mL autosampler vials and spiked with an internal standard solution (50 µL of a methanolic solution containing 40 ng/mL $^{13}C_6$-metolachlor, D_6-tebuconazole, dimoxystrobin). The analytes were separated on a Gemini NX RP18 column (2 x 150 mm, 5 µm, Phenomenex, Torrance,

CA) using a HPLC 1100 Series system (binary pump, micro-vacuum degasser from Agilent, Palo Alto, CA) and a HTS PAL autosampler (CTC Analytics, Zwingen, Switzerland). 1 mL of sample was injected and transferred with an auxiliary HPLC pump (Jasco PU-980, Omnilab, Mettmenstetten, Switzerland) to a pre-column cartridge (2 stacked Gemini NX securityGuard cartridges; 3 x 4 mm; particle size, 5 µm; Phenomenex, Torrance, CA). The analytes were then eluted from the cartridge pre-column to the analytical column by the flow from the gradient HPLC pump. The HPLC conditions were as follows: eluent flow rate, 0.2 mL/min, eluent A, purified water containing 0.1% formic acid; eluent B, methanol containing 0.1% formic acid; gradient elution 0 min 10% B, 1 min 60% B, 11 min 100% B, 14 min 100% B, 14.5 min 10% B, 20 min 10% B. The HPLC column was connected to an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with a turbo ion spray (TIS) source operated in positive ion mode (ion spray voltage, 4.5 kV, 550°C) and multiple reaction monitoring (MRM) with the ion transitions listed in Table S5.

The LOD (signal to noise ratio of all ion transitions > 3) and LOQ (S:N of quantifier mass transition > 10) were 1 resp. 2 ng/L for S-metolachlor, 1 resp. 3 ng/L for epoxiconazole, 5 resp. 10 ng/L for kresoxim-methyl, and 2 resp. 7 ng/L for kresoxim-methyl acid.

Table S5: *MRM mass transitions and corresponding instrument settings used for quantification and confirmation of S-metolachlor and fungicides and the corresponding internal standards on the API 4000 mass spectrometer.*

Analytes	Retention time (min)	Mass transition	Collision Energy	Declustering Potential	
Metolachlor	9.9	284.1 → 252.1	22	40	Quantifier
		284.1 → 176.1	36	40	Qualifier
$^{13}C_6$-Metolachlor (IS)	9.9	290.1 → 258.2	22	40	Quantifier
		290.1 → 182.1	36	40	Qualifier
Kresoxim-methyl	10.4	314.1 → 116.0	17	55	Quantifier
		314.1 → 235.2	19	55	Qualifier
Kresoxim-methyl acid	10.7	300.1 → 116.0	30	40	Quantifier
		300.1 → 192.2	10	40	Qualifier
Dimoxystrobin (IS)	10.3	327.2 → 205.1	15	57	Quantifier
		327.2 → 116.0	30	57	Qualifier
Epoxiconazole	9.8	330.1 → 121.1	30	61	Quantifier
		330.1 → 100.9	70	61	Qualifier
D_6-Tebuconazole (IS)	10.6	314.1 → 72.0	49	59	Quantifier
		314.1 → 125.0	51	59	Qualifier

6 Plant uptake of the neonicotinoids and bromide

6.1 Neonicotinoids

Randomly chosen sugar beet plants were collected on May 9 and June 17 (1 plant of Ribera and Amalia variety), July 9 (2 × Amalia), July 18 (1 × Ribera), and August 20 (1 × Amalia). The Ribera variety was treated with thiamethoxam and Amalia with imidacloprid. After collection, the plants were stored at −18°C in the freezer for 24 hours and subsequently homogenized in a Knife-Mill GM200 (Retsch, Haan, Germany) as an entire plant (May 9 and June 17) or leaves and root tuber separately (other dates). The samples were processed by a QuEChERS method described in Lehotay et al.[4] The resulting extracts were evaporated to complete dryness, dissolved in 400 µL of water/methanol 80:20 (v:v), and analysed in quadruplicates by liquid chromatography tandem mass spectrometry.

6.2 Bromide

Sugar beet plants were collected on June 17 (2×3 plants), July 9 (2×1 plant), July 18 (1 plant), August 20 (1 plant), and October 2 (2×1 plant) for the bromide analysis. The plant samples were divided into leaves and root tuber and either chopped with a knife (June 17 and October 2 samples), or blended with a food processor. The plant samples were stored at −18 °C. Upon analysis, the samples were thawed and oven-dried at 60°C during 69 hours. Bromide was extracted from the plants following the method described by Kohler et al.[1] as follows. The oven-dried plant materials were ground and a subsample (1 g) was shaken in a trichloroacetic acid solution (0.5%). The extracts were then filtered, diluted with distilled water (tenfold) and analyzed for bromide by ion chromatography.

6.3 Neonicotinoid and bromide uptake by sugar beet plants

Figure S3a−c shows the mass recovery of the neonicotinoids in the whole sugar beet plant (root and leaves) 51, 90, 112/120 and 154 days after sowing. Mass recoveries for all substances were calculated from the measured (averaged) content in one plant and the known number of seeds sown on the experimental field (55600 per ha for the varieties Ribera and Amalia each). For clothianidin, the recovery was calculated from the applied rate of thiamethoxam with a conversion for molar mass.

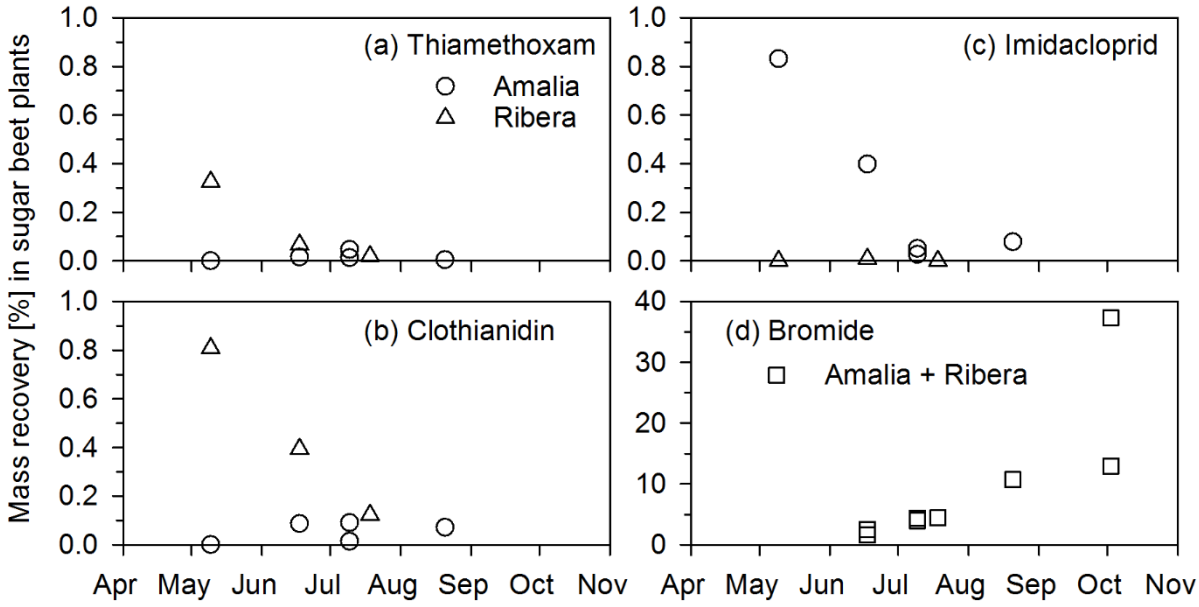

Figure S3. *Mass recovery in the sugar beet plant for (a) thiamethoxam, (b) its metabolite clothianidin, expressed as thiamethoxam equivalents, (c) imidacloprid, and (d) bromide. The sugar beet variety Amalia was treated with imidacloprid and Ribera with thiamethoxam.*

Based on the measured concentrations, the plants were only a minor sink for neonicotinoids with respect to the total mass applied to the field, showing mass recoveries < 1% from day 51 after seeding onwards. However, it should be noted that actual uptake might be higher, depending on the impact of plant metabolism. The absolute content of thiamethoxam (max. 2.0 μg per plant) and clothianidin (max. 4.2 μg per plant) in the variety Ribera and imidacloprid (max. 7.5 μg per plant) in the variety Amalia declined during this time. The variety Ribera, which is treated with thiamethoxam, predominantly accumulated its main metabolite clothianidin. It remained unclear, whether clothianidin was mainly taken up by the roots or was metabolized in the plants.

In the beginning, the plants accumulated only the neonicotinoid from their own seeds. However, low amounts of thiamethoxam (max. 0.094 μg per plant) and clothianidin (max. 0.45 μg per plant) were detected with time in the variety Amalia and imidacloprid in the variety Ribera (max. 0.077 μg per plant) due to the lateral displacement of the substances and steadily growing roots. This clearly showed that sugar beet plants were able to extract soil water containing neonicotinoids, which were released half a meter away.

Table S6. *Mass recoveries with standard error of the mean where applicable for the different substance applied to the experimental fields in 2014 relative to the applied mass on the drainage-relevant, cropped area.*

		Mass recoveries [%] for each sampling date in 2014					
		May 9	**June 17**	**July 9**	**July 18**	**Aug 20**	**Oct 2**
Imidacloprid	Plant	0.831	0.380	–	n.a.	–	n.a.
(Amalia)	Leaves	–	–	0.019±0.008	n.a.	0.030	n.a.
	Tuber	–	–	0.020±0.005	n.a.	0.048	n.a.
Thiamethoxam	Plant	0.326	0.067	n.a.	–	n.a.	n.a.
(Ribera)	Leaves	–	–	n.a.	0.010	n.a.	n.a.
	Tuber	–	–	n.a.	0.010	n.a.	n.a.
Clothianidin	Plant	0.809	0.394	n.a.	–	n.a.	n.a.
(Ribera)	Leaves	–	–	n.a.	0.096	n.a.	n.a.
	Tuber	–	–	n.a.	0.028	n.a.	n.a.
Bromide	Leaves	n.a.	1.80±0.34	4.10±0.27	4.4	10.7	24.2±11.2
	Tuber	n.a.	0.35±0.12	0.08±0.08	< 0.27 [b]	< 0.77 [b]	1.0±1.0

[a] n.a. = not analysed;
[b] Bromide concentration in the extract was below the limit of detection.

Bromide uptake by plants is a well-documented process.[5] In our trial, the mass recovery of bromide in the sugar beet plants increased from 2% of the applied amount on June 17 to 25% on October 2 (Table S6). Bromide accumulated primarily in the leaves. We did not analyze bromide in the plants at harvest, but an extrapolation using a second-order polynomial fitted to measurements resulted in an estimated uptake of 37%. This is somewhat lower than the bromide recovery of 50% in the sugar beet plants found by Kohler et al.[1] upon harvest, who had applied the bromide much earlier (August 23, 1995) than the sowing of the sugar beets (March 30, 1996) in their trial.

7 Temporal dynamics of the concentrations in the drainage water

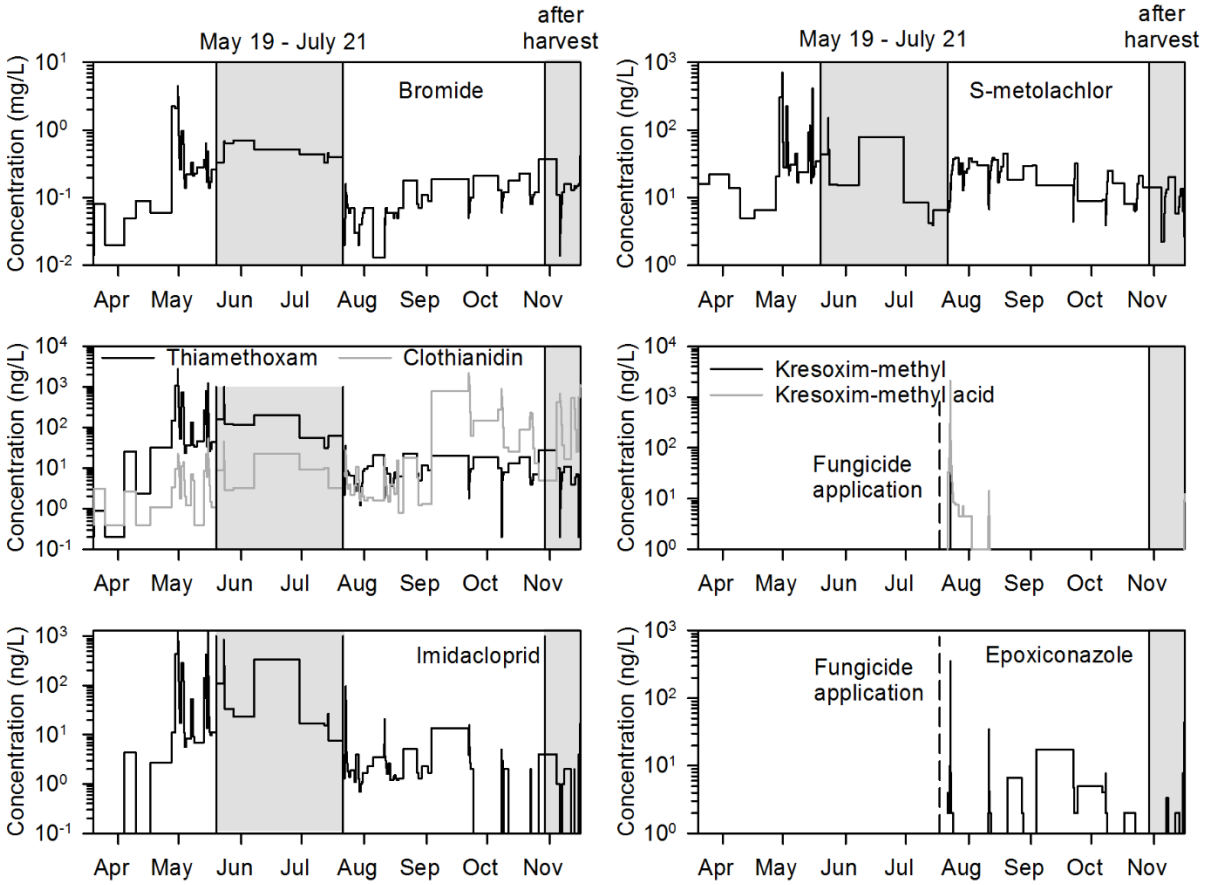

Figure S4. *Breakthrough curves to the tile drains as a function of time of the water tracer bromide, the neonicotinoids thiamethoxam, including its major metabolite clothianidin, and imidacloprid, the herbicide S-metolachlor, and the fungicides epoxiconazole and kresoxim-methyl, including its major metabolite kresoxim-methyl acid for the period from March 19 to November 16, 2014*.

8 Correlations between concentrations in the drainage water

High peak concentrations were measured in the drainage water for bromide and all active substances from March 19 to July 21, with much lower concentrations afterwards. Figures S5 and S6 show the correlations between the log_{10}-transformed concentrations, C_w, in the drainage water of the target substances for the high and low concentration period, respectively.

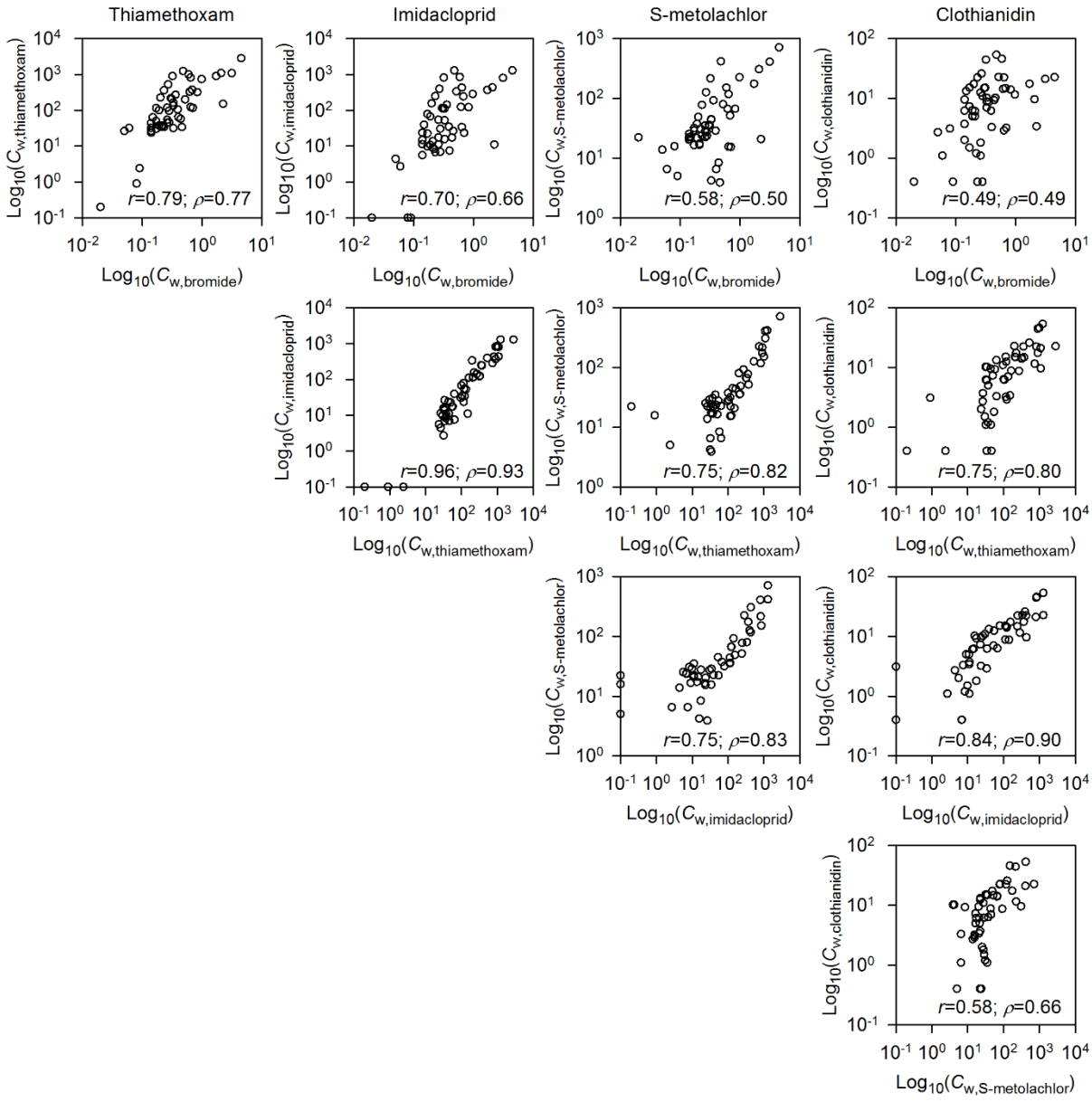

Figure S5. *Correlations between the log_{10}-transformed concentrations, C_w, in the drainage water of the various substances for the high concentration period between March 19 and July 21, expressed by Pearson's correlation coefficient, r, and the Spearman's rank order correlation coefficient, ρ. All coefficients showed a statistically significant relationship between the two variables ($p<0.001$). Bromide concentration is expressed in mg/L, other substances in ng/L.*

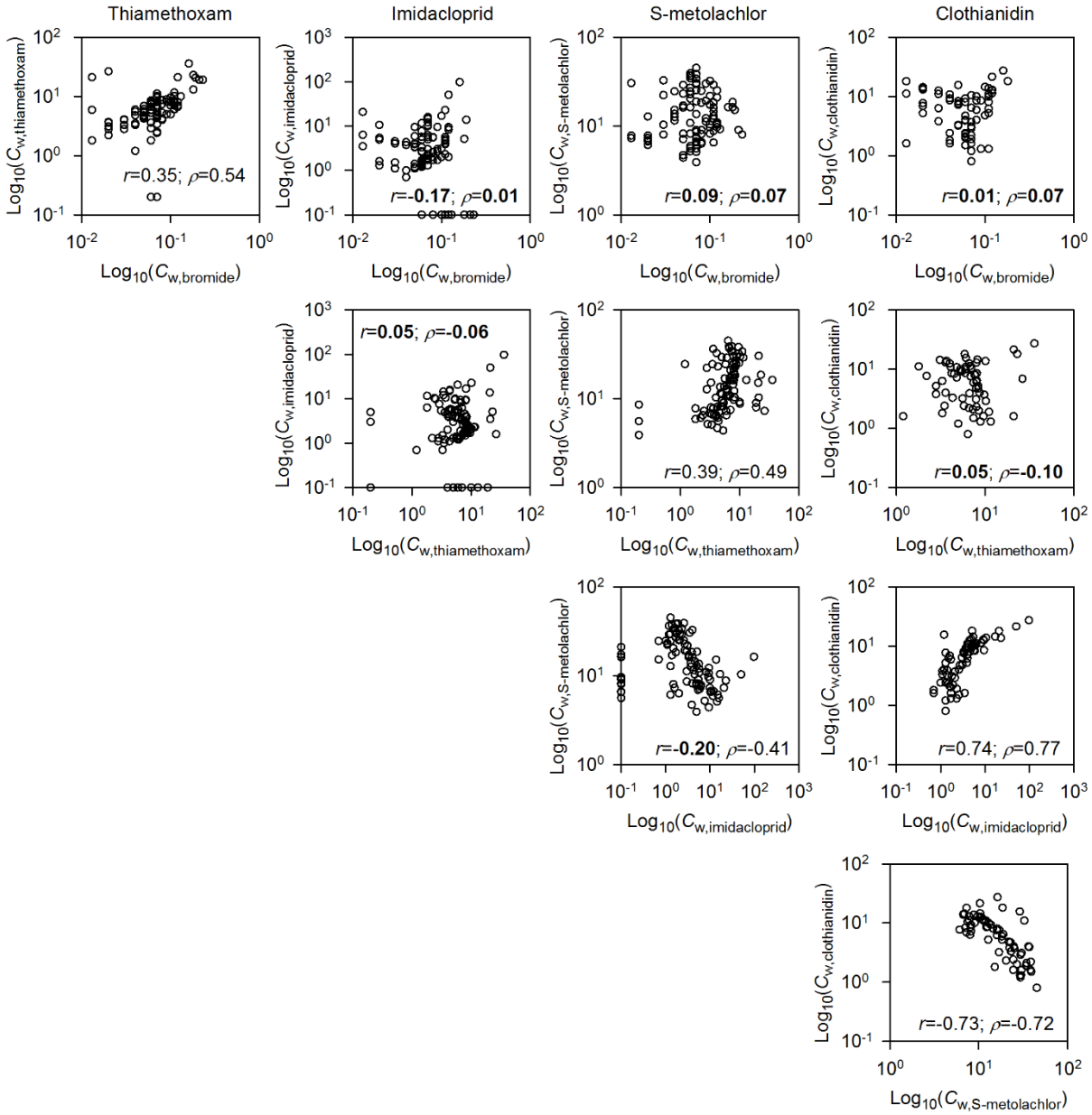

Figure S6. *Correlations between the log_{10}-transformed concentrations, C_w, in the drainage water of the various substances for the low concentration period between July 22 and October 29 (harvest), expressed by the Pearson's correlation coefficient, r, and the Spearman's rank order correlation coefficient, ρ. The coefficients in bold showed no statistically significant relationship between the two variables (p>0.05). Note that for clothianidin only measurements up to September 3 were considered, which were unaffected by sowing of spring oat with a clothianidin dressing. Bromide concentration is expressed in mg/L, other substances in ng/L.*

For the high concentration period, strong positive correlations were found, especially between the active substances themselves (Pearson's correlation coefficient r = 0.75−0.96; Spearman's correlation coefficient ρ = 0.82−0.93) and to a lesser extent between bromide and the organic substances (r = 0.49−0.79; ρ = 0.49−0.77). Note that Pearson's linear correlation coefficient is more sensitive to

outliers, such as concentrations < LOD, than Spearman's rank correlation coefficient. A likely explanation for the lower correlations between bromide and the organic substances is the much higher mobility of bromide.

The correlations between the concentrations deteriorated for the low concentration period, starting on July 22. No statistically significant correlations were found for this period, except for weak correlations between thiamethoxam and both bromide and S-metolachlor, and except for a moderate positive and negative correlation between the metabolite clothianidine and both imidacloprid (r = 0.74; ρ = 0.77) and S-metolachlor (r = −0.73; ρ = −0.72), respectively.

9 Concentration-dependent mobility

In the following, an instantaneous partitioning of a pesticide between the soil solution and the solid phase is assumed, which can be described by the Freundlich sorption isotherm $C_s = K_F C_w^{1/n}$, where C_s (µg/g) and C_w (µg/mL) are the concentration in the solid and liquid phase, respectively, K_F (µg$^{1-1/n}$mL$^{1/n}$/g) is a distribution coefficient, and 1/*n* (-) is the Freundlich exponent. Then, the retardation of a pesticide can be expressed as $R = 1 + \frac{\rho_b}{\theta}\frac{1}{n}K_F C_w^{\frac{1}{n}-1}$, where R (-) is the retardation factor of a pesticide relative to the movement of water, ρ_b (g/cm^3) is the bulk density of the soil, and θ (cm^3/cm^3) is the volumetric water content. Thus, the retardation factor, and consequently mobility, is concentration-dependent and *R* increases with decreasing concentration in the liquid phase. The mass balance equation of a pesticide in a volume of soil is given by $C_t = \rho_b C_s + \theta C_w$, where C_t (µg/mL) is the total pesticide mass per volume of soil. After application, the local concentration in this volume of soil decreases by dilution and degradation.

To assess the effect of sorption nonlinearity on mobility, the retardation factor was calculated for the situation that the pesticide was homogeneously applied to the upper 1 cm of the soil profile. The unknown concentration in the liquid phase was iteratively calculated by solving the mass balance equation for given compound properties (K_F and 1/*n*) and soil properties (ρ_b=1.5 g/cm^3, θ=0.25 cm^3/cm^3, C_{org}=2%). The compound properties were $K_{F,OC}$=189 µg$^{1-1/n}$mL$^{1/n}$/g and 1/*n*=0.89 for S-metolachlor[6, 7], $K_{F,OC}$=225 µg$^{1-1/n}$mL$^{1/n}$/g and 1/*n*=0.80 for imidacloprid,[8] and $K_{F,OC}$=68 µg$^{1-1/n}$mL$^{1/n}$/g and 1/*n*=0.88 for thiamethoxam[6, 9], where $K_{F,OC} = K_F/f_{oc}$ is the Freundlich distribution coefficient normalized to the fraction of the soil`s total organic carbon content, f_{OC} (-). The results for an areal spray application are listed in Table S7.

Table S7. *Retardation factors of the herbicide S-metolachlor and the neonicotinoids imidacloprid and thiamethoxan for an areal application. The values are presented for the actual application rate and for a tenfold dilution.*

Compound	Rate	Areal application rate			Areal application rate × 0.1		
		C_t	C_w	*R*	C_t	C_w	*R*
	(g/ha)	(µg/cm^3)	(µg/cm^3)	(-)	(µg/cm^3)	(µg/cm^3)	(-)
S-metolachlor	450	4.50	0.7359	21.9	0.450	0.05600	28.7
Imidacloprid	50	0.50	0.0377	42.6	0.050	0.00214	74.8
Thiamethoxam	33.4	0.334	0.1154	10.3	0.0334	0.00866	13.7

Only a moderate increase in the retardation factor is estimated for S-metolachlor after a tenfold dilution (R=38 after a hundredfold dilution). The results for a spray application of the neonicotinoids is given for reasons of comparison. The largest increase in the retardation factor for imidacloprid after dilution is caused by the highest degree of sorption nonlinearity (lowest 1/n-value).

The results for a seed treatment are listed in Table S8. The expected, much higher local concentrations resulted in lower retardation factors compared to a spray application. It is, of course, unlikely that the entire neonicotinoid mass in one seed will be available for transport in a soil volume of 1cm^3. However, these calculations provide a range of retardation factors and show that an enhanced mobility is to be expected in the bulk soil (soil matrix), when the neonicotinoids are applied as seed dressings compared to a spray application. The effect is again more pronounced for imidacloprid, with the larger sorption nonlinearity (lower 1/n value).

Table S8. *Retardation factors of the neonicotinoids imidacloprid and thiamethoxan for a seed treatment. The values are presented for the mass in one seed in a soil volume of 1 mL and for a tenfold dilution.*

Compound	Mass	Soil volume of 1 cm^3			Soil volume of 1 cm^3, tenfold dilution		
		C_t	C_w	R	C_t	C_w	R
	(μg/seed)	(μg/cm^3)	(μg/cm^3)	(-)	(μg/cm^3)	(μg/cm^3)	(-)
Imidacloprid	450	450	168.5	8.7	45	9.976	14.6
Thiamethoxam	300	300	228.5	4.7	30	17.70	6.1

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