Text S1:

Quality assurance and quality controls of the measurement of pesticides and their transformation products

Full analytical method description and analytical instrumentation

Preparation of environmental samples (approx. 1 liter) was done by filtering with a folded filter (type 113 P Cellulose ø 240 mm). Supernatant was spiked with the internal standard Diuron-D6 (10 µl of 10 mg L-1). Extraction procedure was a solid phase extraction (SPE). Cartridges (CHROMABOND® HR-X 6 mL/200 mg) were conditioned with 10 mL methanol and washed with 10 mL pure water. Environmental samples were enriched on the cartridges via teflon capillary and a vacuum extraction unit. After enrichment of the samples, cartridges were washed with 5 mL pure water and air dried for about 5-10 minutes. Elution was done with a solvent mixture of methanol and chloroform (v/v; 1:1). The eluted phase was dried with nitrogen to dryness and 200 µl acetonitrile was added. 90 µL of the extract were spiked with 10 µl of Terbutryn-D5 as an internal standard. Each sample was a double determination. Measurements of environmental samples were conducted with a Triple Quadrupole (Agilent Technologies, 1200 Infinity LC-System and 6430 Triple Quad, Waldbronn, Germany).

LC-MS/MS gradient program and analytical instrumentation settings are depicted in table 1 and 2.

Table 1: Gradient Program.

Time (min)	H_2O (0.01 % FA) [%]	ACN [%]	Flow (mL/min)	Oven temperature (°C)	Injection volume [µL]
0	90	10	0.4	30	5
1	90	10	0.4	30	5
11	50	50	0.4	30	5
18	15	85	0.4	30	5
21	10	90	0.4	30	5
24	10	90	0.4	30	5
26	90	10	0.4	30	5
30	90	10	0.4	30	5

Table 2: List of MS/MS transitions (SRM#1 and SRM#2) with corresponding retention times (RT). Substances were analyzed in positive (+) or negative (-) ESI ionization mode (ESI-mode). Internal standard Diuron-D6 was analyzed in both modes (+/-).

	ESI-mode	SRM#1	SRM#2	RT (min)
Fungicides				
Boscalid	+	343.1 → 307.1	343.1 → 140	11.8
Penconazole	+	284.1 → 70.1	284.1 → 159	13.0
Herbicides				
Metazachlor	+	278.1 → 134.1	278.1 → 210.1	10.6
Flufenacet	+	364.1 → 152.0	364.1 → 194.1	12.9
Transformation products				
Metazachlor-ESA	-	324.1 → 69	324.1 → 134.1	2.1
Metazachlor-OA	-	274.1 → 134.0	274.1 → 162.0	2.8
Internal Standard				
Diuron-D6	+/-	239.1 → 78.1	239.1 → 52.1	5.3
Terbutryn-D5	+	247.2 → 191.1	247.2 → 69.0	11.0

Quality assurance and quality control

To enable the assurance and control of the quality of the used method following parameters were evaluated:

Linearity:

Calibration curve were prepared in pure water. The linearity was evaluated by preparing three curves with ten calibration points in the range 1 - 500 µg/L. The standard curves were then extracted according to the protocol and analyzed using LC-MS/MS. The calculated linear regression values (R^2) are shown in table 3. The linearity was very good with R2-values > 0.999.

LOD/LOQ:

The linearity between peak area and concentration of substances were obtained in a range of 0 - 5 µg L^{-1}. Hence limits of detection (LOD) and quantitation (LOQ) were calculated with DINTEST (2003) according to DIN 32645 considering an enrichment factor of 5000. In general, LOD are below 1 ng L^{-1}.

Table 3: Evaluation of the calibration curve of substances.

	Linearity (R^2)	LOD [ng/L]	LOQ [ng/L]
Fungicides			
Boscalid	0.9995	0.37	1.31
Penconazole	0.9994	0.27	0.94
Herbicides			
Metazachlor	0.9997	0.33	1.22
Flufenacet	0.9992	0.35	1.27
Transformation products			
Metazachlor-ESA	0.9996	0.63	2.21
Metazachlor-OA	0.9990	0.47	1.64

Precision:

Measuring precision was evaluated by analyzing one sample at three different time points at concentrations of 500 ng L^{-1} (measuring precision). It reveals variations initiated by the device. Although measuring precision was good for all substances (table 3), we added the internal standard Terbutryn-D5 to eliminate any variation. Method precision reveals random variations of the results. To evaluate the method precision, methodological procedure was implemented three times. Method precision was good for the initial substances, but not for the transformation products which could be explained by the general low recovery. Although the received method precision was good for most of the substances, we implemented a double determination of each sampling point. Eight of them were evaluated and are depicted in table 4. The precision of the double determinations was good with some exceptions (e.g. Metazachlor-ESA).

Table 4: Evaluation of the precision of the measurement and the method.

	Measuring precision [%] n=3	**Method precision [%] n = 3**	**Double determination [%] n=8**
Fungicides			
Boscalid	0.05	12.8	5.9
Penconazole	0.13	6.4	9.3
Herbicides			

Metazachlor	0.26	9.2	5.3
Flufenacet	0.09	7.9	14.9
Transformation products			
Metazachlor-ESA	0.82	39.5	33.5
Metazachlor-OA	0.59	32.2	16.3

Recovery:

For the determination of the recovery of the substances, water samples were spiked with the substances to a final concentration of 200 ng/L. It was analyzed according to the previously described procedure. The experiment was carried out in triplicate. The recoveries were good for the initial substances but not for the transformation products (table 5): Metazachlor-ESA, Metazachlor-OA showed low recoveries in a range of 25-55%.

Carry-over effect:

The carry-over effect was evaluated by analyzing the peak area of blanc samples that were analyzed a few times within the measurement of one sampling campaign. The results reveal that the substances had less than 0.2 % carry-over. One water blank was also injected after each standard curve and after each double sample to avoid carry-over from standards.

Table 1: Recoveries and carry-over effects of the analyzed substances.

	Recovery [%]	**Carry-over effect [%]**
Fungicides		
Penconazole	89.6	0.02
Boscalid	84.3	0.04
Herbicides		
Metazachlor	85.1	0.02
Flufenacet	79.5	0.01
Transformation products		
Metazachlor-ESA	55.0	0.15
Metazachlor-OA	45.2	0.01