Degradation and leaching of bentazone, terbuthylazine and S-metolachlor and some of their metabolites: A long-term lysimeter experiment

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Abstract: The degradation and leaching of bentazone, terbuthylazine and S-metolachlor and their metabolites N-methyl-bentazone, desethyl-terbuthylazine, 2-hydroxy-terbuthylazine, metolachlor ethane sulfonic acid (ESA) and metolachlor oxanilic acid (OA) were investigated using the plant protection products Artett (bentazone/terbuthylazine), Gardo Gold (S-metolachlor/terbuthylazine) and Dual Gold (S-metolachlor) applied to a weighable, monolithic, high precision lysimeter with a loamy, sandy soil. Artett and Gardo Gold were applied at higher doses than recommended according to good agricultural practice. In leachate, S-metolachlor was detected at concentrations of up to 0.15 μg/L, whereas metolachlor-ESA and metolachlor-OA were present at higher concentrations of up to 37 μg/L and 8.4 μg/L, respectively. In a second terbuthylazine application, concentrations of desethyl-terbuthylazine of up to 0.1 μg/L were detected. In soil, bentazone degraded faster than terbuthylazine and S-metolachlor, whereas the metabolization of terbuthylazine after the second application resulted in an enhanced formation of desethyl-terbuthylazine and a highly increased hydroxylation of terbuthylazine. The importance of analysing both parent compounds and metabolites on a long-term scale was demonstrated to better understand the environmental fate and transport.

Keywords: agriculture; herbicide; contamination; metabolism

The use of pesticides to increase agricultural production continues to be an important topic for environmental research. Once applied to the field, pesticides can be degraded by the influence of physical, chemical and biological factors, volatilized, adsorbed by soil colloids and transported through surface runoff and leaching. The transport of pesticides is influenced by the water movement (e.g., infiltration, plant uptake, drainage) and the interaction with the soil matrix (e.g., organic matter, clay content, iron oxides) (Arias-Estévez et al. 2008).

Bentazone, terbuthylazine, and S-metolachlor are important herbicides applied to maize and other crops to control pre-emergence or early post-emergence broadleaf and grass weeds. These herbicides are often used in combination to enhance the herbicidal effect. They transform the environment to form corresponding metabolites such as N-methyl-bentazone, desethyl-terbuthylazine, 2-hydroxy-terbuthylazine, metolachlor ethane sulfonic acid (ESA) and -oxanilic acid (OA). Due to their solubility and mobility, residues of these parent compounds and their metabo-

lites have been detected in surface and groundwater, in some cases at concentrations higher than the European drinking water limit of 0.1 µg/L (Guzzella et al. 2003, Loos et al. 2010, BMLFUW 2013).

Bentazone, terbuthylazine and S-metolachlor and thus their metabolites have different chemical properties (Table 1) linked to different soil sorption and degradation processes. Bentazone poses an environmental risk because of its high mobility and susceptibility to leaching from soil to groundwater (Boesten and Van der Pas 2000, Li et al. 2003). The most stable metabolite of bentazone in the soil is N-methyl-bentazone, which is very prone to microbially-mediated degradation (Wagner et al. 1996). Terbuthylazine became a commonly used triazine herbicide in Austria. Microbial degradation of triazines proceeds mainly via dealkylation, hydroxylation and ring cleavage of the parent compound. Dealkylated products of terbuthylazine can be considered hazardous contaminants for groundwater pollution because they are generally more persistent and water soluble than the parent compound (Gerstl et al. 1997). On the other hand, hydroxylated compounds are characterized by low water solubility and are therefore considered less important potential contaminants for groundwater (Guzzella et al. 2003). The chloroacetanilide herbicide S-metolachlor transforms into the prominent metabolites metolachlor-ESA and metolachlor-OA which are well-known groundwater contaminates. In Austria (BMG 2014) and Germany (Umweltbundesamt 2015), both metabolites are classified as 'non-relevant' metabolites with a threshold value of 3 µg/L in groundwater. 'Non-relevant' metabolites (EC 2003) are either not specifically regulated, or diverse threshold values are applied among EU member states.

The pesticides used in this study are among those used extensively in Austrian agriculture. Due to the lack of long-term degradation experiments, a field-based lysimeter study of three to five years of local agricultural practices was conducted. The fate of bentazone, terbuthylazine and S-metolachlor and the occurrence of their metabolites in leachate and soil at different depths were investigated. The aim was to identify and quantify degradation and migration.

MATERIAL AND METHODS

Experimental site and pesticide application. The experiment was conducted using a weighable, monolithic lysimeter (1 m² surface area, 2 m depth) built in 2004 at the agricultural test site in Wagna (Styria, Austria). The lysimeter could be tilled with

Table 1. Physico-chemical properties based on the pesticide property database (Lewis et al. 2016)

Compound	Bentazone	Bentazone-methyl	Terbuthylazine	Terbuthylazine-desethyl	Terbuthylazine-2-hydroxy	S-Metolachlor	Metolachlor-ESA	Metolachlor-OA
CAS number	25057-89-0	61592-45-8	5915-41-3	30125-63-4	66753-07-9	87392-12-9	171118-09-5	152019-73-3
Molar mass (g/mol)	240.28	254.31	229.71	201.68	211.33	283.79	329.41	279.33
Chemical formula	$C_{10}H_{12}N_2O_3S$	$C_{11}H_{14}N_2O_3S$	$C_9H_{16}ClN_5$	$C_7H_{12}ClN_5$	$C_9H_{17}N_5O$	$C_{15}H_{22}ClNO_2$	$C_{15}H_{23}NO_5S$	$C_{15}H_{21}NO_4$
Solubility in water at 20°C (mg/L)	570	na	6.6	327	7.2	480	212 461	238
Dissociation constant (pK_a)	3.5	na	1.9	na	na	3.1	na	na
Octanol-water partition coefficient (log K_{ow})	0.77	na	3.4	2.3	1.5[a]	na	–1.9	na
Freundlich K_{foc}	60	258	231	78	187	226	na	7.3
DT_{50} in the field (days)	8.0	na	22	29	na	21	70[b]	128

na – not available; [a]Kaune et al. (1998); [b]Bayless et al. (2008); ESA – ethane sulfonic acid; OA – oxanilic acid

Table 2. Soil characteristics of the lysimeter

Depth (cm)	Clay	Silt	Sand	Gravel	Carbon content	Dry bulk density (kg/m³)	pH
			(%)				
0–30	20	33	45	2	1.10	1510	6.3
30–50	20	27	53	0	0.52	1550	6.5
50–80	14	24	62	0	0.35	1550	6.6
80–130	0	1.0	33	66	< 0.08	na	6.8
> 130	0	1.0	25	74	< 0.08	na	7.1

na – not available (1500 kg/m³ assumed)

agricultural machines (e.g., a plough) during which the upper ring of the lysimeter was removed. Leachate was collected at a depth of 180 cm by seven suction cups (total surface 3600 cm^2), which were controlled by a vacuum pump operated to mimic matrix potentials measured next to the lysimeter at a depth of 180 cm. The lysimeter setup has been repeatedly described in detail (Klammler and Fank 2014, Schuhmann et al. 2016, Kupfersberger et al. 2018). The lysimeter was located within a test plot of 1000 m^2 area, which was cultivated with a crop rotation consisting of maize (2010, 2012, 2014), triticale (2011, 2015) and pumpkin (2013). After the crop vegetation periods, typical catch crops were cultivated (ryegrass or forage rye). Soil tillage was done by plough and harrow in early spring and early autumn. Since 2014 the plough has been replaced by ripper to reduce the soil surface treatment. Details about the soil characteristics are given in Table 2.

Since the initial scientific question of the experiment intended to avoid direct pesticide uptake via the leaves

to measure the uptake from the soil into maize (data not available), the maize plants were covered with plastic bags during the pesticide applications in 2010 and 2012. The plastic bags were removed immediately after the application without a wash-off (artificially or by precipitation) of pesticide residues from the plastic bags. Details about the applications are given in Table 3. All plant protection products were applied as suspensions onto the field including the monolithic lysimeter. The applications in 2010 and 2012 were performed using a hand-held spraying apparatus, whereas mechanical sprayers were used in 2013 and 2014. Also, higher pesticide doses than normal in agriculture were used for the applications in 2010 and 2012. The field area chosen for the application ensured an even distribution of the pesticide on the lysimeter surface. All experiments were performed under natural weather conditions without additional irrigation. Precipitation was measured by a meteorological station located at the test site. Table 4 shows the annual amounts of precipitation, evapotranspiration, and leachate from the lysimeter.

Quantification of residues in leachate and soil. Leachate from the lysimeter at depths of 35, 90 and 180 cm were collected by suction cups at an average sampling interval of 10 days. The samples were stored at –18°C and analyzed by direct injection-liquid chromatography-electrospray ionization-tandem mass spectrometry after the addition of an internal standard (bentazone-d$_6$, terbuthylazine-d$_5$, desethyl-terbuthylazine-d$_9$, metolachlor-d$_6$) described in Fuhrmann et al. (2014).

Soil samples at depths of 0–30 cm were taken from the lysimeter surface before the herbicide applications in 2010 and 2012. Immediately after the

Table 3. Details of the pesticide applications at the lysimeter surface

Date	Crop	Formulation	Active ingredients (a.i.)	Application form	Growth stage at time of application	Application dose (kg a.i./ha)
April 28, 2009*	pumpkin	Dual Gold	S-metolachlor (960 g/L)	pre-emergence	no crop cover	2.4
May 12, 2010	maize	Artett	bentazone (150 g/L)/ terbuthylazine 150 g/L	post-emergence	3- to 4-leaf stage	2.7/2.7
May 24, 2012	maize	Gardo Gold	S-metolachlor (312.5 g/L)/ terbuthylazine (187.5 g/L)	post-emergence	6- to 7-leaf stage	3.5/2.1
May 12, 2013	pumpkin	Dual Gold	S-metolachlor (960 g/L)	pre-emergence	no crop cover	1.2
May 10, 2014	maize	Dual Gold	S-metolachlor (960 g/L)	post-emergence	7-leaf stage	0.96

*The first application of Dual Gold in 2009 was done by a local farmer before the start of the project

Table 4. Annual amounts of precipitation (P), real evapotranspiration (ET_r) and leachate (L) together with the annual mean concentrations of S-metolachlor, metolachlor-ESA, and metolachlor-OA from April 2012 to June 2015

Year	Crop	P	ET_r	L	S-Metolachlor	Metolachlor-ESA	Metolachlor-OA
		(mm)			(µg/L)		
2010	maize	1014	599	429			
2011	triticale	730	736	63			
2012	maize	1000	685	325	0.0070	6.4	0.19
2013	pumpkin	952	529	479	0.0019	4.5	0.54
2014	maize	1171	598	561	0.0085	17	1.7
2015	triticale	864	721	88*	0.012	16	0.041

*until June 2015; ESA – ethane sulfonic acid; OA – oxanilic acid

applications, soil samples were taken at a depth of 0–10 cm. The sampling was repeated 12, 30, 80, 150 (in 2010), 476 (in 2011) and 743 (in 2012) days after the application of bentazone and terbuthylazine on May 12, 2010, and 12, 30, 80 and 150 days after the application of S-metolachlor and terbuthylazine on May 24, 2012. Details about the soil sampling procedure are given in Schuhmann et al. (2016). Soil samples were extracted with a modified QuEChERS method specified in Fuhrmann et al. (2014), and the resulting extracts were quantified according to the liquid chromatography-mass spectrometry methods described in Fuhrmann et al. (2014) and Schuhmann et al. (2016).

Estimation of half-life from measured soil residues. The half-life of pesticides belongs together with the sorption coefficient and the Freundlich exponent to the parameters which mainly control degradation and leaching. The DT_{50} (half-life of degradation) values of bentazone, S-metolachlor and terbuthylazine were estimated from the total mass (measured pesticide concentrations multiplied by soil bulk density) in the soil profile between 0–30 cm depth, assuming the first-order degradation according to FOCUS (2006). The initial mass of terbuthylazine and S-metolachlor on day 0 (directly after the application) was calculated from the application amount because the measured data was lower on day 0 compared to day 12. Losses due to leaching or plant uptake were not considered in these simplified estimations.

RESULTS AND DISCUSSION

Leachate. The annual leachate volume varied between 63 mm in 2011 to 561 mm in 2014 (Table 4), which was mainly a consequence of annual precipitation because no additional irrigation was applied. Recently, Klaus et al. (2014) and Meite et al. (2018)

have shown that precipitation characteristics have an important role in pesticide leaching. The experimental duration of 5-years comprised both leaching and non-leaching periods. Almost no leachate was observed during certain periods, especially from June 2011 to mid-May 2012 (in total 10 mm) and from August to October 2013 (in total 0.5 mm) (Figure 1).

Bentazone and terbuthylazine, as well as their metabolites N-methyl-bentazone and 2-hydroxy-terbuthylazine, were not detected, and only traces of the metabolite desethyl-terbuthylazine were found. This might be because low leachate volumes in June (5.4 mm), July (4.4 mm) and August (17 mm) were observed after the application in 2010 and 2-hydroxy-terbuthylazine is a lipophilic compound that is rarely detectable in water samples (Guzzella et al. 2003). After the second application of terbuthylazine in May 2012, the metabolite desethyl-terbuthylazine was detected more frequently at concentrations ranging from 0.055 µg/L to 0.1 µg/L at 180 cm of depth, with the highest concentrations occurring in October and December 2012. It has been reported that repeated application reduces the formation of bound residues and accelerates the rate of metabolite formation (Gevao et al. 2000).

At depths of 35 cm and 90 cm, S-metolachlor was not detected from May 2012 to May 2015. Due to the fact that S-metolachlor was already detected at a depth of 180 cm in April 2012 (0.029 µg/L), which was before the application of S-metolachlor in 2012, the detected concentrations of S-metolachlor in 2012, 2013 and 2014 (Figure 1) seem to originate mainly from the S-metolachlor application in 2009. High precipitation events in 2009 (1360 mm) which led to the rapid translocation of S-metolachlor and dry periods in 2010 and 2011 which decreased the effective degradation rate in the subsoil might be respon-
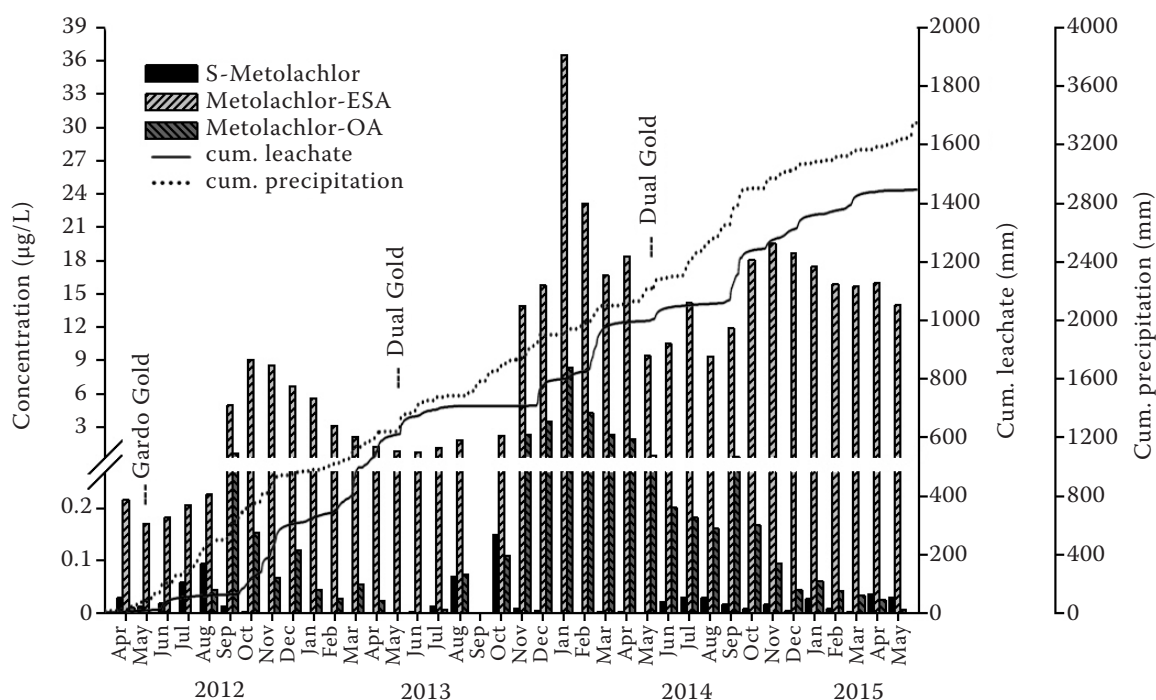
Figure 1. Average concentrations per month of S-metolachlor, metolachlor-ESA (ethane sulfonic acid), and metolachlor-OA (oxanilic acid) in the leachate at the bottom of the lysimeter (180 cm depth) after repeated annual applications together with the cumulative precipitation and the cumulative leachate; no leachate was produced in September 2013. The scale on left *y*-axis has been disrupted for better visibility of low concentrations

sible. Kahl et al. (2014) also stated that substances located in the subsoil could remain there for a very long time and being degraded or leached a long time later. Mean monthly S-metolachlor concentrations were – with one exception in October 2013 – generally lower than 0.1 μg/L (Figure 1). Over the entire investigation period from May 2012 to May 2015, the cumulative leached load of S-metolachlor (8.0 μg) at 180 cm depth was very little in comparison to loads of metolachlor-ESA (15 360 μg) and metolachlor-OA (1300 μg).

Metolachlor-ESA had also already been detected with a background concentration of 0.22 μg/L in the leachate before the S-metolachlor application in May 2012 (Figure 1). Within six months after this application, metolachlor-ESA concentrations in the leachate increased up to 9.1 μg/L in October 2012, followed by a decline to 0.76 μg/L by June 2013. After the S-metolachlor application in 2013, the metolachlor-ESA concentration rose to 37 μg/L in January 2014, which was the maximum value measured during the investigation period. Afterward, the concentrations of metolachlor-ESA dropped to 9.4 μg/L in May 2014 and increased again af-

ter the third application to 20 μg/L in November 2014. In May 2015 a mean concentration of 14 μg/L metolachlor-ESA was still detected in the leachate. Traces of metolachlor-OA initially appeared in August 2012 and reached a relative maximum of 0.64 μg/L in September 2012 (Figure 1). After that peak, the metolachlor-OA concentrations decreased until no metolachlor-OA could be detected between May and June 2013. The highest metolachlor-OA concentration (8.4 μg/L) was detected in January 2014 – eight months after the S-metolachlor application in May 2013. Metolachlor-OA declined to 0.16 μg/L in August 2014 and increased again to 0.29 μg/L in September 2014, after which only traces were detected in leachate.

At a depth of 35 cm, the detected concentrations of both metabolites rapidly increased after each application. The highest concentrations of metolachlor-ESA were detected in September 2014 (52 μg/L), whereas metolachlor-OA showed the greatest measured concentrations in July 2012 (24 μg/L). At a depth of 90 cm, metolachlor-ESA showed a behavior similar to that seen at 35 cm, but concentrations were in general approximately 50% lower with the highest

Table 5. Mean and standard deviation values (µg/kg) of extractable bentazone, N-methyl-bentazone, terbuthylazine, desethyl-terbuthylazine and 2-hydroxy-terbuthylazine on different sampling days at varying soil depths (0–10, 10–20 and 20–30 cm) from 2010 to 2012. The sampling at 10–20 cm depth was initiated on day 12 after the application and at depths of 20–30 cm on day 30 after the application

Day of sampling/ date	Bentazone			N-methyl-bentazone		
	0–10	10–20	20–30	0–10	10–20	20–30
0 (May 12, 2010)*	230 ± 72	–	–	0.65 ± 0.13	–	–
12 (May 24, 2010)	61 ± 23	31 ± 17	–	3.7 ± 1.0	2.5 ± 1.4	–
30 (Jun 14, 2010)	8.3 ± 7.7	1.2 ± 0.38	0.90 ± 0.50	3.1 ± 2.3	0.32 ± 0.14	0.60 ± 0.29
80 (Aug 8, 2010)	1.7 ± 0.39	0.55 ± 0.065	0.19 ± 0.028	3.0 ± 0.95	0.30 ± 0.13	0.16 ± 0.074
150 (Oct 11, 2010)	0.12 ± 0.013	0.21 ± 0.029	0.40 ± 0.16	nd	nd	0.26 ± 0.11
476 (Aug 31, 2011)	0.079 ± 0.042	0.11 ± 0.021	–	nd	nd	–
743 (May 24, 2012)	nd	nd	nd	nd	nd	nd

Day of sampling/ date	Terbuthylazine (TA)			Desethyl-TA			2-hydroxy-TA		
	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30
0 (May 12, 2010)*	38 ± 12	–	–	0.28 ± 0.062	–	–	98 ± 26	–	–
12 (May 24, 2010)	240 ± 88	100 ± 34	–	8.7 ± 2.6	4.2 ± 1.2	–	130 ± 39	58 ± 21	–
30 (Jun 14, 2010)	76 ± 2.9	5.2 ± 4.9	23 ± 3.4	7.4 ± 4.4	0.61 ± 0.32	1.5 ± 0.38	180 ± 160	6.8 ± 5.6	23 ± 3.3
80 (Aug 8, 2010)	26 ± 11	3.1 ± 2.5	0.56 ± 0.45	5.4 ± 1.2	1.1 ± 0.38	0.34 ± 0.071	120 ± 44	13 ± 10	3.3 ± 2.0
150 (Oct 11, 2010)	0.67 ± 0.17	1.8 ± 0.52	3.5 ± 0.20	0.41 ± 0.052	1.3 ± 0.13	1.6 ± 0.12	3.9 ± 0.58	9.3 ± 1.8	20 ± 1.7
476 (Aug 31, 2011)	0.45 ± 0.17	1.3 ± 0.33	–	0.26 ± 0.0049	0.53 ± 0.12	–	2.3 ± 0.67	4.9 ± 0.34	–
743 (May 24, 2012)	0.47 ± 0.35	0.51 ± 0.22	0.50 ± 0.23	0.30 ± 0.097	0.27 ± 0.018	nd	1.6 ± 0.46	2.7 ± 1.6	2.8 ± 0.41

*The sampling on day 0 was immediately after application; – – samples were not taken at these days; *n* = 3; nd – not detected

peak in November 2014 (27 µg/L). The concentrations of metolachlor-OA declined between 35 cm and 90 cm of depth. Because only traces of metolachlor-OA were detected at a depth of 90 cm, it can be assumed that the degradation of metolachlor-OA after the applications in 2012 and 2014 occurred between depths of 35 cm and 90 cm.

Soil. The applied pesticides were not detected in the soil samples taken before the applications in 2010 and 2012. As expected, after the applications the concentrations of bentazone, terbuthylazine and S-metolachlor and their metabolites were highest in the soil surface layer of the lysimeter (Tables 5 and 6) and decreased until 30 cm, confirming the increase of degradation with time. The application in 2010 and 2012 was performed post-emergence with a handheld spraying apparatus, and the maize plants were covered with plastic bags. The low concentrations on day 0 and the higher findings on day 12 can be explained by interception of the applied pesticides on the plastic bags. Because the plastic bags also covered parts of the lysimeter surface (1 m^2), it can

Table 6. Mean and standard deviation values (µg/kg) of extractable S-metolachlor, metolachlor-ESA (ethane sulfonic acid) and metolachlor-OA (oxanilic acid) on different sampling days at varying soil depths (0–10, 10–20 and 20–30 cm) from 2012. The sampling at a depth of 10–20 cm was initiated on day 12 after the application and at depths of 20–30 cm on day 30 after the application

Day of sampling/ date	S-Metolachlor (MET)			MET-ESA			MET-OA		
	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30
0 (May 24, 2012)*	510 ± 180	–	–	5.5 ± 0.81	–	–	6.2 ± 1.6	–	–
12 (Jun 5, 2012)	600 ± 110	11 ± 2.4	–	26 ± 7.8	0.91 ± 0.19	–	33 ± 4.6	0.8 ± 0.27	–
30 (Jun 22, 2012)	270 ± 110	120 ± 94	12 ± 6.0	21 ± 11	15 ± 12	3.4 ± 0.89	27 ± 17	17 ± 11	2.2 ± 0.36
80 (Aug 13, 2012)	63 ± 33	4.6 ± 3.7	1.9 ± 0.56	76 ± 14	62 ± 13	41 ± 15	69 ± 20	16 ± 5.4	12 ± 6.9
150 (Oct 23, 2012)	12 ± 4.2	3.3 ± 1.3	1.5 ± 0.46	6.0 ± 0.77	5.1 ± 0.78	5.1 ± 1.2	4.9 ± 0.89	2.1 ± 0.37	1.2 ± 0.34
	Terbuthylazine (TA)			Desethyl-TA			2-hydroxy-TA		
	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30
0 (May 24, 2012)*	150 ± 50	–	–	1.0 ± 0.29	–	–	190 ± 69	–	–
12 (Jun 5, 2012)	300 ± 45	3.7 ± 0.58	–	30 ± 6.8	1.0 ± 0.45	–	230 ± 54	6.2 ± 0.88	–
30 (Jun 22, 2012)	170 ± 34	68 ± 36	5.7 ± 1.5	20 ± 4.8	9.0 ± 3.8	1.3 ± 0.61	93 ± 25	46 ± 30	6.4 ± 1.7
80 (Aug 13, 2012)	77 ± 27	8.8 ± 8.5	2.9 ± 1.4	18 ± 4.6	3.0 ± 1.7	1.1 ± 0.58	31 ± 9.3	7.1 ± 3.7	5.3 ± 0.27
150 (Oct 23, 2012)	16 ± 1.2	6.5 ± 1.6	1.8 ± 0.36	4.7 ± 0.74	3.2 ± 0.32	1.3 ± 0.30	12 ± 1.6	6.6 ± 1.2	4.5 ± 0.45

*The sampling on day 0 was immediately after application; – – samples were not taken at these days; *n* = 3

be assumed that non-representative samples were collected on day 0. The plastic bags were removed immediately after application before soil samples were taken randomly from six different locations within the lysimeter surface. Thus, the applied pesticide mass on the plastic bags that might have reached to the soil after a wash-off was lost in 2010 and 2012.

The concentrations of bentazone (230 µg/kg) steadily decreased following the application in 2010 until two years later on day 743 no residues were detected. The metabolite N-methyl-bentazone was detected immediately following the application in the top soil (0.65 µg/kg). No residues of N-methyl-bentazone were left at soil depths of 0–10 cm and 10–20 cm after day 80. At 20–30 cm, residues of bentazone and its metabolite N-methyl-bentazone were only detected on days 30, 80 and 150 (i.e., in the year of the application). Within the topsoil, there can be significant within-field spatial variability in pesticide degradation rates, associated with variation

in soil properties controlling degradation processes or the localization of specific pesticide-degrading microbial populations in the topsoil (Walker et al. 2001). Although the application rate of bentazone and terbuthylazine in 2010 was the same, a rise of the soil residue concentration of terbuthylazine (240 µg/kg) was observed on day 12. 2-hydroxy-terbuthylazine (180 µg/kg) was detected at concentrations much higher than those of desethyl-terbuthylazine (8.7 µg/kg). The concentrations of terbuthylazine, desethyl-terbuthylazine and 2-hydroxy-terbuthylazine were still detectable at 0.47, 0.30 and 1.6 µg/kg, respectively, on day 743. At 10–20 cm, the high concentration of terbuthylazine (100 µg/kg) on day 12 rapidly decreased to 5.2 µg/kg by day 30. On day 743, 0.51 µg/kg of terbuthylazine remained in the soil. The highest concentrations of desethyl-terbuthylazine and 2-hydroxy-terbuthylazine were detected on day 12 (4.2 µg/kg and 58 µg/kg). At 20–30 cm, the concentration of terbuthylazine (23 µg/kg) detected

on day 30 finally decreased to 0.50 µg/kg by day 743. After a decline until day 80, the concentrations of both metabolites increased again to 1.6 µg/kg and 20 µg/kg by day 150. On day 743, only 2-hydroxy-terbuthylazine remained in the soil.

Day 743 (May 24, 2012) was the same day as the application (day 0) of S-metolachlor and terbuthylazine. The highest concentration of terbuthylazine (310 µg/kg) was again detected on day 12. On day 150, 16 µg/kg of terbuthylazine remained in the topsoil. High concentrations of 2-hydroxy-terbuthylazine were already found on day 0 (190 µg/kg). At 10–20 cm, the highest concentration of terbuthylazine (68 µg/kg) was detected on day 30. Peak concentrations of desethyl-terbuthylazine and 2-hydroxy-terbuthylazine were also detected on day 30. At 20–30 cm, a terbuthylazine concentration of 5.7 µg/kg was detected on day 30, with levels falling gradually from then on to 1.8 µg/kg by day 150. On day 30, 80 and 150, similar concentrations of the metabolite desethyl-terbuthylazine were measured. Residues of 2-hydroxy-terbuthylazine slightly decreased from 6.4 µg/kg on day 30 to 4.5 µg/kg on day 150.

After the application on May 24, 2012, the concentrations of S-metolachlor peaked on day 12 and then decreased gradually. On day 150, 12 µg/kg of S-metolachlor remained in the topsoil. The metabolites metolachlor-ESA and metolachlor-OA were detected immediately after the application. The concentrations of both have reached their maximum (76 µg/kg and 69 µg/kg, respectively) on day 80. At 10–20 cm, the high concentration of S-metolachlor (120 µg/kg) on day 30 rapidly decreased to 4.6 µg/kg by day 80. Except metolachlor-OA at a depth of 10–20 cm (17 µg/kg on day 30), both metabolites peaked on day 80 in each soil depth. In comparison, higher concentrations of metolachlor-ESA were detected. At 20–30 cm, an S-metolachlor concentration of 12 µg/kg was detected 30 days after the application. Similar concentrations (1.9 µg/kg and 1.5 µg/kg) of S-metolachlor were recorded on days 80 and 150, respectively. Peak concentrations of metolachlor-ESA (41 µg/kg) and metolachlor-OA (12 µg/kg) were detected on day 80.

Bentazone, terbuthylazine, and S-metolachlor showed varying degradation rates. The concentrations of bentazone detected in the soil were generally lower than the concentrations of terbuthylazine. Fitting sum-up residues from 0–30 cm soil depth to the first order decay model resulted in estimated DT_{50} values of 17 and 25 days for bentazone and terbuthylazine,

respectively. According to the estimated DT_{50} values, 26 and 37 days for S-metolachlor and terbuthylazine in 2012, S-metolachlor was mineralized faster than terbuthylazine. These calculated half-lives are apart from bentazone within the range of values in the literature (Table 1; Lewis et al. 2016). Whereas, most of the reported DT_{50} values in literature were normalized to standard conditions.

In conclusion, bentazone, terbuthylazine, N-methyl-bentazone, and 2-hydroxy-terbuthylazine were not detected in leachate. Desethyl-terbuthylazine was found more frequently and at higher concentrations in leachate after the repeated application of terbuthylazine. In contrast to the leachate, where only desethyl-terbuthylazine was detected, 2-hydroxy-terbuthylazine was the predominant metabolite found in soil. While metolachlor-ESA was transported to a depth of 180 cm, metolachlor-OA was mainly degraded at depths of between 35 cm and 90 cm. S-metolachlor residues remained at depths of 0–35 cm after applications in 2012, 2013 and 2014 and were not translocated into deeper soil layers. The S-metolachlor concentrations detected between 2012 and 2014 originated from a previous S-metolachlor application in 2009, which can be explained by a high precipitation rate followed by dry periods in 2010 and 2011.

Acknowledgment

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