Non-invasive method to measure dermal exposure of amphibians to pesticides

Detlef Schenke[1], Jan Sadowski[2], Alexandra Esther[2]

https://doi.org/10.5073/20201029-143153

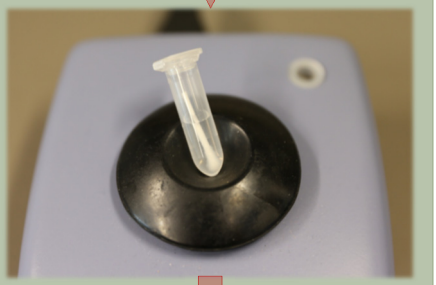
Julius Kühn-Institut
Federal Research Centre for Cultivated Plants

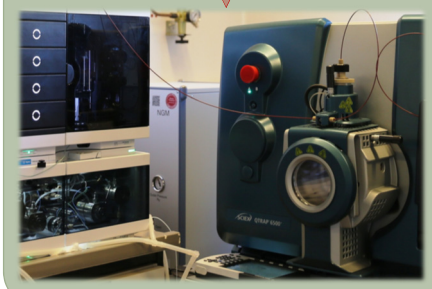
Background

Pesticide exposure of amphibians is difficult to assess due to the various possible exposure routes and the movement behavior between aquatic and terrestrial habitats (EFSA, 2018). In particular, little is known about the dermal uptake of pesticides in field, which appears to be very important for amphibian's exposure risk and survival (Quaranta et al., 2009; Llewelyn et al., 2019). We used swab samples to measure pesticides on the skin of amphibians which possibly originate from contact to contaminated soil, sediment, water, plants or air.

Material and Methods

We investigated adult amphibians, nine common toads (*Bufo bufo*) and one common frog (*Rana temporaria*), which were trapped in and around maize fields in North Rhine-Westphalia (Germany) in summer 2018. About 10 cm² of the ventral and the dorsal side of each animal were swabbed separately using individual sterile Dryswab™ with fine tip rayon buds.
The selection of pesticides based on a proposal for a representative monitoring in the framework of the "Implementation of the National Action Plan on the sustainable use of pesticides" (UBA, 2019).The substances were extracted with a solution of water/methanol (1:1, 1% formic acid) from the swabs. The amounts were measured with liquid and gas chromatography-mass spectrometry. (see supplement for methodical details).





Results

We detected terbuthylazine in samples of three animals (Tab.1). The highest amount of 75 pg /cm² was found on the ventral side of a toad. This amount corresponds to 0.001% of the maximum application rate permitted for maize fields.

Tab. 1: Content of terbuthylazine found in swab samples from five amphibians (all in stage >46 (Gosner, 1960) trapped in and around the same field (n. d. = not detected < 5 pg/cm²).

				Terbuthylazine [pg/cm²]	
No	**Sampling**	**Habitat**	**Species**	**ventral**	**dorsal**
1	26-06-18	Maize field (edge)	Common toad	**75.0**	n. d.
2	04-07-18	Roadside	Common toad	**57.8**	n. d.
5	10-07-18	Maize field	Common frog	**11.5**	**9.2**

Discussion

The detection of terbuthylazine in swab samples from animals in and around maize fields is an expression of the spatio-temporal behaviour of amphibians. The high values at the ventral sides originate possibly from contact of the individuals with residues on the ground after herbicide application.
Plant protection products containing terbuthylazine may be used in the pre- and post-emergence (BBCH 10-17) of maize with maximal 750 g/ha (BVL, 2018). The products contain further herbicidal active substances (i.e. bentazone, bromoxynil, dimethenamid-P, flufenacet and ethoxamid) which were not detected in the samples.

Perspectives

The method allows exposure assessment with an exact spatio-temporal resolution by non-invasive sampling of living amphibians at field sites. This is not possible by analysis of road-killed amphibian (Schenke et al., 2017). Method optimization and evaluation is necessary regarding the selection of other swab bud materials for analysis of other interesting substances.
The relations between environmental concentrations and measured pesticide on the swab bud as well as effects on animals are mostly unknown and requires further efforts.

We thank B. Große, G. Smykalla, Ch. Reichmann, I. Stachewicz-Voigt and S. Weißenberg for analyses and layout of this poster, respectively.

BVL 2018: Pflanzenschutzmittel- Verzeichnis 2018, Teil 1 Ackerbau – Wiesen und Weiden Hopfenbau – Nichtkulturland, 66. Auflage 2018, ISSN 0178-059X.
EFSA, 2018: Scientific Opinion on the state of the science on pesticide risk assessment for amphibians and reptiles. https://efsa.onlinelibrary.wiley.com/doi/pdf/10.2903/j.efsa.2018.5125
Gosner K.L., 1960: A simplified table for staging anuran embryos and larvae with notes on identification. Herpetologica, 16, 183–190.
Llewelyn et al., 2019: Effects of skin region and relative lipophilicity on percutaneous absorption in the toad *Rhinella marina*. Environmental Toxicology and Chemistry 38 (2) 361-367.
Quaranta et al., 2009: Why amphibians are more sensitive than mammals to xenobiotics. PLoS ONE, 4, e7699.
Schenke et al., 2017: Analysis of pesticides in road-killed amphibians. 16th International Conference on Chemistry and the Environment, ICCE 2017. DOI 10.5073/jki.poster.2017.001.
UBA, 2019: Umsetzung des Nationalen Aktionsplans zur nachhaltigen Anwendung von Pestiziden – Teil 2. Texte 08/2019, ISSN 1862-4804.

31st SETAC Europe Annual Meeting,
Virtual Conference, 3rd – 6th May 2021

[1] JKI; Institute for Ecological Chemistry, Plant Analysis and Stored Product Protection, Königin-Luise-Str. 19, D-14195 Berlin
[2] JKI; Institute for Plant Protection in Horticulture and Forests, Vertebrate Research, Toppheideweg 88, D-48161 Münster
detlef.schenke@julius-kuehn.de
www.julius-kuehn.de

Non-invasive method to measure the dermal exposure of amphibians to pesticides

Detlef Schenke[1)], Jan Sadowski[2)], Alexandra Esther[2)]

[1)] Julius Kühn-Institut, Federal Research Centre for Cultivated Plants, (JKI) - Institute for Ecological Chemistry, Plant Analysis and Stored Product Protection, Königin-Luise-Str. 19, D-14195 Berlin, [2)] Julius Kühn Institut (JKI) - Institute for Plant Protection in Horticulture and Forests, Vertebrate Research, Toppheideweg 88, D-48161 Münster

DOI 10.5073/20201029-143153

E-mail: detlef.schenke@julius-kuehn.de

Keywords: bioavailability, monitoring, pesticide, risk assessment

Pesticide exposure of amphibians is difficult to assess due to the various possible exposure routes and the movement behavior between aquatic and terrestrial habitats (EFSA, 2018). In particular, little is known about the dermal uptake of pesticides in field, which appears to be very important for amphibian's exposure risk and survival (Llewelyn et al., 2019). We have used swab samples to measure pesticides on the skin of amphibians which possibly originate from contact to contaminated soil, sediment, water, plants or air. We investigated adult amphibians, nine common toads (*Bufo bufo*) and one common frog (*Rana temporaria*), which were trapped in and around maize fields in North Rhine-Westphalia (Germany) in summer 2018. About 10 cm² of the ventral and dorsal side of each animal were swabbed separately using individual sterile Dryswab™ with fine tip rayon buds. The selection of pesticides based on a proposal for a representative monitoring in the framework of the "Implementation of the National Action Plan on the Sustainable Use of Pesticides" (UBA, 2019). The substances were extracted with a solution of water/methanol (1:1, 1% formic acid) from the swabs. The amounts were measured with liquid and gas chromatography-mass spectrometry. We detected terbuthylazine in samples of three animals. Plant protection products containing terbuthylazine may be used in the pre- and post-emergence (BBCH 10-17) of maize with maximal 750 g/ha (BVL, 2018). The highest amount of 75 pg/cm² was found on the ventral side of a toad. This amount corresponds to 0.001% of the maximum application rate permitted for maize fields. The detection of terbuthylazine in swab samples from animals in and around maize fields is an expression of the spatio-temporal behaviour of amphibians.

References

EFSA, 2018: Scientific Opinion on the state of the science on pesticide risk assessment for amphibians and reptiles. https://efsa.onlinelibrary.wiley.com/doi/pdf/10.2903/j.efsa.2018.5125.

Llewelyn et al., 2019: Effects of skin region and relative lipophilicity on percutaneous absorption in the toad *Rhinella marina*. Environmental Toxicology and Chemistry 38 (2) 361-367.

UBA, 2019: Umsetzung des Nationalen Aktionsplans zur nachhaltigen Anwendung von Pestiziden - Teil 2. Texte 08/2019, ISSN 1862-4804.

BVL, 2018: Pflanzenschutzmittel- Verzeichnis 2018, Teil 1 Ackerbau – Wiesen und Weiden Hopfenbau – Nichtkulturland, 66. Auflage 2018, ISSN 0178-059X.

SUPPLEMENT

Non-invasive method to measure the dermal exposure of amphibians to pesticides

Detlef Schenke[1)], Jan Sadowski[2)] and Alexandra Esther[2)]

31st SETAC Europe Annual Meeting,
Virtual Conference, 3rd – 6th May 2021
Poster Presentation

i) Sampling

ii) Sample processing

iii) Analyses of active ingredients

iv) Validation

i) Sampling

Tab. 1: Origin of samples

No	Date	Habitat	Species	Gender
1	26-06-18	Maize field (edge)	Common toad	Male
2	04-07-18	Roadside	Common toad	Male
3	04-07-18	Ditch	Common toad	Female
4	10-07-18	Corn field	Common toad	Female
5	10-07-18	Corn field	Common frog	Female
6	30-06-18	Maize field (edge)	Common toad	Male
7	30-06-18	Maize field (edge)	Common toad	Female
8	30-06-18	Maize field (edge)	Common toad	Female
9	30-06-18	Maize field (edge)	Common toad	Male
10	30-06-18	Maize field (edge)	Common toad	Male

ii) Sample processing

The fine tip (with rayon bud) of a Dryswab ™ placed in a 2 ml Eppendorf Safe-Lock Tube

↓

Spike with surrogates
atrazine-d_5 (50 pg) and fenpropathrin (25 ng) in 10 µL methanol

↓

Addition of 1 mL methanol/ ethyl acetate (1:1, 1% formic acid)

↓

Vortex 1 min

↓

Ultrasonic bath 15 min

↓

Remove the tip with tweezers and tap off the drops

↓

Transfer the solvent in a conical flask

↓

Repeat the process two times

↓

Evaporate the combined extracts to dryness
(Büchi Rotavapor, 37 °C bath temp.)

↓

Dissolve the extract in 500 µl internal standard solution
bifenthrin-d_6 / trans-cyfluthrin-d_6 (100 pg/µl in acetone, briefly vortex)

↓

Transfer an aliquot (200 µl) through Rotilabo-syringe filter (0.2 µm, PTFE) in a autosampler vial for GC-MSMS measurement

↓

Evaporate another aliquot (200 µl) with N_2 to dryness

↓

Dissolve the extract in 400 µl internal standard solution isoproturon-d_6 / 2,4,5-T(0.5 pg/µl in methanol /water (1:1), briefly vortex)

↓

Transfer the solution through Rotilabo-syringe filter (0.2 µm, PTFE) in a autosampler vial for LC-MSMS measurement

iii) Analysis of active ingredients

LC-MS/MS

C18

Tab. 2: Configuration of LC-MS/MS

LIQUID CHROMATOGRAPHY	**Agilent 1290 Infinity**		
Autosampler temperature	10 °C		
Injection volume	5 µL		
Analytical column	Agilent Zorbax Eclipse (1.8µm, 50 mm, 2.1 mm i.d.)		
Column temperature	40 °C		
Mobile phase A	0.5% formic acid + 5 mM ammonium format in water		
Mobile phase B	0.5% formic acid + 5 mM ammonium format in methanol		
Gradient program	Time (min)	A (%)	B (%)
	0	90	10
	3.3	10	90
	4.5	10	90
	4.6	90	10
	6	90	10
Flow rate	500 µL/min		
MASS SPECTROMETER	**QTRAP 6500+ (SCIEX)**		
Mode	positive ESI		
Ion spray potential	5.0 kV		
Source temperature	450 °C		
Scan type	Multiple Reaction Monitoring/ Enhanced Product Ion		
Dwell time	5 ms		
Software	Analyst 1.7.1		
Quantification	Relative peak area		

Standards: 0.01 – 10 pg/µl

Tab. 3: MS/MS parameters with declustering potential (DP), entrance potential (EP), collision energy (CE) and cell exit potential (CXP)

Q1	**Q3**	**Analyte**	**DP**	**EP**	**CE**	**CXP**
(m/z)			(V)			
213.2	171.0	Isoproturon D6 (IS)	46	10	19	2.5
221.1	179.1	Atrazine D5 (Surr)	21	10	25	2.5
223.1	125.9	Acetamiprid	101	10	33	8
466.0	226.9	Amisulbrom	106	10	21	26
403.9	372.0	Azoxystrobin	51	10	17	24
484.2	452.9	Chlorantraniliprole	91	10	23	20
213.1	72.0	Chlorotoluron	34	11.5	33	1.6
250.1	169.0	Clothianidin	42	10	19	12
325.1	107.9	Cyazofamid	101	10	19	10
406.1	250.9	Difenoconazole	41	9	37	3.3
395.1	266.1	Diflufenican	81	10	35	22
256.1	224.2	Dimethachlor	24	10.5	19	3
276.1	244.1	Dimethenamid-P	86	10	19	12
327.2	205.1	Dimoxystrobin	49	10	15	2.8

274.2	147.1	Fenpropidin	31	10	37	2.3
304.3	147.1	Fenpropimorph	34	11.5	39	2.3
360.0	128.9	Florasulam	21	10	31	16
364.1	194.2	Flufenacet	11	10	17	2.8
383.1	172.8	Fluopicolide	31	10	27	20
376.1	307.0	Fluquinconazole	36	10	33	26
334.2	247.2	Flurtamone	86	10	35	20
453.1	182.2	Foramsulfuron	31	9.5	27	2.6
413.0	156.0	Imazosulfuron	46	10	23	16
507.8	167.0	Iodosulfuron-methyl	71	10	25	16
360.2	244.0	Isopyrazam	56	10	31	22
504.0	182.0	Mesosulfuron-methyl	81	10	31	14
278.1	210.1	Metazachlor	18	9.5	15	2.9
226.1	169.1	Methiocarb	56	10	15	14
417.9	175.0	Metosulam	61	10	35	14
382.1	198.9	Metsulfuron-methyl	34	10.5	27	2.8
272.1	129.1	Napropamide	46	10	21	10
411.0	182.1	Nicosulfuron	41	9	25	2.6
377.1	237.9	Picolinafen	46	10	39	14
239.2	182.3	Pirimicarb	66	10	21	10
256.0	173.1	Propyzamide	39	12	31	2.5
372.9	331.0	Proquinazid	66	10	19	24
252.1	91.2	Prosulfocarb	36	10	29	1.8
420.0	141.0	Prosulfuron	76	10	27	16
388.1	194.0	Pyraclostrobin	19	7	19	2.8
413.0	339.0	Pyraflufen-ethyl	64	11.5	25	4
435.1	194.9	Pyroxsulam	51	10	35	18
284.1	251.9	S-Metolachlor	14	6	19	3.3
732.4	142.1	Spinosyn A	81	10	39	16
746.3	142.1	Spinosyn D	131	10	33	14
298.3	144.2	Spiroxamine	41	12	27	2.3
308.1	70.0	Tebuconazole	86	10	51	10
230.2	174.0	Terbuthylazine	106	10	23	54
252.8	126.0	Thiacloprid	41	10	33	8
388.0	167.0	Thifensulfuron-methyl	29	9	21	2.5
402.1	167.1	Triasulfuron	44	10	25	2.5
409.1	186.1	Trifloxystrobin	19	7.5	23	2.6
336.0	187.0	Zoxamide	36	10	31	16

C18 PS

Tab. 4: Configuration of LC-MS/MS

LIQUID CHROMATOGRAPHY	**Agilent 1290 Infinity**		
Autosampler temperature	10 °C		
Injection volume	5 µL		
Analytical column	Phenomenex Kinetex C18 PS (2.6µm, 50 mm, 2.1 mm i.d.)		
Column temperature	40 °C		
Mobile phase A	0.1% formic acid in water		
Mobile phase B	0.1% formic acid t in methanol		
Gradient program	Time (min)	A (%)	B (%)
	0	90	10
	3.3	10	90
	4.5	10	90
	4.6	90	10
	6	90	10
Flow rate	500 µL/min		
MASS SPECTROMETER	**QTRAP 6500+ (SCIEX)**		
Mode	positive ESI		
Ion spray potential	5.0 kV		
Source temperature	450 °C		
Scan type	Multiple Reaction Monitoring/ Enhanced Product Ion		
Dwell time	10 ms		
Software	Analyst 1.7.1		
Quantification	Relative peak area		

Standards: 0.01 – 10 pg/µl

Tab. 5: MS/MS parameters with declustering potential (DP), entrance potential (EP), collision energy (CE) and cell exit potential (CXP)

Q1	**Q3**	**Analyte**	**DP**	**EP**	**CE**	**CXP**
(m/z)			(V)			
213.2	171.1	Isoproturon D6 (IS)	46	10	19	2.5
265.0	182.1	Aclonifen	36	12	39	2.6
414.1	394.0	Bixafen	76	10	21	24
343.0	307.0	Boscalid	54	10	27	3.6
222.0	92.2	Chloridazon	39	10	35	1.8
350.0	96.7	Chlorpyrifos	51	10	55	11
226.1	76.9	Cyprodinil	41	12	63	1.6
188.1	160.0	Desamino-Metamitron	46	10	23	22
230.0	125.0	Dimethoate	14	10	29	2.1
388.1	301.1	Dimethomorph	41	10	27	3.6
255.0	209.1	Fluroxypyr	49	12	21	2.9
256.1	175.0	Imidacloprid	49	9	25	2.5
207.1	165.1	Isoproturon	46	10.5	19	2.5
235.1	153.1	Lenacil	34	8.5	21	2.4
203.1	175.0	Metamitron	49	12	29	2.5
324.1	134.2	Metazachlor-ESA	61	10	31	8
274.1	134.0	Metazachlor-OA	46	10	29	12
409.1	209.1	Metrafenone	39	8.5	21	2.9

215.1	187.2	Metribuzin	29	10.5	25	2.6
282.1	212.2	Pendimethalin	17	7.5	15	2.9
296.1	131.1	Pethoxamid	39	10	27	2.1
301.1	136.1	Phenmedipham	36	12	25	2.3
189.2	102.0	Propamocarb	16	10	23	1.9
342.1	69.1	Propiconazole	46	10.5	33	1.6
218.1	104.9	Pymetrozine	61	10	29	12
222.0	204.1	Quinmerac	24	10	23	2.8
307.9	162.0	Quinoxyfen	21	12	57	2.4
292.0	211.0	Thiamethoxam	34	8.5	17	2.9

Biphenyl

Tab. 6: Configuration of LC-MS/MS

LIQUID CHROMATOGRAPHY	**Agilent 1290 Infinity**		
Autosampler temperature	10 °C		
Injection volume	5 µL		
Analytical column	Phenomenex Kinetex Biphenyl (2.6µm, 50 mm, 2.1 mm i.d.)		
Column temperature	40 °C		
Mobile phase A	0.1% formic acid in water		
Mobile phase B	0.1% formic acid t in methanol		
Gradient program	Time (min)	A (%)	B (%)
	0	2	98
	3.3	98	2
	4.5	98	2
	4.6	2	98
	6	2	98
Flow rate	500 µL/min		
MASS SPECTROMETER	**QTRAP 6500+ (SCIEX)**		
Mode	negative ESI		
Ion spray potential	-4.5 kV		
Source temperature	450 °C		
Scan type	Multiple Reaction Monitoring/ Enhanced Product Ion		
Dwell time	50 ms		
Software	Analyst 1.7.1		
Quantification	Relative peak area		

Standards: 0.01 – 10 pg/µl

Tab.7: MS/MS parameters with declustering potential (DP), entrance potential (EP), collision energy (CE) and cell exit potential (CXP)

Q1	**Q3**	**Analyte**	**DP**	**EP**	**CE**	**CXP**
(m/z)			(V)			
255.0.	197.0	2.4.5 T (IS)	-65	-10	-20	-17
275.7	81.0	Bromoxynil	-60	-10	-62	-7
247.0	180.0	Fludioxonil	-35	-10	-40	-9
199.0	140.9	MCPA	-60	-10	-20	-9
213.0	140.9	Mecoprop	-65	-10	-20	-17
238.9	132.0	Bentazone	-55	-10	-36	-9
218.9	160.9	2.4 D	-45	-10	-16	-13
232.9	160.8	Dichlorprop	-50	-10	-18	-15

Tab.8: Confirmation of the analytes with MS/MS in linear ion trap mode with dynamic fill time

EPI (enhanced product ion spectra)					
Mass range	CPS	DP	EP	CE	Hit
		(V)			(%)
50 – 450 m/z	> 500	-50/+50 V	-10/+10	-30/+30 (± 15)	>80

GC-MS/MS

Tab. 9: Configuration of GC-MS/MS

GAS CHROMATOGRAPHY	**Trace GC Ultra (Thermo Scientific)**
Autosampler temperature	10 °C
Injector type	Split/Splitless
Injector temperature	210 °C
Injection technique	Splitless (0-3 min) wSurge (200 kPa, 1.5 min)
Injection volume	1 µL (sandwich, rape-spike)
Analytical column	ZB-5-plus (29.5 m, 0.25 mm i.d., 0.25 µm)
Carrier gas	He 5.0 / 1.2 ml/min (const. flow)
Column temperature	70°C (2') > 10 °C/min > 200 °C (5') > 2 °C/min > 250 °C/min (5') > 10 °C/min > 320°C (10')
MASS SPECTROMETER	**TSQ Quantum GC XLS(Thermo Scientific)**
Mode	NICI (negative ion chemical ionisation)
Reactant gas	Methane 5.5 / 3 ml/min
Source temperature	240°C
Transfer line temperature	275 °C
Collision gas	Argon 5.0 / 1.5 mTorr
Scan type	Selected Reaction Monitoring
Software	Xcalibur 3.1.66.10
Quantification	Relative peak area

Standards: 1 - 100 pg/µl

Tab. 10: MS/MS parameters

Analyte	**Q1**	**Q3**
	(m/z)	
Fenpropathrin (Surr)	141-141	141-107
Bifenthrin D6 (IS)	211-167	211-126
trans-Cyfluthrin-D6 (IS)	213-213	215-215
beta-Cyfluthrin	207-207	209-209
Cypermethrin	207-207	209-209
Esfenvalerate	211-167	213-169
lambda-Cyhalothrin	241-205	205-121
Tefluthrin	241-205	241-121

iv) Validation

Tab. 11: Recovery (n = 5) of 0.5 ng/tip for LC- and 5 ng/tip for GC-analytes from fine tip (rayon bud) (LCL = lowest calibration level with relative standard deviation RSD < 20% / n. d. = not detected / in control tips all n. d. (n = 2)

Analyte	**LCL**	**REC**	**RSD**
LC-MSMS	pg/µl	%	
2,4-D	0.05	88	8
Acetamiprid	0.02	94	6
Aclonifen	0.02	20	20
Amisulbrom	1	n. d.	
Azoxystrobin	0.05	65	8
Bentazone	0.01	94	5
Bixafen	0.05	33	17
Boscalid	0.05	63	9
Bromoxynil	0.02	92	6
Chlorantraniliprole	0.1	96	7
Chloridazon	0.5	85	8
Chlorpyrifos	0.05	21	16
Chlorotoluron	0.05	96	7
Clothianidin	0.5	92	14
Cyazofamid	0.5	28	27
Cyprodinil	1	n. d.	
Dichlorprop-P	0.02	91	6
Difenoconazole	0.05	36	14
Diflufenican	0.05	8	25
Dimethachlor	0.05	97	6
Dimethenamid-P	0.05	101	7
Dimethoate	0.05	n. d.	
Dimethomorph	0.05	89	8
Dimoxystrobin	5	62	19
Fenpropidin	0.05	117	8
Fenpropimorph	5	n. d.	
Florasulam	0.1	84	8
Fludioxonil	0.01	38	15
Flufenacet	5	58	22
Fluopicolide	0.05	65	10
Fluquinconazole	0.05	61	15
Fluroxypyr	0.5	95	4
Flurtamone	0.01	60	10
Foramsulfuron	0.5	55	22
Imazosulfuron	1	51	12
Imidacloprid	0.1	79	7
Iodosulfuron-methyl	0.1	74	4
Isoproturon	0.1	119	5
Isopyrazam	0.05	34	18
Lenacil	0.05	107	3

MCPA	0.05	89		8
Mecoprop-P	0.05	92		7
Mesosulfuron-methyl	0.02	62		6
Metamitron	0.1	97		8
Desamino-Metamitron	0.05	91		6
Metazachlor	0.1	101		12
Metazachlor-ESA	5	49		24
Metazachlor-OA	1		n. d.	
Methiocarb	0.5		n. d.	
Metosulam	0.05	84		7
Metrafenone	0.05	29		21
Metribuzin	0.1	94		4
Metsulfuron-methyl	0.5	75		12
Napropamide	0.01	71		7
Nicosulfuron	0.1	45		40
Pendimethalin	0.1		n. d.	
Pethoxamid	0.02	91		5
Phenmedipham	0.05	95		16
Picolinafen	0.05		n. d.	
Pirimicarb	0.05	99		5
Propamocarb	0.02	85		18
Propiconazole	0.1	73		7
Propyzamide	0.1	79		12
Proquinazid	0.05		n. d.	
Prosulfocarb	0.05	45		12
Prosulfuron	0.1	64		11
Pymetrozine	0.02	77		18
Pyraclostrobin	0.05	13		25
Pyraflufen-ethyl	0.1		n. d.	
Pyroxsulam	0.02	73		7
Quinmerac	0.05	84		9
Quinoxyfen	0.05	12		19
S-Metolachlor	0.1	73		11
Spinosad	0.1	62		6
Spiroxamine	0.05	86		8
Tebuconazole	0.1	94		12
Terbuthylazine	0.05	85		5
Thiacloprid	0.02	81		3
Thiamethoxam	0.5	98		10
Thifensulfuron-methyl	0.01	88		6
Triasulfuron	0.02	72		5
Trifloxystrobin	0.05	13		26
Zoxamide	0.1	32		16
Atrazine D5 (Surr)		92		4

GC-MSMS

beta-Cyfluthrin	1	65	2
lambda-Cyhalothrin	1	88	10
Cypermethrin	1	109	1
Esfenvalerate	5	113	7
Tefluthrin	1	86	6
Fenpropathrin (Surr)		124	1