

Supplementary material for:

Ametryn removal by *Metarhizium brunneum*: biodegradation pathway proposal and metabolic background revealed.

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Table S-1. Compound dependant parameters of MRM pairs of ametryn, 2-hydroxy atrazine and terbuthylazine.

Q1	Q3	Dwell time (ms)	ID	DP	EP	CE	CXP
198.100	156.100	25	2-hydroxy atrazine 1	76.000	10.000	25.000	6.000
198.100	86.000	25	2-hydroxy atrazine 2	76.000	10.000	31.000	8.000
228.100	186.000	25	Ametryn 1	76.000	10.000	25.000	8.000
228.100	68.000	25	Ametryn 2	76.000	10.000	57.000	6.000
230.100	174.100	25	Terbuthylazine 1	71.000	10.000	23.000	8.000
230.100	104.000	25	Terbuthylazine 2	71.000	10.000	45.000	8.000

Table S-2. Ametryn metabolites screening LC-MS/MS IDA method parameters.

pMRM scanning		IDA properties	EPI scanning	
Parameter	Value		Parameter	Value
CAD	medium	Intense peaks from 1 to 2 Which exceeds: 1000.000 counts Rolling collision energy: No Exclude former target ions: for 10.000 seconds After 2.0 occurrences Mass Tolerance: 250.000 mDa Use Enhanced Resolution scan to confirm Charge State and/or Isotope Pattern selection: No Exclude 1+ precursors from ER Scan confirmation and MS/MS: No Dynamic Background Subtraction: Yes	CAD	high
EP	10 V		EP	10 V
DP	81 V		DP	81 V
CE	27-35		CE	45-50
CES	N/A		CES	15-20
CXP	6-14		CXP	8-10
Dwell time	5 ms		Fill time	dynamic
Scan speed	10 Da/s		Scan speed	10 000 Da/s

Table S-3. Compound-dependent MRM parameters, linearity and working range for the metabolomics method.

Metabolite Name	Q1	Q3	DP	EP	CE	CXP	RT (min)	Linearity range (ng/ml)	R
Thiamine 1	265.0	122.1	36	10	25	4	0.32	0.25-100	0.99791
Thiamine 2	265.0	143.9	36	10	21	12	0.32		
L-Histidine 1	156.0	110.0	61	10	21	14	0.33	2.5-100	0.99557
L-Histidine 2	156.0	83.1	61	10	35	12	0.33		
L-Lysine 1	147.2	84.2	36	10	21	6	0.33	2.5-100	0.99786
L-Lysine 2	147.2	67.0	36	10	35	10	0.33		
Ornithine 1	133.1	70.0	46	10	23	10	0.33	2.5-100	0.99724
Ornithine 2	133.1	116.1	46	10	13	6	0.33		
L-Arginine 1	175.1	70.2	46	10	29	8	0.34	1-100	0.99877
L-Arginine 2	175.1	60.1	46	10	19	6	0.34		
Diaminopimelic acid 1	191.1	128.1	61	10	21	12	0.36	1-100	0.999761
Diaminopimelic acid 2	191.1	82.0	61	10	31	6	0.36		
L-Cystine 1	241.1	152.0	66	10	21	8	0.37	1-100	0.99616
L-Cystine 2	241.1	73.9	66	10	47	16	0.37		

GABA 1	104.1	86.0	30	4	14	5	0.37	5-250	0.99767
GABA 2	104.1	69.0	30	4	13	6	0.37		
5-Aminopentanoic acid 1	118.0	83.1	21	10	19	6	0.38	1-100	0.99834
5-Aminopentanoic acid 2	118.0	59.2	21	10	25	6	0.38		
Homocysteine thiolactone 1	118.0	90.0	11	10	15	12	0.38	5-250	0.99596
Homocysteine thiolactone 2	118.0	47.0	11	10	39	6	0.38		
L-Alanine 1	90.1	44.0	31	10	15	6	0.39	25-250	0.99743
L-Alanine 2	90.1	45.0	31	10	39	6	0.39		
L-Asparagine 1	133.1	87.0	46	10	13	8	0.39	2.5-100	0.99506
L-Asparagine 2	133.1	74.1	46	10	21	4	0.39		
L-Aspartic acid 1	134.1	88.1	51	10	15	12	0.39	2.5-100	0.99718
L-Aspartic acid 2	134.1	74.0	51	10	27	6	0.39		
Glycine 1	76.0	30.1	41	10	17	8	0.39	10-250	0.9951
Glycine 2	76.0	31.0	41	10	41	8	0.39		
Cytidine 1	244.0	112.1	16	10	21	6	0.39	0.25-100	0.99625
Cytidine 2	244.0	94.9	16	10	55	12	0.39		
Guanidoacetic acid 1	118.0	76.1	46	10	15	8	0.39	2.5-100	0.99659
L-Serine 1	106.0	60.1	1	10	15	4	0.39	5-100	0.99684
L-Serine 2	106.0	42.0	1	10	33	10	0.39		
L-Cysteine 1	122.0	59.1	61	10	35	6	0.4	1-100	0.99736
L-Cysteine 2	122.0	76.1	61	10	19	6	0.4		
L-Glutamine 1	147.1	84.1	36	10	23	4	0.4	1-100	0.99239
L-Glutamine 2	147.1	101.1	36	10	17	8	0.4		
L-Homoserine 1	120.0	44.0	40	5	26	11	0.4	1-100	0.9967
4-Hydroxyproline 1	132.0	86.0	1	10	19	8	0.4	2.5-100	0.99474
4-Hydroxyproline 2	132.0	68.0	1	10	27	4	0.4		
L-Threonine 1	120.0	57.1	6	10	25	6	0.4	5-100	0.99158
L-Glutamic acid 1	148.0	84.0	46	10	21	6	0.4	1-100	0.99642
L-Glutamic acid 2	148.0	102.0	46	10	15	6	0.4		
Betaine 1	118.0	58.0	76	10	39	16	0.41	1-50	0.99718
Betaine 2	118.0	59.1	76	10	27	4	0.41		
DL-Homocystine 1	269.0	136.1	51	10	13	6	0.41	10-250	0.99206
DL-Homocystine 2	269.0	88.0	51	10	47	8	0.41		
Aminoadipic acid 1	162.0	98.1	51	10	21	8	0.42	0.5-100	0.99963
Aminoadipic acid 2	162.0	144.1	51	10	15	6	0.42		
L-Proline 1	116.0	70.1	36	10	19	8	0.42	1-100	0.99807
L-Proline 2	116.0	68.0	36	10	39	4	0.42		
Adenine 1	136.0	119.0	86	10	31	10	0.43	0.5-50	0.99823
Adenine 2	136.0	92.0	86	10	37	8	0.43		
Homocysteine 1	136.0	90.0	40	5	16	6	0.43	2.5-250	0.99898
Homocysteine 2	136.0	56.0	40	5	26	6	0.43		
Pyridoxine 1	170.0	152.1	36	10	19	6	0.43	0.5-25	0.99627
Pyridoxine 2	170.0	134.0	36	10	27	4	0.43		
L-Valine 1	118.1	57.1	66	10	39	14	0.44	5-250	0.99463
L-Methionine 1	150.1	104.1	51	10	15	8	0.47	1-100	0.99805
L-Methionine 2	150.1	133.1	51	10	13	6	0.47		
Nicotinic acid 1	124.0	79.9	26	10	27	8	0.49	1-100	0.99903
Nicotinic acid 2	124.0	53.0	26	10	43	14	0.49		
L-Leucine 1	132.1	85.9	51	10	15	10	0.52	2.5-100	0.99622
L-Leucine 2	132.1	69.3	51	10	23	8	0.52		
Adenosine 1	268.0	136.0	66	10	27	10	0.55	0.25-100	0.99598
Adenosine 2	268.0	119.1	66	10	67	4	0.55		
Uracil 1	113.0	96.0	41	10	23	6	0.55	5-100	0.99902
Uracil 2	113.0	70.0	41	10	19	16	0.55		
Uridine 1	244.9	113.0	31	10	30	10	0.56	0.5-100	0.99882
Uridine 2	244.9	70.0	31	10	45	6	0.56		
L-Tyrosine 1	182.0	165.0	36	10	15	6	0.57	0.5-100	0.99927
L-Tyrosine 2	182.0	91.0	36	10	39	6	0.57		
Hypoxanthine 1	136.9	110.1	31	10	29	8	0.59	0.5-100	0.99922
Hypoxanthine 2	136.9	94.0	31	10	24	6	0.59		
Inosine 1	268.9	137.0	101	10	19	12	0.62	0.25-100	0.99813
Inosine 2	268.9	119.1	101	10	57	8	0.62		
L-Phenylalanine 1	166.1	120.1	26	10	17	10	0.64	1-100	0.99882
L-Phenylalanine 2	166.1	103.0	26	10	39	10	0.64		
Guanosine 1	283.9	152.1	6	10	17	8	0.66	0.1-100	0.99979
Guanosine 2	283.9	135.0	6	10	55	8	0.66		
L-Tryptophan 1	205.1	188.0	41	10	15	8	0.98	1-100	0.99991
L-Tryptophan 2	205.1	146.1	41	10	25	10	0.98		
Cyanocobalamin 1	678.4	147.1	50	10	92	11	1.12	0.05-250	0.99942
Cyanocobalamin 2	678.4	912.5	50	10	50	13	1.12		
Riboflavin 1	377.1	243.0	135	10	44	11	1.15	0.25-250	0.99974
Riboflavin 2	377.1	172.1	135	10	44	11	1.15		
p-Aminobenzoic acid 1	138.0	77.0	56	10	29	10	1.16	0.1-100	0.99987

p-Aminobenzoic acid 2	138.0	94.0	56	10	19	8	1.16		
Biotin 1	245.0	226.9	76	10	21	8	1.21	0.1-100	0.9994
Biotin 2	245.0	97.0	76	10	39	8	1.21		
Kynurenic acid 1	190.1	144.0	55	8	27	5	1.3	0.1-100	0.99915
Kynurenic acid 2	190.1	89.0	55	8	50	7	1.3		

