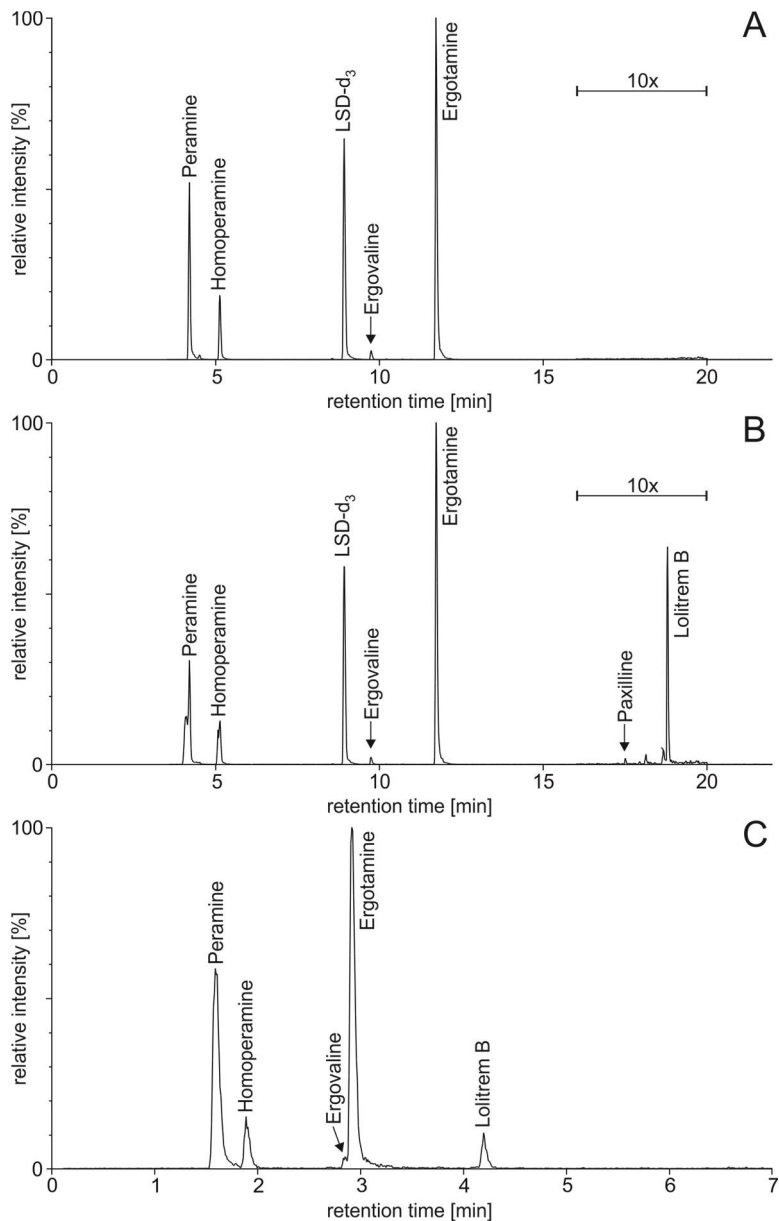


1 Supplemental material

2 **Figure S1**: Chromatograms of analytes analyzed with different methods: **A**: Chromatograms
3 of peramine, homoperamine, LSD-d3, ergovaline and ergotamine analyzed with UPLC-
4 MS/MS method 1 from [1], reconstituted in water/acetonitrile/formic acid 80:20:0.1 (v/v/v),
5 **B**: Chromatograms of peramine, homoperamine, LSD-d3, ergovaline, ergotamine, paxiline
6 and lolitrem B analyzed with UPLC-MS/MS method 1 [1], reconstituted in
7 water/acetonitrile/formic acid 50:50:0.1 (v/v/v), **C**: Chromatograms of peramine,
8 homoperamine, ergovaline, ergotamine and lolitrem B analyzed with UPLC-MS/MS method
9 2 from [2], reconstituted in methanol (80%).



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12 **Table S1:** Study sites with alkaloid concentrations above toxicity thresholds in 2015: Number
13 of samples with concentrations above toxicity thresholds in 2015 for peramine, lolitrem B and
14 ergovaline and number of infected samples at the study site. Sampled in summer
15 (July/August) 2015.

Study site	No. of samples with Peramine concentrations >2 µg/g	No. of samples with Lolitrem B concentrations >1.8 µg/g	No of samples with Ergovaline concentrations >0.3 µg/g	No of infected samples/total sample size
SEG40	2	0	1	2/20
SEG43	1	5	0	5/20
SEG44	2	3	0	3/20
SEG46	6	9	0	13/20
SEG47	2	4	0	8/20

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Table S2: Differences between UPLC-methods used in dataset (3)

Name of the method	Method 1	Method 2
Publications	[1] They used dry plant weight	[2,3] They used fresh plant weight
Detectable alkaloids	Lolitre B, ergovaline, peramine, paxilline	Lolitre B, ergovaline, peramine
Standards	Homoperamine, ergotamine, LSD-d3	Homoperamine, ergotamine
Substances for validation	Peramine, lolitre B, ergovaline, paxilline	Peramine, lolitre B
extraction	One part of the sample was reconstituted in water/acetonitrile/formic acid 50:50:0.1 (v/v/v) for the analysis of lolitre B and paxilline the other in water/acetonitrile/formic acid 80:20:0.1 (v/v/v) for the analysis of peramine and ergovaline	Samples were reconstituted in methanol (80 %)
Analytical method	UPLC-MS/MS	UPLC-MS/MS
Column	Aquity UPLC column (100x2.1 mm; 1.7 µm; Waters GmbH, Eschborn, Germany), Reverse Phase	Acquity UPLC BEH column (50x2.1 mm; 1.7 µm; Waters GmbH, Eschborn, Germany), Reverse Phase
solvents	0.1 % formic acid dissolved in water (solvent A) and acetonitrile containing 0.1 % formic acid (solvent B)	0.1 % formic acid dissolved in water (solvent A) and acetonitrile containing 0.1 % formic acid (solvent B)

Flow rate	0.4 ml/min	0.3 ml/min
gradient	0–1.0 min 98% solvent A, 1.0–3.0 min to 90% solvent A, 3.0–5.0 min to 85% solvent A, 5.0–7.5 min to 80% solvent A, 7.5–10.0 min to 75% solvent A, 10.0–11.5 min to 70% solvent A, 11.5–13.0 min to 65% solvent A, 13.0–14.5 min to 50% solvent A, 14.5–16.0 min to solvent 40% A, 16.0–19.0 min to 0% solvent A, 19.0–22.0 hold 0% solvent A, 22.0–23.0 back to 98% solvent A and hold for another 2 min	from 5% to 25% solvent B in 5 min, followed by 25% to 75% solvent B in 0.5 min, then 75% to 100 % solvent B in 2.5 min
Total run time	25 min	10 min
Injection volume	10 µl for the analyses of peramine and ergovaline 5 µl for the analyses of lolitrem B and paxilline.	5 µl
Limit of detection	Limit of detection (LOD): Paxilline, lolitrem B: 0.05 ng on column Ergovaline, peramine: 0.01 ng on column.	LOD: comparable to method 1

19 **Table S3**: Mean alkaloid concentrations (in [$\mu\text{g/g}$] dry weight (mean \pm SE)) per month on the
20 five study sites in the field in 2018.

Month	Year	Peramine	Lolitrem B
April	2018	0.032 \pm 0.018	0.000 \pm 0.000
June	2018	0.773 \pm 0.158	0.601 \pm 0.113
July	2018	0.939 \pm 0.233	0.367 \pm 0.243
September	2018	3.227 \pm 0.611	0.665 \pm 0.164
November	2018	0.345 \pm 0.110	0.010 \pm 0.008
January	2019	0.242 \pm 0.123	0.001 \pm 0.001

22 **Table S4:** Mean alkaloid concentrations based on plant fresh or dry weight from April until
 23 September 2019 in the common garden experiment (mean \pm SE, n=10 per time point). Date:
 24 dd.mm.yyyy, Week: calendar week. NA: not measured, nd: not detected

sample	Date	Week	Peramine		Ergovaline		Lolitre B		Paxilline	
			fresh	dry	fresh	dry	fresh	dry	fresh	dry
1	09. April 2019	15	NA	26.21 \pm 2.97	NA	0.40 \pm 0.14	NA	0.29 \pm 0.07	NA	0.10 \pm 0.06
2	24. April 2019	17	NA	16.42 \pm 1.71	NA	0.32 \pm 0.12	NA	0.14 \pm 0.07	NA	0.20 \pm 0.10
3	07. May 2019	19	3.02 \pm 0.29	8.44 \pm 1.13	0.11 \pm 0.03	0.48 \pm 0.13	0.59 \pm 0.12	1.46 \pm 0.37	nd	nd
4	21. May 2019	21	NA	1.02 \pm 0.10	NA	0.03 \pm 0.01	NA	0.03 \pm 0.004	NA	nd
5	04. June 2019	23	2.69 \pm 0.31	9.29 \pm 0.99	0.13 \pm 0.05	0.49 \pm 0.14	nd	0.05 \pm 0.02	nd	nd
6	18. June 2019	25	4.21 \pm 0.47	17.28 \pm 2.33	0.26 \pm 0.06	1.33 \pm 0.30	0.01 \pm 0.01	0.10 \pm 0.04	nd	nd
7	02. July 2019	27	4.05 \pm 0.60	13.24 \pm 2.16	0.18 \pm 0.04	0.65 \pm 0.16	0.34 \pm 0.04	1.28 \pm 0.17	nd	nd
8	16. July 2019	29	7.57 \pm 0.92	22.06 \pm 2.76	0.34 \pm 0.06	1.30 \pm 0.26	0.70 \pm 0.13	2.00 \pm 0.32	nd	nd
9	30. July 2019	31	10.78 \pm 0.700	31.81 \pm 3.08	0.31 \pm 0.04	1.03 \pm 0.17	nd	0.03 \pm 0.03	nd	0.05 \pm 0.03
10	14. August 2019	33	13.46 \pm 1.26	35.63 \pm 3.10	0.43 \pm 0.10	1.37 \pm 0.28	2.51 \pm 0.33	6.57 \pm 1.09	nd	0.13 \pm 0.07
11	28. August 2019	35	8.21 \pm 0.98	28.49 \pm 2.80	0.39 \pm 0.08	1.43 \pm 0.24	0.27 \pm 0.07	0.71 \pm 0.14	nd	0.32 \pm 0.13
12	10. September 2019	37	8.58 \pm 0.64	22.76 \pm 1.94	0.51 \pm 0.08	1.43 \pm 0.18	0.63 \pm 0.07	nd	0.02 \pm 0.02	0.56 \pm 0.28
13	25. September 2019	39	5.56 \pm 1.17	16.32 \pm 2.30	0.39 \pm 0.09	0.81 \pm 0.18	0.03 \pm 0.03	nd	nd	0.07 \pm 0.04

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