Supplementary Materials: Multi-Mycotoxin Occurrence and Exposure Assessment Approach in Foodstuffs from Algeria

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Table S1. Performance characteristics of the ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) method for each mycotoxin in barley, maize, rice and wheat samples.

Mycotoxin	Barley				Maize				Rice				Wheat			
	Linear Range (ug/kg)	R^2	LOD (ug/kg)	LOQ (ug/kg)	Linear Range (ug/kg)	R^2	LOD (ug/kg)	LOQ (ug/kg)	Linear Range (ug/kg)	R^2	LOD (ug/kg)	LOQ (ug/kg)	Linear Range (ug/kg)	R^2	LOD (ug/kg)	LOQ (ug/kg)
OTA	4.0–50	0.991	1.2	4.0	2.6–50	0.988	0.8	2.6	3.4–50	0.992	1.0	3.4	4.8–50	0.991	1.4	4.8
FB1	7.5–500	0.986	2.2	7.5	10–500	0.994	3.1	10	9.5–500	0.991	2.8	9.5	2.2–500	0.994	0.7	2.2
FB2	9.9–500	0.990	3.0	9.9	2.8–500	0.995	0.9	2.8	8.8–500	0.997	2.6	8.8	9.5–500	0.995	2.9	9.5
T-2	2.3–500	0.997	0.7	2.3	24–500	0.991	7.1	24	4.0–500	0.997	1.2	4.0	8.7–500	0.994	2.6	8.7
HT-2	4.2–500	0.997	1.3	4.2	4.8–500	0.999	1.4	4.8	4.5–500	0.997	1.4	4.5	4.8–500	0.997	1.5	4.8
CIT	9.2–250	0.995	2.8	9.2	8.5–250	0.994	2.5	8.5	4.3–250	0.996	1.3	4.3	9.7–250	0.995	2.9	9.7
F-X	132–5000	0.990	40	132	174–5000	0.994	52	174	90–5000	0.993	27	90	138–5000	0.982	41	138
DON	92–2000	0.992	28	92	20–2000	0.991	6.0	20	24–2000	0.988	7.1	24	23–2000	0.996	7.0	23
ZEN	23–500	0.995	7.0	23	9.8–50	0.989	2.9	9.8	8.4–50	0.996	2.5	8.4	9.3–50	0.991	2.8	9.3
ENNB	0.9–500	0.994	0.3	0.9	0.9–500	0.996	0.3	0.9	1.3–500	0.997	0.4	1.3	0.6–500	0.996	0.2	0.6
ENNB1	0.6–500	0.992	0.2	0.6	1.5–500	0.991	0.5	1.5	1.4–500	0.993	0.4	1.4	1.6- 500	0.995	0.5	1.6
BEA	0.5–500	0.997	0.2	0.5	0.8–500	0.992	0.2	0.8	0.8–500	0.997	0.2	0.8	1.2–500	0.998	0.4	1.2
ENNA	1.4–500	0.993	0.4	1.4	1.6–500	0.997	0.5	1.6	1.5–500	0.994	0.4	1.5	2.7–500	0.994	0.8	2.7
ENNA1	1.8–500	0.994	0.5	1.8	1.2–500	0.990	0.4	1.2	1.7–500	0.997	0.5	1.7	3.8–500	0.996	1.1	3.8
STE	2.9–50	0.980	0.7	2.9	4.4–50	0.992	1.3	4.4	2.6–50	0.992	0.8	2.6	4.4–50	0.996	1.3	4.4

R^2 = determination coefficient; LOD: limit of detection; LOQ : limit of quantification; OTA: ochratoxin A; FB1: fumonisin B1; FB2: fumonisin B2; T-2: T-2 toxin; HT-2: HT-2 toxin; CIT: citrinin; F-X: fusarenon X; DON: deoxynivalenol; ZEN: zearalenone; ENNB: enniatin B; ENNB1: enniatin B1; BEA: beauvericine; ENNA: enniatin A; ENNA1: enniatin A1; STE: sterigmatocystin.

Table S2. Recovery (%R), intra-day precision (%RSD$_r$) and inter-day precision (%RSD$_R$) for barley, maize, rice and wheat samples (n=9).

Mycotoxin.	Barley			Maize			Rice			Wheat		
	%R	%RSD$_r$	%RSD$_R$	%R	%RSD$_r$	%RSD$_R$	%R	%RSD$_r$	%RSD$_R$	%R	%RSD$_r$	%RSD$_R$
OTA	84.0	6.4	22	78.4	9.1	13	76.6	11	7.3	77.4	7.5	19
FB1	100.1	6.9	9.3	103.6	8.7	10	99.1	11	10	95.7	8.0	12
FB2	94.8	8.3	7.7	90.0	6.1	14	105.5	9.3	4.3	98.5	5.9	9.9
T-2	94.3	4.3	11	87.6	6.5	15	88.9	3.1	4.1	83.4	6.2	12
HT-2	87.5	4.2	12	76.5	14	8.6	82.0	5.3	3.3	96.8	5.6	16
CIT	42.1	7.7	17	60.0	9.6	20	61.2	4.9	4.8	55.1	11	23
F-X	84.4	5.5	7.8	81.1	8.3	18	82.4	7.3	8.5	87.6	6.5	22
DON	83.6	6.0	19	84.5	5.0	7.9	80.5	9.1	4.4	83.8	5.5	14
ZEA	98.9	7.6	20	89.5	8.3	11	94.8	5.5	7.9	87.1	6.9	9.9
ENNB	91.9	2.7	6.1	88.3	3.9	5.7	94.1	3.0	1.7	88.6	2.4	6.7
ENNB1	94.4	2.5	9.8	90.3	5.1	8.4	95.3	2.8	2.0	89.7	2.2	6.3
BEA	84.4	1.9	6.2	88.0	5.3	3.4	91.7	3.8	2.3	91.9	5.3	5.7
ENNA1	98.6	3.1	6.0	93.4	3.4	9.5	105.0	4.1	4.9	93.7	2.9	7.9
ENNA	98.0	1.9	6.9	90.4	4.6	15	105.3	2.7	3.4	93.9	3.2	5.6
STE	76.5	7.3	16	70.6	12	14	65.5	11	17	70.0	8.7	8.4
AVERAGE	**87.5**	**8.6**	**11.8**	**84.8**	**7.3**	**11.4**	**88.5**	**6.2**	**5.7**	**86.2**	**5.8**	**11.9**

Levels: OTA and STE: 25 μg/kg; CIT: 100 μg/kg; FB1, FB2, T-2, HT-2 and ZEA: 250 μg/kg; ENNB, ENNB1, ENNA, ENNA1 and BEA: 400 μg/kg, DON: 1000 μg/kg and F-X: 2500 μg/kg.

Table S3. Co-occurrence of analysed mycotoxins in wheat and maize samples.

Sample Code	Mycotoxins Concentration (μg/kg)											Number of Mycotoxins Found
	DON	HT-2	T-2	ZEN	F-X	CIT	BEA	ENNA	ENNA1	ENNB	ENNB1	
Wheat 10	114.2	–	21.34	–	–	–	–	–	–	–	–	**2**
Wheat 8	68.3	–	20.74	–	–	–	–	–	–	1.16	–	**3**
Wheat 9	92.1	–	34.65	–	–	–	–	–	–	330	282	**4**
Wheat 5	1072	–	33.80	–	–	–	4.30	43.7	–	–	–	
Wheat 25	815	–	17.54	–	–	–	18.5	8.87	–	–	–	
Wheat 2	–	–	25.01	–	156	13.8	–	–	–	85.6	67.1	**5**
Wheat 3	–	–	29.96	10.7	–	22.0	–	–	–	31.6	19.5	
Wheat 7	–	–	30.38	12.7	–	9.75	–	–	–	65.6	49.5	
Wheat 22	396	–	17.48	–	–	32.3	2.80	–	75.9	–	–	
Wheat 23	226	–	16.89	–	–	–	297	–	395	–	265	
Wheat 26	930	–	16.94	15.0	–	–	19.4	–	102	–	–	
Wheat 29	280	–	16.88	–	–	12.2	17.3	–	100	–	–	
Wheat 1	735	–	47.25	22.8	–	–	–	–	22.9	2779	148	**6**
Wheat 6	145	–	27.16	13.1	–	–	–	–	7.04	44.7	31.1	
Wheat 21	1363	36.7	20.74	20.3	–	–	10.7	–	170	–	–	
Wheat 4	270	–	30.55	–	–	13.2	–	–	3.98	2337	197	
Wheat 24	263	–	16.88	9.57	–	–	443	–	28.3	–	299	
Wheat 27	650	27.0	19.93	–	–	16.0	8.68	–	65.0	–	–	
Wheat 11	224	–	17.06	72.6	–	30.4	127	–	–	1828	91.0	**7**
Wheat 16	97.3	–	19.87	40.1	–	11.8	27.8	–	–	159	132	
Wheat 20	770	–	17.00	212	–	–	348	9.45	–	2926	249	
Wheat 12	578	9.82	17.48	163	–	–	473	17.9	–	3865	332	**8**
Wheat 14	724	–	16.64	201	–	10.6	263	8.36	–	2809	151	
Wheat 17	945	–	17.18	257	–	14.7	84.8	87.6	–	5288	4569	
Wheat 18	932	–	17.06	254	–	14.0	486	22.4	–	2540	215	
Wheat 28	285	–	17.42	12.2	139	30.4	33.2	–	160	–	65.3	
Wheat 13	87.0	14.0	18.81	37.5	–	–	133	–	197	50.3	36.0	
Wheat 19	1090	8.35	17.21	295	159	10.1	280	–	–	–	168	
Wheat 30	1189	12.6	16.82	11.2	–	–	28.6	–	155	2006	31.8	
Wheat 15	1053	18.9	17.54	285	–	10.6	57.2	–	18.40	2877	2448	**9**

Table S3. *cont.*

Sample Code	Mycotoxin Concentration (μg/kg)										Number of
	DON	FB1	FB2	T-2	ZEN	F-X	CIT	BEA	ENNA1	ENNB1	Mycotoxins Found
Maize 9	–	–	–	25.0	–	303	–	–	–	–	**2**
Maize 10	–	289	–	25.4	–	267	–	–	–	–	**3**
Maize 29	–	16,082	240	25.0	–	–	13.1	5.63	–	–	
Maize 16	–	1263	7319	25.0	–	314	–	0.88	–	–	
Maize 8	–	9364	84.7	24.5	–	345	–	1.84	–	–	
Maize 17	–	1420	181	25.2	–	398	10.1	–	–	–	
Maize 21	–	5053	237	24.9	–	–	10.6	2.75	–	–	**5**
Maize 24	422	12,347	–	25.2	–	253	–	4.31	–	–	
Maize 30	–	3389	220	25.0	–	–	9.07	1.93	–	–	
Maize 6	–	42,143	6735	25.1	–	–	9.97	1.49	–	–	
Maize 26	–	656	27.5	25.2	–	–	9.40	4.34	–	–	
Maize 3	–	31,122	4711	24.5	–	259	12.2	1.52	–	–	
Maize 7	–	1466	822	24.7	–	315	8.55	2.13	–	–	
Maize 18	–	5893	113	24.8	–	236	11.8	0.91	–	–	
Maize 19	–	930	122	24.6	–	368	15.0	0.85	–	–	**6**
Maize 22	–	3998	1600	24.6	–	477	10.4	2.74	–	–	
Maize 28	368	28,930	5167	24.8	–	–	273	7.90	–	–	
Maize 1	–	4186	184	25.7	–	198	8.79	31.4	–	107	
Maize 5	–	39,038	8603	25.0	–	352	10.8	1.03	11.5	–	
Maize 14	820	2130	353	24.6	–	255	255	0.96	–	–	
Maize 23	47.6	10,967	1991	25.0	–	228	12.4	6.06	–	–	**7**
Maize 25	261	2942	148	24.6	–	391	10.8	1.67	–	–	
Maize 15	913	41,027	3505	25.0	20.4	248	273	–	–	–	
Maize 20	866	17,827	403	24.8	579	211	10.8	–	–	–	
Maize 2	887	17,990	3060	25.4	–	265	14.0	11.9	–	15.0	
Maize 12	2055	27,326	6000	25.0	22.9	194	16.0	0.94	–	–	
Maize 13	482	33,111	7726	25.1	44.7	177	30.0	0.92	–	–	**8**
Maize 27	103	34,816	6118	25.0	13.3	236	12.1	5.09	–	–	
Maize 4	536	18,254	2964	25.3	40.4	281	14.5	1.14	53.9	–	
Maize 11	456	30,411	6680	24.9	39.7	270	12.7	0.95	103	–	**9**

Table S4. Monitored ions of the target analytes and MS/MS parameters.

Compound	Elemental composition	Retention time (min)	Precursor ion (m/z)	Molecular ion	DP [a]	EP [a]	CEP [a]	Product Ions [b]	CE [a]	CXP [a]
DON	$C_{15}H_{20}O_6$	1.27	297.1	$[M+H]^+$	36.0	5.5	16.0	249.2(Q)	17.0	4.0
								161.0(I)	29.0	4.0
F-X	$C_{17}H_{22}O_8$	1.46	355.1	$[M+H]^+$	26.0	12.0	18.0	147.7(Q)	23.0	4.0
								137.1(I)	31.0	4.0
CIT	$C_{13}H_{14}O_5$	2.28	251.2	$[M+H]^+$	26.0	11.0	18.0	233.0(Q)	23.0	23.0
								204.8(I)	73.0	10.0
HT-2	$C_{22}H_{32}O_8$	2.74	442.0	$[M+NH_4]^+$	21.0	5.5	21.0	262.8(Q)	22.0	8.0
								215.4(I)	19.0	4.0
FB 1	$C_{34}H_{59}NO_{15}$	3.00	722.2	$[M+H]^+$	71.0	10.0	30.0	334.2(Q)	51.0	6.0
								352.2(I)	47.0	6.0
T-2	$C_{24}H_{34}O_9$	3.17	484.0	$[M+NH_4]^+$	21.0	10.0	22.0	215.0(Q)	22.0	4.0
								185.0(I)	29.0	4.0
ZEN	$C_{18}H_{22}O_5$	3.53	319.0	$[M+H]^+$	26.0	8.0	20.0	282.9(Q)	19.0	4.0
								301.0(I)	15.0	10.0
OTA	$C_{20}H_{18}ClNO_6$	3.62	404.0	$[M+H]^+$	41.0	7.5	16.0	238.9(Q)	31.0	6.0
								102.1(I)	91.0	6.0
STE	$C_{18}H_{12}O_6$	3.68	325.1	$[M+H]^+$	66.0	3.5	26.0	281.0(Q)	43.0	4.0
								310.0(I)	37.0	4.0
FB 2	$C_{34}H_{59}NO_{14}$	3.81	706.2	$[M+H]^+$	71.0	10.5	20.0	336.3(Q)	43.0	14.0
								318.3(I)	45.0	12.0
ENNB1	$C_{33}H_{57}N_3O_9$	5.20	640.4	$[M+H]^+$	81	8.50	18.0	196.2(Q)	35.0	4.0
								214.2(I)	37.0	4.0
ENNB	$C_{34}H_{59}N_3O_9$	5.30	654.4	$[M+H]^+$	81	7.50	30.0	196.4(Q)	39.0	6.0
								210.1(I)	33.0	6.0
BEA	$C_{45}H_{57}N_3O_9$	5.40	784.5	$[M+H]^+$	81	9.00	26.0	244.2(Q)	39.0	4.0
								262.2(I)	37.0	4.0
ENA 1	$C_{35}H_{61}N_3O_9$	5.50	668.4	$[M+H]^+$	81	10.5	18.0	210.2(Q)	35.0	6.0
								228.2(I)	35.0	4.0
ENA	$C_{36}H_{63}N_3O_9$	5.60	682.4	$[M+H]^+$	76	9.00	26.0	210.2(Q)	35.0	4.0
								228.2(I)	35.0	4.0

[a] Declustering potential (DP), entrance potential (EP), collision cell entrance potential (CEP), collision cell exit potential (CXP) and collision energy (CE). All expressed in voltage. [b] Product ions: (Q) transition used for quantification, (I) transition employed to confirm the identification.

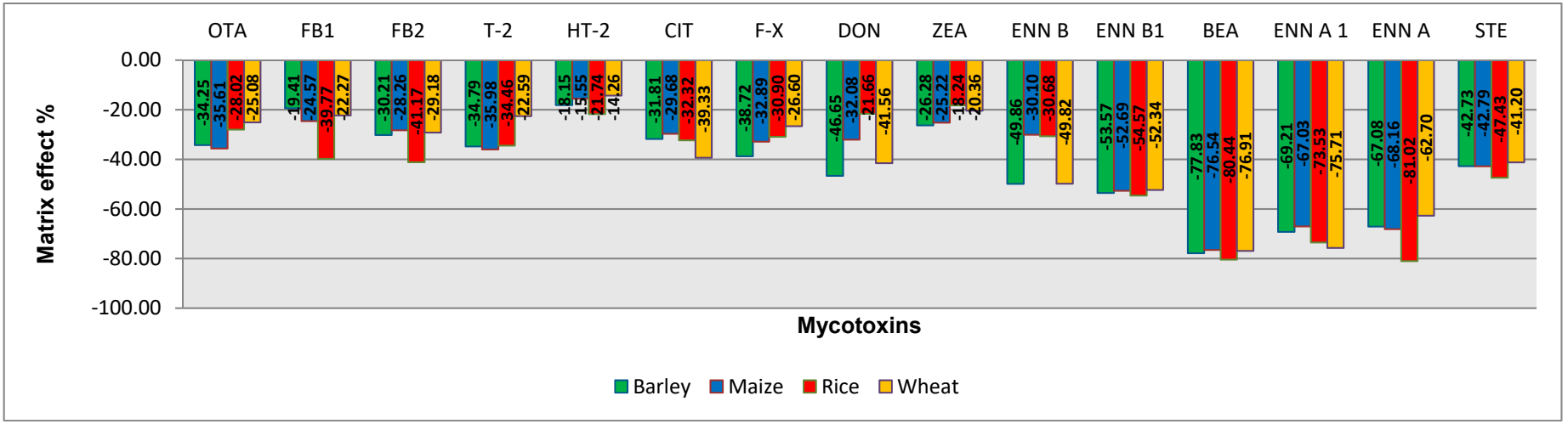

Figure S1. Matrix effect (%) for each studied mycotoxin extracted from barley, maize, rice and wheat samples (concentration levels: OTA and STE: 25 µg/kg; CIT: 100 µg/kg; FB1, FB2, T-2, HT-2 and ZEN: 250 µg/kg; ENNB, ENNB1, ENNA, ENNA1 and BEA: 400 µg/kg, DON: 1000 µg/kg and F-X: 2500 µg/kg).

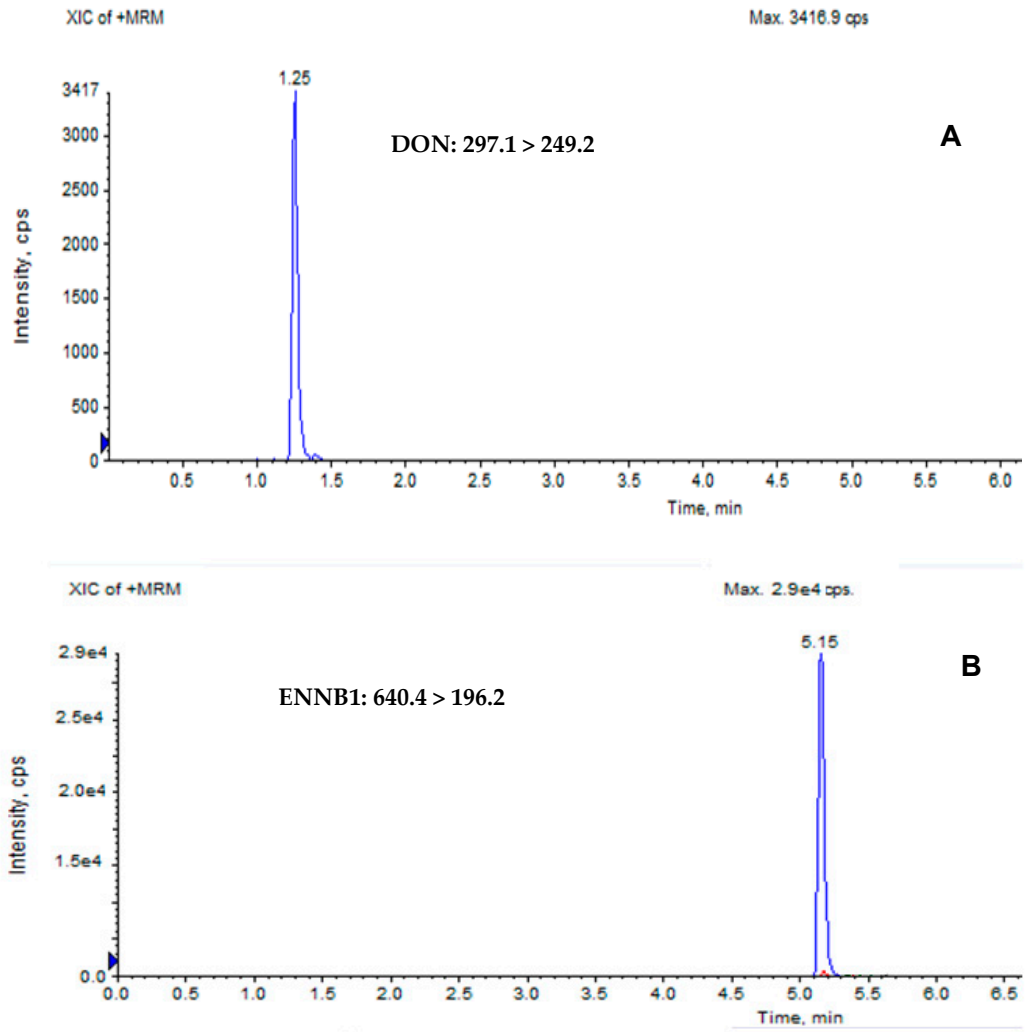

Figure S2. UHPLC-MS/MS multiple reaction monitoring (MRM) chromatogram of two samples of positive wheat contaminated with (**A**) DON (1362 μg/kg) and (**B**) ENNB1 (419 μg/kg).