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REVIEW ARTICLE

Occurrence of Zearalenone and Ochratoxin A in Cereals and Cereal Based Products

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KEYWORDS

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ABSTRACT: The contamination of cereals with toxic secondary metabolites of fungi, mycotoxins, is a permanent challenge in human health. These toxins are produced by a few fungi are mainly of the genera *Fusarium*, *Aspergillus* and *Penicillium*. Ochratoxin A is a nephrotoxic mycotoxin, which possesses carcinogenic, teratogenic, immunotoxic and possibly neurotoxic properties. Zearalenone is a non-steroidal estrogenic toxin, which has been involved in incidents of precocious pubertal changes. In this study, we reviewed recent researches in zearalenone and ochratoxin A contamination in cereals and cereal based products.

INTRODUCTION

Mycotoxins are secondary metabolites produced by fungi. “There is an increasing worldwide awareness of the serious consequences that undesirable levels of mycotoxins may have on human and animal supplies; such as carcinogenic, mutagenic, teratogenic and estrogenic effects” [1]. Cereals are very susceptible to fungal attacks while in the field and during storage. Environmental conditions and different factors are reason to produce fungal mycotoxins. These toxins are stable compounds and do not completely degrade at high temperatures [2]. Based on world standard, five groups of mycotoxins are so important for human health. These are aflatoxins, ochratoxin A (OTA), fumonisins, trichothecenes, and zearalenone (ZEA) [3]. These toxins are mainly produced by fungal species belonging to the genus *Aspergillus*, *Penicillium* and *Fusarium* [2]. Products frequently contaminated with mycotoxins include cereals, coffee, nuts, cocoa, dried

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fruit, dried peas, oil seeds, fruits and beans [4]. Cereals represent the main OTA and ZEA sources of human intake. OTA has been classified in group 2B as a possible carcinogen to humans and ZEA is not classifiable with regard to its carcinogenicity to humans (group 3) [2].

In this study, we reviewed recent researches in ZEA and OTA contamination in cereals and cereal based products.

Zeearalenone

The zearalenone is a mycotoxine, an acid lactone resorcylate and has chemical structure similar to steroid hormones (Figure 1) [5]. Zearalenone produced by *Fusarium* fungi, including *F. graminearum*, *F. cerealis*, *F. culmorum*, *F. crookwellense*, *F. semitectum* and *F. equiseti*, which are common soil fungi. ZEA found corn and colonize, to a lesser extent, oats, wheat, barley, sorghum, rice and millet, too, this toxin has been detected in cereals products like flour, malt, beer, and soybeans. ZEA is rapidly metabolized in animals and humans [6, 7]. ZEA was also shown to be hepatotoxic, and may contribute to the increasing occurrence of cancer [8]. The US Food and Drug Administration (FDA) set tolerable daily intake of 0.2 μg/kg body weight for ZEA. Permissible level for ZEA in maize and other cereals, ranging from 50-1000 μg/kg, have been set in several countries in Europe, Asia, Africa and Latin America [9]. ZEA is a stable toxin and not degrade at high temperatures [7]. ZEA was found in maize, wheat, corn flour, corn cheese snack, barley, corn, wheat bran and silage. We identified 48 studies on occurrence of zearalenone in cereals and cereal based products in worldwide (Table 1).

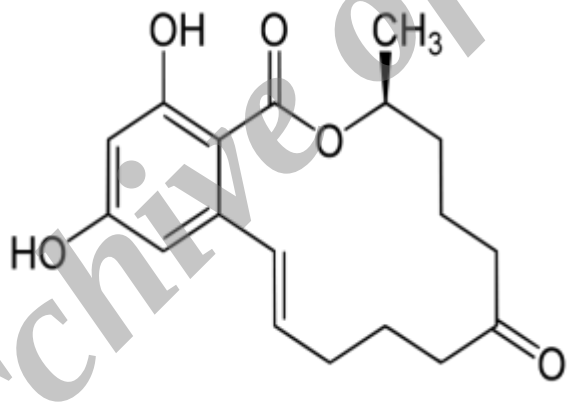

Figure 1. Structure of ZEA ($C_{18}H_{22}O_5$)

Table 1. Occurrence of ZEA in cereals and cereal based products

Sample	Technique	Region	Sample No.	Positive (%)	Mean (μg/kg)	Year	Ref.
Wheat	HPLC	China	59	46.5	198.5	1998	[11]
Wheat	HPLC	China	34	59	23	1999	[11]
Wheat	ELISA	Iran	118	80.5	Range 29-200	2002	[13]
Wheat	HPLC	Iran	175	8.6	72	2004	[16]
Wheat	HPLC	Syria	40	25	13	2009-2010	[19]
Wheat	EIA	Bulgaria	140	69	17	1995	[28]
Wheat	HPLC	Italy	47	34	44	2009-2010	[19]
Wheat	ELISA	Romania	52	69.2	187.74	2010	[43]
Wheat	ELISA	Romania	52	76.9	54.54	2011	[43]

Table 1. Continued

Wheat	TLC	Bulgaria	103	42.7	Range 450 - 884	2003-2005	[33]
Wheat	HPLC	Iran	30	100	54	2011	[21]
Wheat	HPLC	Egypt	15	40	1.55	2013	[27]
Wheat	ELISA	Croatian	51	69	56	2011	[44]
Wheat	LC-MS/MS	Taiwan	13	ND	ND	2011	[23]
Wheat	TLC	Brazil	109	ND	ND	2007-2008	[49]
Wheat	HPLC	Qatar	4	100	Range 0.21–2.13	2002	[15]
Wheat	ELISA	Lithuania	209	54.5	8.05	2003–2005	[32]
Wheat	TLC	Croatia	6	0	ND	2007	[36]
Wheat	ELISA	Croatia	6	66.6	29.1	2007	[36]
Wheat	HPLC	Bulgaria	54	1.9	10	2007	[38]
Wheat	ELISA	Romania	20	10	2.22	2008-2010	[40]
Wheat	GC-MS	Germany	41	63	15	2000-2001	[30]
Wheat Flour	LC	Portugal	42	34.7	19.7	2012-2013	[46]
Wheat Flour	LC	Netherlands	6	75	20.8	2012-2013	[46]
Wheat Flour	ELISA	Poland	23	ND	ND	2009-2010	[42]
Wheat Flour	HPLC-MS/MS	Serbia	15	33.3	4.6	2011	[45]
Wheat Bran	ELISA	Iran	14	ND	ND	2010	[20]
Wheat Flour	ELISA	Romania	16	31.2	9.09	2008-2010	[40]
Maize	TLC	Iran	40	7.5	141	2000	[12]
Maize	HPLC	Indonesia	32	78.1	60.2	2005	[18]
Maize	ELISA	Indonesia	89	36	49.5	2005	[18]
Maize	HPLC	Croatia	15	80	1.70	2002	[31]
Maize	HPLC	Spain	27	14.8	1.4	2004	[34]
Maize	HPLC	France	56	41	26	2004-2007	[35]
Maize	TLC	Bulgaria	104	43.2	Range 398 - 838	2003-2005	[33]
Maize	HPLC	Romania	70	54	326	2009	[41]
Maize	TLC	Brazil	121	0.8	448	2002-2003	[48]
Maize	ELISA	Croatian	63	78	187	2011	[44]
Maize	ELISA	Croatia	12	100	316.5	2007	[36]
Maize	TLC	Croatia	12	25	1481	2007	[36]
Maize	HPLC	Bulgaria	19	21.1	80.6	2007	[38]
Maize	ELISA	Romania	12	33.3	0.57	2008-2010	[40]
Corn	HPLC	Spain	25	64	90.78	2007	[37]
Corn	GC	Spain	25	44	56.82	2007	[37]
Corn	HPLC	Brazil	380	7.8	Range 46.7- 719	1998-1999	[47]
Corn	HPLC	Morocco	20	15	14	2006	[26]
Corn	HPLC	Korea	46	17.4	151	1990-1991	[10]
Corn	ELISA	Iran	8	25	150	2010	[20]
Corn	LC-MS/MS	Taiwan	9	11.1	4.73	2011	[23]
Corn	GC-MS	Germany	41	85	48	2000-2001	[30]
Corn Flour	HPLC	Iran	19	63	377	2005	[17]
Popcorn	TLC	Brazil	51	ND	ND	2007-2008	[49]

Table 1. Continued

Corn Grits	TLC	Brazil	50	2	64	2007-2008	[49]
Yellow Corn	HPLC	Egypt	15	46.6	3.08	2013	[27]
Cornflakes	HPLC	Qatar	5	60	Range 3.88–6.81	2002	[15]
Cornflakes	ELISA	Romania	13	15.3	8.19	2008-2010	[40]
Rice	HPLC	Korea	88	3.4	38.5	2002	[14]
Rice	LC-MS/MS	Taiwan	6	16.7	2.73	2011	[23]
Rice	HPLC	Qatar	9	55.5	Range 0.18- 1.11	2002	[15]
Barley	TLC	Bulgaria	39	36	Range 320 - 378	2003-2005	[33]
Barley	HPLC	Egypt	15	26.6	1.25	2013	[27]
Barley	ELISA	Croatian	34	9	32	2011	[44]
Barley	ELISA	Iran	20	20	136	2010	[20]
Barley	ELISA	Lithuania	112	56.3	9.5	2003–2005	[32]
Barley	ELISA	Croatia	4	100	61.7	2007	[36]
Barley	HPLC	Bulgaria	18	11.1	29	2007	[38]
Oat	TLC	Bulgaria	35	8.5	Range Oats 250- 350	2003-2005	[33]
Oat	ELISA	Croatian	34	6	44	2011	[44]
Oat	HPLC	Qatar	5	20	1.18	2002	[15]
Oat	LC-MS/MS	Taiwan	7	ND	ND	2011	[23]
Oat	ELISA	Lithuania	7	57	7.1	2003–2005	[32]
Oat	ELISA	Croatia	2	50	18.4	2007	[36]
Oat	GC-MS	Germany	17	24	21	2000-2001	[30]
Breakfast cereal	HPLC	Pakistan	237	53	9.91	2012	[24]
Breakfast cereal	LC	Spain	46	39	0.37	2011	[2]
Breakfast cereal	ELISA	Romania	16	31.2	1.63	2008-2010	[40]
Bread	ELISA	Iran	80	100	Range 15 -176.9	2012- 2013	[25]
Bread	ELISA	Romania	26	26.2	2.93	2008-2010	[40]
Beer	ELISA	Poland	91	11	0-546	2009	[4]
Crop	HPLC	Portugal	307	55.7	170	2008	[39]
Rye	ELISA	Lithuania	17	35.3	3.6	2003–2005	[32]
Cheese Snack	HPLC	Iran	19	100	832	2005	[17]
Silage	ELISA	Iran	12	16.7	140	2010	[20]
Rice, Bread, Puffed corn snack and Wheat flour	HPLC	Iran	72	100	1.46	2011	[22]
Cereals and Mixed feed	HPLC	Lithuania	92	58	30	1999	[29]

Ochratoxin A

Ochratoxin A was firstly isolated in 1965 from maize based products contaminated. These are three types ochratoxins includes of A, Band C. Ochratoxins A is common type ofochratoxin (Figure 2.) [50]. OTA is the most common naturally occurring mycotoxin produced by mainly *Penicillium verrucosum* in temperate climates and *Aspergillus ochraceus* and the rare *A. carbonarius* in warm and tropical regions that can contaminate food commodities prior to harvest or more commonly during storage [51]. OTA found in cereal grains, cocoa, spices,

oilseeds, coffee beans and legumes [52]. OTA has nephrotoxic, carcinogenic, teratogenic and immunotoxic properties. OTA contamination was mainly associated with storage; therefore, suitable post-harvest conditions such as temperature and humidity are important in preventing the growth of fungi and the production of the mycotoxin [53]. Based on European Union Scientific Committee for Human Feeding the maximum permissible level of 5 µg/kg in raw wheat, barley and rye [52]. We identified 40 studies on occurrence of zearalenone in cereals and cereal based products in worldwide (Table 2).

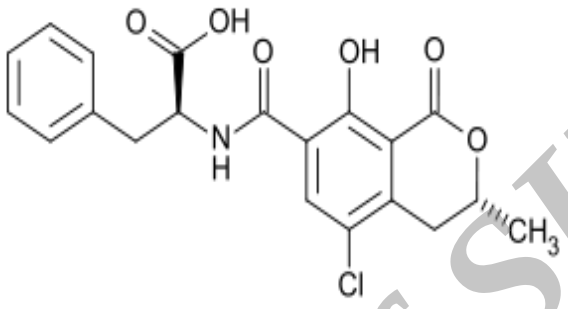

Figure 2. Structure of OTA ($C_{20}H_{18}ClNO_6$)

Table 2. Occurrence and content of OTA in cereals and cereal based products

Sample	Technique	Region	Sample No.	Positive (%)	Mean (µg/kg)	Year	Ref.
Wheat	HPLC	Japan	50	56	0.09	2004-2005	[55]
Wheat	HPLC	India	50	58	5.76	2012	[52]
Wheat	HPLC	Morocco	17	11.7	29.4	2005	[61]
Wheat	ELISA	Romania	52	34.6	6.39	2010	[43]
Wheat	ELISA	Romania	52	92.3	5.71	2011	[43]
Wheat	LC	Italy	70	8.6	1.47	1999- 2000	[65]
Wheat	HPLC	Hungary	36	8.3	0.29	2001	[66]
Wheat	HPLC	Syria	40	30	0.6	2009-2010	[19]
Wheat	LC-MS/MS	Taiwan	13	23.1	Range 0.05 - 0.06	2011	[23]
Wheat	HPLC	Qatar	4	ND	ND	2002	[15]
Wheat	HPLC	Ethiopia	107	23.4	19.6	1999	[60]
Wheat	HPLC	Morocco	20	40	0.42	2006	[26]
Wheat	HPLC	Tunisia	110	42	55	2007	[62]
Wheat	ELISA	Lithuania	29	22.2	6.65	2003–2005	[32]
Wheat	LC	Spain and Portugal	11	36.3	0.84	2005	[69]
Wheat	ELISA	Croatia	6	16.6	2.6	2007	[36]
Wheat Flour	HPLC	Hungary	16	12.5	0.13	2001	[66]
Wheat Flour	HPLC	Taiwan	39	5	Range 0.1–0.5	2002-2004	[53]
White Flour	ELISA	Turkey	34	67.6	4.14	2005-2006	[71]
Wheat Flour	HPLC	Qatar	6	33.3	Range 1.23- 1.95	2002	[15]
Wheat Flour	HPLC	Chile	30	70	Range ND –2.1	2006	[75]

Table 2. Continued

Whole meal Flour	ELISA	Turkey	14	100	9.30	2005-2006	[71]
Maize	LC	Italy	70	27.1	1.7	1999- 2000	[65]
Maize	HPLC	Hungary	6	16.7	0.4	2001	[66]
Maize	HPLC	Croatia	15	33.3	1.40	2002	[31]
Maize	TLC	Brazil	121	0.8	64	2002-2003	[48]
Maize	ELISA	Nigeria	6	100	0.14	2009	[64]
Maize	LC	Spain and Portugal	5	40	0.54	2005	[69]
Maize	ELISA	Croatia	12	25	12.7	2007	[36]
Corn	LC-MS/MS	Taiwan	9	ND	ND	2011	[23]
Corn	HPLC	Morocco	20	40	1.08	2006	[26]
Corn	ELISA	Nigeria	6	100	0.10	2009	[64]
Corn Flour	ELISA	Turkey	10	100	6.39	2005-2006	[71]
Corn Breads	ELISA	Turkey	10	100	4.94	2005-2006	[71]
Cornflakes	HPLC	Qatar	5	ND	ND	2002	[15]
Rice	HPLC	Taiwan	75	ND	ND	2002-2004	[53]
Rice	TLC	Vietnam	25	8	23.75	2000	[54]
Rice	HPLC	Korea	88	9.1	3.9	2002	[14]
Rice	HPLC	Vietnam	100	35	0.75	2006	[56]
Rice	HPLC	Chile	31	42	Range ND–12.5	2006	[75]
Rice	HPLC	Iran	100	69	1.37	2007	[57]
Rice	HPLC	Portugal	42	14.3	Range 0.09- 3.52	2004	[67]
Rice	LC-MS/MS	Taiwan	6	ND	ND	2011	[23]
Rice	HPLC	Qatar	9	ND	ND	2002	[15]
Rice	HPLC	Tunisia	96	27	44	2007	[62]
Rice	LC	Spain and Portugal	9	44.4	2.57	2005	[69]
Oat	LC-MS/MS	Taiwan	7	14.3	0.07	2011	[23]
Oat	LC	Spain and Portugal	5	20	0.5	2005	[69]
Oat	HPLC	Qatar	5	ND	ND	2002	[15]
Oat	ELISA	Croatia	2	ND	ND	2007	[36]
Breakfast Cereal	HPLC	Pakistan	237	48	2.22	2012	[24]
Breakfast Cereal	HPLC	French	45	69	Range 0.2–8.8	2004	[68]
Breakfast Cereal	HPLC	Greece	55	60	0.18	2006-2007	[73]
Breakfast Cereal	LC	Spain	46	48	25.40	2011	[2]
Breakfast Cereal	HPLC	Iran	18	ND	ND	2010	[58]
Breakfast Cereal	HPLC	Spain	21	90	0.265	2005	[70]
Breakfast Cereal	HPLC	Turkey	24	38	0.75	2007	[51]
Bread	HPLC	Portugal	41	66.9	1.24	2009	[74]
Bread	ELISA	Iran	86	52.3	2.61	2010-2011	[59]
Bread	LC	Spain	100	21.65	Range 0.03-19.61	2006	[72]
White Bread	ELISA	Turkey	36	69.4	4.87	2005-2006	[71]
Whole meal Bread	ELISA	Turkey	28	100	7.84	2005-2006	[71]
Barley	HPLC	Ethiopia	103	26.2	61.07	17.2	[60]

Table 2. Continued

Barley	HPLC	Morocco	20	55	0.17	2006	[26]
Barley	HPLC	Tunisia	103	41	96	2007	[62]
Barley	ELISA	Lithuania	71	70.42	4.6	2003–2005	[32]
Barley	LC	Spain and Portugal	4	ND	ND	2005	[69]
Barley	ELISA	Croatia	4	ND	ND	2007	[36]
Sorghum	HPLC	Ethiopia	78	21.8	174.8	1999	[60]
Sorghum	HPLC	Tunisia	113	43	117	2007	[62]
Millet	ELISA	Nigeria	6	100	0.11	2009	[64]
Rye	LC	Spain and Portugal	5	20	5.42	2005	[69]
Nuts	ELISA	Nigeria	50	98	20.6	2007	[63]
Baby Food	HPLC	Spain	20	70	0.187	2005	[70]
Baby Food	HPLC	Turkey	4	17	0.22	2007	[51]
Beer	HPLC	Spain	31	77	0.044	2005	[70]
Beer	HPLC	Turkey	35	14	0.02	2007	[51]
Corn Starch	HPLC	Chile	30	40	Range ND–1.2	2006	[75]
Cereals and Mixed Feed	HPLC	Lithuania	92	92	28	1999	[29]

CONCLUSIONS

Most of cereals and cereal-based products can be contaminated with mycotoxins. Mycotoxins are known as carcinogenic, harmful to the health of humans and animals, and even caused huge economic loss. According to the results, the incidence and contamination levels of ZEA and OTA seem to be an important problem for human health. Therefore, cereals and cereal-based products should be controlled for the occurrence of toxins, storage and humidity, which are major reason in the growth of the *Fusarium* and *Aspergillus* fungi. All so HPLC and ELISA methods are so practical in determining the range of toxins.

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The authors declare that there is no conflict of interests.

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