Profile of major and emerging mycotoxins in sesame and soybean grains in the Federal Capital Territory, Abuja, Nigeria

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ABSTRACT

The spectrum of major and emerging mycotoxins in sesame and soybean grains from the six zones of the Federal Capital Territory (FCT), Abuja, Nigeria was determined using Liquid Chromatography/Tandem Mass Spectrometry (LC-MS/MS). A total of 47 samples (24 sesame and 23 soybean were collected from farmers' stores. Seven regulated mycotoxins in sesame and five in soybean including aflatoxin B_1 (AFB₁), aflatoxin B_2 (AFB₂) and fumonisin B_1 (FB₁) were detected. However, concentrations were generally lower than regulatory limits set in the EU for raw grains with the exception of ochratoxin A (OTA) exhibiting a maximum concentration level of 23.1 μ g kg⁻¹ in one of the soybean samples. This is the first report concerning the contamination of sesame and soybean in Abuja, FCT-Nigeria with the emerging mycotoxins addressed by recent European Food Safety Authority (EFSA) opinion papers totalling 10 in number. These include beauvericin (BEA), moniliformin (MON), sterigmatocystin (STE), altertoxin-I (ATX-I), alternariol (AOH), alternariol methylether (AME) though at relatively low µg kg⁻¹ range. This preliminary data indicate that sesame and soybean might be relatively safe commodities in view of the profile of mycotoxins.

Keywords: Emerging mycotoxins; Nigeria; Liquid chromatography/tandem mass spectrometry; Regulated mycotoxins; Sesame; Soybean.

1. INTRODUCTION

Sesame (*Sesamum indicum* L.) and soybean (*Glycine max* L. Merril) are two very nutritious food items in Nigeria. Just like other crops produce, the occurrence of mycotoxins in these two crops is hardly avoidable. Unimpressive agricultural practices and lack of well-organized and effective regulations in Nigeria and most of sub Saharan Africa make control gloomy. Even where regulatory measures exist, they have little impact in rural areas and subsistence farming communities [1]. Postharvest mishandling of the grains especially before and during storage is one of the major causes of mycotoxin invasion of the crops produce [2].

Sesame stored or marketed in some north central States of Nigeria has been shown over many seasons to be contaminated with agriculturally important toxins [3]. This might be linked to favourable climatic and crop storage conditions which are frequently conducive to fungal growth and mycotoxin production, as much of the population relies on subsistence farming and unregulated local markets. Mycotoxins in soybean have a wide geographical distribution from Argentina [4, 5] to Croatia [6] and their production can be due to the effect of temperature [7]. Health challenges from the synergistic effect of many mycotoxins [8, 9] or through immunomodulation by a variety of cooccurring mycotoxins [10].

Emerging mycotoxins attract an increasing interest among the scientific community due to their high occurrence in feed and food commodities, sometimes at relatively high concentrations, and potential toxicity towards animals and humans. There is not yet existing regulation given to these metabolites despite their established toxicity. The main producers of emerging *Alternaria* metabolites are *A. alternata*, *A. dauci*, *A. cucumerina*, *A. solani*, and *A. tenuissima*, *A. citri*. These mycotoxins are found in wheat, rice, rye, olives, sorghum, tobacco, apples, peppers, sunflower seeds, oilseed rape, pecan nuts, tomatoes and mandarins [11, 12].

The incidence of emerging Fusarium mycotoxins has been reported in different products such as soybean [13], wheat and barley [14], rice [15], grain-based products [16] and infant cereals [17]. Jestoi [18] reported that limited data on emerging, less reported mycotoxins might be due to their late recognition especially because of the late understanding of their role as mycotoxins. Studies focusing on this class of mycotoxins are still quite low in number an extensive review published in 2015 showed that among all mycotoxin-related studies, only 7% were directed toward emerging mycotoxins. Some metabolites such as fusaric acid and fusaproliferin referred to as "emerging mycotoxins" by certain authors such as Jestoi [18] are not yet addressed by EFSA.

In Nigeria, there has been difficulty in determining the actual pecuniary value of food and feed ingredient losses due to mycotoxin load. This was due to paucity of detailed analysis information as well as intervention steps. There has been lack of attention on the probable additive effect and risks posed by emerging mycotoxins. The objective of the present study was to determine the major mycotoxins and emerging fungal metabolite profile of sesame and soybean in the FCT, Abuja Nigeria. This surveillance could be a critical step forward in the cocktail of intervention strategies against mycotoxin contamination in food and feed in Nigeria.

2. MATERIALS AND METHODS

2.1. Sampling

Surveys were conducted the FCT, Abuja Nigeria (between Lat. 9° 40' N, Long. 7° 29' E and Lat. 8° 83'N, Long. 7° 17' E, 388-566 m above the sea level between January and February, 2015. The farmers' stores were located in the six zones of the territory (Table 1). A total of 47 samples (24 sesame and 23 soybean grains) were collected from farmers in the six zones of the FCT namely Abuja Municipal Area Council (AMAC), Abaji, Bwari, Gwagwalada (GWA), Kuje and Kwali. Simple random sampling plan was adopted in the collection of the seed samples. The sampled locations and number of sample types collected from each district were uneven but the quantity were the same. Only samples shelled and stored for less than 30 days after harvest were collected from the farmers. Each sample was collected as a bulk sample (1.8-2 kg) and comprised of four subsamples of 0.5 ± 0.05 kg each. The subsamples were obtained from random points in farmer's basins or other storage containers and mixed to form the bulk. The samples were comminute and quartered such that 100-150 g of representative samples was obtained from each bulk as described by Ezekiel et al. [19]. Representative samples were stored at 4°C until they were analyzed for multiple mycotoxins and microbial metabolites.

2.2. Sampling area

The sampling location in the six zones of the FCT, Abuja is as shown in Table 1.

2.3. Mycotoxin analysis

2.3.1. Chemicals and reagents

Methanol (LC gradient grade) and glacial acetic acid (p.a.) were purchased from Merck

(Darmstadt, Germany), acetonitrile (LC gradient grade) from VWR (Leuven, Belgium), and ammonium acetate (MS grade) from Sigma-Aldrich (Vienna, Austria). Water was purified successively by reverse osmosis and an Elga Purelab ultra analytic system from Veolia Water (Bucks, UK) to $18.2 \text{ M}\Omega$.

Standards of fungal and bacterial metabolites were obtained either as gifts from various research groups or from the following commercial sources: Romer Labs[®] Inc. (Tulln, Austria), Sigma-Aldrich (Vienna, Austria), Iris Biotech GmbH (Marktredwitz, Germany), Axxora Europe (Lausanne, Switzerland) and LGC Promochem GmbH (Wesel, Germany). Stock solutions of each analyte were prepared by dissolving the solid substance in acetonitrile (preferably), acetonitrile/water 1:1 (ν/ν), methanol, methanol/water 1:1 (ν/ν) or water. Thirty-four combined working solutions were prepared by mixing the stock solutions of the corresponding analytes for easier handling, and were stored at -20°C. All solutions were however brought to room temperature before use. The final working solution was freshly prepared prior to spiking experiments by mixing the combined working solutions.

	Total no. of sa	mples/per zone	Communitati				
Zone –	Sesame	Soybean	— Community				
Abaji	3	3	Pandagi, Sabongari, Abaji Centra				
AMAC	3	2	Gwagwa, Kabusa, Karshi, Karu and Orozo				
Bwari	3	2	Bwari Central, Byazhin, Ushafa				
Gwagwalada	6	4	Gwako, Paiko and Tungan Maje				
Kuje	4	6	Chibiri, Gaube, Saaji, Chukuku, Kuje Central, and Kwaku				
Kwali	5	6	Kilankwa, Kwali Central and Yangoji				
Total	24	23					

2.3.2. Extraction procedures

Five grams of each homogenized grain sample, previously pulverized in a mill with a 1 mm² mesh (Cyclotech, Foss Tecator, Höganäs, Sweden), were weighed into a 50 ml polypropylene centrifuge tube (Sarstedt, Nümbrecht, Germany). Ten millilitres of water was added and briefly vortex and allowed to hydrate for ≥ 15 min. 20 ml of the extraction solvent (acetonitrile/water/acetic acid 79:20:1, v/v/v) were added before being vortex for 5-10 min to extract the mycotoxins. The extracts were filtered and centrifuged for 5 min at ≥ 3000 x g (4°C) in order to remove any interfering particles before further clean-up of the supernatant.

For spiking experiments, 0.25 g sample was used for extraction. Samples were extracted for 90 min on a GFL 3017 rotary shaker (GFL, Burgwedel, Germany) and diluted (1 + 1) with dilution solvent (acetonitrile/water/acetic acid 20:79:1, v/v/v). Five

microliters of the diluted extracts were subsequently injected [20].

2.3.3. LC-MS/MS parameters

The LC-MS/MS has been previously described by Malachova et al. [21]. Analysis was performed with a QTrap 5500 LC-MS/MS System (Applied Biosystems, Foster City, CA, USA) equipped with TurboIon Spray electrospray ionization (ESI) source and a 1290 Series HPLC System (Agilent, Waldbronn, Germany). Chromatographic separation was performed at 25°C on a Gemini C18-column, $150 \times 4.6 \text{ mm i.d.}$, 5 µm particle size, equipped with a C18 4 × 3 mm i.d. security guard cartridge (Phenomenex, Torrance, CA, USA).

ESI-MS/MS based Spectrum 380[®] program was performed in the time-scheduled multiple reaction monitoring (MRM) mode both in positive and negative polarities in two separate chromatographic runs per sample by scanning two fragmentation reactions per analyte. The MRM detection window of each analyte was set to its expected retention time ± 27 s and ± 48 s in the positive and the negative modes, respectively. Confirmation of positive analyte identification was obtained by the acquisition of two MRMs per analyte (with the exception of moniliformin that exhibited only one fragment ion). This yielded 4.0 identification points according to the European Union Commission decision 2002/657. In addition, the LC retention time and the intensity ratio of the two MRM transitions agreed with the related values of an authentic standard within 0.1 min and 30%, respectively.

Quantification was performed during external calibration based on serial dilution of a multi-analyte stock solution which was the liquid standards. Results were corrected by apparent recoveries that had been determined by spiking five different blank samples at two concentration levels.

2.3.4. Statistical analysis

Median, mean and standard deviation (SD) were calculated for concentrations of all toxins and metabolites. Pictorial representation of prevalence level was carried out using Excel package 2010.

3. RESULTS

3.1. Occurrence and contamination level of mycotoxins in sesame and soybean grains from the FCT, Abuja, Nigeria

The percentage of contaminated samples, the mean, median and the range of contamination level of the regulated and emerging mycotoxins, in sesame and soybean from the FCT, Abuja are presented Table 2.

	Concentration in sesame (µg kg ⁻¹)*				Concentration in soybean (µg kg ⁻¹)				
Mycotoxin	Positive (n=24) (%)	Median	Mean	Range	Positive (n= 23) (%)	Median	Mean	Range	
Aflatoxin B ₁ (AFB ₁)	3 (13)	1.6	3.6	0.4-7.2	5 (22)	1.2	1.88	0.5-4.02	
Aflatoxin B ₂ (AFB ₂)	2 (8)	1.5	1.5	0.8-1.6	0	-	-	-	
Aflatoxin G1 (AFG ₁)	0	-	-	-	1 (4)	21.1	21.1	21.1	
Ochratoxin A (OTA)	0	-	-	-	2 (9)	16.8	16.8	10.5-23.1	
Fumonisin B ₁ (FB ₁)	5 (21)	17.1	17.3	7.3-26.7	2 (9)	11.84	11.84	10.3-13.4	
Fumonisin B ₂ (FB ₂)	2 (8)	8.6	8.6	6.1-11.2	0	-	-	-	
Fumonisin B ₄ (FB ₄)	1 (4)	5.72	5.72	5.72	0	-	-	-	
Deoxynivalenol (DON)	14 (58)	63.7	78.3	28-171	0	-	-	-	
Zearalenone (ZEN)	11 (46)	3.2	3.6	0.1-18.3	3 (13)	0.7	0.73	0.3-1.4	

Table 2. Occurrence and contamination level of mycotoxins in sesame and soybean grains from the FCT, Abuja, Nigeria.

*Indicated by LC-MS/MS analysis.

The major toxins and emerging metabolites common to both grains were three and seven respectively. Sesame samples had relatively higher occurrence of contamination with regulated mycotoxins such as DON (58.33%), ZEN (45.83%) and FB₁ (20.88%) while 21.7% and 13.4% of the soybean were contaminated with AFB1 and ZEN respectively. AFG1 and OTA were detected in

soyabean but not in sesame, while FB₂ and DON were detected in the sesame but not in soyabean. The highest contamination level was from DON in the sesame samples with median of 63.7 μ g kg⁻¹ while soybean had the highest contamination level from OTA with a median contamination level of $16.8 \ \mu g \ kg^{-1}$.

3.2. Occurrence and contamination level of emerging mycotoxins in sesame and soybean grains

Among the emerging toxins recognized by European Food Safety Authority (EFSA) and the Food and Agriculture Organisation of the United Nations (FAO) and detected in the samples were beauvericin (BEA), moniliformin (MON), sterigmatocystin (STER), alternariolmethylether (AME), alternariol (AOH) and altertoxin-I (ATX-I). Beauvericin (BEA) had the highest occurrence of emerging mycotoxin both in the sesame (66.67%) and in the soybean samples (56.52%) at a respective maximum concentration of 4.2 and 23.04 μ g kg⁻¹ respectively (Table 3). The next higher occurrence (29.16%) was obtained for Alternariol methyl ether (AME), with concentration range of 0.22-11.3 μ g kg⁻¹ in sesame samples. Moniliformin (MON) occurred in the 30.43% of the soybean and with a range concentration of 0.12-33.34 μ g kg⁻¹, while it was detected in 16.67% of sesame with a range of 4.1-17.4 μ g kg⁻¹. Other emerging mycotoxins such as citrinin (CTN) and tenuazonic acid (TeA) were below detectable level.

Table 3. Occurrence of emerging mycotoxins in the samples from the FCT	, Abuja, Nigeria, detected by LC-MS/MS.
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Class of emerging mycotoxin	Emerging mycotoxin	Sesame concentration* (µg kg ⁻¹)				Soybean concentration (µg kg ⁻¹)			
		Positive (n=24) (%)	Median	Mean	Range	Positive (n=23) (%)	Median	Mean	Range
<i>Fusarium</i> metabolites	Beauvericin (BEA)	16 (67)	0.91	0.94	0.08-4.2	13 (57)	0.31	3.69	0.018- 23.04
	Moniliformin (MON)	4 (17)	12.77	11.8	4.1-17.4	7 (30)	2.4	9.4	0.12- 33.34
	Enniatin B (ENN-B)	0	_**	-	-	2 (9)	0.00525	0.005 25	0.005- 0.0055
Aflatoxin precursor	Sterigmatocystin (STER)	4 (17)	0.45	0.43	0.27-0.55	1 (4.3)	0.6	0.6	0.6
<i>Alternaria</i> metabolites	Chanoclavine (CNV)	3 (13)	0.14	0.14	0.06-0.2	0	-	-	-
	Festuclavine (FCV)	2 (9)	1.7	3.21	1.12-8.3	0	-	-	-
	Elymoclavine (ECV)	0	-	-	-	1 (4.3)	1.4	1.4	1.4
	Altertoxin-I (ATX-I)	2 (9)	3.9	4.26	2.82-6.5	1 (4.3)	0.91	0.91	0.91
	Alternariol (AOH)	5 (21)	1.96	8.55	1.14-3.5	1 (4.3)	0.85	0.85	0.85
	Alternariol- methylether (AME)	7 (29)	6.54	5.23	0.22-11.3	1 (4.3)	0.6	0.6	0.6

*Indicated by LC-MS/MS analysis; **= below limit of detection;

The co-occurrence of toxins and metabolites in the ten highest contaminated samples of sesame and in six soybean samples were pictorially presented as scatter plots in Figures 1 and 2. As shown in Figure 1, only in the 5 out of the 10 most contaminated sesame samples (S_1 - S_5) that DON and ZEN co-occurred with other mycotoxins. As shown in Figure 2, only in the 3 out of the 6 most contaminated soyabean samples (S_1-S_3) , that AFB₁ co-occur with other mycotoxins, though at relatively low concentrations below maximum regulatory limits.

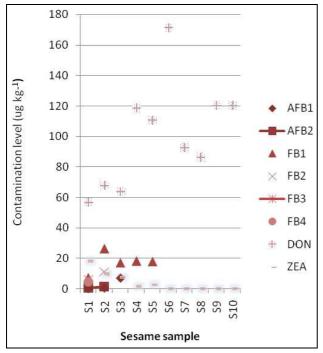


Figure 1. Scatter plots visualizing co-occurrence of major mycotoxins in the ten highest contaminated samples of sesame from the FCT, Abuja Nigeria. Different colour pattern represents each type of metabolite.

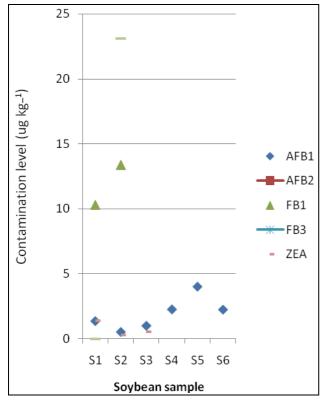


Figure 2. Scatter plots visualizing co-occurrence of major mycotoxins in the six highest contaminated samples of soybean from the FCT, Abuja Nigeria. Different colour pattern represents each type of metabolite.

4. DISCUSSION

The development of LC-MS/MS methods for the simultaneous detection and quantification of a broad spectrum of mycotoxins has facilitated the screening of a larger number of samples for contamination with a wide array of major and less well-known "emerging" mycotoxins [22, 23] Therefore, this analysis was applied in this investigation.

4.1. Occurrence of regulated mycotoxins

In the present study, AFB_1 was observed more frequently in soybean than in sesame. In countries having similar climate, like Burkina Faso and Mozambique, AFB₁ was observed more frequently in soybean-based food and feeds (Burkina Faso, 50% incidence, median = 23.6 μ g kg⁻¹; Mozambique, 46% incidence, median = 69.9 μ g kg⁻¹) than in groundnuts (Burkina Faso, 22% incidence, median = 10.5 μ g kg⁻¹; Mozambique, 14% incidence, median = $3.4 \ \mu g \ kg^{-1}$) [24]. Ezekiel et al. [19] observed that mycotoxin levels were higher in the Nigerian soybean-based kunu-zaki (<LOQ [limit of quantitation] - 123 µg kg⁻¹) and its cereal ingredients $(0.1-31,200 \ \mu g \ kg^{-1})$ than in the sorghumbased pito (<LOQ - 5 µg kg⁻¹) and its cereal base $(1.2-85 \ \mu g \ kg^{-1})$ respectively. Ezekiel et al. [3] reported that up to 13 out of the 16 (81.3%) Nigerian sesame samples analysed had AFs contamination and the concentrations ranged 0.08-1.4 $\mu g kg^{-1}$. Findings in the present study, suggest an association between mycotoxin level and grain size, since soybean is bigger than sesame. There is also the likelihood of more inhibitory compounds in the sesame grains but confirmatory investigation is necessary.

The frequency (20.88%) and the median concentration (17.1 μ g kg⁻¹) of FB₁ was higher in the sesame than in soybeans. This was different in Mozambique where the FB₁ frequency and concentrations in soybean were higher (92% incidence, median = 869 μ g kg⁻¹) than in sesame (75.1%, 107.6 μ g kg⁻¹). This trend might be due to the processing of raw soyabeans into food stuffs in which antifungal factors in the product have been denatured during processing. The occurrence of more FB₁ than FB₂ and FB₃ is consistent with the general pattern of FUM contamination in soybean

and soybean-based foods [25]. Abdus-Salaam et al. [26] reported that *Fusarium* toxins in Nigerian rice had the highest incidence of 79%, but occurred in low amounts with FB₁ having the highest percentage incidence of 39.5% and a mean of 18.5 μ g kg⁻¹. The grains investigated in this study contained relatively lower levels of AFs and FBs below the EU maximum tolerable levels, with highest concentrations of 17.1 μ g kg⁻¹ in FB₁.

It was indicated that DON concentration level was relatively higher in the sesame ranging from 28 to171 μ g kg⁻¹ but below detectable limit in soybean samples. Considering the maximum limits of 750 μ g kg⁻¹ established for DON by EU Regulation in processed cereals in 2012, DON was not of serious health concern as indicated in this study. Also Souza et al. [27] reported a maximum contamination level of 30 μ g kg⁻¹ DON in soybean in Brazil.

Only 8.7% of the soybean grains were contaminated with OTA but there was none detected in sesame. Kayode et al. [28] and Adetunji et al. [29] had a similar report from their analysis of mycotoxins and fungal metabolites in stored soyabean and soyabean-based snacks from Nigeria. Also, Shephard et al. [30] reported that no AFs, OTA, or T-2 or HT-2 toxins were detected on their soybean grains produced in the rural subsistence farmers in Transkei, South Africa. They associated this to the type of varieties planted and good agricultural practices.

In the report of the contamination profile of maize collected from the same store, under similar storage conditions and at the same time was reported by Anjorin et al. [31]. It is obvious that AFB₁, AFB₂, AFG₁, FB₁, FB₂, FB₄ in maize were relatively higher than in sesame and soybean as indicated in this study. For instance, while AFB1 were 17.3 μ g kg⁻¹ and 11.84 μ g kg⁻¹ in sesame and soyabean, respectively, it was as high as 2349 μ g kg⁻¹ in maize grains. This might be due to generic differences in the biochemical and genetic make-up of the crops that might have influenced their resistance level to the prevailing toxigenic fungal species.

There were relatively safe doses of major mycotoxins in the two grains except in OTA found in the soybean (16.8 μ g kg⁻¹) that were slightly above the EU maximum acceptable limit of 5 μ g

kg⁻¹. This limit is also adopted in Nigeria and Kenya thus the only source of health concern.

4.2. Occurrence of emerging mycotoxins

Beauvericin and moniliformin were the two most prevalent emerging mycotoxins in the studied seeds. The incidence and contamination level of BEA was relatively low. In Nigerian rice, analysis revealed that beauvericin were detected with maximum value of 131 µg kg⁻¹ [26] while Sulyok et al. [13] also reported up to 8000 µg kg⁻¹ BEA in soybean-based food samples investigated. BEA, is a *Fusarium* emerging hexadepsi peptides secondary metabolite, has been less frequently investigated by routine methods [32]. BEA is produced by *Fusarium* species such as *F. avenaceum*, *F. subglutinans*, *F. oxysporum F. proliferatum*, *F. poae* and *F. tricinctum* [33-35].

A public health threat cannot completely be ruled out due to their widespread co-occurrence with other mycotoxins and fungal metabolites in the grains [36]. Beauvericin has been implicated in acting on the cellular membranes increasing the permeability and disrupting the cellular homeostasis [37]. MON was also detected in both sesame and soybean samples, but it was at low frequency and concentration. Gutema et al. [38] earlier reported the detection of MON in soybean, wheat, rye, triticale, oats and rice, and their co-occurrence with FUMs.

In this study, the presence of clavines ergot alkaloid such as chanoclavine (CNV), and festuclavine (FCV) mostly in the sesame samples indicated the contamination of such grains with Claviceps purpurea, C. africanana, C. fusiformis, C. fusiformis, C. paspali, and Neotyphodium coenophialum. These toxigenic fungi are also commonly found in wheat, rye, hay, barley, sesame, oats, sorghum, triticale. In soybean-based poultry feed in other parts of Nigeria, Claviceps metabolites were found at concentrations of up to 350 μ g kg⁻¹, with agroclavine (AGV) having the highest concentration with elymoclavin (ECV) was the most prevalent [19]. In this study, frequency of AME in the soybean samples was just 4.35% at a concentration of 0.6 μ g kg⁻¹. This is similar to the report of assessment on the mycotoxins load on Nigerian stored soybean by Adetunji et al. [29] that alternariol methylether (AME) occurred only in one sample (1.7%

contamination) each at concentrations of 106 μ g kg⁻¹. Regardless of the low levels of ergot alkaloids in our samples, there is an impending danger in the continuous consumption of this potent group of non-regulatory toxins [39, 40]. In 2011, EFSA reported that AOH could be potentially harmful to humans and pointed out the need of further investigations to generate toxicity data.

5. CONCLUSION

Multi-mycotoxin analysis by LC-MS/MS is an important step towards gaining a more accurate picture of the extent of mycotoxin contamination in food and feed. The sesame samples analysed were contaminated with, AFB₁ and AFB₂, FB₁ and FB₂, FB₄, DON, and ZEN while the soybean were contaminated with AFB₁, AFG₁, FB₁, OTA and ZEN with their contamination levels below the maximum levels established by the EU with the exception of OTA in soybean. For the first time, the presence of the emerging mycotoxins - beauvericin BEA), sterigmatocystin alternariolmethylether (STER) (AME) chanoclavine (CNV) and elymoclavine (ECV) were confirmed to be present in the sesame and soybean grains in the FCT, Abuja, Nigeria. There is no indication of potential health threat due to the contamination of sesame and soybean with some non-classic mycotoxins which have not been included in conventional mycotoxin monitoring. However, more comprehensive monitoring programs may be needed in the grains in other agroecologies in Nigeria involving both regulated and emerging mycotoxins. This could involve research in possible synergistic interactions with other mycotoxins present.

TRANSPARENCY DECLARATION

The authors declare that there is no conflict of interest regarding the publication of this article.

AUTHORS' CONTRIBUTION

SOF was the study supervisor, rendered technical support and revised the manuscript and ensures compliance with journal standard. TSA acquired the data, interpreted, did extensive literature search and wrote the manuscript. MS and RK analysed the data and developed methodology. All authors read and approved the final manuscript.

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