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Comparative study of mycotoxin occurrence in Andean and cereal grains cultivated in South America and North Europe

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A B S T R A C T

The consumption of high-quality Andean grains (a.k.a. pseudocereals) is increasing worldwide, and yet very little is known about the susceptibility of these crops to mycotoxin contamination. In this survey study, a multi-analyte liquid chromatography–tandem mass spectrometry (LC–MS/MS) method was utilised to determine mycotoxin and fungal metabolite levels in Andean grains (quinoa and kañiwa) in comparison to cereal grains (barley, oats and wheat), cultivated in both South American (Bolivia and Peru) and North European (Denmark, Finland and Latvia) countries. A total of 101 analytes were detected at varying levels, primarily produced by *Penicillium* spp., *Fusarium* spp. and *Aspergillus* spp., depending on the type of crop, geographical location and agricultural practices used. Generally, Andean grains from South America showed lower mycotoxin contamination (concentration and assortment) than those from North Europe, while the opposite occurred with cereal grains. Mycotoxin contamination profiles exhibited marked differences between Andean and cereal grains, even when harvested from the same regions, highlighting the need for crop-specific approaches for mycotoxin risk mitigation. Lastly, the efficacy of grain cleaning in respect to total mycotoxin content was assessed, which resulted in significantly lower levels (overall reduction approx. 50%) in cleaned samples for the majority of contaminants.

1. Introduction

Quinoa (*Chenopodium quinoa*) and kañiwa (*Chenopodium pallidicaule*) are grains that were widely cultivated in the Andean mountains by Pre-Hispanic civilizations, there comes its name *Andean grains* (a.k.a. pseudocereal; Andean grains belong to fam. *Amaranthaceae* while conventional cereals to fam. *Poaceae*). Despite changes in dietary traits during colonial and republican times, the rural consumption of quinoa and kañiwa was relatively common until the early 20th century, mostly, on the Andean plateau. However, the massive importation of wheat severely affected local farmers, leading to reduced cultivation and consumption (Tapia, 1979). Additionally, ethnic discrimination, involving indigenous communities and their traditional food, may have restrained climate-resilient quinoa and kañiwa to areas where no other crop could grow (Hellin & Higman, 2005; Martinez-Zuñiga, 2007), thus becoming staple crops for subsistence farming (Vassas and Viera Pak, 2010). After the revaluation of ancient knowledge, quinoa and kañiwa were found to be formidable food alternatives that could contribute to the world food security (Bazile et al., 2016; FAO, 2011; Jacobsen, 2017; Rodriguez et al., 2020). These gluten-free grains contain not only a complete pool of amino acids, but also a high amount of essential micronutrients and minerals. Those are key features for their nutritional revalorization and growing popularity in the Western World (Repo--Carrasco et al., 2003).

Even though Andean grains are as susceptible to fungal growth and mycotoxin contamination as cereal grains (e.g. maize, wheat), there is scarce information on the contaminating fungi and mycotoxin occurrence in quinoa and kañiwa. The few available studies focused primarily on the investigation of the mycoflora present in Andean grains and not on mycotoxin contamination. Case in point, the presence of *Ascohyta, Altenaria, Phoma, Fusarium, Bipolaris, Cladosporium* and *Pyronochaeta* genera in seeds of *Chenopodium quinoa* from Bolivia, Brazil, Czech Republic and Peru have been reported, but no accompanying mycotoxin data were provided (Boerema et al., 1977; Spehar et al., 1997; Dřímalková, 2003). Amaranth grains from Argentina were analysed to examine mycoflora, which was found to be dominated by the mycotoxin-producing fungal species *A. flavus*, *A. parasiticus*, *P. chrysogenum* and *F. equiseti* (Bresler et al., 1995). Additionally, Pappier et al. (2008) reported that *Penicillium* and *Aspergillus* were the most frequently encountered genera in quinoa harvested from three locations in Argentina. In the same study, processing of the grains for removal of saponins (wet method) caused a decrease in *Aspergillus* incidence, whilst increased the proportion of *Penicillium*, *Eurotium*, *Mucor* and *Rhizopus* that was characterised as internal mycobiota.

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However, analysis of mycotoxins is essential for all types of grains, as these low-molecular-weight toxins can contaminate crops in all climatic regions. Importantly, mycotoxins have been associated with a broad range of toxic effects to both humans and animals, including acute toxicity, immunotoxicity, hepatotoxicity, nephrotoxicity, carcinogenicity and reproductive toxicity (Bhat et al., 2010). Safety of food- and feedstuffs is paramount to consumers and thus, complex regulatory frameworks and monitoring systems have been developed globally that rely on the latest scientific knowledge and analytical tools. In the European Union (EU), maximum levels have been established for a number of mycotoxins in cereals and cereal-derived products (EU Commission Regulation (EC) No 1881/2006). However, no such levels specific to Andean grains exist.

Liquid chromatography–tandem mass spectrometry (LC–MS/MS) is the most widely used method for accurate and reliable determination of multiple mycotoxins at even minute concentrations in complex matrices such as cereal grains and cereal-based foods (Malachová et al., 2018). Recent applications of LC–MS/MS methods for the simultaneous determination of multiple mycotoxins and modified forms include analysis of wheat, barley, maize and cereal-derived products, among others, utilising a variety of matrix-dependent sample preparation techniques (Spaggiari et al., 2019; Ekwomandu et al., 2020; Ostry et al., 2020; Drakopoulos et al., 2021; Rausch et al., 2021).

From the very limited number of studies that have measured mycotoxins in non-cereal grains, zearalenone (ZEN) was determined at levels up to 1980 μg/kg in two samples of *Amaranthus cruentus* grains, which had been stored moist (Bresler et al., 1991). No aflatoxins, ochratoxin A (OT-A) or sterigmatocystin were found, however, the number of samples analysed was very limited. No mycotoxin contamination was reported in the previously mentioned study of Pappier et al. (2008), although the method was only capable of analysing aflatoxins and citrinin. In 2014, Arroyo-Manzanares et al. developed and validated an ultra-high performance liquid chromatography (UHPLC)–MS/MS method for the determination of 15 mycotoxins. It was used to analyse quinoa and amaranth samples purchased from local markets in Spain, but again none were found positive to any of the mycotoxins included in the method. Lastly, commercially available quinoa flour from Italy was recently analysed with enzyme-linked immunosorbent assay (ELISA) and found to contain 4.4 ng/g total aflatoxins (B_1, B_2, G_1 and G_2) and ca. 370 ng/g total fumonisins (B_1 and B_2) (Sacco et al., 2020). In the same study, total aflatoxins at the level of 1.6 ng/g, and fumonisins at 111 ng/g were reported for amaranth (grain).

The aim of the present study was to determine mycotoxins present in commercial varieties of quinoa and kañiwa cultivated in South America and North Europe. This work constitutes the most comprehensive survey of mycotoxin content in Andean grains to date. Data generated herein facilitate comparisons of mycotoxin content between regions and grain types that can be valuable in the identification of mycotoxin-producing fungi and mycotoxins of concern, thus contributing to the safe consumption of Andean grains worldwide.

2. Materials and methods

2.1. Chemicals and reagents

HPLC gradient grade acetonitrile (HiPerSolv Chromanorm) was obtained from VWR Chemicals (Vienna, Austria) and LC–MS Chromasolv grade methanol from Honeywell (Seelze, Germany). LC–MS grade ammonium acetate and glacial acetic acid (p.a.) were purchased from Sigma-Aldrich (Vienna, Austria). Purification of reverse osmosis water was performed using a Purelab Ultra system (ELGA LabWater, Celle, Germany). Analytical standards of mycotoxins and fungal metabolites were isolated in-house at the Department of Agrobiotechnology, IFA-Tulln (Tulln, Austria), received as gifts by external collaborators or purchased from commercial suppliers. The complete list of the analytical standards' details is provided in Sulyok et al. (2020).

2.2. Grains and sample preparation

Grain samples were obtained from Finland, Denmark, Latvia, Peru and Bolivia (latitude descending order; Fig. 1). Andean and cereal grains were collected from plots in close proximity, within the same cultivation area (i.e. Denmark, Peru). Where applicable, a simple random sampling was conducted with resulting specimens mixed into a pool. Grain samples were pre-treated as follows: *Uncleaned*, grains went through mechanical pre-cleaning (removal of large debris, leaves, twigs, etc.) but rinsing was not conducted. *Traditionally washed* grains went through mechanical pre-cleaning (removal of large debris, leaves, twigs, etc.) and rinsing (water at room temperature) until foam was no longer formed (indicative of saponin removal). *Pearled* grains were exposed to an abrasive surface to remove saponin-containing outer layers. *Mechanically cleaned* grains were winnowed and screened but rinsing was not conducted. Detailed information regarding individual pre-treatments and cultivation areas is shown in Table 1 and Fig. 1. All grains were eventually milled using an ultra-centrifugal mill (Retsch ZM 200, Haan, Germany) at 10,000 rpm, weighed (5 g), sorted (3–6 replicates) and stored in falcon tubes at −20 °C. Prior to analysis, Andean and cereal grain samples were extracted using 20 mL of the extraction solution acetonitrile:water:acetic acid (79:20:1, v/v/v) and shaken for 90 min with a rotary shaker (GFL 3017, GFL; Burgwedel, Germany). The supernatants (300 μL) were transferred into HPLC vials and diluted with 300 μL acetonitrile:water:acetic acid (20:79:1, v/v/v).

2.3. LC–MS/MS analysis

The method used for analysis of the Andean and cereal grains was recently published by Sulyok et al. (2020). Briefly, samples were analysed with a 1290 series Agilent Technologies UHPLC system (Waldbronn, Germany) coupled to a QTrap 5500 MS/MS that was equipped with a TurboV electrospray ionisation (ESI) source (Sciex, California, USA). Chromatographic separation was performed on a Gemini C18 column (150 mm × 4.6 mm, 5 μm particle size; Phenomenex, California, USA) with a C18 security guard cartridge (4 mm × 3 mm; Phenomenex). Quantification was based on external calibration (linear, 1/x weighed) using a serial dilution of a multi-analyte working solution. Results were corrected using apparent recoveries obtained through spiking experiments (Sulyok et al., 2020). The accuracy of the method is verified on a continuous basis by participation in a proficiency testing scheme organized by BIPEA (Gennevilliers, France) with a current rate of z-scores between − 2 and 2 of >94% (>1500 results submitted).

2.4. Data processing

Data corresponding to the mycotoxin contaminants from all samples was primarily sorted by cleaning method (cleaned and uncleaned) and collection year (2015 and 2017). Standard normal variate (SNV) was used as pre-treatment method due to its effectiveness in scattering correction. Subsequently, principal component analysis (PCA) was used to observe potential correlations with-in/among samples (a.k.a. loadings) and mycotoxins (a.k.a. scores). Data pre-processing and plotting was done using SIMCA 15.0 software package (v. 13, Umetrics, Sweden). The degree of variation was assessed via Hotelling's T-squared distribution (T^2) at three confidence intervals: 50% (HT^2_50%), 75% (HT^2_75%) and 99% (HT^2_99%). The construction of calibration curves and peak integration were performed using MultiQuant™ v. 2.0.2 software by Sciex.

It is worth noting that siccanol (SIC, 57), dihydrotrichotetronine (DHTTT, 75) and trichotetronine (TTT, 77) were expressed as peak area values, as no analytical standards were available at the time of analysis.

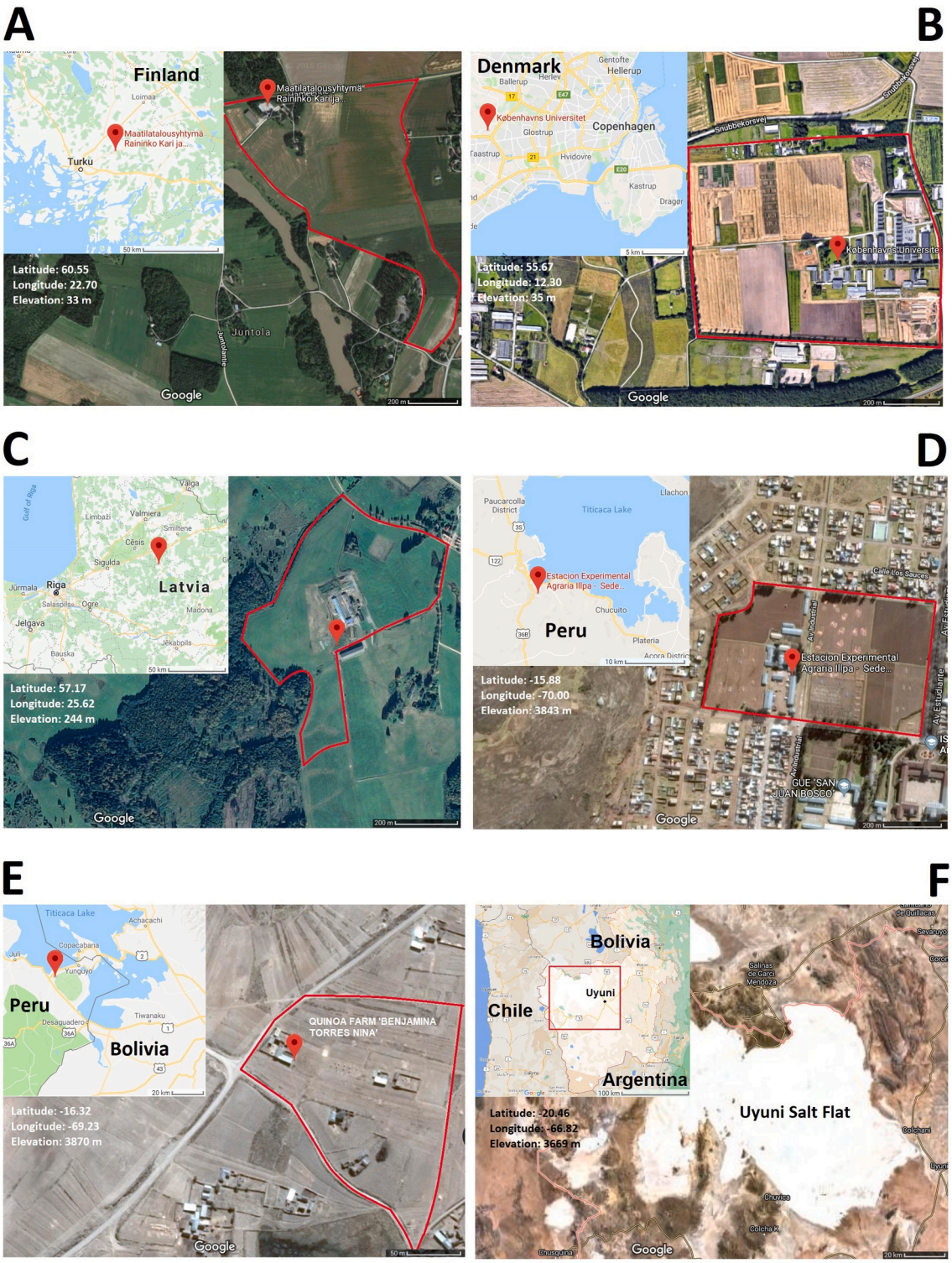

Fig. 1. Cultivation areas of the samples listed in Table 1.
Section 1F: geographic coordinates corresponding to Uyuni Salt Flats (Potosí, Bolivia); exact cultivation area is unknown. Source of the images was Google Inc. (California, USA).

3. Results and discussion

3.1. Method performance

The method was transferred to the new matrices of this study, according to our suggestion in Sulyok et al. (2020), by spiking different individual samples on one concentration level. As considers compliance to official performance criteria, similar results were obtained (Supplementary Table S1). The 70–120% criterion for "recovery" was met for 52–63% and for 83–88% of all investigated analytes for apparent recoveries and recoveries of the extraction step, respectively, whereas the RSD <20% criterion for reproducibility was met for 92–98% of analytes despite using different individual samples for spiking.

Table 1
List of grain samples and their corresponding varieties harvested in 2015 and 2017. Cleaning methods (W, traditional washing; P, pearling; M, mechanical cleaning) and cultivation areas (e.g. 1A = Fig. 1A) are specified.

2015							2017						
Sample	Cleaning methods[a]				Cultivation area	Varietal code	Sample	Cleaning methods[a]				Cultivation area	Varietal code
	U[b]	*W*	*P*	*M*				U[b]	*W*	*P*	*M*		
Quinoa *(Chenopodium quinoa)*							Quinoa *(Chenopodium quinoa)*						
minttumatilda[c]		●	●		1A	QMM	*minttumatilda*[c]	●	●			1A	QMM
kancolla		●			1E	QKA	*Kancolla*	●	●			1E	QKA
kuchivila		●			1E	QKU	*Kuchivila*	●	●			1E	QKU
mistura		●			1E	QM	*Mistura*	●	●			1E	QMM
negra Collana		●			1E	QNC	*negra collana*	●	●			1E	QNC
pasankalla		●			1E	QP	*Pasankalla*	●	●			1E	QP
real[d]		●			1F	QR	*real*[d]	●	●			1F	QR
rosada taraco		●			1E	QRT	*rosada taraco*	●	●			1E	QRT
salcedo INIA		●			1D	QSI	*salcedo INIA*	●	●			1D	QSI
titicaca Denmark	●				1B	QTID	*puno*	●	●			1B	QPU
							titicaca Denmark	●	●			1B	QTID
Kañiwa (Chenopodium pallidicaule)							*vikinga*	●	●			1B	QVI
							titicaca Latvia	●	●			1C	QTIL
cupi INIA				●	1D	KCI	Kañiwa *(Chenopodium pallidicaule)*						
illpa INIA				●	1D	KII							
							cupi INIA	●	●		●	1D	KCI
Barley *(Hordeum vulgare)*							*illpa* INIA	●	●		●	1D	KII
							ramis	●	●			1D	KRA
commercial[e]		●	●		1E	BC	Barley *(Hordeum vulgare)*						
Oat *(Avena sativa)*													
							commercial[e]	●	●			1E	BC
Landsort		●	●		1B	OL	Oat *(Avena sativa)*						
commercial[e]		●	●		1E	OC							
Riegel		●	●		1B	OR	commercial[e]	●	●			1E	OC
Wheat *(Triticum* L.*)*							Wheat *(Triticum* L.*)*						
commercial[e]		●	●		1E	WC	commercial[e]	●	●			1E	WC

[a] Some grain samples went through more than one cleaning procedure.

[b] Uncleaned samples.

[c] Population variety.

[d] Variety cultivated on the Bolivian side of the Andean Plateau. Exact location is unknown.

[e] Cereal grains whose variety could not be specified.

3.2. Mycotoxin profiles

A total of 101 metabolites were detected in all grains (Table 2). The largest array of mycotoxins were produced by *Penicillium* spp. (32 metabolites), followed by *Fusarium* spp. (26 metabolites), *Aspergillus* spp. (10 metabolites), *Alternaria* spp. (6 metabolites), *Trichoderma* spp. (3 metabolites), *Claviceps* spp. (3 metabolites), *Ascochyta* spp. (2 metabolites), *Cladosporium* spp. (2 metabolites), *Metharhizium* spp. (2 metabolites), *Beauvaria* spp. (1 metabolite) and *Ramularia* spp. (1 metabolite). For 13 analytes, no producing species could be attributed and were thus labelled as unspecific metabolites. From all Andean and cereal grains analysed, only two exceeded the maximum levels for mycotoxins in established unprocessed cereals, based on the EU Commission Regulation (EC) No 1881/2006. More specifically, OC from the 2017 harvest contained 64 μg/kg OT-A (22) and 377 μg/kg ZEN (58), both exceeding the limits of 5 μg/kg OT-A (22) and 100 μg/kg ZEN (58), and QTIL contained 5.6 μg/kg OT-A (22). In this section, mean mycotoxin concentration values from both 2015 and 2017 harvest are reported. Detailed mycotoxin levels are provided in Supplementary Table S2 and **S3.**

3.2.1. High contamination levels (>1000 μg/kg)

Flavogaucin (FG, 17) was the *Penicillium*-produced metabolite exhibiting the highest concentration in uncleaned grains; it was mostly abundant in QTIL (18 mg/kg) (Fig. 2A, centre right). Regarding *Fusarium* metabolites, antibiotic Y (AB-Y, 33) and aurofusarin (AUR, 35) were detected in large concentrations in uncleaned OC (3638 μg/kg) and QPU (1041 μg/kg), respectively. Concerning metabolites from *Alternaria* spp., infectopyron (INFE, 72) was present in oat var. *landsort* (OL; 1962 μg/kg), whereas tenuazonic acid (TeA, 74) was mostly detected in QPU (2218 μg/kg) and QTIL (1213 μg/kg) (Fig. 2A, upper left section). The unspecific metabolites neoechinulin A (NC-A, 98; Fig. 2A, right section), asperphenamate (AsP, 90; Fig. 2A, centre) and N-benzoyl-phenylalanine (NBP, 97; Fig. 2A, centre right) were detected in QTIL in the following concentrations: 9784 μg NC-A/kg, 3258 μg AsP/kg and 1062 μg NBP/kg. Asperglaucide (AsG, 89; Fig. 2, centre) was primarily present in quinoa var. *real* (QR; 1008 μg/kg).

3.2.2. Medium contamination levels (100–1000 μg/kg)

A large number of mycotoxins produced by *Fusarium* spp. were detected in concentrations between 100 and 1000 μg/kg. *Fusarium* mycotoxins such as butenolid (BU, 38), chlamydosporol (ChlaD:iol, 40), culmorin (CULM, 42), enniatin A (ENN-A, 45), enniatin A1 (ENN-A1, 46), enniatin B (ENN-B, 47), enniatin B1 (ENN-B1, 48), equisetin (EQ, 51), moniliformin (MON, 54) and nivalenol (NIV, 55) were measured at levels within the 100–1000 μg/kg range. Despite their high concentrations in OC, ENN-A1 (46), ENN-B (47) and ENN-B1 (48) were three out of the only five mycotoxins detected in kañiwa var. *cupi* INIA (KCI), *illpa* INIA (KII) or *ramis* (KRA) (Fig. 2A, lower left section). ENN-A (45) was found in OC and minimally detected in KCI (Fig. 2A, lower right section). QPU and QTIL were the only grains where BU (38) was found, whilst ChlaD:ol (40) was only present in OC. CULM (42) was detected in QPU, QVI, QTIL, quinoa pop. var. *minttumatilda* (QMM) and QTID; NIV (55) was found in oat (OL, OC and OR) (Fig. 2A, upper left section). The highest concentrations of EQ (51) were measured in BC, QPU, OC, and to a lesser extent in QVI (Fig. 2A, upper right section). ZEN (58) was only found in OC at a mean concentration of around 190 μg/kg (Fig. 2a), and no fumonisins were detected in any of the samples.

Altersetin (ALT, 71), produced by *Alternaria* spp., was solely detected in QPU and QTIL (Fig. 2A, far right section). Citreohybridinol (CHOL, 7) and viridicatol (VOH, 32), produced by *Penicillium* spp., were only found in OC (Fig. 2a). Furthermore, mycophenolic acid (MPA, 20) was present in OC, QTIL and to a lesser extent in quinoa var. *kuchivila* (QKU). Pyrenocin A (Pyre-A, 28) was only detected in OL. Calphostin (CAL, 83), attributed to *Cladosporium* spp., was identified at descending levels of concentration in QPU, QTIL, OL, QVI, QTID and QMM. Lastly, unidentified metabolites such as emodin (EMO, 94) and tryptophol (3-IE, 101) were found in almost every sample. For instance, EMO (94) was observed in oats (OL, OR and OC), barley (BC), quinoa (QTIL, QTID, QPU, QMM, QR, QVI and QKU) and kañiwa (KRA) (Fig. 2A, upper left section). 3-IE (101) was found in every sample except for OL and OR (Fig. 2A, lower left section).

3.2.3. Low contamination levels (<99 μg/kg)

A larger array of *Penicillium* mycotoxins were detected at this concentration range (Fig. 2a), in comparison to those from *Fusarium* spp. The occurrence of prominent *Penicillium* mycotoxins, such as OT-A (22) and ochratoxin B (OT-B, 23), in uncleaned grains was relatively low (Fig. 2a, lower right section). QKU and QTIL were contaminated with a mean level of around 5 μg OT-A/kg, whilst OC with 30 μg/kg. The concentration of OT-B (23) in QKU and OC was considerably lower than that of OT-A (22). Similar OT-A concentrations have been previously reported in milled quinoa products, obtained from Canadian markets, where 39% of the analysed samples were found to contain OT-A at a mean level of 1.7 μg/kg (Kolakowski et al., 2016). Among other *Penicillium*-produced contaminants, atlantinol A (AT-A, 5), citrinin (CIT, 8), cyclopenol (COH, 12), viridicatin (VIN, 15), griseophenone B (GSP-B, 19), andrastin A (A-A, 22) and dihydrocitrinone (DH-CIT, 31) were –in some cases– uniquely identified in OC. At lower levels, 7-hydroxypestalotin (7HP, 1), agroclavine (AC, 2), chanoclavin (ChC, 6) and questiomycin A (Qu-A, 29) were detected in QTIL. QKU had only minor concentrations of AT-A (5) and Qu-A (29).

Regarding *Fusarium*-produced metabolites, the type-A trichothecenes HT-2 toxin (HT-2, 53) and T-2 toxin (T-2, 57) were detected in OL and oat var. *riegel* (OR) (Fig. 2A, upper left section). OL was found to contain around 50 μg HT-2/kg and 70 μg T-2/kg. OR, on the other hand, contained around 30 μg HT-2/kg and 10 μg T-2/kg. Apicin (APIC, 34), beauvericin (BEA, 36) and bikaverin (BIKA, 37) were mostly found in OL and OR (Fig. 2A, upper section). Deoxynivalenol (DON, 43) was only detected in OL (Fig. 2A, upper left section) and fungerin (FUN, 52) only in OC. *Cladosporium*-produced cladosporin (CLADO, 84) was identified in OC, QTIL and QSI (Fig. 2A, centre). *Aspergillus*-produced 3-nitropropionic acid (3-NA, 66) and *Metarhizium*-produced destruxin B (D-B, 86) were detected in OC and QTIL (Fig. 2A–a, right section). In contrast to Sacco et al. (2020), who reported aflatoxin contamination in both amaranth and quinoa, no aflatoxins were detected in any of the samples analysed in this study, most likely due to unfavourable geographic and climatic conditions. *Trichoderma*-produced trichodimerol (TCOH, 76) and *Claviceps*-produced ergometrine (ERG, 78) were found in OC and QTIL, respectively. Finally, unspecific metabolites such as cyclo L-Pro-L-Tyr (CDP-Tyr, 92) and cyclo L-Pro-L-Val (CDP-Val, 93) were detected in all the uncleaned grains, whereas citreorosein (91) and fallacinol (96) were mostly found in QTIL.

At trace level concentrations (<10 μg/kg), *Penicillium*-produced mycotoxins represented the largest proportion, followed by mycotoxins produced by *Aspergillus* spp. (mostly in BC and OC), *Alternaria* spp. (mostly in QMM, QPU, QTID and QVI), *Fusarium* (only found in QTIL), *Ascochyta* (OC and QSI), *Metarhizium* (OC), *Romularia* (BC) and *Beauvaria* (QTIL and OL). In this concentration range, only two unspecific metabolites were identified: norlichexanthone (NX, 99) and skyrin (SKY, 100). Most of these metabolites are depicted in Fig. 2a (right section).

3.3. Post-harvest cleaning

Noticeable differences in the content and distribution of mycotoxins were observed by comparing samples before and after cleaning (Figs. 2 and 3). For instance, uncleaned QMM, located on the extreme upper left side of PCA plot (Fig. 2), was initially contaminated with Pyre_A (28), CULM (42), NIV (55), EMO (94) and ENC (95), all of which became nearly undetectable after cleaning, as evidenced by the QMM relocation to the right side of the PCA plot (Fig. 3). Despite this, QMM still contained certain *Fusarium* [e.g. CULM (42)] and *Alternaria* [e.g. ALT (71)]

Table 2
Codified list of detected mycotoxins sorted by pre-treatment and year.

Numerical code	Origin	Mycotoxin	Cleaned		Uncleaned	
			2015	2017	2015	2017
1	Penicillium spp.	7-Hydroxypestalotin		7HP		7HP
2		Agroclavine		AC		AC
3		Anacin		AN		AN
4		Andrastin A		A-A		A-A
5		Atlantinon A		AT-A		AT-A
6		Chanoclavin		ChC		ChC
7		Citreohybridinol		CHOL		CHOL
8		Citrinin[a]		CIT		CIT
9		Communesin B		COM-B		COM-B
10		Curvularin		CURV		CURV
11		Cyclopenin		CIN		CIN
12		Cyclopenol		COH		COH
13		Cyclopeptine		CP		CP
14		Dechlorogriseofulvin		DCGSF		DCGSF
15		Dihydrocitrinone		DH-CIT		DH-CIT
16		Festuclavine				FC
17		Flavoglaucin		FG		FG
18		Griseofulvin		GSF		GSF
19		Griseophenone B		GSP-B		GSP-B
20		Mycophenolic acid	MPA	MPA		MPA
21		Mycophenolic acid IV				MPA-4
22		Ochratoxin A[a]	OT-A	OT-A		OT-A
23		Ochratoxin B[a]		OT-B		OT-B
24		Okaramine B		Ok-B		Ok-B
25		O-Methylviridicatin		OMV		OMV
26		Pestalotin		PES		PES
27		Pinselin		PIN		PIN
28		Pyrenocin A	Pyre_A		Pyre_A	
29		Questiomycin A	Qu-A	Qu-A		Qu-A
30		Quinolactacin A		QuL-A		QuL-A
31		Viridicatin		VIN		VIN
32		Viridicatol		VOH		VOH
33	Fusarium spp.	Antibiotic Y		AB-Y		AB-Y
34		Apicidin	APIC	APIC	APIC	APIC
35		Aurofusarin	AUR	AUR	AUR	AUR
36		Beauvericin	BEA	BEA	BEA	BEA
37		Bikaverin	BIKA		BIKA	
38		Butenolid		BU		BU
39		Chlamydospordiol		ChlaD:iol		ChlaD:iol
40		Chlamydosporol		ChlaD:ol		ChlaD:ol
41		Chrysogin	Chry	Chry	Chry	Chry
42		Culmorin		CULM		CULM
43		Deoxynivalenol	DON		DON	
44		Diacetoxyscirpenol		DAS		DAS
45		Enniatin A	ENN-A	ENN-A	ENN-A	ENN-A
46		Enniatin A1	ENN-A1	ENN-A1	ENN-A1	ENN-A2
47		Enniatin B	ENN-B	ENN-B	ENN-B	ENN-B
48		Enniatin B1	ENN-B1	ENN-B1	ENN-B1	ENN-B1
49		Enniatin B2		ENN-B2		ENN-B2
50		Epiequisetin		epi-EQ		epi-EQ
51		Equisetin	EQ	EQ	EQ	EQ
52		Fungerin		FUN		FUN
53		HT-2 toxin	HT-2		HT-2	
54		Moniliformin	MON	MON	MON	MON
55		Nivalenol	NIV	NIV	NIV	NIV
56		Siccanol	SIC	SIC		SIC
57		T-2 toxin	T-2		T-2	
58		Zearalenone		ZEN		ZEN
59	Aspergillus spp.	Averantin		AVN		AVN
60		Averufin		AVR		AVR
61		Methoxysterigmatocystin		MST		MST
62		Norsolorinic acid		NA		NA
63		Sterigmatocystin		ST		ST
64		Versicolorin A		Ver-A		Ver-A
65		Versicolorin C		Ver-C		Ver-C
66		3-Nitropropionic acid		3-NA		3-NA
67		Sydonic acid		SA		SA
68		Territrem B		T-B		T-B
69	*Alternaria* spp.	Alternariol		AOH	AOH	AOH
70		Alternariolmethylether		AME	AME	AME
71		Altersetin		ALT		ALT
72		Infectopyron	INFE	INFE	INFE	INFE
73		Tentoxin	TEN	TEN	TEN	TEN

(*continued on next page*)

Table 2 (*continued*)

Numerical code	Origin	Mycotoxin	Cleaned		Uncleaned	
			2015	2017	2015	2017
74		Tenuazonic acid		TeA		TeA
75	Trichoderma spp.	Dihydrotrichotetronine		DHTTT		DHTTT
76		Trichodimerol		TCOH		TCOH
77		Trichotetronine		TTT		
78	*Claviceps* spp.	Ergometrine		ERG		ERG
79		Ergometrinine		ERGOE		ERGOE
80		Ergine		LSA		LSA
81	*Ascochyta* spp.	Ascochlorin		Ach		Ach
82		Ascofuranone		AF		AF
83	*Cladosporium* spp.	Calphostin	CAL	CAL	CAL	CAL
84		Cladosporin		CLADO		CLADO
85	*Metarhizium* spp.	Destruxin A		D-A		D-A
86		Destruxin B		D-B	D-B	D-B
87	*Beauvaria* spp.	Bassianolide	BASS		BASS	
88	*Ramularia* spp.	Rubellin D	R-D		R-D	
89	Unspecific	Asperglaucide	AsG	AsG		AsG
90		Asperphenamate	AsP	AsP	AsP	AsP
91		Citreorosein	CTO	CTO	CTO	CTO
92		cyclo(L-Pro-L-Tyr)	CDP-Tyr	CDP-Tyr	CDP-Tyr	CDP-Tyr
93		cyclo(L-Pro-L-Val)	CDP-Val	CDP-Val	CDP-Val	CDP-Val
94		Emodin	EMO	EMO	EMO	EMO
95		Endocrocin	ENC	ENC	ENC	ENC
96		Fallacinol		FOH		FOH
97		N-Benzoyl-Phenylalanine	NBP	NBP		NBP
98		Neoechinulin A	NC-A	NC-A		NC-A
99		Norlichexanthone		NX		NX
100		Skyrin	SKY	SKY	SKY	SKY
101		Tryptophol	3-IE	3-IE	3-IE	3-IE

[a] These mycotoxins have been attributed to Penicillium spp. as the most likely producing species in the samples analysed.

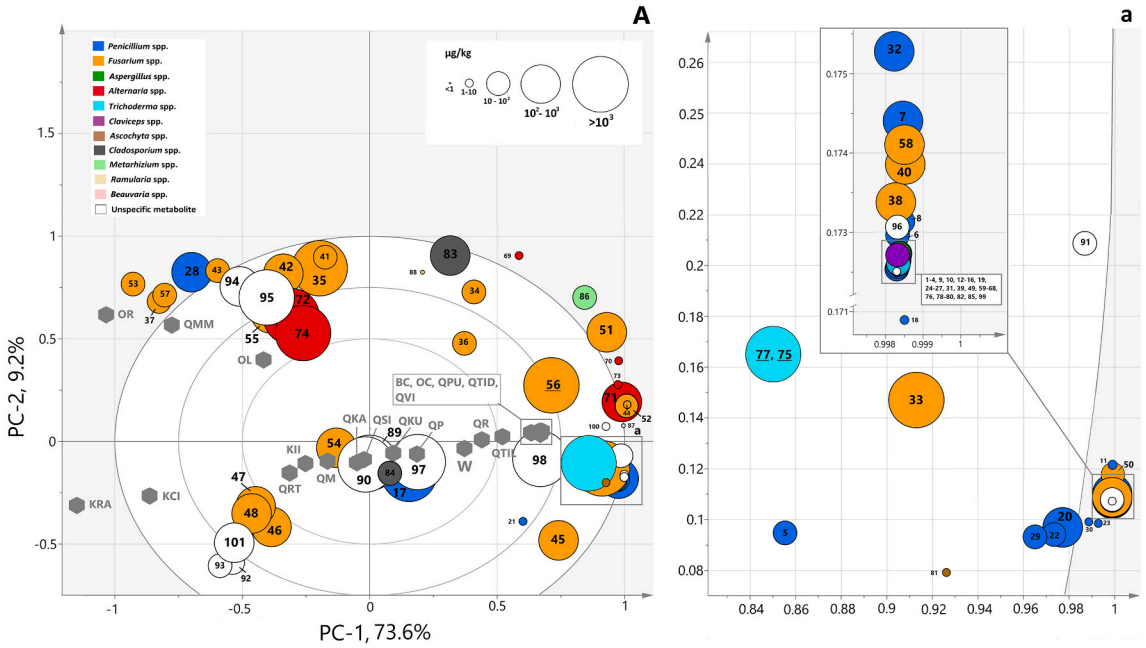

Fig. 2. Principal component analysis bi-plot for mycotoxins detected from uncleaned kañiwa, quinoa, barley, oats and wheat grains (total variance, 82.8%). Numerically coded mycotoxins were colour-labelled based fungal origin. The symbol diameter was set to vary depending on the total occurrence (µg/kg) of a particular mycotoxin in the sample set. The meaning of alphanumerical and numerical codes corresponding to grain varieties and mycotoxins, respectively, are explained in Tables 1 and 2 Plot resulting from the data combination of 2015 and 2017. Siccanol (56), dihydrotrichotetronine (75) and trichotetronine (77) values expressed as absolute peak area. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

mycotoxins. As a matter of fact, the content of 3-IE (101) increased consistently in various grains after cleaning. Presence of mycotoxins after cleaning could be attributed to internal mycobiota that often remains capable of producing mycotoxins even after post-harvest cleaning, as reported in Pappier et al. (2008). Regarding uncleaned QKU, contaminants were mostly unspecific metabolites such as AsG (89), AsP (90) and NBP (97), whose concentrations also reduced dramatically after cleaning. A newly positioned QKU, from the centre (Fig. 2) to the extreme left side (Fig. 3), reflects drastic changes in the mycotoxin profile. In KCI, mycotoxins were practically absent in both cleaned or

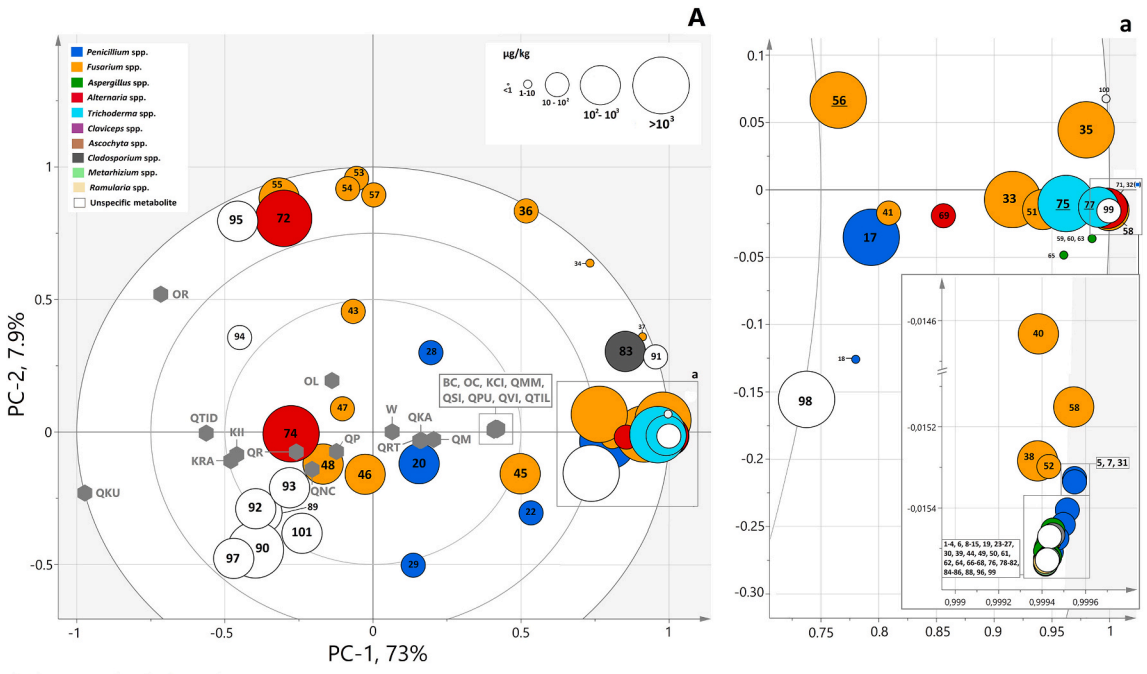

Fig. 3. Principal component analysis bi-plot for mycotoxins detected from cleaned kañiwa, quinoa, barley, oats and wheat grains (total variance, 80.9%). Numerically coded mycotoxins were colour-labelled based fungal origin. The symbol diameter was set to vary depending on the total concentration (expressed as µg/kg) of a particular mycotoxin in the sample set. The meaning of alphanumerical and numerical codes corresponding to grain varieties and mycotoxins, respectively, are explained in Tables 1 and 2 Plot resulting from the data combination of 2015 and 2017. Siccanol (56), dihydrotrichotetronine (75) and trichotetronine (77) values expressed as absolute peak area. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

uncleaned grains. However, SIC (56) was still present in cleaned KCI. Cross-contamination cannot be dismissed given the presence of SIC (56) in barley, oats and quinoa. In Fig. 2, KCI is located in the lower left side of the PCA plot, which indicated a degree of association with *Fusarium* mycotoxins (<1 µg/kg) and unspecific metabolites (<10 µg/kg). After cleaning, KCI migrated to the opposite side of the plot (Fig. 3). Prior to cleaning, KRA presented a very similar mycotoxin profile to KCI (both located on the left side of the PCA plot, Fig. 2). However, upon cleaning, the few contaminants of KRA were reduced [e.g. ENN-B2 (49)]. SIC (56) was not detected in either cleaned or uncleaned KRA. Clearly, KRA moved from the outskirts of the PCA plot (beyond HT^2_99%) towards the centre of the plot (just below HT^2_50%).

Fusarium and *Alternaria* mycotoxins were detected in uncleaned QTID. QTID was initially located on the right side of the PCA plot (just below HT^2_75%) and moved to the opposite side of the plot (beyond HT^2_50%) after cleaning. This occurred in response to a drastic reduction in the concentration of mycotoxins. For instance, the peak of SIC (56) disappeared in cleaned QTID. QPU, QVI and QTIL moved towards the centre of the plot (below HT^2_50%) following cleaning, due to a reduction (though minimal) in the content of *Fusarium* and *Alternaria* mycotoxins. The cleaning of OR and OL was linked to a reduction in the type and concentration of *Fusarium* and *Alternaria* mycotoxins. The differences are noticeable if one compares the strong association of OR and OL with various mycotoxins prior to cleaning (upper left side, Fig. 2), against their newly formed mycotoxin associations (upper left side, Fig. 3). Other samples stayed mostly within the HT^2_50%, meaning that variations in the content of mycotoxins, as a consequence of cleaning, could not be statistically verified. Overall, post-harvest cleaning of cereal grains has been broadly characterised in the literature as an efficient and cost-effective mitigation strategy to significantly reduce grain mycotoxin content (Neme & Mohammed, 2017). The cleaning methods were found to reduce the overall concentration of mycotoxins in tested grains from 2017 by roughly 50% (SIC was omitted from the calculation). In the case of quinoa and kañiwa, where traditional washing is mainly applied for saponin removal, mycotoxin content was significantly reduced, in some cases dropping below the detection level [e.g. FC (16), MPA-4 (21), BASS (87)]; a fact that confirms the effectiveness of this simple mycotoxin mitigation technique also for non-cereal grains.

3.4. South American contaminants

In general, South American samples presented low mycotoxin content as observed in the PCA plot (Fig. 4). South American samples (blue) clearly dominated the centre of the plot, meaning that their differences, in terms of mycotoxins, was minimal. Conversely, KRA, KCI and QKU were located beyond HT^2_75%, indicating differences from the rest of South American samples (Fig. 4). For instance, *Fusarium* mycotoxins [ENN-A1 (46), ENN-B (47) and ENN-B1 (48)] and unspecific metabolites [CDP-Tyr (92), CDP-Val (93) and 3-IE (101)] were detected in uncleaned KRA and KCI (Fig. 4A, cluster b'). After cleaning, KRA and KCI moved to the centre of the PCA plot, as a consequence of the decrease in mycotoxin levels. On the other hand, QKU moved from the centre to the outskirts of the PCA plot after cleaning. This meant that, unlike the rest, QKU remained highly associated to mycotoxins like NBP (97) or AsP (90) (Fig. 4B, lower left section).

From cleaned South American samples (Fig. 4A), those on the farthest right side of the PCA plot (Fig. 4B) contained the largest assortment of mycotoxins. Thus, an in-depth observation was conducted on OC, BC, QSI and KCI (Fig. 5). OC and, to a lesser extent, BC presented a wide array of mycotoxins, including *Fusarium*-, *Metarhizium*- or *Ascochyta*-produced metabolites. It was hard to understand the remarkable presence of mycotoxins in OC, if we consider that it was cultivated in close proximity to other South American samples (Fig. 1D and E). On the other hand, QSI and KCI showed minimal variation in terms of mycotoxins, mostly *Fusarium*-produced metabolites and unspecific metabolites (Fig. 5). Despite the discrepancies, the peak of SIC (56) was still present in OC, BC, QSI and KCI. Interestingly, *Trichoderma*-produced mycotoxins were only found in OC.

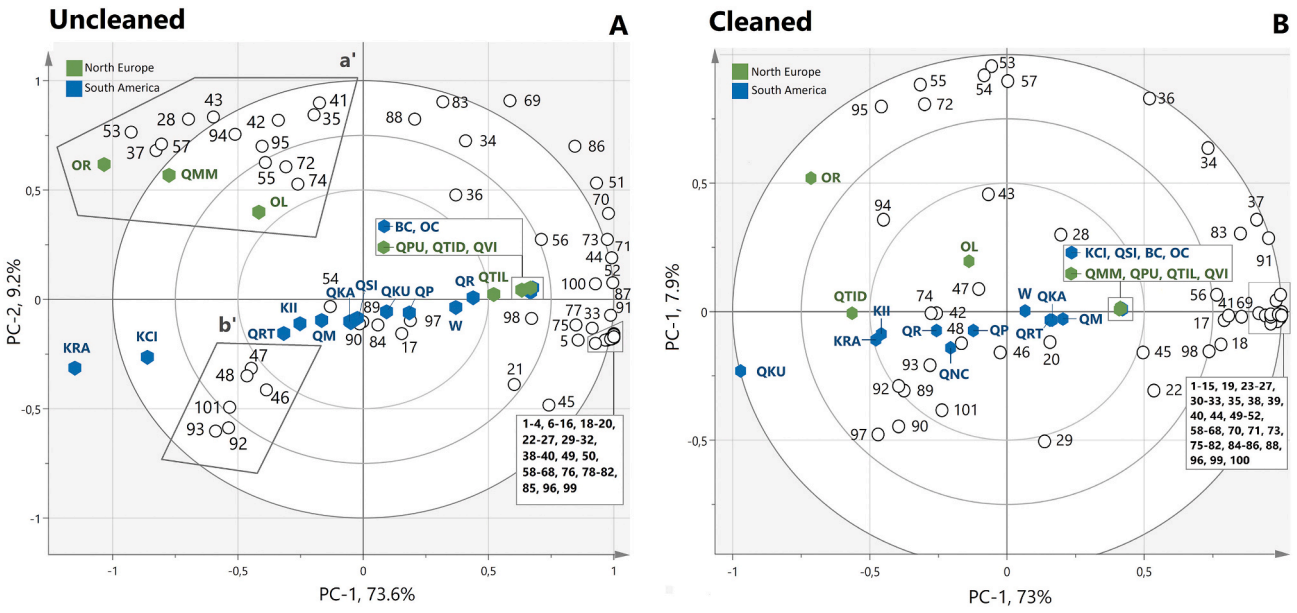

Fig. 4. Principal component analysis bi-plot for mycotoxins detected from uncleaned (A; total variance, 82.8%) and cleaned (B; total variance, 80.9%) kañiwa, quinoa, barley, oats and wheat seeds; theses were colour-labelled based on their continental origin (South America, SA; North Europe, NE). The meaning of alphanumerical and numerical codes corresponding to grain varieties and mycotoxins, respectively, are explained in Tables 1 and 2 Plot resulting from the data combination of 2015 and 2017. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

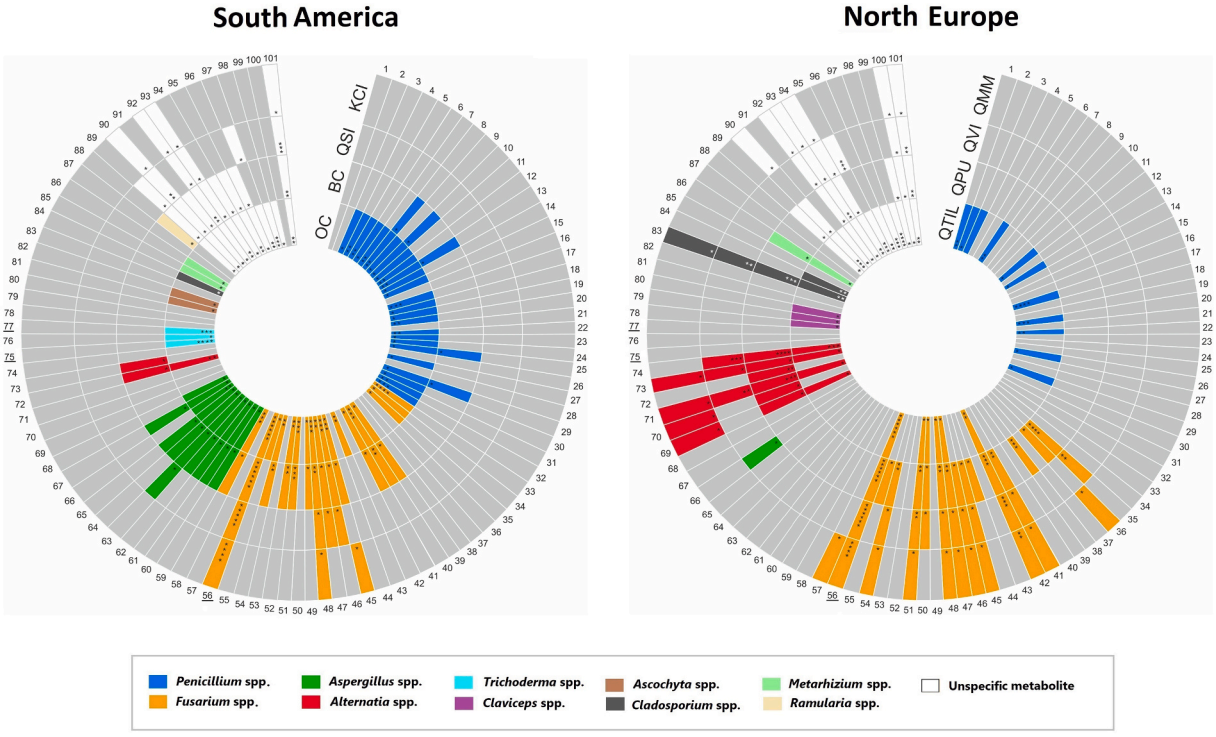

Fig. 5. Mycotoxin profile of cleaned grains with the largest presence and/or concentration of mycotoxins in accordance with the cluster shown in Fig. 4. Results are divided based on the grains' geographical origin. Numerically coded mycotoxins are colour-labelled based fungal origin. Mycotoxin concentration: 0–10 μg/kg (*); 10–10^2 μg/kg(**); 10^2–10^3 μg/kg(***); 10^3–10^4 μg/kg(****); 10^4–10^5 μg/kg(*****); 10^5–10^6 μg/kg(******). Siccanol (56), dihydrotrichotetronine (75) and trichotetronine (77) values expressed as absolute peak area. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.5. North European contaminants

Most samples obtained from North Europe were associated with a large array of mycotoxins, predominantly from *Fusarium* spp., *Alternaria* spp. and *Penicillium* spp.; unspecific metabolites were present in modest amounts (Fig. 4). Unlike South American samples, all North European samples were located outside the centre (beyond HT^2_50%) of the PCA plot (Fig. 4A), denoting that there was a large variation in the content and type of mycotoxins. Among the uncleaned North European samples, two groups were clearly observed: a *low contamination group*, located on

the left upper section of the PCA plot (Fig. 4, cluster a') and a *high contamination group*, located on the right section of the PCA plot (Fig. 4).

Uncleaned OR, OL and QMM were found in the low contamination group, mostly characterised by the presence of *Alternaria*, *Fusarium* and unspecific mycotoxins. Upon cleaning, a noticeable migration was observed. For instance, QMM and OL moved from the far-left side to the centre of the PCA plot, below HT^2_50%. This is in line with a considerable reduction in the content of mycotoxins. On the other hand, the minor changes in OR reflect unremarkable reductions in the content of mycotoxins after cleaning (Fig. 4).

QTIL, QPU, QTID and QVI were allocated in the *high contamination group* due to their strong association with a wide array of mycotoxins, produced mostly by *Fusarium* spp., *Alternaria* spp. and *Penicillium* spp. (Fig. 4A). Interestingly, QTIL was the only sample where *Claviceps*-produced mycotoxins [ERG (78), ERGOE (79) and LSA (80)] were detected. After cleaning, there was considerable reduction in the content of mycotoxins that was reflected in the movement (towards the centre of the PCA plot, below HT^2_50%) of QTIL, QPU, QVI and QMM (Figs. 4B–5). Despite the reduction, QTIL remained strongly associated to various *Penicillium*-produced mycotoxins such as FG (17) and MPA (20) (Fig. 5). In line with their cultivating conditions (Denmark, Fig. 1B), QPU and QVI showed similar mycotoxin profile (Fig. 5). Cleaned QPU and QVI contained mostly *Fusarium*-produced [e.g. AUR (35), CULM (42)] and, to a lesser extent, *Alternaria* mycotoxins [e.g. TeA (71) and ALT (74)]. Despite the observable lower concentrations, QMM also showed adherence to mycotoxins from *Fusarium* and *Alternaria* spp.

Differences in the weather, cultivating/harvesting conditions or post-harvest treatment could help elucidate the reasons behind the remarkable differences among quinoa samples cultivated in North Europe. At first glance, it seems that the farther north quinoa was cultivated, the less contaminated it became. However, this hypothesis could not be applied to samples cultivated in Denmark and Latvia, where the latitudes of the cultivating fields were very similar (Fig. 1B and C), yet they possessed different mycotoxin profiles. Characteristics of the cultivating methods and post-harvest treatments could provide more plausible explanations on mycotoxin variations.

3.6. Andean vs. cereal grain contamination

Cleaned cereal grains were more likely to contain fungal contaminants than cleaned Andean grains, particularly those from South America (Fig. 5). In 2015, conspicuous levels of mycotoxins produced by *Fusarium* spp. [HT-2 (53), MON (54), NIV (55) and T-2 (57)], as well as INFE (72) and some unspecific metabolites [CTO (91), CDP-Tyr (92), CDP-Val (93), EMO (94) and ENC (95)] were detected in OR (Fig. 6A, cereal cluster I) and BC (Fig. 6A, cereal cluster II). These findings are in line with previous surveys indicating high prevalence of *Fusarium* mycotoxins in oats and barley cultivated in Nordic countries (Brodal et al., 2020; Nathanail et al., 2015). On the other hand, cleaned Andean grains presented remarkably low contents of fungal metabolites except from QMM and KCI (Fig. 6A, Andean grains cluster I). From the 2017 harvest samples, cleaned QMM was mainly associated with various *Fusarium* and a few *Alternaria* mycotoxins, but not SIC (56) (Fig. 6B, Andean grains cluster II). QKU was strongly contaminated with certain unspecific metabolites [AsG (89), AsP (90) and NBP (97)]. Cleaned BC and especially OC, both from 2015 to 2017 harvests, were found to contain mycotoxins produced by almost all fungal genera identified in this study (Table 2), except from *Claviceps*, *Beauvaria* and *Ramularia*.

North European cereal grains were found to be consistently less contaminated than Andean grains of the same region, whilst the exact opposite occurred with those from South America (Fig. 5). This outcome could be attributed to the existence of extensive mycotoxin control programmes in European countries, and the implementation of effective mycotoxin contamination prevention strategies for cereal grains (e.g. crop rotation, fertilization, pesticide application) (Agriopoulou et al., 2020). Furthermore, the potentially more favourable climatic/environmental conditions for fungal growth and mycotoxin production of Andean grains cultivated in Europe, in addition to less developed risk mitigation approaches specific to Andean grains, may have be the reasoning behind higher contamination levels. Conversely, cereal grains cultivated in South America were evidently more prone to mycotoxin contamination than South American Andean grains. Inadequate pre-/post-harvesting methods of fungal control or insufficient adaptability of the grains to the environment might explain increased cereal contamination in those regions. Apparently, the resilience of South American Andean grains to the growth of mycotoxin-producing fungi could be due to their formidable biological adaptation to Peruvian mountainous regions (>3000 m.a.s.l.). Something that may drastically change if cultivated away from their natural environment. It could also be argued that saponin-containing Andean grains may prevent the growth of fungi

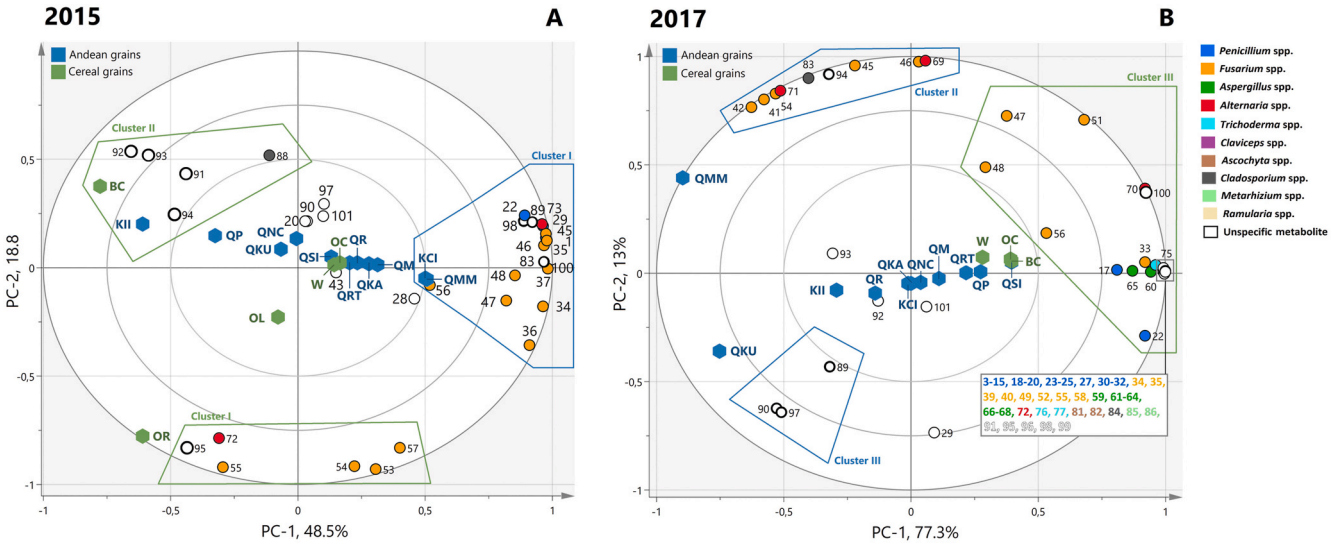

Fig. 6. Principal component analysis bi-plot for mycotoxins detected from cleaned kañiwa quinoa, barley, oats and wheat seeds in 2015 (A; total variance, 67.3%) and 2017 (B; total variance, 90.3%). Mycotoxin occurrence in Andean grains (blue) or cereal grains (green) were highlighted via clusters. Numerically coded mycotoxins were colour-labelled based fungal origin. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(Woldemichael Wink 2001). Herein, the well-documented existence of saponins in various European and South American Andean grains did not seem to at least drastically inhibit fungal growth, particularly in Europe, although the investigation of saponin effects on fungal growth and mycotoxin contamination was out of the scope of this study.

4. Conclusions

A comparative study concerning the natural occurrence of mycotoxins and fungal metabolites was conducted in Andean grains (kañiwa and quinoa) and cereal grains (barley, oats and wheat) cultivated in South America and North Europe. A state-of-the-art LC–MS/MS method was utilised in this study that is capable for the simultaneous determination of several hundreds of analytes within a single run. Significant discrepancies were observed in the contamination profiles between Andean/cereal grains, South America/North Europe and 2015/2017 harvests, attributable to differences in crop physiology, climatic conditions, geographic characteristics, as well as mycotoxin contamination prevention strategies. Moreover, cleaning of grains resulted in significant reductions in the concentration of the majority of mycotoxins, even though certain metabolites, likely produced by internal mycobiota, remained detectable. The present study comprises the most extensive mycotoxin survey of Andean grains to date, providing crucial information on contamination patterns, prevalence of fungal populations and the effect of cleaning in mycotoxin levels. In conclusion, as the value of Andean grains in global food trade increases, more targeted research on this agricultural commodity is needed for the identification of risks, enabling development of effective prevention and mitigation strategies to enhance food safety and promote food security.

CRediT authorship contribution statement

J.M. Ramos-Diaz: Conceptualization, Investigation, Formal analysis, Writing – original draft. **M. Sulyok:** Methodology, Validation, Resources, Writing – review & editing. **S.E. Jacobsen:** Resources, Writing – review & editing. **K. Jouppila:** Resources, Writing – review & editing. **A.V. Nathanail:** Conceptualization, Investigation, Writing – review & editing.

Declaration of competing interest

Please check the following as appropriate:

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

The following authors have affiliations with organizations with direct or indirect financial interest in the subject matter discussed in the manuscript:

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodcont.2021.108260.

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