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 kâniwa) 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 kâniwa (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. pseudocereals; Andean grains belong to fam. Poaceae). Despite changes in dietary traits during colonial and republican times, the rural consumption of quinoa and kâniwa 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-resistant quinoa and kâniwa to areas where no other crop could grow (Hellin & Higman, 2005; Martinez-Zuniga, 2007), thus becoming staple crops for subsistence farming (Vassas and Viera Pak, 2010). After the revaluation of ancient knowledge, quinoa and kâniwa were found to be formidable food alternatives that could contribute to the world food security (Bazile et al., 2016; FAO, 2011; Jacobsen, 2017; Drímková, 2003). Amaranth grains from Argentina were analysed to examine mycospora, 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, Papi er 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 –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 uncleared) 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 *T*² at three confidence intervals: 50% (*HT*²50%), 75% (*HT*²75%) and 99% (*HT*²99%). 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 (DHTT, 75) and trichotetronine (T77, 77) were expressed as peak area values, as no analytical standards were available at the time of analysis.

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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).
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          | Cleaning methods | Cultivation area | Varietal code |
|---------------|------------------|------------------|---------------|
| Sample        | U    | W  | P  | M  |                     | Sample        | Cleaning methods | Cultivation area | Varietal code |
| Quinoa (Chenopodium quinoa) |        |     |     |     |                     | Quinoa (Chenopodium quinoa) |        |                     |
| mintumatilda   | ●    | ●  |     |     |                     | mintumatilda   | ●    | ●  |     |                     |
| kancolla       | ●    |     | ●  |     |                     | Kancolla       | ●    | ●  |     |                     |
| kuchivila      | ●    |     | ●  |     |                     | Kuchivila      | ●    | ●  |     |                     |
| mistura        | ●    |     | ●  |     |                     | Mistura        | ●    | ●  |     |                     |
| negra Collana  | ●    |     | ●  |     |                     | negra collana  | ●    | ●  |     |                     |
| pasankalla     | ●    |     | ●  |     |                     | Pasankalla     | ●    | ●  |     |                     |
| real           | ●    |     | ●  |     |                     | real           | ●    | ●  |     |                     |
| rosada taraco  | ●    |     | ●  |     |                     | rosada taraco  | ●    | ●  |     |                     |
| salcedo INIA   | ●    |     | ●  |     |                     | salcedo INIA   | ●    | ●  |     |                     |
| titicaca Denmark | ●    |     | ●  |     |                     | titicaca Denmark | ●    | ●  |     |                     |
| Katiwa (Chenopodium pallidicaule) |        |     |     |     |                     | Katiwa (Chenopodium pallidicaule) |        |     |     |                     |
| cupi INIA      | ●    |     | ●  |     |                     | cupi INIA      | ●    | ●  |     |                     |
| illpa INIA     | ●    |     | ●  |     |                     | illpa INIA     | ●    | ●  |     |                     |
| Barley (Hordeum vulgare) |        |     |     |     |                     | Barley (Hordeum vulgare) |        |     |     |                     |
| commercial     | ●    | ●  |     |     |                     | commercial     | ●    | ●  |     |                     |
| Oat (Avena sativa) |        |     |     |     |                     | Oat (Avena sativa) |        |     |     |                     |
| Landsort       | ●    | ●  |     |     |                     | Landsort       | ●    | ●  |     |                     |
| commercial     | ●    | ●  |     |     |                     | commercial     | ●    | ●  |     |                     |
| Riegel         | ●    | ●  |     |     |                     | Riegel         | ●    | ●  |     |                     |
| Wheat (Triticum L.) |        |     |     |     |                     | Wheat (Triticum L.) |        |     |     |                     |
| commercial     | ●    | ●  |     |     |                     | commercial     | ●    | ●  |     |                     |

| 2017          | Cleaning methods | Cultivation area | Varietal code |
|---------------|------------------|------------------|---------------|
| Sample        | U    | W  | P  | M  |                     | Sample        | Cleaning methods | Cultivation area | Varietal code |
| Quinoa (Chenopodium quinoa) |        |     |     |     |                     | Quinoa (Chenopodium quinoa) |        |                     |
| mintumatilda   | ●    | ●  |     |     |                     | mintumatilda   | ●    | ●  |     |                     |
| kancolla       | ●    |     | ●  |     |                     | Kancolla       | ●    | ●  |     |                     |
| kuchivila      | ●    |     | ●  |     |                     | Kuchivila      | ●    | ●  |     |                     |
| mistura        | ●    |     | ●  |     |                     | Mistura        | ●    | ●  |     |                     |
| negra Collana  | ●    |     | ●  |     |                     | negra collana  | ●    | ●  |     |                     |
| pasankalla     | ●    |     | ●  |     |                     | Pasankalla     | ●    | ●  |     |                     |
| real           | ●    |     | ●  |     |                     | real           | ●    | ●  |     |                     |
| rosada taraco  | ●    |     | ●  |     |                     | rosada taraco  | ●    | ●  |     |                     |
| salcedo INIA   | ●    |     | ●  |     |                     | salcedo INIA   | ●    | ●  |     |                     |
| titicaca Denmark | ●    |     | ●  |     |                     | titicaca Denmark | ●    | ●  |     |                     |
| titicaca Latvia | ●    |     | ●  |     |                     | titicaca Latvia | ●    | ●  |     |                     |
| Katiwa (Chenopodium pallidicaule) |        |     |     |     |                     | Katiwa (Chenopodium pallidicaule) |        |     |     |                     |
| cupi INIA      | ●    |     | ●  |     |                     | cupi INIA      | ●    | ●  |     |                     |
| illpa INIA     | ●    |     | ●  |     |                     | illpa INIA     | ●    | ●  |     |                     |
| Barley (Hordeum vulgare) |        |     |     |     |                     | Barley (Hordeum vulgare) |        |     |     |                     |
| commercial     | ●    | ●  |     |     |                     | commercial     | ●    | ●  |     |                     |
| Oat (Avena sativa) |        |     |     |     |                     | Oat (Avena sativa) |        |     |     |                     |
| Landsort       | ●    | ●  |     |     |                     | Landsort       | ●    | ●  |     |                     |
| commercial     | ●    | ●  |     |     |                     | commercial     | ●    | ●  |     |                     |
| Riegel         | ●    | ●  |     |     |                     | Riegel         | ●    | ●  |     |                     |
| Wheat (Triticum L.) |        |     |     |     |                     | Wheat (Triticum L.) |        |     |     |                     |
| commercial     | ●    | ●  |     |     |                     | commercial     | ●    | ●  |     |                     |

\(a\) 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 butenolide (BU, 38), chlamydosporol (ChlaDiol, 40), culmoin (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 kaniwa var. cupi INIA (KCI), ilpia INIA (KII) or ramia (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 ChlaDiol (40) was only present in OC. CULM (42) was detected in QPU, QVI, QTIL, quinoa var. minitumatilda (QM) 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). Cytotoxicribodinit (CHOL, 7) and viridicaticol (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. kuchiwila (QKU). Pyrerenocin A (Pyr-A, 28) was only detected in OC, 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 (QTL, QTID, QPU, QMM, QR, QVI and QKU) and kaniwa (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), cirinin (CIT, 8), cyclopelen (COH, 12), viridicatin (VIN, 15), griseophenone B (GSP-B, 19), andrastin A (A-A, 22) and dibhydrocitrinone (DH-CIT, 31) were in some cases– uniquely identified in OC. At lower levels, 7-hydroxypelastatin (7HP, 1), agroclavine (AC, 2), chaonovin (Chc, 6) and ques-tioniainc 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 OC 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 bilavericin (BIKA, 37) were mostly found in OC 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-nitropro-pionic acid (3-NA, 66) and *Metarhizium*-produced destruxin B (D-B, 86) were detected in OC and QTIL (Fig. 2A–s, 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 trichodermolin (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 citreorreosin (91) and falacinol (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), *Metharhizium* (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 Pyr-A (28), CULM (42), NIV (55), EMO (94) and ENC (95), all of which became apparently 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 |
|----------------|-------------|--------------------|----------|-----------|
| 1              | Penicillium | 7-Hydroxypestalotin| 7HP      | 7HP       |
| 2              | Agroclavine | AC                 | AC       | AC        |
| 3              | Anacin      | AN                 | AN       | AN        |
| 4              | Andrastin A | A-A                | A-A      | A-A       |
| 5              | Atlantion A | AT-A               | AT-A     | AT-A      |
| 6              | Chanoclavin | ChC                | ChC      | ChC       |
| 7              | Ciresohydrobinal | CHOL | CHOL     | CHOL     |
| 8              | Citrinin    | CIT                | CIT      | CIT       |
| 9              | Communesin B| COM-B              | COM-B    | COM-B     |
| 10             | Curvularin  | CURV               | CURV     | CURV      |
| 11             | Cyclopenin  | CIN                | CIN      | CIN       |
| 12             | Cyclopelol  | GOH                | GOH      | GOH       |
| 13             | Cyclopeptide| CP                 | CP       | CP        |
| 14             | Dechlorogriseofulvin | DCGSF  | DCGSF    | DCGSF    |
| 15             | Dihydrocitrinine | DH-CIT | DH-CIT   | DH-CIT   |
| 16             | Festuclavine| FC                 | FC       | FC        |
| 17             | Flavoglaicin| FG                 | FG       | FG        |
| 18             | Gristeofulvin| GSF               | GSF      | GSF       |
| 19             | Gristeophenone B | GSP-B   | GSP-B    | GSP-B    |
| 20             | Mycophenolic acid | MPA   | MPA      | MPA       |
| 21             | Mycophenolic acid IV | MPA-4 | MPA-4    | MPA-4    |
| 22             | Ochratoxin A | OT-A              | OT-A     | OT-A      |
| 23             | Ochratoxin B* | OT-B            | OT-B     | OT-B      |
| 24             | Okaramine B | Ok-B               | Ok-B     | Ok-B      |
| 25             | O-Methylviridicat | OMV  | OMV      | OMV       |
| 26             | Pestalotin  | PES                | PES      | PES       |
| 27             | Pimosin A   | PIN                | PIN      | PIN       |
| 28             | Pyrenom A   | Pyre-A             | Pyre-A   | Pyre-A    |
| 29             | Quetiomytin A| Qu-A              | Qu-A     | Qu-A      |
| 30             | Quinolkacin A| QuL-A            | QuL-A    | QuL-A     |
| 31             | Viridicatin  | VIN                | VIN      | VIN       |
| 32             | Viridicato l| VOH                | VOH      | VOH       |
| 33             | Antibiotic Y| AB-Y               | AB-Y     | AB-Y      |
| 34             | Apicadin    | APIC               | APIC     | APIC      |
| 35             | Aurofuranin | AUR                | AUR      | AUR       |
| 36             | Beauvercin  | BEA                | BEA      | BEA       |
| 37             | Bikaverin   | BIKA               | BIKA     | BIKA      |
| 38             | Butenoloid  | BU                 | BU       | BU        |
| 39             | Chlamydospordiol | ChlaD:iol | ChlaD:iol| ChlaD:iol|
| 40             | Chlamydosporol | ChlaD:ol       | ChlaD:ol| ChlaD:ol  |
| 41             | Chrysogin   | Chry               | Chry     | Chry      |
| 42             | Calmodin    | CULM               | CULM     | CULM      |
| 43             | Decoyxylvalenol | DON         | DON      | DON       |
| 44             | Dicetoxyscirpenol | DAS     | DAS      | DAS       |
| 45             | Emanin A    | ENN-A              | ENN-A    | ENN-A     |
| 46             | Emanin A1   | ENN-A1             | ENN-A1   | ENN-A1    |
| 47             | Emanin B    | ENN-B              | ENN-B    | ENN-B     |
| 48             | Emanin B1   | ENN-B1             | ENN-B1   | ENN-B1    |
| 49             | Emanin B2   | ENN-B2             | ENN-B2   | ENN-B2    |
| 50             | Epipodiquitin| epi-EQ            | epi-EQ   | epi-EQ    |
| 51             | Epiquetin   | EQ                 | EQ       | EQ        |
| 52             | Funigerin   | FUN                | FUN      | FUN       |
| 53             | HT-2 toxin | HT-2               | HT-2     | HT-2      |
| 54             | Moniliformin| MON                | MON      | MON       |
| 55             | Nivalenol   | NIV                | NIV      | NIV       |
| 56             | Siccinal    | SIC                | SIC      | SIC       |
| 57             | T-2 toxin  | T-2                | T-2      | T-2       |
| 58             | Zearalenone | ZEN                | ZEN      | ZEN       |
| 59             | Asperigillus ssp. | AVN   | AVN      | AVN       |
| 60             | Averantin   | AVN                | AVN      | AVN       |
| 61             | Averufin    | AVR                | AVR      | AVR       |
| 62             | Methoxysetigmatoctystin | MST | MST       | MST       |
| 63             | Sterigmatocystin | ST   | ST       | ST        |
| 64             | Versicolorin A | Ver-A        | Ver-A    | Ver-A     |
| 65             | Versicolorin C | Ver-C       | Ver-C    | Ver-C     |
| 66             | 3-Nitropropionic acid | 3-NA    | 3-NA     | 3-NA      |
| 67             | Sydonic acid | SA                  | SA       | SA        |
| 68             | Territrem B | T-B                | T-B      | T-B       |
| 69             | Alternariol | AOH                | AOH      | AOH       |
| 70             | Alternariolmethylether | AME   | AME      | AME       |
| 71             | Altersetin  | ALT                | ALT      | ALT       |
| 72             | Infectopyron | INFE              | INFE     | INFE      |
| 73             | Tentoxicyn  | TEN                | TEN      | TEN       |

(continued on next page)
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

Table 2 (continued)

| Numerical code | Origin       | Mycotoxin                | Cleaned 2015 | Cleaned 2017 | Uncleaned 2015 | Uncleaned 2017 |
|----------------|--------------|--------------------------|--------------|---------------|----------------|----------------|
| 74             | Trichoderma spp. | Tenuazonic acid          | TeA          | TeA           |                |                |
| 75             | Dihydrorostrichetorenone | DHTT                  | DHTT         |                |                |                |
| 76             | Trichoderma      | Trichodimerol           | TCOH         | TCOH          |                |                |
| 77             | Trichoderma      | Trichotetone            | TTT          |                |                |                |
| 78             | Claviceps spp.   | Ergometrine             | ERG          | ERG           |                |                |
| 79             | Ergometrinine    | Ergometrinine           | ERGOE        | ERGOE         |                |                |
| 80             | Ergine           | LSA                     | LSA          |                |                |                |
| 81             | Ascochya spp.    | Ascochlorin             | AsG          | AsG           |                |                |
| 82             | Ascochyanone     | AF                      | AF           |                |                |                |
| 83             | Cladosporium spp.| Calphostin              | CAL          | CAL           | CAL            | CAL            |
| 84             | Cladosporin      | CLADO                   | CLADO        |                |                |                |
| 85             | Metarhizium spp. | Destruxin A             | D-A          | D-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       | Aspergaudicete          | AsG          | AsG           |                |                |
| 90             | Asperphenamate   | AsP                     | AsP          | AsP           |                |                |
| 91             | Citrooresein     | CTO                     | CTO          | CTO           |                |                |
| 92             | Cyclo(L-Pro-L-Tyr)| CDP-Tyr                | CDP-Tyr      | CDP-Tyr       |                |                |
| 93             | Cyclo(L-Pro-L-Val)| CDP-Val               | CDP-Val      | CDP-Val       |                |                |
| 94             | Emolin           | EMO                     | EMO          | EMO           |                |                |
| 95             | Endocrocin       | ENC                     | ENC          | ENC           |                |                |
| 96             | Fallacinol       | FOH                     | FOH          | FOH           |                |                |
| 97             | N-Benzoyl-Phenylalanine | NBP                  | NBP          |                |                |                |
| 98             | Neochromin A     | NC-A                    | NC-A         | NC-A          |                |                |
| 99             | Norlichexanthone | NX                      | NX           |                |                |                |
| 100            | Skepin           | SKY                     | SKY          | SKY           |                |                |
| 101            | Tryptophol       | 3-IE                    | 3-IE         | 3-IE          | 3-IE           | 3-IE           |

* 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 kaniwa, 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), dihydrotichetorenone (75) and trichetorenone (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<sub>2</sub>-50%) towards the centre of the plot (just below HT<sub>2</sub>-50%).

Fusarium and Alternaria mycotoxins were detected in uncleaned QTD. QTD was initially located on the right side of the PCA plot (just below HT<sub>2</sub>-75%) and moved to the opposite side of the plot (beyond HT<sub>2</sub>-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 QTD, QPU, QVI and QTL moved towards the centre of the plot (below HT<sub>2</sub>-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<sub>2</sub>-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 kaniwa, 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<sub>2</sub>-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. 4 A, 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.
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$_{50}$) 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 unreducible 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), CIULM (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 (Broadal 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.

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**Fig. 6.** Principal component analysis bi-plot for mycotoxins detected from cleaned kaniwa 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.)
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodcont.2018.02.061.

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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. Nathanall: 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.

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