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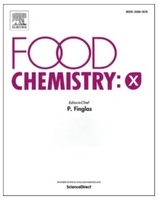

# Determination of 10 mycotoxins in wine, baijiu, and huangjiu of the Chinese market by liquid chromatography tandem mass spectrometry and exposure estimation

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Aflatoxin G1 (PubChem CID: 14421)
Ochratoxin A (PubChem CID: 442530)
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Fumonisins B1 (PubChem CID: 2733487)
Fumonisins B2 (PubChem CID: 2733489)
Fumonisins B3 (PubChem CID: 42608358)
Deoxynivalenol (PubChem CID: 40024)
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## ABSTRACT

In this study, liquid chromatography tandem mass spectrometry (LC–MS/MS) was employed to analyze the prevalence of 10 mycotoxins in 140 samples from the Chinese market, aiming to assess the exposure of Chinese individuals to these mycotoxins through the consumption of wine, baijiu, and huangjiu. Mycotoxins were detected in 98% of the samples, with fumonisins (FBs), deoxynivalenol (DON), and zearalenone (ZEN) exhibiting positive rates exceeding 50%. Regarding the exposure of the Chinese population to mycotoxins resulting from alcoholic beverage consumption, fruit wine intake made a relatively significant contribution to aflatoxin exposure, while baijiu showed a relatively significant contribution to ZEN exposure (1.84%). The analysis of the correlation between grape variety, wine region, and mycotoxin content demonstrated that FBs, ZEN, and DON were significantly influenced by grape variety and wine region. This research holds great significance in protecting human life and health, as well as in the production of safer alcoholic beverages.

## 1. Introduction

Mycotoxins, secondary metabolites produced by fungi, include a variety of compounds such as aflatoxins (AFs), zearalenone (ZEN), ochratoxin A (OTA), and fumonisins (FBs). These mycotoxins are characterized by low molecular weights, diverse structures, and heat stability. The most toxic among these, AFs, along with certain others like OTA and FBs, have been classified as carcinogens by the International Agency for Research on Cancer (IARC). Mycotoxins, when ingested, can cause significant health issues, including immune system damage and disorders in vital organs (Wan, Chen, & Rao, 2020).

According to the World Health Organization, contaminated food causes illness in millions and leads to hundreds of thousands of deaths annually (WHO, 2020). Ensuring food safety, with a focus on

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mycotoxins, is vital as they are commonly found in various agricultural products, including grains, oil-producing crops, fruits, vegetables, animal-derived foods, and fermented products (Liu, Yamdeu, Gong, & Orfila, 2020).

Wine, a key contributor to the global economy, is vulnerable to mycotoxin contamination, notably OTA. This contamination, primarily caused by certain fungi, poses a significant concern, leading to regulatory limits set by the European Commission, the United States, and China at 2 ng/mL. Notably, the concentration of OTA in wine has generally remained below these limits since 2005, attributed to enhanced agricultural practices and evolving climatic conditions (Paterson, Venancio, Lima, Guilloux-Benatier, & Rousseaux, 2018).

Baijiu, a traditional Chinese alcoholic beverage, is recognized as one of the world's distinct distilleries. Qu, a critical ingredient in traditional Chinese liquor production, is made from grains and beans and undergoes fermentation using a complex mix of fungi and bacteria, including varieties like Daqu, Xiaoqu, and Fuqu, essential for flavor development (Liu & Sun, 2018). Baijiu typically has an alcohol content ranging from 38 % to 65 % vol. The production, mainly in the Yangtze and Chishui River basins, faces potential mycotoxin risks due to the complex microbial composition of Qu. Despite the focus on flavor substances and microbial composition in baijiu research, studies on mycotoxins remain limited, highlighting the need for further investigation.

Huangjiu, or yellow rice wine, a traditional Chinese beverage and one of the world's ancient alcoholic drinks is made from rice or millet and fermented with wheat Qu. The microorganisms in wheat Qu, including fungi like *Mucor* and *Aspergillus*, play a critical role in the sensory quality of huangjiu and potentially harmful substance formation (Tian, Zeng, Fang, Zhou, & Du, 2022). Research on huangjiu has focused on flavor substances and functional components (Zhang et al., 2015), yet the analysis of mycotoxins remains unexplored. Given the global increase in alcohol consumption and the significant consumption in China, there is an urgent need to investigate mycotoxins in alcoholic beverages like huangjiu for public health safety (Manthey et al., 2019).

Global alcohol consumption per capita has increased from 5.9 L in 1990 to 6.5 L in 2017, with projections suggesting a rise to 7.6 L by 2030 (Manthey et al., 2019). This growth highlights the potential risk of mycotoxin exposure through alcoholic beverages, a concern particularly relevant in the Chinese market due to its significant consumption levels.

In this study, a liquid chromatography-tandem mass spectrometry (LC–MS/MS) method was developed for the rapid determination of 10 mycotoxins, including AFB1, AFB2, AFG1 (AFs), OTA, OTB (OTs), FB1, FB2, FB3 (FBs), DON, and ZEN, in wine, baijiu, and huangjiu. The levels of these 10 mycotoxins in 140 samples acquired from the Chinese market were determined, and the exposure risk to mycotoxins during consumption was assessed. Additionally, the impact of grape variety and wine region on mycotoxin content in wine was investigated.

## 2. Material and method

### 2.1. Reagents and chemicals

Acetonitrile (ACN) and methanol (MeOH), both LC–MS grade, were purchased from Fisher (IL, USA). Formic acid with a purity of ≥98 % was obtained from Sigma (Merck KGaA, Darmstadt, Germany) and purified for sample preparation and analysis.

### 2.2. Standards

The AFs mix standard, including AFB1, AFB2, and AFG1, was obtained from NIFDC (National Institutes for Food and Drug Control, Beijing, China). Other mycotoxin standards, including OTs (OTA and OTB), FBs (FB1, FB2, FB3), ZEN, and DON, were purchased from Sigma (Merck KGaA, Darmstadt, Germany) with a purity >99 %. The internal standard (IS) 7-methylcoumarin (7-MC), effective in mycotoxin analyses as outlined by De Jesus, Bartley, Welch, and Berry (2017), was procured from tcichemicals (Shanghai, China). All mycotoxins, dissolved in acetonitrile, were stored at −20 °C, with DON at 100 μg/mL and others at 10 μg/mL. Similarly, 7-MC, prepared in a 40 % methanol aqueous solution, was also stored at −20 °C at a concentration of 100 μg/mL.

### 2.3. Samples

A total of 140 samples comprising wine, baijiu, and huangjiu were collected from the Chinese market. Among the 90 wine samples collected, there were 61 red wine, 20 white wine, and 9 fruit wine. The vintage years of the collected red wines ranged from 2002 to 2020, while the vintage years of the white wines ranged from 2015 to 2022. A total of 43 baijiu samples from the Chinese market were collected, including 17 jiangxiangxing, 11 nongxiangxing, 11 qingxiangxing, 1 fengxiangxing, 1 jianxiangxing, 1 texiangxing, and 1 flavored. The alcohol content of the baijiu samples ranged from 35 to 58°. Additionally, 7 huangjiu samples were collected. All baijiu and huangjiu samples were produced in China.

### 2.4. Sample preparation

Prior to analysis, wine, baijiu, and huangjiu samples were thoroughly mixed and stored at −20 °C. Thawed at 4 °C, the samples were prepared at room temperature by adding equal volumes of a 650 ng/mL internal standard (7-MC) solution. After vortexing for 30 s, 200 μL of this mixture was combined with 800 μL of a 40 % methanol aqueous solution. The resulting solution, diluted to a final concentration of 65 ng/mL internal standard, was filtered through 0.22 μm PTFE (polytetrafluoroethylene) microfilters into vials for UPLC–MS/MS analysis. This preparation process was repeated three times for each sample.

### 2.5. LC–MS/MS analysis

The samples were analyzed using a Waters Acquity I-Class UPLC system (Waters, Milford, MA, USA) equipped with a BEH C18 column (2.1 × 100 mm, 1.7 μm) and coupled to a Xevo TQ-S mass spectrometer (Waters, Milford, MA, USA). For chromatographic separation, 5 μL of the prepared samples were injected into the LC–MS/MS system. The column temperature was maintained at 40 °C throughout the analysis, while the samples were kept at 6 °C. The mobile phase consisted of water (mobile phase A) and acetonitrile (mobile phase B), both containing 0.2 % formic acid. A gradient elution program was used as follows: 0 min, 70 % A; 2 min, 40 % A; 4 min, 20 % A; 4.6 min, 0 % A; 4.8 min, 70 % A; 6.0 min, 70 % A. The total run time for the chromatographic analysis was 6.0 min, and the flow rate of the mobile phase was maintained at 0.3 mL/min. The mass spectrometer operated in MRM (multiple reaction monitoring) mode with electrospray ionization in either positive or negative ion mode. The following mass spectrometry parameters were applied: capillary voltage: 3.2 kV; source temperature: 150 °C; desolvation temperature: 500 °C; desolvation gas flow: 1000 L/h; cone gas flow: 150 L/h. Nitrogen was used as the desolvation gas, and argon was employed as the collision gas. Cone voltage, collision energy, and MRM transitions (major precursor ion > fragment ion) were automatically optimized for each analysis.

### 2.6. Method validation

The method validation followed European Commission guidelines (2002, 2006), assessing calibration curve linearity, LOD and LOQ, matrix effects, and accuracy. Linearity was evaluated at eight concentration levels for each mycotoxin, including OTA, OTB, FB1, FB2, FB3, AFG1, AFB1, AFB2, ZEN, and DON, alongside a series of internal standard (7-MC) standards. LOD was determined by multiplying the noise response by a factor of 3, and LOQ by a factor of 10.

Mycotoxin quantification in wine, baijiu, and huangjiu samples used the standard addition method, accounting for matrix interferences. Representative alcoholic beverage samples were fortified, and internal

**Table 1**

Compilation of tolerable daily intake values for mycotoxins.

| Mycotoxins | TDI (ng/(kg·bw·day)) | Reference |
|---|---|---|
| OTA | 17 | (EFSA, 2010) |
| FBs | 1000 | (EFSA, 2018) |
| ZEN | 250 | (EFSA, 2011) |
| DON | 1000 | (SCF, 2002) |

standard (7-MC) was added during sample preparation. Method validation aimed for recoveries between 70 % and 120 % and relative standard deviations under 20 %, with identification criteria based on retention time and product ions response ratio according to the European Commission.

### *2.7. Estimation of mycotoxins daily intake and exposure risk*

In this study, Monte Carlo simulation, was employed for mycotoxin exposure assessment. Mycotoxin concentrations < LOD were replaced with zero, and values between LOD and LOQ were substituted with 1/2 LOQ. The best-fitting probability distributions were selected based on the Akaike Information Criterion (AIC) value, with simulations running 100,000 iterations to reflect the variability in mycotoxin content.

Data on alcohol consumption in China, encompassing wine, baijiu, and huangjiu, were obtained from the International Organisation of Vine and Wine (OIV) (2023), China's National Bureau of Statistics (2023), and industry reports (Finance Sina, 2021). Population demographics and average weight figures for Chinese adults were sourced from the China Statistical Yearbook (2022), and the Chinese National Physical Fitness Surveillance Center (2022). The ratio of male to female alcohol intake, as determined by Manthey et al. (2019), was also considered. These data collectively contributed to the calculation of exposure, integrating demographic and consumption patterns. The following equation (Eq. (1)) was used to calculate the exposure:

$$EDI = (MC^{*}C)/bw \tag{1}$$

where:

EDI = Estimated daily intake of mycotoxins (ng/(kg·bw·day))
MC = Probability function density of mycotoxin concentration in alcoholic drinks (ng/mL)
C = Consumption of alcoholic (mL/day)
Bw = Body weight (kg)

Exposure risk was assessed by comparing the EDI values with the dose reference values of tolerable daily intake (TDI), which can be found in Table 1 (EFSA, 2010, 2011, 2018; SCF, 2002). The comparisons were made using hazard coefficients (HQ), calculated as the ratio between exposure and a reference dose, as shown in Eq. (2). An HQ value of <1 indicated tolerable exposure, while an HQ value of >1 indicated a non-tolerable exposure level (Borg, Lund, Lindquist, & Hakansson, 2013; EFSA, 2013).

$$HQ = EDI/TDI \tag{2}$$

where:

HQ = Hazard Quotient;

**Table 2**

Survey Results of Mycotoxins in Wine, Baijiu, and Huangjiu from China's Market.

| Samples | Mycotoxin | Positive samples (rates) | Mean (μg/L) | P50 (μg/L) | P75 (μg/L) | Range (μg/L) |
|---|---|---|---|---|---|---|
| All kind of samples (n = 140) | OTA | 9 (6.43 %) | 0.050 | 0.046 | 0.072 | 0.006–0.126 |
| | OTB | – | – | – | – | – |
| | FB1 | 50 (35.71 %) | 0.824 | 0.285 | 0.453 | 0.246–22.933 |
| | FB2 | 79 (56.43 %) | 0.314 | 0.277 | 0.292 | 0.269–2.488 |
| | FB3 | 63 (45.00 %) | 0.441 | 0.412 | 0.448 | 0.405–1.597 |
| | AFB1 | 2 (1.43 %) | – | – | – | 3.346–16.415 |
| | AFB2 | 1 (0.71 %) | 2.793 | – | – | – |
| | AFG1 | – | – | – | – | – |
| | ZEN | 96(68.57 %) | 4.056 | 3.718 | 3.874 | 3.685–12.314 |
| | DON | 96(68.57 %) | 47.43 | 20.20 | 37.89 | 1.811–336.081 |
| Wine (n = 90) | OTA | 8 (8.89 %) | 0.0541 | 0.0530 | 0.071 | 0.006–0.126 |
| | FB1 | 26 (28.89 %) | 1.280 | 0.374 | 0.438 | 0.247–22.933 |
| | FB2 | 54 (60.00 %) | 0.322 | 0.277 | 0.284 | 0.269–2.488 |
| | FB3 | 35 (38.89 %) | 0.455 | 0.415 | 0.437 | 0.405–1.597 |
| | AFB1 | 2 (2.22 %) | – | – | – | 3.346–16.415 |
| | AFB2 | 1 (1.11 %) | 2.793 | – | – | – |
| | ZEN | 68 (75.56 %) | 4.159 | 3.727 | 4.064 | 3.685–12.314 |
| | DON | 80 (88.89 %) | 52.837 | 20.337 | 45.744 | 7.125–336.081 |
| Baijiu (n = 43) | OTA | 1 (2.33 %) | 0.015 | – | – | – |
| | FB1 | 21 (48.84 %) | 0.265 | 0.248 | 0.252 | 0.246–0.310 |
| | FB2 | 20 (46.51 %) | 0.284 | 0.274 | 0.284 | 0.269–0.298 |
| | FB3 | 23 (53.49 %) | 0.417 | 0.408 | 0.413 | 0.405–0.479 |
| | AFB1 | – | – | – | – | – |
| | AFB2 | – | – | – | – | – |
| | ZEN | 24 (55.81 %) | 3.885 | 3.715 | 3.741 | 3.685–5.113 |
| | DON | 9 (20.93 %) | 5.430 | 5.174 | 5.66 | 1.811–12.752 |
| Yellow rice wine (n = 7) | OTA | – | – | – | – | – |
| | FB1 | 3 (42.86 %) | 0.848 | 0.438 | 1.065 | 0.413–1.693 |
| | FB2 | 5 (71.43 %) | 0.378 | 0.311 | 0.348 | 0.275–0661 |
| | FB3 | 5 (71.43 %) | 0.470 | 0.465 | 0.497 | 0.431–0.509 |
| | AFB1 | – | – | – | – | – |
| | AFB2 | – | – | – | – | – |
| | ZEN | 4 (57.14 %) | 3.698 | 3.697 | 3.709 | 3.687–3.712 |
| | DON | 7 (100 %) | 39.176 | 31.727 | 41.090 | 21.293–83.755 |

EDI = Estimated daily intake of mycotoxins (ng/(kg·bw·day));
TDI = Tolerable Daily Intake (μg/(kg·bw·day)).

Considering the carcinogenic potential of aflatoxins, the Margin of Exposure (MoE) was calculated for exposure to aflatoxins (Eq. (3)) as a ratio of the Benchmark Dose Lower Confidence Limit ($BMDL_{10}$) and the level of exposure (EDI). MoE indicates the risk level, with MoE ≥ 10,000 considered of low public health concern, and MoE < 10,000 considered of high public health concern (EFSA, 2013). For aflatoxins, the BMDL10 value was determined in accordance with Benford et al. (2010).

$$MoE = BMDL_{10}/EDI \tag{3}$$

where:

MoE = Margin of Exposure;
$BMDL_{10}$ = Benchmark Dose Lower Confidence Limit (0.25 μg/(kg·bw·day));
EDI = Estimated daily intake of mycotoxins (ng/(kg·bw·day)).

### 2.8. Data analysis

Mycotoxin identification and quantitation analyses in alcoholic beverages were performed using MassLynx software version 4.1. Statistical analysis was conducted to calculate means, standard deviations, and relative standard deviations using Microsoft Excel 2019. Significance was determined at a 95 % confidence interval, and $P < 0.05$, using one-way analysis of variance (ANOVA) followed by Duncan's least significant difference test with SPSS 25.0 software (SPSS Inc., Chicago, IL, USA). The statistical analyses were performed using GraphPad Prism 8.0 software (San Diego, CA, USA). Monte Carlo simulation was performed using @Risk® software in Microsoft Excel version 8 (Palisade Corporation, USA). The selection of the best-fitting probability distributions for all mycotoxin concentrations in beer was based on the lowest Akaike Information Criterion (AIC) value. Monte Carlo simulations were conducted with 100,000 iterations, allowing for the consideration of the intrinsic variability of mycotoxin content in wine, baijiu, and huangjiu.

## 3. Results and discussion

### 3.1. Application to wine

In the 90 wine samples analyzed, at least one mycotoxin was detected in each sample, with 65.56 % containing three or more mycotoxins (Table 2). DON was the most frequently detected (88.89 %), followed by FBs (80.00 %), particularly FB2 (60.00 %). Monte Carlo simulation indicated high concentrations of FB1 (Table S1), aligning with Nakagawa, Hashimoto, and Matsuo (2020) who also found FB1 to be most abundant in wines. The results suggest that fumonisins-producing fungi in Chinese wines may differ from those in European wines, where *A. niger*, primarily producing FB2, is predominant. This is further supported by the absence of OTA and OTB in most samples, suggesting *Fusarium* as a likely source. Previous studies by Bolton et al. (2016, 2017) also found *Fusarium* strains in vineyard soils and FBs in wines. The high occurrence of DON, FBs, and ZEN in wine samples indicates a potential increasing trend of these mycotoxins in wines under current climate conditions.

OTA, a primary concern in wine, showed low prevalence in this study, with a maximum value of 0.126 μg/L, which falls below the limits set by China, the United States, and the European Commission for OTA in wine (2 μg/L). Zhong et al. (2014) conducted an analysis of OTA content in 223 wine samples from China and reported OTA detection concentrations ranging from 0.01 to 0.98 μg/L, and Al-Taher et al. (2013), found OTA in 8.3 % of the red wines, with concentrations ranging from 0.11 to 0.43 ng/mL, aligning with the results of this study. However, no other mycotoxins were detected in the wine samples in their study. Studies have indicated a positive correlation between OTA content and high temperatures. A study conducted in Spain sampled a total of 464 vineyards at three different growth stages and observed a positive relationship between the abundance of *A. Niger* and higher temperatures. The incidence of OTA was found to be higher in grapes from warm regions (Belli et al., 2005), and the concentration of OTA in wine was higher in warmer southern European regions compared to northern Europe (Paterson et al., 2018). The lower OTs content in Chinese wines compared to those from Europe and other countries may be attributed to the generally cooler climate in the wine-producing regions of China.

It is important to highlight that although the detection rate of AFs was relatively low, with only 2.22 % (2) of wines testing positive, the detected levels in these two wines were exceptionally high, with a maximum value of 16.42 μg/L. Prolonged consumption of such wines may increase the risk of liver cancer in consumers. It is noteworthy that both of these wines containing high levels of AFs were fruit wines, specifically made from mulberry and sorbus. Currently, there is limited research on sorbus, making it difficult to determine whether sorbus is prone to mold contamination and mycotoxin production. Based on the findings of this study, it is speculated that sorbus may be susceptible to mold infection. Previous studies have demonstrated that mulberry is susceptible to mold contamination and can accumulate AFs. Heshmati, Zohrevand, Khaneghah, Nejad, and Sant'Ana (2017) detected AFs in dried fruits purchased from the Iranian market and found a high positive rate of AFB1 in dried mulberry, reaching 45.5 %, with a high content of 4.12 μg/kg. The elevated levels of AFs observed in the current study samples may be attributed to the raw materials used in the brewing process being susceptible to mold contamination. In the future, it is crucial to emphasize microbial management in the production of fruit wines.

In the analysis of 90 wine samples, DON emerged as the most prevalent mycotoxin. Using Monte Carlo simulation with these samples as input data (Table S1), the P75 concentration of DON was found to be 65.11 μg/L, below the European Commission's limit for baby food. FBs also showed high positive rates, with P75 concentrations within safe limits, except for one fruit wine sample with a high FB1 level of 22.93 μg/L. While the presence of mycotoxins like AFs, FBs, and DON in the Chinese wine market is common, their levels are mostly low. However, wines with elevated mycotoxin levels pose health risks, such as liver and esophageal cancer. To fully understand the impact of wine consumption on mycotoxin exposure in the Chinese population, overall intake patterns must be considered.

### 3.2. Application to baijiu

The starter culture used in baijiu production, known as Qu, consists of a complex combination of microorganisms including molds, yeasts, and bacteria. China's baijiu production regions are predominantly characterized by a subtropical monsoon climate, which is humid and hot, providing favorable conditions for mold growth and mycotoxin accumulation. Due to the susceptibility of baijiu raw materials to mold contamination, it is essential to determine the presence of mycotoxins in baijiu. Of the 43 baijiu samples from the Chinese market analyzed, 93.02 % contained at least one mycotoxin, with up to four mycotoxins detected in a single sample. FBs were the most common mycotoxins, found in 86.05 % of the samples, particularly FB3, which exhibited the highest frequency and concentration range (0.00490–0.486 μg/L, Table S1). ZEN was detected in 55.81 % of the samples. Notably, AFs were absent, and OTA was found in only one sample, indicating that OTs and AFs are not major contaminants in baijiu.

The findings of this study revealed a high occurrence of FBs in baijiu; however, the levels of FBs detected ranged from 0.246 to 1.02 μg/L. Similarly, the concentrations of ZEN and DON ranged from 3.685 to 12.752 μg/L. These values were significantly lower than the limits set by the European Commission for FBs, ZEN, and DON in food. Certain levels

**Table 3**
Estimated Daily Intake for 10 Mycotoxins in Wine, Baijiu, and Huangjiu on the Chinese Market.

| | Mycotoxin | Male-EDI (ng/(kg·bw·day)) | | | | | Female-EDI (ng/(kg·bw·day)) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | P25 | P50 | P75 | P90 | Range (P2.5–P97.5) | P25 | P50 | P75 | P90 | Range (P2.5–P97.5) |
| All kind of samples (n = 140) | OTA | 0.000214 | 0.000516 | 0.001032 | 0.001714 | 0.000019–0.00274 | 0.000073 | 0.000176 | 0.000352 | 0.000585 | 0.000006–0.000938 |
| | OTB | – | – | – | – | – | – | – | – | – | – |
| | FB1 | 0.093200 | 0.192894 | 0.308441 | 0.405371 | 0.00913–0.504 | 0.031829 | 0.065875 | 0.105336 | 0.138438 | 0.00311–0.172 |
| | FB2 | 0.084244 | 0.172513 | 0.270589 | 0.346518 | 0.00831–0.416 | 0.028770 | 0.058915 | 0.092409 | 0.118339 | 0.00283–0.142 |
| | FB3 | 0.133609 | 0.268973 | 0.408592 | 0.499778 | 0.0133–0.559 | 0.045629 | 0.091857 | 0.139538 | 0.170679 | 0.00454–0.190 |
| | AFB1 | 0.005296 | 0.012755 | 0.025509 | 0.042370 | 0.000466–0.0678 | 0.001809 | 0.004356 | 0.008712 | 0.014470 | 0.000159–0.0231 |
| | AFB2 | 0.000748 | 0.001803 | 0.003606 | 0.005990 | 0.000066–0.00959 | 0.000256 | 0.000616 | 0.001231 | 0.002046 | 0.000022–0.00327 |
| | AFG1 | – | – | – | – | – | – | – | – | – | – |
| | ZEN | 1.423189 | 2.877385 | 4.407325 | 5.457069 | 0.141–6.226 | 0.486032 | 0.982654 | 1.505142 | 1.863640 | 0.0483–2.126 |
| | DON | 3.244211 | 5.843809 | 10.144453 | 15.811953 | 1.274–24.540 | 1.107928 | 1.995715 | 3.464425 | 5.399929 | 0.435–8.380 |
| Wine (n = 90) | OTA | 0.000116 | 0.000279 | 0.000559 | 0.000928 | 0.0000102–0.00149 | 0.0000396 | 0.0000954 | 0.000191 | 0.000317 | 0.00000349–0.000508 |
| | FB1 | 0.00892 | 0.0215 | 0.0430 | 0.0714 | 0.000784–0.114 | 0.00305 | 0.00734 | 0.0147 | 0.0244 | 0.000268–0.039 |
| | FB2 | 0.00466 | 0.0112 | 0.0224 | 0.0373 | 0.000410–0.0597 | 0.00159 | 0.00383 | 0.00766 | 0.0127 | 0.00014–0.0204 |
| | FB3 | 0.00426 | 0.0103 | 0.0205 | 0.0341 | 0.000375–0.0547 | 0.00146 | 0.00351 | 0.00702 | 0.0117 | 0.000128–0.0187 |
| | AFB1 | 0.00530 | 0.0128 | 0.0255 | 0.0424 | 0.000466–0.0679 | 0.00181 | 0.00436 | 0.00871 | 0.0145 | 0.000159–0.0232 |
| | AFB2 | 0.000748 | 0.00180 | 0.00361 | 0.00599 | 0.000066–0.00960 | 0.000256 | 0.000616 | 0.00123 | 0.00205 | 0.0000225–0.00328 |
| | ZEN | 0.0758 | 0.183 | 0.365 | 0.606 | 0.00667–0.972 | 0.0259 | 0.0623 | 0.125 | 0.207 | 0.00228–0.332 |
| | DON | 1.132 | 2.728 | 5.456 | 9.062 | 0.0997–14.519 | 0.387 | 0.932 | 1.863 | 3.095 | 0.0341–4.958 |
| Baijiu (n = 43) | OTA | 0.0000982 | 0.000237 | 0.000473 | 0.000786 | 0.00000864–0.00126 | 0.0000335 | 0.0000808 | 0.000162 | 0.000268 | 0.0000003–0.00043 |
| | FB1 | 0.0773 | 0.155 | 0.232 | 0.278 | 0.00774–0.302 | 0.0264 | 0.0528 | 0.0792 | 0.0951 | 0.00264–0.103 |
| | FB2 | 0.0744 | 0.149 | 0.223 | 0.268 | 0.00745–0.290 | 0.0254 | 0.0508 | 0.0762 | 0.0915 | 0.00254–0.0991 |
| | FB3 | 0.119 | 0.239 | 0.358 | 0.430 | 0.0119–0.466 | 0.0408 | 0.0816 | 0.122 | 0.147 | 0.00408–0.159 |
| | ZEN | 1.276 | 2.551 | 3.826 | 4.592 | 0.128–4.974 | 0.436 | 0.871 | 1.307 | 1.568 | 0.0436–1.699 |
| | DON | 0.342 | 0.825 | 1.649 | 2.740 | 0.0301–4.389 | 0.117 | 0.282 | 0.563 | 0.936 | 0.0103–1.499 |
| Huangjiu (n = 7) | FB1 | 0.00694 | 0.0167 | 0.0335 | 0.0556 | 0.000611–0.0890 | 0.00237 | 0.00571 | 0.0114 | 0.0190 | 0.000209–0.0304 |
| | FB2 | 0.00516 | 0.0124 | 0.0249 | 0.0413 | 0.000454–0.0662 | 0.00176 | 0.00425 | 0.00850 | 0.0141 | 0.000155–0.0226 |
| | FB3 | 0.00986 | 0.0197 | 0.0296 | 0.0355 | 0.000987–0.0385 | 0.00337 | 0.00674 | 0.0101 | 0.0121 | 0.000337–0.0131 |
| | ZEN | 0.0719 | 0.144 | 0.216 | 0.259 | 0.00719–0.281 | 0.0246 | 0.0491 | 0.0737 | 0.0884 | 0.00246–0.0958 |
| | DON | 1.770 | 2.291 | 3.039 | 4.010 | 1.145–5.632 | 0.604 | 0.782 | 1.038 | 1.369 | 0.391–1.923 |

**Table 4**

Risk characterization of aflatoxins through the determination of Margin of Exposure (MoE) and Combined MoE (MoET) based on the occurrence data for 10 Mycotoxins in Wine on the Chinese Market.

| Gender | Wine | | P25 | P50 | P75 | P90 | Range (P2.5–P97.5) |
|---|---|---|---|---|---|---|---|
| Male | MoE | AFB1 | 47,203 | 19,601 | 9800 | 5900 | 536549–3683 |
| | | AFB2 | 334,067 | 138,625 | 69,329 | 41,735 | 3795441–26052 |
| | MoET | | 41,359 | 17,173 | 8587 | 5170 | 470094–3226 |
| Female | MoE | AFB1 | 138,218 | 57,394 | 28,697 | 17,277 | 1571113–10784 |
| | | AFB2 | 978,207 | 405,920 | 203,007 | 122,207 | 11113728–76285 |
| | MoET | | 121,106 | 50,284 | 25,143 | 15,137 | 1376519–9448 |

of ZEN and DON were detected in some baijiu samples, which may be due to the relatively high levels of ZEN and DON in alcoholic fermentative grains and trace amounts of mycotoxins entering the baijiu with distillation. Further determination of ZEN and DON contents in wheat, Daqu, alcoholic fermentative grains, and crude baijiu samples is needed to explore the sources of ZEN and DON in baijiu. Zhang, Qi, et al. (2021) employed LC–MS/MS to analyze AFs and OTA in wheat, Daqu, alcoholic fermentative grains, and crude baijiu samples. Positive samples were detected in wheat, Daqu, and alcoholic fermentative grains. The incidence and content of AFs in Daqu were relatively high, with rates of 30 % (4.56–8.14 μg/kg) and 20 % (0.56–4.20 μg/kg), respectively. However, no AFs or OTA were detected in crude baijiu samples, aligning with the results of this study. Existing research indicates that the variety of mold species in Baijiu starters is quite diverse. Zhang, Shen, et al. (2021) analyzed the microbial composition of Daqu made from wheat, finding that the mycotoxin-producing genus *Fusarium* predominates within the mature Daqu. This accounts for the high incidence rate of FBs in Baijiu samples. The content of harmful substances in alcoholic fermentative grains significantly decreases through the distillation, suggesting that the concentration of FBs in alcoholic fermentative grains could be considerable, potentially even exceeding that of OTs and AFs. Mycotoxins may have a high boiling point and remain in solid form during the distillation process. Nevertheless, it is essential to assess whether alcohol consumption increases mycotoxin exposure among the relevant Chinese population in light of these findings.

### 3.3. Application to huangjiu

Huangjiu, commonly used in Chinese cooking for its flavor-enhancing properties, is regularly consumed both as a beverage and a seasoning. Despite its widespread use, studies on mycotoxin presence in huangjiu are lacking. To address this, our study applied a specific method to analyze 10 mycotoxins in 7 huangjiu samples from the Chinese market, with the results detailed in Table 2.

Huangjiu is made from rice, glutinous rice, or millet through Wheat Qu fermentation. Raw rice can be susceptible to environmental or fungal contamination, leading to the production of mycotoxins such as DON, OTA, and ZEA on the rice's surface (Juraschek, Kappenberg, & Amelung, 2022). During alcohol fermentation, these mycotoxins can transfer into the huangjiu. All huangjiu samples tested in this study exhibited the presence of two or more mycotoxins, with a single sample containing up to five mycotoxins. Among the 10 mycotoxins examined, DON was the most commonly detected, with a detection rate of 100 % and concentrations exceeding 21.29 μg/L. Prolonged and excessive consumption of huangjiu may lead to adverse reactions such as nausea and vomiting in consumers. Furthermore, FBs emerged as the second most frequently detected mycotoxin in huangjiu, being present in 85.71 % of the samples, with concentrations ranging from 0.275 to 2.862 μg/L. The two alcoholic beverages, baijiu and huangjiu are both grain-fermented using different types of Qu as starter cultures. After distillation, the mycotoxin content in Baijiu is lower than that in huangjiu, and the distillation process reduces mycotoxin levels in alcoholic beverages. It is worth noting that none of the 10 mycotoxins mentioned above exceeded the limits set by the European Commission Decision No 2023/915 for mycotoxins in food (European Commission, 2023). This study demonstrates that OTs and AFs are not significant contaminants in huangjiu. Nevertheless, to assess whether FBs and DON have an impact on consumer health, it is essential to integrate these findings with data on the consumption of huangjiu in the Chinese population.

### 3.4. Estimation of daily intake and exposure risk of mycotoxins in Chinese

In the analysis of 140 alcoholic beverage samples, 97.86 % tested positive for mycotoxins, with FBs, ZEN, and DON showing particularly high detection rates. This underscores the prevalence of these mycotoxins in the Chinese market's wine, baijiu, and huangjiu. To understand the potential risk to the Chinese population, we estimated dietary exposure to these mycotoxins using Monte Carlo simulations based on the detected results. The Estimated Daily Intake (EDI) was calculated for the 25th percentile, mean, 75th percentile, and the 95 % confidence interval (ranging from the 2.5th to the 97.5th percentile) values derived from the simulation. The results of these estimations are presented in Table 3.

Considering the carcinogenic potential of aflatoxins, the Margin of Exposure (MoE) was calculated for exposure to aflatoxins, which is considered high risk when the value of MoE is less than 10,000. In the detection of wine, baijiu, and huangjiu, aflatoxins were detected only in wine. Therefore, aflatoxins exposure risk in wine was assessed, and the results were shown in Table 4. Male are more likely to be exposed to AFs through wine consumption than female. For the drinking data of Chinese men, the MOEs of P75 and above were all lower than 10,000, indicating that the consumption of wine, especially fruit wine, can cause potential health problems to human health. Among them, AFB1 was the major contributor. For women, the risk of potential health problems caused by AFs through wine is low, and there may only be a risk above P97.5. Prolonged consumption of wine containing AFs may lead to chronic toxicity, characterized by growth disorders and subacute or chronic liver damage. Consumers should be mindful of these potential risks.

Table 5 presents the results of risk characterization for OTA, ZEN, DON, and FBs using HQ (individual mycotoxins) and HI (combined mycotoxins), which were determined by estimating mycotoxin exposures through a probabilistic approach. It is worth noting that, for males, the cumulative P97.5 exposure to DON in wine, baijiu, and huangjiu reached 1.45 %. These results align with a previous study by Raad, Nasreddine, Hilan, Bartosik, and Parent-Massin (2014), which detected mycotoxins in common foods in France and estimated a 2.35 % HQ for DON exposure in alcoholic beverages. When it comes to baijiu consumption, there appears to be a slight risk of ZEN exposure in the Chinese population. Based on the P90 data HQ, the estimated risk of ZEN exposure in males is approximately 1.84 %. For regular or heavy drinkers, exposure to mycotoxins in baijiu may have more significant health implications, potentially leading to symptoms such as nausea, chills, and headaches. On the other hand, the exposure risk of OTA in wine, which was a major concern, is relatively low, with male exposure to OTA being less than 0.006 %. It is believed that there is no significant

**Table 5**
Risk characterization of mycotoxins through determination of Hazard Quotient (HQ) based on the occurrence data for 10 Mycotoxins in Wine, Baijiu, and Huangjiu on the Chinese Market.

| | | Mycotoxin | Male | | | | | Female | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | P25 | P50 | P75 | P90 | Range (P2.5–P97.5) | P25 | P50 | P75 | P90 | Range (P2.5–P97.5) |
| Wine | HQ | OTA | 0.00000682 | 0.0000164 | 0.0000329 | 0.0000546 | 0.000000601–0.0000874 | 0.00000233 | 0.00000561 | 0.0000112 | 0.0000186 | 0.000000205–0.0000299 |
| | | ZEN | 0.000303 | 0.000730 | 0.00146 | 0.00243 | 0.0000267–0.00389 | 0.000103 | 0.000249 | 0.000499 | 0.000828 | 0.00000911–0.00133 |
| | | DON | 0.00113 | 0.00273 | 0.00546 | 0.00906 | 0.0001–0.0145 | 0.000387 | 0.000932 | 0.00186 | 0.00309 | 0.0000341–0.00496 |
| | | FB1 | 0.00000892 | 0.0000215 | 0.0000430 | 0.0000714 | 0.000000784–0.000114 | 0.00000305 | 0.00000734 | 0.0000147 | 0.0000244 | 0.000000268–0.000039 |
| | | FB2 | 0.00000466 | 0.0000112 | 0.0000224 | 0.0000373 | 0.00000041–0.0000597 | 0.00000159 | 0.00000383 | 0.00000766 | 0.0000127 | 0.00000014–0.0000204 |
| | | FB3 | 0.00000426 | 0.0000103 | 0.0000205 | 0.0000341 | 0.000000375–0.0000547 | 0.00000146 | 0.00000351 | 0.00000702 | 0.0000117 | 0.000000128–0.0000187 |
| | HI | FBs | 0.0000178 | 0.0000430 | 0.0000859 | 0.000143 | 0.00000157–0.000229 | 0.00000609 | 0.0000147 | 0.0000294 | 0.0000488 | 0.000000536–0.0000781 |
| Baijiu | HQ | OTA | 0.00000578 | 0.0000139 | 0.0000278 | 0.0000462 | 0.000000508–0.0000741 | 0.00000197 | 0.00000475 | 0.00000951 | 0.0000158 | 0.000000174–0.0000253 |
| | | ZEN | 0.00510 | 0.0102 | 0.0153 | 0.0184 | 0.00051–0.0199 | 0.00174 | 0.00348 | 0.00523 | 0.00627 | 0.000174–0.0068 |
| | | DON | 0.000342 | 0.000825 | 0.00165 | 0.00274 | 0.0000301–0.00439 | 0.000117 | 0.000282 | 0.000563 | 0.000936 | 0.0000103–0.0015 |
| | | FB1 | 0.0000773 | 0.000155 | 0.000232 | 0.000278 | 0.00000774–0.000302 | 0.0000264 | 0.0000528 | 0.0000792 | 0.0000951 | 0.00000264–0.000103 |
| | | FB2 | 0.0000744 | 0.000149 | 0.000223 | 0.000268 | 0.00000745–0.00029 | 0.0000254 | 0.0000508 | 0.0000762 | 0.0000915 | 0.00000254–0.0000991 |
| | | FB3 | 0.000119 | 0.000239 | 0.000358 | 0.000430 | 0.0000119–0.000466 | 0.0000408 | 0.0000816 | 0.000122 | 0.000147 | 0.00000408–0.000159 |
| | HI | FBs | 0.000271 | 0.000542 | 0.000814 | 0.000976 | 0.0000271–0.00106 | 0.0000926 | 0.000185 | 0.000278 | 0.000333 | 0.00000927–0.000361 |
| Huangjiu | HQ | ZEN | 0.000288 | 0.000575 | 0.000863 | 0.00104 | 0.0000288–0.00112 | 0.0000983 | 0.000197 | 0.000295 | 0.000354 | 0.00000983–0.000383 |
| | | DON | 0.00177 | 0.00229 | 0.00304 | 0.00401 | 0.00114–0.00563 | 0.000604 | 0.000782 | 0.00104 | 0.00137 | 0.000391–0.00192 |
| | | FB1 | 0.00000694 | 0.0000167 | 0.0000335 | 0.0000556 | 0.000000611–0.000089 | 0.00000237 | 0.00000571 | 0.0000114 | 0.0000190 | 0.000000209–0.0000304 |
| | | FB2 | 0.00000516 | 0.0000124 | 0.0000249 | 0.0000413 | 0.000000454–0.0000662 | 0.00000176 | 0.00000425 | 0.00000850 | 0.0000141 | 0.000000155–0.0000226 |
| | | FB3 | 0.00000986 | 0.0000197 | 0.0000296 | 0.0000355 | 0.000000987–0.0000385 | 0.00000337 | 0.00000674 | 0.0000101 | 0.0000121 | 0.000000337–0.0000131 |
| | HI | FBs | 0.0000220 | 0.0000489 | 0.0000879 | 0.000132 | 0.00000205–0.000194 | 0.00000750 | 0.0000167 | 0.0000300 | 0.0000452 | 0.000000701–0.0000662 |

OTA exposure risk to the Chinese population. This is consistent with previous studies that analyzed 223 Chinese wines, where OTA intake for the average adult consumer ranged from 0.86 to 1.08 ng/kg body weight per week, significantly lower than the 5 % tolerable intake per week (Zhong et al., 2014).

### 3.5. *Effects of wine grape varieties and region on mycotoxin of Chinese wines*

The study analyzed the correlation between wine types, grape varieties, and mycotoxin levels in 90 wine samples, classified into red wine, white wine, and fruit wine. The results (Fig. 1A–C) indicated that wine type significantly influenced FBs, ZEN, and DON content, with fruit wines showing higher FBs and ZEN levels, and white wines having more DON. This may be due to different susceptibility to mold infections in the fruits used for fruit wines and white grapes. Further, an analysis of grape varieties revealed that Port wine, a sweet fortified wine from Portugal, had significantly higher FB2 levels (Fig. 1D). Port wine is a sweet fortified wine originating from the Douro Valley in Portugal. Abrunhosa, Calado, and Venancio (2011) isolated black aspergilli species from the surfaces of Portuguese wine grapes and assessed their toxigenic potential. The study revealed that the primary producer of FB2 among the black aspergilli species is *A. niger*, with the highest percentage of FB2-producing strains found in the Douro Valley region (38 %), the production area for Port wine. This may explain the significantly higher FB2 content in Port wine compared to other varieties in the Chinese market. Although *A. niger* has been reported to be associated with OTA levels, the research demonstrated that out of the 597 strains of *A. niger* examined, only 10 strains were found to simultaneously produce FB2 and ochratoxin A (Abrunhosa et al., 2011). This aligns with the findings of this study, which did not detect OTA in the tested Port wines. It is suggested that the predominant contaminating fungus in Port wine in the Chinese market is *A. niger*, which does not produce OTA. Wine made from Carmena and Syrah has significantly higher ZEN levels than the other grape varieties. The content of DON in Prince, China's native grape variety, is significantly higher than other grape varieties. This may be because Carmena, Syrah, and Prince are more susceptible to infection by DON and ZEN-producing mold.

China has eight major wine-producing regions, namely Jiaodong Peninsula, Ningxia, Changli-Huailai, Xinjiang, Southwest, Northeast, Qingxu in Shanxi province, and Wuwei in Gansu province. Despite being the capital of China, Beijing is not included among these eight regions. However, due to its advantageous geographical location, Beijing has witnessed rapid development in the wine industry in recent years, resulting in the production of many exceptional wines. As limited research has been conducted on wines produced in Beijing, this study considers Beijing as a wine-producing region for analysis. Samples were primarily collected from Beijing, Changli-Huailai, Ningxia, and Xinjiang. The analysis, as shown in Fig. 1G, revealed significant regional differences in mycotoxin content, with ZEN levels higher in Beijing and Changli-Huailai red wines compared to those from Ningxia and Xinjiang ($P < 0.05$). Similarly, DON content was elevated in wines from Beijing and Ningxia ($P < 0.05$). These variations in mycotoxin levels across regions may be influenced by differing climatic conditions, which affect the growth of toxigenic molds.

### 3.6. *Method validation and recovery*

In this study, we adapted the method developed by Al-Taher et al. (2013) for detecting mycotoxins in beer to analyze wine, baijiu, and huangjiu, aligning with European Commission Decision No. 2002/657 (2002) and No. 401/2006 (2006). The optimized MS/MS parameters enabled the detection of 10 mycotoxins in a single run with high sensitivity. The method's performance, including LOD, LOQ, and linearity, met the required standards, as detailed in Table 6.

ZEN showed the lowest linearity ($R^2 = 0.9989$), while other

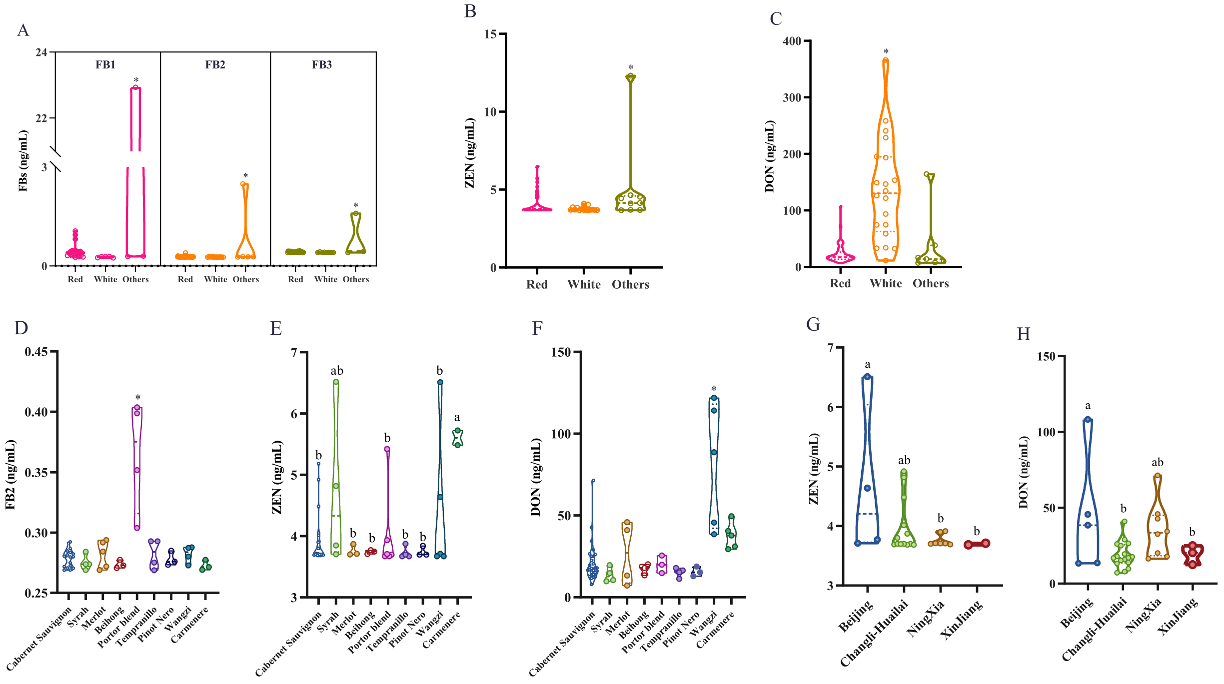

**Fig. 1.** Impact of grape varieties and regions on mycotoxin levels. (A–C) The influence of wine types on mycotoxin content. (D–F) The impact of grape varieties on mycotoxin levels. (G and H) Effects of wine regions in China on mycotoxin concentrations. Using one-way analysis of variance (ANOVA) followed by Duncan's least significant difference test.

mycotoxins exhibited $R^2$ values exceeding 0.999. The method enabled quantification of OTA and OTB above 0.005 μg/L and AFB1 above 0.056 μg/L. Compared with the European Commission Decision No 2023/915 limits (European Commission, 2023), the LOQ values for these mycotoxins were satisfactorily lower. All 10 mycotoxins had relative standard deviations below 5 %, fulfilling the European Commission's criteria. In conclusion, this method is considered to meet the criteria specified by the European Commission.

The validation of the method was conducted following the performance criteria outlined by the European Commission (2002). Two levels of mycotoxins were added to two wine samples (one red wine and one white wine), one baijiu sample, and one huangjiu sample. The low concentrations of mycotoxins were OTA, OTB, FB1, FB2, FB3, AFG1 (1 ng/mL), AFB1 (1.08 ng/mL), AFB2 (0.66 ng/mL), ZEN, and DON (10 ng/mL). The high concentration was twice that of the low concentration. The recovery (Rec%) and standard deviation (RSD%) were evaluated.

Matrix effects, influencing the analyte signal through suppression or enhancement, were evident in our study, as detailed in Table 7. These effects, impacting various mycotoxins differently in red wine, baijiu, and huangjiu, originated from sample components and chromatographic conditions. Specifically, FB1 showed ion enhancement in lower concentrations, while AFs experienced ion suppression in red wine, with both effects decreasing at higher concentrations. ZEN's matrix effects were minimal in wine and baijiu but showed ion suppression in huangjiu at low concentrations. In contrast, DON's matrix effect in baijiu was negligible, but its recovery in wine and huangjiu was low. These findings are in line with Al-Taher et al. (2013), who also observed varied matrix effects for mycotoxins in wine using LC–MS/MS. Overall, the recovery percentages of the 10 mycotoxins in the spiked alcoholic beverages ranged from 74.79 to 118.55 %, with RSD% values within acceptable limits. These results indicate that the method complies with the regulations set by the European Commission and is suitable for the analysis of wine, baijiu, and huangjiu.

## 4. Conclusion

A validated LC–MS/MS method that is rapid, sensitive, and reliable has been successfully employed to quantitatively detect 10 mycotoxins in wine, baijiu, and huangjiu samples. This method complies with the standards outlined in European Commission No. 657/2002 and No. 401/2006 and demonstrates mycotoxin levels below the limits specified in European Commission No. 2023/915. Spiked recovery tests in wine, baijiu, and huangjiu samples have confirmed the reliability of this method for the analysis of these diverse mycotoxins. Applying this method, a total of 90 wine, 43 baijiu, and 7 huangjiu samples purchased from the Chinese market were analyzed to assess the prevalence of mycotoxins and evaluate the exposure of the Chinese population to mycotoxins through the consumption of alcoholic beverages. Mycotoxins were detected in 97.86 % of the samples, with FBs, DON, and ZEN exceeding the 50 % threshold. Wine consumption significantly contributes to the exposure of AFs and DON, while baijiu consumption has a more substantial impact on ZEN exposure, particularly in men. Furthermore, a correlation analysis was conducted to investigate the influence of grape varieties and wine regions on mycotoxin content. ZEN and DON were found to be significantly affected by grape variety and wine region, whereas FBs showed a significant association with grape variety. This research holds great significance in the pursuit of producing higher quality and safer wine, baijiu, and huangjiu. It plays a crucial role in the development of food safety policies, regulatory frameworks, and the establishment and implementation of effective food safety systems both within China and globally.

## CRediT authorship contribution statement

**Tianyang Wu:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Jie Gao:** Validation. **Bing Han:** Data curation. **Huan Deng:** Validation. **Xiaoyu Han:** Data curation. **Yiding Xie:** Visualization. **Chenyu Li:** Writing – original draft. **Jicheng Zhan:** Supervision. **Weidong Huang:** Project administration, Funding acquisition. **Yilin You:** Supervision, Funding acquisition.

**Table 6**
Analysis of Mass Spectrometry Parameters, Calibration Curve, Linear Range, Correlation Coefficient (R$^2$), Limit of Detection (LOD), Limit of Quantification (LOQ), and Precision of 10 Mycotoxins.

| Mycotoxin | RT (min) | Structural formula | Mass (g/mol) | Ion Mode | Parent/Daughters (*m/z*) | Cone Voltage | Collision Energy | Linear equation | R$^2$ | LOD (ng/mL) | LOQ (ng/mL) | Recision (RSD, %) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| OTA | 3.1 | C20H18ClNO6 | 403.813 | [M + H]$^+$ | 403.99 > 238.93[a]<br>403.99 > 220.91[b] | 26 | 22<br>34 | y = 21799.3x + 5536.55 | 0.9994 | 0.000 | 0.0045 | 1.37 |
| OTB | 2.61 | C20H19NO6 | 369.368 | [M + H]$^+$ | 370.09 > 205.02[a]<br>370.09 > 187[b] | 4 | 18<br>34 | y = 34055.9x + 9562.16 | 0.9992 | 0.000 | 0.005 | 1.64 |
| FB1 | 1.7 | C34H59NO15 | 721.83 | [M + H]$^+$ | 722.48 > 334.28[a]<br>722.48 > 352.36[b] | 2 | 38<br>34 | y = 6623.8x + 52.26 | 0.9992 | 0.032 | 0.056 | 2.37 |
| FB2 | 2.15 | C34H59NO14 | 705.8306 | [M + H]$^+$ | 706.43 > 336.36[a]<br>706.43 > 318.34[b] | 10 | 36<br>34 | y = 11353.3x-1233.48 | 0.9992 | 0.035 | 0.047 | 2.82 |
| FB3 | 1.97 | C34H59NO14 | 705.8306 | [M + H]$^+$ | 706.43 > 336.36[a]<br>706.43 > 318.34[b] | 10 | 36<br>34 | y = 10634.97x-308.51 | 0.9993 | 0.075 | 0.088 | 2.34 |
| AFB1 | 2.09 | C17H12O6 | 312.2736 | [M + H]$^+$ | 313.1 > 284.94[a]<br>313.1 > 241.08[b] | 6 | 36<br>20 | y = 6693.1x + 2407.15 | 0.999 | 0.014 | 0.056 | 2.92 |
| AFB2 | 2.09 | C17H14O6 | 314.2895 | [M + H]$^+$ | 314.22 > 285.92[a]<br>314.22 > 242.06[b] | 4 | 32<br>18 | y = 3408.9x + 189.97 | 0.9991 | 0.101 | 0.300 | 2.32 |
| AFG1 | 1.93 | C17H12O7 | 328.273 | [M + H]$^+$ | 329.15 > 243.03[a]<br>329.15 > 199.77[b] | 6 | 26<br>40 | y = 6015.6x + 1668.5 | 0.9994 | 0.061 | 0.375 | 2.08 |
| ZEN | 3.15 | C18H22O5 | 318.3643 | [M−H]$^-$ | 317.18 > 174.89[a]<br>317.18 > 159.87[b] | 2 | 24<br>30 | y = 78.109x-85.157 | 0.9989 | 0.682 | 0.739 | 3.60 |
| DON | 1.01 | C15H20O6 | 296.3157 | [M + H]$^+$ | 297.16 > 203.08[a]<br>297.16 > 249.08[b] | 4<br>4 | 8<br>12 | y = 1000.6x + 155.89 | 0.9992 | 1.411 | 4.468 | 2.49 |
| 7-MC | 2.14 | C10H8O3 | 176.1687 | [M + H]$^+$ | 177.02 > 118[a]<br>177.02 > 90.85[b] | 80 | 20<br>26 | y = 547.22x + 222.2 | 0.9992 | 7.950 | 25.073 | 2.12 |

**Table 7**
Validation Parameters for LC–MS/MS Method in Mycotoxin Analysis of Wine, Baijiu, and Huangjiu.

| Sample Type | Red Wine | | | | White Wine | | | | Baijiu | | | | Huangjiu | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mycotoxin | Rec[a] (%) | RSD[a] (%) | Rec[b] (%) | RSD[b] (%) | Rec[a] (%) | RSD[a] (%) | Rec[b] (%) | RSD[b] (%) | Rec[a] (%) | RSD[a] (%) | Rec[b] (%) | RSD[b] (%) | Rec[a] (%) | RSD[a] (%) | Rec[b] (%) | RSD[b] (%) |
| OTA | 99.29 | 1.66 | 101.67 | 1.11 | 106.33 | 1.89 | 105.53 | 1.54 | 98.31 | 1.8 | 106.82 | 0.59 | 99.73 | 1.34 | 104.07 | 1.46 |
| OTB | 98.52 | 1.99 | 103.91 | 1.51 | 101.43 | 1.49 | 105.01 | 1.05 | 102.04 | 1.42 | 107.08 | 0.43 | 103.21 | 1.23 | 107.73 | 0.71 |
| FB1 | 118.55 | 3.52 | 103.97 | 3.43 | 111.92 | 2.46 | 102.27 | 1.53 | 106.38 | 2.31 | 97.52 | 1.02 | 116.92 | 2.67 | 106.67 | 1.24 |
| FB2 | 106.37 | 3.2 | 101.72 | 3.81 | 105.71 | 2.39 | 104.50 | 2.49 | 96.21 | 1.72 | 99.52 | 2.71 | 109.92 | 1.21 | 104.15 | 1.47 |
| FB3 | 103.44 | 3.42 | 102.94 | 2.78 | 104.53 | 2.4 | 101.29 | 1.12 | 106.86 | 2.82 | 100.64 | 2.28 | 108.37 | 1.83 | 105.09 | 0.61 |
| AFB1 | 90.66 | 3.58 | 95.39 | 3.56 | 99.22 | 3.75 | 102.42 | 3.09 | 99.02 | 2.35 | 103.79 | 0.96 | 100.11 | 3.12 | 102.98 | 1.37 |
| AFB2 | 86.56 | 2.92 | 91.54 | 3.59 | 93.48 | 2.59 | 98.38 | 3.8 | 96.73 | 2.45 | 100.16 | 1.22 | 99.70 | 1.24 | 98.21 | 1.09 |
| AFG1 | 90.12 | 2.78 | 97.50 | 3.88 | 102.47 | 2.12 | 110.42 | 1.87 | 98.53 | 2.08 | 110.73 | 1.19 | 104.75 | 2.48 | 112.18 | 2.08 |
| ZEN | 100.57 | 3.61 | 105.45 | 3.32 | 98.53 | 2.9 | 109.62 | 2.6 | 99.07 | 2.92 | 99.90 | 3.29 | 72.89 | 2.45 | 104.94 | 2.43 |
| DON | 75.00 | 3.32 | 82.07 | 3.17 | 76.38 | 3.44 | 83.85 | 2.19 | 97.14 | 1.72 | 102.91 | 3.6 | 74.79 | 3.22 | 82.33 | 2.85 |
| 7-MC | 100.70 | 1.36 | | | 108.08 | 1.07 | | | 98.04 | 1.57 | | | 103.14 | 2.5 | | |

[a] Samples spiked at concentration of OTA, OTB, FB1, FB2, FB3, AFG1 (1 ng/mL), AFB1 (1.08 ng/mL), AFB2 (0.66 ng/mL), ZEN and DON (10 ng/mL).

[b] Samples spiked at concentration of 2 times higher than above.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2024.101301.

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