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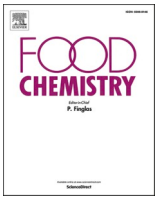

Isotopic, mycotoxin, and pesticide analysis for organic authentication along the production chain of wheat-derived products

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ABSTRACT

Wheat-based products are staples in diets worldwide. Organic food frauds continuously threaten consumer trust in the agri-food system. A multi-method approach was conducted for the organic authentication and safety assessment of pasta and bakery products along their production chain. Bulk and Compound-Specific (CS) Isotope Ratio Mass Spectrometry (IRMS) suggested the $\delta^{15}N_{bulk}$, $\delta^{15}N_{leucine}$ and $\delta^{15}N_{proline}$ as promising organic markers, with CS able to distinguish between pairs which bulk analysis could not. Processing significantly affected the values of $\delta^{15}N_{leucine}$, $\delta^{13}C_{proline}$ and $\delta^{13}C_{leucine}$. Multi-mycotoxin analysis (HT-2, T-2, DON, ZEN, OTA, AFB1) revealed higher contamination in conventional than organic samples, while both milling and baking significantly reduced mycotoxin content. Lastly, from the evaluation of 400 residues, isopyrazam was present at the highest concentration (0.12 mg/kg) in conventional wheat, exhibiting a 0.12 Processing Factor (PF), while tebuconazole levels remained unchanged in pasta production (90 °C) and reduced below LOQ in biscuits and crackers (180–250 °C).

1. Introduction

Cereals are the most produced commodities globally (FAO, 2022), with wheat supplying a fifth of the food calories and protein to the world's population (Erenstein et al., 2022). Sales of non-organic cereal grains being sold as certified organic have led to consumers paying millions of dollars on the fraudulent products (U.S. Department of Justice, 2023; Parker, 2021), with studies finding such cases to threaten consumer confidence in the integrity of the agri-food system (Giannakas & Yiannaka, 2023). Therefore, the development of robust testing regimes, able to effectively monitor product authenticity and quality are necessary.

The relative isotope abundance of natural materials is affected by their metabolic turnover and environmental growing conditions. Consequently, Isotope Ratio Mass Spectrometry (IRMS) can be used in food authentication cases to trace the geographical origin of plant and animal products, distinguish between agricultural practices and detect fraudulent addition or substitution of ingredients (Zhang, 2015). The technique has proved effective in differentiating between organic and conventional products (Giannioti, Ogrinc, Suman, Camin, & Bontempo, 2024; Liu et al., 2023), based on the principle that the two categories involve distinct farming practices. The most promising organic marker has proved to be $\delta^{15}N$, with higher values reported for organic rice (Chung et al., 2017; Trapp et al., 2021; Yuan et al., 2018), potatoes (Gatzert et al., 2021; Magdas, Dehelean, Feher, & Radu, 2017; Trapp et al., 2021), tomatoes (Trandel, Vigardt, Walters, Lefticariu, & Kinsel, 2018) and spring barley (Buša, Bērtiņš, Vīksna, Legzdiņa, & Kobzarevs, 2021), compared to their conventional counterparts. However, organic wheat was not distinguished from conventional wheat based solely on bulk $\delta^{15}N$ values. Specifically, Bontempo, Camin, Paolini, Micheloni, and Laursen (2016) reported average values ranging from 1.5 to 4.7‰ for conventional and 1.4 to 4.9‰ for organic durum wheat (dependent on sampling region), while Gatzert et al. (2021) reported average $\delta^{15}N$ ranges from 2.7 to 3.9‰ and 2.4 to 3.9‰ for organic and conventional common wheat, respectively. $\delta^{13}C$ and $\delta^{34}S$ have also been investigated as organic markers. However, their values in organic products can

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overlap with those grown conventionally, as noted in durum wheat (Bontempo et al., 2016), common wheat (Gatzert et al., 2021), and spring barley (Buša et al., 2021). Compound-Specific (CS) IRMS methods can overcome the limitations exhibited by bulk analysis. Promising CS organic markers include the $\delta^{15}N$ and $\delta^{13}C$ of amino acids extracted from plant-based samples (Bontempo et al., 2020; Chung et al., 2019; Paolini, Ziller, Laursen, Husted, & Camin, 2015).

The contamination of organic cereals and cereal-based products with mycotoxins is another relevant parameter in their distinction from conventional products. Multi-mycotoxin contamination, which is the most common type, can pose a threat to humans and lead to hyper-estrogenism, nephrotoxicity, hepatotoxicity and carcinogenicity (Bol, Araujo, Veras, & Welke, 2016). Wheat and wheat-based products have a high likelihood of contamination by mycotoxins produced from the fungal genus Fusarium, mainly at the pre-harvesting stage. Examples predominantly occurring in Europe include the trichothecenes deoxynivalenol (DON), T-2 toxin (T-2) and HT-2 toxin (HT-2), along with zearalenone (ZEA), which is often co-produced with DON (Luo, Du, Kebede, Liu and Xing, 2021; Schaarschmidt and Fauhl-Hassek, 2018). Mycotoxins can also be associated with improper storage or warm and humid field conditions, like in the case of ochratoxin A (OTA), which is widely occurring in small grains, and aflatoxin B1 (AFB1), which is the most worldwide recognised mycotoxin (Leslie et al., 2021). It has been hypothesized that organic products would be more prone to contamination, since the use of fungicides in organic agriculture is limited (Regulation 2018/848, 2024). However, recent agronomy studies have highlighted factors other than the cultivation type, such as diverse crop rotations, N fertilizer content, soil organic matter content and tillage, to have a bigger influence on mycotoxin contamination risk (Bernhoft, Wang and Leifert, 2022).

It is widely known that consumers who prefer to buy organic over conventional food products expect them to be free of synthetic residues. However, trace amounts are regularly detected in organic food, since pesticides can be present in all environmental compartments (soil, water, air)due to their application in the wider area or to historical usage (Schleiffer & Speiser, 2022). The 2018 EU report on pesticides in foods, employing >30,000 food samples, noted quantifiable residues in 6.5% of the organic samples and in 44.5% of the conventional samples analysed (European Food Safety Authority (EFSA), 2018). Residues reported in wheat and wheat products include the fungicides carbendazim and tebuconazole (Tao et al., 2021), the plant growth regulator chlormequat (Wang et al., 2020), the post-harvest insecticides pirimiphos-methyl and chlorpyrifos-methyl (Nougadère et al., 2012), as well as glyphosate-based herbicides (GBHs) (Xu, Smith, Smith, Wang, & Li, 2019).

Considering that wheat is generally consumed in processed forms, it is important to assess the pesticide residues and mycotoxin contamination in the processed commodities rather than the raw materials. This approach also allows for more realistic dietary exposure risk assessments. Additionally, examining the processing effects on the stable isotope ratios of wheat-derived products can provide valuable information for traceability purposes.

In this work, pairs of organic and conventional samples of common and durum wheat were collected and subsequently milled, in order for the the resulting flours to be used in the preparation of bakery products (biscuits, crackers) and pasta, simulating industrial conditions. Bulk analysis of C, N, S was carried out by Elemental Analyzer (EA)-IRMS, while a multi-step sample preparation process was performed for the Gas Chromatography (GC)- Combustion (C)-IRMS analysis of $\delta^{15}N$ and $\delta^{13}C$ of 8 wheat amino acids. Moreover, multi-mycotoxin analysis (HT-2, T-2, DON, ZEN, OTA, AFB1) by Ultra-High Performance Liquid Chromatography coupled with High Resolution Mass Spectrometry (UHPLC-HRMS) was conductedafter solid phase extraction (SPE). Lastly, the presence of a broad spectrum of 400 pesticide residues was evaluated by LC- and GC-MS/MS, after employing QuEChERS (quick, easy, cheap, effective, rugged, and safe) with dispersive SPE and Quick Polar Pesticide (QuPPe) techniques.

2. Materials and methods

2.1. Sample collection

Five pairs of durum wheat (organic and conventional) and two pairs of common wheat (organic and conventional) were collected directly from producers in Italy or grown in experimental fields (Table 1.A). The dimensions of the cultivation fields were in the average order of the hectare. The organic crops, grown within the same municipality of origin as the conventional ones (for each couple taken into consideration), complied with EC Regulation No. 889/2008, which lays down separation distance criteria to be met by organic farms to minimise the risk of contamination from conventional crops using synthetic chemicals. The quantity collected was circa 2 kg per sample.

2.2. Wheat grains conditioning & milling

The grains were conditioned for milling by the addition of water, in order to achieve the desired humidity (15 - –16.5 %) which prevents the bran from breaking into smaller pieces and ensures optimal separation from the endosperm (Scholz et al., 2022). The humidity of the grains was measured using the Infratec™ Grain Analyzer (Foss Analytics A/S), and the quantity of added water was measured according to the formula:

$$\frac{\text{Theoretical Humidity (\%)} - \text{Actual Humidity (\%)}}{100\ (\%) - \text{Theoretical Humidity (\%)}} * \text{Sample Weight (g)}$$

The grains with the added water were placed on roller mixers for a total of 24 h and the humidity was measured again to make sure that the desired condition was reached. Thereafter, the wheat samples were milled (Bona mill, Monza, Italy) and the flour/semolina was collected and stored at 10 °C. The yields ranged from 51 to 61%.

2.3. Wheat-based products preparation

Biscuits were prepared using ca. 500 g of the 4 common wheat flour samples (or 480 g according to the sample availability). The ingredients can be found in Table 2.A. The biscuits were baked for 10 min at 180 °C and then dried at 100 °C for 10 min.

Crackers were prepared using 1000 g of the same 4 common wheat flour samples. The ingredients can be found in Table 3.A. The crackers were baked in a static oven at 250 °C for 4 min and dried at 100 °C for 15 min.

Durum wheat semolina was mixed with water for the preparation of pasta. The tagliatelle-shaped samples were dried in a desiccator at 90 °C for 24 h.

All samples were homogenized (IKA® A11 Basic, Staufen, Germany) and stored at room temperature in sealed containers prior to analysis.

2.4. Bulk IRMS analysis

Samples were weighed (ca. 2 mg) and placed in tin capsules to measure the $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ values simultaneously, using an isotope ratio mass spectrometer (Elementar Analysensysteme GmbH, Langenselbold, Germany) after total combustion in an elemental analyser (Vario Isotope Cube; Elementar Analysensysteme GmbH). All samples were measured in triplicate.

The isotope ratios were expressed in δ ‰ versus atmospheric nitrogen for $\delta^{15}N$, V-PDB (Vienna – Pee Dee Belemnite) for $\delta^{13}C$ and and the Vienna-Canyon Diablo Troilite (VCDT) for $\delta^{34}S$, according to the equation below, where R is the ratio of the heavy (^{i}E) to light (^{j}E) isotope of an element E:

$$\delta^{i}\left(E_{sample/standard}\right) = \frac{R\left({}^{i}E/{}^{j}E\right)_{sample}}{R\left({}^{i}E/{}^{j}E\right)_{standard}} - 1$$

International reference materials (U.S. Geological Survey), and an in-house working standard (wheat flour), were used to normalise the isotopic values, namely, USGS90 (millet flour, δ^{15}N: 8.84 ‰, δ^{13}C: -13.75 ‰, δ^{34}S: -15.14 ‰) and USGS88 (collagen, δ^{15}N: 14.96 ‰, δ^{13}C: -16.06 ‰, δ^{34}S: 17.1 ‰).

2.5. Compound-specific IRMS analysis

2.5.1. Reagents and materials

L-Amino acid standards at ≥98% purity (alanine, aspartic acid, glutamic acid, glycine, isoleucine, norleucine, leucine, phenylalanine, proline, and valine) and analytical grade cation-exchange resin (Amberlite IR120 hydrogen form) were purchased from Sigma-Aldrich. All other solvents (isopropanol, acetone, and ethyl acetate) and reagents (triethylamine and acetic anhydride) used were of analytical grade and purchased from Sigma-Aldrich and VWR (Milan, Italy).

2.5.2. Sample preparation and analysis

A multi-step sample preparation process was followed for the GC-C-IRMS analysis of δ^{15}N and δ^{13}C wheat amino acids, as described by Paolini et al. (2015). This involved defatting the samples with a mixture of petroleum ether/ethyl ether, followed by protein hydrolysis with HCl, and amino acid purification using an ion-exchange chromatography resin. *N*-acetyl isopropyl derivatization was the final phase, which required acidified isopropanol for esterification and a mixture of acetic anhydride/trimethylamine/acetone for acetylation.

The isotopic values of the amino acids alanine (Ala), aspartate and asparagine (Asx), glutamate and glutamine (Glx), glycine (Gly), leucine (Leu), phenylalanine (Phe), proline (Pro), threonine (Thr), and valine (Val), were determined by a Trace GC Ultra (GC IsoLink + ConFlo IV, Thermo Scientific) interfaced with an IRMS (DELTA V, Thermo Scientific) through an open split interface and with a single-quadrupole GC–MS (ISQ Thermo Scientific). Due to the conversion of asparagine (Asn) and glutamine (Gln) into aspartate (or aspartic acid) (Asp) and glutamate (or glutamic acid) (Glu), after the acid-hydrolysis step, the δ^{15}N and δ^{13}C reported in the samples represent their summaries as Asx and Glx (Paolini et al., 2015).

All samples were measured in duplicate. Corrections accounting for the measured δ^{13}C values of the derivatized amino acids were carried out as reported in Paolini et al. (2015).

2.6. Mycotoxins analysis

2.6.1. Reagents and materials

Methanol, acetonitrile, acetic acid and ammonium acetate for HPLC, gradient grade ≥ 99.0%, were purchased from VWR International, Ltd. (Poole, United Kingdom). For the preparation of the mobile phase and all sample preparations experiments, water was purified using a Milli-Q system (Millipore, Bedford, MA). Standard mycotoxin solutions and ^{13}C-labeled mycotoxin solutions ($^{13}C_{15}$DON, $^{13}C_{22}$HT2) were purchased from Romer Labs GmbH (Tulln, Austria). Oasis® HLB (3 mL, 60 mg) columns were purchased from Waters (Milan, Italy). Filter papers were obtained from Whatman International Ltd. (Maidstone, UK). Certified reference materials were obtained from FAPAS (FERA Science Ltd. York, UK).

2.6.2. Sample preparation and analysis

All grain, flour and semolina samples, as well as the derived products (bakery and pasta) were analysed by a multi-mycotoxin (HT-2, T-2, ZEA, DON, AFB1 and OTA) method, based on the one described by Lattanzio, Gatta, Suman, and Visconti (2011). Recovery levels and LOQs of all mycotoxins can be found in Tables 4.A and 5.A, respectively.

Briefly, 10 g of ground sample (IKA® A11 Basic, Staufen, Germany) were extracted with acetonitrile/water (84:16, *v*/v); the extract was filtered, evaporated to dryness under N_2 stream, purified through Oasis® HLB columns, spiked with an appropriate amount of ^{13}C-labeled internal standard mix, dried and finally redissolved with methanol: water (20:80 v/v) with 0.5% acetic acid, and 1 mM ammonium acetate, prior to UHPLC-MS/MS analysis. Ultrahigh-performance liquid chromatography (UHPLC) was performed using a Dionex Ultimate® 3000 LC systems (Thermo Fisher Scientific Inc., Waltham, MA, USA) and a Kinetex Biphenyl column (2.6 mm; 100 2.10 mm; Phenomenex) with a binary gradient composed of (A) water (0.5% acetic acid, 1 mM ammonium acetate) and (B) methanol (0.5% acetic acid, 1 mM ammonium acetate).

Before UHPLC-MS/MS analysis, all samples were filtered through centrifugal filter units. ESI-MS/MS was carried out by a Q-Exactive (Thermo Fisher Scientific Inc., Waltham, MA, USA) mass spectrometer. Experiments were performed in full MS data scan for quantification and data-dependent scan. All equipment control and data processing were performed on Xcalibur™ software (Thermo Fisher Scientific Inc., Waltham, MA, USA).

2.7. Pesticides analysis

2.7.1. Reagents and materials

Pesticide reference standards (purity ranging between 90 and 99%) were obtained from Merck KGaA (Darmstadt, Germany) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). Stock solutions of 5000 μg L^{-1} were prepared in acetonitrile. An internal standard, triphenyl phosphate (TPP), was purchased from Merck KGaA (Darmstadt, Germany). For chemical analysis, methanol, acetonitrile and magnesium sulfate were obtained from Sigma-Aldrich (Milan, Italy). Ultrapure water was produced in the laboratory using an Arium pro UV (Sartorius Stedim, Gottingen Germany) water purification system.

2.7.2. Sample preparation and analysis

For the analysis of 390 residues (including insecticides/acaricides, fungicides and herbicides), the samples were prepared according to the QuEChERS procedure as reported by the official European Union method, namely EN 15662:2018 (European Committee for Standardization (CEN) Standard Method EN 15662, 2018). Briefly, samples were weighed in falcon tubes as follows: 5 g wheat, 5 g pasta, 2 g biscuits, 2 g crackers, and spiked with 100 μL TPP internal standard solution. Then, 8 mL and 5 mL distilled water were added to the biscuits/crackers and wheat/pasta, respectively, followed by 10 mL ACN. After agitating for 2 min, EN 15662:2018 QuEChERS salt mixture was added and agitated for another 2 min. The samples were then put in the freezer (−25 °C) for 30 min, agitated for 1 min, with 5 mL of the supernatant transferred to tubes (Eppendorf® Safe-Lock Microcentrifuge Tubes) containing 150 mg PSA and 900 mg $MgSO_4$ and finally centrifuged for 5 min (5000 rpm). The supernatant was filtered (0.22 μm) and was taken for GC–MS/MS and LC-MS/MS analysis.

Moreover, for the screening of polar pesticides (glyphosate), the EURL-SRM QuPPe-PO-Method was followed as described by Anastassiades et al. (2021) for cereal matrices. Briefly, samples were weighed in falcon tubes as follows: 5 g wheat, 5 g pasta, 2 g biscuits, 2 g crackers, and spiked with 100 μL internal standard solution (IL-IS Glyphosate 1,2-$^{13}C_2$ ^{15}N. Then, 8 mL and 5 mL distilled water were added to the biscuits/crackers and wheat/pasta, respectively, followed by 10 mL MeOH containing 1% formic acid and extra 100 μL formic acid. Thereafter, 1 mL 10% aqueous EDTA solution was added, the tubes were shaken mechanically for 15 min and centrifuged for 20 min (10,000 rpm, −10 °C). 2 mL of the supernatant were transferred into a tube containing 2 mL ACN, shaken for 1 min, centrifuged for 5 min (3000 rpm) and filtered prior to LC-MS/MS analysis.

LC-MS/MS analysis was carried out by an ACQUITY ultra-high-pressure liquid chromatography system (UHPLC Waters Corporation,

Milford, MA, USA) coupled to a Xevo TQ MS mass spectrometer (Waters Corporation) operating in MRM mode (Multiple Reaction Monitoring). GC–MS/MS was done on a GC System 8890 (Agilent Technologies, Santa Clara, CA, USA) coupled to a triple quadrupole (7010 TQ, Agilent Technologies) operating in MRM mode. The list of all screened residues and the validation parameters can be found in Table 6.A.

2.7.3. Processing factor (PF)

To calculate the processing factors (PFs), the residue levels measured in the products were corrected according to the points a) and c) of Article 20 of Regulation (EC) 396/2005, referring to the humidity changes due to water addition/evaporation and the fraction of wheat flour contained in the recipe, respectively. Furthermore, we used the PFs available on the EU database for wheat milling (Zincke et al., 2022a) to account for the residue losses from grain to flour.

PF was calculated from the corrected residue level in the processed commodity divided by the residue level in the raw material, i.e. the wheat grain (European Commission (EC), 2022):

$$\mathrm{PF} = \text{Residue in product (mg/kg)} / \text{Residue in wheat grain (mg/kg)}$$

PF was only calculated in cases where the residue level was greater than the LOQ. PF > 1 indicates an increase in the residue during processing. PF < 1 indicates a decrease in the residue.

2.8. Statistical analysis

The least significant difference test was performed at the 0.05 probability level. Boxplots were drawn using R (version 4.3.0). The Shapiro-Wilk Test was conducted to check the normality of the IRMS data, Fisher's F-test was used to compare the variances of two samples and the paired Student's *t*-test was used to compare the differences between the organic and conventional groups.

3. Results and discussion

3.1. Isotopes

3.1.1. Bulk IRMS analysis

All measurements are reported for the wheat sample pairs in Table 7.A. The outlier seen in the δ^{15}N conventional box plot corresponds to the conventional Parma 3 sample, which exhibited a similar value to its organic pair (Fig. 1). Overall, bulk analysis of wheat showed that the δ^{15}N values of organic samples exhibited significantly higher values than those of their conventional counterparts ($p < 0.05$) (Fig. 1). This trend is very frequently noted in literature (Buša et al., 2021; Trapp et al., 2021; Yuan et al., 2018), since fertilizer is the main source of N necessary for plant growth and there are significant differences between the δ^{15}N of organic and synthetic fertilizers. Specifically, fertilizers used in conventional agriculture have δ^{15}N values ranging from −6 to 6‰, whereas the animal manures and composts used in organic farming have δ^{15}N values varying between 1 and 37‰ (Bateman & Kelly, 2007). The range of all wheat δ^{15}N values from the Emilia Romagna provinces, i.e. Piacenza, Parma and Ravenna, were in a similar range in our study (−0.1 to 5.2 ‰) as those of wheat from the same region in the study of Bontempo et al. (2016) (0.7 to 7.0 ‰).

No significant difference was observed between the δ^{13}C values of the two cultivation types ($p > 0.05$) (Table 7.A). δ^{13}C can be predominantly influenced by the plant photosynthetic pathway or the local growing conditions, rather than fertilization strategy (Georgi, Voerkelius, Rossmann, Graßmann, & Schnitzler, 2005). Specifically, C4 plants (−20 ‰ to −9‰) have higher values than C3 plants (−35 ‰ to −21 ‰), whereas CAM plant values range between those of C4 and C3 plants (Badeck, Tcherkez, Nogués, Piel, & Ghashghaie, 2005). The values reported herein (−28 ‰ to −24 ‰) are consistent with those of C3 plants, as well as with those reported by Gatzert et al. (2021) and Bontempo et al. (2016), ranging between approximately −27 to −26 ‰ and − 27 to −23 ‰, respectively.

Conventional samples generally exhibited lower δ^{34}S values compared to their organic counterparts in the majority of cases (Fig. 1), however the difference was not statistically significant ($p > 0.05$). The same was noted by Gatzert et al. (2021) for common wheat, and by Bontempo et al. (2020) for tomatoes. On the other hand, δ^{34}S was an organic marker for wheat from one region (Basilicata) of the four included in the study of Bontempo et al. (2016), with the first exhibiting negative and the latter positive values. This observation also applies to the majority of our δ^{34}S values (Table 7.A). Generally, synthetic fertilizers exhibit variable δ^{34}S values, which often overlap with those of organic fertilizers, due to the different sulfate sources used in their production. These sources could be marine evaporites exhibiting values between 10 ‰ to 35 ‰, or sulfuric acid exhibiting δ^{34}S values between −5‰ to 12‰ (Vitòria, Otero, Soler, & Canals, 2004). In our study there was a single case (Pesaro Urbino), where the conventional sample exhibited a higher value (c. 4 ‰) (outlier) than the organic sample from the same area (−3.3 ‰).

3.1.2. Compound-specific (CS) IRMS analysis

The δ^{15}N values of leucine, proline, aspartic acid, glutamic acid and phenylalanine were higher in the organic than the conventional samples in the majority of the areas (Table 1). The biggest difference between the two categories was circa +6‰ for phenylalanine in the Parma area, however the most promising organic markers were the δ^{15}N values of leucine and proline ($p < 0.05$). It is worth noting that CS analysis could distinguish between pairs which could not be differentiated by bulk analysis, such as Parma 3 and Piacenza.

Few studies have investigated the potential of amino acid isotope values as organic markers. Paolini et al. (2015) found no statistically significant differences between organic and conventional durum wheat samples, while the δ^{15}N values of conventionally grown winter wheat

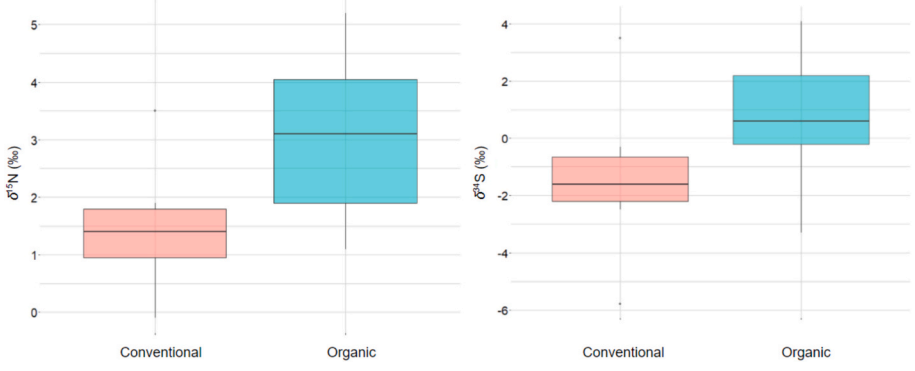

Fig. 1. Boxplots of δ^{15}N and δ^{34}S values of wheat grain organic and conventional samples. Significant difference found for δ^{15}N ($p < 0.05$) but not for δ^{34}S ($p > 0.05$).

Table 1
δ^{15}N values of wheat amino acids (O stands for organic and C stands for conventional samples). Different letters indicate statistically significant differences ($p < 0.05$).

δ^{15}N AA (‰)	alanine		valine		leucine		glycine		proline		aspartic acid		glutamic acid		phenylalanine	
	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C
Piacenza	0.8	1.8	2.9	2.2	0.2	1.1	2.1	2.8	3.4	3.7	1.0	1.8	4.4	2.7	9.5	9.3
Pesaro e Urbino	2.0	3.2	1.4	3.5	3.0	−0.7	2.8	3.3	5.5	4.3	4.0	1.9	5.3	3.2	10.2	9.6
Ravenna	0.2	0.3	−1.6	3.0	0.3	−1.2	0.4	1.3	5.2	3.2	3.5	1.8	1.6	2.6	8.7	6.7
Parma 1	3.7	0.7	6.2	2.0	0.7	0.5	0.9	1.9	7.6	5.5	3.6	1.3	5.2	3.2	11.8	10.1
Parma 2	7.6	4.8	7.9	5.3	6.8	3.8	3.4	2.7	7.7	4.7	5.8	3.6	7.6	5.8	14.8	8.8
Parma 3	1.6	2.8	1.3	1.9	0.0	0.1	1.3	1.2	3.6	4.7	1.8	4.1	2.2	4.3	8.0	9.6
Experimental	3.5	1.8	4.9	3.0	4.9	1.8	0.9	3.7	3.6	3.2	3.4	3.5	5.2	4.3	9.5	9.6
Mean	2.8	2.2	3.3	3.0	2.3^{a}	0.8^{b}	1.7	2.4	5.2^{a}	4.2^{b}	3.3	2.6	4.5	3.7	10.4	9.1
S.D.	2.5	1.5	3.3	1.2	2.7	1.7	1.1	1.0	1.8	0.9	1.6	1.1	2.1	1.1	2.3	1.1

exhibited significantly lower values than those of organic wheat grown with animal manure, with differences over +5‰ for alanine, aspartic acid, isoleucine, phenylalanine, threonine, and valine. Moreover, Chung et al. (2019) demonstrated that the δ^{15}N values of glutamic acid, glycine, isoleucine, methionine, proline, serine, and threonine could effectively differentiate organic and pesticide-free rice samples from conventional samples. Lastly, Bontempo et al. (2020) found that $\delta^{15}N_{Isoleucine}$, $\delta^{15}N_{Glutamic\ acid}$, and $\delta^{15}N_{Phenylalanine}$ could be used as organic authentication markers for tomatoes, with differences of approximately +5‰ between organic and conventional samples.

The differences between the organic markers identified for rice and wheat have been attributed to the different metabolic and growth mechanisms of the two crop types (Chung et al., 2019).

No statistically significant differences were found for the δ^{13}C values of wheat amino acids for the differentiation between organic and conventional samples in this study (Table 8.A) ($p > 0.05$). In other cases, the δ^{13}C compound-specific values were promising organic markers. Paolini et al. (2015) successfully differentiated organic winter and durum wheat on the basis of the δ^{13}C values of glutamic acid, which were greater in organic than conventional samples. The same δ^{13}C amino acid values were again found to be effective organic markers for tomatoes, when differentiation was not possible through bulk analysis, by Bontempo et al. (2020). Lastly, Chung et al. (2019) were able to identify organic rice samples by their $\delta^{13}C_{tyrosine}$ and $\delta^{13}C_{lysine}$ values, with an average −32.6 ‰ and − 26.28 ‰ for conventional and − 30.9 ‰ and − 24.8 ‰ for organic samples, respectively.

3.1.3. *Processing effects on bulk and CS IRMS values*

Processing effects are depicted in Figs. 2 and 3, considering the differences between the isotope values measured for the wheat grains and those of the finished products ($\Delta\delta$). The exact measurements are reported in Table 9.A. Student's *t*-test showed that leucine was the only amino acid exhibiting a significant change in δ^{15}N following processing ($p < 0.05$), which can affect its reliability as an organic marker. Leucine, as well as proline, also exhibited a significant increase in the δ^{13}C value ($p < 0.05$).

Bulk values (C, N, S) did not change significantly after processing. This is consistent with the findings of Bontempo et al. (2016), who noted

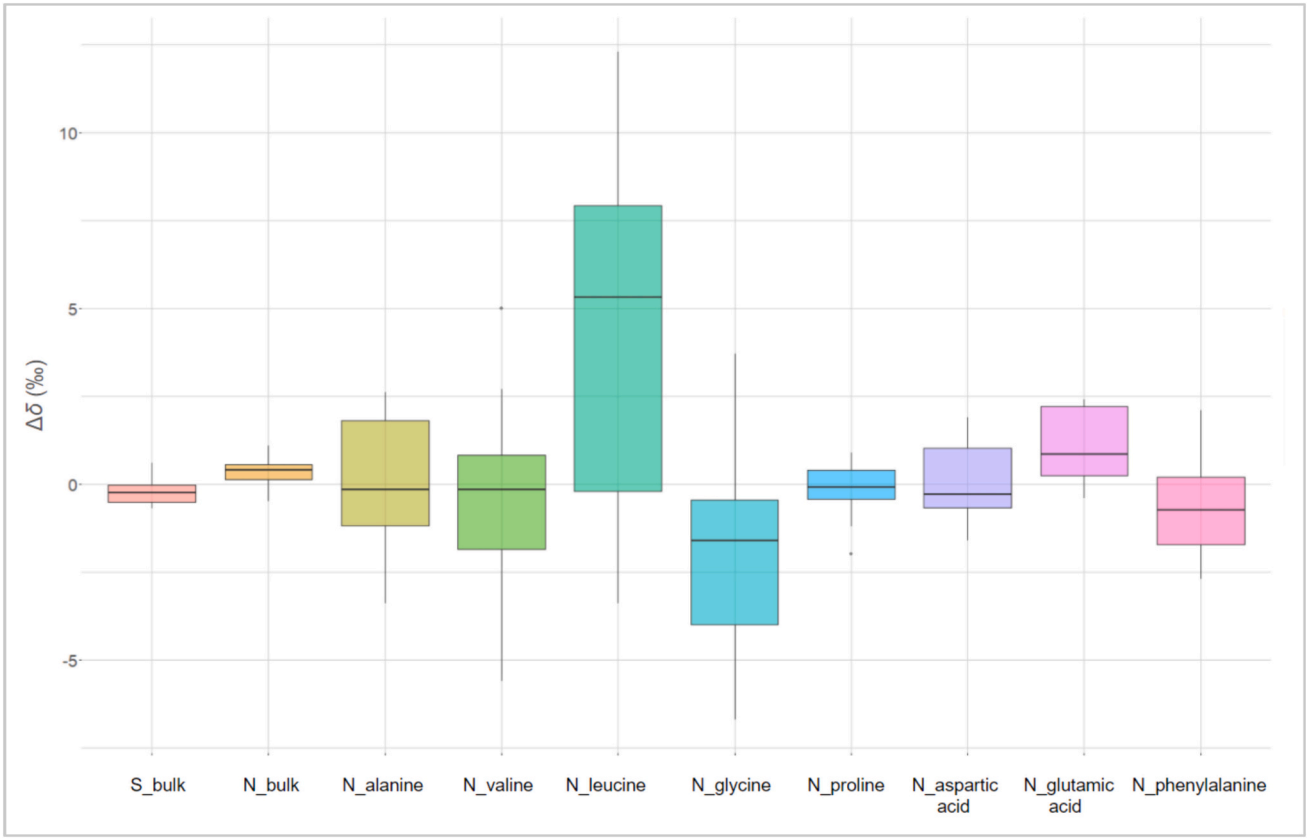

Fig. 2. $\Delta\delta$S and $\Delta\delta$N between the raw materials (wheat grains) and the final products.

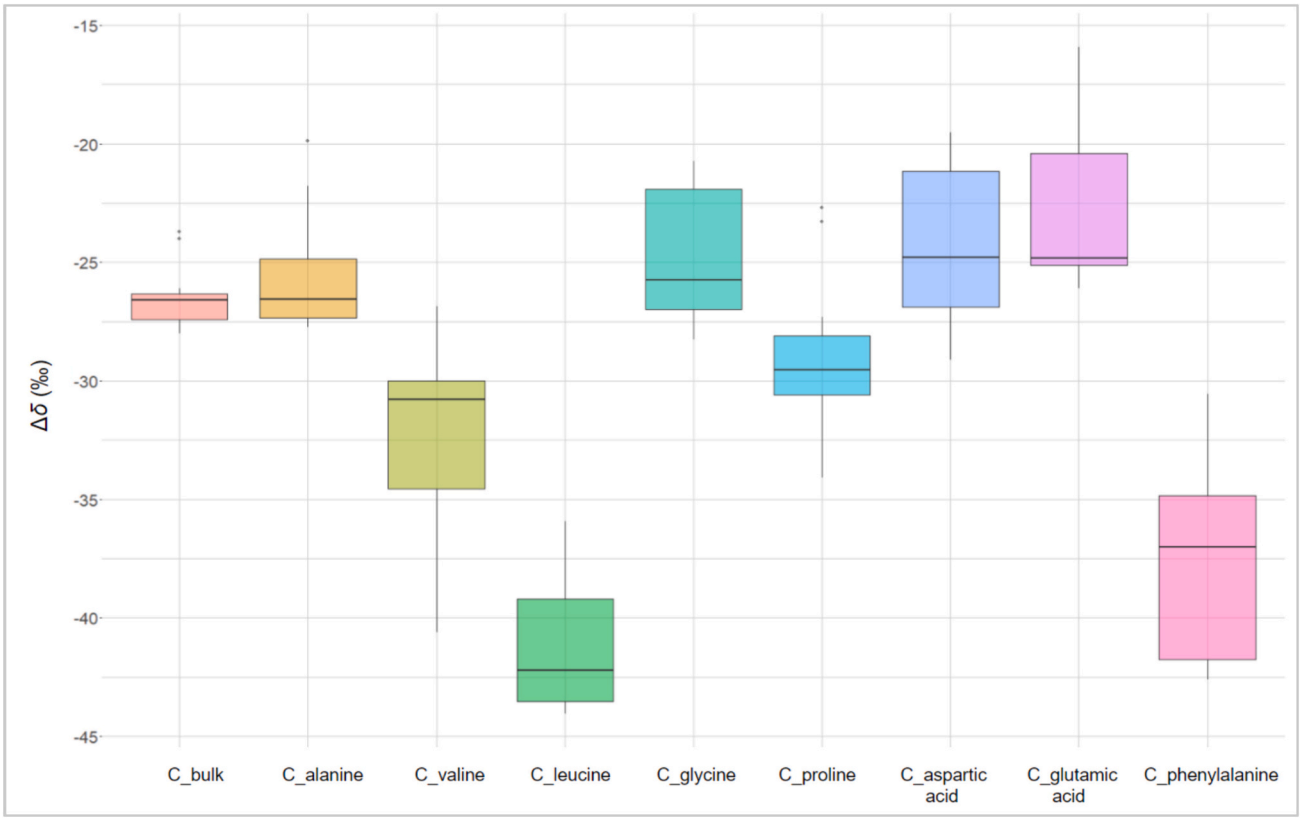

Fig. 3. Δδ C between the raw materials (wheat grains) and the final products.

no statistically significant differences between the bulk $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ values of wheat, flour and pasta. Studies have examined the effects of cooking on amino acid content but not the effects of food processing on the stable isotope values of amino acids. Patel, Kar, Pradhan, Mohapatra, and Nayak (2019) investigated the effects of baking temperature on protein fortified biscuits and found that some amino acids decreased up to 35% with an increase in the baking temperature from 180 to 220 °C. Variations of amino acid content were also noted in pizza crust (Tsen, Bates, Wall, & Gehrke, 1982) and balady breads baked at different high temperatures (248–343 °C) and short times (3.5–7.0 min) (El-Samahy & Tsen, 1981). Therefore, changes in amino acid content caused by heat processing may be linked to changes in amino acid stable isotope values. Other contributing factors could include the ingredients added in the preparation of the products – predominantly in the case of bakery recipes - such as eggs or butter.

3.2. Mycotoxins

Two of the six mycotoxins of interest were detected in the grain samples, with conventional common wheat exhibiting the highest levels of contamination (82.0 ± 14.8 μg/kg) (Table 10.A). Co-existence of HT-2 and DON was noted mainly in conventional durum wheat samples at concentrations of 15 ± 4.9 and 17 ± 9.9 μg/kg, respectively. Organic common wheat contained levels below LOQ in all mycotoxins analysed, while two samples of organic durum wheat exhibited low levels of contamination (7.0 μg/kg HT-2 and 8.0 μg/kg DON). HT-2 toxin is a major metabolite of T-2. In our study, T-2 was not detected at levels above LOQ in any of the samples. Indicative levels for the sum of T-2 and HT-2 have been set by the European Commission (Recommendation 2013/165, 2024) at 100 μg/kg for unprocessed wheat, 50 μg/kg for cereal milling products and 25 μg/kg for bakery products and pasta. Maximum permissible limits have been set for DON, AFB1, OTA and ZEN as per the Regulation 2023/915, 2024. The levels of DON detected in all our samples were significantly below these limits, which are 1750 μg/kg in unprocessed durum wheat, 750 μg/kg in cereal flours and pasta, and 500 μg/kg in bakery products.

Our results clearly show that mycotoxin contamination was significantly more prominent in the conventional rather than the organic samples. The same conclusion was reached in a recent review article, with lower occurrence of Fusarium mycotoxins (DON, ZEA, and T-2 + HT-2) having been reported in organic than conventional cereals production, in the majority of studies included (Bernhoft et al., 2022). Organic farming systems have been able to keep mycotoxin contamination at low levels specifically in wheat (Lazzaro, Moretti, Giorni, Brera, & Battilani, 2015; Polišenská, Jirsa, Salava, Sedláčková, & Frydrych, 2021) and wheat flour (Vrček et al., 2014), with the authors suggesting that production and environmental parameters could have a bigger influence on the presence of mycotoxins than the farming method itself. Fusarium mycotoxin contamination risks are potentially lowered by factors such as diverse crop rotations, improved soil organic matter and biological activity, while the use of high mineral nitrogen fertilizers and certain fungicides and herbicides could have the opposite effect (Bernhoft et al., 2022). As noted by the authors, such agronomic variables may explain the lower contamination in organic fields, even though more studies are required to assess the exact effects. Different findings have been reported by Sacco et al. (2020), with Italian organic flour yielding higher fungal recovery and mycotoxin detection than conventional. No significant differences between the two cultivation types were reported in Croatian wheat and wheat-based products (Pleadin et al., 2017), as well as in UK and German wheat flours (Wang et al., 2020), even though DON occurrence was 20% higher in organic flour samples.

Both the mechanical (milling) and the thermal (baking/drying) processing had significant effects on the mycotoxin concentrations of our samples (Fig. 4). Considering the low levels of contamination in most cases, the specific percentages may not reflect the exact trend

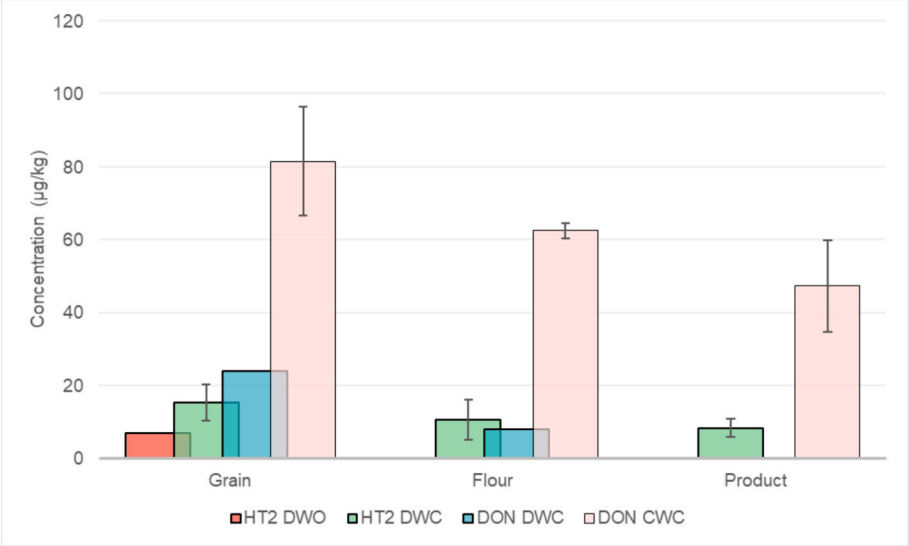

Fig. 4. Comparison between mycotoxin levels detected in the grains and their derived flours and products. DW: Durum Wheat, CW: Common Wheat, O: Organic, C: Conventional. Error bars (± SD) added where contamination was seen in more than a single sample.

beyond this study. However, a decreasing trend has clearly been noted for all detected mycotoxins. HT-2 reduction ranged between 30 and 100% and 46–100% when comparing wheat grain to flour/semolina and wheat grain to final products, respectively. Similarly, Pascale et al. (2011) noted an overall 89% reduction of T-2 and HT-2 toxins in semolina produced from wheat contaminated artificially at levels between 97 and 5954 µg/kg (sum of both toxins). The authors also noted that in the samples exhibiting toxin concentrations below 250 µg/kg (levels likely to occur in naturally contaminated wheat), the resulting semolina had negligible levels of T-2 and HT-2. Significant processing effects were also observed in pasta (99% reduction) by Silvestri (2010), while HT-2 and T-2 reduction has been reported in bread production (De Angelis, Monaci, Pascale, & Visconti, 2013; Dropa, Hajšlová, Lancová, & Burešová, 2014).

We found DON levels to also be affected by processing. Specifically, DON reduction ranged between 23 and 67% and 42–100% when going from wheat grain to flour/semolina and to final products, respectively. Processing effects have been investigated in bread-making from pre-contaminated wheat with DON concentrations from <500 to >5000 µg/kg and reduction rates from flour to bread were found to range between 38 and 100% (Tibola et al., 2018). Even if contradictory results have been reported in the last decade on the evolution of DON and the formation of degradation/conversion products (Suman, 2021), baking, kneading and fermentation have significantly affected DON levels in bread (depending on sourdough use and flour contamination levels) (Generotti et al., 2017; Stadler et al., 2019; Vidal, Marín, Morales, Ramos, & Sanchis, 2014; Wu, Kuca, Humpf, Klìmova, & Cramer, 2017), while 63% reduction was reported in semolina, with a further 8% and 41% in dry and cooked pasta, respectively (Brera et al., 2013).

3.3. Pesticides

No residues were detected in the organic wheat and wheat-derived samples analysed in this study. Low-level contamination of organic wheat was noted in the 2018 EU report on pesticide residues in foods, with 44.7% of the 716 conventional wheat samples analysed exhibiting contamination at or above LOQ, while residues were detected in 1.5% of the 134 organic wheat samples (European Food Safety Authority (EFSA), 2018). Moreover, results of a 2-year retail survey in the UK and Germany suggested 25% of organic wheat flour samples considered were contaminated with pesticides residues, with the plant growth regulator chlormequat being the most frequently detected compound (Wang, Hasanalieva, Wood, Anagnostopoulos, et al., 2020).

Fig. 5 shows the levels of contamination found in the conventional samples in our study. All residues were detected at concentrations below the EU maximum residue levels (MRLs). Isopyrazam, which is a broad-spectrum foliar fungicide, was the compound exhibiting the highest concentration, being half of the maximum permissible limit set by the EU in wheat (0.2 mg/kg) (Regulation 2019/552, 2024). Isopyrazam concentration was reduced 5 times after the processing of wheat into pasta, exhibiting a PF of 0.12. The available EU database on processing factors does not include data for durum wheat processing or composite foods such as bread and pasta (Zincke et al., 2022b). However, the PF reported in the database for isopyrazam in common wheat milling is 0.22 (Zincke et al., 2022a), which is higher than our value, indicating that pasta-making further decreases isopyrazam levels after milling. Tebuconazole levels remained nearly unchanged after durum wheat processing into pasta, while they reduced to <LOQ in bakery products. Complementary to our findings is the study of Hrynko, Kaczyński, Wołejko, and Łozowicka (2023), who reported that grinding (including milling and homogenizing) reduced tebuconazole in wheat only by 2%, while bread-baking (180 °C, 60 min) resulted in 50% average reduction. The baking temperatures in our case, as mentioned in Section 2.3, were 180 °C for biscuits, 250 °C for crackers, while pasta was dried at 90 °C. Therefore, it is understood that tebuconazole fungicide reduction can be achieved at higher temperatures. Azoxystrobin, which is another systemic broad-spectrum fungicide, was significantly reduced in our pasta samples compared to the raw material, with a PF of 0.12. This value is lower than the one reported in the EU database for common wheat flour (PF = 0.24) (Zincke et al., 2022a), which could be an indicator that pasta-making has a comparable effect with grain milling in azoxystrobin reduction. The major chiral metabolite of the fungicide prothioconazole, prothioconazole-desthio, was recently found to follow a decreasing trend during bread baking (Fang et al., 2023), while it reduced to levels below LOQ after wheat was processed into pasta in our study. Similarly, the levels of pyrethroid insecticide fluvalinate tau became non detectable in our finished products. The compound has been demonstrated to readily degrade after heat treatment even up to 100% (European Food Safety Authority (EFSA) et al., 2018). Lastly, metconazole fungicide was reduced below LOQ in our study from wheat to pasta, while the reported PF is 0.22 for common wheat flour (Zincke et al., 2022a), suggesting that heat processing in our study affected this compound.

The majority of pesticide residues considered in our study were not detected in the samples. However, other works have made noteworthy

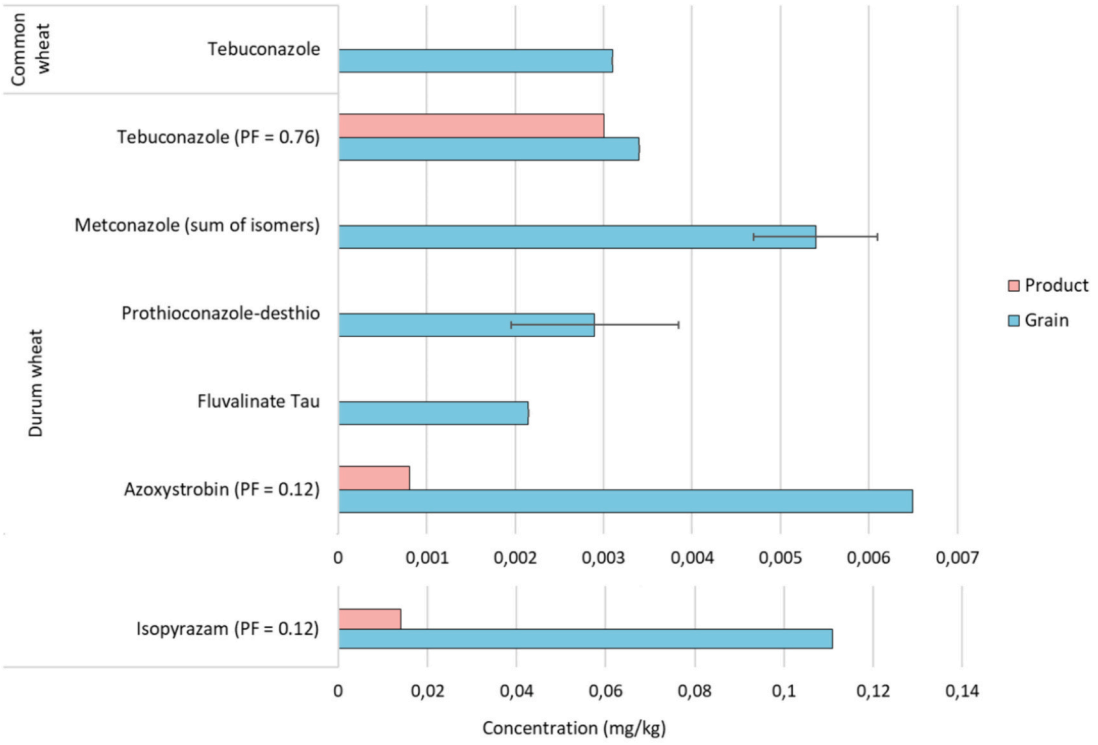

Fig. 5. Residues and PFs in the conventional wheat grains (blue) and derived products (pink). Error bars added where >1 sample contained the respective residue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

observations; Tittlemier et al. (2020) found significant contamination reduction from glyphosate and its main metabolite amino-methylphosphonic acid (AMPA) after wheat milling but no change after bread-baking (30 min, 205 °C). Glyphosate is the most-used pesticide globally in terms of quantity and is also associated with several environmental and health concerns, leading to discussions about the ban of its application (Finger, Möhring, & Kudsk, 2023). Studies have also noted the degradation of several organophosphorus pesticides, including malathion and chlorpyrifos-methyl in wheat during pasta (Uygun, Senoz, & Koksel, 2008) and cookies (Uygun, Senoz, Öztürk, & Koksel, 2009) processing, as well as chlorpyrifos in wheat-based Chinese steamed breads production (Liang, Duan, Gao, Li, & Zhang, 2022; Yu et al., 2021).

4. Conclusions

The present study investigated the differences between organically and conventionally grown wheat grains based on their stable isotope fingerprints ($\delta^{15}N$, $\delta^{34}S$, $\delta^{13}C$), as well as the levels of multi-mycotoxin and pesticide contamination. The latter proved the most effective for authentication purposes, since no residues were detected in the organic products. Moreover, differences between organic and conventional products were seen in their $\delta^{15}N_{bulk}$, $\delta^{15}N_{leucine}$ and $\delta^{15}N_{proline}$ values. While processing did not affect the bulk IRMS values, it caused a decreasing trend in the mycotoxin and residue contamination going from the wheat grain to the final products.

By simulating industrial processing, we hereby examined how the IRMS values were affected as food traceability markers and followed a realistic approach to the exposure of consumers to mycotoxins and pesticide residues, which is important since wheat is consumed in processed forms. To gain a deeper understanding of the changes of stable isotope ratios in complex matrices such as biscuits and crackers, future studies could include the IRMS values of all ingredients prior to mixing, as well as monitor the relationship between amino acid content and stable isotope ratios.

CRediT authorship contribution statement

Zoe Giannioti: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Michele Suman:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Conceptualization. **Alberto Roncone:** Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Eleonora Rollo:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation. **Loris Tonidandel:** Writing – review & editing, Validation, Methodology, Investigation. **Alice Barbero:** Writing – review & editing, Validation, Investigation, Data curation. **Dante Catellani:** Validation, Methodology, Investigation. **Roberto Larcher:** Writing – review & editing, Validation, Resources, Project administration, Methodology. **Luana Bontempo:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Zoe Giannioti reports financial support was provided by European Commission Marie Sklodowska-Curie Actions. If there are other authors, they 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

Data will be made available on request.

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Appendix A. Appendix

Table 1.A
List of grain samples. Regional pairs are indicated by the same number.

Samples	Cultivation	Area	Year
Common Wheat	Conventional	Parma[1]	2022
Common Wheat	Organic	Parma[1]	2022
Common Wheat	Conventional	Parma[2]	2022
Common Wheat	Organic	Parma[2]	2022
Durum Wheat	Organic	Parma[3]	2021
Durum Wheat	Conventional	Parma[3]	2021
Durum Wheat	Organic	Ravenna[1]	2022
Durum Wheat	Conventional	Ravenna[1]	2022
Durum Wheat	Organic	Piacenza[1]	2022
Durum Wheat	Conventional	Piacenza[1]	2022
Durum Wheat	Organic	Pesaro Urbino[1]	2022
Durum Wheat	Conventional	Pesaro Urbino[1]	2022
Durum Wheat	Organic	Experimental[1]	2022
Durum Wheat	Conventional	Experimental[1]	2022

Table 2.A
Biscuits ingredients list.

Ingredients:
Butter
Sugar
Sunflower oil
Ammonium bicarbonate
Sodium bicarbonate
Water
Whole eggs
Flour

Table 3.A
Crackers ingredients list.

Ingredients:
Flour
Malt
Fine salt
Soybean oil
Sodium bicarbonate
Malted barley flour
Yeast base (lievito madre)
Natural yeast
Water

Table 4.A
Recovery levels for the mycotoxins included in this study.

		Recovery, % (RSD_r, %)								
	Spiking level	DON	AFG_2	AFG_1	AFB_2	AFB_1	HT-2	T-2	ZEA	OTA
Barley flour	1	101 (1)	100 (6)	97 (8)	114 (13)	108 (4)	102 (10)	106 (2)	91 (9)	93 (3)
	2	99 (5)	93 (7)	99 (8)	89 (1)	101 (3)	103 (2)	93 (4)	89 (8)	94 (5)
	3	108 (9)	100 (13)	104 (4)	101 (8)	98 (3)	112 (3)	114 (2)	95 (8)	95 (4)
Durum wheat flour	1	95 (2)	90 (8)	82 (4)	84 (6)	89 (4)	95 (4)	92 (4)	95 (9)	74 (7)
	2	94 (3)	93 (111)	90 (7)	93 (11)	87 (6)	100 (1)	99 (1)	70 (4)	81 (14)
	3	100 (1)	89 (5)	99 (9)	102 (12)	93 (8)	100 (3)	100 (1)	91 (6)	87 (4)
Oat flour	1	99 (2)	n.d.	101 (4)	91 (10)	99 (9)	100 (5)	98 (6)	97 (12)	88 (11)
	2	104 (7)	84 (4)	103 (6)	93 (12)	107 (5)	98 (9)	97 (5)	96 (9)	97 (8)

(*continued on next page*)

Table 4.A (*continued*)

		Recovery, % (RSD_r, %)								
	Spiking level	DON	AFG_2	AFG_1	AFB_2	AFB_1	HT-2	T-2	ZEA	OTA
	3	99 (3)	85 (5)	109 (4)	105 (1)	103 (1)	104 (1)	100 (2)	87 (11)	98 (2)
Wheat-based crisp bread	1	100 (0)	102 (5)	106 (5)	85 (10)	102 (6)	107 (2)	108 (6)	84 (5)	101 (3)
	2	100 (5)	112 (3)	107 (9)	100 (10)	104 (8)	105 (3)	103 (4)	97 (10)	96 (5)
	3	99 (3)	101 (6)	98 (2)	96 (10)	101 (16)	102 (1)	99 (3)	95 (11)	102 (4)
Rye-based crisp bread	1	95 (3)	n.d.	n.d.	n.d.	77 (3)	97 (2)	91 (3)	96 (7)	82 (2)
	2	90 (1)	n.d.	98 (4)	97 (8)	73 (3)	94 (6)	85 (1)	79 (3)	84 (1)
	3	89 (9)	100 (8)	77 (3)	91 (9)	79 (2)	90 (40)	84 (3)	64 (4)	67 (2)
	Volume of spiking solution (μL)	Spiking level (μg/kg)								
		DON	AFG_2	AFG_1	AFB_2	AFB_1	HT-2	T-2	ZEA	OTA
Level 1	40	300	2	0.4	1.2	0.4	20	20	30	1.2
Level 2	100	750	5	1	3	1	50	50	75	3
Level 3	200	1500	10	2	6	2	100	100	150	6

Table 5.A
LOQs of the mycotoxins.

Mycotoxin	LOQ (μg/kg)
DON	5
ZEN	3
HT2	6
T2	6
OTA	0.5
AFB1	0.2

Table 6.A
Molecules analysed with the relative validation parameters in the wheat matrix.

Pesticide (EN 15662:2018 method)	LOQ (μg/kg)	Instrumetal tecnique	10 (μg/kg)		50 (μg/kg)		200 (μg/kg)			
			Rec%	RSD%	Rec%	RSD%	Rec%	RSD%	Calibration range (μg/kg)	R^2
2,4-DDD	10	GC–MS/MS	88%	7%	91%	4%	122%	2%	10–200	0,9909
2,4-DDE	10	GC–MS/MS	88%	5%	80%	5%	70%	2%	10–200	0,9807
2,4-DDT	10	GC–MS/MS	87%	3%	80%	2%	79%	2%	10–200	0,9809
2-Phenylphenol	30	GC–MS/MS	118%	20%	109%	12%	95%	5%	30–250	0,9976
3,5 dichloroaniline	30	GC–MS/MS	111%	27%	71%	10%	106%	4%	30–250	0,9945
3-Hydroxycarbofuran	3	LC-MS/MS	71%	3%	98%	2%	78%	3%	3–200	0,9979
3-Ketocarbofuran	3	LC-MS/MS	121%	5%	111%	6%	115%	6%	3–200	0,9905
4,4-DDE	10	GC–MS/MS	97%	10%	95%	8%	114%	7%	10–200	0,9908
4,4-DDT	10	GC–MS/MS	100%	7%	95%	8%	113%	4%	10–200	0,981
6-Benzyladenine	3	LC-MS/MS	99%	7%	108%	6%	69%	5%	3–200	0,9928
Abamectin (B1a)	10	LC-MS/MS	97%	20%	85%	26%	120%	6%	10–200	0,9854
Acephate	5	LC-MS/MS	85%	3%	106%	2%	70%	2%	5–200	0,9867
Acetamiprid	3	LC-MS/MS	83%	15%	84%	11%	81%	2%	3–200	0,9805
Acetochlor	10	GC–MS/MS	113%	8%	90%	8%	112%	6%	10–200	0,9842
Acibenzolar-*S*-methyl	3	LC-MS/MS	81%	20%	95%	12%	83%	5%	3–200	0,9856
Acrinathrin	10	GC–MS/MS	88%	7%	92%	5%	115%	3%	10–200	0,993
Alachlor	30	GC–MS/MS	76%	3%	86%	3%	70%	3%	30–250	0,9961
Aldicarb	30	LC-MS/MS	115%	8%	99%	6%	101%	4%	10–200	0,9911
Aldicarb sulfone	3	LC-MS/MS	106%	20%	88%	21%	111%	14%	3–200	0,9827
Aldicarb sulfoxide	5	LC-MS/MS	107%	18%	71%	16%	76%	10%	5–200	0,9805
Aldrin	10	GC–MS/MS	122%	2%	88%	3%	106%	2%	10–200	0,9813
Allethrin	10	LC-MS/MS	96%	3%	95%	3%	95%	2%	10–200	0,9847
Ametocradin	3	LC-MS/MS	114%	22%	77%	19%	114%	20%	3–200	0,9862
Ametryn	3	LC-MS/MS	73%	12%	90%	8%	120%	5%	3–200	0,9853
Amidosulfuron	3	LC-MS/MS	78%	2%	84%	3%	78%	4%	3–200	0,9969
Amisulbron	30	LC-MS/MS	103%	4%	98%	3%	76%	2%	10–200	0,9848
Amitraz	30	LC-MS/MS	104%	4%	87%	4%	103%	3%	10–200	0,9974
Atrazine	3	LC-MS/MS	93%	4%	86%	4%	93%	3%	3–200	0,9805
Azaconazole	3	LC-MS/MS	105%	12%	80%	25%	86%	19%	3–200	0,9887
Azinphos-ethyl	30	LC-MS/MS	93%	12%	95%	15%	106%	15%	10–200	0,9859
Azinphos-methyl	10	LC-MS/MS	100%	15%	62%	11%	108%	16%	10–200	0,9951
Azoxystrobin	3	LC-MS/MS	83%	5%	71%	4%	72%	3%	3–200	0,988
Beflubutamid	5	LC-MS/MS	94%	13%	104%	7%	73%	2%	5–200	0,9958
Benalaxyl	3	LC-MS/MS	113%	20%	78%	13%	91%	7%	3–200	0,9892
Bendiocarb	3	LC-MS/MS	88%	7%	84%	5%	90%	3%	3–200	0,9821
Benfluralin	10	GC–MS/MS	88%	18%	68%	21%	120%	18%	10–200	0,9967
Benfuracarb	10	LC-MS/MS	82%	16%	115%	25%	111%	10%	10–200	0,9956

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Table 6.A (*continued*)

Pesticide (EN 15662:2018 method)	LOQ (μg/kg)	Instrumetal tecnique	10 (μg/kg)		50 (μg/kg)		200 (μg/kg)			
			Rec%	RSD%	Rec%	RSD%	Rec%	RSD%	Calibration range (μg/kg)	R^2
Benomyl	50	LC-MS/MS	102%	8%	96%	7%	78%	8%	50–400	0,994
Bensulfuron-methyl	10	LC-MS/MS	83%	21%	74%	12%	119%	6%	10–200	0,9846
Benthiavalicarb Isopropyl	3	LC-MS/MS	85%	15%	97%	9%	110%	5%	3–200	0,9901
Benzoximate	10	LC-MS/MS	93%	7%	88%	6%	105%	5%	10–200	0,9925
Benzoylprop-ethyl	3	LC-MS/MS	73%	19%	93%	10%	92%	17%	3–200	0,9997
Bifenazate	3	LC-MS/MS	111%	12%	90%	11%	107%	19%	3–200	0,9808
Bifenox	10	GC–MS/MS	77%	7%	93%	5%	92%	3%	10–200	0,9934
Bifenthrin	3	LC-MS/MS	73%	6%	113%	7%	121%	5%	3–200	0,9858
Bitertanol	10	LC-MS/MS	76%	11%	93%	10%	99%	7%	10–200	0,9938
Boscalid	3	LC-MS/MS	119%	11%	104%	9%	98%	8%	3–200	0,9828
Bromacil	3	LC-MS/MS	84%	15%	98%	13%	109%	11%	3–200	0,9871
Bromadiolone	30	LC-MS/MS	75%	5%	80%	4%	69%	3%	10–200	0,9846
Bromophos-ethyl	10	GC–MS/MS	122%	5%	82%	4%	116%	3%	10–200	0,9805
Bromophos-methyl	3	LC-MS/MS	101%	12%	85%	6%	119%	5%	3–200	0,9807
Bromopropilate	10	GC–MS/MS	115%	12%	94%	10%	109%	3%	10–200	0,9909
Bromoxynil	5	LC-MS/MS	100%	6%	86%	5%	82%	3%	5–200	0,9937
Bromuconazole (sum)	3	LC-MS/MS	109%	3%	88%	3%	98%	3%	3–200	0,983
Bupirimate	3	LC-MS/MS	86%	4%	99%	3%	104%	3%	3–200	0,9817
Buprofezin	3	LC-MS/MS	88%	21%	69%	18%	96%	18%	3–200	0,9959
Cadusafos	3	LC-MS/MS	117%	4%	76%	4%	86%	2%	3–200	0,9968
Captan (THPI)	30	GC–MS/MS	117%	7%	95%	5%	71%	3%	30–250	0,9856
Carbaryl	3	LC-MS/MS	84%	8%	95%	9%	71%	6%	3–200	0,9927
Carbendazim	3	LC-MS/MS	84%	15%	85%	9%	102%	4%	3–200	0,9968
Carbofuran	3	LC-MS/MS	74%	5%	106%	5%	108%	4%	3–200	0,9955
Carbosulfan	10	LC-MS/MS	100%	21%	122%	15%	105%	19%	10–200	0,9806
Carboxin	3	LC-MS/MS	86%	6%	85%	5%	120%	5%	3–200	0,9949
Carfentrazone Ethyl	3	LC-MS/MS	120%	11%	105%	10%	113%	9%	3–200	0,9923
Chinomethionat	10	GC–MS/MS	105%	12%	115%	13%	98%	8%	10–200	0,9906
Chlorantranilprole	10	LC-MS/MS	112%	8%	96%	4%	104%	2%	10–200	0,9867
Chlorfenapyr	30	GC–MS/MS	72%	4%	110%	5%	122%	5%	30–250	0,9966
Chlorfenson	10	GC–MS/MS	121%	19%	87%	9%	112%	5%	10–200	0,9924
Chlorfenvinphos	5	LC-MS/MS	121%	5%	103%	5%	111%	4%	5–200	0,993
Chlormephos	30	GC–MS/MS	119%	19%	86%	18%	119%	13%	30–250	0,9923
Chlorothalonil	30	GC–MS/MS	79%	12%	105%	23%	83%	14%	30–250	0,9868
Chlorpropam	30	GC–MS/MS	82%	10%	66%	6%	100%	2%	30–250	0,9809
Chlorpyrifos	3	LC-MS/MS	74%	11%	98%	8%	69%	3%	3–200	0,9943
Chlorpyrifos Methyl	10	GC–MS/MS	105%	14%	79%	13%	70%	20%	10–200	0,9902
Chlozolinate	10	LC-MS/MS	104%	21%	70%	19%	85%	16%	10–200	0,998
Chlozolinate	10	GC–MS/MS	95%	3%	99%	3%	121%	3%	10–200	0,9907
Chromafenozide	10	LC-MS/MS	77%	4%	99%	4%	104%	4%	10–200	0,9925
Clethodim Isomer A	30	LC-MS/MS	119%	4%	93%	4%	103%	3%	10–200	0,9992
Clethodim Isomer B	3	LC-MS/MS	115%	5%	93%	4%	97%	3%	3–200	0,9853
Clofentezine	10	LC-MS/MS	84%	15%	83%	9%	93%	4%	10–200	0,9972
Clopyralid	100	LC-MS/MS	93%	10%	92%	6%	109%	5%	50–400	0,983
Cloquintocet	30	LC-MS/MS	118%	7%	62%	16%	109%	16%	10–200	0,9941
Cloquintocet-mexyl	3	LC-MS/MS	113%	5%	91%	3%	91%	3%	3–200	0,9872
Clothianidin	3	LC-MS/MS	90%	4%	95%	3%	98%	2%	3–200	0,9836
Coumaphos	3	LC-MS/MS	106%	25%	119%	24%	87%	19%	3–200	0,9929
Cyanazine	3	LC-MS/MS	92%	21%	110%	20%	104%	15%	3–200	0,9833
Cyantraniliprole	5	LC-MS/MS	90%	14%	107%	11%	103%	10%	5–200	0,9924
Cyazofamid	3	LC-MS/MS	80%	12%	115%	9%	122%	7%	3–200	0,9809
Cycloxydim	3	LC-MS/MS	84%	20%	74%	19%	98%	12%	3–200	0,9932
Cyflufenamid	3	LC-MS/MS	103%	11%	119%	12%	86%	4%	3–200	0,9961
Cyflumetofen	3	LC-MS/MS	88%	9%	78%	7%	83%	5%	3–200	0,9916
Cyfluthrin	30	GC–MS/MS	75%	12%	118%	15%	118%	20%	30–250	0,9957
Cyhalofop-butyl	10	GC–MS/MS	116%	15%	85%	14%	115%	27%	10–200	0,9949
Cymoxanil	10	LC-MS/MS	105%	12%	90%	12%	96%	8%	10–200	0,9994
Cypermethrin	30	GC–MS/MS	97%	19%	91%	15%	97%	9%	30–250	0,982
Cyproconazole	3	LC-MS/MS	77%	18%	100%	16%	113%	10%	3–200	0,9955
Cyprodinil	3	LC-MS/MS	113%	14%	91%	14%	77%	10%	3–200	0,9831
dazomet	100	GC–MS/MS	122%	15%	84%	12%	110%	10%	30–250	0,9884
Deltamethrin	10	GC–MS/MS	87%	8%	97%	5%	113%	2%	10–200	0,9902
Demeton-*S*-methyl	30	LC-MS/MS	104%	4%	104%	5%	92%	5%	10–200	0,991
Demeton-*S*-methylsulfone	3	LC-MS/MS	104%	7%	95%	7%	113%	6%	3–200	0,9848
Desethyl-Atrazine	5	LC-MS/MS	95%	7%	93%	7%	80%	5%	5–200	0,9913
Desisopropyl-Atrazine	3	LC-MS/MS	80%	8%	72%	19%	89%	10%	3–200	0,9961
Desmedipham	3	LC-MS/MS	112%	12%	97%	10%	96%	5%	3–200	0,9871
Desmethyl-pirimicarb	3	LC-MS/MS	93%	9%	119%	9%	84%	5%	3–200	0,9985
Diazinon	3	LC-MS/MS	69%	25%	102%	19%	106%	18%	3–200	0,9947
Dicamba	50	LC-MS/MS	101%	3%	117%	2%	81%	1%	50–400	0,9888
Dichlobenil	10	GC–MS/MS	100%	5%	86%	4%	79%	4%	10–200	0,9877
Dichlofenthion	10	GC–MS/MS	103%	9%	101%	5%	116%	2%	10–200	0,9834
Dichlofluanid	30	GC–MS/MS	108%	7%	79%	6%	119%	3%	30–250	0,9959

(*continued on next page*)

Table 6.A (*continued*)

Pesticide (EN 15662:2018 method)	LOQ (μg/kg)	Instrumetal tecnique	10 (μg/kg)		50 (μg/kg)		200 (μg/kg)			
			Rec%	RSD%	Rec%	RSD%	Rec%	RSD%	Calibration range (μg/kg)	R^2
Dichlorvos	3	LC-MS/MS	70%	3%	100%	2%	105%	1%	3–200	0,9874
Dicloran	30	GC–MS/MS	97%	6%	88%	4%	96%	2%	30–250	0,9904
Dicofol	30	GC–MS/MS	114%	12%	72%	12%	85%	10%	30–250	0,9807
Dicrotophos	3	LC-MS/MS	69%	8%	98%	9%	107%	9%	3–200	0,9882
Dieldrin	30	GC–MS/MS	85%	9%	99%	8%	93%	6%	30–250	0,9936
Diethofencarb	3	LC-MS/MS	101%	10%	112%	14%	103%	13%	3–200	0,9955
Difenoconazole	3	LC-MS/MS	114%	17%	116%	13%	77%	8%	3–200	0,9732
Diflubenzuron	30	LC-MS/MS	119%	19%	112%	3%	118%	6%	10–200	0,9805
Diflufenican	10	GC–MS/MS	115%	8%	94%	5%	80%	5%	10–200	0,9841
Dimethoate	3	LC-MS/MS	118%	15%	102%	16%	73%	12%	3–200	0,9893
Dimethomorph	3	LC-MS/MS	118%	13%	98%	25%	111%	15%	3–200	0,9977
Dimoxystrobin	3	LC-MS/MS	109%	4%	89%	3%	91%	3%	3–200	0,9801
Diniconazole	3	LC-MS/MS	117%	7%	103%	7%	94%	5%	3–200	0,9808
Dinotefuran	30	LC-MS/MS	89%	7%	100%	5%	69%	3%	10–200	0,9819
Dioxathion	30	GC–MS/MS	117%	5%	79%	5%	99%	4%	30–250	0,9826
Diphenamid	3	LC-MS/MS	92%	13%	98%	10%	114%	8%	3–200	0,9915
Diphenylamine	30	GC–MS/MS	77%	11%	107%	8%	73%	5%	30–250	0,9993
Disulfuton	10	GC–MS/MS	82%	7%	101%	8%	92%	3%	10–200	0,9944
Ditalimfos	10	LC-MS/MS	95%	10%	87%	7%	79%	3%	10–200	0,9868
Diuron	3	LC-MS/MS	70%	5%	91%	4%	109%	2%	3–200	0,9847
Dodemorph	3	LC-MS/MS	93%	13%	84%	8%	119%	4%	3–200	0,9952
Dodine	10	LC-MS/MS	106%	15%	72%	16%	87%	3%	10–200	0,9929
Emamectin Benzoate B1a	3	LC-MS/MS	78%	9%	127%	11%	104%	9%	3–200	0,9962
Endosulfan-alfa	10	GC–MS/MS	72%	4%	94%	3%	113%	2%	10–200	0,9956
Endosulfan-beta	30	GC–MS/MS	107%	6%	114%	6%	92%	5%	30–250	0,9992
Endosulfan-sulfate	30	GC–MS/MS	100%	11%	109%	9%	103%	6%	30–250	0,9907
EPN	30	GC–MS/MS	79%	21%	78%	12%	69%	5%	30–250	0,9919
Epoxiconazole	3	LC-MS/MS	89%	4%	92%	3%	101%	3%	3–200	0,9873
Etaconazole Isomer	3	LC-MS/MS	89%	6%	77%	8%	74%	7%	3–200	0,9948
Ethalfluralin	10	GC–MS/MS	89%	17%	91%	15%	92%	8%	10–200	0,9911
Ethion	10	LC-MS/MS	91%	3%	54%	10%	92%	7%	10–200	0,9804
Ethirimol	3	LC-MS/MS	91%	9%	99%	8%	72%	6%	3–200	0,9915
Ethofumesate	5	LC-MS/MS	94%	5%	101%	6%	80%	4%	5–200	0,9889
Ethoprophos	3	LC-MS/MS	80%	18%	100%	10%	85%	6%	3–200	0,9874
Ethoxyquin	3	LC-MS/MS	103%	9%	97%	16%	115%	18%	3–200	0,993
Etofenprox	3	LC-MS/MS	72%	3%	97%	3%	107%	1%	3–200	0,9911
Etoxazole	3	LC-MS/MS	73%	8%	97%	6%	122%	3%	3–200	0,9815
Etridiazole	10	GC–MS/MS	109%	15%	109%	13%	86%	7%	10–200	0,9856
Etrimfos	3	LC-MS/MS	100%	12%	90%	8%	101%	3%	3–200	0,9946
Famoxadone	10	GC–MS/MS	106%	4%	92%	3%	111%	3%	10–200	0,9928
Fenamidone	3	LC-MS/MS	102%	11%	88%	7%	92%	3%	3–200	0,9923
Fenamiphos	3	LC-MS/MS	119%	13%	87%	9%	115%	4%	3–200	0,9884
Fenarimol	10	LC-MS/MS	118%	9%	78%	6%	81%	2%	10–200	0,9913
Fenazaquin	3	LC-MS/MS	80%	2%	84%	3%	70%	4%	3–200	0,9996
Fenbuconazole	3	LC-MS/MS	74%	3%	84%	3%	109%	3%	3–200	0,992
Fenbutatin-oxide	3	LC-MS/MS	80%	12%	101%	13%	120%	13%	3–200	0,9927
Fenchlorphos	10	GC–MS/MS	117%	4%	97%	3%	89%	2%	10–200	0,9888
Fenhexamid	5	LC-MS/MS	84%	5%	94%	3%	74%	2%	5–200	0,9978
Fenitrothion	10	GC–MS/MS	107%	4%	91%	4%	73%	3%	10–200	0,9813
Fenothiocarb	3	LC-MS/MS	81%	20%	92%	12%	74%	4%	3–200	0,9907
Fenoxaprop	50	LC-MS/MS	109%	4%	84%	4%	110%	4%	50–400	0,9868
Fenoxycarb	3	LC-MS/MS	106%	8%	98%	5%	98%	2%	3–200	0,9986
Fenpropathrin	10	GC–MS/MS	98%	3%	90%	3%	119%	2%	10–200	0,988
Fenpropidin	3	LC-MS/MS	92%	9%	101%	14%	74%	6%	3–200	0,9911
Fenpropimorph (sum of isomers)	3	LC-MS/MS	93%	5%	103%	10%	116%	5%	3–200	0,9888
Fenpyrazamide	3	LC-MS/MS	98%	13%	83%	9%	118%	4%	3–200	0,9905
Fenpyroximat	3	LC-MS/MS	76%	3%	119%	5%	71%	4%	3–200	0,9858
Fenson	10	GC–MS/MS	87%	9%	114%	6%	119%	3%	10–200	0,9944
Fenthion	3	LC-MS/MS	72%	19%	62%	18%	121%	7%	3–200	0,9821
Fenthion-sulfone	30	GC–MS/MS	121%	5%	91%	4%	69%	3%	30–250	0,9951
Fenthion-sulfoxide	3	LC-MS/MS	86%	6%	102%	5%	69%	3%	3–200	0,9903
Fenvalerate	10	GC–MS/MS	114%	4%	84%	8%	93%	7%	10–200	0,9998
Fipronil	5	LC-MS/MS	75%	4%	86%	7%	112%	7%	5–200	0,9891
Fipronil-sulfone	3	LC-MS/MS	75%	18%	88%	18%	107%	19%	3–200	0,997
Flazasulfuron	10	LC-MS/MS	117%	3%	82%	3%	72%	3%	10–200	0,9849
Flonicamid	3	LC-MS/MS	85%	6%	105%	6%	90%	5%	3–200	0,9918
Florasulam	3	LC-MS/MS	86%	8%	93%	8%	99%	8%	3–200	0,9974
Fluazifop	10	LC-MS/MS	91%	10%	116%	9%	105%	7%	10–200	0,9891
Fluazifop-P-Butyl	3	LC-MS/MS	88%	4%	98%	3%	121%	3%	3–200	0,9859
Fluazinam	5	LC-MS/MS	120%	6%	118%	6%	98%	4%	5–200	0,9971
Flubendiamide	30	LC-MS/MS	88%	7%	116%	5%	70%	4%	10–200	0,9851
Flucythrinate	10	GC–MS/MS	93%	18%	97%	9%	105%	3%	10–200	0,9879
Fludioxonil	10	LC-MS/MS	110%	9%	99%	6%	116%	4%	10–200	0,9977

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Table 6.A (*continued*)

Pesticide (EN 15662:2018 method)	LOQ (μg/kg)	Instrumetal tecnique	10 (μg/kg)		50 (μg/kg)		200 (μg/kg)			
			Rec%	RSD%	Rec%	RSD%	Rec%	RSD%	Calibration range (μg/kg)	R^2
Fludioxonil	30	GC–MS/MS	102%	3%	69%	3%	104%	3%	30–250	0,9939
Flufenacet	3	LC-MS/MS	75%	3%	98%	4%	79%	4%	3–200	0,9923
Flufenoxuron	3	LC-MS/MS	108%	3%	90%	3%	80%	2%	3–200	0,9896
Fluopicolide	5	LC-MS/MS	76%	13%	81%	11%	116%	9%	5–200	0,9978
Fluopyram	3	LC-MS/MS	103%	4%	92%	3%	122%	2%	3–200	0,9911
Flupyradifurone	3	LC-MS/MS	73%	12%	94%	7%	104%	3%	3–200	0,9962
Fluquinconazole	10	LC-MS/MS	106%	16%	100%	15%	95%	12%	10–200	0,9846
Fluroxypyr	10	LC-MS/MS	121%	7%	110%	6%	113%	4%	10–200	0,9855
Fluroxypyr-1-methylheptyl ester	5	LC-MS/MS	97%	11%	119%	8%	119%	4%	5–200	0,9859
Flusilazole	3	LC-MS/MS	120%	23%	92%	14%	93%	6%	3–200	0,9985
Flutriafol	10	LC-MS/MS	118%	14%	98%	11%	102%	9%	10–200	0,983
Fluvalinate Tau	3	LC-MS/MS	111%	7%	99%	5%	101%	2%	3–200	0,981
Fluxapyroxad	3	LC-MS/MS	101%	8%	89%	4%	91%	3%	3–200	0,9955
Folpet (Phtalimide)	30	GC–MS/MS	112%	16%	87%	16%	79%	16%	30–250	0,9962
Fonofos	3	LC-MS/MS	107%	15%	89%	12%	98%	9%	3–200	0,9974
Fosthiazate	3	LC-MS/MS	123%	23%	79%	17%	76%	10%	3–200	0,9865
Fuberidazole	3	LC-MS/MS	114%	18%	86%	10%	77%	5%	3–200	0,9837
Furalaxyl	3	LC-MS/MS	83%	10%	81%	7%	76%	5%	3–200	0,9887
Furathiocarb	3	LC-MS/MS	96%	4%	79%	5%	94%	4%	3–200	0,9965
Heptachlor	10	GC–MS/MS	95%	11%	84%	6%	118%	3%	10–200	0,9835
Heptenophos	3	LC-MS/MS	79%	11%	109%	9%	93%	6%	3–200	0,9987
Hesachlorobenzene	30	GC–MS/MS	90%	13%	87%	8%	107%	3%	30–250	0,9923
Hexaconazole	3	LC-MS/MS	91%	10%	71%	18%	116%	21%	3–200	0,9857
Hexaflumuron	30	GC–MS/MS	104%	10%	88%	7%	85%	6%	30–250	0,9851
Hexythiazox	3	LC-MS/MS	109%	4%	80%	6%	102%	4%	3–200	0,9917
Imazalil	3	LC-MS/MS	76%	4%	98%	3%	118%	2%	3–200	0,9958
Imazaquin	10	LC-MS/MS	97%	10%	96%	10%	98%	2%	10–200	0,9968
Imazosulfuron	10	LC-MS/MS	116%	3%	98%	3%	96%	2%	10–200	0,9956
Imidacloprid	3	LC-MS/MS	77%	5%	83%	4%	115%	4%	3–200	0,9836
Indoxacarb	3	LC-MS/MS	75%	5%	107%	6%	112%	6%	3–200	0,9955
Ipconazole Isomer	3	LC-MS/MS	115%	5%	90%	4%	73%	3%	3–200	0,982
Iprodione	30	GC–MS/MS	110%	7%	89%	8%	79%	7%	30–250	0,993
Iprovalicarb	3	LC-MS/MS	113%	10%	86%	6%	114%	2%	3–200	0,9836
Isofenphos	30	GC–MS/MS	103%	23%	110%	15%	109%	10%	30–250	0,9937
Isofetamid	3	LC-MS/MS	94%	10%	83%	6%	120%	5%	3–200	0,9821
Isopropalin	10	LC-MS/MS	117%	7%	81%	9%	114%	7%	10–200	0,983
Isoproturon	3	LC-MS/MS	96%	3%	87%	4%	82%	5%	3–200	0,9851
Isopyrazam	3	LC-MS/MS	79%	7%	72%	12%	79%	13%	3–200	0,9827
Kresoxim Methyl	10	GC–MS/MS	102%	4%	108%	3%	79%	2%	10–200	0,994
lambda-Cyhalothrin	30	GC–MS/MS	85%	6%	110%	4%	118%	3%	30–250	0,9884
Lenacil	3	LC-MS/MS	116%	7%	85%	5%	86%	4%	3–200	0,9862
Linuron	3	LC-MS/MS	84%	10%	98%	15%	80%	7%	3–200	0,9846
Lufenuron	10	LC-MS/MS	92%	13%	104%	13%	70%	6%	10–200	0,9824
Malaoxon	3	LC-MS/MS	99%	13%	85%	11%	83%	11%	3–200	0,983
Malathion	10	GC–MS/MS	76%	20%	85%	15%	108%	9%	10–200	0,9827
Mandipropamid	3	LC-MS/MS	70%	8%	96%	6%	86%	4%	3–200	0,994
MCPA	30	LC-MS/MS	102%	14%	92%	8%	83%	4%	10–200	0,9915
Mecarbam	3	LC-MS/MS	77%	3%	92%	2%	78%	2%	3–200	0,9849
Mecoprob	30	LC-MS/MS	120%	6%	93%	5%	78%	4%	10–200	0,9804
Mepanipyrim	10	LC-MS/MS	111%	7%	108%	6%	80%	5%	10–200	0,9809
Mepronil	3	LC-MS/MS	107%	4%	86%	3%	77%	3%	3–200	0,9858
Mepronil	10	GC–MS/MS	75%	4%	106%	3%	103%	2%	10–200	0,9919
Mepthyldinocap	50	LC-MS/MS	117%	10%	96%	20%	72%	14%	50–400	0,9856
Metalaxyl	3	LC-MS/MS	112%	4%	90%	3%	96%	3%	3–200	0,9898
Metamitron	3	LC-MS/MS	85%	5%	105%	6%	94%	6%	3–200	0,9833
Metazachlor	3	LC-MS/MS	121%	9%	93%	9%	87%	8%	3–200	0,9825
Metconazole (sum of isomers)	3	LC-MS/MS	84%	10%	75%	15%	111%	20%	3–200	0,9883
Methamidophos	3	LC-MS/MS	116%	12%	80%	9%	84%	7%	3–200	0,9923
Methidathion	3	LC-MS/MS	73%	25%	71%	17%	108%	10%	3–200	0,9882
Methiocarb	3	LC-MS/MS	90%	15%	100%	15%	106%	14%	3–200	0,9951
Methiocarb Sulfone	3	LC-MS/MS	74%	6%	92%	6%	77%	4%	3–200	0,9839
Methiocarb-sulfoxyde	3	LC-MS/MS	101%	12%	90%	10%	119%	10%	3–200	0,9911
Methomyl	3	LC-MS/MS	114%	10%	98%	21%	85%	11%	3–200	0,9817
Methoxyfenozide	10	LC-MS/MS	93%	3%	89%	3%	99%	3%	10–200	0,9879
Metolachlor	3	LC-MS/MS	85%	10%	88%	6%	121%	3%	3–200	0,9904
Metolachlor	10	GC–MS/MS	70%	3%	97%	3%	121%	2%	10–200	0,9921
Metoxychlor	10	GC–MS/MS	97%	6%	86%	4%	78%	2%	10–200	0,9932
Metrafenone	3	LC-MS/MS	101%	3%	91%	3%	105%	3%	3–200	0,9976
Metribuzin	3	LC-MS/MS	120%	8%	85%	6%	77%	4%	3–200	0,9927
Mevinphos	10	LC-MS/MS	91%	6%	81%	7%	84%	7%	10–200	0,9826
Monocrotophos	3	LC-MS/MS	71%	8%	75%	14%	101%	7%	3–200	0,9834
Monolinuron	3	LC-MS/MS	120%	3%	81%	3%	90%	2%	3–200	0,9804
Monuron	3	LC-MS/MS	71%	3%	98%	4%	121%	4%	3–200	0,9822

(*continued on next page*)

Table 6.A (*continued*)

Pesticide (EN 15662:2018 method)	LOQ (μg/kg)	Instrumetal tecnique	10 (μg/kg)		50 (μg/kg)		200 (μg/kg)			
			Rec%	RSD%	Rec%	RSD%	Rec%	RSD%	Calibration range (μg/kg)	R^2
Myclobutanil	5	LC-MS/MS	91%	14%	95%	8%	69%	6%	5–200	0,9986
Napropamide	3	LC-MS/MS	99%	5%	86%	10%	102%	10%	3–200	0,9868
Nicosulfuron	3	LC-MS/MS	69%	14%	109%	12%	71%	10%	3–200	0,9826
Nitenpyram	3	LC-MS/MS	105%	6%	93%	4%	107%	3%	3–200	0,9978
Nitrofen	30	GC–MS/MS	87%	3%	110%	5%	81%	5%	30–250	0,9801
Nuarimol	3	LC-MS/MS	111%	9%	88%	7%	96%	7%	3–200	0,9908
Omethoate	5	LC-MS/MS	73%	6%	93%	4%	115%	2%	5–200	0,9887
Oryzalin	30	LC-MS/MS	78%	11%	84%	6%	85%	3%	10–200	0,9933
Oxadiazon	3	LC-MS/MS	72%	4%	113%	7%	84%	2%	3–200	0,9864
Oxadixyl	3	LC-MS/MS	116%	7%	84%	5%	119%	4%	3–200	0,9948
Oxamyl	3	LC-MS/MS	74%	4%	84%	4%	108%	4%	3–200	0,9952
Oxathiopiprolin	30	LC-MS/MS	102%	9%	102%	10%	110%	13%	10–200	0,9923
Oxycarboxin	3	LC-MS/MS	103%	9%	88%	7%	72%	4%	3–200	0,9906
Paclobutrazol	5	LC-MS/MS	120%	7%	75%	5%	114%	3%	5–200	0,9966
Paraoxon	3	LC-MS/MS	108%	6%	91%	4%	89%	2%	3–200	0,9902
Paraoxon Methyl	10	GC–MS/MS	104%	9%	92%	6%	103%	4%	10–200	0,9866
Parathion Ethyl	30	GC–MS/MS	105%	5%	94%	3%	90%	2%	30–250	0,9866
Parathion Methyl	10	GC–MS/MS	82%	5%	112%	6%	74%	5%	10–200	0,9811
Penconazole	3	LC-MS/MS	110%	12%	103%	15%	94%	13%	3–200	0,9915
Pencycuron	3	LC-MS/MS	75%	10%	86%	8%	73%	4%	3–200	0,9947
Pendimethalin	10	LC-MS/MS	104%	4%	105%	2%	91%	2%	10–200	0,9994
Penoxsulam	3	LC-MS/MS	108%	9%	80%	5%	107%	3%	3–200	0,9846
Penthiopyrad	3	LC-MS/MS	80%	28%	92%	21%	79%	16%	3–200	0,9933
Permethrin	10	GC–MS/MS	76%	5%	85%	4%	88%	3%	10–200	0,9865
Permethrin (sum)	5	LC-MS/MS	86%	12%	106%	10%	82%	10%	5–200	0,994
Pethoxamid	3	LC-MS/MS	70%	3%	94%	4%	72%	4%	3–200	0,997
Phosalone	10	GC–MS/MS	83%	17%	96%	21%	103%	11%	10–200	0,994
Phosmet	10	GC–MS/MS	110%	7%	102%	10%	88%	8%	10–200	0,9915
Phoxim	10	LC-MS/MS	120%	3%	110%	6%	105%	5%	10–200	0,987
Picoxystrobin	3	LC-MS/MS	80%	5%	90%	4%	87%	3%	3–200	0,9862
Piperonyl Butoxide	3	LC-MS/MS	89%	5%	84%	4%	84%	3%	3–200	0,983
Pirimicarb	3	LC-MS/MS	120%	16%	76%	11%	113%	5%	3–200	0,986
Pirimiphos-methyl	3	LC-MS/MS	119%	5%	83%	4%	107%	2%	3–200	0,9926
Prochloraz	3	LC-MS/MS	107%	6%	88%	4%	72%	2%	3–200	0,9995
Procymidone	10	GC–MS/MS	108%	8%	113%	6%	105%	3%	10–200	0,9974
Profenofos	3	LC-MS/MS	91%	8%	91%	9%	120%	4%	3–200	0,9834
Profluralin	10	GC–MS/MS	77%	7%	106%	8%	120%	5%	10–200	0,9859
Promecarb	3	LC-MS/MS	69%	8%	111%	13%	113%	7%	3–200	0,9849
Prometon	10	LC-MS/MS	100%	5%	84%	15%	122%	6%	10–200	0,9804
Prometryn	3	LC-MS/MS	89%	13%	110%	10%	105%	8%	3–200	0,998
Propamocarb	3	LC-MS/MS	111%	22%	92%	6%	108%	12%	3–200	0,999
Propanil	3	LC-MS/MS	72%	10%	81%	4%	89%	7%	3–200	0,981
Propaquizafop	3	LC-MS/MS	115%	7%	92%	3%	105%	4%	3–200	0,9955
Propargite	3	LC-MS/MS	76%	6%	99%	2%	82%	3%	3–200	0,9962
Propham	30	LC-MS/MS	113%	3%	75%	7%	97%	2%	10–200	0,9974
Propiconazole	3	LC-MS/MS	120%	3%	107%	7%	123%	2%	3–200	0,9857
Propoxur	3	LC-MS/MS	121%	11%	85%	4%	114%	3%	3–200	0,9865
Propoxycarbazone	50	LC-MS/MS	71%	7%	110%	11%	93%	5%	50–400	0,9837
Propyzamide	10	LC-MS/MS	113%	7%	83%	9%	76%	3%	10–200	0,9887
Proquinazid	3	LC-MS/MS	108%	17%	101%	3%	93%	6%	3–200	0,9965
Prosulfocarb	3	LC-MS/MS	70%	14%	94%	2%	101%	7%	3–200	0,9835
Prosulfuron	10	LC-MS/MS	122%	5%	94%	5%	76%	2%	10–200	0,9987
Prothioconazole	30	LC-MS/MS	78%	4%	89%	14%	112%	1%	10–200	0,9923
Prothioconazole-desthio	5	LC-MS/MS	97%	5%	93%	5%	105%	3%	5–200	0,9857
Prothiophos	10	GC–MS/MS	93%	14%	85%	4%	74%	14%	10–200	0,9851
Pyraclostrobin	3	LC-MS/MS	78%	8%	63%	27%	93%	3%	3–200	0,9917
Pyraflufen	30	LC-MS/MS	110%	4%	99%	4%	110%	3%	10–200	0,9958
Pyraflufen Ethyl	3	LC-MS/MS	79%	10%	86%	4%	80%	14%	3–200	0,9968
Pyrazophos	3	LC-MS/MS	120%	7%	102%	15%	113%	3%	3–200	0,9923
Pyrethrum (Cinerin I)	10	LC-MS/MS	111%	6%	91%	10%	103%	3%	10–200	0,9906
Pyrethrum (Cinerin II)	5	LC-MS/MS	83%	16%	88%	3%	73%	11%	5–200	0,9966
Pyrethrum (Jasmolin I)	30	LC-MS/MS	86%	13%	84%	3%	77%	5%	10–200	0,9902
Pyrethrum (Jasmolin II)	30	LC-MS/MS	90%	4%	75%	6%	74%	3%	10–200	0,9866
Pyrethrum (Pyrethrin I)	3	LC-MS/MS	110%	4%	69%	12%	102%	3%	3–200	0,9866
Pyrethrum (Pyrethrin II)	5	LC-MS/MS	81%	9%	95%	6%	120%	2%	5–200	0,9811
Pyridaben	3	LC-MS/MS	113%	19%	107%	8%	74%	13%	3–200	0,9915
Pyridaphenthion	10	LC-MS/MS	80%	9%	91%	4%	80%	4%	10–200	0,9947
Pyrifenox (sum)	3	LC-MS/MS	86%	13%	58%	10%	74%	5%	3–200	0,9994
Pyrimethanil	3	LC-MS/MS	120%	4%	90%	6%	73%	4%	3–200	0,9846
Pyriofenone	3	LC-MS/MS	118%	10%	90%	5%	117%	16%	3–200	0,9933
Pyriproxyfen	3	LC-MS/MS	73%	10%	84%	16%	70%	2%	3–200	0,9865
Quinalphos	3	LC-MS/MS	101%	6%	97%	3%	94%	2%	3–200	0,994
Quinoxyfen	3	LC-MS/MS	90%	24%	113%	17%	114%	10%	3–200	0,997

(*continued on next page*)

Table 6.A (*continued*)

Pesticide (EN 15662:2018 method)	LOQ (μg/kg)	Instrumetal tecnique	10 (μg/kg)		50 (μg/kg)		200 (μg/kg)			
			Rec%	RSD%	Rec%	RSD%	Rec%	RSD%	Calibration range (μg/kg)	R^2
Quintozene	10	GC–MS/MS	111%	10%	78%	5%	75%	17%	10–200	0,994
Quizalofop Ethyl	3	LC-MS/MS	109%	12%	90%	4%	81%	15%	3–200	0,9915
Sedaxane	30	LC-MS/MS	118%	10%	89%	3%	112%	5%	10–200	0,987
Sethoxydim	3	LC-MS/MS	107%	9%	80%	3%	93%	4%	3–200	0,9862
Simazine	30	LC-MS/MS	100%	7%	103%	3%	98%	3%	10–200	0,9986
Spinetoram (sum)	3	LC-MS/MS	122%	4%	85%	4%	80%	2%	3–200	0,988
Spinosad A	3	LC-MS/MS	115%	15%	101%	8%	71%	19%	3–200	0,9911
Spinosad D	3	LC-MS/MS	111%	6%	88%	3%	96%	5%	3–200	0,9888
Spirodiclofen	3	LC-MS/MS	96%	18%	104%	19%	123%	3%	3–200	0,9905
Spirotetramat	3	LC-MS/MS	97%	4%	80%	3%	86%	2%	3–200	0,9858
Spirotetramat BYI 03380-enol	5	LC-MS/MS	91%	5%	72%	7%	123%	2%	5–200	0,9944
Spirotetramat BYI 03380-enol-glucoside	5	LC-MS/MS	76%	5%	80%	11%	111%	2%	5–200	0,9821
Spirotetramat BYI 03380-ketohydroxy	10	LC-MS/MS	88%	5%	77%	10%	69%	4%	10–200	0,9951
Spiroxamine	3	LC-MS/MS	100%	7%	76%	11%	89%	7%	3–200	0,9903
Sulfotep	3	LC-MS/MS	109%	4%	94%	5%	111%	2%	3–200	0,9998
Sulfoxaflor	10	LC-MS/MS	100%	10%	100%	12%	117%	15%	10–200	0,9891
Tebuconazole	5	LC-MS/MS	106%	3%	66%	4%	92%	2%	5–200	0,997
Tebufenozide	5	LC-MS/MS	106%	12%	71%	8%	84%	3%	5–200	0,9849
Tebufenpyrad	3	LC-MS/MS	108%	8%	87%	7%	105%	6%	3–200	0,9918
Tebupirimifos	3	LC-MS/MS	69%	7%	78%	9%	96%	6%	3–200	0,9974
Tecnazene	10	GC–MS/MS	95%	7%	98%	4%	82%	7%	10–200	0,9891
Teflubenzuron	30	LC-MS/MS	102%	7%	97%	9%	87%	3%	10–200	0,9859
Tefluthrine	30	GC–MS/MS	72%	13%	102%	6%	103%	12%	30–250	0,9971
Tembotrione	3	LC-MS/MS	84%	5%	84%	16%	123%	1%	3–200	0,9851
Tepraloxydim	30	LC-MS/MS	113%	4%	109%	3%	107%	4%	10–200	0,9879
Terbufos	30	LC-MS/MS	118%	12%	92%	3%	94%	3%	10–200	0,9977
Terbumeton	3	LC-MS/MS	113%	6%	102%	8%	123%	7%	3–200	0,9939
Terbuthylazine	3	LC-MS/MS	117%	4%	94%	4%	123%	2%	3–200	0,9923
Terbutryn	3	LC-MS/MS	120%	13%	96%	7%	103%	4%	3–200	0,9896
Tetrachlorvinphos	3	LC-MS/MS	108%	8%	72%	9%	111%	4%	3–200	0,9978
Tetraconazole	3	LC-MS/MS	91%	13%	61%	19%	116%	17%	3–200	0,9911
Tetradifon	10	GC–MS/MS	116%	4%	76%	5%	73%	3%	10–200	0,9928
Tetramethrin (sum)	3	LC-MS/MS	120%	5%	74%	3%	108%	3%	3–200	0,9854
Thiabendazole	3	LC-MS/MS	121%	6%	88%	7%	86%	7%	3–200	0,9842
Thiacloprid	3	LC-MS/MS	112%	16%	103%	4%	114%	4%	3–200	0,9856
Thiamethoxam	3	LC-MS/MS	93%	10%	110%	6%	121%	13%	3–200	0,993
Thifensulfuron-methyl	10	LC-MS/MS	110%	8%	96%	3%	117%	19%	10–200	0,9961
Thiobencarb (4-chlorobenzyl methyl sulfone)	3	LC-MS/MS	120%	9%	75%	9%	111%	2%	3–200	0,9931
Thiodicarb	3	LC-MS/MS	112%	19%	81%	15%	98%	2%	3–200	0,9827
Thiometon	30	GC–MS/MS	90%	4%	86%	3%	79%	2%	30–250	0,9805
Thiophanate-methyl	3	LC-MS/MS	112%	11%	89%	3%	91%	7%	3–200	0,9813
Tolcofos methyl	10	LC-MS/MS	101%	8%	117%	3%	100%	2%	10–200	0,9847
Tolylfluanid	30	GC–MS/MS	72%	9%	70%	8%	106%	4%	30–250	0,9862
Triadimefon	10	LC-MS/MS	74%	15%	78%	9%	89%	15%	10–200	0,9969
Triadimenol	30	GC–MS/MS	110%	25%	114%	16%	81%	11%	30–250	0,9848
Tri-allate	3	LC-MS/MS	113%	4%	81%	5%	96%	2%	3–200	0,9974
Triasulfuron	10	LC-MS/MS	75%	5%	93%	12%	80%	2%	10–200	0,9805
Triazamate	3	LC-MS/MS	108%	5%	65%	18%	119%	2%	3–200	0,9887
Triazophos	5	LC-MS/MS	106%	14%	71%	10%	75%	12%	5–200	0,9859
Trichlorfon	3	LC-MS/MS	93%	15%	87%	10%	78%	4%	3–200	0,9951
Triclopyr	30	LC-MS/MS	103%	18%	72%	13%	102%	2%	10–200	0,988
Tricyclazole	3	LC-MS/MS	122%	7%	96%	6%	91%	5%	3–200	0,9958
Trifloxystrobin	3	LC-MS/MS	107%	7%	72%	6%	111%	3%	3–200	0,9892
Triflumizole	3	LC-MS/MS	86%	18%	93%	8%	76%	8%	3–200	0,9821
Triflumuron	3	LC-MS/MS	112%	11%	87%	10%	76%	14%	3–200	0,9906
Trifluralin	30	GC–MS/MS	114%	3%	87%	3%	77%	3%	30–250	0,9966
Triticonazole	3	LC-MS/MS	110%	15%	86%	14%	72%	11%	3–200	0,9902
Tritosulfuron	3	LC-MS/MS	101%	15%	94%	2%	71%	6%	3–200	0,9866
Valifenalate	5	LC-MS/MS	112%	10%	85%	4%	80%	5%	5–200	0,9866
Vamidothion	3	LC-MS/MS	81%	9%	74%	7%	99%	4%	3–200	0,9811
Vinclozolin	10	GC–MS/MS	75%	7%	86%	5%	101%	6%	10–200	0,9915
Zoxamide	3	LC-MS/MS	120%	14%	107%	9%	119%	9%	3–200	0,9947

Pesticide (QuPPe-PO- method)	**LOQ (mg/kg)**	**Instrumetal tecnique**	**100 μg/kg**		**500 μg/kg**		**2000 μg/kg**			
			Rec %	**RSD%**	**Rec %**	**RSD%**	**Rec %**	**RSD%**	**Calibration range**	**R2**
Glyphosate	0,1	LC-MS/MS	90%	10%	91%	6%	97%	5%	100–2000	0,989

Table 7.A
Bulk IRMS analysis results (N, C, S). Pairs indicated by the same letter.

Sample Type	Origin	Cultivation	δ^{15}N (‰)	δ^{13}C (‰)	δ^{34}S (‰)
Durum wheat	Piacenza	Organic[a]	1.4	−26.7	0.6
		Conventional[a]	1.4	−27.8	−2.5
Durum wheat	Pesaro e Urbino	Organic[a]	3.1	−26.1	−3.3
		Conventional[a]	1.0	−26.3	3.5
Durum wheat	Ravenna	Organic[a]	2.4	−26.6	4.1
		Conventional[a]	−0.1	−26.6	−5.8
Common wheat	Parma 1	Organic[a]	4.7	−28.0	2.0
		Conventional[a]	1.7	−27.2	−1.6
Common wheat	Parma 2	Organic[b]	5.2	−27.7	2.4
		Conventional[b]	1.9	−27.5	−1.9
Durum wheat	Parma 3	Conventional[c]	3.5	−26.6	−1.0
		Organic[c]	3.4	−26.4	−0.7
Durum wheat	Experimental	Organic[a]	1.1	−23.7	0.3
		Conventional[a]	0.9	−24.0	−0.3

Table 8.A
δ^{13}C values of wheat amino acids. O: Organic, C: Conventional.

δ^{13}C AA (‰)	alanine		valine		leucine		glycine		proline		aspartic acid		glutamic acid		phenylalanine	
	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C
Piacenza	−25.3	−27.8	−30.7	−30.1	−42.5	−43.8	−25.8	−27.3	−29.5	−30.7	−24.1	−26.3	−25.2	−25.8	−41.9	−37.7
Pesaro e Urbino	−27.7	−24.8	−40.6	−30.0	−43.6	−39.5	−26.8	−25.6	−29.7	−29.1	−25.5	−20.9	−25.0	−20.7	−42.1	−35.2
Ravenna	−27.5	−24.4	−35.0	−30.3	−44.0	−40.4	−28.1	−26.2	−30.1	−27.9	−27.8	−21.4	−24.8	−20.0	−42.6	−34.8
Parma 1	−27.5	−26.9	−31.8	−33.2	−42.0	−43.6	−28.3	−27.0	−30.3	−28.7	−25.4	−27.1	−25.0	−24.8	−30.6	−36.8
Parma 2	−26.8	−25.1	−30.9	−29.2	−39.1	−38.8	−25.7	−24.6	−31.2	−27.3	−21.6	−21.1	−21.2	−20.3	−37.3	−33.6
Parma 3	−26.7	−26.4	−36.6	−35.6	−43.4	−42.9	−20.9	−21.0	−34.1	−33.5	−29.1	−27.6	−26.1	−25.8	−41.4	−42.3
Experimental	−21.8	−19.9	−27.6	−26.9	−35.9	−36.5	−20.8	−21.0	−23.3	−22.7	−20.3	−19.5	−17.2	−15.9	−32.0	−35.3
Mean	−26.2	−25.0	−33.3	−30.7	−41.5	−40.8	−25.2	−24.7	−29.7	−28.5	−24.8	−23.4	−23.5	−21.9	−38.3	−36.5
S.D.	2.1	2.6	4.4	2.8	3.0	2.8	3.2	2.7	3.2	3.3	3.1	3.4	3.2	3.7	5.1	2.9

Table 9.A
δ^{15}N and δ^{13}C values of wheat-derived products.

			δ^{15}N							
Cultivation	Grain Origin	Product	alanine	valine	leucine	glycine	proline	aspartic acid	glutamic acid	phenylalanine
Organic	Piacenza	Pasta	1,18	2,57	7,42	1,77	2,91	2,86	4,24	9,40
Conventional	Piacenza	Pasta	1,13	3,01	−1,55	0,77	4,13	1,19	3,74	8,15
Organic	Pesaro e Urbino	Pasta	1,95	4,13	12,77	6,49	6,27	4,39	6,01	11,28
Conventional	Pesaro e Urbino	Pasta	−0,23	−2,16	11,56	−0,30	2,25	0,36	2,80	7,36
Organic	Ravenna	Pasta	0,06	3,39	−1,32	−0,10	5,11	1,87	3,72	7,11
Conventional	Ravenna	Pasta	−0,46	3,74	−0,93	0,10	3,23	0,89	3,05	6,34
Organic	Parma 1	Biscuit	5,79	7,07	3,86	3,27	7,95	4,72	7,38	11,34
Organic	Parma 1	Cracker	5,42	3,28	9,31	−2,44	7,36	3,66	7,33	13,86
Conventional	Parma 1	Biscuit	3,31	0,51	8,23	−3,68	5,11	2,75	5,62	9,08
Conventional	Parma 1	Cracker	2,99	1,47	7,86	−4,80	4,35	2,23	4,80	7,99
Organic	Parma 2	Biscuit	5,33	7,90	3,39	2,33	7,18	5,29	7,19	12,09
Conventional	Parma 2	Biscuit	2,25	1,12	7,24	−2,58	5,61	2,93	6,20	9,98
							δ^{13}C			
Cultivation	Grain Origin	Product	alanine	valine	leucine	glycine	proline	aspartic acid	glutamic acid	phenylalanine
Organic	Piacenza	Pasta	−28,32	−29,61	−40,23	−26,67	−25,73	−26,22	−20,08	−34,51
Conventional	Piacenza	Pasta	−26,24	−31,92	−41,55	−27,65	−25,22	−24,93	−24,59	−38,30
Organic	Pesaro e Urbino	Pasta	−25,20	−28,98	−40,05	−27,47	−27,10	−21,69	−19,74	−31,73
Conventional	Pesaro e Urbino	Pasta	−25,66	−35,69	−40,05	−20,66	−22,52	−30,33	−23,70	−37,49
Organic	Ravenna	Pasta	−25,65	−30,84	−37,88	−24,60	−26,89	−18,39	−20,10	−36,32
Conventional	Ravenna	Pasta	−24,44	−27,05	−39,87	−27,31	−24,86	−23,92	−18,99	−35,13
Organic	Parma 1	Biscuit	−26,75	−29,84	−37,97	−25,03	−17,40	−21,70	−22,85	−32,57
Organic	Parma 1	Cracker	−26,97	−27,81	−40,20	−24,01	−18,07	−21,40	−21,71	−29,82
Conventional	Parma 1	Biscuit	−26,13	−31,48	−39,09	−25,85	−17,83	−19,13	−21,41	−29,85
Conventional	Parma 1	Cracker	−27,36	−33,49	−42,38	−28,19	−19,29	−20,63	−22,48	−32,36
Organic	Parma 2	Biscuit	−25,49	−28,18	−37,17	−26,01	−16,25	−22,40	−22,28	−35,37
Conventional	Parma 2	Biscuit	−26,89	−29,67	−39,89	−26,12	−20,01	−20,48	−21,19	−32,21

Table 10.A
Summary of mycotoxin levels detected in the wheat grain samples.

Sample Type	Mycotoxin	Min (μg/kg)	Max (μg/kg)	Mean (μg/kg)	SD (%)
Conventional Common Wheat	HT-2	<LOQ	<LOQ	<LOQ	–
	DON	71.0	92.0	82.0	14.8
Organic Common Wheat	HT-2	<LOQ	<LOQ	<LOQ	–
	DON	<LOQ	<LOQ	<LOQ	–
Conventional Durum Wheat	HT-2	12.0	21.0	15.0	4.9
	DON	10.0	24.0	17.0	9.9
Organic Durum Wheat	HT-2	<LOQ	7.0	7.0	–
	DON	<LOQ	8.0	8.0	–

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