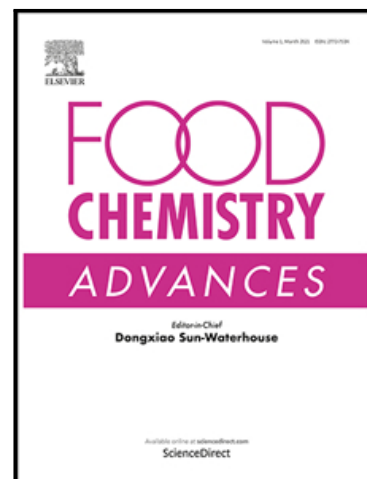


## Journal Pre-proof

Maize Landrace and Post-Harvest Traits are reflected in the Volatile Profile and Nutritional Composition of Italian Maize Porridge (Polenta): A preliminary study

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## Highlights

- Physio-chemical properties of four Italian flint maize landraces were analyzed.
- SPME GC-MS and PTR-TOF-MS were applied for volatilome characterization.
- Flours volatilome and nutritional traits are preserved into polenta.
- Cooking triggered Maillard reaction, lipid oxidation and VOCs evaporation.

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## Maize Landrace and Post-Harvest Traits are reflected in the Volatile Profile and Nutritional Composition of Italian Maize Porridge (Polenta): A preliminary study

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### Abstract:

Maize porridge, known as "polenta" in Italy, is a global staple food. This study aims to characterize the quality of four Italian flint maize landraces by investigating physical properties and macronutrients composition. By using SPME GC-MS and PTR-ToF-MS we analyzed the flours volatilome and changes in aroma profile post-cooking. Cooking induced the formation of 5 compounds and the loss of up to 25 compounds, primarily through evaporation. Post-cooking, the concentrations of some sulphur compounds (methanethiol, dimethyl sulfide and dimethyl trisulfide), lipid oxidation compounds (2-pentylfuran and hexanal) and Maillard reaction compounds including some aldehydes (nonanal, benzaldehyde, phenylacetaldehyde), pyridine and furans (furfural and furfuryl alcohol) increased. Differences in volatilome and macronutrients contents among landraces were also observed with Marano samples having on average a significantly higher concentration of proteins (13.67%), while the Nostrano samples had the highest fat content (5.00%). Fatty acid profile differences were mirrored in the volatilome. Spin flours had the highest level of linoleic acid, leading to elevated levels in cooked polenta due to linoleic acid oxidation. The differences in volatilome and macronutrients contents among the samples confirmed that local landraces are not only important for biodiversity and cultural heritage but also lead to unique aroma compounds profiles.

**Keywords:** flint maize, polenta, volatilome, SPME GC-MS, PTR-TOF-MS

**Abbreviations:** VOCs, volatile organic compounds; SPME GC-MS, solid phase micro extraction-gas chromatography-mass spectrometry; FA, fatty acid; PUFA, polyunsaturated fatty acid; PTR-ToF-MS, proton transfer reaction-time of flight-mass spectrometry; DMS, dimethyl sulfide

## 1. Introduction

Maize, one of the world's most popular cereal grains, had a production of approximately 1.134 million tonnes in 2017 (FAO, 2017). In Europe, maize production reaches around 110 million tons annually, with Northern Italy alone accounting for up to 5.2% of the total European maize production (FAO, 2017). While most of the production is used as animal feed, maize serves as a staple food in many countries, particularly in Africa and Mexico. It is a good source of starch (74.4-76.8%), protein (8.05-8.62%), lipids (up to 5.91%) and also contains polyphenols, carotenoids, vitamins and dietary fibre (Singh et al., 2019).

One of the primary methods of consuming maize is by cooking maize flour in hot water, commonly referred to as maize porridge. In Italy, this dish is known as "polenta" and carries a profound historical association with times of famine and hunger. It has served as a dietary staple for rural populations in northern Italy for centuries (Tesio & Follis, 2012). Flint maize (*Zea mays indurata*), a specific maize category, is traditionally used for polenta preparation. In Italy, the primary flint maize varieties are *Marano*, *Nostrano dell'Isola*, *Pignoletto* and *Ottofile*, mainly cultivated in mountain regions (Tesio & Follis, 2012). Flint maize is preferred over other maize varieties, due to its high content of hard starch endosperm, which maintains a better particle texture during cooking and preserves its flavour better during the cooking procedure. Porridge flavour and aroma play a key role in determining consumer acceptance and preferences by determining its organoleptic characteristics (Ekpa et al., 2020).

Previous research has utilized gas chromatography mass spectrometry (GC-MS) to identify and quantify volatile organic compounds (VOCs) in fresh maize, maize kernel, maize flour and starch, and other maize products like canned maize, popcorn, maize oil and breakfast cereal (Buttery et al., 2002; Flora & Wiley, 1974; Goicoechea & Guillén, 2014; Zhang et al., 2023). These analyses found mostly aldehydes, ketones and alcohols and a small amount of terpenes, alkadienal, esters and furans (Buttery et al., 2002). Recently, (E)-2-nonenal, 1-octen-3-ol,  $\beta$ -myrcene, dimethyl trisulfide and D-limonene were indicated as characteristic VOCs in sweet corn after steaming, blanching and roasting (Zhang et al., 2023). Ekpa and co-workers highlighted the impact of post-harvest operations and storage on aroma compounds stability of a variety of provitamin A biofortified maize (Ekpa et al., 2021). However, research regarding the influence of cooking on flint maize aroma profile remains limited.

The growing awareness of the need for sustainable food systems is fueling consumers' increasing desire for indigenous, locally grown crops, fostering stronger connections with local food systems (Upright, 2023). This trend has prompted the regional valorization of local and native landraces properties (Posadinu et al., 2023) which are preserved and selected by smallholder farmers (Barcaccia et al., 2003). These landraces are essential for maintaining biodiversity and are valued for their unique nutritional and sensory profiles. While scientific researches have focused on evaluating and characterizing maize landraces to preserve and valorize ancient varieties, agronomical traits and biodiversity heritage (Palumbo et al., 2017), differences in sensory, physicochemical and nutritional properties have been insufficiently characterized. It is not clear whether these differences are retained during the cooking process, which can affect the aroma profile through thermal degradation, evaporation, lipid oxidation and Maillard reaction.

The present study aims to characterize different local landraces of flint maize flour from Northern Italy and whether these characteristics are preserved after the cooking process. Physical properties, including moisture content, water activity ( $a_w$ ) and texture, macronutrients composition (fat and protein content and composition) and volatiles were investigated. A combination of SPME GC-MS and proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) was deployed to investigate changes in the aroma profile occurring during the cooking process by comparing flour and polenta volatile fingerprints. We hypothesize that the cooking process will lead to the depletion of certain VOCs through evaporation, while simultaneously generating new aroma compounds through fatty acids oxidation and Maillard reaction, thereby preserving the distinctive landraces characteristics.

## 2. Materials and Methods

### 2.1. Materials

#### 2.1.1. Sample collection

Three flint maize flours from Trentino region and one from Veneto region, namely *Nostrano di Storo* (N=14), *Spin di Caldonazzo* (N=4), *Dorotea di Primiero* (N=4) and *Marano Vicentino* (N=5), were obtained from local producers. In addition, one commercially available instant polenta (VLC) was included in the sampling, resulting in a total of 28 distinct samples. Instant polenta is a type of cornmeal that has been partially pre-cooked (by heat and steam) and dried to reduce its cooking time when compared to traditional polenta.

Maize flour samples were collected directly from farmers, from consortia or from a local supermarket in 2018. Samples were chosen to capture the authenticity of landraces, acknowledging the inherent variability resulting from diverse growing conditions and post-harvest processes (*i.e.* drying, milling and storage), typical of regional and limited smallholder production. For the *Nostrano* flours (INT, GbM, GSNV, GS, C1-C4, P1-P4, BC and FM), samples were collected from a consortium (36 producers) and directly from producers in Chiese valley. For the *Spin* flours (181227, 926, 120 and SP), different lots with different producing dates (range 0-3 months) were obtained from the same producer (Valsugana valley). The *Dorotea* samples (LM, FS, RC and LP) were obtained from producers located in the Primiero valley. These samples were subjected to varying durations of sun-drying exposure and different storage conditions. Meanwhile, *Marano* samples (L283A, L270, L331, 414 and 9) had scattered production dates (range 0.5-4 months). Information about the samples were obtained directly from the farmers or the cooperatives that supplied the products through interviews. Additional samples information can be found in Table S1.

### 2.1.2. Polenta cooking

Polenta was made using Thermomixer (Bimby TM-31 Vorwerk, Italy) by pouring 100 g of flour into 400 mL of boiled distillate water at 100 °C for 2 minutes on velocity setting 2. After that, the speed was increased to 3 for 1 minute to ensure homogeneity before cooking for 40 minutes at 100 °C at the velocity setting 2 (Thermomix recipe, Vorwerk).

## 2.2. Methods

### 2.2.1. Moisture content and water activity of raw maize flours

All maize flours were measured in triplicates for moisture content and  $a_w$  (AquaLab Ser. 3 Water Activity Meter, USA). The moisture content was measured by weighting 1 g of flour before and after drying it for one hour at 130 °C (AACC method 44-15-02). The  $a_w$  meter was calibrated using water ( $a_w=1.000\pm 0.003$ ) prior to sample analysis.

### 2.2.2. Fat and protein content in raw maize flours

The protein content was determined by analyzing the nitrogen content of the samples using DUMAS with a conversion factor of 6.25. The total fat content was measured using Soxhlet extraction with petroleum ether at 40-60 °C for 6 hours. After that, the mixing solution was evaporated by rotary evaporator and left in a fume hood overnight before weighting the final extracted fat.

### 2.2.3. Polyunsaturated fatty acid (PUFA) content in raw maize flours

PUFA content was determined based on ISO 5509E method (ISO, 2000). The lipid extract was dissolved in hexane (20 g maize flour in 230 mL of hexane soaked for 20 hours at room temperature) and centrifuged 1900 g for 5 minutes before evaporating the supernatant by rotary evaporator.

Fatty acids (FAs) were then determined through GC-FID (Thermo Fisher Scientific Inc., Waltham, MA, US) analysis by using a capillary column WCOT Fused Silica Coating Selecting FAME (dimensions: 100 m x 0.25 mm ID x 0.2  $\mu\text{m}$  film thickness). Samples were placed within 2 mL autosampler vials. The injector and detector temperatures were set at 250 °C with hydrogen as a carrier gas. The initial column temperature was held at 60 °C for 5 minutes, then raised at 15 °C  $\text{min}^{-1}$  until reached 165 °C and maintained for 1 minute before raised to 225 °C with a rate of 2 °C  $\text{min}^{-1}$  for 20 minutes (ISO/IDF, 2015). FAs identification was based on elution order and by comparing retention times with corresponding peaks in a standard solution (GLC-36). Individual FAs semi-quantification was based on peaks areas and expressed in percentage of total peaks area. The analysis was run in duplicates on a selected sample set: C1-C4 and P1-P4 for *Nostrano*, L283A, L270, L331, 414 and 9 for *Marano*, 926 for *Spin* and LM for *Dorotea*.

#### 2.2.4. Texture properties of polenta

After preparation, polenta samples were immediately poured in a plastic-cylinder with 55 mm diameter and 15 mm thickness before being incubated at 40 °C for one hour to allow temperature equilibration. The polenta was then tested for hardness and stickiness by the puncture test through a texture analyzer (TA.XT.Plus from Stable MicroSystems, UK). A load cell of 5 kg with a cylinder probe P/25 (25 mm x 40 mm) were used. The probe height was set at 20 mm and the penetration rate was 2 mm/s while the post-test speed was 5 mm/s. The analysis was performed in triplicate to obtain the peak force to rupture (N).

#### 2.2.5. SPME GC-MS for raw maize flours and polenta

All analyses were performed with a GC-MS (Thermo Fisher Scientific Inc., Waltham, MA, US) equipped with a Stabilwax DA capillary column (30 m x 0.25 mm ID x 0.25  $\mu\text{m}$  film thickness) and a SPME fibre assembly DVB/CAR/PDMS (Divinylbenzene/Carboxen/Polydimethylsiloxane) 53/30  $\mu\text{m}$  diameter, 2 cm length (Supelco, Bellefonte, USA). 2 g of maize flour or polenta were placed in a 10 mL vial and incubated at 40 °C for 15 min, including 10 min agitation and 5 min acceleration for equilibrium. Volatiles were trapped by exposing the fibre to the vial's headspace for 10 min (40 °C) without agitation and then desorbed for 10 min into the GC injection port (260 °C) in splitless mode. The oven temperature was set at 40 °C for 2 min, increased at 10 °C/min to 200 °C and then held for 5 min. The helium flow-rate was

constant at 1 ml/min. Spectra were acquired at 50 spectra/s in the range 30–380 Da. The detector voltage was set at 2500 V with an electron energy of 70 eV. The N-alkane standard C7-C40 series was injected with the same setting condition and using split ratio of 1:40. The obtained retention times (RTs) were used to calculate the linear retention index (LRI) and the NIST library was used for identification. The analysis was run in duplicates for all maize flour samples and, for the polenta, on the samples selection used for the PUFA analysis.

#### 2.2.6. PTR-ToF-MS for raw maize flours and polenta

All headspace measurements were performed by using a multipurpose GC sampler (Gerstel GmbH, Mulheim am Ruhr, Germany) connected to a PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) through a heated PEEK capillary tube (D=1 mm, T= 110 °C) as described previously (Pedrotti et al., 2021). For each sample, 2 g of maize flour and 4 g of polenta were weighed into 25 mL vials. The PTR-ToF-MS instrumental conditions for all the measurements were as follows: drift voltage 628 V, drift temperature 110 °C, drift pressure 2.80 mbar affording an E/N value of 128 Td (1 Td=10<sup>-17</sup> V· cm<sup>2</sup>). Sampling was performed headspace direct injection with a flow rate of 40 sscm for 60 seconds followed by 60 seconds of nitrogen to reduce memory effects. The mass resolution (m/Δm) was at least 3800 and data were collected for the mass range *m/z* from 20 to 250. The measurement order was randomized and empty vials were used as blanks. Maize flours samples were stored in coolers at 10 °C and then incubated at 40 °C for 30 min before PTR-TOF-MS analysis. Polenta samples were measured directly after cooking with the same procedure. All samples were measured in five replicates each. Flours measurements were performed in one day while polenta samples were performed in four consecutive days. Polenta samples measured on the initial day (C2, GS, LP, L331, P3, SP and FM) were removed from the dataset due to instrumental malfunction.

#### 2.2.7. Data processing and statistical analysis

To better investigate landraces characteristics, data were aggregated per landraces (*Nostrano*, *Spin*, *Dorotea*, *Marano* and sample VLC). Proximate analysis, texture and FAs data were summarized using mean ± SD for each maize landrace. After checking normality and variance homogeneity assumptions by using Shapiro and Levene tests, differences in terms of landraces were assessed through one-way ANOVA (*P*<0.01) followed by a Tukey honest significant difference (HSD) *post-hoc* test whether a statistically significant difference was observed.



SPME GC-MS data were integrated and extracted using Chromeleon 7 (ver. 7.2 SR4). Aroma compounds were identified by comparing mass spectra with the National Institute of Standards and Technology (NIST) database and the LRI. Absolute and normalized peak areas (% X/TIC) were obtained for each selected compound. One-way ANOVA followed by a Tukey HSD was performed on both flour and polenta GC-MS data to see which compounds were significantly different ( $P < 0.01$ ) for each landrace.

PTR-ToF-MS data sets of flours and polenta samples were integrated and extracted using TOFO MATLAB according to a procedure described elsewhere (Pedrotti et al., 2021) and by averaging 30 sec for each measurement. A mass selection procedure was then applied to select mass peaks that were significantly higher than the blanks ( $P < 0.01$ ) and by eliminating  $^{13}\text{C}$  isotopologues and signals related to interfering ions (Pedrotti et al., 2020). For both data sets (flours and polenta) the median values over the five replicates were obtained. Then a Principal Component Analysis (PCA) was run by previously mean centring and scaling each mass peak by its standard deviation. This holistic exploration was followed by a univariate approach where the mass peaks were analyzed with separate one-way ANOVA ( $P < 0.01$ ) with Bonferroni correction followed by Tukey HSD *post-hoc* test to find VOCs markers for each landrace. Multiple Factor Analysis (MFA) was performed on flours data (protein and fat content, water activity and moisture, GC-MS and PTR-MS data) to better visualize landraces clustering.

All data analyses were run in R 3.6.3 with core functions and external packages (ChemometricsWithR, mixOmics, multcomp, vegan, FactoMineR).

### 3. Results and discussion

#### 3.1. Proximate and physical analysis

In Table 1 are presented the results of proximate and physical analysis of the flours and the textural analysis of polenta samples.

*Table 1 here*

On average, *Dorotea* samples had the highest moisture content (14.15%), mostly due to FS sample which had 18.29%. This value exceeded the CODEX limit of 15% while the rest of the samples ranged between 10.9-13.9%, except for two samples: BC (8.62%) and FM (9.56%) from *Nostrano* flours. Moisture content fluctuation mostly depended on post-harvest operations including drying and storage time and conditions, moisture migration, condensation and packaging type (Meena et al., 2017). In the case of the

*Dorotea* sample (FS), the observed high moisture content may be attributed to the combination of traditional sun-drying, which is dependent on weather conditions and is less predictable, and subsequent storage at relatively high temperatures (12-17 °C) in paper bags. Conversely, the majority of *Nostrano* and *Spin* samples, which exhibited a lower moisture ( $12.16\pm 1.39\%$  and  $12.41\pm 0.99\%$  respectively), were dried using industrial ovens under controlled conditions and packaged in propylene bags known for their effectiveness in maintaining low moisture levels (Likhayo et al., 2018).

The  $a_w$  correlated significantly with moisture content ( $R^2=0.943$ ,  $P<0.05$ ) and ranged from 0.39 to 0.84 with FS sample having the highest value.  $a_w$  was significantly different ( $P<0.05$ ) only for the precooked sample due to the prior cooking process. To the best of the authors' knowledge, there is no official quality standard for maize flour  $a_w$  but values above 0.7-0.8 can favour mold, yeast and bacteria growth (Barbosa-Cánovas et al., 2007).

Flour macronutrients data were comparable to those reported for other maize varieties, with the exception of the pre-cooked sample: all samples had a protein content within the range of typically observed for commercial corn varieties (8-14%).

*Marano* samples had a significantly higher protein content (14%,  $P<0.05$ ) than other samples, followed by *Doreotea* samples (13%). *Nostrano* landrace samples showed a protein content around 11%, comparable to the average value of 10% found by Lucchin *et al.* (2003). The same study on *Nostrano* landrace showed comparable values also in terms of fat content (5%). The other samples also have a similar fat content, except for samples from *Spin* landrace, which, on average, had a significant lower fat content (3%,  $P<0.05$ ). Differences in macronutrients between the landraces were expected since maize variety might affect both physical and chemical characteristics of maize and its products (Colín-Chávez et al., 2020). In our case, pre- and post-harvest conditions (*i.e.* growing and drying conditions, milling and storage) might also had an effect. For example, in the case of *Spin* samples, the maize kernels are degermed during dry milling which can reduce both fat and protein content. Similarly, in the pre-cooked sample the maize kernels are dehulled and degermed during milling. The removal of the bran and the germ is known to decrease the nutritional value (Suri & Tanumihardjo, 2016). This, together with the combination of heat and moisture applied during the pre-cooking process – which can affect final product nutritional attributes – can explain the lowest value on protein and fat content in the VLC sample. In terms of texture, this sample showed the highest hardness and lowest stickiness, probably because of prior cooking conditions and the associated loss of soluble

compounds (leaching). A weak correlation of protein content with hardness ( $R^2=0.47$ ,  $P<0.05$ ) and protein content with stickiness ( $R^2=0.38$ ,  $P<0.05$ ) was found. This indicates that protein content only marginally influences polenta texture. Starch content, due to its dominant presence in maize (around 74.4-76.8%), plays a more important role in predicting polenta texture (Singh et al., 2019). Amylopectin, one of the two constituents of starch, during the cooking leaks from the protein-network and envelops the gelatinized granules and therefore increases the stickiness (Li et al., 2016). It is possible that the maize landraces with higher starch content will have higher hardness and lower stickiness, as these two parameters were found to be negatively correlated ( $R^2=0.88$ ,  $P<0.05$ ). However, in this study no significant differences were found in the textural properties of the polenta made with the maize flours from the different landraces.

### 3.2. Fatty acid composition in maize

Data about samples composition in terms of main fatty acids (FAs) are shown in Figure 1 while the exact FAs composition can be found in Table S2 (supplementary materials). The polyunsaturated fatty acids (PUFA) in maize flours were dominated by linoleic acid (C18:2n6) and oleic acid (C18:1n9) while palmitic acid (C16:0) and stearic acid (C18:0) had the highest content, as previously found in cold-pressed corn oil (Carrillo et al., 2017). *Spin* landrace samples showed significantly higher values for linoleic, vaccenic acid and  $\alpha$ -linolenic acids compared to the other landraces ( $P<0.05$ ). *Marano* landrace samples showed, on average, the highest levels of palmitic, oleic and arachidic acids but the lowest levels of linoleic acid. On average, *Dorotea* landrace samples had the highest concentration of stearic acid.

#### **Figure 1 here**

Differences in FAs profile of the maize flours may be negligible in terms of nutritional characteristics but can have a marked effect on the sensory properties. Each FAs profile can generate different VOCs, mainly through thermal oxidation during the cooking process, impairing the final product's sensory characteristics. For example, oleic acid oxidation was found to produce high amounts of octanal and nonanal, while linoleic acid autoxidative degradation resulted in high quantities of hexanal, decatrienal, methyl octanoate, 2,4-heptadienal, 3-hexenal, 2-pentenal, propanal and ethane. In the following paragraphs, the VOCs profile of both raw flours and polenta from the different samples is discussed, by considering FAs profile differences.

### 3.3. Volatiles analysis using SPME GC-MS

The GC-MS analysis on maize flours detected 42 compounds (Table 2). Based on VOCs relative concentrations, hydrocarbons (11 compounds) were the most abundant compound followed by aromatics (6 compounds), acids (6 compounds), alcohols (5 compounds), aldehydes (4 compounds), ketones (2 compounds), terpenes (4 compounds), esters (2 compounds), one furan and one sulphur-containing-compounds. More specifically, focusing on the VOCs identified by the GC-MS analysis, univariate data analysis revealed 17 compounds with significant differences in relative abundance ( $P < 0.01$ ) among the maize landraces (Table 2). In terms of composition, ethanol was the dominant compound for most of the landraces, including *Nostrano* (59%), *Spin* (36%), *Marano* (33%) and the pre-cooked (28%) samples. On average, *Dorotea* samples had acetone as the most dominant compound (21%), followed by ethanol (12%). *Marano* samples had significantly higher relative abundance levels of some acids (heptanoic, octanoic and nonanoic acids) and alcohols (1-pentanol, 1-hexanol and 1-decanol). Some of these compounds may originate from the oleic acid oxidation which had the highest levels in *Marano* landrace (Figure 1). As well, some of the detected hydrocarbons like tetradecane and toluene, aldehydes like hexanal, nonanal and benzaldehyde, and ethyl hexanol could be the result of oxidative and/or thermal degradation of unsaturated fatty acids, mostly from oleic and linoleic acid (Diez-Simon et al., 2019). Compounds like benzaldehyde and 2-pentylfuran may result from Strecker degradation while 2-pentylfuran has been indicated as a typical oxidation compound from linoleic acid (Smith & Peterson, 2020). The analysis highlighted the presence of some contaminants that could be caused by fungi. Compounds such as naphthalene could result from *Fusarium spp.* metabolism which is a well-known maize pathogen (Oldenburg et al., 2017), while *o*-xylene and 3-butenic acid were detected in cracked corn infected by isolates of *Aspergillus flavus*, a phytopathogenic fungus present on pre-harvest corn (De Lucca et al., 2012). All these compounds were present only at trace levels.

#### **Table 2 Here**

The SPME GC-MS analysis of polenta found 23 compounds in the samples (Table 2). The VOCs consisted of hydrocarbons (6 compounds), alcohols (3 compounds), acids (5 compounds), aldehydes (4 compounds), one ketone, one terpene, one furan and one sulphur-containing-compounds. In terms of composition, the cooking process generated 5 new compounds while 25 compounds were lost during the cooking process from maize flour to polenta including some primary alcohols like ethanol, 1-hexanol and 1-decanol. The

cooking process effect in reducing some aroma compounds was already observed during the cooking of sweet corn (Zhang et al., 2023) due to the evaporation of some compounds. The cooking process induced the formation or increased the concentration of some typical Maillard reaction compounds including nonanal, benzaldehyde (Cepeda-Vázquez et al., 2018) and acetoin (Diez-Simon et al., 2019). Some compounds derived from lipid oxidation reactions like 2-pentylfuran (Smith & Peterson, 2020) and hexanal also increased their concentrations after cooking. Hexanal was the most abundant compound for the *Spin* landrace samples and showed a significant ( $P < 0.01$ ) higher concentration than the polenta samples from the other landraces. These high levels may be correlated to the high levels of linoleic acid in the *Spin* flour (Figure 1), as hexanal originates from linoleic acid oxidation. Finally, the polenta making process resulted also in an increase of dimethyl sulfide (DMS) and some hydrocarbons like dodecane (Ekpa et al., 2020).

In terms of aroma differences among the landraces, only three compounds showed significant differences ( $P < 0.01$ ) among the polenta samples: acetoin, hexanal, nonanal. Across all these compounds, the *Dorotea* landrace samples exhibited lower concentrations. The aroma differences between the landraces were further explored through PTR-ToF-MS analysis.

#### 3.4. Volatiles analysis using PTR-ToF-MS

The data extracted from the PTR-ToF-MS analysis resulted in 267 mass peaks for the maize flours and 273 mass peaks for polenta samples. The mass peaks selection procedure resulted in 171 and 134 mass peaks for the flours and the polenta samples respectively. On these mass peaks, PCA was conducted. Preliminary analysis of both raw maize flours and polenta detected the FS sample as an outlier due to the highest moisture content and  $a_w$ , thus FS was removed from further statistical analysis.

#### Figure 2 here

In Figure 2 are presented the PCA loadings plots for the flours (Figure 2A) and the polenta (Figure 2B) samples respectively. Both the PCAs revealed a partial separation of the landraces based on their volatilome. The PCA score plot in Figure 2A explains about 46% of the total variance in maize flours. The variance in the first principal component (explained variance: 26.6%) mainly distinguishes *Nostrano* samples (except for samples FM, BC, GbM) from other flour samples. On the second principal component (explained variance: 19.8%) it is possible to observe a separation of the pre-cooked sample and *Spin* samples from *Marano* and

some of *Nostrano* samples. *Marano* and *Dorotea* samples showed lower volatiles emission than the other samples (loadings, Figure S1).

As observed in SPME GC-MS data, the cooking process affected samples volatilome (Figure 2B, total explained variance 48.1%). *Marano* landrace samples and the RC sample from *Dorotea* landrace were separated from other samples on the first principal component (explained variance: 33.7%). As for the flours, the loading plot (Figure S2) confirms that this separation is related to a lower concentration of most of the detected VOCs. The PC2 (explained variance: 15.8%) divided some of the *Nostrano* samples and sample LM (*Dorotea*) from the rest of the samples. Figure 2B (score plot) indicates that the cooking process induced some differences inside the *Nostrano* samples since two clusters are visible. Still, the loading plot (Figure S2) indicates that *Nostrano* samples had higher concentrations for most of the selected mass peaks. *Spin* samples were still clustered together as in the flours. Finally, it is interesting to notice that when cooked, the VLC sample (pre-cooked) lost most of its aroma compounds (Figure S2).

The selected mass peaks were further investigated using univariate data analysis to find VOCs markers' of each landrace. Mass peaks which resulted to be significantly different ( $P < 0.01$ ) for at least one of the landrace samples and with a concentration of at least 0.3 ppbV are reported in Table 3. 52 compounds of maize flour and 45 compounds of polenta were tentatively identified based on their sum formula, fragmentation pattern (correlation analysis) and literature data.

#### **Table 3 here**

The post hoc test analysis in Table 3 highlights differences in the volatilome of the maize flour landraces. *Nostrano* landrace flours were characterized by significant higher levels ( $P < 0.01$ ) of  $m/z$  45.03, 47.054, 63.028, 73.065 and 87.082 tentatively identified as acetaldehyde, ethanol, DMS and the ketone/aldehyde mixtures 2-butanone/butanal and 2/3-methylbutanal/2/3-pentanone (Pico et al., 2018). The higher levels observed in the *Nostrano* flours for the ketones may be due to the significantly higher fat content ( $P < 0.05$ ) and relatively high linoleic acid content (Figure 1). Regarding the aldehydes, which are usually produced by the deamination of amino acids such as isoleucine and leucine (Meng et al., 2021), this was not expected since the *Nostrano* landrace samples did not showed the highest protein content (Table 3).

More specific protein content analysis should be performed to draw definitive conclusions. Additionally, different post-harvest conditions such as higher temperatures during the drying procedure,

could have had an effect (Table S1). *Spin* landrace samples, together with the pre-cooked samples, were characterized on average by significantly higher ( $P<0.01$ ) concentrations of  $m/z$  61.029 and 103.076 tentatively identified as acetic acid and as a mixture of pentanoic acid/ 2-methylbutanoic acid and propyl acetate. These compounds can be formed from lipid oxidation (Annan et al., 2003; Goicoechea & Guillén, 2014; Pico et al., 2018), most probably from linoleic acid given the high levels detected in the *Spin* landrace from our analysis (Figure 1). 2-methylbutanoic acid may also derive from the degradation of isoleucine through the Ehrlich pathway by microorganisms present in the flours (Karolkowski et al., 2021). *Spin* landrace samples showed the highest release ( $P<0.01$ ) also of  $m/z$  135.117 identified as a terpene mixture (Ekpa et al., 2020). *Doreotea* landrace samples showed significantly higher concentrations ( $P<0.01$ ) for  $m/z$  60.053, 77.061, 81.071, 85.102 and 99.117 tentatively identified as acetone isotopologue, a compounds fragment, a fragment of monoterpenes, cyclohexane and 1-heptene/cycloheptane. The last three compounds were also detected in the GC-MS analysis. The pre-cooked samples showed higher concentrations for different mass peaks including  $m/z$  83.085, 101.097 and 127.111 tentatively identified as a fragment of hexanal, hexanal and a mixture of 1-octen-3-ol/2-octenal which have been reported in previous studies on maize volatilome (Alves et al., 2020; Ekpa et al., 2020). 2-octenal was suggested among the main odor- and aroma-related volatile in Portuguese maize open-pollinated varieties and is a by-product of linoleic acid oxidation (Alves et al., 2017). Hexanal is also a well-known marker of lipid oxidation. The higher levels observed for the pre-cooked flour by both GC and PTR analysis may be attributed to the industrial processing, during which is exposed to high temperatures.

$m/z$  43.02, 45.03, 47.051, 51.044, 60.053, 61.029, 63.028 and 63.045 tentatively identified as a non-specific fragment, acetaldehyde, ethanol, methanol (cluster with water), acetic acid, acetone, DMS and ethanediol were the most abundant mass peaks in the flours. These mass peaks, (excluding  $m/z$  61.029 and 63.045) showed the highest concentration also in the polenta samples and were also among the most abundant in a similar study on maize flour and in porridge from Nigeria (Ekpa et al., 2020). Most of these VOCs have been identified in GC-MS analysis on maize (Flora & Wiley, 1974; Goicoechea & Guillén, 2014). Moreover, acetaldehyde, ethanol and acetone have been associated with the fruity and sulphurous aroma of sweet corn (Flora & Wiley, 1974).

The cooking process decreased the concentration of most of the detected mass peaks, as observed in the GC-MS data. However, the polenta-making process also generates some aroma compounds and increased the

levels of some others. For example, the cooking process increased the concentration of  $m/z$  69.035, 69.047 and 80.050, 83.052, 85.031, 97.031, 97.065, 107.051, 139.115 which have been all tentatively identified as compounds originating from the Maillard reaction including aldehydes, furans, pyridines and pyrroles. Increased levels of three sulphur compounds ( $m/z$  49.012, 63.028 and 126.968) tentatively identified as methanethiol, DMS and dimethyl trisulfide were observed in polenta over flour samples. The same trend for DMS was observed in the SPME GC-MS analysis. This compound is known as one of the compound responsible for the “corny” aroma in processed corn (Flora & Wiley, 1974). DMS is mainly formed by two pathways: the thermal degradation of S-methyl-L-cysteine with pectin as the methyl donor (Breedon & Juvik, 1992) and by methanethiol oxidation. The *Dorotea* and the *Spin* landrace samples showed, on average, significantly higher ( $P<0.01$ ) levels of DMS (Table 3). Previous studies suggested that increasing kernel maturation and different genotypes may have a role in influencing DMS concentrations during cooking (Breedon & Juvik, 1992).

When cooked, the *Nostrano* landrace samples were characterized by high levels of  $m/z$  69.035, 75.064, 80.050, 87.047 and 99.045 tentatively identified as furan, propanoic acid, pyridine, 3-butenic acid/ethyl acetate and furfuryl alcohol which have been reported in previous studies on maize products (Annan et al., 2003; Goicoechea & Guillén, 2014). Pyridines are formed from hexose and amino acids in the final stages of Maillard reaction through Strecker degradation (Diez-Simon et al., 2019). Furan can be formed from different precursor classes upon thermal treatment, including ascorbic acid, Maillard reaction systems, lipids, organic acid and carotenes (Limacher et al., 2008) which are naturally contained in flint maize. Furfuryl alcohol is also a product from Maillard reaction and is known as a food contaminant that results from thermal processing like heating or roasting (Okaru & Lachenmeier, 2017). Considering the relatively high content of carbohydrates in maize flour, it is reasonable to hypothesise that most of the generated furan comes from the glucose moiety during the starch cooking process. The above-cited acids may be formed from the corresponding aldehydes during lipid thermal oxidation (Goicoechea & Guillén, 2014).

*Dorotea* landrace samples were characterized by significantly higher levels of  $m/z$  69.054 tentatively identified as pyrazole. Pyrazole traces may derive from compounds formed during the Maillard reaction (Yaylayan & Haffenden, 2003). On average, *Spin* and *Nostrano* samples had higher levels for  $m/z$  139.112 tentatively identified as 2-pentylfuran, which may be correlated to their higher concentration of linoleic acid (Figure 1). *Dorotea* and *Marano* samples were characterized by lower levels of  $m/z$  121.067 tentatively



identified as phenylacetaldehyde (Annan et al., 2003). Phenylacetaldehyde is a degradation product from phenylalanine and is a precursor for the formation of benzaldehyde, especially in wet condition (Chu & Yaylayan, 2008). Lower levels of phenylacetaldehyde and benzaldehyde may be used as quality marker since both compounds were associated with off-flavour/ food spoilage in other food matrixes (Chu & Yaylayan, 2008).

The VOCs number detected with SPME GC-MS was less than the one detected by PTR-TOF-MS, both in maize flours and polenta. This is due to differences in sensitivity, limit of detection, selectivity and specificity of the two methods. For example, hydrocarbons and halocarbons are not effectively measured by PTR-MS due to their low proton affinity. For these compounds, alternative ionization modes ( $O_2^+$ ) should be used. Despite these differences, several correspondences were found with 17 VOCs detected by both analytical methods including some key aroma compounds like DMS, acetoin, ethyl acetate, butanoic acid, hexanal and nonanal.

The volatilome analysis (Figure 2, Table 2 and 3) highlighted that the polenta-making process induced the formation of Maillard reaction compounds including some aldehydes (nonanal, benzaldehyde, phenylacetaldehyde), pyridine and furans (furfural, furfuryl alcohol), volatile fatty acids originating from lipids thermal oxidation (propanoic acid, pentanoic acid, 2-methylbutanoic acid and propyl acetate) and some sulphur compounds (methanethiol, DMS and dimethyl trisulfide).

In the individual plot derived from the MFA presented in Figure 3, the high variability inherent in small-scale productions is evident. Despite this variability, discernible differences among the flours are apparent, as highlighted by the clustering patterns observed for each landrace.

### Figure 3 here

The *Nostrano* and *Marano* samples are separated along the first dimension (22.2% explained variance), which is predominantly shaped by VOCs data (Figure S3). While the two varieties share related genetic traits, with *Nostrano* originating from *Marano*, the aroma differences could be attributed to factors such as open pollination seeding of both varieties (Barcaccia et al., 2003), as well as other pre and post-harvest factors. The second dimension, explaining 19.1% of the data variance, serves to distinguish *Nostrano* and *Spin* samples. This dimension is primarily influenced by data related to fat and protein content along with PTR-MS data (Figure S3). The MFA and the PTR-ToF-MS results indicated more compounds similarity

between *Dorotea* and *Marano* flours. Figure 3 illustrates that *Dorotea* samples exhibit considerable variability, with the widest spread on both dimensions. This variability is likely attributable to the differences in the post-harvest operations of drying and storage among the samples. Sun drying, employed for varying durations, is a less controlled process and resulted in higher  $a_w$ . Additionally, the four *Dorotea* samples were subjected to different storage conditions (Table S1). The milling procedure (stone vs cylindrical milling) appears to have a limited effect on *Nostrano* flour samples. Upon closer examination of postharvest storage conditions, GC-MS data from individual samples revealed that freshly milled *Dorotea* (LP and LM) and *Marano* (414 and 9) samples exhibited higher levels of acetaldehyde, DMS, linalool and butanoic acid compared to samples that underwent milling and subsequent storage (data not shown). However, it is important to note that the sample set under investigation was not specifically collected to examine the effects of these postharvest factors. Rather, as a preliminary study, our aim was to explore whether any differences among local landraces of flint maize flour from Northern Italy were present and if these differences were retained after the cooking process. A more comprehensive sample set is needed to validate conclusion on drying procedure, milling and storage conditions. Moreover, future studies should also include discriminative sensory test (e.g. triangle tests) by a (semi)trained panel or a consumer test to validate if aroma differences in the various landraces are perceivable. In the same vein, quantitative descriptive analysis by a trained panel or the application of GC-olfactometry could help in better characterizing the impact of single VOC on polenta's flavour.

#### 4. Conclusions

In this study flours and porridges (polenta) from different maize landraces cultivated in Northern Italy were investigated. Despite the inherent variability in smallholder productions, clear effects of the landraces before and after cooking were observed. Variations in macronutrient content (protein, fat, and FA composition) among the landraces were noted; nevertheless, these did not impact the textural properties of the polenta samples. However, it was observed that the FAs composition played a significant role in determining the aroma of the flours. The significantly higher levels of fatty acids in *Nostrano* flours resulted in higher concentrations of aldehydes and ketones such as hexanal, 2-butanone and 2/3-pentanone. Similarly, higher levels of oleic acid in *Marano* samples resulted in significantly higher levels of heptanoic, octanoic and nonanoic acids and 1-pentanol, 1-hexanol and 1-decanol. Cooking the flours into polenta, induced the

formation of some key aroma compounds such as DMS, methanethiol and Maillard compounds such as nonanal, benzaldehyde, acetoin, pyridine, and furans. The cooking process also induced the formation of 2-pentylfuran and hexanal due to thermal lipid oxidation but as well to the losses of numerous VOCs due to evaporation. Even after cooking, distinctive differences in the volatilome profiles of each landrace persisted, providing justification and valorizing the utilization of specific maize landraces. Post-harvest operations (drying, milling, storage and packaging conditions) had an effect not only on VOCs profile but also on moisture content and water activity indicating that these variables.

While following the convenience culture trend, instant polenta consumption is increasing due to its lower preparation time, our data confirm the importance of preserving ancient local maize landraces. Local landraces are not only essential to preserve biodiversity and small-scale farming but also to retain unique nutritional characteristics and aroma traits. Future studies may continue exploring the impact of landraces, post-harvest operation and cooking on porridge, particularly polenta, volatilome. Monitoring the cooking process through PTR-MS on-line measurement could provide a more detailed information on the dynamic of formation or degradation of key VOCs.

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**Table 1** Proximate, physical analysis and fatty acids content of the different varieties of maize flours and textural analysis of polenta The letters indicate significant differences ( $P<0.05$ ) between varieties according to Tukey *post-hoc* test.

	Variety				
	Nostrano	Marano	Dorotea	Spin	Pre-cooked
<b>Moisture content (%)</b>	12.16±1.39 <sup>bc</sup>	13.18±0.59 <sup>ab</sup>	14.15±2.53 <sup>a</sup>	12.41±0.99 <sup>abc</sup>	10.75±0.95 <sup>c</sup>
<b>a<sub>w</sub></b>	0.59±0.08 <sup>a</sup>	0.65±0.02 <sup>a</sup>	0.68±0.09 <sup>a</sup>	0.63±0.05 <sup>a</sup>	0.46±0.00 <sup>b</sup>
<b>Protein content (%)</b>	11.42±0.70 <sup>c</sup>	13.67±0.53 <sup>a</sup>	12.56±0.92 <sup>b</sup>	10.63±0.82 <sup>c</sup>	7.65±0.24 <sup>d</sup>
<b>Fat Content (%)</b>	5.00±0.41 <sup>a</sup>	4.75±0.38 <sup>a</sup>	4.47±0.52 <sup>a</sup>	3.48±0.62 <sup>b</sup>	0.62±0.10 <sup>c</sup>
<b>Hardness (N)</b>	9.43±2.60 <sup>b</sup>	7.98±0.75 <sup>b</sup>	7.30±1.45 <sup>b</sup>	9.68±0.48 <sup>b</sup>	20.03±0.37 <sup>a</sup>
<b>Stickiness (N)</b>	-2.95±0.82 <sup>a</sup>	-2.85±0.29 <sup>a</sup>	-2.57±0.45 <sup>a</sup>	-3.14±0.37 <sup>a</sup>	-5.09±0.64 <sup>b</sup>



**Table 2** Relative abundance (%) of the compounds identified in the headspace SPME GC-MS analysis of maize flour and polenta samples. Only the compounds with a relative abundance above 0.5% for at least one of the sample are reported. For each compound the chemical formula, the molecular weight are indicated. For each landrace the mean and its standard error. Means with different letters (considering maize flour and polenta separately) were found significantly different (ANOVA, Tukey post hoc,  $P < 0.01$ , Bonferroni correction).

Volatile compounds	Formula	MW	Raw maize (% R.A)					Polenta (% R.A)			
			Nostrano	Dorotea	Spin	Marano	Pre-cooked	Nostrano	Dorotea	Spin	Marano
<i>Hydrocarbons</i>											
2-methylbutane <sup>1</sup>	C <sub>5</sub> H <sub>12</sub>	72	1.34±0.40	0.96±0.21	0.70±0.18	4.87±2.48	0.81±0.00	14.02±1.61	7.07±2.49	21.24±7.2	10.53±2.04
3-Methylpentane	C <sub>6</sub> H <sub>14</sub>	86	1.19±0.31	0.98±0.46	0.66±0.12	3.39±0.82	0.81±0.00	21.86±7.61	41.2±26.68	2.38±0.99	24.87±10.42
Octane <sup>1,2</sup>	C <sub>8</sub> H <sub>18</sub>	114	0.60±0.21	1.27±0.4	0.51±0.1	0.97±0.17	0.19±0.00				
3-Ethylhexane	C <sub>8</sub> H <sub>18</sub>	114	0.29±0.19	1.06±0.46	0.20±0.07	0.23±0.14					
Isododecane	C <sub>12</sub> H <sub>26</sub>	170	0.11±0.06	11.86±11.72	0.29±0.1	0.03±0.02	0.20±0.00				
Decane <sup>2</sup>	C <sub>10</sub> H <sub>22</sub>	142	1.13±0.18 <sup>a</sup>	0.91±0.37 <sup>a</sup>	2.00±0.40 <sup>ab</sup>	2.21±0.46 <sup>ab</sup>	3.74±0.00 <sup>b</sup>				
Undecane <sup>1,2</sup>	C <sub>11</sub> H <sub>24</sub>	156	1.35±0.40 <sup>a</sup>	0.74±0.47 <sup>a</sup>	3.25±0.68 <sup>a</sup>	2.4±0.82 <sup>a</sup>	11.12±0.00 <sup>b</sup>				
Dodecane <sup>1,3</sup>	C <sub>12</sub> H <sub>26</sub>	170						3.6±0.49	1.24±0.86	0.82±0.51	3.27±1.15
Tridecane	C <sub>13</sub> H <sub>28</sub>	184						1.2±0.23	0.48±0.83	0±0	0.38±0.27
Tetradecane <sup>1,3</sup>	C <sub>14</sub> H <sub>30</sub>	198	2.28±0.48	2.03±0.67	1.41±0.33	3.89±0.68	4.56±0.00	11.88±1.78	8.3±2.8	8.43±5.3	11.98±3.42
Hexadecane <sup>1,4</sup>	C <sub>16</sub> H <sub>34</sub>	226	0.16±0.03 <sup>a</sup>	0.15±0.04 <sup>a</sup>	0.14±0.03 <sup>a</sup>	0.27±0.03 <sup>ab</sup>	0.50±0.00 <sup>b</sup>	0.62±0.07	0.33±0.13	0.54±0.26	0.67±0.14
Naphthalene <sup>1,4,5</sup>	C <sub>10</sub> H <sub>8</sub>	128	0.13±0.03 <sup>a</sup>	0.21±0.02 <sup>ab</sup>	0.46±0.11 <sup>a</sup>	0.35±0.09 <sup>b</sup>	0.25±0.00 <sup>ab</sup>				
2-bromo-2-methylbutane	C <sub>5</sub> H <sub>11</sub> Br	150	0.42±0.06 <sup>a</sup>	0.37±0.16 <sup>a</sup>	0.35±0.07 <sup>a</sup>	0.9±0.14 <sup>b</sup>	1.69±0.00 <sup>c</sup>				
<i>Aromatics</i>											
Toluene <sup>1,3</sup>	C <sub>7</sub> H <sub>8</sub>	92	1.02±0.26 <sup>b</sup>	5.21±1.94 <sup>ac</sup>	7.7±2.18 <sup>c</sup>	2.25±0.5 <sup>ab</sup>	0.53±0.00 <sup>a</sup>				
Cyclohexane <sup>*1</sup>	C <sub>6</sub> H <sub>12</sub>	84	0.12±0.02	0.52±0.41	0.27±0.09	0.79±0.17	0.47±0.00				
Ethylbenzene <sup>1</sup>	C <sub>8</sub> H <sub>10</sub>	106	0.20±0.11	0.41±0.30	0.30±0.10	0.79±0.25	1.69±0.00				
o-Xylene <sup>11</sup>	C <sub>8</sub> H <sub>10</sub>	106	5.53±3.76	6.51±3.04	9.31±3.43	2.09±0.3	0.90±0.00				
1,3,5-Trimethylbenzene <sup>1,11</sup>	C <sub>9</sub> H <sub>12</sub>	120	0.07±0.02 <sup>a</sup>	0.81±0.51 <sup>ab</sup>	2.98±1.51 <sup>b</sup>	0.27±0.10 <sup>a</sup>	0.09±0.00 <sup>ab</sup>				
1,2,3-Trimethylbenzene <sup>11</sup>	C <sub>9</sub> H <sub>12</sub>	120	0.23±0.05 <sup>a</sup>	1.79±0.97 <sup>a</sup>	7.4±3.53 <sup>b</sup>	1.00±0.45 <sup>a</sup>	0.25±0.00 <sup>ab</sup>				
<i>Alcohols</i>											
Ethanol <sup>*</sup>	C <sub>2</sub> H <sub>6</sub> O	46	59.23±7.75	11.81±5.98	35.78±12.38	33.34±6.41	27.55±0.00				
Furfuryl alcohol <sup>*4,5</sup>	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	98						0.65±0.17	0.06±0.03	0.31±0.11	0.16±0.07
1-Pentanol <sup>1,4,7,8</sup>	C <sub>5</sub> H <sub>12</sub> O	88	0.71±0.06 <sup>a</sup>	1.4±0.76 <sup>a</sup>	0.72±0.14 <sup>a</sup>	2.75±0.33 <sup>b</sup>	2.54±0.00 <sup>ab</sup>	1.02±0.13	1.32±0.45	1.7±0.32	1.06±0.25
1-Hexanol <sup>1,3,5,7,8</sup>	C <sub>6</sub> H <sub>14</sub> O	102	1.79±0.24 <sup>a</sup>	4.96±3.3 <sup>a</sup>	3.1±1.09 <sup>a</sup>	12.45±2.09 <sup>b</sup>	2.33±0.00 <sup>a</sup>				
1-Decanol	C <sub>10</sub> H <sub>22</sub> O	158	0.15±0.02 <sup>a</sup>	0.15±0.04 <sup>a</sup>	0.13±0.03 <sup>a</sup>	0.3±0.04 <sup>b</sup>	0.43±0.00 <sup>b</sup>				
Benzyl Alcohol <sup>*4,5</sup>	C <sub>7</sub> H <sub>8</sub> O	108	0.06±0.01	0.07±0.02	0.2±0.15	0.13±0.01	0.05±0.00	0.95±0.07	0.48±0.17	0.61±0.12	0.87±0.21
<i>Aldehydes</i>											

Hexanal <sup>*1,4,5,6,8,9</sup>	C <sub>6</sub> H <sub>12</sub> O	100	4.04±2.00	0.97±0.37	2.02±1.12	1.12±0.13	13.45±0.00	9.09±1.16 <sup>a</sup>	7.73±3.2 <sup>a</sup>	15.96±3.33 <sup>b</sup>	12.26±3.51 <sup>a</sup>
Nonanal <sup>*1,2,4,7</sup>	C <sub>9</sub> H <sub>18</sub> O	142	0.82±0.28	0.47±0.19	0.77±0.39	0.99±0.17	2.74±0.00	5.39±0.74 <sup>a</sup>	3.69±1.28 <sup>ab</sup>	6.62±1.71 <sup>a</sup>	9.53±1.8 <sup>b</sup>
Benzaldehyde <sup>*</sup>	C <sub>7</sub> H <sub>6</sub> O	106	0.21±0.07 <sup>a</sup>	0.11±0.03 <sup>a</sup>	0.16±0.04 <sup>a</sup>	0.21±0.03 <sup>a</sup>	1.28±0.00 <sup>b</sup>	1.93±0.25	1.15±0.43	1.53±0.26	1.3±0.19
Acetaldehyde <sup>*6,9,10</sup>	C <sub>2</sub> H <sub>4</sub> O	44	1.86±0.36	1.60±0.49	1.20±0.22	1.63±0.43	2.04±0.00	2.79±1.44	1.92±3.33	5.57±2.44	1.9±0.68
<b>Ketones</b>											
Acetone <sup>*6,9,10</sup>	C <sub>3</sub> H <sub>6</sub> O	58	5.13±0.91	20.8±11.57	3.72±0.9	6.72±1.17	7.52±0.00				
Acetoin <sup>*4,5</sup>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88						1.96±0.18 <sup>b</sup>	0.66±0.27 <sup>a</sup>	1.41±0.28 <sup>ab</sup>	0.61±0.13 <sup>ab</sup>
Acetophenone <sup>*5</sup>	C <sub>8</sub> H <sub>8</sub> O	120	0.12±0.02 <sup>a</sup>	0.06±0.01 <sup>a</sup>	0.1±0.03 <sup>a</sup>	0.14±0.02 <sup>a</sup>	0.60±0.00 <sup>b</sup>				
<b>Acids</b>											
Acetic acid <sup>*1,3,4,7</sup>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60	3.11±0.23	2.02±0.59	5.15±1.06	4.39±1.06	3.74±0.00	2.92±0.43	1.83±0.67	2.62±0.48	2.58±0.48
Butanoic acid <sup>*1,3</sup>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88	0.38±0.06	0.36±0.07	0.42±0.21	0.86±0.26	0.72±0.00				
3-Butenoic acid <sup>*1,1</sup>	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	86	0.26±0.02	0.35±0.06	0.36±0.07	0.32±0.04					
Hexanoic acid <sup>1,3,7</sup>	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116						1.66±0.21	1.66±1.25	3.24±2.07	2.45±0.3
Heptanoic acid <sup>1,3</sup>	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	130	0.07±0.01 <sup>a</sup>	0.11±0.03 <sup>ab</sup>	0.08±0.02 <sup>a</sup>	0.18±0.03 <sup>b</sup>	0.08±0.00 <sup>ab</sup>	0.75±0.08	0.4±0.22	0.71±0.34	0.74±0.11
Octanoic Acid <sup>1,3</sup>	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	144	0.12±0.01 <sup>a</sup>	0.16±0.03 <sup>ab</sup>	0.12±0.02 <sup>a</sup>	0.27±0.04 <sup>b</sup>	0.12±0.00 <sup>ab</sup>	1.49±0.17	0.65±0.27	0.95±0.26	1.13±0.15
Nonanoic acid <sup>1,3</sup>	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	158	0.18±0.02 <sup>a</sup>	0.22±0.04 <sup>ab</sup>	0.15±0.03 <sup>a</sup>	0.38±0.06 <sup>b</sup>	0.17±0.00 <sup>ab</sup>	2.31±0.35	0.83±0.3	1.11±0.21	1.36±0.22
<b>Esters</b>											
Ethyl acetate <sup>*1,2,8</sup>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88	1.82±0.91	1.02±0.45	1.29±0.16	0.77±0.1	2.15±0.00				
Hexyl acetate <sup>4</sup>	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	144	0.64±0.33	0.04±0.02	0.29±0.1	0.62±0.15	2.70±0.00				
<b>Terpenes</b>											
γ-Terpinene	C <sub>10</sub> H <sub>16</sub>	136	1.10±0.29	11.26±9.66	2.03±0.38	2.4±0.33	0.59±0.00				
Terpinolene	C <sub>10</sub> H <sub>16</sub>	136	0.57±0.3	1.69±0.86	1.26±0.95	0.5±0.26	0.04±0.00				
Linalool <sup>1,4</sup>	C <sub>10</sub> H <sub>18</sub> O	154	0.18±0.03 <sup>b</sup>	0.93±0.2 <sup>a</sup>	0.35±0.08 <sup>ab</sup>	0.49±0.05 <sup>a</sup>	0.16±0.00 <sup>ab</sup>				
1-Terpinen-4-ol	C <sub>10</sub> H <sub>18</sub> O	154	0.01±0.003	0.01±0.01		0.02±0.02		2.35±0.26	1.68±1.02	2.11±0.49	2.97±0.49
<b>Furans</b>											
2-Pentylfuran <sup>*1,3,5,7</sup>	C <sub>9</sub> H <sub>14</sub> O	138	0.16±0.05	1.53±1.28	1.22±0.53	0.26±0.06	0.12±0.00	5.11±0.62	3.98±1.83	11.49±2.51	4.34±0.63
<b>Sulfur containing compounds</b>											
Dimethyl sulfide <sup>*10</sup>	C <sub>2</sub> H <sub>6</sub> S	62	0.53±0.174	0.76±0.35	0.63±0.23	0.52±0.12	0.13±0.00	3.05±0.42	10.18±4	6.64±1.77	1.01±0.21

<sup>1</sup>Goicoechea and Guillén, 2014, <sup>2</sup>Macku and Shibamoto, 1991, <sup>3</sup>Sayaslan, 2006, <sup>4</sup>Pico et al., 2018, <sup>5</sup>Buttery, Ling and Chan, 1978), <sup>6</sup>Hougen, Quilliam and Curran, 1971, <sup>7</sup>Annan et al., 2003, <sup>8</sup>Onyango et al., 2004, <sup>9</sup>Ory et al., 1978), <sup>10</sup>Flora and Wiley, 1974, <sup>11</sup>De Lucca et al., 2012 \* Compound detected also by PTR-MS analysis.

**Table 3** Selection of tentatively identified mass peaks in the PTR-MS analysis of both maize flours and polenta samples. The mean and standard deviation of each landrace are reported. Means with different letters (considering maize flour and polenta separately) were found significantly different (ANOVA, Tukey post hoc,  $P < 0.01$ , Bonferroni correction).

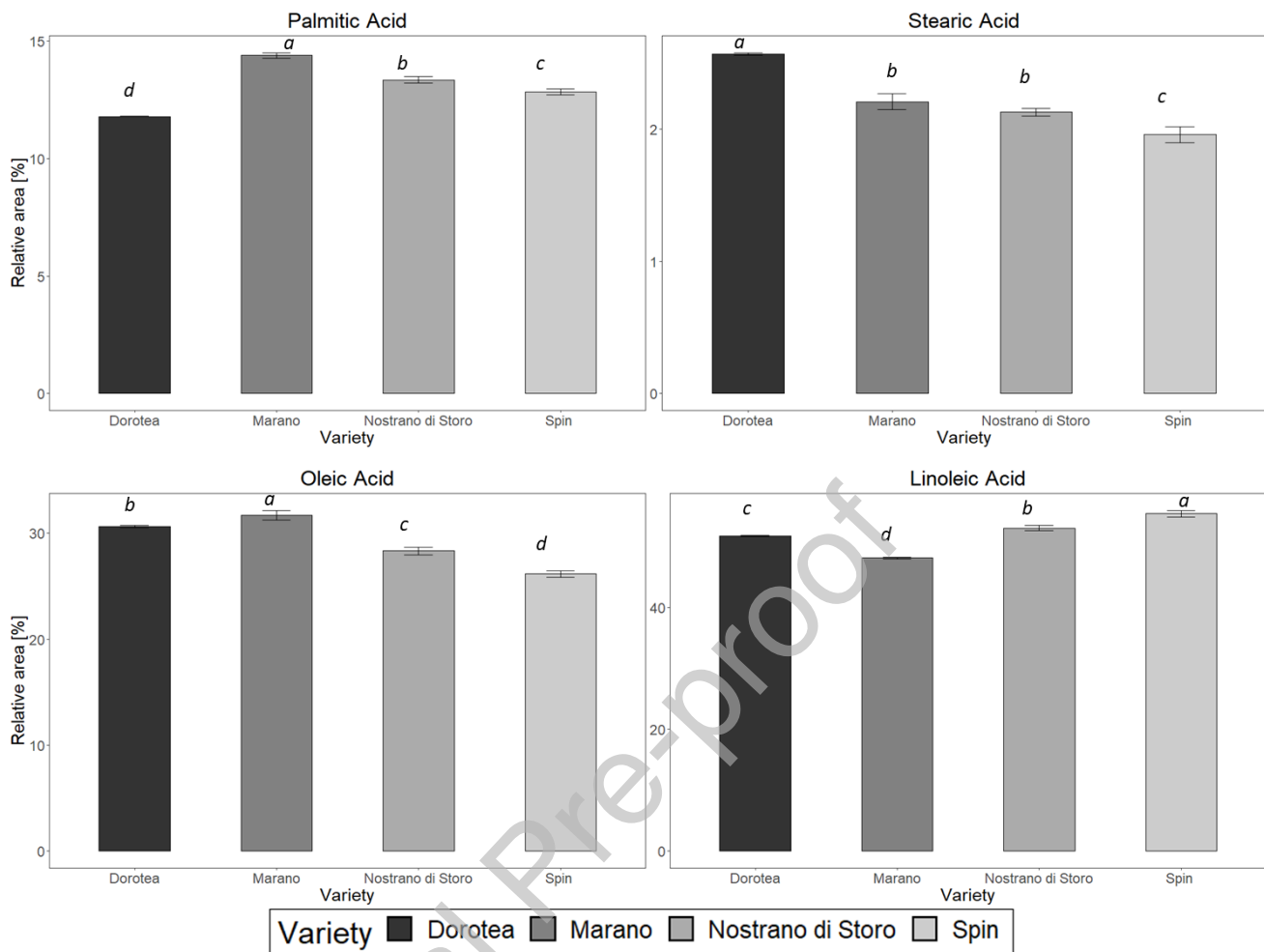
m/z	Formula	Tentative identification	Maize flour					Polenta				
			Dorote a	Maran o	Nostran o	Pre- cooked	Spin	Dorote a	Maran o	Nostra no	Pre- cooked	Spin
41.039	C3H5+	Alkyl fragment alcohol	12.94±5.6 2b	8.08±3.23 a	8.55±4.46 b	24.98±1.0 4b	19.43±11. 87a	2.18±1.12 b	1.71±0.25 a	2.39±0.37 b	2.85±0.23 b	2.11±0.2 3a
42.022	C2H2N2+		5.76±3.21 c	1.47±0.45 a	7.92±4.59c	6.21±0.21 bc	2.21±1.06 ab	1.93±0.34 a	1.71±0.25 a	2.41±0.4b	2.85±0.23 b	2.11±0.2 3a
43.02	C2H3O+	Acetic acid fragment	15.92±2.8 3a	12.8±2.08 a	32.65±13. 75b	17.88±2.1 2a	27.76±8.4 a	13.05±1.8 9a	12.29±2.7 7a	13.76±3.8 9a	10.53±0.5 2a	14.67±2. 09a
43.055	C3H7+	Alkyl fragment	6.59±2.07 a	5.96±2.83 a	4.76±2.66a	12.59±5.6 6ab	17.52±15. 39b					
44.025	C2H3OH+	Fragment	0.99±0.13 a	0.87±0.19 a	2.86±1.84 b	1.05±0.06 a	1.82±0.92 a					
44.983	CO2H+	Carbon dioxide						0.92±0.23 c	0.37±0.06 a	0.57±0.11 b	0.28±0.02 a	0.65±0.1 5bc
45.035 *	C2H4OH+	Acetaldehyde	61.63±4.0 4a	48.3±2.49 a	163.23±15 .76b	34.19±1.2 4a	87.95±11. 68a	49.62±8.8 8a	40.29±6.4 8a	91.17±30 b	38.77±4.1 1a	46.63±5. 38a
46.994	CH2SH+							2.86±0.62 b	1.7±0.24a	2.15±0.45 b	1.23±0.08 a	2.06±0.3 1b
47.051 *	C2H6OH+	Ethanol	59.01±8.0 8a	77.17±11. 02a	453±75.43 b	59.84±5.1 0a	222±45a	2.67±0.67 a	2.87±1.81 a	14.23±10. 41b	7.27±0.43 ab	8.07±4.4 9a
48.01	CH3SH+							1.5±0.12b d	1.23±0.05 a	1.32±0.1c	1.3±0.01a bc	1.46±0.0 8d
49.012	CH4SH+	Methanethiol	1.84±0.65 bc	1.71±0.39 b	2.36±1c	0.29±0.03 a	1.66±0.62 b	18.62±2.8 7a	16.96±3.2 a	21.59±5.0 7b	11.79±0.8 4a	13.67±1. 27a
49.029	CH4O2H+		0.6±0.55b	0.1±0.03a	0.42±0.16 b	0.36±0.02 b	0.15±0.07 a					
51.046	CH4OH*H 3O+	Methanol cluster	47.19±27. 58b	10.77±3.8 8a	63±46.68b	32.93±5.0 4ab	14.97±9.7 7a	70.29±13. 15d	48.57±7.4 4bc	50.37±16. 2c	19.43±2.5 2a	44.28±7. 17b
53.013	C2N2H+		0.17±0.01 a	0.13±0.06 a	0.57±0.44 b	0.26±0.02 ab	0.35±0.2a					
53.042	C4H4H+		0.55±0.12 b	0.27±0.08 a	0.69±0.34 b	1.11±0.06 c	0.53±0.15 b	0.51±0.08 bc	0.37±0.05 a	0.48±0.11 b	0.41±0.03 ab	0.42±0.0 5ac
57.040	C3H4OH+	Unknown fragment	3.56±0.58	3.18±0.78	3.01±0.94a	3.35±0.39	3.91±0.75					

			b	a		a	a					
57.071	C4H9+	alkyl/alcohol fragment	10.2±7.22 b	3.16±0.64 a	5.77±3.68c	4.96±0.26 abc	5.89±1.9a bc	0.8±0.06a b	0.74±0.1a	0.85±0.11 b	0.9±0.06a b	0.84±0.0 4ab
59.051 *	C3H6OH+	Acetone						21.63±6.7 1a	18.1±4.05 a	41.01±13. 41b	28.78±3.3 2ab	20.03±3. 26a
60.053 *	C2[13]CH6 OH+	Acetone isotope	3.64±1.9c	1.11±0.12 a	2.49±1.76 b	1.6±0.07a b	1.43±0.14 a					
61.029 *	C2H4O2H+	Acetic acid	15.71±3.4 a	17.04±2.3 1a	32.44±11. 3b	17.64±2.1 a	33.7±8.27 b					
63.028 *	C2H6SH+	Dimethyl sulfide (DMS)	9.85±2.1b	2.7±1.5a	22.57±6.4 2c	0.85±0.95 a	12.40±3.2 1b	33.67±12. 74c	3.7±0.65a	9.72±2.71 b	2.85±0.12 a	23.94±7. 91c
63.045	C2H6O2H+	Ethenediol	12.33±2.2 2a	7.38±1.19 a	15.09±5.1 5b	6.51±0.7a	10.58±1.3 5a					
63.988	CH3OSH+							0.48±0.22 a	0.85±0.21 ab	0.63±0.22 ab	0.87±0.04 ab	0.85±0.1 3b
65.025	CH4O3H+							2.96±0.71 c	1.36±0.15 a	1.75±0.24 b	1.12±0.04 a	2.52±0.3 5c
67.06	C5H7+	Unknown (Fragment)	0.43±0.16 ab	0.32±0.12 a	0.79±0.48c	0.64±0.05 ac	0.65±0.21 bc					
69.035	C4H4OH+	Furan						1.44±1.68 b	0.87±0.28 a	3.17±0.84 c	0.79±0.09 a	2.28±0.3 1b
69.054	C <sub>4</sub> H <sub>2</sub> NH+	Pyrazole	0.54±0.3c	0.12±0.05 a	0.63±0.53 bc	0.23±0.05 ab	0.15±0.11 a	1.51±0.21 d	1.19±0.18 bc	1.35±0.22 cd	0.42±0.07 a	1.17±0.1 8b
69.070	C5H8H+	Isoprene	1.38±0.15 c	0.95±0.28 a	2.24±0.68 bc	2.63±0.11 bc	1.72±0.47 ab	1.3±0.17b	0.99±0.14 a	1.47±0.18 c	1.82±0.14 d	1.15±0.0 7ab
71.050	C4H6OH+		0.46±0.07 b	0.36±0.04 a	0.6±0.13c	0.76±0.05 d	0.59±0.07 c	0.51±0.05 ab	0.42±0.04 a	0.7±0.11c	0.6±0.03b cd	0.63±0.0 9d
71.087	C5H11+	Unknown (Fragment)	3.17±1.39 b	1.63±0.63 a	2.32±1.51a	2.27±0.14 ab	2.22±0.77 ab	0.33±0.18 a	0.24±0.01 b	0.35±0.06 b	0.68±0.07 c	0.27±0.0 2a
73.065	C4H8OH+	2-butanone/ butanal	5.91±1.3b	3.88±1.03 a	8.16±2.94c	2.68±0.2a	5.94±1.37 ab					
75.044	C3H6O2H+	Propanoic acid	1.12±0.13 b	1.11±0.11 a	1.81±0.48 b	1.72±0.14 ab	1.6±0.16b	1.23±0.25 a	1.25±0.17 a	1.78±0.38 b	1.19±0.02 a	1.34±0.1 6a
77.061	C3H8O2H+	Fragment	2.05±1.01 c	0.56±0.11 a	1.36±1.11 b	0.8±0.07a b	0.81±0.13 ab	1.2±0.31a	1.06±0.2a	2.16±0.65 b	1.58±0.17 ab	1.15±0.1 7a
80.050	C5H4NH+	Pyridine						0.29±0.02 b	0.30±0.04 b	0.32±0.04 c	0.23±0.01 a	0.30±0.0 2b
81.071	C6H8H+	Monoterpene fragment (m/z 137)	8.66±6.24 c	1.57±0.48 a	1.53±1.04a	2.84±0.16 ab	5.12±3.13 b	0.67±0.11 b	0.48±0.08 a	0.66±0.13 b	0.75±0.03 b	0.75±0.1 4b
83.052	C5H6OH+	2-methylfuran						1.29±0.14 ab	1.05±0.18 a	1.27±0.35 b	0.87±0.05 a	1.07±0.1 1a

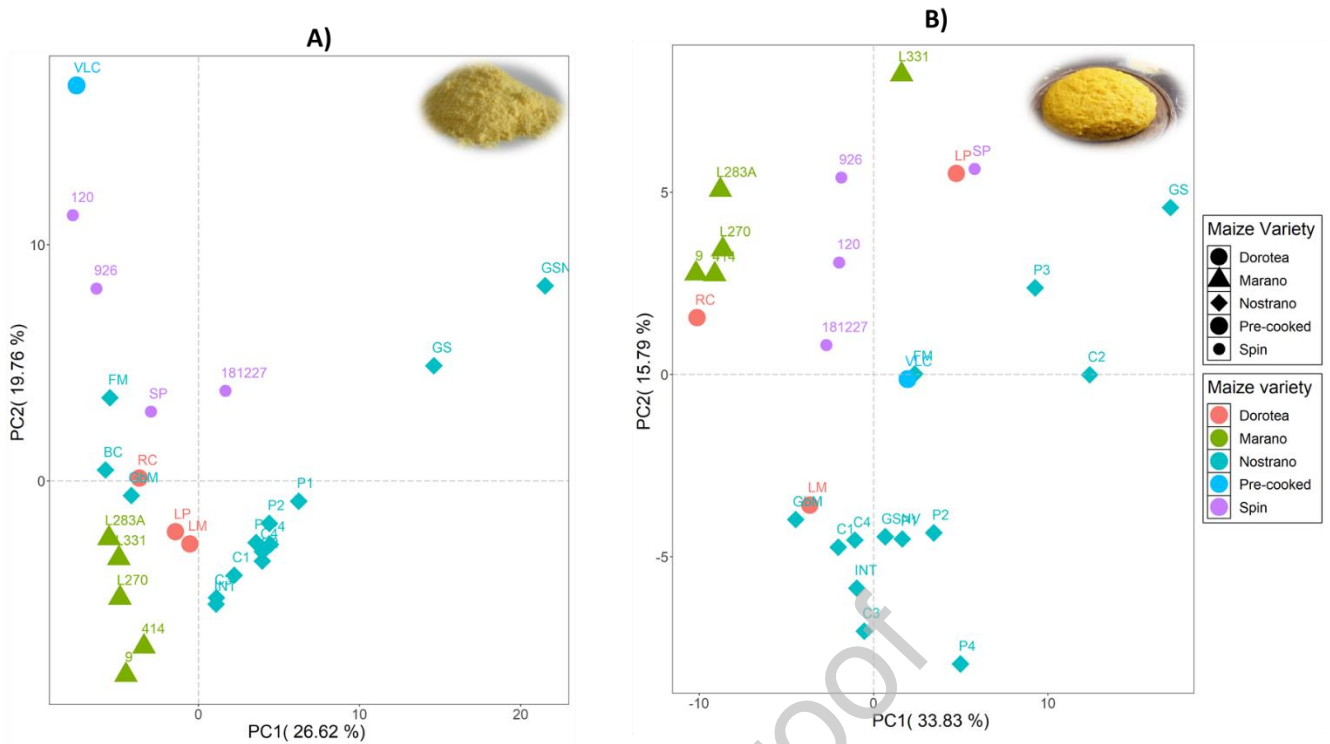
83.085	C6H11+	Hexanal fragment	2.4±0.52a b	1.48±0.77 a	4.3±4.41b	10.29±0.3 8c	3.55±1.72 ab	1.71±0.43 ab	1.33±0.34 a	2.19±0.67 c	2.86±0.21 c	1.89±0.3 8bc
85.031	C4H4O2H+	2(5H)-Furanone						0.35±0.04 a	0.34±0.06 a	0.55±0.13 b	0.27±0.01 a	0.37±0.0 3a
85.067	C5H8OH+	2-Pentenal / 3-Penten-2-one	0.18±0.47 a	0.14±0.02 a	0.23±0.07 b	0.48±0.02 c	0.24±0.04 b	0.48±0.08 a	0.44±0.06 a	0.57±0.12 b	0.5±0.05a b	0.43±0.0 5a
85.102 *	C6H13+	Cyclohexane	4±2.62b	2.12±1.1a	1.42±1.28a	1.15±0.06 a	1.79±0.4a					
87.045 *	C4H6O2H+	3-Butenoic acid / ethyl acetate	1.54±0.38 bc	1.06±0.19 a	1.89±0.69c d	1.13±0.07 ab	2.13±0.44 d	1.85±0.2b c	1.32±0.12 a	2.4±0.33d	1.42±0.1a b	2.08±0.3 1c
87.082	C5H10OH+	2/3-methylbutanal / 2/3-pentanone	0.62±0.11 ab	0.43±0.09 a	1.47±0.54c	0.82±0.03 ab	0.82±0.16 b	0.41±0.09 ab	0.3±0.03a	0.57±0.15 c	0.55±0.04 bc	0.41±0.0 5ab
89.062 *	C4H8O2H+	Acetoin / Butanoic acid / Ethyl acetate						0.43±0.1a	0.4±0.08a	0.59±0.21 b	0.37±0a	0.63±0.1 5b
91.062	C4H10SH+	Butanethiol	1.53±1.11 bc	0.5±0.11a	1.13±0.73 b	0.77±0.03 ab	2.18±1.42 c	1.55±0.24 ab	1.36±0.14 a	1.58±0.23 ab	1.86±0.18 b	1.47±0.3 6ab
93.04	C3H8OSH+		3.46±0.63 bc	3.06±0.51 b	2.35±0.45a	2.08±0.16 a	3.65±0.69 c					
95.019	C2H6O2SH +	Dimethyl sulfone	0.63±0.22 bc	0.6±0.07d	0.53±0.07 b	0.4±0.03a	0.57±0.08 cd					
95.050	C6H6OH+		1.36±0.54 ab	0.89±0.08 a	1.08±0.52a	0.92±0.03 ab	1.35±0.35 b					
95.087	C7H11+	Fragment of monoterpenes	1±0.37c	0.59±0.29 b	0.4±0.13a	0.83±0.05 bc	0.91±0.41 c					
97.031	C5H4O2H+	Furfural						0.68±0.06 a	0.53±0.04 a	1.58±0.42 b	0.63±0.06 a	0.73±0.0 5a
97.065	C6H8OH+	2-ethylfuran						0.37±0.02 b	0.28±0.02 a	0.41±0.06 b	0.54±0.04 c	0.39±0.0 2b
97.103	C7H13	Heptanal fragment	0.39±0.26 b	0.4±0.25b	0.2±0.06a	0.42±0.07 bc	0.55±0.18 c					
99.045 *	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub> H+	Furfuryl alcohol						0.24±0.04 b	0.24±0.02 b	0.29±0.04 c	0.19±0.00 a	0.25±0.0 2b
99.117	C7H15+	1-Heptene / Cycloheptane	0.61±0.65 c	0.08±0.03 ab	0.07±0.05a	0.21±0.01 ab	0.25±0.12 b					
101.06	C5H9O2H+	2,3-Pentanedione	0.52±0.37 ab	0.31±0.05 ab	0.33±0.08 b	0.25±0.02 a	0.34±0.04 b	0.35±0.07 a	0.36±0.06 a	0.56±0.1b	0.34±0.01 a	0.38±0.0 4a
101.09 7*	C6H12OH+	Hexanal	0.68±0.31 ab	0.35±0.15 a	1.24±1.48 b	3.14±0.1c	1.17±0.64 ab	0.53±0.14 ab	0.43±0.11 a	0.69±0.21 c	0.93±0.08 c	0.6±0.12 bc
103.07 7	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> H+	Pentanoic acid/ 2-methylbutanoic acid/ propyl acetate	0.19±0.03 a	0.2±0.02a	0.23±0.02 b	0.35±0.00 c	0.31±0.04 c	0.18±0.03 ab	0.15±0.02 a	0.18±0.03 b	0.15±0.00 a	0.16±0.0 2ab

105.07 2	C8H8H+	Styrene	0.36±0.03 a	0.29±0.06 a	0.58±0.29 b	0.57±0.04 ab	0.95±0.4c						
107.05 1*	C7H6OH+	Benzaldehyde						0.37±0.09 b	0.28±0.03 a	0.56±0.11 c	0.79±0.09 d	0.34±0.0 9b	
108.95 9	CO4SH+		2.03±0.06 b	2.04±0.04 b	1.94±0.09a	2.02±0.07 ab	2.02±0.06 b						
109.06 9*	C7H8OH+	Benzyl alcohol						0.44±0.09 b	0.35±0.04 a	0.44±0.07 b	0.47±0.05 b	0.35±0.0 4a	
109.09 9	C8H13+		0.44±0.1a	0.45±0.16 a	0.55±0.19a	1.22±0.08 c	0.76±0.21 b						
111.04 7	C6H6O2H+	5-methyl furfural	0.69±0.17 bc	0.7±0.16c	0.58±0.16a b	0.48±0.05 a	0.67±0.11 ac						
119.09 4	C9H10+		0.29±0.01 a	0.23±0.04 a	0.33±0.16a	0.59±0.05 b	0.76±0.4b						
121.06 7*	C8H8OH+	Acetophenone						0.39±0.05 a	0.41±0.02 a	0.55±0.06 b	0.54±0.02 b	0.51±0.0 4b	
125.96 1	C2H5S3H+		0.69±0.01 b	0.69±0.01 b	0.66±0.03a	0.68±0.01 ab	0.68±0.02 b						
126.96 8	C2H6SH3+	Dimethyl trisulfide	0.6±0.04a b	0.62±0.06 a	0.54±0.08 b	0.47±0.03 ab	0.58±0.06 ab	1.12±0.03 a	1.14±0.03 ab	1.13±0.03 a	1.15±0.00 ab	1.16±0.0 3b	
127.11 1	C8H14OH+	1-octen-n-ol / 2-octenal	0.18±0.04 ab	0.17±0.05 a	0.23±0.11 b	0.54±0.04 c	0.24±0.05 ab						
135.11 7	C10H15+	Terpene (unknow)	0.34±0.10 a	0.23±0.15 a	0.16±0.07a	0.43±0.04 a	2.05±1.47 b						
139.11 5*	C9H14OH+	2-pentylfuran						0.65±1.27 b	0.44±0.05 a	0.67±0.17 a	1.49±0.14 b	0.64±0.1 4a	
143.14 2*	C9H18OH+	2-Nonanone/Nonanal	0.23±0.06 a	0.19±0.06 a	0.24±0.12a	0.94±0.07 c	0.41±0.25 b	0.63±0.14 ab	0.44±0.05 a	0.66±0.17 b	1.49±0.14 c	0.64±0.1 4b	

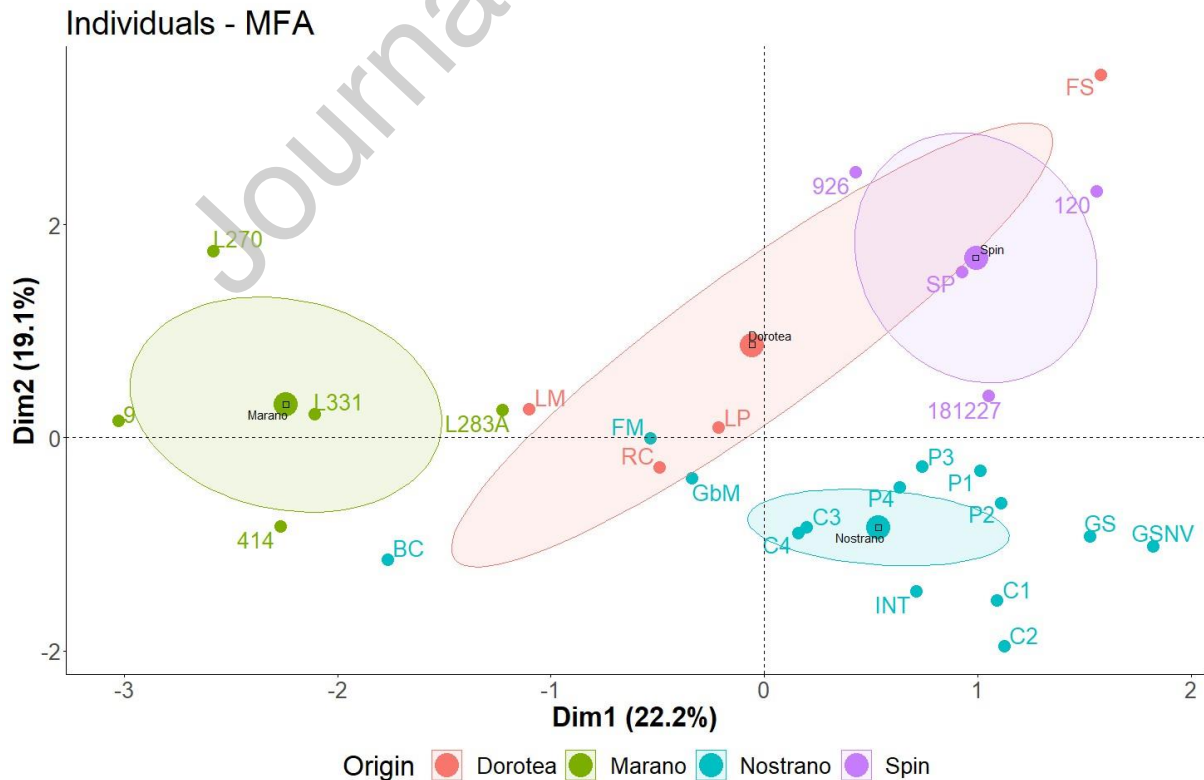
\* Compound detected also by SPME-GC-MS analysis.



**Figure 1:** Fatty acids (FAs) content of the different varieties of maize flours. The letters indicate significant difference of fatty acids between varieties ( $P < 0.05$ ). The results are expressed in % area. In the figures only the four main FAs in terms of content are considered. A complete overview of the maize flours FAs content is given in Table S2.



**Figure 2:** PCA score plots of the selected PTR-MS mass peaks for the maize flour (A) and polenta sample (B). The first two principal components are shown. The different colors and shapes indicate the different maize landraces. For each sample the average of the five replicates are shown.





**Figure 3:** The individual map (samples) from the MFA on the four different datasets (proximates, fat and protein content, GC-MS and a selection of PTR-MS mass-peaks) of the maize flours (VLC sample was not included). The different colors and shapes indicate the different maize landraces together with the confidence ellipses for each group. For each sample the average of the replicates is shown. The variables map and the contribution of each variable to the first two dimensions are presented in the supplementary materials (Figure S3).

### Author contributions

**Pedrotti M.:** Conceptualization, Formal analysis, Investigation, Methodology, Validation, Supervision, Visualization, Writing – original draft, Writing - review & editing **Linarty L:** Formal analysis, Investigation, Visualization, Writing – original draft; **Peng C.:** Formal analysis, Investigation, Writing – original draft **Oliviero T.:** Investigation, Project, administration, Methodology, Supervision, Writing – review & editing **Fogliano V.:** Funding acquisition, Resources, Writing – review & editing **Biasioli F.:** Conceptualization, Resources, Supervision, Writing – review & editing

### Declaration of interests

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.

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

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