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ICP-MS triple quadrupole as analytical technique for the characterization of metal contamination processes in commercial flours for food safety

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ABSTRACT

This study focuses on the analysis of the elemental composition of different commercial flours focusing the attention on toxic trace metals. The goal is to search markers for contaminations, due to the growth of the cereal in polluted soil, and / or due to the working process to which the cereals are subjected to obtain flour. To do that, different kind of flour (wheat, durum wheat, oats, corn, spelt and rice) were bought and analysed using ICP-MS triple quadrupole located in an ISO 6 cleanroom. Arsenic, cadmium, and lead founded could be related to soil contamination. Vanadium is therefore identified as a useful marker of process contamination as it is commonly scarce in the soil, but it is very common in the heavy-duty milling cylinders. Poor maintenance, wear conditions, economic reasons could be some of the causes of process contamination. Finally, a possible marker for type 00 wheat flours was identified, having observed the tendency of caesium to accumulate in the internal parts of the wheat grain.

1. Introduction

Pollution is an alteration of the natural environment due to anthropic impact by contaminating elements. It produces temporary discomfort, disease, or permanent damage to life in a specific area and can place the area in imbalance with existing natural cycles. This alteration can be of different origins, chemical, physical, or biological, and can cause different effects on the environment and human health.

Pollution is also closely related to food risk, i.e., the probability and severity of a harmful effect on health, resulting from the presence of a biological, chemical, or physical agent contained in food or feed, capable of causing a harmful effect on the human and environmental health (EC Regulation No. 178/2002).

Among the pollutants of a chemical nature there are heavy metals and toxic trace elements (TTEs), some of which are necessary for the proper functioning of the organism (Skalnaya and Skalny, 2018). In fact, with a maximum intake limit, they play a beneficial role for the human body, but if taken in large quantities they could turn into a harmful compound.

Among these, some are defined as toxic, as they can cause, at certain doses or concentrations, disturbances, or damage to living organisms to which they have been administered or with which they have come into contact (Rai et al., 2019).

Humans can be exposed to TTEs mainly through the environment or the food, and since the most significant source of exposure is food (Istituto Superiore di Sanità, 2019), limits of TTEs have been introduced by the EC regulation No. 1881/2006 replaced by the EC regulation No. 915 (2023).

The present work is focused on the research of the metal contaminants, such as As, Cd and Pb present in flours that are controlled by the European Community regulation, but also on different much less investigated elements like V, Co, Cr and Ni trying to identify possible markers for the contaminations deriving from the production process. In this regard, the quantification of V content is an extremely useful indicator for potential industrial process contamination as it is commonly not found in the soil, but it is very common in the industrial alloys used in milling cylinders.

Flour samples were analysed with a triple quadrupole mass spectrometer (ICP-MS QQQ) in ISO 6 cleanroom to reduce the presence of external contamination.

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In particular, the elements arsenic, cadmium, and lead were analysed as markers of soil contamination and because they are dangerous for human health.

Arsenic (As) is a metal present in all the environmental matrices, emitted by natural activities such as volcanic eruptions or soil erosion by water, or freed from anthropogenic products such as insecticides or herbicides. The effects of an intoxication of this metal are cardiovascular diseases, developmental anomalies, diabetes, and an increased risk of developing carcinomas (Farkhondeh et al., 2018).

Cadmium (Cd) is carcinogenic and suspected mutagen for the European Chemical Agency. Exposure to high levels of cadmium leads to imbalances in the human body of the levels of other elements such as Zn, Mg, and Cu and can cause problems in the human reproductive system, neurological disorders, and kidney failure (Zhang and Reynolds, 2019).

High lead (Pb) poisoning can inhibit the synthesis of haemoglobin (leading to anaemia) and are responsible for damage to the nervous system (Singh et al., 2018).

Different types of flours were analysed, as flour is a bio-accumulator of these metals, especially cadmium and lead, and because flour is the basis of bread, pasta, sweets, and many other foods present in the diet of every man and animal.

Flour is the product of the grinding of dried vegetable products (fruit or seeds). In addition to diversifying for ground cereal, flours can be classified according to refining, that is, according to the amount of the external part of the grain removed. For example, soft wheat flour is classified in 00 (highly refined), 0, 1, 2 and finally wholewheat flour which is obtained by grinding the grain without refining or eliminating any part of the seeds content (the bran).

For cereal derivatives, the sources of contamination can be of two types: contamination due to plant growth (the contaminant was present in the soil); contamination due to subsequent processing due to a release of metals from the milling equipment. This kind of contamination can occur due to normal wear or due to tribocorrosion as demonstrated by Addai et al. (2024) for Cr and Ni, the same kind of tribological contamination can be identified also in manual or rudimental metal mills used in developing countries (Mugume et al., 2023).

It may happen that the soil where the cereal grows is contaminated. However, there are toxic and harmful metals of which some cereals, especially wheat, tend to absorb and bioaccumulate. Pollution of these metals in the soil can be due to the administration of sludge, compost or fertilizers containing lead, industrial activities, residues from the second world war, etc. However, considering that many of these pollutants are not easily removable from the soils, to protect human health it is necessary to continuously monitor, as well as the soils themselves, also the cultivated cereal and the final flours to be sure to put non-toxic or harmful food products on the market. Generally, these metal contaminants are often present in flours, especially both wheat and durum wheat, but it is necessary to define their concentrations which must obviously remain below the legal limits (EC regulation No. 915, 2023).

Regarding the contamination due to process, there are two main types of grain grinding: stone and cylinder. Stone grinding is the oldest and consists of two millstones with a variable external diameter in the order of 60–120 cm: the lower millstone is stationary while the upper millstone rotates, and therefore the grain size of the product is adjusted by acting on the rotation axis (Cai et al., 2023). An important aspect of grinding is the type of material used to make millstones, generally consisting of gritstone, a siliceous sedimentary rock. A disadvantage of this methodology is the overheating of the flour produced due to the high rotation speeds of the upper grinder, which leads to a degradation of the starch contained in the endosperm. Furthermore, the flour yield obtained with stone mill is lower than by cylinder mill, preventing the product from being optimally refined. For this reason, stone grinding is mainly suitable for the production of whole wheat flour.

Cylindrical grinding is a technique introduced in the nineteenth century and is aimed at obtaining a product with a higher yield. It is performed with a pair of cylinders rotating in the same direction that do not touch each other (Katyal et al., 2022). The grain of cereal passes through these cylinders and is crushed to obtain a more refined product, since it is possible to repeat the milling operation several times without penalizing the quality of the mill, keeping the product temperatures low and thus limiting deterioration. Metals such as nickel, chromium and vanadium are present in the alloys of the milling of cylinders, and it cannot be excluded that, with normal wear or due to tribocorrosion they may contaminate the processed flours. The contamination is expected to be higher in the much more refined flours as we also found in the samples of the present study.

Before being ground, the grain is cleaned to eliminate dirt (earth, residues, small stones, metal elements). The cereal is also wet to soften the endosperm. To resist the corrosive action of water, coupled with the friction generated by the process, the cylinders are made of stainless steel, or hard cast iron, with a high chromium content that superficially protects the underlying metal or alloy for greater resistance to oxidation and corrosion. To increase corrosion resistance, it is also possible to add other alloying elements in addition to chromium, including nickel, and creating the Ni-Cr alloys, such as AISI 304 steel (18–20 % Cr; 8–10 % Ni). Also in this case, therefore, the machinery used could release metals if damaged or worn (Cubadda et al., 2005; Addai et al., 2024).

An excess content of chromium in flour can be harmful to human health, as chromium has been classified by the IARC as a human carcinogen (class I – IARC website), as it can create mutations in DNA, it can attack the respiratory system if inhaled in large quantities and create permanent damage to the eyes as well as to the skin and mucous membranes.

The risk assessment of contaminants in the food chain is based on the monitoring and study of environmental contaminants which is currently one of the priorities for the international scientific community to be able to predict health emergencies, including those relating to Food Safety. Continuously monitoring the possible presence of harmful toxic pollutants, especially in flours, allows us to safeguard human beings in most of the diet, as flour is the main ingredient of many foods, especially in children's nutrition.

This scientific work is based on the use of a triple quadrupole ICP-MS spectrometer in an ISO 6 cleanroom which allows to reduce possible external pollutants and to analyse even small quantities of pollutants with greater precision. The focus on arsenic, cadmium and lead allows to identify a possible natural pollution, for example due to the soil, while the detailed analysis of chromium and nickel, but also of vanadium, allows to hypothesize a pollution from flour production process due to tribocorrosion.

2. Materials and methods

In this section the samples used in the experiment and the methodology for preparing the samples themselves will be described.

2.1. Sample collection

Different types of commercial flours have been bought in supermarkets in Bologna (Emilia Romagna region, Italy) for a total of 108 samples (name and place of origin of the samples are expressed in Table S1 in Supplementary Material). All samples were made of Italian flours:

- 60 wheat flours (*Triticum aestivum*)
  - 21 samples related to 00 flour type.
  - 20 samples related to 0 flour type.
  - 7 samples related to 1 flour type.
  - 3 samples related to 2 flour type.
  - 9 samples related to wholewheat.

- 16 durum wheat flours (*Triticum durum*)
- 6 oats flours (*Avena sativa*)

- 15 corn flours (*Zea mays)*
- 6 spelt flours *(Triticum spelta)*
- 6 rice flours (*Oryza sativa*)

2.2. Laboratory facilities

For the characterization of toxic trace metals in commercial flours, a specific ICP-MS Facility was used. The high-level laboratory facility for trace element/isotopic analysis was located in ENEA C.R. Brasimone (Emilia Romagna region, Italy), which is composed by a Clean Laboratory for sample treatment and a Clean Room ISO 14644–1 with controlled parameters such as pressure, temperature, and humidity, satisfying all standard request for food trace analysis with a maximum concentration limits of 1×10^6 (particles/m^3) for particles ≥ 0.1 μm for ISO Class 6. (Telloli et al., 2023). The operation conditions of the Clean Room are controlled by a Programmable Logic Controller (PLC) located in the technical compartment that guarantee the maintenance of the parameter: air flow 9400 m^3/h; humidity ≤ 50 % and temperature between 20.8 and 21.5 °C.

A triple quadrupole inductively coupled plasma mass spectrometer (ICP-MS-QQQ) 8800 model (Agilent Technologies, Santa Clara, CA, USA) was the analytical technique used in this experiment. The instrument is located in the clean room to guarantee the control quality which reduce the limit of detection of all the elements, reducing the presence of pollutants.

The Clean Laboratory was specifically designed for sample handling and preparation. Prior to ICP-MS-QQQ analysis, samples undergo microwave digestion to mineralize them. The Clean Laboratory is equipped with a system of absolute HEPA H14 filters, which effectively eliminates contaminants from the external environment. This ensures a suitable working space for trace analysis, in compliance with EN 1822:2009 standards. All sample preparation procedures were conducted within this controlled environment.

2.3. Chemicals

All the flour samples were prepared before the ICP-MS-QQQ analysis to obtain a transparency solution, using analytical-reagent grade: TraceSELECT® grade 69 % HNO_3 and ultra-pure grade 30 % H_2O_2 were acquired from Sigma-Aldrich (St. Louis, MO, USA) and Carlo Erba Reagents (Milan, Italy), respectively.

Milli-Q® Advantage A10 water purification system (Millipore, Bedford, MA, USA) produced high purity deionized water (resistivity 18.2 MΩ cm-1).

For the analyses of the contaminants, a multi-element standard stock solution (IV-ICP-MS71A - 10 mg L-1 each in 3 % HNO3) supplied by Inorganic Ventures (Christiansburg, USA) was used for calibration curves. The multi-element standards include 43 elements, but we focus the attention only on As, Pb, Cd, Ni, Cr, Co, V, Cs, Mn, Fe, Cu, and Zn.

Standards and samples were prepared daily in an acidic aqueous solution used as carrier solution during the ICP-MS-QQQ analysis. The acidified aqueous solution used for the carrier solution during the ICP-MS-QQQ analysis, and the blanks were prepared by adding 40 mL of HNO_3 (69 %) to 20 mL of HCl (37 %) and the solution was brought to volume (2 l) using ultrapure water (specific resistivity 18.2 mΩ cm).

All the solutions, prepared in the Clean Laboratory in order to minimize any chance of sample contamination and consequent analytical artefacts, were stored in pre-cleaned and conditioned polypropylene containers.

2.4. Sample treatment

A Speedwave Four (Berghof, Germany) microwave digestion system was used for samples mineralization. The system is equipped with temperature and pressure parameters control.

Each flour samples were weighted 400 mg into TFM™-PTFE vessels, adding 13.8 mL of ultrapure H_2O, 2.8 mL of HNO_3 (69 %) (Fluka, traceSELECT®) and 3.4 mL of H_2O_2 (30 %) (Carlo Erba Reagents, Milan, Italy), as suggested by Correia et al. (2017). In addition, as confirmed after the experiment published in Telloli et al. (2023), hydrogen peroxide is essential for the success of the digestion of the flour sample in solution.

The digestion cycles were programmed according to the microwave heating program:

- Constant pressure at 30 bar;
- step 1 with a linear increase of temperature from ambient to 190 °C in 5 min and stay in the same condition for 10 min (pressure 30 bar);
- step 2 with a linear increase of temperature from 190 °C to 200 °C in 5 min and stay in the same condition for 5 min (pressure 30 bar).

The total duration of a digestion cycle is 25 min.

After the digestion, the acid mixture was left to cool to room temperature (about 20 min). After checking the clearly of the resulting solution, it was quantitatively transferred into plastic vials (Falcon® 50 mL Polypropylene Conical Tubes) and made up to a final volume of 10 mL with H_2O.

2.5. Multivariate analysis

Software XLSTAT by Addinsoft was used to perform statistical analyses.

In food chemistry studies, Principal Component Analysis (PCA) is widely used to minimize the dimensionality of data resulting from ICP-MS-QQQ analysis allowing to investigate the differences between the samples and to the detection of environment-related contamination.

3. Results

3.1. Method validation

The Limit of Detection (LOD) and the Limit of Quantification (LOQ) for Instrument and Process for the contaminants analysed and described in this research work is reported in Table S2 in Supplementary Materials, compared with the Agilent Technologies method detection limits (Sakai, 2015).

The data reliability check was completed not only with the calibration curves but also with the quality control (QC), which is the analysis of solutions at a known concentration every five samples analysed (Figure S1 in Supplementary Materials).

To evaluate the instrumental efficiency, the data obtained in ICP-MS-QQQ of wheat flours (types 00, 0, 1, 2 and wholewheat) were compared with the data published by (Telloli et al., 2024), in which the same samples were analysed. The results obtained are comparable to each other, confirming the good performance of the instrument (Table S3).

3.2. Flour samples data analysis

Firstly, chemometric analysis was used to discriminate samples from different type of flours characterized by common features, and to gain a first understanding of the distribution of toxic trace metals in flours grouped into clusters.

For the PCA model, only the first two principal components (PCs) were selected explaining the 47.36 % of the variance (as shown in Table S4 and in the Scree plot in Fig. S3, both in Supplementary Materials).

Fig. 1 shows the biplot scores in which the samples are separated into different clusters, representing the different type of flours.

Rice and spelt flour samples (coloured in light blue and red respectively) are clustered in the lower part of the graph in Fig. 1, represented by toxic metals as Pb, Cs and Tl.

On the opposite, on the top of the graph, there is the cluster of the

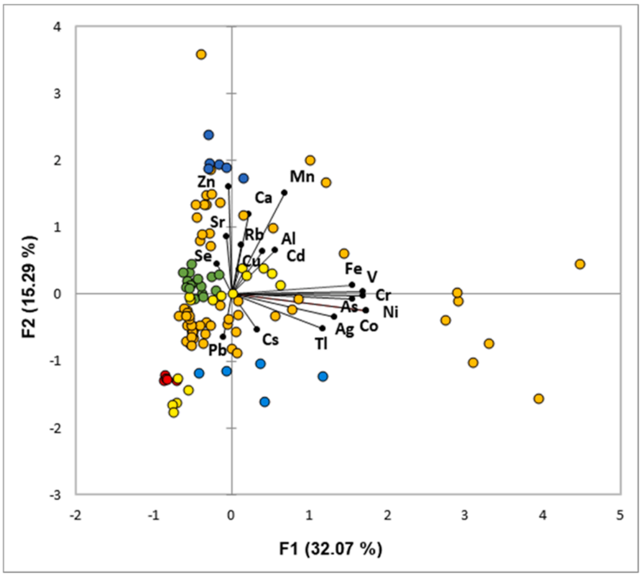

Fig. 1. Biplot obtained from PCA scores using XLSTAT software by Addinsoft. In black the active variables and with colored circles the samples: wheat flour in dark yellow, durum wheat in green, oats in blue, corn in yellow, spelt in red and rice in light blue.

oats flour samples (coloured in blue), represented by Zn and Sr toxic trace elements.

In the central part of the graph in Fig. 1 on the left, durum wheat flour samples (coloured in green) appear to be enriched in Se.

Wheat and corn flour samples are not clearly distinguishable. This occurs because in this samples we consider all the different kind of wheat samples (types 00, 0, 1, 2 and whole wheat) and the different grade of refining probably generate flours with different values of the elements analysed. However, there could be more evident differences of corn flour samples, which are represented by two cluster, one that appear to be enriched in Pb and the other less.

3.3. Aluminium, arsenic, cadmium and lead average concentration

Food safety is ensured when the concentrations of toxic trace metals in commercial flours are kept under control. The main indicators of metal pollutant in flours are related to the concentration of aluminium, arsenic, cadmium and lead.

Fig. 2 shows the average concentration, expressed in μg/kg, of aluminium (coloured in green), arsenic (coloured in orange), cadmium

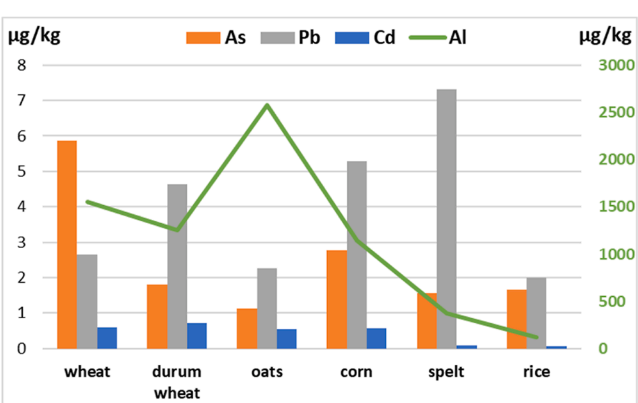

Fig. 2. Average concentrations of contaminants detected in the flours of the various cereals analysed and expressed in μg/kg: Al (green line), As (orange bar), Cd (blue bar) and Pb (grey bar).

(coloured in blue) and lead (coloured in grey) for all the samples analysed in this scientific work. The wheat samples 00, 0, 1, 2 and wholewheat are represented by the column named wheat, because they are all *Triticum aestivum*.

The green line in Fig. 2 represents the average value of the aluminium which is much higher respect to the other three contaminants analysed (bar scale in green on the right side of the graph). Comparing the green line and the bars, the aluminium shows different trend respect to the other elements. The highest value is in oats, followed by wheat, durum wheat, corn and less in spelt and finally in rice, with a difference between the two extreme values of 2579 μg/kg (in oats flour) and 121 μg/kg (in rice flour). The aluminium value on wheat is similar to those compared by Ertl and Goessler (2018) but less than that published by Vrček and Vinković (2012).

Fig. 2 shows, also, that lead is a high abundant contaminant in all the different type of samples, with the highest average value for spelt, follow by corn, durum wheat and wheat 00. The lowest value for rice, oats, wholewheat and wheat 0 and 1.

The high value of lead in all the flour samples is not surprising because, despite being much less bioavailable than cadmium, in Italian agricultural soils its average concentration is higher than that of cadmium (Abollino et al., 2002; Buccolieri et al., 2010).

Wheat and durum wheat have similar trend for the three contaminants, with Pb which shows the higher values (2.650 and 4.637 μg/kg respectively) than the two other contaminants, then As (2.056 and 1.805 μg/kg respectively) and finally Cd, which instead shows lower values (0.567 and 0.710 μg/kg respectively). The Pb value of wheat is similar to that proposed by Nardi et al. (2009), but low respect to Vrček and Vrček (2012). Cd in wheat and durum what is present with low values in all the samples, compared to data in literature (Nardi et al., 2009; Vrček and Vinković, 2012) and respect the other two contaminants, as being uniformly distributed in the cereal it has a relatively low *removal rate* (10 %) compared to other metals (i.e., Pb around 60 %). The *removal rate* represents the decrease in the metal content in the flour compared to the cereal after cleaning, sieving, and milling. The average metal content is then lowered during processing, by removing the external parts of the grain (Cubadda et al., 2005). Finally, the value of As of the samples analysed show lower value than literature data, as for example by Nardi et al. (2009) and Thosago et al. (2022).

Oats flour shows similar value of wheat flour samples: Pb 2.261 μg/kg, As 1.124 μg/kg and Cd 0.540 μg/kg, which are higher respect to those found in rice except for As (1.652 μg/kg). The Pb value in rice is lower respect to that presented by Stakheev and Stolboushkina (2022). Also, for oats and rice, Cd is the lowest contaminant which shows very low value, also compared to data in literature (Li et al., 2022; Stakheev and Stolboushkina, 2022; Rubio et al., 2023).

Corn flour is not much studied but comparing the literature data with those obtained by ICP-MS-QQQ, the values are lower, for example for Cd and Pb compared to Hatami et al. (2022) and Rubio et al. (2023). Also, the value of As are lower respect to literature data (Supadmi et al., 2023).

Finally, also for spelt flours there are not a lot of publication regarding multielement analysis. Despite this, the As data obtained by ICP-MS-QQQ are low respect to that published from 1.57 μg/kg (our data) to 1.67 mg/kg (Wiwart et al., 2016) but probably for spelt the difference in the type of *Triticum* makes different data. The same is for Cd, 0.093 μg/kg (our data) compared to 1.54 mg/kg by Wiwart et al. (2016); and for Pb 7.317 (our data) and 1.12 mg/kg by Wiwart et al. (2016). Same comparison for other literature data (Slepecka et al., 2016).

3.4. Arsenic, cadmium and lead compared to the maximum level permitted

The concentrations of arsenic, lead, and cadmium were also analysed in all the flour samples of all cereals to identify a possible environmental contribution of these metals.

The maximum level set for cereals is a maximum concentration of lead of 0.200 mg/kg (EC regulation No. 915, 2023). Related to cadmium, the maximum level permitted is for *Triticum durum* 0.180 mg/kg and for rice 0.150 mg/kg. (EC regulation No. 915, 2023) of dry matrices, while the quantities of arsenic have been regulated only in rice (0.250 mg/kg) (EC regulation No. 915, 2023).

Fig. 3 shows the values obtained for the three contaminants for all the flour samples analysed which highlighted that all the elements analysed are lower the regulatory limit, but with different trend.

As regards type 00 wheat flours (Fig. 3a), the lead concentration remains below 6 µg/kg except for one sample in which the lead is 17 µg/kg and the As concentration remain below 8 µg/kg.

Fig. 3b shows that all the samples of type 0 wheat flour have lead values below the regulatory limit, putting the attention in four samples, with lead value slightly higher than all other samples, where lead is lower than 1 µg/kg. Cadmium is similar in all the samples and only two samples has slightly higher arsenic value as compared to each other (with a maximum value of 10.190 µg/kg).

The graph in Fig. 3c combines the samples of flour type 1 (samples F20, F25, F60, F61, F65, F66 and F82), flour type 2 (samples F24, F67 and F71) and wholewheat flour (samples F11, F17, F19, F29, F33, F62, F69, F80 and F78). The wholewheat flour samples show the lower value of the three contaminants analysed, respect to the other two type of flour. The same trend is obtained by other research study, but our data are lower, as for example Ertl and Goessler (2018) founded As value of 9 µg/kg respect to the average of 4.569 µg/kg calculated for the wholewheat samples analysed, the same for Cd 34 µg/kg compared to the average value of 1.262 µg/kg and finally Pb < 4 µg/kg compared with 0.705 µg/kg of our research work. On the opposite, flour type 2 samples show the highest value of all the three contaminants, especially for lead. In all the samples lead is the contaminant present with higher values.

Anomalies were also found for durum wheat (Fig. 3d). Some samples show more concentration of lead than all the others, in accordance with the *removal rate* for Pb suggested by Cubadda et al. (2005), equal to just 50 %. Durum wheat flours represent 50 % of the total contaminated flours.

The corn samples show different trend to each other (Fig. 3e): some samples have high value of arsenic (around 6 µg/kg) respect other in which the data obtained are lower than 2 µg/kg. The same is for lead, which in some samples is lower than 2 µg/kg and in other higher than 6 µg/kg, arriving at the value of 14 or 16 µg/kg. The As average value (2.772 µg/kg) is comparable to those reported by Sigrist et al. (2016)

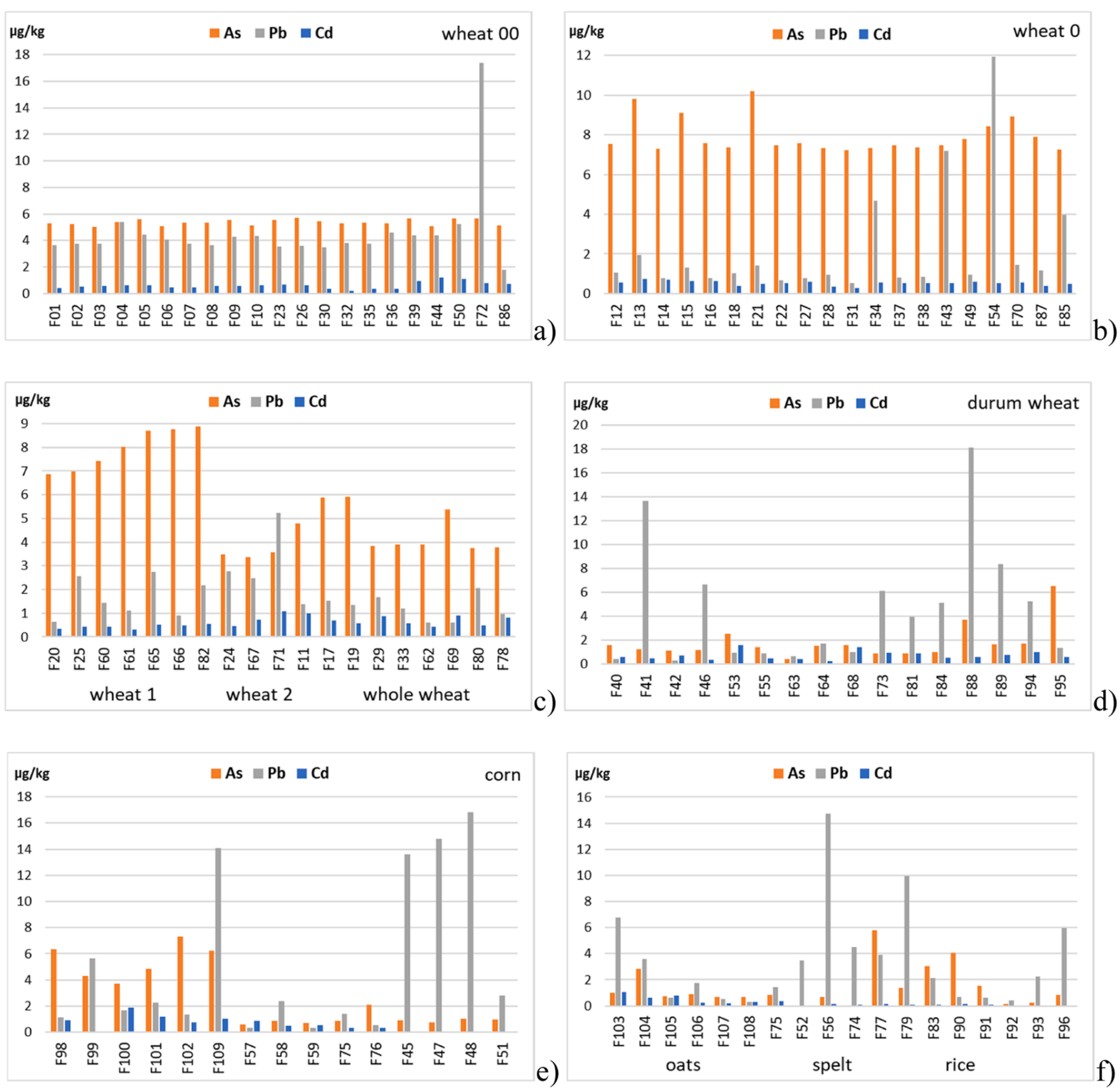

Fig. 3. Detailed concentration of contaminants As (coloured in orange), Cd (coloured in blue) and Pb (coloured in grey) detected in all the flour samples: a) wheat type 00; b) wheat type 0; c) wheat types 1, 2 and wholewheat; d) durum wheat; e) corn; f) oats, spelt and rice.

(3 μg/kg). On the opposite Cd (0.580 μg/kg) and Pb (5.276 μg/kg) are lower respect to those published by Rubio et al. (2023) (Cd = 147 μg/kg and Pb = 19 μg/kg).

The graph in Fig. 3f shows the results of three different kind of samples: oats (from F103 to F108), spelt (from F75 to F79) and rice (from F83 to F96). A single oat flour has a high Pb concentration; in general, lead remains the contaminant present in higher concentrations than the other two contaminants. The same for spelt, in which the value of lead arrives at 15 μg/kg, as for corn flour samples. The data obtained are partially comparable with those in literature: As is 1.570 μg/kg respect to < 2 μg/kg for Ertl and Goessler (2018); Pb is 7.317 which is double of the value proposed by Ertl and Goessler (2018), and finally Cd is 0.093 which is very low respect to 24 μg/kg analysed by Ertl and Goessler (2018).

Finally, rice flours have only one sample with a slightly higher lead value (5.975 μg/kg), but low arsenic value and cadmium close to zero. The average data obtained in rice flour samples (As = 1.652 μg/kg, Pb = 2.008 μg/kg, Cd = 0.062 μg/kg) are lower respect to those in literature: the average value of As is 1.652 similar to those reported by Adomako et al. (2011) present value of arsenic in white rice around 140 μg/kg; value of cadmium around 20 μg/kg and finally, lead 10 μg/kg. Other literature data for comparison are those of Ertl and Goessler (2018), which have underlain an average value of arsenic in white rice flour of 6 μg/kg, lead of 8 μg/kg and Cd 11 μg/kg, all of them are higher to those obtained in our research work. Related to the data published by Punshon and Jackson (2018), only lead could be comparable (4 μg/kg), As and Cd in our research work are lower.

3.5. Chromium, cobalt, nickel, and vanadium data

To investigate the potential contribution of metal contamination from the refining process, we analyzed flours for chromium, cobalt, nickel, and vanadium, in addition to the main toxic trace metals (aluminum, arsenic, cadmium, and lead).

Table 1 lists the minimum, maximum, and average concentrations of chromium, cobalt, nickel, and vanadium calculated for all the type of flours collected.

Oats and corn flour samples show the lowest average value of all the contaminants respect to the other type of flours. Spelt shows the highest average value of Cr but with low value respect to Wiwart et al. (2016) and Sinkovič et al. (2023), and wheat the highest values of Co, Ni and V, which show high value respect to that in literature (Thabit et al., 2020).

The average concentration of Ni in wheat (326 μg/kg) is five times higher respect to corn and oats and also durum wheat, and three times higher respect to rice and spelt. The value of Ni in wheat flour samples is lower respect to that published by Ertl and Goessler (2018) but higher to that by Thabit et al. (2020). The same for the other contaminants. This large difference in concentration between the various data present in the literature could be linked both to the origin of the grain, but also to the production process to which the cereal is subjected to become flour. The range of variation of these contaminants in wheat is much higher than in the types of flours, probably because wheat includes all the flours resultant from *Triticum aestivum* (00 flour type, 0 flour type, 1 flour type, 2 flour type and wholewheat): for chromium it varies from a minimum of 3.846 (00 type) to a maximum of 4330.920 (0 type, followed by 2471.448 in 00 type); for cobalt it varies from a minimum of 0.068 (00 type) to a maximum of 112.372 (0 type, followed by 104.815 in 00 type); for nickel it varies from a minimum of 4.617 (00 type) to a maximum of 3802.255 (0 type, followed by 3557.357 in 00 type); for vanadium it varies from a minimum not detected in 00 type to a maximum of 23.844 in 0 type (followed by 14.622 in 00 type). It is interesting to note, that also the minimum and the maximum value are present in the refined flour samples (00 and 0 type), while in less refined flours the difference between minimum and maximum value is not so high. We know that these contaminants can be both present in the soil and therefore transferred to the plant and then consequently into the grain, but also derive from pollution of the milling production process. In fact, at least in Italy, milling is almost no longer done with stone, but generally, especially for commercial flours, metal rollers are used, which are uncontrolled, can wear and deteriorate therefore releasing metals to the final flour product.

The fact of finding such different values (between minimum and maximum) especially in refined flours supports the thesis of a more probable contamination due to the industrial alloys with which industrial mills are built. The transfer of the alloy metals into the finished product could occur as a result of excessive wear of the grinding rollers and/or late replacement of the rollers themselves. This could put refined flours with different levels of contaminants on the market, while remaining below the legal limits.

Some flour samples had relatively high values of nickel, chromium, and vanadium compared to the average concentration detected. In particular, finding vanadium concentrations which normally stood below the Limit of Detection (LOD), was a stimulus to repeat the analysis to exclude any errors due to the instrument. The fact that metals typically used in the production of high-strength metal alloys have unusually high concentrations has suggested the hypothesis of contamination downstream of the flour production process, that is, grinding. To corroborate this thesis is also the type of sample; the flour samples with highest value of these contaminants are of wheat type flour (especially wheat type 00 – Fig. 4) subjected to repeated grinding processes and therefore more likely to be contaminated during a grinding phase.

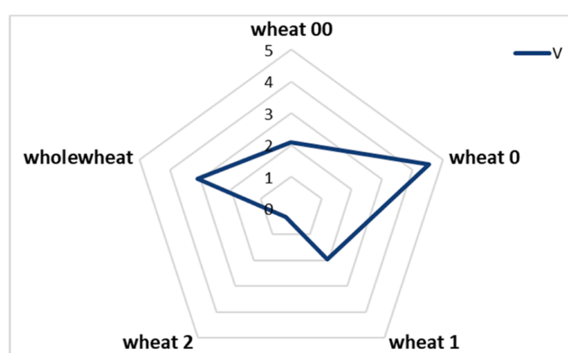

Fig. 4. Average concentrations of vanadium (V) contaminant detected in wheat flour samples and expressed in μg/kg.

Table 1
Minimum, maximum, and average value concentration of Cr, Co, Ni, and V, expressed in μg/kg, in all the different type of flour samples analysed.

	Cr (μg/kg)			Co (μg/kg)			Ni (μg/kg)			V (μg/kg)		
	average	min	max	average	min	max	average	min	max	average	min	max
Wheat	390.944	3.846	4330.920	9.613	0.068	112.372	326.219	4.617	3802.255	2.402	n.d.	23.844
Durum wheat	305.120	15.681	2068.721	1.724	0.221	10.842	73.903	11.084	442.349	1.478	0.027	5.631
Oats	122.428	80.328	226.950	1.037	0.630	1.672	64.735	33.256	96.002	1.030	0.510	2.045
Corn	170.678	23.707	419.851	1.367	0.353	3.136	61.027	18.282	181.998	1.064	n.d.	2.673
Spelt	436.110	19.065	1538.866	2.904	0.273	9.931	121.754	16.520	402.772	1.934	n.d.	5.763
Rice	366.676	81.885	917.568	2.675	0.658	6.663	108.867	29.397	265.804	2.343	0.303	6.412

Fig. 4 shows the mean concentrations of vanadium (V) of all the wheat flour samples analysed and underlines that V is concentrated more in wheat flour “0”, followed by type “1”. Even if the differences are minimal between the different types of flour samples, it can be noted how V follows the refinement of the flour, except for whet type “00”. Finding vanadium concentrations higher than the LOD and unusually high concentrations of the other metals selected for the analysis could lead to the hypothesis of typical pollution due to the use of high-strength metal alloys in cereal crushing processes to obtain flour.

3.6. Caesium data

We have studied with specific focus the content of caesium in the flours because the radioactive isotopes of this element (Cs137 and Cs134) are among the more abundant nuclear fission products, that may be dispersed in case of nuclear power plant reactor accident. Any nuclear accident, with consistent fall down may have strong impact in the content of this element in the agriculture products, through both foliar and root uptake (Kubo et al., 2020). As cereals are the most important source of food all over the world with 60 % of calories and protein consumed provided by cereals, it will be important to have specific data about the content of this element in the flours.

As shown in Fig. 5a, caesium is more abundant in wheat flours compared to other type of flours (around 0.1 μg/kg). These data could drive the focus on caesium as a specific marker for wheat flours as wheat is the richest in caesium compared to the other types of flours.

Durum wheat shows second higher concentration of caesium, followed by oats and corn.

Spelt and rice have very low value of caesium, below 0.1 μg/kg, closed to the detection limit.

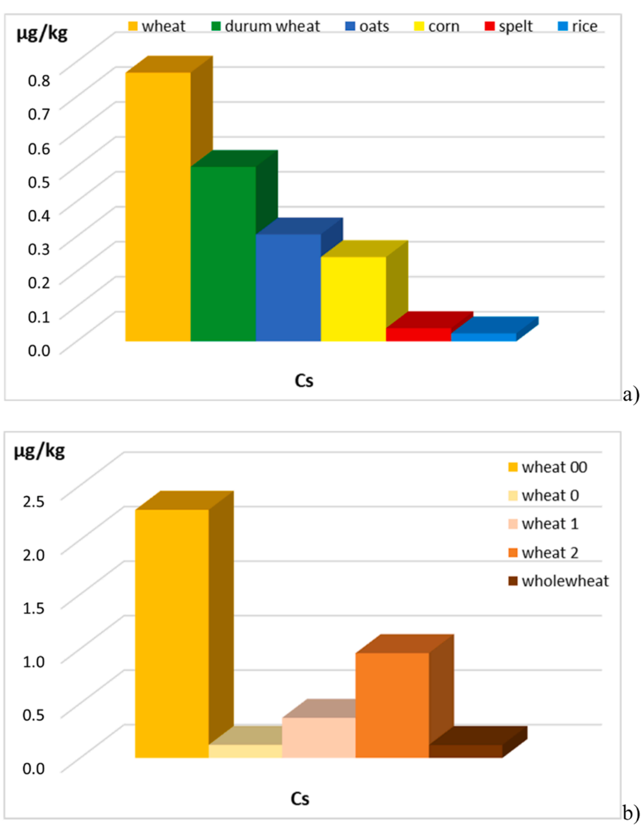

Fig. 5. Average concentrations of caesium (Cs) contaminant detected in the flours of the various cereals analysed and expressed in μg/kg: a) wheat flour in dark yellow, durum wheat in green, oats in blue, corn in yellow, spelt in red and rice in light blue; b) wheat 00 in dark yellow, wheat 0 in light yellow, wheat 1 in light orange, wheat 2 in orange, whole wheat in brown.

Analysing in detail the different kind of wheat flour samples, it is important to note that the average value obtained in the graph of Fig. 5a is due to different value of the detailed samples. Fig. 5b, in fact, shows that the wheat flours analysed are characterized by different value of caesium: type “00” wheat shows the highest value (close to 2 mg/kg). In fact, it has a well-defined tendency, which leads it to be more present in the internal parts of the seed (endosperm) than in the bran. This feature leads to the observation that the endosperm of the wheat is preferentially accumulating caesium in comparison with the bran. As a matter of fact, the wholewheat exhibit lower values of caesium concentration than type “00” one, cause to the average value between endosperm and bran. It is worth to observe that any accidental spread of radioactive caesium in the environment could cause an accumulation of these isotopes in the endosperm, affecting the whole quality of the flours. This may also have consequences on the choice and management of strategic reservoirs in case of adverse events. Another observation affecting the content of caesium is the granulometry of the flours, so that flours with finer particles size (type “00” and type “2”), exhibit higher concentration of caesium.

Further studies will be needed to assess the uptake and accumulation factor of the different components of the wheat, also considering the texture and granulometry of the flours.

4. Discussion

For all types of cereals, the sources of contamination can be of two types: contamination due to the growth of the plant into contaminated soil (Rizvi et al., 2020); contamination due to subsequent processing (Pirhadi et al., 2020). In this research work we want to focus on the possible contamination of the flour matrices due to milling.

Usually, in fact, cereals are not consumed as they are but undergo different production processes that transform the cereal into the desired product. Processing effects can alter the outcome, increasing levels of contaminating metals due to equipment metal release. This is because even the machinery used for crushing, if damaged or worn, could release metals into the flour (finished product), as previously confirmed by Cubadda et al. (2005) and by Addai et al. (2024) in relation to the elements Iron, Nickel, Cadmium, Chromium and Lead.

To resist the corrosive action of water during the moisture activity, the cylinders must be made of stainless steel or hard cast iron (Magallanes López et al., 2019). Stainless steels are characterized by greater resistance to oxidation and corrosion, especially in humid environments, compared to normal carbon steels (Berndt and Becerra, 2023). This ability is mainly due to the presence of chromium in the alloy, capable of passivating itself, that is, of covering itself with a thin and adherent layer of oxides with a thickness of the order of 0.3–5 nm, which superficially protects the metal of the alloy. It is also possible to add other alloying elements in addition to chromium, capable of increasing the degree of passivation. The most common element is nickel, obtaining Ni-Cr alloys, such as AISI 304 steel (18–20 % Cr; 8–10 % Ni). While to protect the hard cast iron cylinders they are coated with a special paint made up of chromium, manganese, silicon and nickel powders.

It is clear that with all these metals present in the cereal processing process to obtain flour, if the machinery throughout the process is not properly maintained, the risk of having high concentrations of metals in the finished product is high. Although the metal content remains below the legal limits, a constant increase in metals in the finished product also leads to an increase in metals in the human body, which, associated with certain pathologies, can favor the development of serious diseases.

5. Conclusions

Flours are the basis of any human diet, and often require pre-treatment before being consumed. Cereals grinding processes could create a potential risk of invisible contamination that could escape normal quality control analyses. The reasons can be the most disparate, from purely technical and economic ones (a good quality cylinder in AISI 304 steel has very high prices, in addition to the lost income due to the necessary downtime of machines for replacement), to those due to a search for a virtually absent contamination and much rarer than that due to Pb or Cd.

Commercial flours are generally produced through industrial process that involves the use of metal rollers. This research work shows how much these metals could accumulate in flours during the flour milling process, even if of small quantities.

Vanadium has been identified as a relevant element that can be monitored to unveil the tribocorrosion and milling process contamination as it is unequivocally transferred by the industrial alloys.

A solution to avoid or minimize the chromium, cobalt, nickel, and vanadium content on the flours could be the tempestive replacement of metal rolls and by increasing the process maintenance. Furthermore, these elements should be regularly checked by the competent authorities.

Intellectual property

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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CRediT authorship contribution statement

Telloli Chiara: Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Data curation, Supervision. **Cicconi Flavio:** Writing – original draft, Software, Formal analysis, Data curation. **Iapalucci Maria:** Project administration, Conceptualization. **Rizzo Antonietta:** Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Borgognoni Fabio:** Writing – review & editing. **Salvi Stefano:** Methodology, Formal analysis. **Lombardi Pasquale:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation.

Declaration of Competing Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2025.107387.

Data availability

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

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