Comparative elemental analysis of dairy milk and plant-based milk alternatives

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Abstract

Together with essential elements, toxic elements can also be found in food. In this study, we analysed the content of 41 elements in milk from mammals (cow, goat, and donkey) and plant-based milk alternatives (from soy, rice, oat, spelt, almond, coconut, hazelnut, walnut, cashew, hemp, and quinoa) using inductively coupled plasma mass spectrometry and cold vapour generation atomic fluorescence (for Hg). The analytical methods were validated using both milk certified reference materials and recovery experiments for different milk samples, obtaining satisfactory results in all cases. Only cow and goat milks were important sources of all major mineral elements like Ca, K, Mg, Na and P, and some minor elements like Se and Zn, while soy milk contained significant amounts of Cu and Fe, coconut milk contained Cr and Se, and hemp milk contained Mo. The level of toxic trace elements, including As, Cd, Hg, and Pb was very low in all analysed samples and did not pose any threat to consumers. The study is of significance for consumers of plant-based beverages from nutritional and food safety point of view.

Keywords

Essential elements; toxic elements; plant-based milk beverages; dietary intakes; inductively coupled plasma mass spectrometry; cold vapour generation atomic fluorescence spectrometry.

1. Introduction

Various human and industrial activities are sources of environmental contamination, resulting in damage to the food chain and products consumed by humans (Manigrasso et al., 2019; Canepari et al., 2018; Marconi, Canepari, Astolfi, & Perrino, 2011; D'Ilio, Petrucci, D'Amato, Di Gregorio, Senofonte, & Violante, 2008; Licata et al., 2004). Therefore, environmental pollution as well as manufacturing and packaging processes can alter the elemental composition of milk and non-dairy milk beverages (Ziarati, Shirkhan, Mostafidi, & Zahedi, 2018; Rao & Murthy, 2017; Abdallah, 2005). Together with essential elements, toxic elements can also be found in these products (Ziarati et al., 2018; Pilarczyk, Wójcik, Czerniak, Sablik, Pilarczyk, & Tomza-Marciniak, 2013). For Pb, the European Union (EU) with Commission Regulation (CR) No. 1881/2006 established a 0.020 mg kg^{-1} wet weight (w.w.) maximum level in raw milk, heat-treated milk, milk for the manufacture of milk-based products, as well as infant and follow-on formula (Commission Regulation (EC), 2006). In some EU countries, national action levels have been set for As and Cd as well (D'Ilio et al., 2008).

Milk is a staple in the human diet and a primary natural source of nutrition for infants (Tripathi, Raghunath, Sastry, & Krishnamoorthy, 1999). Health problems, such as dietary restrictions, allergies, and lactose intolerance in addition to ethical issues regarding the use of animals have influenced consumer demand for alternatives to cow's milk (Vanga & Raghavan, 2018; Sethi, Tyagi, & Anurag, 2016). These alternative milk options include other dairy milks from mammals (non-standard dairy milks) such as goat, donkey, and camel, as well as plant-based milk alternatives including soy, almond, rice, and coconut milks (Vanga & Raghavan, 2018; Ziarati et al., 2018). Other sources have also been used to produce plant-based milks, but are less common and include hemp, hazelnuts, macadamia nuts, flax, oats, and spelt (Vanga & Raghavan, 2018). Plant-based milk alternatives have become increasingly popular but most lack nutritional balance when compared to cow’s milk. However milk alternatives contain functionally active components with health promoting properties that appeal to health-conscious consumers (Sethi et al., 2016). Recent studies regarding plant-based milk compositions have focused mainly on protein and energy content and a select few nutrients and vitamins (Vanga & Raghavan, 2018; Singhal, Baker, & Baker, 2017; Sethi et al., 2016). Therefore, it is necessary to determine and monitor the levels of toxic and essential elements in all beverages meant for human consumption, as they can significantly affect human health (Astolfi et al., 2019a; Licata et al., 2004; Singh, Sharma, Agrawal & Marshall, 2010; Tripathi et al., 1999). To date only few studies on the major and minor element composition of milk have been published, with most focused on human milk contamination (Khan et al., 2014; D’Ilio et al., 2008; Cava-Montesinos, Cervera, Pastor, & de la Guardia, 2005; Martino, Sánchez, & Sanz-Medel, 2001). The concentrations of some elements have been reported for soy and dairy yogurts (Llorent-Martínez, De Córdova, Ruiz-Medina, & Ortega-Barrales, 2012), goat milk (Singh, Yadav, Garg, Sharma, Singh, & Sharma, 2015), and donkey milk (Fantuz et al., 2015). To the best of our knowledge, no comprehensive studies have been performed on the presence of major, minor, and trace elements concentration in commercially available non-standard dairy milk and plant-based milk alternatives.

Good quality measurements are essential for quality control and assessing the quality of milk products for manufacturing trade and research (Kira & Maihara, 2007). Sample digestion is critical for elemental analysis due to the preparation time, risk of contamination, and analyte loss which may contribute towards systematic analysis errors (Kira & Maihara, 2007). Generally, HNO_3 and H_2O_2 mixed in various proportions is used for sample digestion (D'Ilio et al., 2008). Cold vapour generation atomic fluorescence spectrometry (CV-AFS) is a common used technique for Hg determination, while inductively coupled plasma mass spectrometry (ICP-MS) is the most suited and fastest technique for analysis of many other elements (Astolfi et al., 2019b; D'Ilio et al., 2008). Both instrumental techniques exhibit high sensitivity, high sample throughput, and wide linear concentration range (Di Dato et al., 2017; D'Ilio et al., 2008; Cava-Montesinos, Ródenas-Torralba, Morales-Rubio, Cervera, & de la Guardia, 2004).

This study was performed to provide updated information regarding the concentrations of a wide range of toxic and essential elements (Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, U, V, W, Zn, and Zr) in various dairy milks and plant-based beverages samples collected randomly from markets in Italy. The method performances were evaluated in terms of detection and quantification limits, precision, accuracy, and recovery, using both milk standard reference materials and fortified milk samples. The obtained results were compared to literature values and to critical levels specified by the World Health Organization (WHO) and Food and Nutrition Board (FNB).

2. Materials and methods

2.1. Instrumentation

The quadrupole ICP-MS used herein was an 820-MS (Bruker, Bremen, Germany) equipped with a collision-reaction interface (CRI) and glass nebuliser (0.4 mL min^{-1}; MicroMistTM; Analytik Jena AG, Jena, Germany). Standard mode was used to quantify all elements except for As, Cr, Fe, Mn, Se, and V, which were determined by CRI with He and H_2 (99.9995% purity; SOL Spa, Monza, Italy) as cell gases. The data were collected according to a previously reported method (Astolfi et al., 2018). Before each experiment, the instrument was tuned for daily performance using a multi-standard stock solution containing Ba, Be, Ce, Co, In, Pb, Mg, Tl, and Th (10.00 ± 0.05 mg L^{-1}; Spectro Pure, Ricca Chemical Company, Arlington, TX, USA). A standard solution of Y (5 µg L^{-1} from 1000 ± 2 mg L^{-1}; Panreac Química, Barcelona, Spain), Sc, Rh, In, and Th (10 µg L^{-1} from 1000 ± 5 mg L^{-1}; Merck KGaA, Darmstadt, Germany) in 1% HNO_3 (v/v) was used as an internal standard to control the nebuliser efficiency, as previously reported (Astolfi et al., 2018; Conti, Canepari, Finoia, Mele, & Astolfi, 2018; Astolfi, Di Filippo, Gentili, & Canepari, 2017).

A CV-AFS (AFS 8220 Titan, FullTech Instruments, Rome, Italy) was used for Hg determination. The instrumental conditions for CV-AFS analysis were described in a previous study in detail (Astolfi et al., 2019b).

An ICP-optical emission spectrometer (Vista MPX CCD Simultaneous; Varian, Victoria, Mulgrave, Australia) in axial view mode equipped with a cyclonic spray chamber was used to determine the residual C content of the final digests using a previously reported method (Astolfi et al., 2018).

2.2. Reagents

All calibration standard solutions for ICP-MS were prepared from a multi-element standard solution (1.000 ± 0.005 mg L^{-1} As, Al, Ba, Be, Bi, Cd, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Te, Ti, Tl, U, V, W, and Zr; 5.00 ± 0.03 mg L^{-1} Ce and Co; 10.00 ± 0.05 mg L^{-1} Fe and Zn; 50.00 ± 0.25 mg L^{-1} P and Si; 55.00 ± 0.25 mg L^{-1} B and Sr; 500.0 ± 2.5 mg L^{-1} K, Mg, and Na; 1000 ± 5 mg L^{-1} Ca and S; Ultra Scientific/Agilent Technologies, North Kingstown, RI, USA) and for CV-AFS from the Hg standard solution (1002 ± 7 mg L^{-1}; SCP Science, Baie D’Urfé, Canada) by dilution with 3% (v/v) HNO_3 (same percentage of acid present in the sample) in deionised water. Analytical reagent grade concentrated HNO_3 (67–70%; super pure) was obtained from Carlo Erba Reagents S.r.l. (Milan, Italy) and HCl (assay >36%; residue <3 mg L^{-1}) and H_2O_2 (assay >30%) were obtained from Promochem, LGC Standards GmbH (Wesel, Germany). The 5% HCl was used as a carrier and 0.05% $NaBH_4$ (Sigma-Aldrich Chemie GmbH, St. Louis, USA) in 0.05% NaOH (assay >98%, anhydrous pellets, RPE for analysis, ACS – ISO; Carlo Erba Reagents, Milan, Italy) as reducing agent for CV-AFS. Deionised water with a resistivity ≤18.3 MΩ cm was obtained using an Arioso Power I RO-UP Scholar UV water purification system (Human Corporation, Songpa-Ku, Seoul, Korea). The European reference material ERM®-BD150 and ERM®-BD151, consisting of skimmed milk powder materials certified for their elemental mass fractions were purchased from the Joint Research Centre, Institute for Reference Materials and Measurements (Geel, Belgium).

All plastic containers, polypropylene flasks, pipette tips, quartz digestion tubes, and reagents that contacted the samples or standards were checked for contamination.

2.3. Sample preparation and digestion

A total of 43 samples of commercially available dairy milks and plant-based milk alternatives were collected from the local supermarkets of Rome in central Italy. The samples consisted of 12 freshly pasteurised or long-life cow milk (5 whole, 4 partially skimmed, 3 skimmed), 2 freshly pasteurised and 2 long-life whole goat milk, 1 freshly pasteurised whole donkey milk, and 26 plant-based beverages (4 soy, 4 rice, 2 oat, 1 spelt, 4 almond, 4 coconut, 2 hazelnut, 2 walnut, 1 cashew, 1 hemp, and 1 quinoa milks). For each type of milk, the samples of different brands or flavours were purchased in triplicate at different times from January 2018–July 2019. All samples were kept in their original packages and transferred to the laboratory in an ice box, properly labelled, and stored in a refrigerator. The samples were processed for analysis before their respective expiry dates.

Five different portions of 1 mL were withdrawn from the same sample and weighed using an analytical balance (sensitivity, 0.1 mg; Europe 60; Gibertini Elettronica, Milan, Italy) to calculate the mean densities of the different milks. This value was used to calculate the final concentration of the analytes in the milk samples (mg kg^{-1}).

For the acid digestion, ~0.5 g of samples was accurately weighed and placed in polypropylene tubes (Artiglass s.r.l., Due Carrare, PD, Italy). Subsequently, 1 mL 67% HNO_3 and 0.5 mL 30% H_2O_2 were added and the sample was digested using a water bath (WB12; Argo Lab, Modena, Italy) with an electronic temperature control at 95 °C (temperature accuracy, ± 0.2 °C) (Astolfi et al., 2018). The digestion was completed in approximately 30 min, as indicated by the appearance of a colourless solution. Only the digested soymilk the sample presented a residue and was filtered. The mixture was left to cool and the contents of the tubes were diluted to 5 mL with 3% HCl or 20 mL with deionised water for the CV-AFS or ICP-MS analyses, respectively.

At regular intervals during the analysis (immediately after the calibration curve, after every 20 samples, and at the end of the analytical sequence), intermediate calibration standards were analysed to monitor instrument drift. Furthermore, blanks (3% HNO_3) were periodically analysed alongside the samples to check for any losses or cross contamination. Blanks were treated as samples for subtraction of the background signal from the reagents.

2.4. Calibration procedure

For quantitative analysis of the samples, the external calibration technique was followed. Standard solutions were prepared in 3% (v/v) HNO_3 (same percentage of acid present in the samples) by diluting a multi-element standard solution containing all elements or only Hg. The calibration curves for the analytes by ICP-MS were prepared using seven different concentrations in the range of 0.5–50 $\mu g\ L^{-1}$ for As, Al, Ba, Be, Bi, Cd, Cr, Cs, Cu, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Te, Ti, Tl, U, and V; 2.5–250 $\mu g\ L^{-1}$ for Co, Fe, and Zn; 27.5–2750 $\mu g\ L^{-1}$ for B and Sr; 250–25000 $\mu g\ L^{-1}$ for K, Mg and Na; and 500–50000 $\mu g\ L^{-1}$ for Ca. Hg was determined by CV-AFS using nine different standard concentrations ranging from 0.01 to 1.5 $\mu g\ L^{-1}$. All measurements were performed using full quantitative mode analysis. The correlation coefficients for all calibration curves were at least 0.999, showing good linear relationships throughout the ranges of the concentrations studied. Moreover, the linear concentration range was verified using at least five levels (including zero) by Mandel fitting test, as indicated in the Commission Decision (CD) No. 657/2002 (Brüggemann, Quapp, & Wennrich, 2006; European Commission, 2002). The dynamic range is related both to the variability of the elemental concentrations in the studied matrices and to the features of the used instrument. The dynamic range was, respectively, 2.0 log for all elements determined with ICP-MS and 2.3 for Hg determined with CV-AFS. The comparison of dynamic range with previously published methods is shown in Table S1.

2.5. Quality assurance

Several parameters were evaluated to validate the analytical methods for determination of major, minor, and trace elements in dairy and plant-based beverages. The summary of performance characteristics of the proposed method was reported in Table S1.

The limits of detection (LODs) and quantification (LOQs) were calculated as three and ten times the standard deviation of the blank sample, respectively (Table 1). The LOD and LOQ values ranged from 0.00002 (Tl, and U) to 10 (Ca) mg kg^{-1} and 0.0001 (Cs, Tl, and U) to 40 (Ca) mg kg^{-1}, respectively. For Pb, CR No. 333/2007 (Commission Regulation (EC), 2007) a maximum LOQ value of 8 μg kg^{-1} is necessary and the present method achieved a LOQ of 5 μg kg^{-1}. Comparison of the method proposed in the present study with others already developed for elemental determination in milk samples showed that the LODs of some selected elements are similar or lower than the values reported by Chen et al. (2020) and Llorent-Martínez et al. (2012); in contrast the LODs are higher than the values reported by Khan et al. (2014) (Table S1).

To check the method accuracy, samples of certified skimmed milk powder material (six replicates; ERM®-BD150 and ERM®-BD151) were analysed for Ca, Cd, Cu, Fe, Hg, K, Mg, Mn, Na, P, Pb, Se, and Zn contents. The obtained results are shown in Fig. 1 along with the certified values.

Detailed data for Fig. 1 were provided in the “Supplementary material” (Table S2). Good agreement between the obtained and certified values was found, with trueness bias percentages ranging from -7% (Se in ERM®-BD150) to 8% (Cu in ERM®-BD150) and precision as repeatability of <5%.

Because of the lack of certified reference materials for milk in liquid form for trace elements, the analytical quality control was also verified using recovery experiments for the 41 considered elements in cow, almond, coconut, oat, rice, soy, and spelt milk matrices by spiking samples with all the considered elements at three concentrations (Tables 1, S3, and S4). The three added concentrations were selected based on the criterion indicated in CD No. 657/2002 (Commission Decision, 2002) as 1, 1.5, and 2 times the eligible concentrations (Table S3). For Pb, additions of 0.5, 1.0, and 1.5 the maximum level for milk (0.020 mg kg^{-1}) were chosen (Commission Regulation (EC), 2006). An acceptance limit between 90 and 110% was used in compliance with the CD No. 657/2002 (Commission Decision, 2002). The obtained recoveries of spiked cow milk samples ranged from 91–107% (Table 1), confirming that no significant loss occurred during digestion. Moreover, the residual C present in the final digest ranged from 15 mg kg^{-1} for donkey milk to 57 mg kg^{-1} for cow milk and did not significantly interfere with the analysis, in accordance with previously reported results (Astolfi et al., 2018). The results for the plant-based milk alternatives are reported in Tables S4a and S4b. Acceptable recoveries were obtained for all elements at third selected concentration level, except for Zr in spelt (83%), almond (79%), and coconut milks (85%), as shown in Table S4b. The differences in the recovery between the cow milk and plant-based milk alternatives were likely due to the different elemental contents present in the matrices without addition.

Method precision was evaluated as repeatability for each addition level. The obtained percent coefficient of variation (CV%) ranged from 0.1–15% (Tables 1, and S4) except at level 1 for Al in rice milk (19%); As in rice (16%), spelt (33%), and oat milks (22%); Ba in oat milk (20%); and Se in spelt milk (24%). The CV% of Al, Ba, Cu and Si were >10% for addition at level 1 in cow’s milk, probably because the concentration of addition was ≤LOQ; CV% of other elements in the plant-based milk alternatives were >10% because the addition level was small compared to the natural content.

2.6. Statistical analysis

Data obtained from the different types of milk were reported as mean and standard deviation of triplicate measurements. Significant differences ($p < 0.05$) between the means were processed by analysis of variance (ANOVA one way) and Tukey's honestly significant difference (HSD) test using SPSS Statistics Software Version 25 (IBM Corp., Armonk, NY, USA). The obtained values below the LOD were designated as half the LOD.

3. Results and discussion

The digestion method was optimised to allow sample preparation in one vessel. This sample preparation avoided as much as possible sample loss due to the transfer in different vessels and reduced the risk of contamination. The proposed method uses HNO3 and H2O2 respectively as the acid and oxidising agent for the sample digestion, which are commonly used in the literature for milk samples (Table S1). Microwave assisted digestion is the most widely used procedure (Table S1); however sample preparation can be slow due to the need to clean the vessels after each analysis. The digestion method using a water bath appears the fastest procedure (time of digestion, 30 min for 120 samples) compared to the other sample treatments reported by literature (Table S1) and can be easily applied to the routine screening analyses. The validated methods offered satisfactory detection limits and provided precise and accurate procedures with high sample throughput (Fig. 1, and Tables 1, S1, S2 and S4).

3.1. Differences in element concentrations

The concentrations of 41 analysed elements obtained for each sample are provided in Tables 2a and 2b. The elements that showed significant differences ($p < 0.05$) among the samples of different varieties are reported in Table 3. The data of different varieties of cow milk were not significantly different ($p > 0.05$) for all elements; therefore, they were considered as a single sample type and the same was true for the goat milk samples. Ca data in the fortified plant-based milk alternatives fortified (soy, hazelnut, and walnut milks) were not processed by ANOVA. No significant differences were observed in the concentrations of all considered elements among the following types of milk: soy-hemp, rice-quinoa, rice-spelt, rice-cashew, quinoa-spelt, quinoa-cashew, spelt-cashew, and hazelnut-walnut. In Tables 2a and 2b the elements are categorised into major elements (with concentrations of >10 mg kg^{-1} = Ca, K, Mg, Na, and P), minor elements (with concentrations between 10 and 0.01 mg kg^{-1} = Al, B, Ba, Cu, Fe, Li, Mn, Mo, Ni, Rb, Se, Si, Sr, Ti, and Zn) and trace elements (with concentration of <0.01 mg kg^{-1} = As, Be, Bi, Cd, Ce, Co, Cs, Ga, Hg, La, Nb, Pb, Sb, Sn, Te, Tl, U, V, W, and Zr).

The level of toxic elements is important for the safety and quality of dairy milk and plant-based milk alternatives. Dietary intakes for all elements from each type of sample were established (Table S5). Intake levels of major elements (Fig. 2), and some minor (Cu, Fe, Mn, Mo, Se and Zn) and trace (Cr) elements (Table S5) were compared with the recommended daily allowance (RDA) or with adequate intakes (AIs) if the RDA was not set, as recommended by the FNB (Food and Nutrition Board, 2001). Intake levels of toxic elements (Fig. 3 and Table S5) were estimated and compared with the provisional tolerable weekly intake (PTWI) recommendations (JECFA, 2011a, 2006; Food and Nutrition Board, 2001; WHO, 1996, 1982) or tolerable daily intake (TDI) (WHO, 2004). The portion size of dairy milks and plant-based milk alternatives was set to 240 mL in accordance with the literature (Vanga & Raghavan, 2018; Singhal et al., 2017). The density of different varieties of milk ranged from 1.004 ± 0.002 (donkey milk) to 1.043 ± 0.002 g mL^{-1} (whole cow milk) at 21 °C. Intake levels were determined assuming a body weight (BW) of 60 kg. The most significant results are discussed in following sub-sections in detail.

3.1.1. Major elements

The human body is an extensive and complex functioning system that manages and maintains the amount of essential elements within a normal range (Vanga & Raghavan, 2018). To the best of our knowledge, only a few studies have reported the concentrations of major elements in dairy milks and plant-based milk alternatives (Vanga & Raghavan, 2018; Singhal, Baker, & Baker, 2017; Sethi et al., 2016). The dietary reference intake (DRI) values for Ca, K, Mg, Na, and P range from 1000–1300, 2300–3400, 240–420, 1200–1500, and 700–1250 mg/day, respectively (Food and Nutrition Board, 2001). Table 2 and Fig. 2 show that the only cow and goat milks are important sources of minerals, in particular Ca, which is required by the human body for the maintenance of bone health especially during childhood and adolescence (Vanga & Raghavan, 2018). In accordance with the literature, Ca is added to most brands of plant-based alternative milks to mimic the levels present in cow's milk (1340 ± 86 mg kg^{-1}) (Vanga & Raghavan, 2018). Considering the purchased samples, Ca was added in soy, hazelnut, and walnut milks. In the other plant-based samples, the Ca concentrations were much lower: 39 ± 11 mg kg^{-1} in rice milk, 174 ± 36 mg kg^{-1} in oat milk, 109 ± 34 mg kg^{-1} in spelt milk, 202 ± 130 mg kg^{-1} in almond milk, 71 ± 32 mg kg^{-1} in coconut milk, 111 ± 7 mg kg^{-1} in cashew milk, 177 ± 8 mg kg^{-1} in hemp milk, and <10 mg kg^{-1} in quinoa milk (Tables 2a and 2b). Other minerals are available in considerable quantities in cow's milk, including K (1490 ± 78 mg kg^{-1}), Mg (111 ± 6 mg kg^{-1}), Na (346 ± 26 mg kg^{-1}), and P (481 ± 25 mg kg^{-1}). Most of the alternative milks contained comparable quantities of the major elements i.e. 50–70% compared to cow's milk, with some exceptions (Table 3). In particular, donkey, oat, and spelt milks contained significantly ($p < 0.05$) lower amounts of Ca, K, and P; rice milk contained all major elements except Na; almond milk Ca and K; coconut milk Ca; hazelnut and walnut milks K and P; hemp milk Ca and P; and quinoa milk K, Mg, and P. A few brands of goat milk contained K, Mg, and Na, soy milk and coconut milk for Mg, and hazelnut milk for Na were even higher (>120%, but not significantly different; p >0.05) compared to cow's milk.

3.1.2. Minor elements

The results of mean concentrations of minor elements in dairy milks and plant-based milk alternatives ranged from <0.02 (cow milk, and goat milk) to 0.542 ± 0.007 mg kg^{-1} (walnut milk) for Al, <0.05 (donkey milk, rice, oat, and spelt) to 1.00 ± 0.03 mg kg^{-1} (hemp milk) for B, <0.01 (quinoa milk) to 0.219 ± 0.023 mg kg^{-1} (hazelnut milk) for Ba, 0.0336 ± 0.0037 (donkey milk) to 1.27 ± 0.91 mg kg^{-1} (coconut milk) for Cu, 0.127 ± 0.056 (rice milk) to 3.43 ± 0.28 mg kg^{-1} (soy milk) for Fe, 0.00098 ± 0.00024 (hemp milk) to 0.020 ± 0.018 mg kg^{-1} (goat milk) for Li, <0.007 (donkey milk) to 2.5 ± 2.9 mg kg^{-1} (coconut milk) for Mn, 0.00466 ± 0.00076 (donkey milk) to 0.411 ± 0.028 mg kg^{-1} (hemp milk) for Mo, <0.002 (quinoa milk) to 0.61 ± 0.44 mg kg^{-1} (coconut milk) for Ni, 0.100 ± 0.028 (rice milk) to 5.2 ± 4.5 mg kg^{-1} (coconut milk) for Rb, <0.008 (all types of milk except cow, goat, and coconut milks) to 0.019 ± 0.018 mg kg^{-1} (coconut milk) for Se, 3.76 ± 0.36 (donkey milk) to 18 ± 12 mg kg^{-1} (coconut milk) for Si, 0.0172 ± 0.0027 (quinoa milk) to 0.931 ± 0.022 mg kg^{-1} (hazelnut milk) for Sr, 0.0048 ± 0.0017 (rice milk) to 0.061 ± 0.034 mg kg^{-1} (soy milk) for Ti, and <0.2 (quinoa milk) to 4.54 ± 0.76 mg kg^{-1} (cow milk) for Zn (Tables 2a and 2b). The concentrations of Ba and Se were similar for all varieties of milks studied, except for Se in coconut milk which was significantly (p <0.05) higher than in soy, rice, and almond milks (Table 3). In coconut milk, Ni and Rb were comparatively higher with respect to all other milks except for Rb in goat milk and Mn with respect to cow, goat, rice, oat, and almond milks, Si with respect to cow, goat, donkey, soy, almond, and cashew milks, and Ti with respect to cow and rice milks. The contents of Al and Sr in hazelnut and walnut milks, B and Mo in soy milk, and Zn in cow and goat milks were significant higher than all other non-standard dairy milks alternatives except for B in hazelnut and hemp milks and Sr in goat, oat, almond, and walnut milks. The concentrations of Cu and Fe in soy and coconut milks were significantly higher than in cow, goat, rice, and oat milks.

A comparison of the results obtained herein with the published literature showed that Fe and Zn in almond, soy, and coconut milks were higher than those reported by Vanga & Raghavan (2018) (0.18 ± 0.13 and 0.56 ± 0.46 mg kg^{-1}; 0.84 ± 0.78 and 0.75 ±0.19 mg kg^{-1}; and 0.1 ± 0.065 and 0.66 ± 0.4 mg kg^{-1}, respectively), while Fe in rice milk (0.13 ± 0.18 mg kg^{-1}) was the same and Zn in rice milk (0.75 ± 0.27 mg kg^{-1}) was lower. In accordance with other authors (Llorent-Martínez et al., 2012), the highest differences in the levels of minor elements between cow and soy milks were observed for Al, Cu, Fe, Mn, Mo, and Ni, which were found in much higher levels in soybean milk. The concentrations of minor elements in cow milk were lower than those reported previously (Llorent-Martínez et al., 2012) for Al and Fe; (Martino et al., 2001) for Al, Ni, and Sr; and (Khan et al., 2014) for Cu, Li, Mn, Ni, Rb, Se, and Sr; whereas they were higher than those reported by Llorent-Martínez et al. (2012) for Zn; by Martino et al. (2001) for Cu, Fe, Mn, Se and Zn, and in the same range as those reported by Llorent-Martínez et al. (2012) for Ba, Cu, Mn, Mo and Ni, and by Khan et al. (2014) for Ba and Zn. It was not possible to compare the obtained data for B, Si, and Ti because these elements were not studied by other authors. In goat milk, Fe and Zn concentrations were lower while Cu was higher (9.1 ± 5.5, 5.1 ± 1.7, and <0.025 mg L^{-1}, respectively) than the values reported by Singh et al. (2015). In donkey milk, the Rb, Sr, and Ti contents were lower, whereas Mo was high than the previously reported results (0.339 ± 0.082, 0.0773 ± 0.0077, 0.882 ± 0.270, and 0.0045 ± 0.0016 mg L^{-1}, respectively) (Fantuz et al., 2015).

According to the WHO (WHO, 1996), minor elements such as Cu, Mo, Se, and Zn are essential, whereas B, Mn, Ni, and Si are probably essential, while Al and Li are potentially toxic elements, although they have essential functions. Several critical levels have been reported for these minor elements (JECFA, 2011b; Food and Nutrition Board, 2001; WHO, 1996, 1982). According to these values (Table S5), the DRIs for Cu, Fe, Mn, Mo, Se, and Zn are in the ranges of 0.7–0.9, 8–18, 1.6–2.3, 0.034–0.045, 0.040–0.055, and 8–11 mg/day, respectively; while the specified upper level (UL) for B, Cu, Fe, Mn, Mo, Ni, Se, and Zn range from 11–20, 5–10, 40–45, 6–11, 1.1–2.0, 0.6–1, 0.28–0.40, and 23–40 mg/day, respectively, and the PTWI value for Al is 2 mg kg^{-1} BW/week assuming a BW of 60 kg (JECFA, 2011b). Thus, soy and coconut milks provide good contributions of Cu, Fe, Mn, Mo, and Ni, whereas sufficient Zn is provided by cow and goat milks with reference to the DRIs for consumers and there is no known risk to healthy people based on consumption of 240 mL of the beverages. The results obtained for these nutritional elements are within the specified limits. It should be considered that dairy milks and/or plant-based milk alternatives are not the only sources of these minor elements in a typical diet.

3.1.3. Trace elements

Trace elements included those with concentrations of <0.010 mg kg^{-1} in dairy milks and plant-based milk alternatives samples are listed in Tables 2a and 2b. The concentrations of As, Be, Bi, Cd, Ce, Co, Cr, Cs, Ga, La, Pb, Sn, Tl, U, V, W, and Zr differed significantly ($p < 0.05$) among the samples from different varieties (Table 3). As ranged from <0.005 (cow, goat, donkey, spelt, and almond milks) to 0.0172 ± 0.0082 mg kg^{-1} (hazelnut milk), Be from <0.0001 to 0.00017 ± 0.00013 mg kg^{-1} (hazelnut milk), Bi from <0.0001 (all milks except cow milk) to 0.00123 ± 0.00068 mg kg^{-1} (cow milk), Cd from <0.0001 (cow, goat, and donkey milks) to 0.00458 ± 0.00012 mg kg^{-1} (hemp milk), Ce from <0.0002 (cow, goat, and donkey milks) to 0.00213 ± 0.00045 mg kg^{-1} (walnut milk), Co from 0.000669 ± 0.000012 (donkey milk) to 0.0111 ± 0.0042 mg kg^{-1} (coconut milk), Cr from <0.003 to 0.024 ± 0.029 mg kg^{-1} (coconut milk), Cs from 0.000080 ± 0.000020 (rice milk) to 0.025 ± 0.024 mg kg^{-1} (coconut milk), Ga from <0.0005 (donkey, rice, and spelt milks) to 0.0047 ± 0.0036 mg kg^{-1} (goat milk), La from <0.0001 (cow and goat milks) to 0.00242 ± 0.00037 mg kg^{-1} (walnut milk), Pb from <0.001 (hemp and quinoa milks) to 0.015 ± 0.016 mg kg^{-1} (cashew milk), Sn from <0.0002 (cow, oat, spelt, almond, hazelnut, walnut, cashew, hemp, and quinoa milks) to 0.00811 ± 0.00020 mg kg^{-1} (donkey milk), Tl from 0.000023 ± 0.000011 (hemp milk) to 0.00112 ±

0.00091 mg kg^{-1} (coconut milk), U from <0.00002 (quinoa milk) to 0.0019 ± 0.0018 mg kg^{-1} (coconut milk), V from <0.003 (coconut and walnut milks) to 0.00555 ± 0.00059 mg kg^{-1} (walnut milk), W from <0.002 (cow, donkey, spelt, walnut, and hemp milks) to 0.014 ± 0.019 mg kg^{-1} (goat milk), and Zr from <0.0002 (cow, goat, donkey, oat, spelt, cashew, hemp, and quinoa milks) to 0.0032 ± 0.0027 mg kg^{-1} (coconut milk). Bi in cow milk, Ce in walnut milk, Cd in hemp milk, Co, Cs, Sn, and Tl in coconut milk, La in walnut milk, and Sn in donkey milk were significantly ($p < 0.05$) higher with respect to all the other milks except for Cd in soy, hazelnut, cashew, and coconut milks; Ce in almond and hazelnut milks; Co in hazelnut and walnut milks; and Cs in hazelnut and cashew milks. The As content in cow milk was significantly lower than in soy, rice, and hazelnut milks; similar Ga levels were found in rice milk with respect to goat, soy, and coconut milks. Pb in cashew milk was significantly higher than that found in cow, goat, and soy milks, along with U, V, and Zr in coconut milk with respect to cow and goat milk, and W in cow milk with respect to goat milk. Other trace elements (Hg, Nb, Sb, and Te) were not statistically different among the samples from different varieties, but the highest results were: Hg in donkey milk (0.00022 ± 0.00014 mg kg^{-1}), Nb in cow and coconut milks (0.00127 ± 0.0014 and 0.0013 ± 0.0015 mg kg^{-1}, respectively), and Sb and Te in walnut milk (0.00386 ± 0.00028 and 0.00134 ± 0.00006 mg kg^{-1}, respectively).

To the best of our knowledge, the literature has mainly reported studies of trace elements in dairy milk and soymilk (Khan et al., 2014; Lorent Martínez et al., 2012; Licata et al., 2004; Martino et al., 2001). The obtained values in soy milk for Be, Cd, Co, Hg, Pb, Sn, Tl, and V were similar to the literature, whereas the As and Sb values were higher, and Cr content was lower (Llorent-Martínez et al., 2012). In contrast, in cow milk, As was the same concentration as determined by Khan et al. (2014), Llorent-Martínez et al. (2012) and Licata et al. (2004); Be, Co, Tl, and V were the same concentrations as determined by Llorent-Martínez et al. (2012), but lower than those reported by Khan et al. (2014); Bi was the same content as determined by Khan et al. (2014); Cd and Pb were the same contents as determined by Lorent-Martínez et al. (2012), Licata et al. (2004) and Martino et al. (2001), but lower than reported by Khan et al. (2014); Cr, Ce, Ga, and U showed lower concentrations than those reported by Khan et al. (2014); Hg, Sb, and Sn were the same concentrations as reported by Llorent-Martínez et al. (2012). No data were found in the literature for Ce, La, Nb, Te, W, and Zr.

Cr is considered to be an essential element, V a probable essential element, while As, Cd, Hg, Pb, and Sn are potentially toxic elements, but some possibly exhibit essential functions (WHO, 1996). All others trace elements are not known for any prominent nutritional significance. Bi toxicity has been reported after exposure during the therapeutic treatment of affected livers and kidneys (Medeiros et al., 2012). The DRIs for Cr and V range from 0.020–0.035 as AI and 1.8 as TUI, respectively. The TDI for U is 0.6 µg kg^{-1} BW/day (WHO, 2004), while the PTWI for As, Cd, and Pb are specified as 0.015, 0.007, and 0.025 mg kg^{-1} BW/week, respectively (Food and Nutrition Board, 2001; WHO, 1996, 1982), and for Hg it is 0.004 mg kg^{-1} BW/week (JECFA, 2011a).

The trace element concentrations detected herein were very low in all samples and pose no health concern to consumers. The Pb results for all types of milks and plant-based milk alternatives were lower than the maximum level specified by CR No. 1881/2006 (Commission Regulation (EC), 2006). Considering a daily intake of 240 mL of the tested products, the values of toxic trace element fall within permissible levels (Table S5).

4. Conclusion

Herein, the determination of major, minor, and trace elements in dairy milk (cow, goat, and donkey milks) and plant-based milk alternatives (soy, rice, oat, spelt, almond, coconut, hazelnut, walnut, cashew, hemp, and quinoa milks) from an Italian market was performed. The analysis involved 43 different milk samples and 41 elements, allowing an extensive and detailed comparison of elemental compositions. The analytical methods, validated using certified reference milk materials and recovery experiments for different types of dairy milks and plant-based substitutes yielded satisfactory results for all samples tested.

The results presented herein showed that dairy milks and plant-based milk alternatives are quite safe with low contamination from toxic trace elements including As, Cd, Hg, and Pb. Only cow and goat milks were significant sources of the key minerals Ca, K, Mg, Na, and P, while soy and coconut milks were good sources of Mg, and hazelnut milk provided a large amount of Na. The levels of nutritional elements were appropriate and soy and coconut milk were determined to provide a good contribution to the daily nutrition of consumers in terms of Fe and Cu, coconut milk for Cr and Se, hemp milk for Mo, and cow and goat milks for Se and Zn. Soymilk was the best alternative to replace cow or goat milk in the human diet. Other non-standard dairy milk alternatives represent possible options for soybean-allergic consumers, but various essential nutrients must be obtained through other sources in the diet in adequate quantities.

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Table 1

Limits of detection (LODs; mg kg^{-1}) and quantification (LOQs; mg kg^{-1}), percent spike recovery (R%; three concentrations in cow milk) and precision [percent coefficient of variation (CV%)] for the analysed elements.

Element	LODs	LOQs	Level 1		Level 2		Level 3	
			R%	CV%	R%	CV%	R%	CV%
Al	0.02	0.07	121	12	110	5	108	3
As	0.005	0.02	91	10	90	8	91	8
B	0.05	0.2	110	3	110	2	110	1
Ba	0.01	0.04	97	12	97	8	90	1
Be	0.0001	0.0002	92	1	91	3	92	0.2
Bi	0.0001	0.0005	92	3	91	3	90	1
Ca	10	40	99	3	106	4	105	2
Cd	0.0001	0.0003	91	1	90	2	90	1
Ce	0.0002	0.0006	96	3	96	2	94	1
Co	0.0001	0.0003	98	2	97	2	95	2
Cr	0.003	0.01	91	1	91	5	90	4
Cs	0.00003	0.0001	96	3	96	2	95	1
Cu	0.003	0.009	106	11	102	3	100	1
Fe	0.04	0.1	105	2	96	5	92	3
Ga	0.0005	0.002	90	1	94	3	95	2
Hg	0.00008	0.0003	103	7	97	2	95	3
K	2	6	99	4	107	3	105	2
La	0.0001	0.0003	94	3	95	2	93	1
Li	0.0001	0.0005	103	2	104	2	103	2
Mg	0.2	0.6	99	4	102	2	99	2
Mn	0.007	0.02	109	10	98	8	95	6
Mo	0.0001	0.0006	99	3	102	4	101	1
Na	0.2	0.7	102	3	107	3	106	2
Nb	0.0001	0.0003	96	2	97	2	96	1
Ni	0.002	0.006	98	3	99	3	95	1
P	0.6	2	98	3	105	4	105	1
Pb	0.001	0.005	90	5	91	3	90	1
Rb	0.0003	0.0008	100	5	106	2	105	2
Sb	0.0002	0.0007	90	2	90	2	90	1
Se	0.008	0.03	90	10	99	7	90	11
Si	1	4	99	15	90	12	90	2
Sn	0.0002	0.0007	91	2	91	3	91	1
Sr	0.005	0.02	110	3	110	4	93	1
Te	0.0005	0.002	90	4	90	1	90	5
Ti	0.002	0.008	106	3	106	3	101	2
Tl	0.00002	0.0001	93	4	93	3	91	1
U	0.00002	0.0001	94	3	94	3	92	1
V	0.003	0.008	90	10	92	6	91	4
W	0.002	0.006	95	3	96	3	95	0.1
Zn	0.2	0.8	101	3	105	5	100	3

Zr	0.0002	0.0008	90	2	90	6	91	1

Table 2a

Concentrations of elements [mean and standard deviation (SD); mg Kg^{-1}] in dairy milk and plant-based milk alternatives.

	Dairy milks						**Plant-based milk**							
							Legume-based		**Cereal-based**					
Element	**Cow**		**Goat**		**Donkey**		**Soy**		**Rice**		**Oat**		**Spelt**	
Major elements	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***
Ca[a]	1340	86	1209	99	329	21	1200[a]	-	39	11	174	36	109	34
K	1490	78	1829	140	271	6	1000	250	154	81	394	57	571	35
Mg	111	6	134	21	37.3	0.7	142	16	21.0	2.3	60	21	24.0	2.6
Na	346	26	507	150	118	1	251	22	275	180	364	93	329	26
P	481	25	534	71	104	3	311	100	76	36	147	37	105	7
Minor elements														
Al	<LOD	-	<LOD	-	0.053	0.016	0.190	0.095	0.050	0.038	0.065	0.048	0.067	0.025
B	0.15	0.10	0.112	0.101	<LOD	-	0.900	0.069	<LOD	-	<LOD	-	<LOD	-
Ba	0.109	0.093	0.097	0.033	0.094	0.068	0.110	0.065	0.061	0.011	0.102	0.012	0.0558	0.0030
Cu	0.0612	0.0048	0.121	0.022	0.0336	0.0037	1.08	0.03	0.080	0.082	0.103	0.036	0.166	0.009
Fe	0.227	0.065	0.247	0.056	0.244	0.017	3.43	0.28	0.127	0.056	0.33	0.13	0.233	0.011
Li	0.00159	0.00068	0.020	0.018	0.00582	0.00018	0.0032	0.0025	0.0046	0.0033	0.018	0.015	0.00305	0.00059
Mn	0.0200	0.0000	0.0478	0.0060	<LOD	-	1.44	0.16	0.23	0.17	0.45	0.26	0.567	0.039
Mo	0.0531	0.0064	0.0144	0.0053	0.00466	0.00076	0.361	0.073	0.060	0.015	0.129	0.029	0.0828	0.0073
Ni	0.0237	0.0032	0.0254	0.0050	0.0145	0.0033	0.119	0.023	0.030	0.024	0.127	0.071	0.0301	0.0051
Rb	1.32	0.33	3.51	0.41	0.194	0.004	0.46	0.10	0.1000	0.028	0.55	0.14	0.895	0.059
Se	0.0149	0.0054	0.0181	0.0037	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Si	6.26	0.97	7.33	0.69	3.76	0.36	12.5	3.8	10.3	1.7	13.1	5.3	11.2	1.2
Sr	0.430	0.088	0.76	0.18	0.209	0.008	0.420	0.042	0.16	0.13	0.59	0.36	0.0410	0.0058
Ti	0.0242	0.0025	0.055	0.046	0.00897	0.00038	0.061	0.034	0.0048	0.0017	0.019	0.013	0.0055	0.0011
Zn	4.54	0.76	3.25	0.80	0.537	0.029	2.06	0.24	0.47	0.12	0.386	0.069	0.62	0.37
Trace elements														

As	<LOD	-	<LOD	-	<LOD	-	0.016	0.012	0.0163	0.0098	0.008	0.010	<LOD	
Be	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	
Bi	0.00123	0.00068	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Cd	<LOD	-	<LOD	-	<LOD	-	0.00303	0.00044	0.0012	0.0017	0.00049	0.00042	0.000675	0.000091
Ce	<LOD	-	<LOD	-	<LOD	-	0.00050	0.00015	0.00029	0.00018	0.00085	0.00088	<LOD	-
Co	0.00254	0.00024	0.0039	0.0027	0.000669	0.000012	0.00632	0.00089	0.00095	0.00092	0.00125	0.00091	0.00078	0.00020
Cr	<LOD	-	<LOD	-	<LOD	-	0.0061	0.0029	0.0048	0.0036	<LOD	-	<LOD	-
Cs	0.00283	0.00054	0.0083	0.0015	0.00028	0.00002	0.00126	0.00027	0.000080	0.000020	0.00049	0.00025	0.00146	0.00007
Ga	0.00230	0.00016	0.0047	0.0036	<LOD	-	0.0039	0.0023	<LOD	-	0.0013	0.0012	<LOD	-
Hg	<LOD	-	0.00019	0.00013	0.000220	0.000014	0.000111	0.000058	0.000128	0.000085	0.000139	0.000070	0.000115	0.000007
La	<LOD	-	<LOD	-	0.000083	0.000023	0.00054	0.00013	0.00033	0.00034	0.00076	0.00081	0.000075	0.000011
Nb	0.00127	0.00014	<LOD	-	<LOD	-	<LOD	-	0.00130	0.00012	<LOD	-	<LOD	-
Pb	0.0015	0.0018	0.0019	0.0010	0.00326	0.00003	0.0027	0.0016	0.0057	0.0082	0.0029	0.0027	0.0015	0.0012
Sb	<LOD	-	0.00021	0.00022	<LOD	-	0.0023	0.0022	0.0012	0.0018	0.0022	0.0024	<LOD	-
Sn	<LOD	-	0.00028	0.00013	0.00811	0.00020	0.00034	0.00033	0.00033	0.00049	<LOD	-	<LOD	-
Te	<LOD	-	<LOD	-	<LOD	-	0.0011	0.0015	<LOD	-	0.00068	0.00073	<LOD	-
Tl	0.000115	0.000039	0.000186	0.000058	0.000085	0.000011	0.000101	0.000051	0.000030	0.000017	0.000049	0.000042	0.000043	0.000020
U	0.00005	0.00011	0.000043	0.000033	0.000188	0.000025	0.00073	0.00054	0.00054	0.00083	0.00111	0.00069	0.000078	0.000017
V	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-
W	<LOD	-	0.014	0.019	<LOD	-	0.0052	0.0042	0.0066	0.0064	0.0085	0.0073	<LOD	-
Zr	<LOD	-	<LOD	-	<LOD	-	0.00096	0.00026	0.00039	0.00040	<LOD	-	<LOD	-

[a] Ca added post processing to mimic the cow’s milk calcium levels.

Table 2b

Concentrations of elements [mean and standard deviation (SD); mg Kg^{-1}] in other plant-based milk alternatives.

	Plant-based milk													
	Nut-based										Seed-based		Pseudo-cereal based	
Element	**Almond**		**Coconut**		**Hazelnut**		**Walnut**		**Cashew**[a]		**Hemp**[b]		**Quinoa**[c]	
Major elements ***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	***mean***	***SD***	
Ca[d]	202	130	71	32	1200[a]	-	1200[a]	-	111	7	177	8	<LOD	-
K	230	75	1460	1000	306	1	223	4	217	1	982	38	224	4
Mg	95	28	165	120	71.9	0.5	77.1	1.1	70.3	0.5	121	4	32.7	0.7
Na	383	200	226	140	497	6	332	4	308	5	130	4	410	4
P	214	92	410	180	93.7	1.1	122	2	98.2	2.0	212	8	73.5	1.2
Minor elements														
Al	0.22	0.12	0.27	0.15	0.520	0.072	0.542	0.007	0.224	0.061	0.189	0.013	0.090	0.064
B	0.693	0.095	0.171	0.097	0.743	0.012	0.452	0.011	0.230	0.006	1.00	0.03	0.090	0.018
Ba	0.127	0.031	0.21	0.23	0.219	0.023	0.115	0.079	0.118	0.045	0.058	0.004	<LOD	
Cu	0.304	0.084	1.27	0.91	0.645	0.009	0.495	0.009	0.452	0.001	0.59	0.01	0.0605	0.0077
Fe	1.26	0.10	3.4	3.7	1.77	0.01	1.19	0.09	1.33	0.05	3.29	0.28	0.36	0.26
Li	0.0145	0.0083	0.0075	0.0046	0.00317	0.00085	0.0029	0.0016	0.0035	0.0025	0.00098	0.00024	0.0049	0.0014
Mn	0.689	0.056	2.5	2.9	0.955	0.054	0.987	0.032	1.08	0.02	0.90	0.05	0.0766	0.0029
Mo	0.0159	0.0060	0.036	0.015	0.0374	0.0026	0.0109	0.0012	0.0117	0.0051	0.411	0.028	0.0682	0.0061
Ni	0.018	0.022	0.61	0.44	0.044	0.019	0.157	0.016	0.095	0.011	0.153	0.003	<LOD	-
Rb	0.338	0.093	5.2	4.5	1.02	0.01	0.145	0.003	0.731	0.001	0.731	0.018	0.195	0.015
Se	<LOD	-	0.019	0.018	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Si	7.9	6.2	18	12	5.96	0.57	6.77	0.10	4.79	0.24	11.0	0.1	10.86	0.50
Sr	0.64	0.23	0.32	0.25	0.931	0.022	0.734	0.026	0.226	0.006	0.176	0.004	0.0172	0.0027
Ti	0.0302	0.0033	0.061	0.042	0.0375	0.0029	0.0403	0.0008	0.0268	0.0004	0.0524	0.0023	0.0152	0.0026
Zn	0.88	0.12	1.6	1.2	0.742	0.008	0.947	0.065	1.02	0.16	1.43	0.09	<LOD	
Trace elements														

As	<LOD	-	0.0059	0.0040	0.0172	0.0082	0.0065	0.0085	0.0057	0.0004	0.0085	0.0038	0.0108	0.0076
Be	<LOD	-	<LOD	-	0.00017	0.00013	0.000169	0.000034	<LOD	-	<LOD	-	<LOD	-
Bi	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Cd	0.00040	0.00033	0.0028	0.0015	0.0022	0.0024	0.00063	0.00046	0.0034	0.0025	0.00458	0.00012	0.00130	0.00073
Ce	0.00120	0.00074	0.00086	0.00050	0.00165	0.00025	0.00213	0.00045	0.000535	0.000010	0.00043	0.00002	<LOD	-
Co	0.0036	0.0014	0.0111	0.0042	0.00803	0.00073	0.0104	0.0003	0.00397	0.00015	0.00485	0.00071	0.00083	0.00014
Cr	<LOD	-	0.024	0.029	<LOD	-	0.0066	0.0027	<LOD	-	0.0038	0.0017	<LOD	-
Cs	0.00059	0.00019	0.025	0.024	0.00601	0.00001	0.00026	0.00011	0.00584	0.00026	0.00145	0.00023	0.000777	0.000085
Ga	0.00185	0.00030	0.0047	0.0032	0.00125	0.00007	0.00150	0.00017	0.00109	0.00019	0.00283	0.00038	0.00096	0.00020
Hg	0.000182	0.000013	0.000201	0.000039	0.000122	0.000001	0.000133	0.000064	0.000160	0.000007	0.000107	0.000028	0.000166	0.000062
La	0.0011	0.0010	0.00089	0.00090	0.00161	0.00012	0.00242	0.00037	0.00036	0.00011	0.00022	0.00013	0.000119	0.000007
Nb	<LOD	-	0.00130	0.00015	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Pb	0.00244	0.00063	0.0060	0.0062	0.00303	0.00005	0.0094	0.0094	0.015	0.016	<LOD	-	<LOD	-
Sb	0.0016	0.0016	0.0031	0.0017	0.0027	0.0012	0.00386	0.00028	0.0033	0.0013	0.0035	0.0017	<LOD	-
Sn	<LOD	-	0.0018	0.0014	<LOD	-	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Te	0.00063	0.00064	0.00051	0.00099	0.00069	0.00091	0.00134	0.00006	0.00069	0.00091	<LOD	-	<LOD	-
Tl	0.000111	0.000059	0.00112	0.00091	0.000263	0.000008	0.0000765	0.0000001	0.0000697	0.0000061	0.000023	0.000011	0.000181	0.000034
U	0.00115	0.00041	0.0019	0.0018	0.00073	0.00012	0.00116	0.00021	0.000062	0.000015	0.000313	0.000001	<LOD	-
V	<LOD	-	0.0045	0.0040	<LOD	-	0.00555	0.00059	<LOD	-	<LOD	-	<LOD	-
W	0.0058	0.0036	0.0031	0.0016	0.0039	0.0034	<LOD	-	0.0044	0.0025	<LOD	-	0.00811	0.00069
Zr	0.0019	0.0027	0.0032	0.0027	0.00066	0.00019	0.00062	0.00023	<LOD	-	<LOD	-	<LOD	-

[a] Cashew milk with almond and hazelnut.

[b] Hemp milk with soy and rice.

[c] Quinoa milk with rice.

[d] Ca added post processing to mimic the cow's milk calcium levels.

Table 3

Significant differences ($p < 0.05$) within means of the analysed elements and among all samples from different varieties by analysis of variance (ANOVA) and Tukey's honestly significant difference (HSD) test.

	Cow 1	Goat 2	Donkey 3	Soy4	Hemp7	Rice9	Quinoa10	Oat11	Spelt12	Almond13	Halzenut14	Cashew15	Walnut16	Coconut17
Goat2	Bi, Li, Sr, W, Zn	-												
Donkey3	Bi, Ca, K, P, Sn, Zn	Ca, K, Na, P, Sn, Sr, Zn	-											
Soy4	Al, As, B, Bi, Cd, Co, Cu, Fe, Mo, P, Ti, Zn	Al, B, Cd, Cu, Fe, K, Li, Mo, Na, P, Rb, Sr	B, Cd, Co, Cu, Mo, Sn	-										
Hemp7	B, Bi, Ca, Cd, Fe, Mo, P, Zn	B, Ca, Cd, Mo, Na, P, Sr	B, Cd, Mo, Sn	-	-									
Rice9	As, Bi, Ca, K, Mg, P, Sr, Zn	Ca, Ga, K, Li, Mg, Na, P, Rb, Sr, Ti, Zn	Sn	B, Cd, Co, Cu, Fe, Ga, K, Mg, Mo, P, Ti, Zn	B, Cd, Mo, Ti	-								
Quinoa10	Bi, Ca, K, P, Zn	Ca, K, P, Sr, Zn	Sn	B, Co, Mo, P	B, Cd, Mo	-	-							
Oat11	Bi, Ca, Ce, K, Li, Mo, P, Zn	Ca, K, Mo, P, Zn	Mo, Sn	B, Cd, Co, Cu, Fe, Mo, Zn	B, Cd, Mo	Mo, Sr	Sr	-						
Spelt12	Bi, Ca, K, P, Zn	Ca, K, P, Sr, Zn	Sn	B, Co, Cu, Mg, Mo	B, Cd, Mo	-	-	Sr	-					
Almond13	Al, B, Bi, Ca, Ce, K, La, Li, P, U, Zn	Al, B, Ca, Ce, K, La, P, Rb, Zn	B, Ce, Sn	As, B, Cd, Ce, Cu, K, Mo	B, Cd, Sr, Mo	Al, As, B, Ce, Sr	B, Ce, Sr	B, Mo	B, Ce, Sr	-				
Halzenut14	Al, As, B, Be, Bi, Ce, Co, K,	Al, B, Be, Ce, K, La, P, Zn	Al, B, Be, Ce, Co, Na, Sn, Sr	Al, Be, Ce, Mo, Sr	Al, Be, Ce, Mo, Sr	Al, B, Be, Ce, Co, Sr	Al, B, Be, Ce, Co, Sr	Al, B, Be, Co, Mo	Al, B, Be, Ce, Co, Sr	Al, Be, Co	-			

	La, P, Sr, Zn													
Cashew15	Al, Bi, Ca, Cd, K, P, Pb, Zn,	Ca, Cd, K, P, Pb, Sr, Zn	Cd, Sn	B, Mo, Pb	B, Mo	-	-	Cd, Mo	-	B, Cd	Al, B, Be, Sr	-		
Walnut16	Al, B, Be, Bi, Ce, Co, K, La, P, Rb, Zn	Al, B, Be, Ce, Co, K, La, P, Zn	Al, B, Be, Ce, Co, La, Sn	Al, B, Be, Ce, La, Mo	Al, B, Be, Cd, Ce, La, Mo	Al, Be, Ce, Co, La, Sr	Al, B, Be, Ca, Ce, Co, La, Sr	Al, B, Be, Ca, Ce, Co, La, Mo	Al, B, Be, Ca, Ce, Co, La, Sr	Al, Be, Co	-	Al, Be, Ce, Co, La	-	
Coconut17	Al, Bi, Ca, Cd, Ce, Co, Cs, Cu, Fe, La, Mn, Ni, Rb, Sn, Si, Ti, Tl, U, V, Zn, Zr	Al, Ca,Cd, Ce, Co, Cs, Cu, Fe, Mn, Na, Ni, Si, Sn, Sr, Tl, U, V, Zn, Zr	Al, Cd, Co, Cs, Cu, K, Mg, Ni, P, Rb, Si, Sn, Tl	B, Co, Cr, Cs, Mo, Ni, Rb, Se, Sn, Tl, Zr	B, Co, Cr, Cs, Mo, Ni, P, Rb, Sn, Tl	Al, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Mg, Mn, Ni, P, Rb, Se, Sn, Ti, Tl, U, Zr	Co, Cs, Cu, K, Mg, Ni, P, Rb, Sn, Tl, U	Al, Cd, Co, Cs, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Rb, Sn, Tl, Zr	Co, Cs, Cu, Mg, Ni, P, Rb, Sn, Tl	B, Cd, Co, Cu, Cs, K, Mn, Ni, P, Rb, Se, Si, Sn, Tl	Al, B, Be, K, Ni, P, Rb, Sn, Sr, Tl	Co, Cu, K, Ni, P, Rb, Sn, Tl	Al, B, Be, Ce, Cs, K, La, Ni, P, Rb, Sn, Tl	-

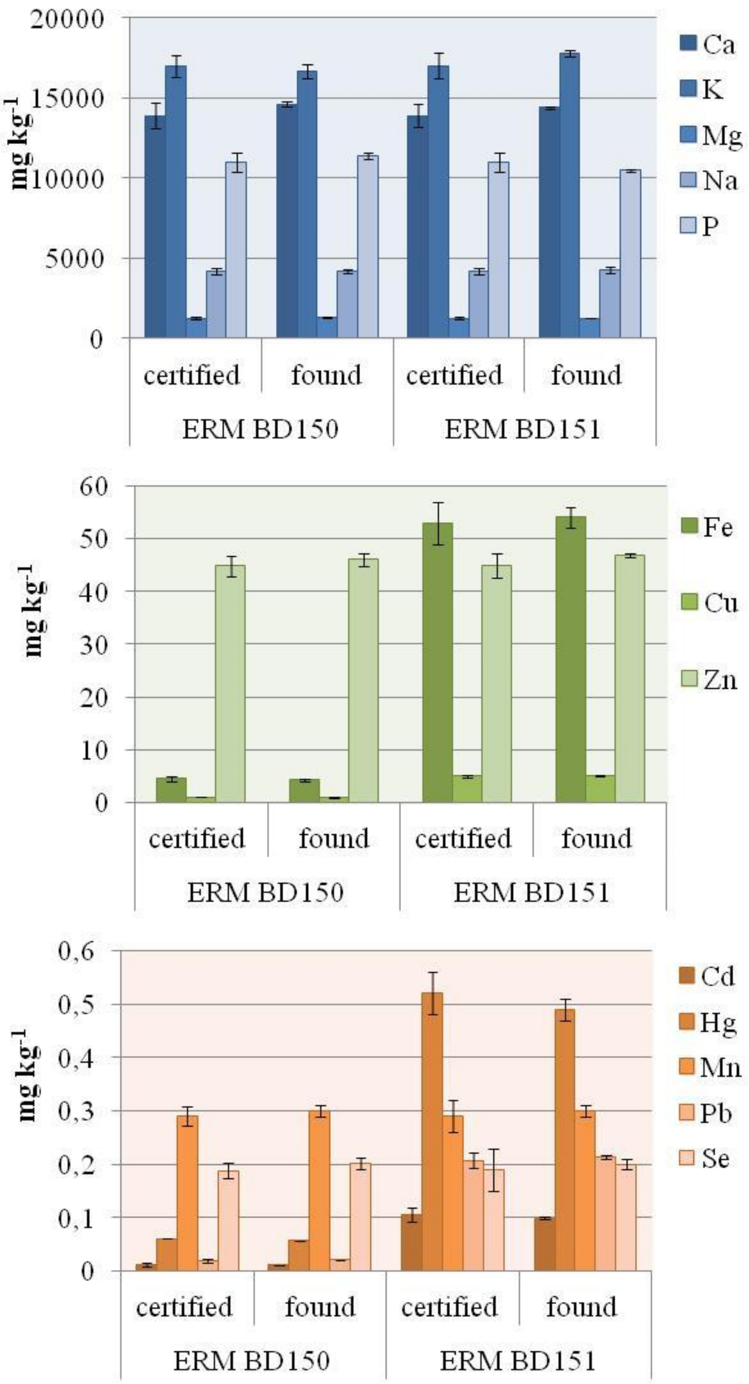

Fig. 1. Certified and found concentrations [mg Kg^{-1}; mean ± standard deviation (SD)] for major (Ca, K, Mg, Na, and P), minor (Fe, Cu, and Zn), and trace (Cd, Hg, Mn, Pb, and Se) elements in skimmed milk powder certified material (ERM®-BD150 and ERM®-BD151).

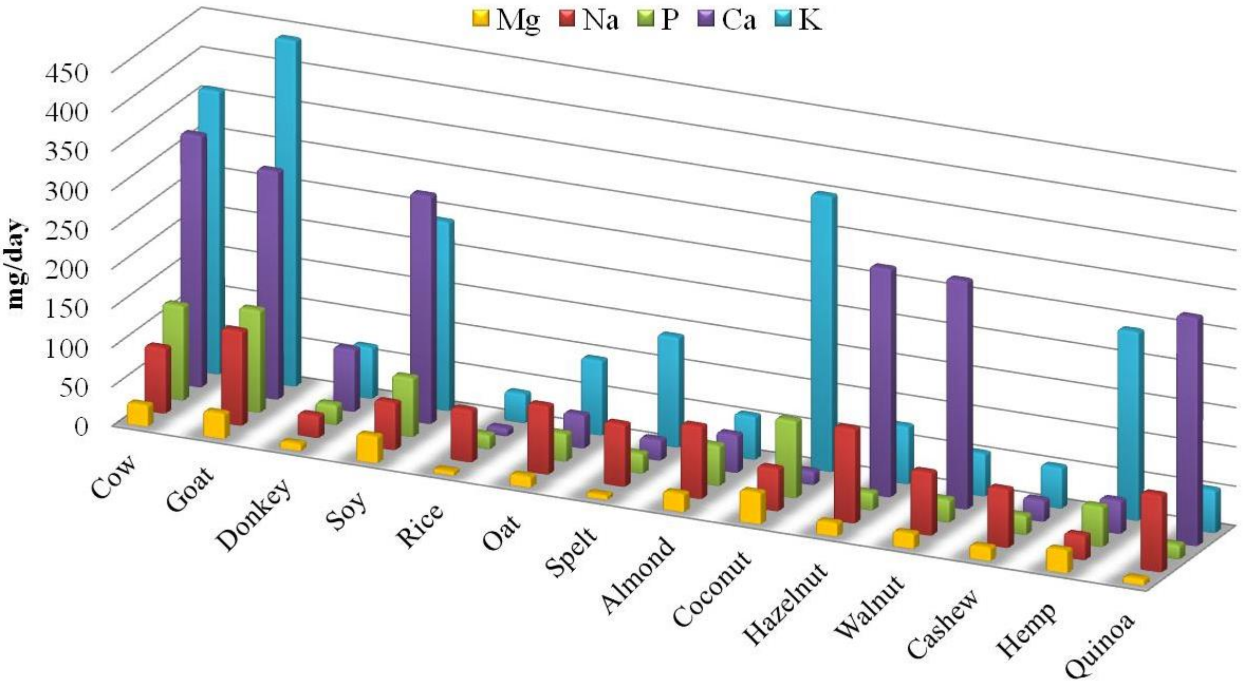

Fig. 2. Major element contents (mg/day) in cow's milk and plant-based beverages (per 240 mL = 1 serving).

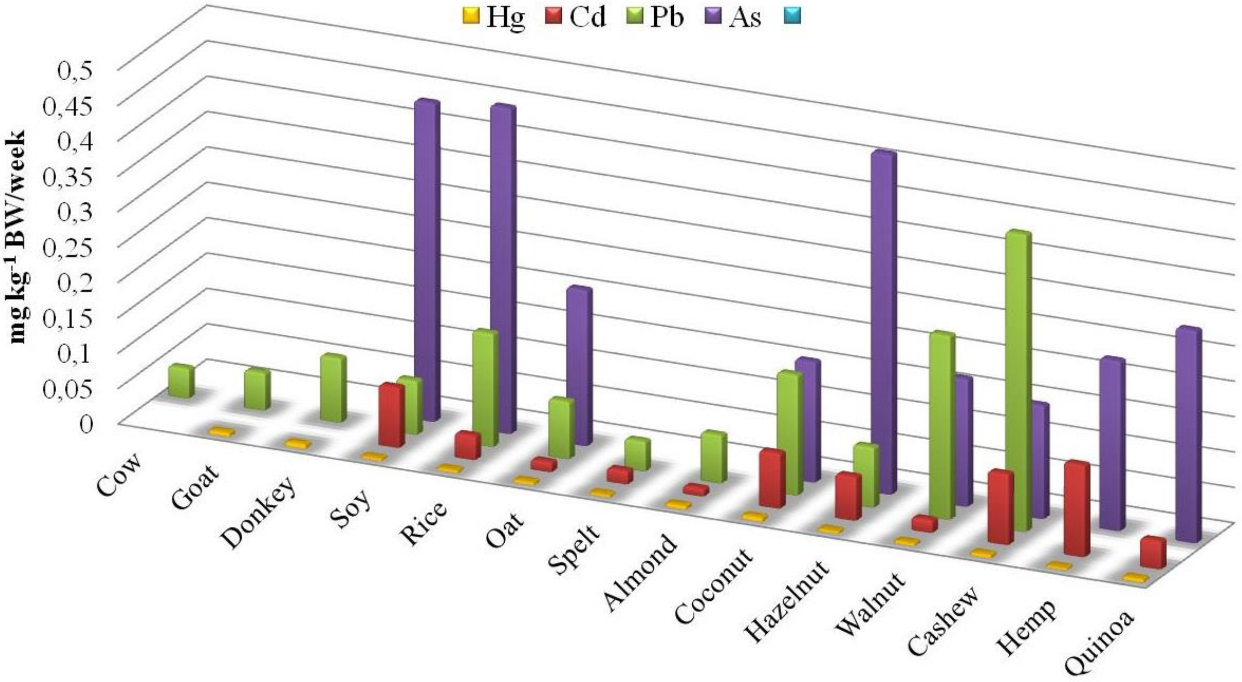

Fig. 3. Intake estimations for some toxic elements [body weight, BW = 60 kg; μg kg^{-1} BW/week] in cow's milk and plant-based beverages (per 240 mL = 1 serving). The data not shown are lower than the determination limits.