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ARTICLE

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ABSTRACT

The aim of this work was to determine Ni, Cr, Cu, Zn, Pb, and As levels in raw milk and Oaxaca and ranchero type cheeses, produced in areas irrigated with waste water from Puebla in Mexico. Milk results showed a mean Pb level of 0.03 mg kg^{-1}, which is above the maximum limit as set by Codex Alimentarius and the European Commission standards. For As a mean value of 0.12 mg kg^{-1} in milk was obtained. Mean As and Pb levels in milk were below the Mexican standard. Milk whey and ranchero cheese had mean Pb levels of 0.07 and 0.11 mg kg^{-1}, respectively. As was higher in Oaxaca and ranchero cheese at 0.17 and 0.16 mg kg^{-1}, respectively. It was concluded that cheeses made from cow's milk from areas irrigated with waste water are contaminated with Pb and As, which may represent a health risk.

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Heavy metal; lead; arsenic; cheese; milk; whey; environment; pollution

Introduction

Milk is a food of great importance for its nutritional content mainly for children. However, milk can be contaminated in different ways, where heavy metals are important because they can appear in milk due to cows that consume environmental water and/or contaminated feed. Milk contamination can be transferred to dairy products such as cheeses, which are considered as a healthy food and important for the human diet, due to its high protein, fat, and mineral content (Yuzbası et al. 2003; Pattnaik et al. 2008). Among the many factors involved in the contamination of cheeses by heavy metals is the use of milk produced in areas contaminated by irrigation with waste water from the industry. These may also present contamination with heavy metals due to the processing practices and equipment used during the process (Moreno Rojas et al. 1994; Garau et al. 2007).

This is important because children are the ones who consume milk and their by-products, being more sensitive to the absorption of heavy metals (Tripathi et al. 1999). In addition, regular intake of small amounts can cause serious health of growing children by affecting mental development (Salma et al. 2000). On the other hand, the International Agency for Research on Cancer (IARC 2016) classifies arsenic (As) and chromium (Cr) as being carcinogenic metals and in the case of Pb as a possible carcinogen. Such metals can cause different types of cancer due to dermal contact, inhalation, and ingestion.

Therefore, the aim of this work was to determine the content of heavy metals (Ni, Cr, Zn, Pb, and As) in raw milk and in Oaxaca and Ranchero type cheeses in an area irrigated with waste water in the state of Puebla, Mexico.

Material and methods

Location

The work was carried out in June (summer) 2016, in Santa Ana Xalmimilulco, belonging to the municipality of Huejotzingo in the state of Puebla at the geographical coordinate's latitude 19.12′30.81″ N and longitude 98.24′36.78″ O and an altitude of 2228 m. This site concentrates on the production of milk used to make cheeses. The milk comes from different neighbouring communities that together produce an estimated total of 45 tons of raw milk. For that milk production fodder is used which is irrigated by water of the river Atoyac and its effluents (Xopanac and Xochiac river) that receive effluents of different industries located in textile city Quetzalcoatl industrial park and a petrochemical plant.

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Sampling

Milk samples were randomly taken from milk storage tanks from the different locations in the centre-west of Puebla, where forage is irrigated with waste water. A total of 5 samples of milk, 7 of pasta (curd), 7 of milk whey, 1 of Oaxaca cheese, and 1 of ranchero cheese were collected in triplicate, weekly during 4 weeks. Milk sample sizes were 16–21 ml and cheese sample sizes were 22–38 g. Liquid samples were collected in polypropylene flasks previously rinsed with nitric acid and three times with deionised water to remove acidic debris. At a later stage, 50 ml Falcon tubes were applied, prepared in the same manner as the polypropylene flasks. All samples were transferred in a refrigerator to the laboratory where they were frozen at −80ºC. The samples were then lyophilised over a freeze dry system (FreeZone 4.5 Litre Benchtop, Kansas City, MO, USA). Milk, milk whey, curd, and cheeses were digested in a microwave oven (CEM MarsX, CEM Corporation, Mathews, NC, USA). A 0.5 g lyophilised portion from each of the components was weighed and 10 ml HNO_3 was added (High purity 65%, Suprapur, Merck, Darmstadt, Germany). The tubes were placed in the microwave oven at a power of 1600 W, 15 min on the ramp at a pressure of 800 psi and 200ºC and on hold for 15 min. After full digestion, the samples were filtered on Whatman grade 42 paper (GE Healthcare, Little Chalfont, UK), diluted to 50 ml with deionised water, and refrigerated upon analysis.

Determination of metals

Pb, Ni, Cu, Cr, Zn, and As were determined in milk, milk whey, curd, and cheese by inductively coupled plasma optical emission spectroscopy (ICP–OES, Varian 730, Varian Australia, Mulgrave, Victoria) which has a nebuliser seaspray, ezylok, and a spray chamber glass spantion (Agilent Technologies, Santa Clara, CA, USA). For the determination of As, the hydride technique of ICP–OES was used. All chemicals employed were of analytical reagent grade. The solutions were prepared in 18.2 MΩ cm^{-1} deionised water.

The calibration standards for each metal were prepared using a multi-element standard XVI solution for ICP, composed of 21 elements in HNO_3 Suprapure 6%, with a density of 1.032 g/cm^3 and 20ºC of Merck (Darmstadt, Germany).

Levels of precision and accuracy were realised with 5 blanks with 10 repetitions. Quality control was performed using a control standard and control sample, which were used in every series of 20 samples analysed. Analytical recovery values were determined at 104% on average and the correlation coefficients (r^2) were 0.9999. The limits of detection and of quantification were calculated with 3 and 10 times the standard deviation of the blank divided by the slope of the analytical curve, respectively. This allows to determine the minor and trace elements in the sample (Khan et al. 2014).

Results

LOD and LOQ were 0.0001 and 0.0003 mg/kg respectively. A significant content of Pb and As was found in raw milk used for cheese production. Values found for As, Cu, and Ni during the cheese-making process showed ($p < 0.001$) a significant difference (Table 1), where milk whey had the highest values with respect to the other components. In the case of Pb, it was the ranchero cheese that obtained the highest content with respect to the other stages of the process of elaboration, with an ascending order of Ranchero cheese > milk whey > Oaxaca cheese > milk > curd. Cr and Zn showed higher values in raw milk and Oaxaca cheese compared to the other components at different stages of cheese production. During cheese processing, heavy metals were found (Table 1), where milk whey was the component that showed the highest As content, with a decreasing order of milk whey > Oaxaca cheese > ranchero cheese > milk > curd.

Table 1. Metals in milk (mean ± standard deviation; mg kg^{-1}) obtained in an area irrigated with waste water in Puebla, Mexico, and at different stages of cheese processing.

Metal	Milk $n = 60$	Curd $n = 84$	Whey $n = 84$	Oaxaca cheese $n = 12$	Ranchero cheese $n = 12$
As	0.12 ± 0.08^{b}	0.07 ± 0.05^{b}	0.52 ± 0.4^{a}	0.17 ± 0.1^{b}	0.16 ± 0.07^{b}
Pb	0.03 ± 0.01^{d}	$0.02 \pm 0.0d^{d}$	0.07 ± 0.02^{b}	0.05 ± 0.03^{c}	0.11 ± 0.04^{a}
Cu	0.01 ± 0.01^{b}	0.02 ± 0.01^{b}	0.05 ± 0.03^{a}	0.02 ± 0.01^{b}	0.02 ± 0.01^{b}
Cr	0.03 ± 0.02^{a}	0.03 ± 0.02^{ab}	0.02 ± 0.01^{abc}	0.01 ± 0.01^{c}	0.02 ± 0.01^{bc}
Ni	0.01 ± 0.02^{b}	0.002 ± 0.003^{b}	0.06 ± 0.02^{a}	0.003 ± 0.005^{b}	0.01 ± 0.01^{b}
Zn	0.71 ± 0.09^{a}	0.69 ± 0.2^{a}	0.23 ± 0.09^{b}	0.18 ± 0.09^{a}	0.74 ± 0.1^{b}

Different literals (a, b, c) present significant differences ($p < 0.001$).

Discussion

Evaluating Pb content found in this study, it was observed that it was above the maximum level according to European (European Commission 2006) and Codex standards (Codex Alimentarius 1995) of 0.020 mg kg^{-1} for milk and cheeses. As content was 0.12 mg kg^{-1} in milk, which is in the range of 0.10–0.30 mg kg^{-1} for EU limits in different categories of rice and rice products only. This might be a reason to pay attention to it, since it is a very dangerous element for human health and may cause a carcinogenic effect due to increased oxidative stress, direct genotoxicity, altered DNA repair, and expression of the growth factor (Ghosh and Sil 2015). However, the values found in this study for As and Pb are lower than those established by the Mexican Official Standard (NOM-184-SSA1-2010), which are 0.1 and 0.2 mg kg^{-1}, respectively.

Several authors have conducted research on metals in milk. Kazi et al. (2009), in Pakistan, found 51.1 µg Pb l^{-1} in milk. Rahimi (2013) reported 1.93 ng l^{-1} in Iran and stated that this value can vary due to the sampling area and the time of year. Similarly Patra et al. (2008), in India reported a Pb value of 0.85 µg l^{-1} in zones with mining and iron manufacturing activities. Ismail et al. (2015), in Punjab province, Pakistan, found in the main industrial zone values for Pb of 0.023, for Cu of 0.84, and for Ni of 0.032 mg kg^{-1} in cow milk. Kim et al. (2016), in Korea, reported a content of 1.48 µg kg^{-1} for Pb in milk, below levels found in this work. In an area irrigated with waste water of industrial origin in Puebla and Tlaxcala, Mexico, Castro-Gonzalez et al. (2017) reported 0.048 mg kg^{-1} for Pb, which is higher than in this study and for As a value of 0.038 mg kg^{-1}, that is below as found in this study. On the other hand, Bilandžić et al. (2011) reported for Pb a value of 58.7 µg l^{-1} in the northern part of Croatia and 36.2 µg l^{-1} for the southern regions, both value higher than as established in this study.

Moreno-Rojas et al. (2010) analysed 50 varieties of Spanish cheeses and reported an average value of 32.8 ± 19.9 µg kg^{-1} for Pb, lower than the value obtained in this study for the two varieties of cheese (Ranchero and Oaxaca). Yüzbasi et al. (2009) compared the different stages of the Kasar-type cheese-making process by evaluating Pb content in milk, milk whey, curd, and fresh cheese in Turkey, obtaining 0.63, 0.14, 0.91, and 0.37 mg kg^{-1} for Pb, respectively, values higher than those measured in this study. In Italy, Anastasio et al. (2006) reported Pb values of 0.58 µ g^{-1} in mature cheese and 0.39 µg g^{-1} in ricotta, values higher than those measured in this study.

The highest Pb content was found in ranchero cheese and milk whey. This is probably due to the process of making this type of cheese. When the enzyme (rennet) is added to the milk, it initiates the hydrolysis of the milk protein (*κ*-casein) into two compounds: curd and milk whey. Curd is mainly composed of saturated fats, lactose, and casein. Milk whey is the precursor of ranchero cheese, which contributes to increase the Pb content. Increasing the level of protein increases the content of this metal due to the affinity of this metal for the proteins of the milk whey (Ayar et al. 2009). Another important aspect is the moisture content present in the cheeses, because with a higher water content, the metals are diluted (Moreno-Rojas et al. 2010). Thus, in ranchero cheese, having a final pressing to shape and pack it by applying a mechanical press, removal of excess moisture raises the As level as well. As has a high affinity for lipids and tends to be found in higher levels in milk whey, showing similar values in both types of cheeses.

According to Castro-González et al. (2017), milk could be considered as a high risk for health due to the content of Pb and As found, which showed that although the content of these metals is below the allowable values, the health risk is high because of the amount of milk ingested daily. On the contrary, in relation to the cheeses, Moreno-Rojas et al. (2010) mentioned this represents no danger for human health, because the consumption of cheese is low. In Mexico, the per capita consumption of cheese is only 2.1 kg year^{-1} (Cesin-Vargas 2014). Therefore, if a daily consumption of Pb of 25 µg/kg body weight/week is considered, the intake of a consumer of cheese would be 0.17 µg/kg body weight/week of Pb. In case of As, with a total weekly intake of 15 µg/kg/body weight/week (FAO/WHO 1993), according to consumption in Mexico, a person would be ingesting 4.8 µg kg/body weight/week, which is below the weekly intake. However, it has to be considered that people could consume both products, so the risk could be even greater, also due to more items of the daily consumption.

Conclusion

According to the results obtained, it is concluded that the milk produced in regions irrigated with waste water were contaminated with heavy metals such as Pb and As. Also, during cheese processing, the metals were distributed in different fractions, where the Ranchero cheese and milk whey were the ones that had the highest content of these toxic metals. It is important to carry out health risk assessment studies on the consumption of both products in the population on, as well as to search for nutritional alternatives for cows, as to obtain milk free of heavy metals and to prevent diseases in the population.

Disclosure statement

No potential conflict of interest was reported by the authors.

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