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RESEARCH ARTICLE

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Some toxic metals (Al, As, Mo, Hg) from cow's milk raised in a possibly contaminated area by different sources

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Abstract

Milk can be considered as an indicator of the degree of environmental contamination of the place where it is produced and this is especially important when assessing its content in toxic metals. Therefore, 36 bovine milk samples from 7 farms with a semi-extensive grazing system were analysed, located in Asturias (Spain), in an area with high probability of being highly contaminated due to a mining zone, with important industrial activity and near high-density highway traffic. The samples were lyophilised to achieve total dehydration, further analysed using inductively coupled plasma mass spectrometry (ICP-MS). The metals titrated were aluminium (Al), arsenic (As), molybdenum (Mo) and mercury (Hg) in the lyophilised samples and subsequently extrapolated their values to whole milk. All samples analysed showed levels of Al and Mo above the limit of detection, with mean values of Al of 140.89 ± 157.07 in liquid milk and 1065.76 ± 1073.45 in lyophilised milk and Mo of 20.72 ± 14.61 μg/kg and 152.26 ± 96.82 μg/kg in whole and lyophilised milk. Only As was detected in four samples with mean values of 18.45 ± 6.89 and 166.45 ± 42.30 μg/kg in liquid and lyophilised milk, respectively, and no Hg was found in any of them. In no case do the values found indicate a significant hazard to the population and are in agreement with those found in other investigations. Although the various anthropogenic activities of the area (industrial, mining, traffic density) could, a priori, indicate a possibly contaminated area.

Keywords Heavy metals · Bovine milk · Environmental contamination · Mining · Caudal River

Introduction

Until a few years ago, the quality of milk has been valued exclusively for its chemical composition, microbiological quality and CCS. However, its level in minerals has rarely been thought about and especially in those potentially toxic. The growing interest in the content of mineral elements in milk is given by its use as an indicator of quality, whose ultimate objective is to ensure and offer a safe food, with adequate nutritional wealth. Today, the consumer is more demanding than in the past and expects "healthy" milk, rich in nutrients, with high biological value, but without health risks (Licata et al. 2004). Therefore, milk mineral levels are both a direct indicator of the hygienic state of milk and an indirect indicator of the degree of environmental contamination of the place where milk is produced (Simsek et al. 2000; Serdaru et al. 2001; Licata et al. 2004; Pavlovic et al. 2004; Baranowska et al. 2006; Gonzalez-Montaña et al. 2012).

Minerals in milk can be classified into macrominerals and microminerals, which in turn are subdivided into four categories: (1) essential, required in man's diet and some animal species such as iron, zinc, copper, manganese, molybdenum, cobalt, selenium, iodine, and fluoride; (2) possibly essential, probably required in the diet of some animals under strict surveillance, but are not considered necessary for man, indicating chromium, nickel, silicon, tin, and vanadium; (3) toxic substances, those that cause problems more because of their excess than because of their deficiency under normal conditions of life in man and animals such as aluminium, arsenic,

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cadmium, lead, and mercury; and (4) other elements considered as sporadic contaminants in animals, which with the advances in techniques of analysis and other scientific findings can change in category (Olson 2007; Suttle 2010).

Living beings "need", in small quantities, many of these elements. However, both a deficiency and an excessive concentration can alter a great variety of biochemical and/or physiological processes in the organism. The so-called trace elements or microminerals, which although they are required in minimum quantities by the organism—micrograms to milligrams/day—, sometimes their accumulation can trigger a series of harmful effects, ranging from infertility to chronic diseases—liver failure, kidney failure—or cancerous diseases.

Metals are found naturally in the soil and in the environment, usually at such concentrations that do not harm the different life forms. Although there are a multitude of factors to consider when assessing the presence of metals in food of animal origin, we can point out four large groups of factors that affect the levels of metals in the environment and therefore in animals and their milk. This includes factors dependent on the animal, factors dependent on climatic and edaphic factors, factors dependent on food and factors related to anthropogenic activities (Perween 2015; Tunegová et al. 2016).

Many of these elements are related to the industrial, mining, agricultural and livestock contamination present in the area favouring greater exposure to these pollutants (Serdaru et al. 2001; Baranowska et al. 2006; Vidovic et al. 2005). There are many examples relating high levels of lead, cadmium, mercury and other metals with animals that live in areas of extensive steel activity and with industrial plants of all kinds, near coal-fired power plants, petroleum-related facilities—wells, oil pipelines and refineries—, in areas of great mining extraction—iron, lead, gold and especially coal—, in the vicinity of highways and roads with a large influx of vehicles and in cities with a high concentration of people (Simsek et al. 2000; Serdaru et al. 2001; Baranowska et al. 2006; Vidovic et al. 2005; Perween 2015; Norouzirad et al. 2018).

Metals reach the milk through the ingestion, on the part of the animals, of the plants that settle in the zone of grass, in the fields of production of cereals or through the water of drink and thus are incorporated into the food chain, finally reaching people (Dwivedi et al. 2001; Baranowska et al. 2006; Patra et al. 2008; Jigam et al. 2011; Perween 2015). There is a direct relationship between atmospheric deposits of heavy metals and distribution in the food chain (Serdaru et al. 2001; Vidovic et al. 2005; Tunegová et al. 2016).

Lead, cadmium, zinc and other metals can cross the breast barrier, making milk a high-risk factor for consumers (Serdaru et al. 2001). Although most research is inclined to value the levels of various metals, they should always be below the values recommended by international law (Codex Alimentarius, European Union Regulations, FAO/OMS) so that milk is suitable for human consumption. In other cases, the main interest is to discard the presence of some metals, especially toxic, such as Hg and As (Rahimi 2013). Therefore, it is important to monitor the metals present in the milk produced in the Caudal mining area (Asturias, Spain), a potentially contaminated area. We must consider this research as a continuation of the one conducted in the same area, measuring the amount of Pb and Cd present in the milk samples (Gonzalez-Montaña et al. 2012).

The aim is to evaluate the concentrations of aluminium (Al), arsenic (As), manganese (Mn) and mercury (Hg) in raw milk from cows from the Caudal River area (Asturias, Spain). Therefore, in addition to checking whether the milk produced in this area is suitable for human consumption, we want to correlate the concentrations indicated above with the various anthropogenic activities of the area—industrial activity, mining and traffic density of the area. We will try to correlate the concentrations of the different metals present in the milk, trying to justify if possible the relationship that exists among them. Finally, we intend to compare the measured values with those found by other researchers in milk produced in similar areas.

Material and methods

Collection and preparation of the samples

The animals sampled, the farms where the animals were selected and the collection system were described in Gonzalez-Montaña et al. (2012). All the samples were collected from the Asturian Valley cattle breed. Each animal was approximately 8 years old and having lived in this area for at least the last 3 years. The cattle were fed predominantly with local forage. However, on some occasions, they were also given locally produced hay and silage. The farms sampled were randomly chosen, but always bearing in mind that they were representative of the type and number of farming in the area. Recall that 36 raw milk samples were obtained from healthy animals, reared in a medium and extensive production system and were collected in seven farms located in the Caudal area (Asturias, Spain). We consider that different levels of contamination were due to their location close to the steel industry, mineral extraction and deposit areas or thermal power stations (Fig. 1).

Farms I and VII are located at a distance of 2000 and 500 m respectively from the Mineral Treatment Plant in Reicastro, considered as one of the most important mineral deposits in Asturias. In addition, farm I is situated at approximately 500 m from one of the main glass transformation factories in South-Europe. Farms II, III and V are a priori considered as the highest risk areas due to their particular location. Farm II is located very close to La Pereda Thermal Power Station and at hardly 500 m away from an important mining waste depot. Farm III is situated in the Black River Valley, which takes its

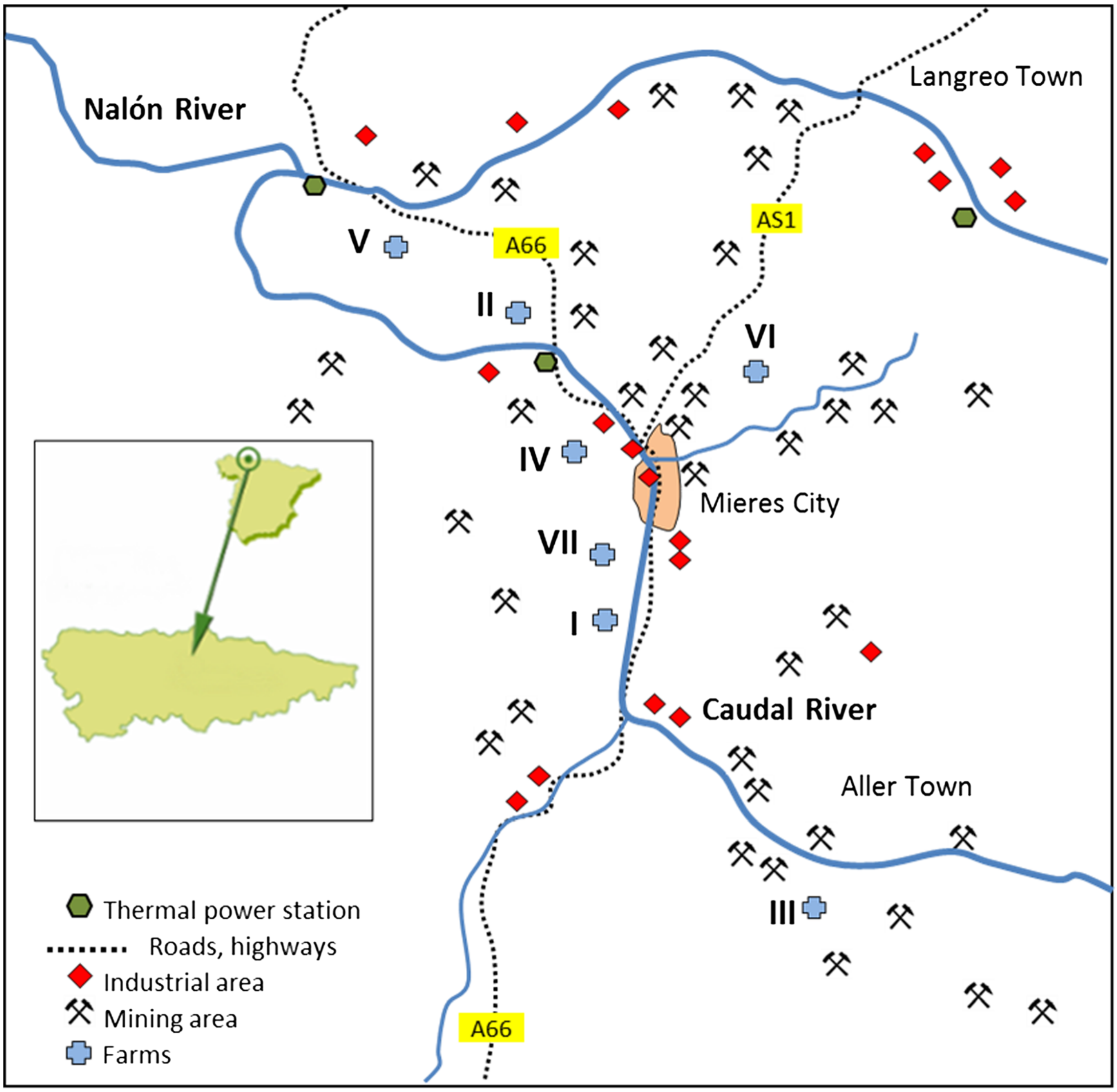


Fig. 1 Sampled farms and pollutant related areas

name from the fact that it was used to wash the coal of several mines of the valley during decades. Farm V is located on the top of a hill which is only at 300-m distance from the thermal power station of Soto de Ribera, which is one of the most productive in Spain, and close to several mines from the Morcin district. Farms IV and VI are placed close to urban areas and also to former mining zones and, apart from this, farm IV is located next to the main road that connects Asturias with the rest of Spain, although farm VI is on top of the old mining centre of Rioturbio.

Milk samples were collected in sterile precleaned polypropylene tubes of 50 ml, close to 118 postpartum days, between October and February. After being identified, they were frozen (KOMA, 80/20 System) under − 20 °C until their analysis. All samples were lyophilized to achieve their total dehydration. The analyses were made in the Laboratory of Instrumental Technologies (LTI) at the University of León.

Analytical method

Measured metals were aluminium (Al), arsenic (As), molybdenum (Mo) and mercury (Hg) in samples of lyophilised milk, and later their values were extrapolated to whole milk. The method used for the analysis was that of Pavlovic et al. (2004), modified to suit our circumstances. The quantification was performed by inductively coupled plasma mass spectrometry (ICP-MS, Varian; ICP-MS, Perkin Elmer Optima 4300 DV), capable of detecting elements in liquid matrices with sensitivities less than 0.1 μg/kg. To check the accuracy of the analytical method, a mixture of internal elements (Sc, Y, Pt, Pd and Rh) and a multi-element standard solution (Merck) of different known concentrations (0.2, 50 and 100 μg/kg) was used, with a recovery rate between 82.9 and 104.7%. The technique has been described in more detail in Gonzalez-

Montaña et al. (2012). The concentrations of the metals were expressed in μg/kg.

Statistical analysis

At first, we carried out an explorative statistical analysis (SPSS v. 13.0) of the concentration values measured. The number of samples (n), mean (m), maximum value (max), minimum value (min) and standard deviation (SD) are indicated. Subsequently, a correlation analysis was performed to measure the relationship between the different metals present in the samples. The p value < 0.05 was chosen for statistical significance.

Results

Metal levels in liquid and f lyophilized milk

The values of Al, As, Mo and Hg—aluminium, arsenic, molybdenum and mercury—obtained in the analysed milk samples are presented in Tables 1 and 2 and Fig. 2. All samples had levels of Al and Mo above the limit of detection. Only As was detected in some samples, whereas no Hg was found in any of them.

Aluminium mean value is 140.89 ± 157.07 μg/kg in liquid milk and 1065.76 ± 1073.45 μg/kg in lyophilised milk, with values between 9.99 and 684.60 μg/kg in liquid milk and 67.29 and 4265.59 μg/kg in lyophilised milk. Aluminium levels for farm are very different, ranging from the highest in farm II (280.88 μg/kg) and farm III (206.71 μg/kg) and the lowest in livestock VI (22.78 μg/kg) in liquid milk and between 150.04 and 1951.71 μg/kg in lyophilised milk.

Table 1 Statistical values about metal levels (Al, As and Mo) in lyophilized milk and liquid milk

	Lyophilised milk			Liquid milk		
	Al	As	Mo	Al	As	Mo
N	36	4	36	36	4	36
Mean	1065.76	166.45	152.26	140.89	18.45	20.72
Geometric mean	625.30	162.55	113.32	80.48	17.63	14.59
Median	688.98	158.43	141.06	93.49	15.91	17.93
Min.	67.290	129.650	18.530	9.990	13.410	2.060
Max.	4265.59	219.30	326.37	684.60	28.58	52.75
Lower quartile	234.89	132.36	59.00	36.18	14.22	7.63
Upper quartile	1608.15	200.54	223.63	187.43	22.68	28.18
SD	1073.45	42.297	96.82	157.06	6.89	14.61
Std. error	178.91	21.15	16.14	26.18	3.45	2.44

All values in μg/kg. *Min.*, minimum value; *Max.*, maximum value

Table 2 Metal values (Al, As and Mo) in bovine milk (lyophilised milk and liquid milk) by farm

	Lyophilized milk			Liquid milk		
Farm	Al	As	Mo	Al	As	Mo
1	1090.08		133.67	142.82		18.25
2	1951.71		102.79	280.88		13.98
3	1751.35	177.18	56.24	206.71	21.81	6.78
4	1181.29	155.72	122.69	166.40	15.10	16.57
5	728.02		219.08	95.20		29.04
6	150.04		220.57	22.78		30.32
7	594.79		205.38	71.05		29.06

All values in μg/kg

We have only found arsenic values above the limit of detection in 4 milk samples, specifically in farms III and IV, with mean values of 18.45 ± 6.89 and 166.45 ± 42.30 μg/kg in liquid milk and lyophilised milk, respectively. The highest value (28.6 μg/kg) was found in farm III.

Mean values of Mo detected in all liquid milk samples were 20.72 ± 14.61 μg/kg and in freeze-dried milk samples of 152.26 ± 96.82 μg/kg. Values in liquid milk ranged from 2.06 μg/kg to 52.75 μg/kg and from 18.53 to 307.58 μg/kg in lyophilised milk. With respect to the average values per farm of molybdenum, we found that the highest values were detected in farm VII, being close to 50 μg/kg (52.75 and 47.19 μg/kg in liquid milk). A similar value was found on farm V (46.57 μg/kg w.w.). The lowest values were detected at farm III, with values slightly higher than 2 μg/kg (2.06, 2.95, 2.48 and 2.87 μg/kg).

We found no mercury in any of the analysed milk samples.

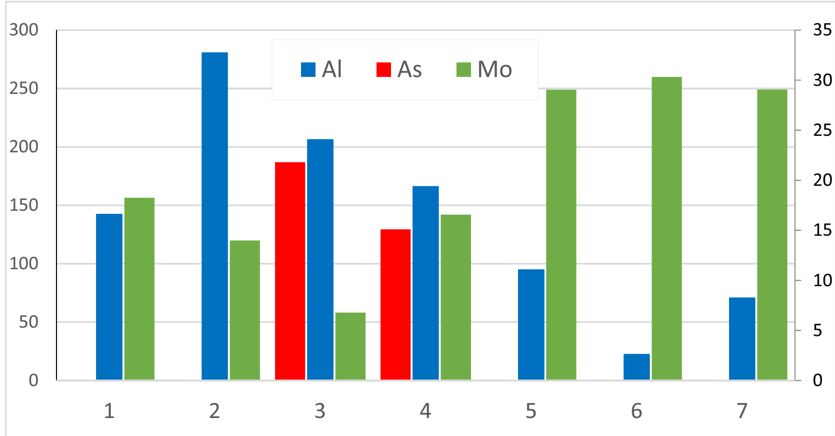
Correlations among different metals

No correlation was observed between the metals analysed in this research nor with Pb and Cd, described in Gonzalez-Montaña et al. (2012). As expected, we found an important correlation between the levels of each of the metals studied in the liquid milk sample and in the lyophilised milk sample, with values $p < 0.000$ and positive correlation between 96 and 98%.

Discussion

In general, what really makes metals toxic, and especially heavy metals, is not their own characteristics, but the concentrations at which they can occur and, almost more importantly, the type of compound they form in a given medium. Its toxicity comes from the interaction of metals with proteins

Fig. 2 Metal values (Al, As and Mo) in liquid bovine milk by farm (μg/kg). Al by the scale on the left; As and Mo by the scale on the right



(enzymes) and that inhibits multiple metabolic processes (Underwood and Suttle 2002).

Although the effects depend on each particular mineral, and taking into account that even some of these elements are essential for normal animal physiology and for proper production, both acute and chronic exposure to some minerals can trigger significant toxic effects, ranging from slight discomfort and decrease of the productions until teratogenic effects, induction of serious pathologies, increase of tumoral processes and even death (Rahimi 2013; Salehipour et al. 2015; Lane et al. 2015). Toxicity is especially important in children, who consume large quantities of milk and are among the most vulnerable population (Codex Alimentarius 2011a, b; Chao et al. 2014).

The average level of milk metals obtained in this research was within the ranges indicated by Puls (1994) and Knowles et al. (2006). Aluminium and molybdenum were detected in all samples, while mercury was not detected in any of them. Arsenic was only detected in 0.89% of the samples, a percentage similar to the samples in which the presence of cadmium was detected and regarding lead, the detection level was 69.64% of the analysed samples (Gonzalez-Montaña et al. 2012).

Arsenic content

There is little information on arsenic concentrations in milk and dairy products, so it is very important to measure their levels and correlate them with the ecological environment and with the many different management practices that surround the production units.

Arsenic has been the only human carcinogen with registered evidence of carcinogenic risk by both inhalation and ingestion and has been connected with certain types of cancer, including lung, liver, skin and bladder cancer in humans (Kapaj et al. 2006). It is also directly toxic and is accumulative (Bilandzic et al. 2011).

Some examples of the release of arsenic are the process of combustion at high temperatures of both fossil fuels or vegetation, as well as mining and volcanic activity (Rosas et al. 1999; Gutiérrez 2009; Singh et al. 2011; Perween 2015).

The arsenic water level could affect human health through milk consumption (Rosas et al. 1999; Ayar et al. 2009). The As, an environmental pollutant, is present in minimal amounts but unchanged in food, potable water and air. However, if the groundwater contains As and it is not treated to be eliminated, it can be incorporated into the food chain when used for irrigation or for drinking animals. Arsenic is found in subsoil rocks, so when aquifers are full, arsenic is diluted in water, but in times of drought, it increases its concentration, increasing the levels of arsenic in drinking water (Gutiérrez 2009).

Cows can eat grass, hay and drink contaminated water but their milk could be kept free of the toxicant (Rosas et al. 1999). However, it was found that the As content was raised in cow's milk from some affected villages. It should be noted that an estimated 5% of the water sources in the USA exceed the 0.01 ppm (10 ppb) of As and that the consumption of water from these naturally contaminated aquifers led to chronic As poisoning in many of these locations (Jones 2007). This contaminated milk also arrives at dairy processing units (Rosas et al. 1999; Ayar et al. 2009).

In our case, we have only detected this metal in 4 milk samples, specifically in livestock III and IV. It is important to note that both farms are located in areas of greater risk. So farm III is located in the Black River Valley, named that way because it was used to wash coal for decades. This farm also showed the highest average level of lead (9.40 ± 5.08) (Gonzalez-Montaña et al. 2012) related to the high extractive activity and the excessive density of deposits of mining waste in the area, being frequent that the cows graze directly on the mining deposits. Farm IV is close to both urban areas and old mining areas, and next to the A-6 highway, with a high traffic density.

Both Gutiérrez (2009) in León (Spain) and Ayar et al. (2009) in Anatolia (Turkey) only detected arsenic in a sample of raw milk, whose value was 32.08 μg/kg and 0.08 mg/kg, respectively. In Spain, the arsenic content in Valencia was 0.14 and 0.77 ng/g in commercial milk (Cervera et al. 1994) and in Huelva, it ranged from undetected (nd) to 4.98 μg/kg (Bordajandi et al. 2004). Robberecht et al. (2002) in Belgium analysed 9 milk samples and all of them were below the limit of detection. In other countries, the arsenic content varies significantly, so in Denmark, arsenic content has been found to range from 0.25 to 23.0 ng/g milk (Hermansen et al. 2005); in Calabria (Italy), arsenic values of 37.9 μg/kg have been found in milk (Licata et al. 2004); in Torino (Italy), it was 50.0 μg/l in commercial milk (Abollino et al. 1998); in Turkey, the arsenic content was 17.5 μg/kg in milk (Erdogan et al. 2004), 42.0–49.0 μg/kg (Ulman et al. 1998), 0.20–50, 0 μg/kg (Simsek et al. 2000) and n.d. to 0.08 μg/kg (Ayar et al. 2009) and in France, 3.0 μg/kg has been recorded in milk (Leblanc et al. 2005). In The USA, arsenic values have been reported in milk from < 0.4 ng/g (Dabeka and Lacroix 1987); in Chile, concentrations of 12.0 ng/g have been observed in milk (Muñoz et al. 2005), while in Mexico, concentrations ranging from 0.9 to 27.4 ng/g have been detected (Rosas et al. 1999) and in Córdoba (Argentina), levels were between 2.8 and 10.5 ng/g in milk (Pérez-Carrera and Fernández-Cirelli 2005).

In recent years, only Bilandzic et al. (2011), in Croatia, has cited much higher values, ranging from 1 to 283 μg/l and to 1019 μg/l, while Rey-Crespo et al. (2013) in Spain, Arianejad et al. (2015) in Iran, Cadar et al. (2015) in Romania, Dhanalakshmi and Gawdaman (2013) in India, Li et al. (2016) in China and Mends (2016) in Ghana have found similar or even lower values than those reported in our research. Simsek et al. (2000) compared the arsenic levels of three regions (with heavy traffic, industrial region and rural region), proving that the highest values were found in the first two, while it was found in a single point in the rural area. Licata et al. (2004) indicate that the high levels of arsenic observed could be due to the use of pesticides and environmental disinfectants (arsenical compounds) used in farmland areas. Arsenic levels in milk, in addition to other sources, are increased by the presence of arsenic in the drinking water of the animals (Pérez-Carrera and Fernández-Cirelli 2005), although an increase in the levels of arsenic in drinking water supplying the animals (10 μg/l) did not show an increase in collected milk samples (Gutiérrez 2009). The research carried out by Ayar et al. (2009), surprisingly, detected higher concentrations of arsenic in dairy products, while only detecting arsenic in one of the samples in raw milk, although the levels of arsenic in both milk and dairy products were always below the limits of Codex (Ayar et al. 2009).

Codex Alimentarius (2011a, b) indicates values of 0.001–0.15 mg/kg (1–150 μg/kg) as maximum concentrations of arsenic in milk and milk powder and the European Union (European Union 1881/2006; European Union 2015/1006; Unión Europea 2017) indicates 0.10 mg/kg (100 μg/kg) as the maximum content of arsenic in liquid milk, ready for consumption. Therefore, the values found were always below the recommendations of these institutions.

Aluminium content

Aluminium has historically been considered to be relatively non-toxic in healthy individuals, without any apparent harmful effects. However, there is now abundant evidence that Al may cause adverse effects on the nervous system and high intakes of it—through such sources as buffered analgesics and antacids—may lead to pathological changes (Ayar et al. 2009).

The average values of aluminium found, 140.89 μg/kg in liquid milk, are similar to those reported by Gutiérrez (2009) in tank milk in León, Spain (192.16 μg/kg), being lower than those obtained in other researches carried out in Spain by Viñas et al. (1997) in Murcia (0.796 μg/ml in bottled milk) and by Fernández-Lorenzo et al. (1999) in Galicia (0.700 mg/kg milk) or by Sola-Larrañaga and Navarro-Blasco (2009) in Navarra (indicating values between 47.0 and 1598.0 μg/l in milk). In a study carried out in the same province (Asturias), the results were much lower, with values of 31.0 μg/l in ultrapasteurised milk and 26.0 μg/l in raw milk (Rivero-Martino et al. 2001).

The values of aluminium per farm are very different, with the highest values in farm II (280.88 μg/kg) and farm III (206.71 μg/kg) and the lowest in livestock VI (22, 78 μg/kg). As indicated above, farms II and III could be considered as the areas of greatest risk, since they are located near a thermal power station and very close to an important deposit of mining waste. However, farm VI, with the lowest values, is also on top of an old mining operation.

Aluminium content in human milk and in infant formulas having much lower values of 27 ng/ml of milk has been reported in Koo et al. (1988), while concentrations ranging from 95 to 100 ng/ml have also been found in the USA (Andersson 1992), in Australia (Weintraub et al. 1986) and in Italy (de Curtis et al. 1989). On the contrary, much higher values (460 μg/l) were found by Abollino et al. (1998) in Torino (Italy) in semi-skimmed commercial milk, and especially in Anatolia (Turkey) with values much higher, ranging from 5650 to 8920 μg/kg of raw cow milk (Ayar et al. 2009).

This increase in aluminium values could be due to the addition of chemical substances—polyphosphates—as stabiliser to the uperisation reaction (Fernández-Lorenzo et al. 1999), although it has also been proven that Al contamination results from the uncontrolled use of low-quality materials made from Al used in the processing of milk, as well as the use of aluminized carton boxes where milk is marketed (Ayar et al. 2009).

Molybdenum content

The mean values of Mo detected in all liquid milk samples were 20.72 ± 14.61 μg/kg and 152.26 ± 96.82 μg/kg in lyophilised milk samples. The highest values, close to 50 μg/kg, were detected on farms VII and V, while the lowest values were detected on farm III, with several values slightly higher than 2 μg/kg. Farm VII is located next to the Mineral Treatment Plant considered as one of the most important mineral deposits in the Region, while livestock V is located in areas with great mining activity and very close to a thermal power plant. However, cattle ranching III, as mentioned above, is located in areas with high coal mining activity, showing high levels of other minerals measured.

When comparing our values with the data quoted in other researches, we have seen that Andersson (1992) in the USA found a concentration of molybdenum of 22 μg/kg in cow's milk and also coincides with the data reported by Benincasa et al. (2008) who describe a molybdenum content of 29.0 μg/kg of milk in the Calabria region (Italy). However, Abollino et al. (1998) found values higher than our results when analysing bovine milk samples in Torino, Italy, citing an average value of 73.0 μg/l and of 45.20 μg/kg in milk samples in León (Spain) collected in tank (Gutiérrez 2009). Similar results were described in Murcia (Spain) by Viñas et al. (1997) who mention that the concentration range of molybdenum in milk ranged from 37 to 325 μg/kg. Also higher values were found in Galicia, in the Northwest of Spain by Rey-Crespo et al. (2013), with slightly higher values in milk produced in organic farms (45.2 μg/l, with values between 27.0 and 111.2) than in conventional farms or in market milk (between 33.1 and 49.5 and between 36.8 and 44.3 μg/l, respectively).

Mercury content

Mercury is a naturally occurring metallic element which can be present in foodstuffs by natural causes. The most important anthropogenic sources of mercury pollution in the environment are mining and combustion, agricultural materials and industrial and urban discharges (Zhang and Wong 2007; Bilandzic et al. 2011; Codex Alimentarius 2011a, b). While methylmercury and also total mercury levels in terrestrial animals and plants are usually very low, the fungicidal treatment with organomercurial seed dressings have traditionally been a major source of mercury for farm animals, while the recent practice of adding fish meal to feed is the main source of mercury for livestock (López-Alonso et al. 2007; Codex Alimentarius 2011a, b).

As with molybdenum, there is not too much data on mercury residues in milk in comparison with other trace metals, since in multiple investigations, the values are very low or below the limit of detection. All milk samples we analysed were below the established detection limit.

The European Union (European Union 2015; Unión Europea 2017) indicates 0.01 mg/kg (100 μg/kg) as the maximum mercury content in any food, thus including milk. Therefore, the values found are below the recommendations of these institutions. Joint FAO/WHO Food Standards Programme Codex Committee on contaminants in foods (Codex Alimentarius 2011a, b) does not indicate levels of mercury in milk, although it does indicate for other foods like water, salt or fish (0.001, 0.1 and 0.5 mg/kg).

Several reports refer to concentrations of mercury in milk ranging from undetected to 2.0 μg/kg (Simsek et al. 2000; Muñoz et al. 2005; Rey-Crespo et al. 2013; Dhanalakshmi and Gawdaman 2013; Cadar et al. 2015; Li et al. 2016). However, Puls (1994) mentions that this concentration of mercury in cow's milk can be quite higher, with values ranging from 3.0 to 10.0 μg/l, as well as Caggiano et al. (2005) who, in Italy, report similar results when analysing sheep milk samples and record values between 1.2 and 3.7 μg/kg; Anastasio et al. (2006), also in Italy, report values between 1.4 and 2.9 μg/kg and Bilandzic et al. (2011), in Croatia, indicate values between 1.59 and 7.1 μg/l. In Iran, Arianejad et al. (2015), when comparing milk from cows from industrialized versus traditional farms, found that the highest values appeared in farms with older systems (7.29 vs 14.95 μg/l). The highest values we have found are cited by Mends (2016), with values of 124.38 μg/l in cow's milk and slightly higher in human milk (132.83 μg/l), which could be attributed in part to the release of toxic mercury into the environment by the crude electronic waste recycling activities at the Agbogbloshie dumpsite where these cattle are reared. This place is considered to be the largest landfill in the world for electronic scrap from Europe and North America and possibly the most contaminated place on the African continent by metals such as lead, beryllium, cadmium or mercury.

There is not always a direct relationship with the degree of industrialisation of the area, so in Turkey, no differences have been found between a "Traffic Intensity Region", an "Industrial Region" and a "Rural Region" (Simsek et al. 2000), since none of the collected milk samples detected mercury at a level above 0.005 mg/kg, limit of detection of the method used in this research (Simsek et al. 2000).

It has been shown that some metals have no biological function and are toxic, as well as that they can be accumulated in the body, and can be classified into various categories: those that are carcinogenic to humans (group I), probably carcinogenic to humans (group 2A) or those possible human carcinogen (group 2B) (Codex Alimentarius Commission 2011a; IARC 2006, 2017). Thus, aluminium, arsenic and inorganic arsenic compounds and chromium (chromium (VI) compounds) are considered to be carcinogenic to humans in group I (*group 1. The agent (mixture) is carcinogenic to humans,* *according to the IARC classification* (IARC 2006, 2017)), while others such as the molybdenum and the methylmercury are classified in group 2B (*group 2B: The agent (mixture) is possibly carcinogenic to humans*). In contrast, chromium (metallic), the chromium (III) compounds, the mercury and inorganic mercury compounds 3 and the arsenobetaine and other organic arsenic compounds that are not metabolised in humans are included in group 3 ((*group 3. The agent (mixture or exposure circumstance) is not classifiable as to its carcinogenicity to humans*), always using the IARC classification (IARC 2006, 2017).

Finally, we cannot forget the various interactions and synergies that occur between different minerals, leading to significant undesirable effects. In this research, we have not been able to verify any correlation between the metals analysed, nor with Pb and Cd, measured in an earlier publication; however, there are multiple interactions described in the literature.

Thus, it is mentioned that Cd interacts with Zn, Cu, Fe, Mn and Ca, while Cu levels influence and are influenced by other minerals such as Zn, Mo, Fe, Cd, P and S (Serdaru et al. 2001; Underwood and Suttle 2002; Radostits et al. 2007; Suttle 2010), wehreas arsenic may exert an antagonistic effect on iodine, Se, Hg and Pb (Puls 1994). Copper is strongly affected by the synergism between Mo and sulphur, which is the case of ruminants form highly insoluble complexes in the rumen (Puls 1994; Underwood and Suttle 2002; Bustamante et al. 2008; Suttle 2010). Studies in rats with a marginal zinc deficiency have revealed increased and significant uptake of mercury (Kul'kova et al. 1993) and cadmium (Reeves and Chaney 2004). Thus, a marginal zinc deficiency is important in areas of heavy metal contamination (Underwood and Suttle 2002; Suttle 2010). There are many known interactions for aluminium. It can replace calcium in cases of hypocalcaemia and interfere with the metabolism of magnesium and phosphorus, although high concentrations of aluminium favour iron, copper, magnesium and zinc deficiency (Puls 1994).

Conclusions

As conclusion, we can indicate that all milk samples analysed showed levels of Al and Mo above the limit of detection, whereas only As was detected in four samples and no Hg was found in any of them. In no case do the values found indicate a significant danger to the population and are in agreement with those found in other researches, although the various anthropogenic activities of the area—industrial, mining and traffic density—could, a priori, indicate one possibly contaminated area, advising periodic monitoring.

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Authors' contributions González-Montaña and Senis designed the study; Senís carried out the samplings and analyses; González-Montaña, Senis, Casas and Alonso carried out the data analysis; Gonzalez Montaña wrote the draft; Senís, Casas and Alonso y Domínguez contributed to the preparation of the manuscript and revised it critically. All authors have read and approved the final version of the manuscript.

Compliance with ethical standards

Conflict of Interest The authors declare that they have no competing interests.

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