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Section: Environmental protection

Cd and Pb concentrations in the main groups of foodstuff

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Abstract

Various chemicals such as pesticide residues, heavy metals, environmental pollutants and some other trace elements in the food chain can be accessed directly and indirectly. A large part of the heavy metals in human living environment comes from anthropogenic sources of business. Food intake is one of the main ways for contaminants from entering the human body. Over the past decades, a growing number of scientific food research related to pollution by heavy metals and other pollutants. Cd and Pb are among the heavy metals that have caused most concern in terms of adverse effects on human health.

The aim of this study was to determine Cd and Pb concentrations in various foodstuff groups that are sold in Lithuanian supermarkets.

Cd and Pb were measured by atomic absorption method using an atomic absorption spectrometer Shimadzu AA-6800th. Samples were purchased from the major supermarkets in Lithuania and market. Producers and suppliers were from different countries. Collection of samples was carried out in 2012–2013 (October-March). A total of 37 samples were collected. Were analyzed: meat, fish and seafood, vegetables, oil and baby food.

Maximum concentration of Pb was found in Iceberg lettuce (0.5042±0.0148 mg/kg). Maximum concentration of Cd was found in squid (0.8669±0.3561 mg/kg). The analysis had revealed that the supplier and the foodstuff are statistically not significant ($p>0.005$) for the concentration of Cd and Pb. Wilks test value indicates that more influence for Cd and Pb concentration had the producer than the product (0.87; $p<0.05$). Supplier did not have the influence for Cd and Pb concentration, because as the results showed it was statistically not significant ($p>0.05$).

These procedures are rapid and accurate, and can be considered useful for the routine determination of Pb and Cd in the quality control of food samples.

Keywords: Heavy metals; Cd, Pb; Atomic absorption method; Cd, Pb in the fuddstuff groups.

1. Introduction

A variety of chemicals may enter the food chain by means of intentional and unintentional addition. These chemicals include many substances like food additives, pesticide residues, environmental contaminants, mycotoxins, flavouring substances and micronutrients. Packaging materials are also a source of chemicals in food products and beverages. It is recognised that chemicals from packaging and other food-contact materials can migrate into the food itself and can be ingested by consumer [1].

As well a large part of the heavy metals in human living environment comes from anthropogenic sources of business [2]. Food intake is one of the main ways for contaminants from entering the human body. Over the past decades, a growing number of scientific food research related to pollution by pesticides, heavy metals and other pollutants [3]. Toxic elements can be very harmful, even at low concentrations, when fall in the body continuously and for a long time period.

The negative effects of heavy metals are often invisible because the changes in the body become apparent after several or even dozens of years, sometimes they occur only to other generations [4].

Metals like iron, copper and zinc are essential metals since they play an important role in biological systems, whereas lead, cadmium and tin are non-essential metals as they are toxic even in trace amounts [5, 6].

Cd and Pb are among the heavy metals that have caused most concern in terms of adverse effects on human health. This is because they are readily transferred through food chains and are not known to serve any essential biological function [7]. Children have been shown to be more sensitive to Cd and Pb than adults are and the effects are cumulative; the elements build up in the tissues [8].

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Pb and Cd are one of the most common heavy metals and are highly toxic. According to the literature data for basic foodstuffs, Cd and Pb accumulated in relatively small quantities. The maximum Pb were determined in the flesh of fish, molluscs (from 0.2 to 2.5 mg/kg) caught from contaminated water with heavy metals [9]. The highest concentration of Cd determined in rice, wheat, oysters, mussels and animal kidneys [10].

Pb and Cd are toxic elements, even at low concentrations [11]. Both metals have an adverse effect on human health. The entrance of Pb at levels >0.5–0.8 µg/ml into blood causes various abnormalities. Pb accumulates in the skeleton, especially in bone marrow. It is a neurotoxin and causes behavioral abnormalities, retarding intelligence and mental development. It interferes in the metabolism of calcium and vitamin D and affects hemoglobin formation and causes anemia [5]. The regular absorption of small amounts of certain elements, such as Pb, may cause serious effects on the health of growing children, including retardation of mental development (e.g. reading and learning disabilities) and deficiencies in concentration, adverse effects on kidney function, blood chemistry and the cardiovascular system, as well as hearing degradation [12].

Cd in the body also have a negative impact: lung cancer, bone fractures, kidney dysfunction and hypertension and skin lesions are associated with an increased concentration of Cd in the environment [13].

Cd accumulation in the human body can lead to kidney failure, skeletal and reproductive disorders. Moreover, Cd displaces calcium from the bone, is carcinogenic, teratogenic and may cause genetic mutations [14].

The long-term effects of low Cd concentrations caused by chronic obstructive pulmonary (chronic obstructive pulmonary disease-a progressive respiratory disease that distorts the permeability and gas exchange in the lungs and tissues) [15].

The aim of this study was to determine Cd and Pb concentrations in various foodstuff groups that are sold in Lithuanian supermarkets.

2. Methods

2.1. Collection of samples

The main foodstuff groups, which the European Union in all the member states concerning the maximum allowable Cd and Pb concentration (MAC) were chosen for this study. Analyzed foodstuff groups were: meat, fish and seafood, vegetables, oil and baby food (Table 1). Foodstuff samples were purchased from main supermarkets in Lithuania and market. Producers and suppliers were from different countries. Collection of samples were carried out in 2012–2013 (October-March). A total of 37 samples were collected.

Table 1. Studied foodstuff samples

No.	Foodstuff	Producer/Supplier
1.	Olive pomace oil	Italy
2.	Canola oil	Lithuania
3.	Sunflower oil	Argentina
4.	Potatoes *(Capsicum annuum)*	Lithuania (supplier 1)
5.	Potatoes *(Capsicum annuum)*	Lithuania (supplier 2)
6.	Potatoes *(Capsicum annuum)*	Lithuania (supplier 3)
7.	Potatoes *(Capsicum annuum)*	Lithuania (supplier 4)
8.	Mushrooms *(Agaricus bisporus)*	Lithuania (supplier 1)
9.	Mushrooms *(Agaricus bisporus)*	Lithuania (supplier 2)
10.	Mushrooms *(Agaricus bisporus)*	Lithuania (supplier 3)
11.	Mushrooms *(Agaricus bisporus)*	Lithuania (supplier 4)
12.	Baby food	Lithuania
13.	Baby food	Germany (supplier 1)
14.	Baby food	Germany (supplier 2)
15.	Peking cabbage *(Brassica rapa pekinensis)*	Spain
16.	Spinach *(Spinacia oleracea)*	Italy
17.	Spinach *(Spinacia oleracea)*	Spain
18.	Iceberg lettuce *(Lactuca sativa var. capitata)*	Italy
19.	Iceberg lettuce *(Lactuca sativa var. capitata)*	Spain
20.	Lettuce "Lollo Biondo" *(Lactuca sativa)*	Lithuania (supplier 1)
21.	Lettuce "Aficion" *(Lactuca sativa)*	Lithuania (supplier 1)
22.	Lettuce *(Lactuca sativa)*	Spain
23.	Lettuce *(Lactuca sativa)*	Estonia
24.	Rucola *(Eruca sativa)*	Italy
25.	Pork tenderloin	Lithuania (supplier 1)
26.	Pork tenderloin	Lithuania (supplier 2)
27.	Pork neckloin	Lithuania (supplier 1)
28.	Pork neckloin	Lithuania (supplier 2)
29.	Pork neckloin	Lithuania (supplier 3)
30.	Pork neckloin	Lithuania (supplier 4)

End of Table 1

No.	Foodstuff	Producer/Supplier
31.	Pork loin	Lithuania
32.	Salmon fillet *(Salmonibus ordinarius)*	Norway (supplier 1)
33.	Salmon fillet *(Salmonibus ordinarius)*	Norway (supplier 2)
34.	Carp fillet *(Carpere ordinarius)*	Lithuania (supplier 1)
35.	Carp fillet *(Carpere ordinarius)*	Lithuania (supplier 2)
36.	Squid *(Calce ordinarius)*	Spain
37.	Squid *(Calce ordinarius)*	France

2.2. Analysis of samples

Before analysis all samples were homogenized. After what 0.5 g of sample was precisely weighted, then 6 ml of 65% HNO_3 and 2 ml of 30% H_2O_2 was added. Samples were digested for 15 min (180 °C). Mixture was finally diluted to 25 ml by deionized water.

Concentration of Cd and Pb was measured by atomic absorption method and atomic absorption spectrometer Shimadzu AA-6800th was used. The analysis was performed electrothermal mode with deuterium background correction. Electromagnetic radiation used items to the hollow cathode with the resonant lines (nm): Cd 228.8; Pb 283.3. Analysis of the use of high-density graphite tubes, inert gas – argon. For calibrations curves standard solutions of Cd and Pb were used. A total of 37 samples with the replays were analyzed.

2.3. Statistical analysis

The independent-samples *t*-test was applied to estimate difference between means of cases. The levels of significance for differences between all cases were analysed using one-way ANOVA. P value <0.05 was the threshold for significance. Statistical analysis were performed by *Statistica. WizArd* and *Microsoft Excell* programs were used for data analysis.

3. Results and discussion

Multi-element surveys of foods have been published because of growing interest in trace element concentrations in infant foods and the need to establish limits for infant exposure to such elements from the diet. Lead and cadmium are toxic elements, and the European Commission has proposed a regulation which sets maximum limits for these metals in certain foods [16].

In this paper were analysed concentrations of Cd and Pb in various wet foodstoofs, measured by atomic absorption method using an atomic absorption spectrometer Shimadzu AA-6800th. The products were purchased from Lithuanian supermarkets, as well as from different producers and suppliers, in case to compare what is the dependence from the geographic product location.

The most important sources of lead exposure are industrial emission, soils, car exhaust gases and contaminated food. Vegetables with a relatively large leaf area, such as spinach and cabbage can contain high levels when grown near lead sources. Cadmium ions are easily absorbed by vegetables and, in animal-based food, are principally distributed in the liver and kidneys [2].

In the Figure 1 is shown that the main Cd concentration was in baby food that was purchased from German supplier 1, 0.0031±0.0007 mg/kg. Furthermore, the concentration of Cd in all investigated baby foods were quite higher than in determined oil.

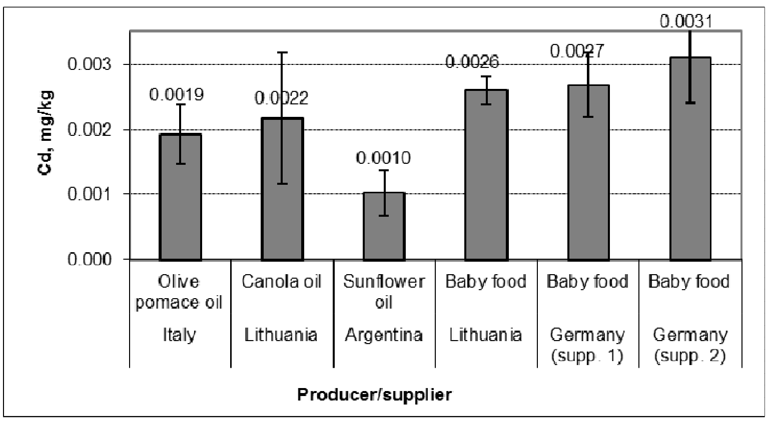

Fig. 1. Concentration of Cd in oil and baby food

The concentration of Pb was determined mainly in olive pomace oil from Italy-0.1549±0.0700 mg/kg, while the maximum allowable concentration (MAC) of Pb is 0.1 mg/kg (Fig. 2). And the lowest concentration of Pb was in baby food from Germany 0.0142±0.1100 mg/kg. It also has been pointed out the the maximum allowable concentration-0.02 mg/kg, whereas, the maximum concentration of Pb was determined in baby food from Lithuania-0.0379±0.0076 mg/kg, while the maximum allowable concentration is 0.02 mg/kg, that's mean almost 2 times exceeded.

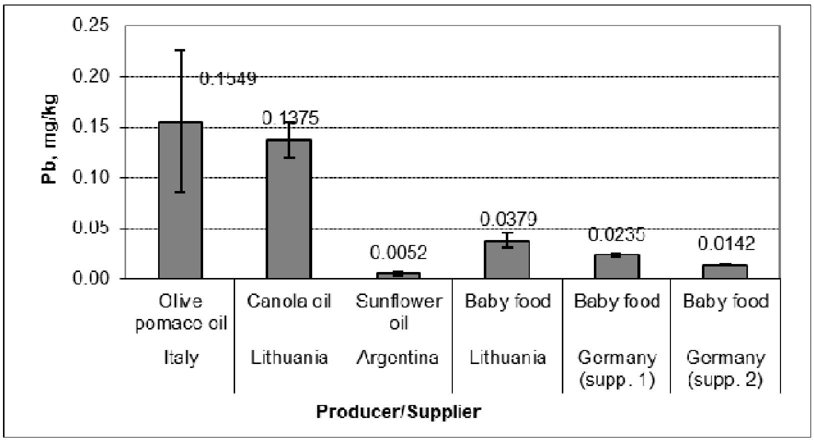

Fig. 2. Concentration of Pb in oil and babyfood (MAC (mg/kg), oil-0.1 mg/kg; baby food-0.02 mg/kg)

It has also been investigated the concentration of Pb and Cd in potatoes grown in a family farm and purchased from Lithuanian supermarkets. It was found out that the concentration of Cd in potatoes from the private economy – 0.0389± 0.0040 mg/kg (Fig. 3, 4), while potatoes from supermarkets have to contain more concentration of Cd. Such an outcome could lead to a different distribution of the soil in which the vegetables were grown. The most common heavy metals accumulate in the upper soil layer, which is available to the plant roots.

Concentrations of Cd tested in potatoes did not exceed MAC (0.1 mg/kg), and the concentration of Pb exceeded the MAC (0.1 mg/kg).

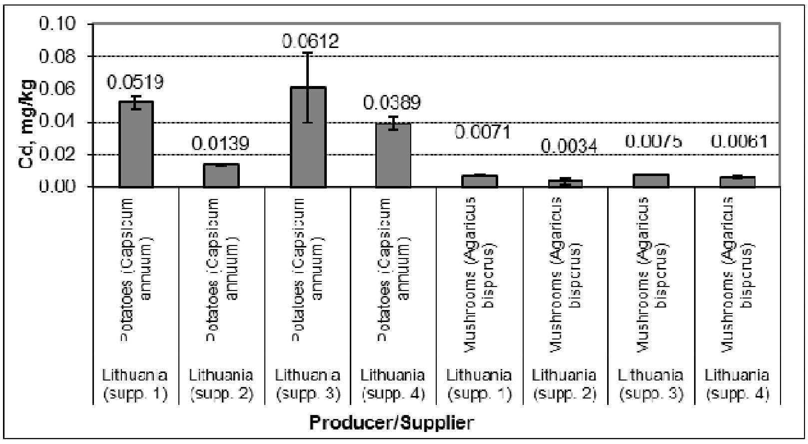

Fig. 3. Concentration of Cd in potatoes and mushrooms (MAC (mg/kg), potatoes-0.1 mg/kg; mushrooms-0.2 mg/kg)

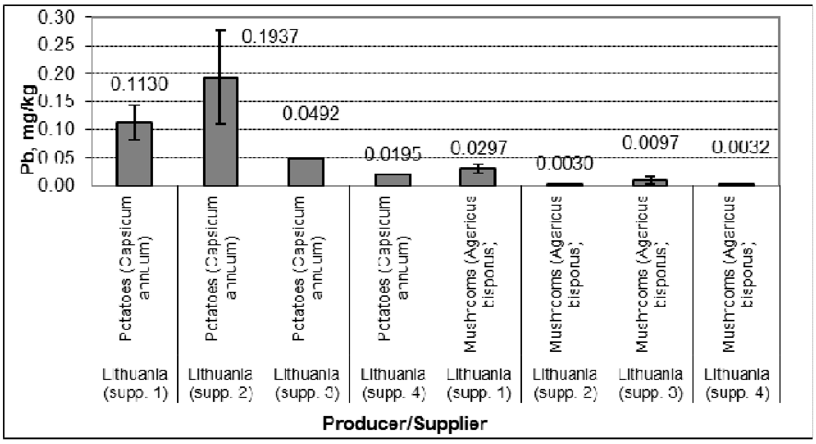

Fig. 4. Concentration of Pb in potatoes and mushrooms (MAC (mg/kg), potatoes-0.1 mg/kg; mushrooms-0.3 mg/kg)

Concentrations of Pb and Cd were also determined in Agaricus bisporus mushrooms (champignons) (Fig. 3, 4). No MACs were exceeded. Different concentrations of Pb and Cd distribution between the same products, but purchased from different places, could not lead to a uniform growing conditions, i.e. different environment, where mushrooms are grown, as well as the amounts of nutrients needed for the growth of the fungus [17].

According to the determination of Pb and Cd concentrations in various lettuce, was found that the highest concentration of Cd is in lettuce from Spain – 0.0582±0.0074 mg/kg, the minimum amount – in Peking cabbage (Spain) – 0.0018±0.0004 mg/kg (Fig. 5). The highest concentration of Pb found in Iceberg lettuce from Spain – 0.5042 ± 0.1973 mg/kg, the lowest concentration was in Rucola from Italy (0.0028±0.0024 mg/kg) (Fig. 6).

Lithuanian vegetables grown in higher concentrations of Cd and it was found in lettuce "Lollo Biondo" – 0.0167±0.0009 mg/kg, Pb concentrations were also higher in the lettuce – 0.0676±0.0150 mg/kg. Lettuce grown in Estonia, the concentration of Cd is 0.0124±0.0005 mg/kg, whereas Pb concentration – 0.0358±0.0148 mg/kg.

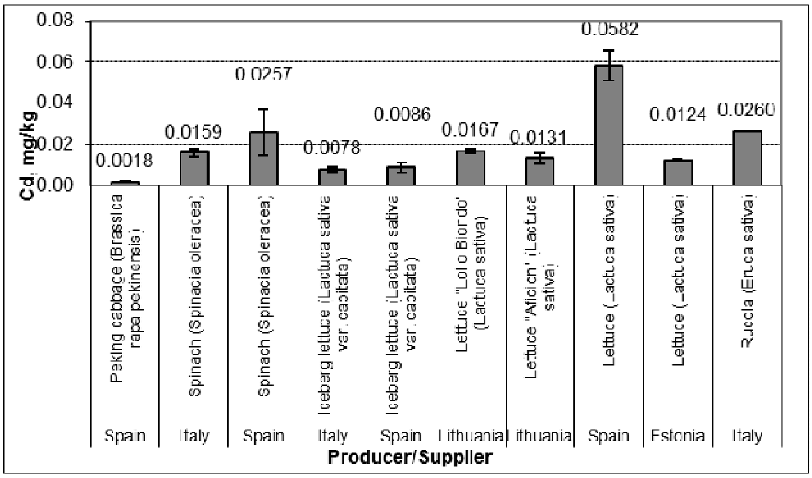

Fig. 5. Concentration of Cd in various lettuce (MAC-0.2 mg/kg)

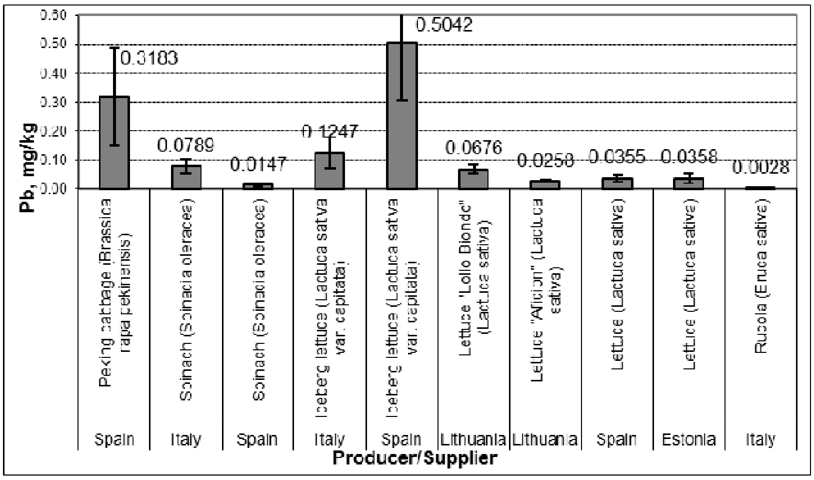

Fig. 6. Concentration of Pb in various lettuce (MAC-0.3 mg/kg)

The investigations also demonstrate the concentration of Cd and Pb in different parts of pork. The large majority of Cd concentration was set in the pork neckloin-0.0140±0.0124 mg/kg (Fig. 7). In the other samples the distributions of concentrations' are very similar. The minimum concentration of Cd were detected in pork neckloin – 0.0012±0.0002 mg/kg. Pb concentrations in all samples were similar, except for the pork tenderloin and pork neckloin, where the concentrations are 0.4407±0.0124 mg/kg and 0.2305±0.0714 mg/kg, respectively (Fig. 8).

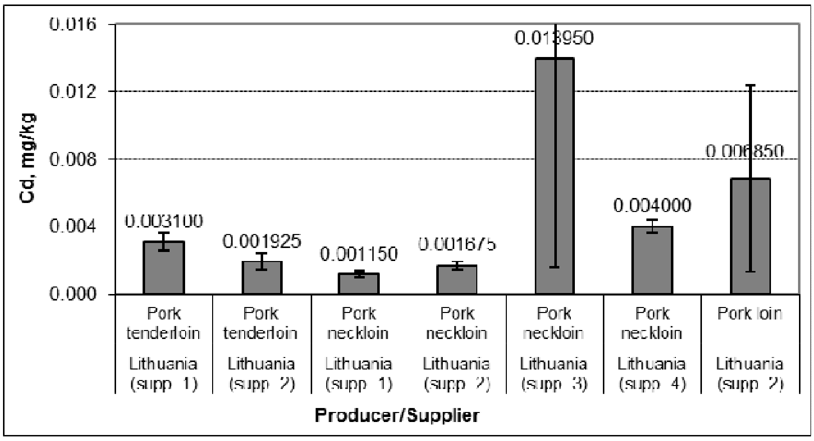

Fig. 7. Concentration of Cd in different parts of pork (MAC-0.05 mg/kg)

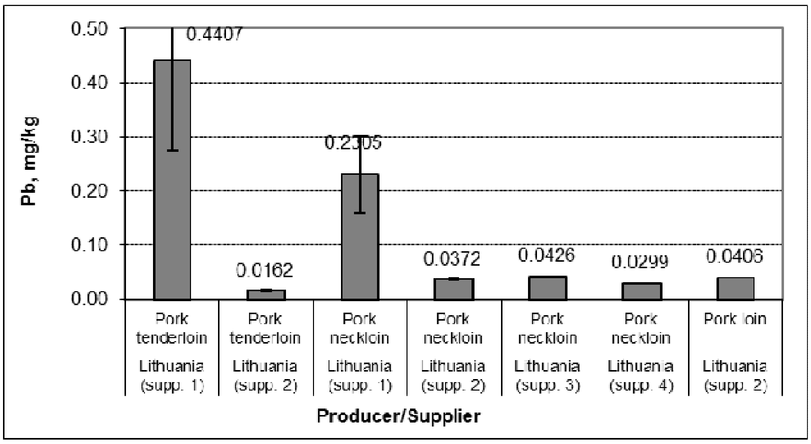

Fig. 8. Concentration of Pb in different parts of pork (MAC-0.1 mg/kg)

In the evaluation of Pb and Cd in the distribution of fish, the results show that the main majority of Cd was in squid from France and Spain: 0.5868±0.3561 mg/kg and 0.5868±0.1799 mg/kg, respectively. In the other samples the distributions of concentrations' were similar (Fig. 9).

The highest concentration of Pb was determined in carp fillet which was purchased in Lithuanian supermarket-0.1025± 0.0313 mg/kg (Fig. 10).

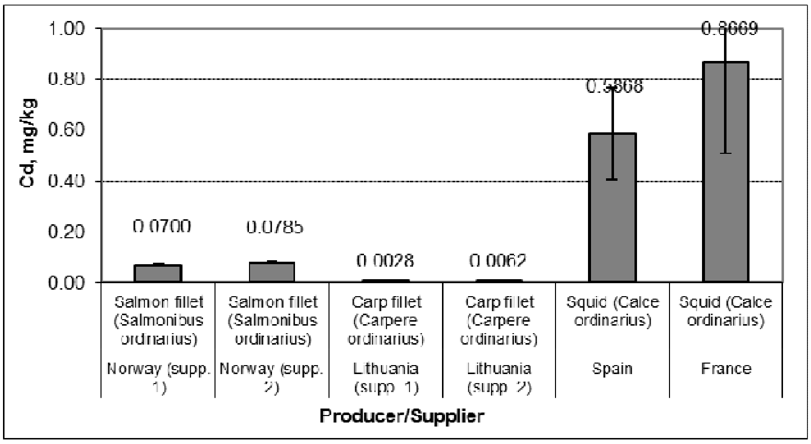

Fig. 9. Concentration of Cd in fish and seafood (MAC-0.05 mg/kg)

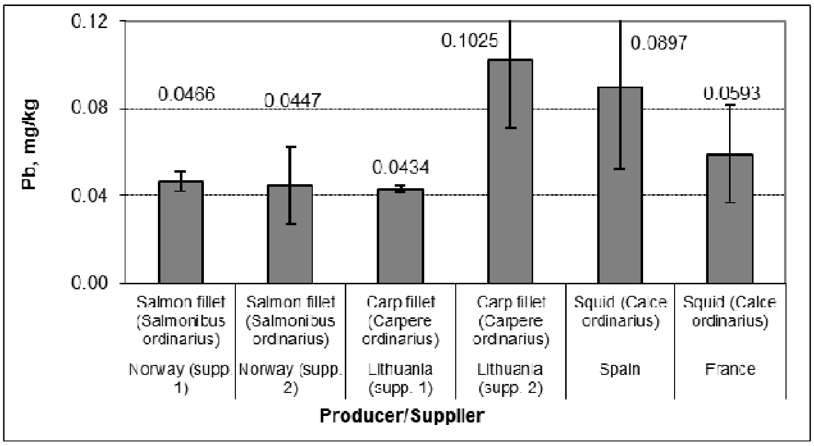

Fig. 10. Concentration of Pb in fish and seafood (MAC-0.3 mg/kg)

After our analysis we analysed the literature sources to make a comparison with other countries, what kind of maximum allowable concentration are there.

According the literature, in the analysis of Pb concentrations in dairy products and baby food was found a large amount of Pb. It could be affected by vessels in which the milk was considered and devices, because Pb may enter into food and glazed or metal utensils or pots. The similar results were obtained by Rahimi (2012) studies in Iran. In his report was designated that the concentration of Pb in milk samples exceeded the MAC-9.88 ng/ml [12]. The concentration of Cd in milk and baby food has not been evaluated, because there are no regulations for it.

Karavoltsos 2008, determined that in Greek commercially available potatoes the concentration of Pb is 11.8 ng/g ± 2.8 and Cd-8.6 ng/g ±2.7 [18].

In Turkey Oymak (2009) has performed studies and showed that the concentration of Pb and Cd in fish did not exceed the permitted limits [19]. Pb content-6.63 ng/g and Cd-4.24 ng/g. In Turkey Tuzen (2009) performed studies of Cd concentrations in fish ranged from 0.09 to 0.48 mg/g, Pb-from 0.22 to 0.85 mg/g. In the same year he determined the concentrations of Cd and Pb in mushrooms: Cd-7.50±0,56 mg/kg and Pb-4.17±0.35 mg/kg [17].

Edible oils also play an important role in human nutrition worldwide. In this case it is important to pursue the development of analytical procedures to check their chemical quality. In addition to the major components and minor compounds that affect their nutritional quality, edible oils contain very small quantities of metals. Monitoring the presence of these low concentrations is of some relevance since, besides the toxic nature of some of these metals, they may affect certain oxidation reactions that will result in the formation of toxic compounds [20]. The European Union has fixed the maximum level of Pb at 100 ng/g in oil samples. However, the levels reported for Pb and Cd in edible oils vary over a wide range [21-24]. Spain researches in oil samples detected the limits of 0.6 and 10.0 ng/kg for Cd and Pb, respectively [25].

According to the Codex Alimentarius Commission [26], the maximum levels for Cd is 100 ng/g for vegetables, legumes and cereals, and for Pb are 100, 500 and 500 ng/g for vegetables, legumes and cereals, respectively. Comparing the values obtained for spinach samples [27] with the maximum levels recommended, spinach samples showed higher Pb values: 296.5 ±29.5 ng/g and 45.5±1.2 ng/g for Cd.

Electrothermal atomic absorption spectrometry is one of the most sensitive techniques with limits of detection in the range from µg/L to ng/L, it requires only low sample volumes, tolerates high matrix concentrations and is therefore often chosen for such determinations [28], thereby, in lettuce was determined low limit of detection [27].

Since 2004 Brazil is the world's largest beef and poultry and fourth-largest pork exporter. Future increase in meat exports and greater access to global markets will depend on the success of current efforts to eliminate this disease and to implement and maintain strict sanitary controls. It was detected of 1.9 µg/kg kg for Pb and 0.13 µg/kg kg for Cd [29], while in European Union the maximum allowable concentrations are: 0.05 mg/kg for Cd and 0.1 mg/kg for Pb.

In this sense the development of fast, reliable and inexpensive screening methods of analysis is of great importance in order to increase the number of samples that can be analysed on a routine basis and to provide results within the shortest time possible. The presence of heavy metals in animal tissues and meat products may result from natural occurrence in the soil, from where they are taken up by the plants that feed the animals, or due to contamination from anthropogenic sources.

Several trace metals such as As, Cd, Pb and Hg, are among the toxic substances controlled by the Brazilian Ministry of Agriculture. The control of these residues in meat within the Brazilian program of residue control in products of animal origin has the purpose of getting information about regional levels, making possible the identification of areas of environmental pollution [30]. In this way atomic absorption spectrometry (AAS) provides the necessary performance for multielement determination concerning achievable limits of detection without detriment of repeatability and reproducibility.

4. Conclusions

Pb and Cd can be determined reliably in different types of foodstuffs. The experimental procedure is simple, that is mean that it reduces the risks of contamination. The addition of hydrogen peroxide and nitric acid to the samples considerably reduces the deposition of carbonaceous residues, which improves reproducibility.

Common deuterium background correction is appropriate, which allows the procedures to be applied in most laboratories with no need for more sophisticated correction systems.

In conclusion, based on the results' maximum concentration of Pb was found in Iceberg lettuce (0.5042±0.0148 mg/kg); maximum concentration of Cd was found in squid (0.8669±0.3561 mg/kg). Also the analysis revealed that the supplier and the foodstuff are statistically not significant ($p>0.005$) for the concentration of Cd and Pb. Wilks test value indicates that more influence for Cd and Pb concentration had the producer than the product (0.87; $p<0.05$). Supplier did not have the influence for Cd and Pb concentrations', because as the results showed it was statistically not significant ($p>0.05$).

These procedures are rapid and accurate, and can be considered useful for the routine determination of Pb and Cd in the quality control of food samples.

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