Arsenic, Cadmium and Lead in Beers from the Italian Market

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ABSTRACT

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Nineteen beer brands from the Italian market were surveyed for the presence of arsenic, cadmium and lead in January of 2007. Detection was performed by means of inductively coupled plasma-mass spectrometry (ICP-MS). Average arsenic content was 10.82±5.54 µg/L, while cadmium (0.16±0.15 µg/L) and lead (1.84±3.24 µg/L) were significantly lower ($P<0.05$). Overall, this survey indicated that beer may contribute heavy metals to the diet. Nevertheless, the dietary exposure to these contaminants is unlikely to constitute a hazard to the consumer's health due to the low level of contamination found and to the low annual per capita consumption of beer in Italy.

Key words: Arsenic, cadmium, food security, heavy metals, Italian beers, lead.

INTRODUCTION

Contaminants are substances that have not been intentionally added to food. They may be present in food as a result of the various stages of production, packaging, transport or holding. They also might result from environmental contamination. Heavy metals and semi-metals such as arsenic are no exception. In fact, they can be naturally found at different concentrations in the earth's crust or they can occur in the environment as a result of human activities such as industrial release, improperly disposed chemicals or inappropriate application of pesticides and traffic fumes. Although an authoritative definition of heavy metals does not exist, the term heavy metals can be considered "a group name for metals and semi-metals that have been associated with contamination and potential toxicity and ecotoxicity."[15] These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Some heavy metals have nutritional functions and are essential to maintain the metabolism of the human body[7,12,23,39]. Others can cause serious illnesses. All of them may be harmful if excessive amounts are consumed. Poisoning of the general population may result from water contamination, food intake or air pollution. Additionally workers in a variety of occupations are potentially exposed to lead, cadmium, arsenic and their selected organic and inorganic compounds[1,47,49]. Heavy metal toxicity varies according to their oxidation state, solubility and many different inorganic and organic forms[45]. In addition, their toxicity depends on the exposure dose, frequency and duration of exposure, targeted biological species, age, gender, individual susceptibility, genetic and nutritional factors[20,38,46]. Lead contamination is mainly the result of anthropogenic activity with exposition to lead from air and food in nearly equal proportions[24]. The International Agency for Research on Cancer (IARC) classified lead as a possible human carcinogen in 1987. Specifically inorganic lead compounds are probably carcinogenic to humans and are classified in group 2A, while organic lead compounds are not classifiable as to their carcinogenicity to humans and are inserted into group 3[28]. Manifestations of lead poisoning include effects on the haematopoiesis, renal and central nervous systems[28,42]. In turn, cadmium and cadmium compounds are classified 2A by the IARC as probably carcinogenic to humans[27,48] due to epidemiological data that link cadmium and pulmonary and prostate cancer[19,39,51]. Apart from smokers, food is the most important source of cadmium exposure for the general population[24,52]. Additionally chronic exposure may lead to kidney damage, pulmonary emphysema, osteomalcia and osteoporosis[32,33]. The IARC classifies the semimetal arsenic in group I as a known human carcinogen[26] due to the causative role of arsenic in the genesis of cancer of the bladder, lung, kidney, liver, colon, prostate and skin[26,40]. It follows that exposure to arsenic through food and water should be as low as reasonably practicable. The main source of exposure to arsenic is drinking water contaminated by natural geological sources, as arsenic occurs naturally in the environment, or by pollution of aquifers due to uncontrolled industrialization[44]. Since heavy metals are ubiquitous[35] they are likely to be present in all foodstuffs, although to a different extent, with water, agricultural foodstuff and fish being a major source. Therefore, the intake of heavy metals in very small concentrations by humans is almost unavoidable. Referring to the brewing industry, heavy metals may enter the beer chain from a number of sources. They can be picked up from contaminated soil and water or be deposited on the grain from traffic fumes and other pollution in the air. Since water is the main ingredient in beverages, the purity of water is of prime importance as the final concentration of toxic metals is likely to be related to the amount contributed via water employed in the production process.

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Table I. List of beers analyzed for lead, arsenic and cadmium. Arsenic, cadmium and lead per beer sample are reported.

Sample	Origin	Beer type	Raw materials	ABV (%)	Arsenic (µg/L)	Cadmium (µg/L)	Lead (µg/L)
1	Italy	Munich Dark Bock	Malted barley and maize	6.5	13.8	<D.L.[a]	<D.L.
2	Belgium	Pale Ale	Malted barley	7.2	8.64	0.18	<D.L.
3	Italy	Munich Dark Bock	Malted barley	5.6	15.4	0.15	2.07
4	Italy	Irish Red	Malted barley and maize	6.6	15.4	0.07	1.14
5	Germany	Hefe Weizen Hell	Malted barley and wheat	5.5	5.47	0.22	3.32
6	Germany	Hefe Weizen Hell	Malted wheat and malted barley	5.0	2.85	0.13	0.07
7	Germany	Hefe Weizen Hell	Malted wheat and malted barley	5.3	6.55	0.19	2.48
8	Germany	Hefe Weizen Hell	Malted wheat and malted barley	5.5	7.47	0.47	3.25
9	Italy	Europilsner	Malted barley	5.2	10.3	<D.L.	<D.L.
10	Italy	Europilsner	Malted barley and maize	4.7	8.10	<D.L.	<D.L.
11	Europe	American lager	Malted barley and glucose syrup	5.0	9.69	0.14	4.12
12	Italy	Europilsner	Malted barley	5.0	8.98	0.17	<D.L.
13	Italy	American lager	Malted barley and rice	5.0	14.9	0.21	<D.L.
14	Ireland	Stout	Malted barley	4.2	2.77	0.01	<D.L.
15	Mexico	American Lager	Malted barley, maize and rice	4.6	6.37	0.05	<D.L.
16	Spain	American Lager	Malted barley and maize	4.6	23.8	0.10	0.11
17	Denmark	Strong Ale	Malted barley and maize	7.7	15.1	0.58	5.17
18	Japan	American lager	Malted barley and rice	5.0	10.5	0.18	<D.L.
19	Scotland	Strong lager	Malted barley	9.0	19.5	0.25	13.30
			Mean and standard deviation		10.82±5.54	0.16±0.15	1.84±3.24

[a] D.L.: Detection limit.

As regards cereals intended for brewing, the uptake from the environment depends upon many variables which include: 1) differences between cereal varieties; 2) differences between cultivars[34]; 3) soil type and pH of the site where cereals are grown[29,31,51]; 4) organic matter composition of soil[31,50]; 5) specific bioclimatic conditions; 6) rural or urban location of the crop; 7) chemicals applied to agricultural practices; 8) the type of enterprises established on a territory; 9) species assortment of the plants prevailing in a specific area; 10) recycling of sludge to agricultural land[11].

Usually hops contain a higher level of toxic metals than do the cereals from which beer is brewed, although the total amount introduced via hops lies far below the hazard limit for human health due to the low hop amount employed in brewing. Highest values are recorded for lead[14,18,36]. Fortunately purified CO_2 extracts and stabilised hop products are reported to effectively reduce the final heavy metal content contributed to beer through hopping.

At present limited data exist on heavy metals such as lead, cadmium and particularly arsenic in beers on sale in Italy. In order to bridge this gap, this study investigated the levels of these elements in beers from the Italian market in order to ascertain if arsenic, cadmium and lead are a health concern for beer consumers in the Italian marketplace. Descriptive population statistics are reported. The contribution of beer to the weekly intake through the diet is also considered.

MATERIALS AND METHOD

Nineteen beers from the Italian beer market were bought in a supermarket in Varese, Italy. They represented the common brands readily available to consumers in the off-premises chain in Italy. Beers can be differentiated on the basis of the raw materials from which they are brewed, on the basis of the fermentation technology and on the basis of the final % ABV. They can also be differentiated on the basis of the production plant location. All but one of the beer samples were non returnable bottled beers. The split of 18:1 is representative of the packaging types from which beer is consumed in Italy. Glass containers had a 79.2% market share, while the canned beer share was 7.96% in 2006 according to the Assobirra[2] Annual Report 2007. Beer containers were of different volume i.e. 0.33 L, 0.50 L, and 0.66 L. All the brands surveyed had nearly the same remaining shelf-life. As nearly 97% of the beers consumed in Italy belong to the non specialty lager type pilsner, only a few stout or ale or other top fermented beers were considered in this study. Beer main features are displayed in Table I.

HEAVY METAL ANALYSIS

Detection was performed by means of inductively coupled plasma-mass spectrometry (ICP-MS). Analytical procedures are hereunder reported in detail.

Reagent, solutions and instrumentation

Standard solutions were prepared by dilution of a multi element standard (100 mg L^{-1}) obtained from CPI international (Amsterdam, The Netherlands). Reagent water was ultra-pure and de-ionized water (18MΩ-cm resistance, Millipore® system, Millipore, Bedford, MA). Sub-pure nitric acid was obtained with sub-boiling system (Milestone mod. Subpure). Nitric acid and hydrogen peroxide (30%) were used for the mineralization of the samples.

Elemental analyses were carried out on Agilent 7500 Ce inductively coupled plasma mass spectrometer (Agilent Technologies, USA) equipped with an ORS system (octapole reaction system). Table II shows the operating conditions used for each element, as well as the instrumental conditions. The interference of $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$ was rejected using collision cell with helium gas. There were no significant differences in no gas mode and collision (helium) mode. For lead 206, 207 and 208 masses were monitored and interference equation applied.

Table II. Operating parameters for ICP-MS (Agilent mod. 7500ce).

Power RF	1500 W
Carrier gas flow rate	Ar 0.75 L min^{-1}
Auxiliary gas flow rate	Ar 0.40 L min^{-1}
Sampling depth	8.0 mm
Nebulizer	Quarz, MicroMist
Spray chamber	Quarz, Scott double pass, chilled to 2°C
Sample flow rate	0.1 L min^{-1}
m/z	^{75}As, ^{111}Cd, ^{206}Pb, ^{207}Pb, ^{208}Pb

Beer samples and analysis of mineral content

Beer samples were stocked in plastic containers and stored at −25°C. Prior to analysis, all beer samples were degassed using an ultrasonic bath for 30 min. A 10 mL of a degassed sample was mixed with 2 mL of nitric acid and 2 mL of hydrogen peroxide in a plastic flask (Digitube 50 mL). The mixture was heated in Digiprep system (Scp Science, Quebec, Canada) for 1 h (100°C) until complete clarification. Once the sample was at room temperature, it was diluted with de-ionized water and filtered. Four blanks were prepared in an identical way, but omitting the sample. The average of blank ICP-MS signals was subtracted from analytical signals of samples before interpolation on calibration graphs.

STATISTICS

The analysis of variance (ANOVA) and Tukey's post-hoc HSD test were performed to find differences between the means of each heavy metal species and to know specifically which groups differed from the other groups. Pearson's R was compute to measure the relationship between the variables. Data were analyzed by means of the SPSS® statistical package version 13.5 (SPSS Inc., Chicago, IL, USA).

RESULTS AND DISCUSSION

A summary of the heavy metal content per sample is reported in Table I and visually displayed in Fig. 1. The detection limits of ICP-MS determination in the beer sample were 5.1 ng/L for arsenic, 2.5 ng/L for cadmium and 8.6 ng/L for lead. Descriptive statistical analysis showed quite a variation in heavy metal content across beer brands as displayed in Table I. The arsenic average content was 10.82±5.54 µg/L (min. 2.77; max. 23.8 µg/L), while the lead average was 1.84±3.24 µg/L (min. < D.L.; max. 13.3 µg/L) and the cadmium average was 0.16±0.15 µg/L (min. < D.L.; max. 0.58 µg/L). Nine out of nineteen samples were below the detection limits for lead with a 52.6% of samples with a quantifiable residue level, three for cadmium and none for arsenic. Moreover nine samples were over the legal limit set for arsenic by the Italian regulations for drinking water. Additionally, Tukey post-hoc test indicated that arsenic was found at a significantly higher level than lead and cadmium. A significant correlation at the 0.034 level (Pearson's R = 0.489) was found between cadmium and lead. Also, a highly statistically significant correlation (Pearson's R = 0.620) at the 0.01 level was found between % ABV and total arsenic content.

The results of this study are in line with previous surveys, which showed a low level of lead and cadmium in beer from different marketplaces. In 2003, Soares and de Moraes[41] analyzed Brazilian beer samples from six different states for their cadmium and lead content. Lead ranged from not detected to 290 µg/L. The cadmium concentrations varied from not detected to 14.3 µg/L. Both metals were below the regulatory limit (0.5 mg/L) for alcoholic beverages set by the Brazilian Ministry of Health. In addition in 1993, Matsushige and Oliveira[30] reported lead content varying from 13 to 52 µg/L in Brazilian samples. In 1998, Tahvonen[43] reported a far less content of 9 µg/L for lead and of 1 µg/L for cadmium in Finnish beers. These results are in line with Biurrum et al.[4] who reported a lead level from 3 to 15 µg/L in Spanish beers. A more complete survey was administered by Sherlock et al.[37] who monitored lead in beers from the UK market in 1986 showing a minimum of 10 µg/L and a maximum of 200 µg/L. Also Binns et al.[3] in 1978 presented results for the level of arsenic and lead in 144 samples of lager beers. Lead was below 60 µg/L and ar-

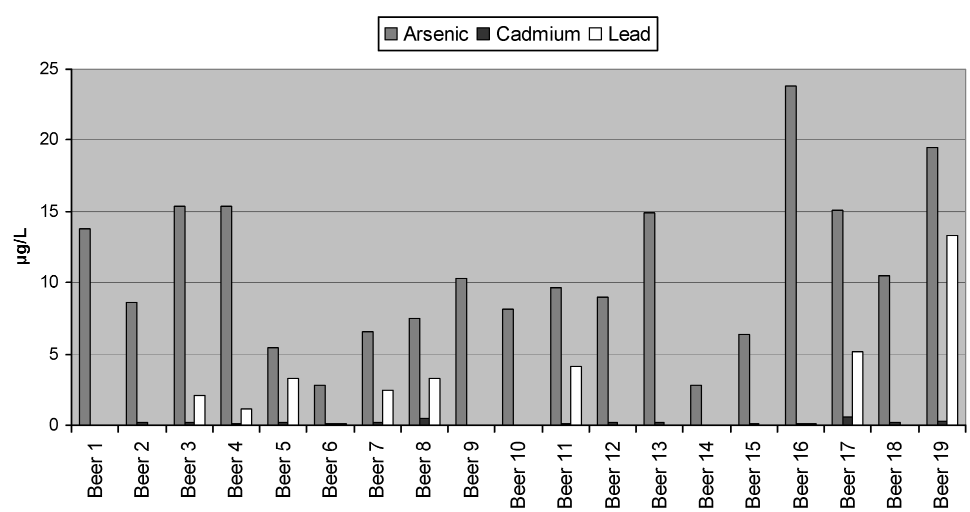

Fig. 1. Heavy metal content per beer sample.

senic below 20 µg/L in all samples. Ferzik et al.[16] in 2004 reported a content of 0.46–4.74 µg/L for lead, 0.02–0.15 µg/L for cadmium in samples available on the Czech market. In 2002, the Bundesamt für Verbraucherschutz und Lebensmittelsicherheit[5] reported that beers (n = 251) from the German market showed an average cadmium content of 0.0017 mg/kg with a 13.5 share of samples with a quantifiable residue level in the period 1995–2002. A higher average lead content was found (13.9 µg/kg) with a 15.1 share of positive samples. Additionally the Scientific Co-operation (SCOOP) Task 3.2.11[13] confirmed such low cadmium amounts in 126 beer samples. As far as Italy is concerned, in 1990 Finoli et al.[17] reported a lead content in seven samples of Italian beers from less than 30 to 120 µg/L.

As far as arsenic is concerned, historically beer from several breweries was linked with the incidence of arsenic poisoning in the Manchester area, arising from the use of contaminated sulphuric acid[25] at the beginning of the twentieth century. More recently, Cervera et al.[9] analyzed the arsenic content of different brands from Spain and other European countries. All the samples respected the legal regulations of Spain. Herce-Pagliai et al.[22] found arsenic at a level of 1.5–12.4 µg/L. No differences were found between bottled and canned beers, as well as no correlation existed with the specific gravity of the beers[9]. The process employed in the production of alcohol free beers is reported to influence the level of the final arsenic species found in beer. Monomethylarsonic acid is the most abundant species in alcoholic beers, while inorganic arsenic (III) is similar to the organic species in alcohol free beers[22]. Furthermore in 2002, the Bundesamt für Verbraucherschutz und Lebensmittelsicherheit[5] reported an average arsenic content of 7.4 µg/L for the German market. Hefe Weizen Hells in this study had a similar arsenic content. All the top fermented beers brewed from malted wheat were produced in Germany, mainly in Bavaria. The concentration of naturally occurring arsenic in ground water is reported to vary with climate and geology[53]. Moreover literature results indicate that there are differences among the cereals in the ability to accumulate heavy metals in grains[10]. Also intra cultivar variations are reported[21]. As far as wheat is concerned, different cadmium accumulations in grains was related to variations in the translocation from root to shoot and to the cadmium concentration in shoot, flag leaf, and grain coats, but not to the uptake of cadmium by roots[21]. Significant cultivar effects were also identified in kernel heavy metal accumulation for barley (*Hordeum vulgare* L.)[57] indicating a potential for developing cultivars that are low accumulators. Cereal crops, from which beers selected for our study were brewed, were grown in different sites all over Europe and different soil compositions can be expected. Soil composition is reported to play a fundamental role in metal speciation, and in particular, in the amount of metal in exchangeable form. For example, soils having an acidic pH value and a lower organic matter content are not able to bind the metals, which are consequently sorbed by plants in high amounts[6].

The SCOOP Task 3.2.11 assessed the dietary exposure to arsenic, cadmium, lead and mercury of the population of the EU member states in the period 2002–2004[13]. Italian participation provided the EU mainly with data concerning the presence of cadmium in different foodstuffs. Unfortunately a limited amount of occurrence data for lead and arsenic was submitted. Cereals and vegetables were seen as the main sources of cadmium in the diet, representing approximately two thirds of the mean cadmium intake. As far as fermented beverages were concerned, wine from Italy was reported to contain an average level of cadmium equal to 0.003 mg/kg in the triennium 1996–1998. Unfortunately no data on beer were presented. This study showed that some samples were above the regulatory limit (10 µg/L) established by the Italian Ministry of Health for arsenic in drinking water. Nevertheless, the arsenic content of beer should not be a cause of concern due to the low annual per capita beer consumption in Italy. Considering an annual per capita consumption[8] of 30 L in the year 2003, a weekly intake (WI) of 0.104 µg/kg body weight (bw) can be calculated. This represents only 0.69% of the provisional total weekly intake (PTWI) for dietary arsenic set by the World Health Organization (WHO)[55]. Likewise, a 0.017 µg/kg bw weekly intake for lead and a 0.0015 µg/kg bw weekly intake for cadmium can be calculated. This means that beer contributes 0.022% of the provisional total weekly intake of cadmium per kg of body weight and a 0.070% of the provisional total WI of lead set by the WHO[54,56] per kg of body weight.

Overall the survey indicates that beer's contribution to the dietary exposure to heavy metals is unlikely to constitute a hazard to health. This could be a consequence of the effectiveness of the total quality and safety management implemented by the producers and of the environmental policies implemented by the EU Member States. It can also be due to the fact that, if present, only traces of heavy metals are carried over during the brewing process. In fact despite that hops, malts and adjuncts can contribute heavy metals to the finished beer, brewing is reported to be efficient in removing heavy metals entering the production chain[16]. Cadmium and lead, if present, can fortunately accumulate in the spent grains and wort sludge, thus reducing the carryover effects[16]. Nevertheless some warnings could arise in cases of beers brewed from raw materials that come from polluted environments.

CONCLUSIONS

This survey shows that beer does not pose a serious risk for consumers' health on the basis of the detected levels of arsenic, cadmium and lead. Moreover beer is not a dietary staple in Italy and the heavy metal contribution to the diet is thus irrelevant. Samples that were surveyed comprised both domestic and imported brands, but we are bound to say that any beer from undeveloped countries was not taken into consideration, due to their irrelevant market share in Italy.

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