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Temporal trend of the dietary exposure to metals/metalloids: A case study in Tarragona County, Spain

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ABSTRACT

In 2018, samples of various food groups were randomly purchased in different establishments of Tarragona County (Catalonia, Spain). The levels of As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Sn, Tl and V were determined in the analyzed foodstuffs and their dietary intakes were estimated. Manganese was the element showing the highest concentration, while Be, Cr and Tl were not detected in any of the samples. Fish and shellfish was the only food group with detectable traces of all the remaining elements. The current levels were compared with the results of two previous surveys conducted in 1998 and 2013 in the same area. Although the levels of the analyzed elements in foodstuffs increased during the period 2013–2018, their intakes decreased by an average of 60%, due to consumption patterns changes by the population. Children and adolescents exceeded the maximum recommended intake of Ni set by the EFSA, while the dietary exposure to Pb for children was also above safety values. Compared with the concentrations found in 2013, Ni was the only element showing an increase, as well as an increase of human dietary intake. Meat, vegetables and milk were identified as the main contributors to Ni exposure. This trend was also correlated with changes in the biological burden of the same elements previously reported for the population of the area, for whom an increase of Ni in lungs was reported. Based on these results, Ni should be included as a target metal by food safety authorities, being suggested its inclusion in future Total Diet Studies.

1. Introduction

Nowadays, it is well established that the diet is the main exposure pathway to chemical and microbiological contaminants. Food can be a vehicle for pathogens and environmental pollutants, being therefore a potential source of disease (Gallo, Ferrara, Calogero, Montesano, & Naviglio, 2020). In fact, foodstuffs can result contaminated in any of the steps of the food chain, and consequently, food safety is an issue of great importance (Domingo, 1994). In this sense, public authorities must provide sufficient confidence to the population by applying mechanisms to assure food safety. The ultimate goal should be to retrieve data on the occurrence of chemical and microbial contaminants in food.

While duplicate diet has been used as a possible method to assess dietary exposure to food nutrients and/or contaminants (Domingo, Perelló, & Giné-Bordonaba, 2012), the Total Diet Study (TDS) is the most internationally recognized cost-effective way to conduct this kind of evaluations (Wong, Chung, Chan, Ho, & Xiao, 2013; Muñoz, Zamorano, Garcia, & Bastías, 2017; Kolbaum, Berg, Müller, Kappenstein, & Lindter, 2019; Babaali et al., 2020; Wang et al., 2020). TDS provides representative and realistic data for assessing the dietary intake of chemicals, either contaminants or residues, for general populations (Turrini et al., 2018).

Since 2000, a TDS aimed at evaluating the health risks of the general population of Catalonia (Spain) to chemical contaminants in food, is periodically performed in our laboratory. Arsenic (As) and various metals are a group of particular interest (González et al., 2019; Llobet, Falcó, Casas, Teixidó, & Domingo, 2003; Martorell et al., 2011; Perelló, Vicente, et al., 2015). Prior to the first survey, in 1998, we conducted a specific TDS focused on the population of Tarragona County (Catalonia, Spain), aimed at assessing the dietary exposure to metals/metalloids by the local population living in the vicinity of a large petrochemical complex (Llobet, Granero, Schuhmacher, Corbella, & Domingo, 1998a). This first TDS was promoted by local authorities, in accordance with the scientific community of the area, as a pre-operational survey prior to the building of a new hazardous waste incinerator (HWI) located in the village of Constantí (Tarragona County). That new facility arose an important concern in the population of the area, based on the potential health risks mainly derived from polychlorinated dibenzo-*p*-dioxins and

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dibenzofurans (PCDD/Fs) and various metals/metalloids released to air by the HWI. Therefore, PCDD/Fs, As and a number of metals were included in a surveillance program on the impact of the facility on the environment and public health. For 20 years, data on the occurrence of metals/metalloids have been periodically obtained, while the changes in human exposure and the associated health risks have been updated (Bocio, Nadal, & Domingo, 2005; Llobet, Granero, Schuhmacher, et al., 1998b; Martí-Cid, Perelló, & Domingo, 2009; Perelló, Nadal, & Domingo, 2015).

While the TDS performed across Catalonia focused on a rather reduced number of toxic elements (i.e., As, Cd, Hg and Pb; including a specific speciation study of the contents of inorganic As (InAs) and methylmercury (MeHg)), the TDS performed in Tarragona County included a longer list of trace elements. Since chromium (VI) is a human carcinogen and some nickel compounds are also carcinogenic to humans (IARC, 1990), Cr and Ni were also included as target elements, together with Be, Mn, Sn, Tl and V.

The present study was aimed at updating the data on the dietary exposure to a number of metals/metalloids by individuals living in Tarragona County, 20 years after the first TDS was conducted in that area. The dietary intake for various age groups was estimated and compared with the most recent health-based Guidance Values (HBGVs) set by the European Food Safety Authority (EFSA).

2. Materials and methods

2.1. Food sampling

In January-February 2018, food samples were randomly purchased in different food establishments of Tarragona County (Catalonia, Spain). The selected food items were the same as in previous surveys (Perelló, Nadal, et al., 2015). In order to diversify food origins and to simulate the behavior of consumers, food samples were obtained in hypermarkets, supermarkets, local markets and grocery stores. The following 43 food items, classified into 12 groups, were purchased: meat and meat products (pork, sausage, boiled ham, chicken, veal, lamb), fish and seafood (mussel, shrimp, hake, sardine, canned tuna, canned sardine), pulses (lentils, beans, chickpeas), cereals (bread, rice, pasta), vegetables (lettuce, tomato, green beans, cabbage, cauliflower), fruits (apple, orange, pear, banana), tubers (potato, carrot), cow milk (whole milk, semi-skimmed milk), dairy products (soft cheese, semi-mature cheese, mature cheese, yoghurt, custard), eggs, oils and fats (olive oil, sunflower oil, margarine, butter, locally produced “D.O. Siurana” extra virgin olive oil), and sugar. Fourteen individual samples of each food item were collected for the subsequent analyses, with the exception of the “D.O. Siurana” extra virgin olive oil, for which 12 different samples were collected. Therefore, 600 individual food samples were analyzed. After sampling, foodstuffs were treated as for consumption, being the edible parts separated, shredded, homogenized and properly stored at −20 °C until analysis.

2.2. Chemical analysis

For metal extraction, a portion of sample (0.5 g) was digested with 5 mL of HNO_3 (65% Suprapur, E. Merck, Darmstadt, Germany) for 8 h at room temperature and additionally for 8 h at 80 °C in hermetic Teflon vessels. Samples were filtered and made up to 25 mL with deionized water. Afterwards, they were stored at a temperature of −20 °C until analysis (Martí-Cid et al., 2009; Perelló, Vicente, et al., 2015). The concentrations of As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Sn, Tl and V were determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan 6000), using rhodium (Rh) as internal standard. The limits of detection (LOD) for each trace element were: 0.025 μg/g for Tl; 0.05 μg/g for Be, Sn, Pb and Cd; 0.10 μg/g for Hg, Mn, As and V; 0.25 μg/g for Ni, and 0.50 μg/g for Cr. In turn, the limit of quantification (LOQ) ranged between 0.08 μg/g, for Tl, and 1.50 μg/g, for Cr. The accuracy of the instrumental equipment and the reliability of the analytical procedure was checked by using blank samples, as well as two different certified materials as reference standards: *Dogfish Liver* (NRC Canada, DOLT-5) and *Trace Elements in Spinach Leaves* (NIST 1570-A, Gaithersburg, USA). Blanks, duplicate samples and standards were analyzed every batch of 10 samples. Recovery percentages ranged between 51%, for Cr, and 98%, for Hg. Specific data of the recoveries for each element are given in Supplementary Information (SI; Table S1).

2.3. Data analysis

The statistical analysis of the results was performed by using the SPSS 27.0 software. Firstly, the Levene test was executed to determine the homogeneity of the variances. Depending on the data distribution, ANOVA or Kruskal-Wallis statistical tests were applied for normally and non-normally distributed data, respectively. A probability less than 0.05 ($p < 0.05$) was considered as statistically significant. Undetected elements were assumed to have a concentration equal to one-half of the respective limit of detection (ND = 1/2LOD) (González et al., 2019).

The dietary intake of each metal/metalloid was calculated by multiplying the concentration of that element in each food item by their respective consumption and then summing the results for all the food items. Consumption data were obtained from two national food surveys (AECOSAN, 2016a,b) conducted in Spain in recent years. One was focused on children and adolescents (ENALIA), and the other one was targeted to the adult population, including seniors and pregnant women (ENALIA2). ENALIA is a cross-sectional survey that was carried out between November 2012 and July 2014, which included a representative sample of 1862 Spanish children and adolescents (Cuadrado-Soto et al., 2020). In the current study, data from two age groups were used: children aged 3–9 years and adolescents aged 10–17 years. In turn, ENALIA2 is a dietary survey conducted to collect food consumption data, as well as other information on eating habits and physical activity of the Spanish adult population. It was based on data from 1033 individuals (AECOSAN, 2016b).

In this survey, human dietary exposure to metals/metalloids was estimated for 3 population groups classified according to age: 18–39 years old, 40–64 years old, and 65–74 years old. As an especially sensitive group, the dietary intake of the analyzed elements was also calculated for pregnant women. This is the very first TDS conducted in Tarragona County that provides data on children, adolescents and pregnant women, as our previous food surveys were focused only on the adult population (Bocio, Nadal, & Domingo, 2005; Llobet, Granero, Schuhmacher, et al., 1998b; Martí-Cid, Perelló, & Domingo, 2009; Perelló, Nadal, et al., 2015). In order to establish the temporal trends with respect to previous surveys, the intake of the analyzed elements was also estimated for a general adult population aged between 18 and 74 years.

3. Results and discussion

3.1. Concentrations in foodstuffs

The mean levels of the analyzed elements in food samples are summarized in Table 1. Manganese showed the highest concentrations, especially in cereals (6.87 μg/g) and pulses (3.60 μg/g). In contrast, Be, Cr and Tl levels were below their respective detection limits in all samples (<0.05, <0.50 and < 0.025 μg/g, respectively). Fish and seafood was the only food group where detectable amounts of the remaining elements were found. Very high levels of As were detected in fish and seafood (3.67 μg/g), in comparison to the As concentrations found in other food groups where this metalloid could be detected (e.g., pulses, cereals, dairy products, and oils and fats). Moreover, fish and seafood showed the maximum concentrations of Cd (0.074 μg/g), Pb (0.077 μg/g, the same as in vegetables) and V (0.067 μg/g). On the other hand, the highest levels of Mn, Ni and Sn corresponded to cereals, meat

Table 1
Concentrations of a number of elements (in μg/g of fresh weight) in food samples purchased in several establishments of Tarragona County in 2018.

Food group	*As*	*Cd*	*Hg*	*Mn*	*Ni*	*Pb*	*Sn*	*V*
Meat and meat products	0.051 ± 0.002	ND	ND	0.142 ± 0.076	0.806 ± 0.440	0.027 ± 0.004	0.031 ± 0.007	ND
Fish and seafood	3.67 ± 2.33	0.074 ± 0.066	0.092 ± 0.064	0.653 ± 0.713	0.471 ± 0.272	0.077 ± 0.052	0.040 ± 0.013	0.067 ± 0.036
Pulses	0.053 ± 0.006	ND	0.052 ± 0.003	3.60 ± 2.08	0.794 ± 0.096	0.039 ± 0.025	0.101 ± 0.066	ND
Cereals	0.081 ± 0.043	0.026 ± 0.002	ND	6.87 ± 0.784	0.233 ± 0.136	0.027 ± 0.002	0.036 ± 0.005	ND
Vegetables	ND	0.029 ± 0.006	ND	2.18 ± 0.890	0.693 ± 0.467	0.078 ± 0.107	0.026 ± 0.002	ND
Tubers	ND	ND	ND	0.567 ± 0.157	0.348 ± 0.009	ND	ND	ND
Fruits	ND	ND	ND	0.653 ± 0.803	0.301 ± 0.205	ND	0.027 ± 0.002	ND
Milk	ND	ND	ND	0.053 ± 0.004	0.359 ± 0.276	0.035 ± 0.014	0.045 ± 0.021	ND
Dairy products	0.053 ± 0.007	ND	ND	0.212 ± 0.148	0.341 ± 0.244	0.029 ± 0.005	0.031 ± 0.004	0.053 ± 0.005
Eggs	ND	ND	ND	0.267 ± 0.00	0.318 ± 0.000	ND	ND	ND
Sugar	ND	ND	ND	ND	0.154 ± 0.000	ND	0.042 ± 0.000	ND
Oils and fats	0.051 ± 0.002	ND	ND	0.125 ± 0.123	0.464 ± 0.222	0.047 ± 0.027	0.032 ± 0.006	ND

Data are given as means ± standard deviations. ND: Not detected. Be, Cr and Tl were not detected in any sample.

and meat products, and pulses (6.87, 0.806 and 0.101 μg/g, respectively). However, it must be highlighted that the levels of Pb and Sn were very similar independently of the food group, with their concentrations ranging between 0.027 and 0.078 μg/g for Pb, and between 0.026 and 0.101 μg/g for Sn. Finally, V could be only detected in dairy products, in addition to the fish and seafood group.

Individual concentrations of the food items are shown in Supplementary Information (SI; Table S2). Shrimp, sardine and hake contained the highest levels of As (7.30, 4.78 and 4.20 μg/g, respectively). Canned sardine also presented relatively high amounts of As, contrasting with canned tuna (3.17 vs. 0.59 μg/g). In turn, Hg showed an opposite profile, being the mean concentrations found in canned tuna (0.21 μg/g) higher than those detected in the remaining fish and seafood species. Cd and Pb were found at higher concentrations in the two shellfish species here analyzed (mussel and shrimp). Interestingly, the maximum amount of Pb was found in lettuce (0.27 μg/g), while the highest levels of Ni were observed in chicken breast and tomato (1.61 and 1.51 μg/g, respectively).

Fig. 1 depicts the temporal trends in the levels of As and various metals found in food samples purchased in Tarragona County in relation to the results obtained 20 years (in 1998) and 5 years (in 2013) ago. With respect to As, a slight increase of its concentrations in fish and shellfish was observed in the period 2013–2018. Nevertheless, this increase was not statistically significant ($p > 0.05$). For Cd, a metal that could be only detected in the groups of fish and seafood, vegetables and cereals, its mean levels significantly increased in the first two groups, while a certain stabilization of Cd levels was noted in cereals. As in the current study, fish and shellfish was the only group showing detectable amounts of Hg in the previous surveys. Notwithstanding, no significant differences were found when comparing the data of 2018 with those reported in 1998 and 2013. Likewise, Mn levels did not show significant changes with respect to our previous surveys. However, some fluctuations with time were noticed in Mn levels. With respect to Ni, pulses showed a significant reduction of concentrations compared to the

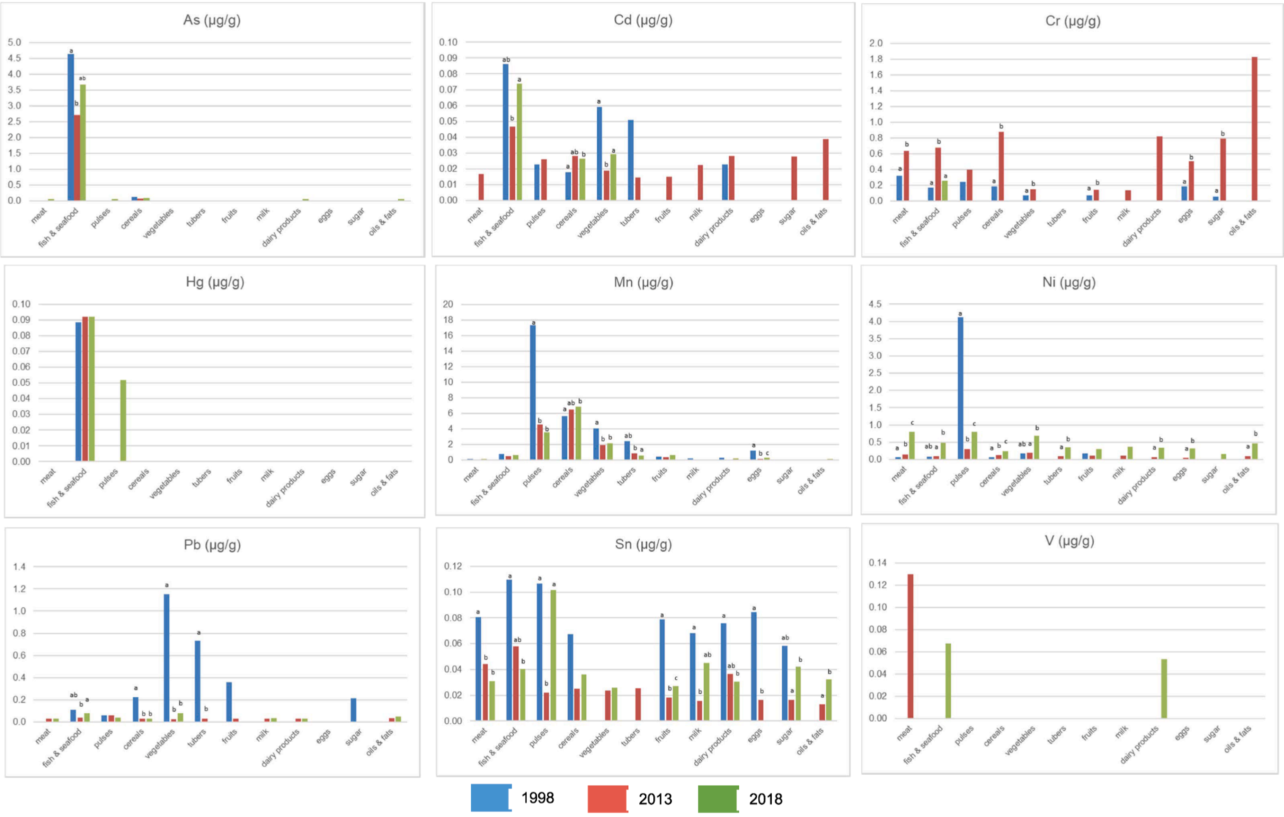

Fig. 1. Concentrations of the indicated elements in food samples purchased in 1998, 2013 and 2018 in Tarragona County. Different superscripts (a,b,c) indicate statistically significant differences ($p < 0.05$) between surveys.

baseline (1998) study, decreasing from 4.12 to 0.794 μg/g. By contrast, the levels of Ni increased between 2013 and 2018 in the rest of food groups. Interestingly, the current survey is the first one in which Ni could be detected in sugar.

On the other hand, there was a significant decrease of Pb levels in vegetables compared to those found in the baseline (1998) survey: 1.15 vs. 0.078 μg/g. This reduction would be associated to the ban of leaded gasoline introduced by the Spanish government in 2002. A significant decrease of Pb in vegetables (Capdevila, Nadal, Schuhmacher, & Domingo, 2003), as well as in other environmental matrices (Nadal, Schuhmacher, & Domingo, 2004; MacKinnon et al., 2011; Walraven, van Os, Klaver, Middelburg, & Davies, 2014), has been largely reported in the scientific literature after the obligatory use of unleaded gasoline. Moreover, there was also important reduction of the concentrations of this toxic metal in cereals and sugar. With respect to Sn, a general reduction was found, being Sn levels in foodstuffs much lower than those found in the baseline (1998) study. In turn, when the results of the last two surveys (2013 and 2018) were compared with those of the current one, it was seen that Sn concentrations fluctuated differently depending on each food group. Thus, a significant increase of Sn in pulses, sugar, and oils and fats was noted, while Sn levels were significantly reduced in meat and meat products, fish and seafood, and dairy products. Finally, in 2013, V could be only detected in meat and meat products, while in 2018, traces of this metal were found only in fish and shellfish and in dairy products. In general terms, the concentrations of most analyzed elements were slightly higher than those found in the previous survey (2013) (Perelló, Nadal, et al., 2015), but lower than those observed in the baseline study (1998) (Llobet, Granero, Schuhmacher, et al., 1998a).

3.2. *Dietary intake*

The daily dietary intakes of As and metals notably differed between the current study and the two previous (1998 and 2013) surveys. Data on daily food consumption for an adult living in Tarragona County are given in Table 2. In 1998, the mean total food consumed daily by an adult was 1198 g (Arija et al., 1996). This intake increased to 1505 g in 2013, when new updated data were available (Capdevila et al., 2000). In the most recent food consumption survey performed by the AECOSAN (2016b), the average amount of food daily consumed by the adult Spanish population was estimated to be 661 g, which is only 43% of the quantity estimated some years ago. Milk was the most consumed product (21%), while the contribution of fruits, cereals, meat and meat products, and vegetables was also notable: 16%, 13%, 12% and 12%, respectively. In spite of the differences in the daily amount of consumed food, the contribution percentages of each food group were similar in the different food consumption surveys. However, fruits, instead of milk, showed the highest contribution in the previous food consumption surveys (Arija et al., 1996; Capdevila et al., 2000).

Table 2
Food consumption by an adult man of 70 kg of body weight in Tarragona County in 1998, 2013 and 2018.

Food group	1998	2013	2018
Meat and meat products	173	185	82
Fish and seafood	72	92	18
Pulses	16	24	8
Cereals	194	206	88
Vegetables	122	226	81
Tubers	66	74	48
Fruits	269	239	103
Milk	178	217	141
Dairy products	44	106	34
Eggs	29	34	17
Sugar	35	61	6
Oils and fats	NA	41	35
TOTAL	**1198**[a]	**1505**[b]	**661**[c]

Data from [a]Llobet et al. (1998), [b]Perelló et al. (2015), and [c]AECOSAN (2016b).
NA: not available.

The dietary intake of the analyzed elements by the adult population living in Tarragona County is given in Table 3. The contribution of each food group to the total intake is also summarized. Since Mn and Ni showed the greatest concentration values in food, the highest intakes also corresponded to these trace elements (947 and 289 μg/day, respectively). The group of cereals was the most important contributor to Mn intake, meaning 63% of the total. This percentage would be linked to the high levels of Mn in cereals together with the high consumption of this food group. In turn, meat and meat products showed the largest contribution of Ni intake (23%), although the consumption of Ni through vegetables and milk was also relevant (19% and 17%, respectively). Since fish and seafood showed the highest concentrations of As and Hg, this food group was identified as the main pathway of the dietary intake of both elements, with contributions above 80%. On the other hand, vegetables group was the main contributor to the intake of Pb, resulting from the relatively high Pb levels and the important consumption of vegetables. This is in accordance with data reported by Malavolti et al. (2020) and De Vasconcelos Neto, Silva, Araújo, and Souza (2019), who pointed out that vegetables are one of the main contributors to Pb exposure. Finally, V intake was only calculated for fish and seafood and for dairy products, the only two groups where this metal could be detected.

A specific study of the dietary intake of the analyzed elements for different population groups -classified according to age- was done (Table 4). Furthermore, as pregnant women are considered an especially vulnerable/sensitive population group and specific warning messages are addressed to them, calculations were also carried out for pregnant women. Without any exception, adolescents presented the maximum intake of all elements. However, a remarkable high intake of Hg was estimated for children (2.67 μg/day), being this very close to the intake estimated for adolescents (2.74 μg/day).

The daily intake of the analyzed elements was also calculated according to the mean body weight of each population group. As expected, children showed the greatest intake values, followed by adolescents. On the other hand, the dietary intake of toxic elements, given as μg/kg body weight/day (μg/kg bw/day), was very similar in adults, seniors and pregnant women. For example, the estimated As intake by children and adolescents was estimated in 4.05 and 2.05 μg/kg bw/day, respectively, while it ranged 1.06–1.27 μg/kg bw/day in the other groups of population. A specific speciation study was not performed, since only the concentrations of total As were determined. In a recent study, González et al. (2019) evaluated the dietary intake of both InAs and total As by the average general population of Catalonia (Spain). It was found that the intake of InAs was approximately 2% of that of total As. Using that percentage, all the population living in Tarragona County, including children, would show an ingestion of As much lower than the limit set by the EFSA (2009a), which considers a benchmark dose lower confidence limit ($BMDL_{01}$) of 0.3–8.0 μg/kg bw/day (EFSA, 2009a).

The dietary intake of Cd, Hg, Ni and Pb by individuals of different age groups, and according to the mean body weight, is depicted in Fig. 2. The results are also compared with the safety limits established by the EFSA. In 2009, the EFSA re-evaluated the data about Cd and fixed a new tolerable weekly intake (TWI) of 2.5 μg/kg bw/week (EFSA, 2009b). This threshold is far above the current dietary intake of Cd for all the groups of population. Regarding Hg, a speciation study was not here performed, since the amounts of inorganic Hg and MeHg in foodstuffs were not separately analyzed. However, a worst-case scenario was considered by assuming that all the Hg in food could be in the form of MeHg, which is the most toxic species. Therefore, the daily intake of total Hg was compared to the TWI of MeHg recommended by the EFSA (2012). Even in an unrealistic worst-case scenario, the current dietary exposure to Hg for the population of Tarragona County, including children, would be below the threshold values. With respect to Pb, the

Table 3
Dietary intake of a number of elements (in µg/day) by the adult population of Tarragona County in 2018.

Food group	*As*	*Cd*	*Hg*	*Mn*	*Ni*	*Pb*	*Sn*	*V*
Meat and meat products	4.13	–	–	11.5	65.7	2.23	2.51	–
Fish and seafood	67.1	1.35	1.69	11.9	8.60	1.40	0.733	1.23
Pulses	0.422	–	0.409	28.4	6.27	0.312	0.801	–
Cereals	7.13	2.31	–	601	20.5	2.40	3.16	–
Vegetables	–	2.36	–	175	55.8	6.29	2.08	–
Tubers	–	–	–	27.3	16.7	–	–	–
Fruits	–	–	–	67.6	31.1	–	2.81	–
Milk	–	–	–	7.40	50.5	4.88	6.37	–
Dairy products	1.83	–	–	7.33	11.8	0.988	1.06	1.84
Eggs	–	–	–	4.58	5.46	–	–	–
Sugar	–	–	–	–	0.922	–	0.252	–
Oils and fats	1.78	–	–	4.38	16.2	1.65	1.13	–
TOTAL	**82.4**	**6.02**	**2.10**	**947**	**289**	**20.1**	**20.9**	**3.07**

Table 4
Dietary intake of As and various metals (in µg/day) by the population of Tarragona County in 2018 classified according to the age group.

Element	Children	Adolescents	Young adults	Adults	Seniors	Pregnant women
As	97.1	104	76.6	85.5	89.7	70.8
Cd	4.82	6.59	5.39	6.55	6.00	5.39
Hg	2.67	2.74	1.92	2.17	2.39	1.79
Mn	840	1191	889	1001	930	819
Ni	308	362	278	301	282	272
Pb	21.1	24.8	19.0	21.4	19.0	19.7
Sn	25.2	28.3	20.2	21.5	20.6	19.8
V	4.66	4.71	3.05	3.09	3.06	3.07

EFSA (2010) proposed to assess the Pb risks with BMDLs derived from Pb levels (in µg/L) in blood, according to data on neurotoxicological development, $BMDL_{01}$ 12 (0.50), effects on systolic blood pressure, $BMDL_{01}$ 36 (1.50), and the effects on the prevalence of chronic kidney disease, $BMDL_{10}$ 15 (0.63) (EFSA, 2010). Taking into account this information, children exceeded the safety level for neurotoxicological effects (0.88 µg Pb/kg bw/day), but not for the effects on blood pressure and kidney disease.

Nickel is a toxic metal of special relevance. In 2015, the EFSA received a specific request for a scientific opinion on the risk to human health from the presence of Ni in food, and particularly in vegetables. The assessment was also extended to drinking water. The reproductive and developmental toxicity in experimental animals was selected as the critical effect for the assessment of chronic effects of Ni (EFSA, 2015). As a result, a tolerable daily intake (TDI) of 2.8 µg Ni/kg bw/day was derived. Recently, the EFSA (2020) updated the data on risk assessment of Ni in food and drinking water by using more than 47,000 analytical results on Ni occurrence to calculate chronic and acute dietary exposure. A $BMDL_{10}$ of 1.3 mg Ni/kg bw/day was selected as the reference point for the establishment of a TDI of 13 µg/kg bw. However, a BMDL could not be derived for the evaluation of the acute exposure. Instead, a lowest-observed-adverse-effect-level (LOAEL) of 4.3 µg Ni/kg bw was selected as reference value. According to the current results, the youngest population groups living in Tarragona County, both children and adolescents, had a much higher dietary intake of Ni (12.82 and 7.10 µg/kg bw/day, respectively) than the LOAEL. In fact, the intake of Ni through the diet is dangerously very close to the TDI established by the EFSA in terms of chronic exposure. Furthermore, although Ni intake for the other population groups was below the LOAEL, the current values are also very close to that threshold, being especially relevant for

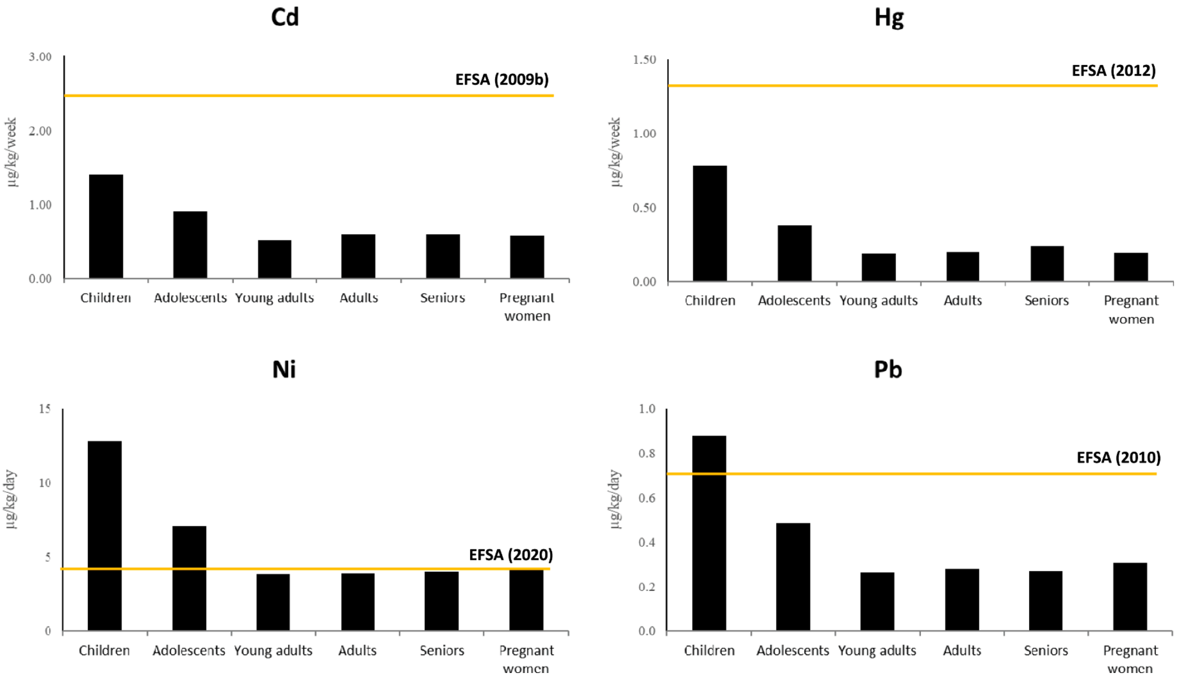

Fig. 2. Human dietary intake of Cd, Hg, Ni and Pb according to age, and comparison with EFSA threshold levels.

pregnant women (4.19 μg/kg bw/day). This is the very first study performed in Catalonia (Spain) in which the updated scientific information of the EFSA on Ni has been used. Our results clearly indicate that Ni is a potentially toxic metal, whose food concentrations should be controlled in future dietary studies, not only conducted in Tarragona County, but also at regional/national/international levels. Therefore, we recommend that Ni is included as one of the target elements in food surveillance programs.

The current dietary exposure to As and various metals by the population of Tarragona County was compared with data obtained from the scientific literature. Since children and adolescents exceeded the HBGVs, special attention was paid to Ni. Recently, Marini, Angouria-Tsorochidou, Caro, and Thomsen (2021) evaluated the daily intake of heavy metals and minerals by analyzing the levels in Danish food items. Four different Danish diets (i.e., standard, carnivore, vegetarian and vegan) were considered. The risk of exceeding the provisional TDI across the four dietary profiles was 60%, 17% and 16% for Cd, Hg and Pb, respectively, while the risk of exceeding the provisional daily intake of As was 33%. The dietary intake of Ni of a person following a standard diet was estimated in 102 μg/day, a value clearly lower than the mean dietary intake estimated for the population of Tarragona County (289 μg/day). In a very comprehensive recent TDS, Cubadda et al. (2020) assessed the dietary exposure of the Italian population to Ni. The mean chronic dietary exposures for children, adolescents, adults and the elderly to this metal were estimated in 4.57, 2.57, 1.55, and 1.47 μg/kg bw/day, respectively. These levels mean a dietary intake of Ni, which is around 2.5-times lower than those calculated for the same population groups in Tarragona County, evidencing that local residents would be highly exposed to Ni through the diet. Cubadda et al. (2020) also summarized data from the scientific literature regarding dietary exposure assessment to Ni via TDS in various countries. All the studies, which included data from France (Arnich et al., 2012), Lebanon (Nasreddine et al., 2010) and United Kingdom (Rose, Baxter, Brereton, & Baskaran, 2010), showed a mean children exposure to Ni notably lower than that found in Tarragona County. However, it must be highlighted that the comparison of TDS data from different countries cannot be easily carried out (Dofkova et al., 2016). Sirot et al. (2018) found that exposure levels to InAs, Pb and Ni were higher than the HBGVs for a part of children, which was considered as a concern, therefore requiring management measures to reduce the exposure. Although the target population was French children under 3 years of age, the authors already identified Ni and Pb as two metals of special interest. Furthermore, they also suggested that data should be integrated in future work on cumulative and aggregated risk assessment for several substances and exposure routes, something not usually considered in exposure assessment studies.

Humans are mainly exposed to chemical contaminants through the diet. Consequently, for the general population, the body burdens of toxic elements essentially depend on their dietary intakes. Since 1998, a biological monitoring program of the population living in Tarragona County was initiated in parallel to the TDS. Blood and autopsy tissues for the adult population (Llobet, Granero, Schuhmacher, et al., 1998b; Llobet, Granero, Torres, Schuhmacher, & Domingo, 1998), and human hair for children (Granero, Llobet, Schuhmacher, Corbella, & Domingo, 1998), were selected as biomonitors to evaluate the exposure to trace elements. In successive 5-year periods, new surveys were conducted by periodically measuring the levels of metals and As in the same biological tissues (Nadal, García, Schuhmacher, & Domingo, 2019). In the last survey, performed in 2017–2019, updated information was retrieved (Esplugas et al., 2019, 2020; García et al., 2020). The results were compared with those of the baseline survey. In general, an increasing trend was not observed in any of the matrices, as most elements showed non-significant differences after 20 years. The concentrations of most elements in whole blood collected in 1998 and 2017 were very similar, with only Hg and Mn showing a significant decrease. In human hair, the levels of most elements were again statistically similar in 1998 and 2017, although Cd, Cr and Pb showed a significant reduction. It must be remarked that the levels of Ni in both matrices, blood and hair, showed a slight, non-significant reduction, in the last surveys (Esplugas et al., 2019, 2020). Moreover, the concentration of Ni in lung, as well as those of Cr in kidney and bone from autopsied subjects, significantly increased between 1998 and 2019 (García et al., 2020).

4. Conclusions

In the current food survey, Mn was the most abundant element in the 600 analyzed food items. Fish and shellfish was the only group with detectable traces of all the remaining elements, presenting the highest concentrations of As, Cd, Pb and V. In turn, meat and vegetables were the food groups showing the greatest levels of Ni. The intake of trace elements decreased by an average of 60% as a consequence of consumption patterns changes among the population. Remarkably, Ni was the only element showing increased concentrations in most food items, resulting in an increase of human exposure. Moreover, the dietary intake of Ni for children and adolescents exceeded the most recent guidance values set by the EFSA. This Authority is paying special attention to Ni, given that its opinion on Ni in food and drinking water was updated twice in only five years, eventually changing the HBGVs. The current exposure values of Ni by the local population were currently much higher than those reported in other countries for the same age groups. The increase in the dietary Ni exposure correlates well with the increase of the concentrations of this metal found in lungs of subjects who had been living in Tarragona County at least for the last 10 years. In summary, our current findings clearly indicate that Ni may be a metal of notable concern. The results also highlight the importance of including Ni in TDSs performed not only in Tarragona County, but also elsewhere the populations present similar food consumption patterns.

CRediT authorship contribution statement

Neus González: Formal analysis, Investigation, Writing - review & editing. **Montse Marquès:** Validation, Methodology, Writing - review & editing. **Martí Nadal:** Resources, Investigation, Writing - original draft, Supervision. **José L. Domingo:** Conceptualization, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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