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Total arsenic and water-soluble arsenic species in foods of the first German total diet study (BfR MEAL Study)

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ABSTRACT

Arsenic can occur in foods as inorganic and organic forms. Inorganic arsenic is more toxic than most water-soluble organic arsenic compounds such as arsenobetaine, which is presumed to be harmless for humans. Within the first German total diet study, total arsenic, inorganic arsenic, arsenobetaine, dimethylarsinic acid and monomethylarsonic acid were analyzed in various foods. Highest levels of total arsenic were found in fish, fish products and seafood (mean: 1.43 mg kg^{-1}; n = 39; min–max: 0.01–6.15 mg kg^{-1}), with arsenobetaine confirmed as the predominant arsenic species (1.233 mg kg^{-1}; n = 39; min–max: 0.01–6.23 mg kg^{-1}). In contrast, inorganic arsenic was determined as prevalent arsenic species in terrestrial foods (0.02 mg kg^{-1}; n = 38; min–max: 0–0.11 mg kg^{-1}). However, the toxicity of arsenic species varies and measurements are necessary to gain information about the composition and changes of arsenic species in foods due to household processing of foods.

1. Introduction

Arsenic (As) as a ubiquitous metalloid can be found in both inorganic and organic forms in foods (Edmonds, Francesconi, & Stick, 1993; Francesconi, 2010). Fish and seafood (including seaweed) are the major sources of dietary As exposure for most human populations, where As is primarily present as organic compounds such as arsenobetaine (AsB), arsenosugars and arsenolipids (Taylor et al., 2017). Arsenobetaine is the predominant water-soluble As species in marine food and is considered to be non-toxic for humans as there are no toxicological data to indicate otherwise (Francesconi, 2010; Kaise, Watanabe, & Itoh, 1985). In contrast, the prevalent As species in drinking water and terrestrial foods is inorganic As (iAs) as arsenite (As(III)), arsenate (As(V)) or a combination of both. Dimethylarsinic acid (DMA(V)) and monomethylarsonic acid (MMA(V)) (termed DMA and MMA in the following) are the main metabolites of iAs and can occur in terrestrial as well as in marine foods (Lynch, Greenberg, Pollock, & Lewis, 2014).

The International Agency for Research on Cancer (IARC) classified As and iAs as “carcinogenic to humans” (Group 1). Both, DMA and MMA are classified as “possibly carcinogenic to humans” (Group 2B) and toxicological evaluations of both As species are still in process (IARC, 2012). Due to the toxic potential of iAs, the European Food Safety Authority (EFSA) recommends minimizing the intake of iAs. As rice is among the most consumed grain in many countries and is known to contain higher levels of iAs compared to other grains (Davis et al., 2017), the European Commission has set maximum levels (MLs) of iAs in rice and rice-based products (European Commission, 2015). A number of studies examined As species in rice and rice-based products and investigated the impact of different influences on their levels in these food items. These studies indicate varying concentrations of iAs in rice depending on their geographical origins, on effects of the water to rice ratio during cooking, on the contamination of the used cooking water as well as on the type of rice and processing factors (Althobiti, Sadiq, & Beauchemin, 2018; Carbonell-Barrachina et al., 2012; Devesa, Vélez, & Montoro, 2008; Meharg et al., 2008; Rasheed, Kay, Slack, & Gong, 2018; Sharafi, Yunesian, Mahvi, Pirsaheb, Nazmara, & Nabizadeh Nodehi, 2019; Upadhyay, Shukla, Yadav, & Srivastava, 2019; Williams et al., 2006; Zhao, Zhu, & Meharg, 2013).

Although investigations of As species were carried out in drinking water, rice, fish and seafood, the majority of dietary exposure and risk

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assessment is presently based on occurrence data of total As. Further data on As species in foods are required to improve dietary exposure and risk assessment. To gain representative data about levels of substances in foods, a total diet study (TDS) as standardized methodology is recommended by EFSA, the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) in 2011 (EFSA/FAO/WHO, 2011). A TDS establishes the average levels of substances in foods considering three criteria: (i) covering more than 90% of the foods consumed by the population, (ii) foods are typically prepared as in private households prior to analyses and (iii) similar foods are pooled in one sample (EFSA/FAO/WHO, 2011; Moy & Vannoort, 2013). Other European countries, such as France, Ireland, Spain and Portugal have carried out TDSs, but the determination of iAs was only conducted in the TDSs of Ireland and Spain (Valencia) (FSAI, 2016; Llobet, Falcó, Casas, Teixidó, & Domingo, 2003; Marín, Pardo, Báguena, Font, & Yusà, 2017; Martí-Cid, Llobet, Castell, & Domingo, 2008; Millour et al., 2011; Ventura et al., 2020). Speciation of further As species was not performed in any European TDSs. The first German TDS called BfR MEAL Study (meals for exposure assessment and analytics in food) (Sarvan, Bürgelt, Lindtner, & Greiner, 2017) was conducted following the recommendation by EFSA/FAO/WHO and determined besides others, total As and As species. Representative levels of total As in most commonly consumed foods in Germany were determined and speciation of iAs, AsB, DMA and MMA was performed for various foods such as fish, seafood, and rice for the first time in a TDS.

2. Materials and methods

2.1. Sample collection and preparation

The BfR MEAL Study followed the international recommended design of a TDS and was briefly described elsewhere (Sarvan et al., 2017). The list of foods (MEAL food list) to be analyzed was established based on consumption data of 24-h recalls of the National Nutrition Survey II (NVS II; 2006, n = 13,926) of the Max Rubner Institute (MRI) (Krems et al., 2006; MRI, 2008a; 2008b) and 24-h recalls of the German consumption survey for children (VELS; 2002, n = 804) (Banasiak, Heseker, Sieke, Sommerfeld, & Vohmann, 2005; Heseker, Oeppining, & Vohmann, 2003).

Here, most consumed foods were selected from the respective main food group using FoodEx2 classification (European Food Safety Authority, 2015). The MEAL food list contained 356 different foods in total and covered at least 90% of the average German diet across genders and age groups from 0.5 to < 5 years and 14 to 80 years. Foods with an assumed impact on various production types, regions or seasons were identified (EFSA/FAO/WHO, 2011; Moy & Vannoort, 2013). A distinction was made between organic and conventional production for 106 foods of the MEAL food list. For regionally sampled foods (n = 70), Germany was divided into four regions (north, east, south, west) with three sampling points each (rural area, small and big city). Foods with seasonal variations (n = 57), i.e. one season with expected higher local production and one season with expected higher import rates, were sampled twice. If a food was collected several times according to the previous criteria, the pooled sample contained 15 individual food items (called subsample). Otherwise, pooled samples were composed of 20 subsamples and were only sampled in the area of Berlin.

In order to represent the purchasing behavior of German consumers, market share data, e.g. brands, varieties, origins and shopping locations were evaluated to compile a shopping list. Pooled samples were prepared to be analyzed in a manner considered to be typical of an average German household. Therefore, information about the household behaviors, e.g. about browning degree preferences, sources of recipes, materials of used kitchen utensils or information about out-of-home consumption, was collected and evaluated using surveys.

After preparation, equally sized subsamples were ground using a knife mill (GRINDOMIX GM 300 or GRINDOMIX GM 200; Retsch GmbH, Haan, Germany) to obtain a pooled sample. Where necessary, a weighed aliquot of water (16.9 MΩ cm; Milli-Q® Integral 5, Merck Chemicals GmbH, Darmstadt, Germany) or liquid nitrogen were added to ensure a homogeneous distribution. All pooled samples were stored in polypropylene (PP) vessels at −20 °C until analysis.

Due to multiple sampling of foods a total of 870 pooled samples were prepared for the analysis of total As between December 2016 and May 2019. The As speciation was performed for rice, rice-based meals and products from the food groups “grains and grain-based products” and “composite dishes” as well as for all samples of the main food group “fish, fish products and seafood”. The pooled samples organic rice and conventional rice included brown and white rice according to market share data for Germany. In addition to the MEAL food list, brown and white rice were sampled separately to ensure a comparison of both food items. Since rice is known to be prone to iAs contamination, rice-based breakfast cereals and rice flakes for infants were analyzed additionally. Furthermore, selected terrestrial samples of the MEAL food list with comparable higher total As levels were analyzed to gain more information about the composition of water-soluble As species in foods.

2.2. Determination of total arsenic

Total As determination was outsourced to the accredited contract laboratory (Institut Kirchhoff Berlin GmbH) and was performed as described in the following: Total As was determined using an inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion. Each sample was analyzed in duplicate. The pressure digestion was performed according to DIN EN 13805:2014 (pressure digestion) by weighing 0.4 g ± 0.1 mg of solid samples and 2.0 g ± 0.1 mg of liquid samples. After adding 4.0 mL HNO_3 and 2.0 mL H_2O_2, the samples were gradually heated to 210 °C and maintained at this temperature for 25 min using a MARS 6 microwave digestion system (CEM, Kamp-Linfort, Germany). After cooling to room temperature, the samples were diluted with purified water up to a total volume of 25 mL. Total As concentration in the digests was determined by ICP-MS X-Series II and ICP-MS iCAP Q (Thermo Fischer Scientific, Bremen, Germany) systems, as well as by an ICP-MS 7800 (Agilent Technologies) system. Helium was used as cell gas to remove polyatomic interferences from argon chloride ($^{40}Ar^{35}Cl$ on ^{75}As). For internal standardization, Nb (2 μg L^{-1}) was directly added during the injection of the digested samples to ICP-MS. Instruments were optimized daily for maximum sensitivity. Further information on the used reagents and standards and instrumental parameters is listed in Tables S1 and S2, Supplementary data. Limits of detection (LOD) were 0.001 mg kg^{-1} for moist food and 0.002 mg kg^{-1} for dry food. Limits of quantification (LOQ) were 0.002 mg kg^{-1} for moist food and 0.01 mg kg^{-1} for dry food.

2.3. Determination of water-soluble arsenic species

The determination of As species was performed at the University of Potsdam. The method based on Raber et al., 2012 was used and carried out in duplicate for each sample (Raber, Stock, Hanel, Murko, Navratilova, & Francesconi, 2012). For extraction, about 1 g ± 0.1 mg of a sample was weighed and 20 mL of 0.02 M trifluoroacetic acid with 6% (V/V) H_2O_2 were added. Latter was added for oxidation of As(III) to As (V). The suspensions were sonicated for 15 min at 35 °C and extracted for 60 min at 95 °C in a water bath. Sonication was repeated and the extracts were centrifuged for 15 min at 7,164 rcf. An aliquot of 2 mL was centrifuged for 15 min at 21,380 rcf.

The supernatant (200 μL) was directly used for analysis with anion exchange high-performance liquid chromatography (HPLC)-ICP-MS/MS. An HPLC 1260 series instrument coupled to ICP-QQQ-MS 8800 from Agilent Technologies was used. Instruments were optimized daily for maximum sensitivity. Separation was performed on a Hamilton PRP-X100 column (150 × 4 mm; 10 μm) at 40 °C using 3.5 mM malonic acid with 1% (V/V) H_2O_2 (adjusted to pH 5.6 with 25% (V/V) NH_4OH)

as mobile phase. Concentrations of iAs are determined only as As(V) since As(III) was converted to As(V) by oxidation with H_2O_2. Both, DMA and MMA were determined in +5 oxidation state. The quantification was done by external calibration against standard arsenic species (iAs, DMA, MMA) based on peak areas. Obtained LOD and LOQ for all As species were 0.001 mg kg^{-1} and 0.003 mg kg^{-1}, respectively.

Since AsB eluted in the void volume of the anion exchange method, samples that showed signals at low retention times were subjected to cation exchange HPLC-ICP-MS/MS, to confirm the presence of AsB. For this purpose, a Hamilton PRP-X200 column (250 × 4 μm; 10 μm) at 40 °C and 10 mM pyridine (adjusted to pH 2.6 with formic acid) as mobile phase was used. The quantification was done by external calibration against iAs standard based on peak areas.

Further information on the used reagents and standards and instrumental settings is given in Tables S1 and S3, Supplementary data. The data evaluation was carried out by using OrginPro 2018b (version b9.5.5.409, OriginLab).

2.4. Statistical methods

Results below the LOD or LOQ were substituted using the modified lower bound (MDL) approach, i.e. results below the LOD were set to zero and the results below the LOQ and above the LOD were replaced by the value reported as the LOD. In addition, the upper bound (UB) approach was used by replacing results below the LOD by the value reported as the LOD and the results below the LOQ and above the LOD by the value reported as the LOQ. Results of the UB approach are given in Table S4, Supplementary data. Calculation of mean values, median, 95th percentile (P95), minimum (min) and maximum (max) levels of the main food groups were carried out using Microsoft Excel 2016 (version 16.16.23) and are given in Table 1. The P95 was only calculated for main food groups of at least 20 pooled samples using the QUANTIL.EXKL command. Results of samples analyzed additionally to the MEAL food list were not included in the calculations for the main food groups.

3. Results and discussion

3.1. Total arsenic

Quantifiable levels of total As were found in 544 (63%) of the 870 pooled samples analyzed. In the main food groups "fish, fish products and seafood" as well as in "products for non-standard diet, food imitates and food supplements", all samples contained quantifiable levels of total As. In the other main food groups, the amount of quantifiable levels of total As varied depending on the matrices. In 221 (25%) pooled samples, the levels of total As were below the LOQ and in 105 (12%) pooled samples below the LOD, e.g. in samples of the main food groups "animal and vegetable fats and oils" and "water and water-based beverages" no levels of total As were quantified (see Table S5, Supplementary data).

Highest mean levels of total As were measured in the main food group "fish, fish products and seafood" (1.433 mg kg^{-1}, n = 39), followed by "vegetable and vegetable products" (0.02 mg kg^{-1}, n = 152) and "legumes, nuts, oil seeds and spices" (0.009 mg kg^{-1}, n = 24) and "food products for young population" (0.009 mg kg^{-1}, n = 15) (see Table 1).

Within the main food group of "fish, fish products and seafood" the highest mean total As levels in decreasing order of subgroups were found in marine fish (2.82 mg kg^{-1}, n = 10), seafood (1.72 mg kg^{-1}, n = 3), fish products (1.68 mg kg^{-1}, n = 9), migratory fish (0.73 mg kg^{-1}, n = 6) and freshwater fish (0.03 mg kg^{-1}, n = 2) (see Table 2). However, Plaice (*Pleuronectes platessa*)/ sole (*Solea solea*), canned cod liver, smoked spiny dogfish (*Squalus acanthias*) and cod (*Gadus morhua*) showed the highest total As concentrations in the main food group "fish, fish products and seafood" (6.15 mg kg^{-1}, 6.00 mg kg^{-1}, 5.70 mg kg^{-1}, 4.25 mg kg^{-1}, respectively). Lowest concentrations were found in fish from freshwater sources, such as carp (*Cyprinus*) and striped catfish (*Pangasianodon hypophthalmus*) (0.04 mg kg^{-1}, 0.01 mg kg^{-1}, respectively).

The highest levels in the main food group of "vegetable and vegetable products" were determined in algae, boletus (*Boletus edulis*), cultivated mushrooms (*Agaricus bisporus*), culinary fresh herbs and pickled cucumber (2.500 mg kg^{-1}, 0.047 mg kg^{-1}, 0.016 mg kg^{-1}, 0.015 mg kg^{-1}, 0.014 mg kg^{-1}, respectively).

Highest levels for the main food group "legumes, nuts, oilseeds and spices" were found in pistachios (*Pistachia vera*) and spices (dry) (0.034 mg kg^{-1}, 0.033 mg kg^{-1}, respectively).

In the main food group "food products for young population" highest levels of total As were found in cereal porridge for infants (powder) (0.027 mg kg^{-1}), ready-to-eat-mixed-meal for children (0.021 mg kg^{-1}) and cereal porridge (millet) for infants (powder) (0.021 mg kg^{-1}).

For the remaining main food groups, the mean levels of total As

Table 1
Levels of total arsenic by food group (MLB values in mg kg^{-1}).

Main food group	Pooled samples (n)	Foods (n)	<LOD / LOQ (%)	Mean	Median	P95	Min - max
Alcoholic beverages	11	8	64	0.002	0.001	**	0 – 0.003
Animal and vegetable fats and oils	13	8	100	0.001	0.002	**	0 – 0.002
Coffee, cocoa, tea and infusions	11	8	55	0.005	0.000	**	0 – 0.040
Composite dishes	170	52	24	0.007	0.003	0.025	0 – 0.325
Eggs and egg products	10	2	80	0.001	0.001	**	0 – 0.002
Fish, seafood, amphibians, reptiles and invertebrates	39	30	0	1.433	0.855	6.000	0.010 – 6.150
Food products for young population	15	11	27	0.009	0.003	**	0 – 0.028
Fruit and fruit products	64	22	50	0.002	0.002	0.004	0 – 0.008
Fruit and vegetable juices and nectars	12	10	67	0.001	0.001	**	0 – 0.004
Grains and grain-based products	97	40	22	0.008	0.005	0.039	0 – 0.130
Legumes, nuts, oilseeds and spices	24	20	38	0.009	0.004	0.040	0.002 – 0.043
Meat and meat products	101	35	32	0.003	0.002	0.009	0 – 0.012
Milk and dairy products	38	24	74	0.001	0.001	0.004	0 – 0.007
Products for non-standard diet, food imitates and food supplements	8	7	0	0.005	0.005	**	0.002 – 0.011
Seasoning, sauces and condiments	19	16	16	0.004	0.004	0.019	0 – 0.019
Starchy roots or tubers and products thereof, sugar plants	26	8	50	0.002	0.002	0.006	0 – 0.007
Sugar, confectionery and water-based sweet desserts	18	15	83	0.004	0.002	**	0 – 0.017
Vegetables and vegetable products	153	34	31	0.020	0.003	0.016	0 – 2.500
Water and water-based beverages	41	6	100	0.000*	0.000*	0.001	0 – 0.001
Total	**870**	**356**	**38**	**0.071**	**0.002**	**0.049**	**0 – 6.150**

*Left censored-data were analyzed using the modified lower bound (MDL) approach, i.e. results below the LOD were set to zero and the results below the LOQ and above the LOD were replaced by the value reported as the LOD. All pooled samples of this main food group were below LOD or LOQ, therefore the calculated mean is zero.

**The P95 was only calculated for main food groups of at least 20 pooled samples.

Table 2
Levels of total arsenic, inorganic arsenic (iAs), arsenobetaine (AsB), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) in the food group "fish, fish products and seafood" (in mg kg^{-1}).

Sub food group	Food	Total As	iAs	AsB	DMA	MMA	∑As species	% ∑As species
Fish products	Cod liver (*Gadus morhua*), canned	6.000	0.408	2.972	0.419	1.227	5.026	84
	Fish fingers (sticks) (*Gadus chalcogrammus*)	0.855	ND	0.886	0.087	ND	0.973	114
	Fish fillet, gratinated	0.810	ND	0.620	0.070	ND	0.690	85
	Herring (*Clupea harengus*), canned	1.200	0.011	0.295	0.034	0.152	0.492	41
	Herring (*Clupea harengus*), fried herring	1.500	0.023	0.324	0.103	0.275	0.725	48
	Herring (*Clupea harengus*), pickled ("Matjes"."Bismarckhering")	1.600	0.100	0.145	0.124	0.428	0.797	50
	Herring (*Clupea harengus*), pickled(Roll mop)	1.100	0.013	0.147	0.043	0.194	0.398	36
	Tuna (*Thunnus*), canned	0.835	ND	0.792	ND	ND	0.792	95
	Tuna (*Thunnus*), canned in oil	1.200	ND	0.827	ND	ND	0.827	69
	Mean	**1.678**	**0.062**	**0.779**	**0.098**	**0.253**	**1.192**	**71**
Freshwater fish	Striped catfish (*Pangasianodon hypophthalmus*)	0.010	0.006	0.008	ND	ND	0.014	140
	Carp (*Cyprinus*) (region 1)	0.052	ND	0.011	ND	0.030	0.041	79
	Carp (*Cyprinus*) (region 2)	0.030	ND	0.017	ND	0.014	0.031	103
	Carp (*Cyprinus*) (region 3)	0.033	ND	0.010	ND	0.015	0.025	76
	Carp (*Cyprinus*) (region 4)	0.058	ND	0.017	ND	0.033	0.050	86
	Mean	**0.037**	**0.008**	**0.013**	**ND**	**0.023**	**0.032**	**97**
Marine fish	Cod (*Gadus morhua*)	4.250	ND	3.621	0.523	ND	4.144	98
	Plaice (*Pleuronectes platessa*)/ sole (*Solea solea*)	6.150	ND	6.227	0.708	ND	6.935	113
	Halibut (*Hippoglossus hippoglossus*)	2.075	ND	1.706	0.210	ND	1.916	92
	Halibut (*Hippoglossus hippoglossus*), smoked	3.150	ND	3.124	0.290	ND	3.414	108
	Herring (*Clupea harengus*), smoked	1.850	0.102	0.316	0.119	0.397	0.934	50
	Ocean perch (*Sebastes norvegicus*)	2.100	ND	1.929	0.240	ND	2.169	103
	Pollack (*Pollachius virens*)	1.550	ND	1.355	0.149	ND	1.504	97
	Spiny dogfish (*Squalus acanthias*)	5.700	ND	4.356	ND	ND	4.356	76
	Tuna (*Thunnus*)	0.850	ND	0.872	ND	ND	0.872	103
	Tuna (*Thunnus*), smoked	0.530	ND	0.423	0.055	ND	0.478	90
	Mean	**2.821**	**0.010**	**2.393**	**0.229**	**0.040**	**2.672**	**95**
Migratory fish	Eel (*Anguilla anguilla*)	0.990	0.024	0.035	0.029	0.095	0.183	18
	Eel (*Anguilla anguilla*), smoked	1.250	0.018	0.040	0.039	0.128	0.225	18
	Salmon (*Salmo salar*)	0.545	ND	0.421	0.072	ND	0.493	90
	Salmon (*Salmo salar*), smoked	0.660	ND	0.677	0.098	ND	0.775	117
	Trout (*Salmo trutta*) (region 1)	0.770	ND	0.724	0.063	ND	0.787	102
	Trout (*Salmo trutta*) (region 2)	0.480	ND	0.420	0.039	ND	0.459	96
	Trout (*Salmo trutta*) (region 3)	0.350	ND	0.364	0.029	ND	0.393	112
	Trout (*Salmo trutta*) (region 4)	0.430	ND	0.344	0.032	ND	0.376	87
	Trout (*Salmo trutta*), smoked (region 1)	0.375	ND	0.401	0.039	ND	0.440	117
	Trout (*Salmo trutta*), smoked (region 2)	0.435	ND	0.451	0.047	ND	0.498	114
	Trout (*Salmo trutta*), smoked (region 3)	0.365	ND	0.357	ND	ND	0.357	98
	Trout (*Salmo trutta*), smoked (region 4)	0.610	ND	0.723	ND	ND	0.723	119
	Mean	**0.605**	**0.021**	**0.413**	**0.049**	**0.112**	**0.476**	**91**
Seafood	Mussels (*Mytilus edulis*, *Pecten* spp., *Ostera edulis)*	1.550	0.003	0.737	0.098	0.573	1.411	91
	Shrimps / prawns	1.400	0.048	1.030	0.103	0.105	1.286	92
	Squid (*Loligo vulgaris)* / octopus (*Octopus vulgaris*)	2.200	ND	1.900	0.283	ND	2.183	99
	Mean	**1.717**	**0.017**	**1.222**	**0.161**	**0.226**	**1.626**	**95**

Table 3
Levels of total arsenic, inorganic arsenic (iAs), arsenobetaine (AsB) dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) in rice, rice-based products and meals (in mg kg^{-1}).

Sub food group	Food	Total As	iAs	AsB	DMA	MMA	∑As species	% ∑As species
Rice	Rice, organic	0.042	0.034	ND	0.001	ND	0.035	83
	Rice, conventional	0.039	0.033	ND	0.008	ND	0.041	105
	White rice	0.036	0.021	ND	0.012	ND	0.033	92
	Brown rice	0.033	0.023	ND	0.016	ND	0.039	118
Rice-based products	Rice wafers, organic	0.100	0.088	ND	0.014	ND	0.102	102
	Rice wafers, conventional	0.130	0.106	ND	0.019	ND	0.125	96
	Rice-based breakfast cereals	0.124	0.078	ND	0.022	ND	0.100	81
	Rice flakes for infants	0.124	0.088	ND	0.018	ND	0.106	85
	Rice drink	0.011	0.010	ND	ND	ND	0.010	91
Rice-based meals	Rice pudding, organic	0.033	0.024	ND	0.014	ND	0.038	115
	Rice pudding, conventional	0.025	0.018	ND	0.007	ND	0.025	100
	Rice-based mixed meals	0.044	0.027	0.008	0.016	ND	0.051	116
	Rice-based meals with vegetables	0.033	0.031	ND	0.008	ND	0.039	118
	Risotto	0.034	0.024	ND	0.013	ND	0.037	109
	Sushi	0.325	0.003	0.164	0.010	0.136	0.313	96

ranged from below LOD (0.001 mg kg^{-1}) ("water and water-based beverages") to 0.009 mg kg^{-1} ("food products for young population"). In these food groups, the highest concentrations of total As were found in composite dishes containing fish or seafood, e.g. pizza with fish or seafood (0.145 mg kg^{-1}) and sushi (0.325 mg kg^{-1}). Furthermore, higher As concentrations were found in rice (0.038 mg kg^{-1}), rice-based meals (0.034 mg kg^{-1}) and rice-based products (0.098 mg kg^{-1}) (see Table 3).

High concentrations are not necessarily resulting in high exposure if the respective foods are rarely consumed. But fish and seafood are already described as major dietary source of total As in many human populations (Taylor et al., 2017). Similar to the present study, the main food group of "fish, fish products and seafood" was also found to be the most As contaminated food with concentrations ranging from 1.5 mg kg^{-1} to 4.8 mg kg^{-1} in other European TDSs (FSAI, 2016; Llobet et al., 2003; Marín et al., 2017; Martí-Cid et al., 2008; Millour et al., 2011; Ventura et al., 2020). However, the mean level of total As presented here was slightly lower. Results (mean 2.382 mg kg^{-1}; lower bound) of the data collection of the EFSA (2009) were higher compared to the present study, but in the range of other European TDSs. This might be explained by different fish species and seafood analyzed as well as by different preparation methods.

Similar to the results of the present study, higher As concentrations were reported for marine fish than in freshwater fish and explained by higher accumulation and retention of As in marine organisms (Edmonds, Shibata, Francesconi, Rippingale, & Morita, 1997; Upadhyay et al., 2019). Moreover, fish species mainly living at the bottom of the sea (e.g. flat fishes) contained higher total As levels compared to other species (Sirot, Guérin, Volatier, & Leblanc, 2009; Uneyama, Toda, Yamamoto, & Morikawa, 2007).

The high mean level of the main food group "vegetable and vegetable products" mainly resulted from the total As level in algae. If algae would be excluded from this main food group, the mean level of total As would be reduced from 0.020 mg kg^{-1} to 0.004 mg kg^{-1}. Classification of algae to the main food group "vegetables and vegetable products" was in accordance to the FoodEx2 classification by EFSA (EFSA, 2015), but in other studies algae were considered as seafood according to their sea origin (Taylor et al., 2017; Uneyama et al., 2007). Moreover, total As concentrations in algae were reported to be higher than in fish or other seafood (Uneyama et al., 2007).

High levels in the main food group "food products for young population" resulted from samples containing rice or fish, e.g. "cereal porridge for infants (powder)" and "ready-to-eat-mixed-meal for children". In contrast to the study design, the samples "cereal porridge for infants", "cereal porridge for infants (millet)", "infant milk formula" and "milk-based porridge" were analyzed unprocessed, i.e. as powder. Thus, levels of total As would be decreased during the preparation to the ready-to-eat meal by uncontaminated water.

In regards to other food groups in other European TDSs, the food group of grains (including rice) showed higher mean contamination levels of total As compared to other food groups (FSAI, 2016; Llobet et al., 2003; Marín et al., 2017; Martí-Cid et al., 2008; Millour et al., 2011; Ventura et al., 2020). In the present study, average total As levels of the main food group "grain and grain based products" were lower than in "food products for young population", however they were not considered in other studies. The higher total As levels in the main food group "food products for young population" could be due to pooled samples containing rice within this main food group as well as the number of foods and pooled samples were lower compared to the main food group "grains and grain products".

Similar to other studies (Chekri et al., 2019; Dabeka et al., 1993; Fontcuberta et al., 2011), higher As concentrations were quantified in rice and rice-based meals and products, but one to two orders of magnitude lower than those measured in "fish, fish products and seafood". Differences in the mean As levels of rice and rice-based meals in comparison to rice-based products of about 2.7-fold lower may be due to the extremely low water content in rice-based products. This factor of approx. 2.7 is consistent to the processing factor of 2.8 reported by the German Nutrient Data Base (German: Bundeslebensmittelschlüssel (BLS)). Dabeka et al. (1993) showed a similar factor (2.96) for As concentrations in cooked and dry rice (0.096 mg kg^{-1} and 0.284 mg kg^{-1}, respectively). In rice drink containing approx. 12.5% rice, As levels were one order of magnitude lower compared to the other pooled samples containing rice (0.011 mg kg^{-1}). Guillod-Magnin et al. (2018) also reported similar findings.

Rice and other foods (e.g. pasta or vegetables) absorb water during cooking. Since drinking water is contaminated in many parts of the world (EFSA, Panel on Contaminants in the Food Chain (CONTAM), 2009), levels of As in the water used for preparation could have an influence on the As levels in the foods (Devesa et al., 2008). In contrast to this, other foods (e.g. fish and meat) might lose water during preparation (Dabeka et al., 1993). Different studies (Dabeka et al., 1993; Devesa et al., 2008) reported both an increase and decrease of total As after cooking in the context of water loss. Nevertheless, the effect of cooking on As concentrations in foods depends on different factors such as As levels in the water used for preparation and the type of preparation (e.g. draining of rice).

3.2. Water-soluble arsenic species

3.2.1. Fish, fish products and seafood

Highest levels of iAs were found in canned cod liver (0.408 mg kg^{-1}) and lowest levels of iAs were determined in mussels (*Mytilus edulis*, *Pecten* spp., *Ostera edulis)* (0.003 mg kg^{-1}) (see Table 2). Levels of iAs contributed from < 1% (mussels) up to 60% (striped catfish) to total As. AsB was quantified in all pooled samples and varied from 0.008 mg kg^{-1} (striped catfish) to 6.227 mg kg^{-1} (plaice / sole). Similarly, proportions of AsB to total As varied from 3% (smoked eel (*Anguilla anguilla*)) to 100% (e.g. plaice / sole, trout (*Salmo trutta*) and tuna (*Thunnus*)). For DMA, quantifiable levels were found in 56% of the pooled samples, ranging from 0.029 mg kg^{-1} (eel) to 0.708 mg kg^{-1} (plaice / sole). DMA accounted for about 8.2% of the total As level in marine fish, seafood, migratory fish and fish products. In pooled samples of freshwater fish, no DMA was detected. The arsenic species MMA was quantified in all pooled samples containing iAs except striped catfish. The highest concentration of MMA was found in canned cod liver (1.227 mg kg^{-1}), but could not be detected in the cod sample (filet). Summarizing the concentrations of the As species analyzed at least 70% of total As concentrations were represented. Samples containing eel or herring, the water-soluble As species covered only 18% to 50% of total As concentrations (see Fig. 1).

Maximum iAs concentrations in fish and seafood were higher compared to the TDS of Ireland with a maximum of 0.05 mg kg^{-1} (n = 11) (FSAI, 2016). In contrast, the Spanish TDS (Valencia) reported a median of 0.11 mg kg^{-1} for iAs in fish and seafood, which is higher than in the present study (0.021 mg kg^{-1}) (Marín et al., 2017). Deviations in the results of the studies might be caused by investigating of partly different species of fish and seafood. Comparing fish species of the present study, ESFA (2014) estimated the highest iAs levels in mussel (*Mytilus edulis*) with 0.042 mg kg^{-1}, which is much higher compared to the pooled sample mussels (0.003 mg kg^{-1}) of the present study. However, in the present study, the pooled sample mussels contained 85% of mussel (*Mytilus edulis*), 10% of scallop (*Pecten* spp.) and 5% of oyster (*Ostera edulis*). Concentrations of iAs for mussels of the present study were in the range of concentrations reported by other European studies varying from < 0.002 mg kg^{-1} to 0.116 mg kg^{-1} (Fontcuberta et al., 2011; Larsen, Engman, Sloth, Hansen, & Jorhem, 2005; Muñoz et al., 2000; Raber et al., 2012).

The other As species AsB, DMA and MMA were not analyzed in the TDS of France, Ireland, Portugal and Spain (Catalonia and Valencia) (FSAI, 2016; Llobet et al., 2003; Marín et al., 2017; Millour et al., 2011; Ventura et al., 2020). However, a number of studies investigated these

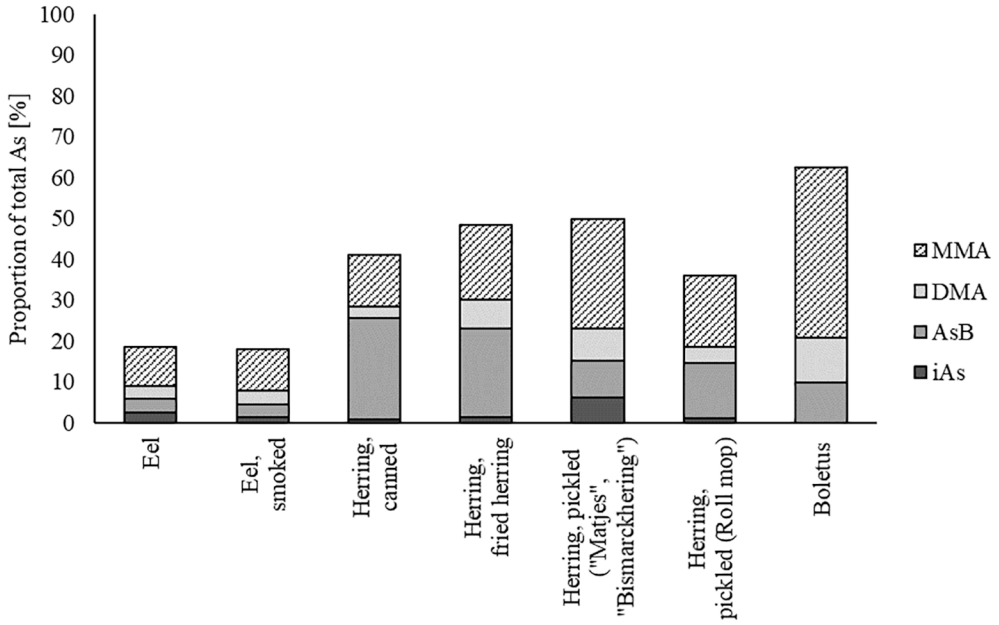

Fig. 1. Proportions of total arsenic from inorganic arsenic (iAs), arsenobetaine (AsB), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) in samples containing eel or herring and boletus.

As species in fish and seafood (Francesconi, 2010; Larsen et al., 2005; Liao, Wang, Li, & Zhao, 2018; Muñoz et al., 2000; Sirot et al., 2009). There, the predominant organic water-soluble As species in most fish and seafood was AsB (Francesconi, 2010; Taylor et al., 2017), like in the current study. The proportion of AsB to total As reported by Liao et al. (2018), Raber et al. (2012) and Sirot et al. (2009) ranged between 49,5% to 100% and was similar to the present study (3% to 100%).

For methylated As species, such as DMA and MMA only small amounts have been reported in fish and seafood (Liao et al., 2018; Lynch et al., 2014; Sirot et al., 2009; Taylor et al., 2017). The results of the present study are in accordance with the literature, but levels of DMA and MMA in canned cod liver (DMA: 0.419 mg kg^{-1}; MMA: 1.227 mg kg^{-1}) and pooled samples containing herring (*Clupea harengus*) (DMA: 0.034 mg kg^{-1} – 0.124 mg kg^{-1}; MMA: 0.152 mg kg^{-1} – 0.428 mg kg^{-1}) were much higher. Amayo et al. (2014) and Schmeisser et al. (2006) analyzed arsenolipids and their degradation products in cod liver oil. Although arsenolipids still need to be fully characterized in their chemical structure, toxicity and bioaccessibility, these species are associated to fatty fish and fish oil (Taylor et al., 2017). In cod liver oil, DMA was reported as major degradation product of arsenolipds (Amayo, Raab, Krupp, & Feldmann, 2014; Schmeisser, Goessler, & Francesconi, 2006), thus the higher DMA levels in the current pooled sample might be explained. However, MMA has not been identified as degradation product of arsenolipids (Amayo et al., 2014). Therefore, investigations on the relation between the occurrence of iAs and MMA are necessary.

In the present study, samples containing eel or herring contained approx. 27% and 16% of fat, respectively. Therefore, the presence of arsenolipids could be assumed, which would explain the deviation between the sum of the water-soluble As species analyzed and total As levels. Also, the type of food processing might effecting the concentrations and composition of As species (Devesa et al., 2008; Liao et al., 2018). In shellfish, Liao et al. (2018) showed a significant decrease of iAs, DMA and AsB after washing and cooking, while a decrease in MMA concentration was not significant. A conversion of DMA and MMA to iAs was assumed due to the slightly higher decrease in levels of DMA and MMA compared to iAs. Moreover, the results of Liao et al. (2018) demonstrated an adverse effect on As removal by further ingredients, such as salt and lemon. As concluded by Devesa et al. (2008) from several studies, arsenobetaine decarboxylates at temperatures above 150 °C and an increase of iAs and DMA might be the result from degradation of other As compounds.

Nevertheless, the present results in combination with results from other studies demonstrate considerable variations in the concentrations of total As and As species for different fish species and seafood. Concentrations can vary substantially within the same species (Larsen et al., 2005; Muñoz et al., 2000; Sirot et al., 2009; Taylor et al., 2017).

3.2.2. *Rice, rice-based meals and products*

Levels of iAs and DMA were found in all pooled samples, ranging from 0.003 mg kg^{-1} (sushi) to 0.106 mg kg^{-1} (conventional rice wafers) and 0.001 mg kg^{-1} (organic rice) to 0.022 mg kg^{-1} (rice-based breakfast cereals), respectively (Table 3). The levels of iAs accounted for 1% (sushi) to 94% (rice-based meals with vegetables) of the total As levels. The DMA concentrations represented 23% of total As on average.

For rice samples, iAs concentrations and proportions to total As were similar, comparing organic rice (0.034 mg kg^{-1}, 81%) with conventional rice (0.033 mg kg^{-1}, 85%), and negligible higher in brown rice (0.023 mg kg^{-1}, 70%) than in white rice (0.021 mg kg^{-1}, 58%). In case of DMA, concentrations and proportions in organic rice (0.001 mg kg^{-1}, 2,4%) were lower compared to conventional rice (0.008 mg kg^{-1}, 21%), and in white rice (0.012 mg kg^{-1}, 33%) slightly lower compared to brown rice (0.016 mg kg^{-1}, 48%). As expected, AsB was quantifiable in pooled samples containing fish or seafood ingredients, e.g. “rice-based dishes” (0.008 mg kg^{-1}) and sushi (0.164 mg kg^{-1}). MMA was detected only in sushi (0.136 mg kg^{-1}). The sum of As species covered at least 80% of total As concentration.

The iAs levels of the present study were higher compared to those of the Irish and Spanish TDS (FSAI, 2016; Marín et al., 2017). Ireland published data for the food groups “cereals” (including rice) and “breakfast cereals” (including rice-based cereals) with maximum iAs concentrations of 0.02 mg kg^{-1} and 0.06 mg kg^{-1}, respectively (FSAI, 2016). Since iAs concentrations in rice were typically 10-fold higher than in other grains (Davis et al., 2017), the maximum iAs concentrations within these food groups could be associated with rice. Similarly, data obtained in Spain (Valencia) reported 0.006 mg kg^{-1} as median for cereals including rice (Marín et al., 2017).

Mean concentrations of iAs in raw rice were estimated by EFSA (2014) to be 0.101 mg kg^{-1} (medium bound). In contrast to the present

study, iAs concentrations reported for brown rice (0.152 mg kg^{-1}) were practically 2-times higher as in white rice (0.089 mg kg^{-1}) (EFSA, European Food Safety Authority, 2014). Results of the German food monitoring program of 2016 showed similar iAs concentration in (raw) brown rice (0.121 mg kg^{1}) compared to (raw, white) round-grain rice (0.129 mg kg^{-1}) and long grain rice (0.100 mg kg^{-1}) (BVL, 2016). In contrast, iAs concentrations in (white) Basmati rice (0.047 mg kg^{-1}) were more than 2-times lower. However, in 2017 reported iAs concentrations of long grain rice (0.071 mg kg^{-1}) were lower compared to brown rice (0.107 mg kg^{-1}) and the results of 2016 (BVL, 2016; BVL, 2017). In the present study, iAs concentrations of brown rice were only marginally higher than in white rice. Further investigations would be necessary to conclusively assess differences between brown and white rice. However, deviations in the results of the studies could be caused by the influence of irrigation, geographical location, rice genotype and rice grain processing (Meharg et al., 2009; Upadhyay et al., 2019; Williams et al., 2006; Zhao et al., 2013). In rice and rice-based products, concentrations of iAs and DMA ranged from < 0.003 mg kg^{-1} to 0.750 mg kg^{-1} and < 0 mg kg^{-1} to 0.570 mg kg^{-1}, respectively (Carbonell-Barrachina et al., 2012; EFSA, European Food Safety Authority, 2014; Fontcuberta et al., 2011; Guillod-Magnin, Brüschweiler, Aubert, & Haldimann, 2018; Lynch et al., 2014; Meharg et al., 2008; BVL, 2016). In the literature (Althobiti et al., 2018; Fontcuberta et al., 2011; Rasheed et al., 2018; Sharafi et al., 2019; Upadhyay et al., 2019), reduced iAs concentrations were described caused by washing and boiling with uncontaminated water between 15% and 86% depending on the water to rice ratio. In the present study, rice was prepared according to the different manufacturers' instructions. There was almost no instruction to wash the rice before cooking. Most manufacturers recommended a 1 : 2 or 1 : 8 rice : water ratio or did not give precise instructions. For cooking, tap water sourced at the location of the study kitchen in Berlin was used to prepare the pooled samples. This tap water was analyzed to reveal total As concentrations below LOD, thus contamination by tap water could be excluded.

In the present study, MMA was not detectable in rice samples (except sushi), which might be caused by interconversions during cooking. Results of Althobiti et al. (2018) indicated interconversions such as MMA convert to iAs, by comparing As species in raw, unwashed rice and washed, cooked rice. Guillod-Magnin et al. (2018) found MMA only in low levels (<3%) in uncooked rice and rice-based products as well.

Previous studies (Carbonell-Barrachina et al., 2012; EFSA, European Food Safety Authority, 2014; Meharg et al., 2008) indicated high iAs exposure of infants caused by the intake of rice-based products. Concentrations of iAs in baby rice ranged from 0.06 mg kg^{-1} to 0.16 mg kg^{-1}, averaging 52% of the total As levels (Meharg et al., 2008). Meharg et al. (2008) and Carbonell-Barrachina et al. (2012) pointed to a linear increase of iAs concentration up to 0.25 mg kg^{-1} of total As and a plateau or decrease with higher total As concentrations in infant food (except fish-based samples). In the present study, high concentrations of iAs were found in unprepared rice flakes for infants (0.088 mg kg^{-1}) as well. However, these high concentrations would be diluted by preparation with water to rice porridge for infants.

In 2016, the European Commission raised MLs of iAs in raw rice and rice-based products from 0.10 mg kg^{-1} to 0.30 mg kg^{-1} (European Commission, 2015). In the present study, iAs levels in the pooled samples of "rice wafers" and "rice flakes for infants" were in compliance with these regulatory limits. Since the MLs only apply to raw commodities, evaluation of TDS rice samples is not possible. Assuming a processing factor of 2.8 for raw to cooked rice, iAs levels from 0.059 mg kg^{-1} to 0.095 mg kg^{-1} were calculated for the rice samples of the present study, which are still below the MLs. Nevertheless, based on Margin of Exposure assessments, the German Federal Institute for Risk Assessment (BfR) concluded that iAs concentrations in foods should be "as low as reasonably achievable" (ALARA principle) (BfR, 2014).

3.2.3. Further selected foods

Concentrations of iAs were determined in all pooled samples except pizza with fish or seafood; iAs concentrations ranged from 0.003 mg kg^{-1} (organic salad with dressing) to 0.300 mg kg^{-1} (algae) (see Table 4). For salad with dressing, the results of seasonal and regional sampling were comparable and were aggregated within the production type "organic" and "conventional".

The levels of iAs represented up to 100% of the total As levels. Quantifiable values of DMA were found in increasing order in infants millet porridge (0.001 mg kg^{-1}), cereal wafers (0.003 mg kg^{-1}), pizza with fish or seafood (0.015 mg kg^{-1}) and algae (0.200 mg kg^{-1}). Compared to iAs, proportions of DMA to total As reached 10% at the maximum. AsB was determined in algae (0.800 mg kg^{-1}), pizza with fish or seafood (0.126 mg kg^{-1}), organic salad with dressing (0.010 mg kg^{-1}) and conventional salad with dressing (0.011 mg kg^{-1}) as expected, since

Table 4
Levels of total arsenic, inorganic arsenic (iAs),arsenobetaine (AsB), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) in selected foods (in mg kg^{-1}).

Main food group	Food	Total As	iAs	AsB	DMA	MMA	∑As species	% ∑As species
Grains and grain-based products	Cereal wafers, organic	0.053	0.054	ND	0.003	ND	0.056	105
Vegetables and vegetables products	Algae	2.500	0.300	0.800	0.200	1.500	2.800	112
	Broccoli (*Brassica oleracea* var. *italica*)(season 1, region east)	0.003	0.003	ND	ND	ND	0.003	100
	Broccoli (*Brassica oleracea* var. *italica*)(season 2, region east)	0.02	0.024	ND	ND	ND	0.024	118
	Cucumber (*Cucumis sativus*),organic (season 1)*	0.005	0.005	ND	ND	ND	0.005	99
	Cucumber (*Cucumis sativus*),organic (season 2)*	0.016	0.017	ND	ND	ND	0.017	104
	Cucumber *Cucumis sativus*,conventional	0.005	0.005	ND	ND	ND	0.005	101
	Culinary fresh herbs, organic	0.012	0.012	ND	ND	ND	0.012	100
	Culinary fresh herbs, conventional	0.017	0.018	ND	ND	ND	0.018	103
	Boletus (*Boletus edulis*)	0.072	ND	0.007	0.008	0.030	0.045	63
Meat and meat products	Bovine liver, organic (season 1)	0.012	0.006	ND	ND	0.007	0.008	93
	Bovine liver, organic (season 2)	0.009	0.005	ND	ND	0.003	0.013	107
Food products for young population	Cereals porridge for infants (millet)	0.021	0.019	ND	0.001	ND	0.020	98
	Cereals porridge for infants, conventional	0.026	0.024	ND	ND	ND	0.024	94
Composite dishes	Ready-to-eat mixed meal for children, conventional	0.021	0.005	0.014	0.002	ND	0.021	100
	Salad with dressing, organic*	0.012	0.003	0.010	ND	ND	0.013	113
	Salad with dressing, conventional*	0.016	0.004	0.011	ND	ND	0.015	96
	Pesto	0.019	0.020	ND	ND	ND	0.020	104
	Pizza with fish or seafood	0.145	ND	0.126	0.015	ND	0.141	97

* Results of seasonal and regional sampling were comparable and were aggregated within the production type "organic" and "conventional".

these pooled samples contained fish, seafood or algae. Concentrations of AsB contributed for 32% (algae) up to 87% (pizza with fish or seafood and salad with dressing) to total As with an average of 69%. MMA was quantifiable only in algae (1.500 mg kg^{-1}) and organic bovine liver from two seasons (0.003 mg kg^{-1} and 0.007 mg kg^{-1}), conventional bovine liver was not investigated. For broccoli, cucumber and bovine liver, the results showed similar proportions of the detected As species even if the total As levels were different between the pooled samples of the various foods. The sum of As species for the samples of this section represented about 93% up to 100% of the total As concentrations, with exception of boletus (*Boletus edulis*) (63%; see Fig. 1).

Similar results of iAs levels to the present study were reported by the TDS of Ireland in vegetables (0.01 mg kg^{-1}; n = 30) and meat including meat products (0.01 mg kg^{-1}; n = 13); the results of Ireland were shown as maximum iAs levels (UB) (FSAI, 2016). In order to compare the results from vegetables (broccoli and cucumber), the results from algae were excluded since they were not included in the Irish TDS, but contained high levels of iAs. For herbs and spices, iAs levels ranged from 0.03 mg kg^{-1} to 0.16 mg kg^{-1} in the Irish TDS, which is higher compared to the results for culinary fresh herbs (0.015 mg kg^{-1}) in the present study. Results of the Spanish TDS (Valencia) were comparable by taking the different compositions of food groups in TDSs into account (Marín et al., 2017). For vegetables and meat, iAs levels were presented as median levels, 0.007 mg kg^{-1} and 0.019 mg kg^{-1}, respectively. EFSA (2014) estimated iAs concentrations for cucumber (0.011 mg kg^{-1}), edible offal from farmed animals (0.007 mg kg^{-1}), mixed herbs (0.099 mg kg^{-1}), unspecified follow-on formula (powder) (0.031 mg kg^{-1}), pizza (0.011 mg kg^{-1}) and unspecified prepared salads (0.015 mg kg^{-1}). If iAs concentrations were not available for a sample, EFSA calculated iAs concentrations as a fraction of 70% of total As reported. Results of the present study were comparable to those reported by EFSA with exception of herbs, pizza and salads. For unspecified prepared salads, EFSA excluded salads with fish, since the conversion factor is only 1% iAs to total As levels. In the present study, canned tuna was contained in pooled samples of salad with dressing resulting in higher AsB levels within these pooled samples.

Studies of As species in marine algae showed a varying composition of As species in algae depending on their taxonomy and location (García-Salgado, Quijano, & Bonilla, 2012; Llorente-Mirandes, Ruiz-Chancho, Barbero, Rubio, & López-Sánchez, 2011; Narukawa, Hioki, & Chiba, 2012). In the present study, the pooled sample algae mainly consisted of wakame (*Undaria pinnatifida*), nori (*Porphyra purpurea*) and further unspecified algae. In the literature, for nori and wakame concentrations of iAs and DMA were reported up to 4.5 mg kg^{-1} and up to 2.08 mg kg^{-1}, respectively (EFSA, European Food Safety Authority, 2014; García-Salgado et al., 2012; Llorente-Mirandes et al., 2011; Narukawa et al., 2012). The As species MMA and AsB were either not detected or not analyzed in nori and wakame in the cited studies (EFSA, European Food Safety Authority, 2014; García-Salgado et al., 2012; Llorente-Mirandes et al., 2011; Narukawa et al., 2012). The high MMA concentration in algae (1.5 mg kg^{-1}) in the present study may be caused by the unspecified algae, since MMA was quantified in other algae species, e.g. kombu (*Laminaria saccharina*; 0.21 mg kg^{-1} and 0.46 mg kg^{-1}) (Llorente-Mirandes et al., 2011; Narukawa et al., 2012). The sum of As species analyzed represented the whole total As level, however, arsenosugars are associated as major As species in algae and accounted for more than 50% of the total As (Narukawa et al., 2012; Taylor et al., 2017). Investigations of the effect of washing and soaking on As concentration showed a reduction of up to 60% of the total As concentrations (Hanaoka, Yosida, Tamano, Kuroiwa, Kaise, & Maeda, 2001). Nevertheless, most studies of As speciation in algae focused on raw or dry algae in contrast to the present study. Thus, differences in the levels and composition of As species between the cited results and the results of the present study could be due, e.g. to the compositions of the pooled sample (containing more nori algae) or analyses after preparation. Regulations of maximum iAs levels in algae were set in France (3 mg kg^{-1} per dry weight) as well as in Australia and New Zealand (1 mg kg^{-1} based on 85% hydration) individually (CEVA, 2020; FSANZ, 2016). Concentrations of iAs in algae (0.300 mg kg^{-1}) of the present study cannot be compared directly to these MLs since the current sample contained fresh and prepared algae.

For other foods, fewer studies of As speciation were available as compared to studies on fish, seafood, algae and rice. However, Fontcuberta et al. (2011) found iAs concentrations of 0.19 mg kg^{-1} in mixed herbs and 0.08 mg kg^{-1} in parsley, which is much higher compared to the present study. Dabeka et al. (1993) showed a relation between weight loss (e.g. loss of water) and increasing As concentrations during the cooking process for some meat and fish samples. Assuming that the cited samples were dry, as it was not described differently, deviation of the iAs concentrations may be explained by a higher water content of culinary fresh herbs in the present study. Concentrations of MMA were also reported for beef muscle (0.007 mg kg^{-1}), which was similar to the results of the present study (Batista, Nacano, De Souza, & Barbosa, 2012).

For boletus, the sum of As species analyzed represented only 63% of total As concentrations, which might be explained by the presence of other As species. Similar results were found in the study of Komorowicz et al. (2019) (Komorowicz, Hanć, Lorenc, Barałkiewicz, Falandysz, & Wang, 2019; Nearing, Koch, & Reimer, 2014). Here the authors reported the present of iAs, AsB, DMA and MMA and also of another undefined As species. Furthermore, Nearing et al. (2014) (Nearing et al., 2014) found ten different As compounds in edible mushrooms such as trimethylarsine oxide (TMAO) and tetramethylarsonium (TETRA) in boletus. Both studies reported wide variations in the composition of As species in different mushrooms (Komorowicz et al., 2019; Nearing et al., 2014).

3.3. Limitations and uncertainties of the study

Due to the pooling of foods, information about the variability of substance concentrations in individual food samples are missing. This uncertainty is accepted, since the TDS design was established to collect representative occurrence data, i.e. partially high or low contaminated foods are included to gain mean levels. Regional and seasonal variabilities as well as organic and conventional types of production were covered for foods with an assumed impact on these factors by multiple sampling in the present study. In comparison to other TDSs, the MEAL food list contained 356 different foods and the aggregation level of foods is lower.

The consumption surveys VELS and NVS II used for establishing the MEAL food list covered the age groups between 0.5 to < 5 years (VELS) and 14 to 80 years (NVS II), leading to a gap of 9 years between both data sets. An identification of foods for this gap was not assumed in the present study. The collection of the data sets of the consumption surveys was conducted in 2002 (VELS) and 2006 (NVS II). Changes in the consumption behavior might be possible and new food items or eating trends might occur. But from 2008 to 2012/2013, the MRI conducted a follow-up study of NVS II with part of the panelists (n = 1,840) and found no significant deviations in eating behavior for the main food groups (Gose, Krems, Heuer, & Hoffmann, 2016).

Furthermore, consumption data were collected on three non-consecutive days for VELS and on two non-consecutive days for NVS II by 24-h recalls. A long-term food consumption may be not represented appropriately, especially for rarely consumed foods.

The MDL approach used for the analysis of left-censored data leads to deviation from the actual concentrations for calculated statistics such as mean levels.

The use of two different laboratories for analysis of total As and As species may have contributed to the observed difference between total As concentrations and the sum of As species concentrations (see Fig. 1). For samples analyzed on As species, levels of total As were confirmed in the range of contract laboratory's measurement uncertainty (30%) by a similar method using the same ICP-MS as for As speciation (see Table S6,

Supplementary data). Within the present study, the water-soluble As species iAs, AsB, DMA and MMA were determined only, however for samples containing fatty fish (e.g. eel or herring), algae or mushrooms further As speciation would be required to determine As species such as arsenolipids, arsenosugars, TMAO or TETRA.

Lastly, the composition of As species and concentrations could depend on preparation methods. For example, preparation of rice was performed according to manufacturer's instructions in the present study. However, practices in households could differ.

Concentrations in drinking water and tap water used for food preparation could vary and have an influence on the composition of the sample.

4. Conclusion

The determination of the water-soluble As species iAs, AsB, DMA and MMA of various foods was performed for the first time in a European TDS. The data of the present study provide a sound database for a refined exposure and risk assessment of As content in food considering also the different As species. This study showed highest total As levels in pooled samples containing fish or seafood and algae. Levels and composition of As species widely varied in fish, fish products and seafood. Even AsB was the predominant water-soluble As species, iAs, DMA and MMA were also found in the samples. Thus, the evaluation of fish, fish products and seafood require a speciation of these and further As species, especially arsenolipids in fatty fish and fish oil. DMA and MMA were also found in some terrestrial foods, however iAs being the prevalent As species and represented at least 50% of the total As amount. Thus, levels of total As in terrestrial foods could be used to evaluate MLs for iAs. However, the European Commission raised MLs for iAs in rice and rice-based products only. In mushrooms, further As speciation is necessary due to the presence of other As species, e.g. TMAO and TETRA.

In general, monitoring of As species in foods should be further extended and taken into account for dietary exposure assessment. Furthermore, regulations for iAs should be considered for further foods and for DMA and MMA.

CRediT authorship contribution statement

Christin Hackethal: Investigation, Formal analysis, Writing - original draft. **Johannes F. Kopp:** Formal analysis. **Irmela Sarvan:** Project administration, Supervision. **Tanja Schwerdtle:** Resources, Supervision, Formal analysis. **Oliver Lindtner:** Conceptualization, Funding acquisition, Project administration.

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 data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2020.128913.

References

Althobiti, R. A., Sadiq, N. W., & Beauchemin, D. (2018). Realistic risk assessment of arsenic in rice. *Food Chemistry, 257*, 230–236. https://doi.org/10.1016/j.foodchem.2018.03.015.

Amayo, K. O., Raab, A., Krupp, E. M., & Feldmann, J. (2014). Identification of arsenolipids and their degradation products in cod-liver oil. *Talanta, 118*, 217–223. https://doi.org/10.1016/j.talanta.2013.09.056.

Banasiak, U., Heseker, H., Sieke, C., Sommerfeld, C., & Vohmann, C. (2005). Abschätzung der Aufnahme von Pflanzenschutzmittel-Rückständen in der Nahrung mit neuen Verzehrsmengen für Kinder. Bundesgesundheitsblatt – Gesundheitsforschung – Gesundheitsschutz, 48(1), 84–98. https://doi.org/10.1007/s00103-004-0949-6.

Batista, B. L., Nacano, L. R., De Souza, S. S., & Barbosa, F., Jr (2012). Rapid sample preparation procedure for As speciation in food samples by LC-ICP-MS. *Food Additives & Contaminants: Part A, 29*(5), 780–788. https://doi.org/10.1080/19440049.2011.645218.

BfR, The German Federal Institute for Risk Assessment. (2014). Arsenic in Rice and Rice Products. BfR Opinion, No. 018/2015 of 24 June 2014.

BVL, Bundesamt für Verbraucherschutz und Lebensmittelsicherheit. (2016). Berichte zur Lebensmittelsicherheit 2014 – Monitoring. Gemeinsamer Bericht des Bundes und der Länder. BVL-Reporte (Vol. 10.3). Basel, CH: Springer International Publishing.

BVL, Bundesamt für Verbraucherschutz und Lebensmittelsicherheit. (2017). Berichte zur Lebensmittelsicherheit 2016 – Monitoring. Gemeinsamer Bericht des Bundes und der Länder. BVL-Reporte (Vol. 12.4). Berlin, DE: Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (BVL).

Carbonell-Barrachina, Á. A., Wu, X., Ramírez-Gandolfo, A., Norton, G. J., Burló, F., Deacon, C., & Meharg, A. A. (2012). Inorganic arsenic contents in rice-based infant foods from Spain, UK, China and USA. *Environmental Pollution, 163*, 77–83. https://doi.org/10.1016/j.envpol.2011.12.036.

CEVA, Centre d'Étude et de Valorisation des Algues. (2020). Edible seaweed and microalgae - Regulatory status in France and Europe.

Chekri, R., Le Calvez, E., Zinck, J., Leblanc, J.-C., Sirot, V., Hulin, M., Noël, L., & Guérin, T. (2019). Trace element contents in foods from the first French total diet study on infants and toddlers. *Journal of Food Composition and Analysis, 78*, 108–120. https://doi.org/10.1016/j.jfca.2019.02.002.

Dabeka, R. W., McKenzie, A. D., Lacroix, G. M. A., Cléroux, C., Bowe, S., Graham, R. A., … Verdier, P. (1993). Survey of arsenic in total diet food composites and estimation of the dietary intake of arsenic by Canadian adults and children. *Journal of AOAC International, 76*(1), 14–25. https://doi.org/10.1093/jaoac/76.1.14.

Davis, M. A., Signes-Pastor, A. J., Argos, M., Slaughter, F., Pendergrast, C., Punshon, T., … Karagas, M. R. (2017). Assessment of human dietary exposure to arsenic through rice. *Science of The Total Environment, 586*, 1237–1244. https://doi.org/10.1016/j.scitotenv.2017.02.119.

Devesa, V., Vélez, D., & Montoro, R. (2008). Effect of thermal treatments on arsenic species contents in food. *Food and Chemical Toxicology, 46*(1), 1–8. https://doi.org/10.1016/j.fct.2007.08.021.

Edmonds, J. S., Francesconi, K. A., & Stick, R. V. (1993). Arsenic compounds from marine organisms. *Natural Product Reports, 10*(4), 421–428. https://doi.org/10.1039/NP9931000421.

Edmonds, J. S., Shibata, Y., Francesconi, K. A., Rippingale, R. J., & Morita, M. (1997). Arsenic Transformations in Short Marine Food Chains studied by HPLC-ICP MS. *Applied Organometallic Chemistry, 11*(4), 281–287. https://doi.org/10.1002/(sici)1099-0739(199704)11:4<281::Aid-aoc581>3.0.Co;2-s.

EFSA, European Food Safety Authority. (2014). Dietary exposure to inorganic arsenic in the European population. *EFSA Journal, 12*(3), 68. https://doi.org/10.2903/j.efsa.2014.3597.

EFSA, Panel on Contaminants in the Food Chain (CONTAM). (2009). Scientific Opinion on Arsenic in Food. *EFSA Journal, 7*(10), 199. https://doi.org/10.2903/j.efsa.2009.1351.

EFSA/FAO/WHO. (2011). Towards a harmonised Total Diet Study approach: A guidance document. EFSA Journal, 9(11), 2450. https://doi.org/10.2903/j.efsa.2011.2450.

European Commission. (2015). COMMISSION REGULATION (EU) 2015/1006 of 25 June 2015 amending Regulation (EC) No 1881/2006 as regards maximum levels of inorganic arsenic in foodstuffs. Official Journal of the European Union (Vol. L 161, pp. 14–16).

European Food Safety Authority. (2015). The food classification and description system FoodEx 2 (revision 2). EFSA Supporting Publication 2015:EN-804, 12(5), 90. https://doi.org/10.2903/sp.efsa.2015.EN-804.

Fontcuberta, M., Calderon, J., Villalbí, J. R., Centrich, F., Portañ a, S., Espelt, A., Duran, J., & Nebot, M. (2011). Total and Inorganic Arsenic in Marketed Food and Associated Health Risks for the Catalan (Spain) Population. *Journal of Agriculture and Food Chemistry, 59*(18), 10013–10022. https://doi.org/10.1021/jf2013502.

Francesconi, K. A. (2010). Arsenic species in seafood: Origin and human health implications. *Pure and Applied Chemistry, 82*(2), 373–381. https://doi.org/10.1351/PAC-CON-09-07-01.

FSAI, Food Safety Authority of Ireland. (2016). Report on a Total Diet Study carried out by the Food Safety Authority of Ireland in the period 2012–2014. Monitoring & Surveillance Series, Chemical. Dublin, IE: Food Safety Authority of Ireland.

FSANZ, Food Standards Australia New Zealand. (2016). Australia New Zealand Food Standards Code – Standard 1.4.1 – Contaminants and natural toxicants. (124).

García-Salgado, S., Quijano, M. A., & Bonilla, M. M. (2012). Arsenic speciation in edible alga samples by microwave-assisted extraction and high performance liquid chromatography coupled to atomic fluorescence spectrometry. *Analytica Chimica Acta, 714*, 38–46. https://doi.org/10.1016/j.aca.2011.12.001.

Gose, M., Krems, C., Heuer, T., & Hoffmann, I. (2016). Trends in food consumption and nutrient intake in Germany between 2006 and 2012: Results of the German National Nutrition Monitoring (NEMONIT). *British Journal of Nutrition, 115*(8), 1498–1507. https://doi.org/10.1017/S0007114516000544.

Guillod-Magnin, R., Brüschweiler, B. J., Aubert, R., & Haldimann, M. (2018). Arsenic species in rice and rice-based products consumed by toddlers in Switzerland. *Food Additives & Contaminants: Part A, 35*(6), 1164–1178. https://doi.org/10.1080/19440049.2018.1440641.

Hanaoka, K., Yosida, K., Tamano, M., Kuroiwa, T., Kaise, T., & Maeda, S. (2001). Arsenic in the prepared edible brown alga hijiki,Hizikia fusiforme. *Appl. Organometal. Chem., 15*(6), 561–565. https://doi.org/10.1002/aoc.195.

Heseker, H., Oeppining, A., & Vohmann, C. (2003). *Verzehrsstudie zur Ermittlung der Lebensmittelaufnahme von Säuglingen und Kleinkindern für die Abschätzung eines akuten Toxizitätsrisikos durch Rückstände von Pflanzenschutzmitteln (VELS)*. Paderborn DE: Universität Paderborn.

IARC, International Agency for Research on Cancer. (2012). A review of human carcinogens - Part C: arsenics, metals, fibres and dusts. IARC Monographs, 100.

Kaise, T., Watanabe, S., & Itoh, K. (1985). The acute toxicity of arsenobetaine. *Chemosphere, 14*(9), 1327–1332. https://doi.org/10.1016/0045-6535(85)90153-5.

Komorowicz, I., Hanć, A., Lorenc, W., Barałkiewicz, D., Falandysz, J., & Wang, Y. (2019). Arsenic speciation in mushrooms using dimensional chromatography coupled to ICP-MS detector. Chemosphere, 233, 223-233. https://doi.org/https://doi.org/10.1016/j.chemosphere.2019.05.130.

Krems, C., Bauch, A., Götz, A., Heuer, T., Hild, A., Möseneder, J., & Brombach, C. (2006). Methoden der Nationalen Verzehrsstudie II. *Ernährungs Umschau, 53*(2), 44–50. https://www.ernaehrungs-umschau.de/print-artikel/13-02-2006-methoden-der-nationalen-verzehrsstudie-ii/.

Larsen, E. H., Engman, J., Sloth, J. J., Hansen, M., & Jorhem, L. (2005). Determination of inorganic arsenic in white fish using microwave-assisted alkaline alcoholic sample dissolution and HPLC-ICP-MS. *Analytical and Bioanalytical Chemistry, 381*(2), 339–346. https://doi.org/10.1007/s00216-004-2815-7.

Liao, W., Wang, G., Li, K., & Zhao, W. (2018). Change of Arsenic Speciation in Shellfish after Cooking and Gastrointestinal Digestion. *Journal of Agriculture and Food Chemistry, 66*(29), 7805–7814. https://doi.org/10.1021/acs.jafc.8b02441.

Llobet, J. M., Falcó, G., Casas, C., Teixidó, A., & Domingo, J. L. (2003). Concentrations of Arsenic, Cadmium, Mercury, and Lead in Common Foods and Estimated Daily Intake by Children, Adolescents, Adults, and Seniors of Catalonia, Spain. *Journal of Agriculture and Food Chemistry, 51*(3), 838–842. https://doi.org/10.1021/jf020734q.

Llorente-Mirandes, T., Ruiz-Chancho, M. José., Barbero, M., Rubio, R., & López-Sánchez, J. F. (2011). Determination of Water-Soluble Arsenic Compounds in Commercial Edible Seaweed by LC-ICPMS. *Journal of Agriculture and Food Chemistry, 59*(24), 12963–12968. https://doi.org/10.1021/jf2040466.

Lynch, H. N., Greenberg, G. I., Pollock, M. C., & Lewis, A. S. (2014). A comprehensive evaluation of inorganic arsenic in food and considerations for dietary intake analyses. *Science of The Total Environment, 496*, 299–313. https://doi.org/10.1016/j.scitotenv.2014.07.032.

Marín, S., Pardo, O., Báguena, R., Font, G., & Yusà, V. (2017). Dietary exposure to trace elements and health risk assessment in the region of Valencia, Spain: A total diet study. *Food Additives & Contaminants: Part A, 34*(2), 228–240. https://doi.org/10.1080/19440049.2016.1268273.

Martí-Cid, R., Llobet, J. M., Castell, V., & Domingo, J. L. (2008). Dietary Intake of Arsenic, Cadmium, Mercury, and Lead by the Population of Catalonia, Spain. *Biological Trace Element Research, 125*(2), 120–132. https://doi.org/10.1007/s12011-008-8162-3.

Meharg, A. A., Sun, G., Williams, P. N., Adomako, E., Deacon, C., Zhu, Y.-G., Feldmann, J., & Raab, A. (2008). Inorganic arsenic levels in baby rice are of concern. *Environmental Pollution, 152*(3), 746–749. https://doi.org/10.1016/j.envpol.2008.01.043.

Meharg, A. A., Williams, P. N., Adomako, E., Lawgali, Y. Y., Deacon, C., Villada, A., . . . Yanai, J. (2009). Geographical Variation in Total and Inorganic Arsenic Content of Polished (White) Rice. Environmental Science & Technology, 43(5), 1612-1617. https://doi.org/10.1021/es802612a.

Millour, S., Noël, L., Kadar, A., Chekri, R., Vastel, C., Sirot, V., Leblanc, J.-C., & Guérin, T. (2011). Pb, Hg, Cd, As, Sb and Al levels in foodstuffs from the 2nd French total diet study. *Food Chemistry, 126*(4), 1787–1799. https://doi.org/10.1016/j.foodchem.2010.12.086.

Moy, G. G., & Vannoort, R. W. (Eds.). (2013). *Total Diet Studies*. New York, NY: Springer New York.

MRI, M. R.-I. (2008a). Nationale Verzehrs Studie II: Ergebnisbericht, Teil 1. Die bundesweite Befragung zur Ernährung von Jugendlichen und Erwachsenen.

MRI, M. R.-I. (2008b). Nationale Verzehrs Studie II: Ergebnisbericht, Teil 2. Die bundesweite Befragung zur Ernährung von Jugendlichen und Erwachsenen.

Muñoz, O., Devesa, V., Suñer, M. A., Vélez, D., Montoro, R., Urieta, I., Macho, M. L., & Jalón, M. (2000). Total and Inorganic Arsenic in Fresh and Processed Fish Products. *Journal of Agriculture and Food Chemistry, 48*(9), 4369–4376. https://doi.org/10.1021/jf000282m.

Narukawa, T., Hioki, A., & Chiba, K. (2012). Aqueous Extraction of Water-soluble Inorganic Arsenic in Marine Algae for Speciation Analysis. *Analytical Sciences, 28*(8), 773–779. https://doi.org/10.2116/analsci.28.773.

Nearing, M. M., Koch, I., & Reimer, K. J. (2014). Arsenic Speciation in Edible Mushrooms. *Environmental Science & Technology, 48*(24), 14203–14210. https://doi.org/10.1021/es5038468.

Raber, G., Stock, N., Hanel, P., Murko, M., Navratilova, J., & Francesconi, K. A. (2012). An improved HPLC–ICPMS method for determining inorganic arsenic in food: Application to rice, wheat and tuna fish. *Food Chemistry, 134*(1), 524–532. https://doi.org/10.1016/j.foodchem.2012.02.113.

Rasheed, H., Kay, P., Slack, R., & Gong, Y. Y. (2018). Arsenic species in wheat, raw and cooked rice: Exposure and associated health implications. *Science of The Total Environment, 634*, 366–373. https://doi.org/10.1016/j.scitotenv.2018.03.339.

Sarvan, I., Bürgelt, M., Lindtner, O., & Greiner, M. (2017). Expositionsschätzung von Stoffen in Lebensmitteln: Die BfR-MEAL-Studie – die erste Total-Diet-Studie in DeutschlandDietary exposure assessment of substances in foods: The BfR MEAL study – the first German total diet study. *Bundesgesundheitsbl, 60*(7), 689–696. https://doi.org/10.1007/s00103-017-2566-1.

Schmeisser, E., Goessler, W., & Francesconi, K. A. (2006). Human metabolism of arsenolipids present in cod liver. *Analytical and Bioanalytical Chemistry, 385*(2), 367–376. https://doi.org/10.1007/s00216-006-0401-x.

Sharafi, K., Yunesian, M., Mahvi, A. H., Pirsaheb, M., Nazmara, S., & Nabizadeh Nodehi, R. (2019). Advantages and disadvantages of different pre-cooking and cooking methods in removal of essential and toxic metals from various rice types-human health risk assessment in Tehran households, Iran. *Ecotoxicology and Environmental Safety, 175*, 128–137. https://doi.org/10.1016/j.ecoenv.2019.03.056.

Sirot, V., Guérin, T., Volatier, J.-L., & Leblanc, J.-C. (2009). Dietary exposure and biomarkers of arsenic in consumers of fish and shellfish from France. *Science of The Total Environment, 407*(6), 1875–1885. https://doi.org/10.1016/j.scitotenv.2008.11.050.

Taylor, V., Goodale, B., Raab, A., Schwerdtle, T., Reimer, K., Conklin, S., Karagas, M. R., & Francesconi, K. A. (2017). Human exposure to organic arsenic species from seafood. *Science of The Total Environment, 580*, 266–282. https://doi.org/10.1016/j.scitotenv.2016.12.113.

Uneyama, C., Toda, M., Yamamoto, M., & Morikawa, K. (2007). Arsenic in various foods: Cumulative data. *Food Additives and Contaminants, 24*(5), 447–534. https://doi.org/10.1080/02652030601053121.

Upadhyay, M. K., Shukla, A., Yadav, P., & Srivastava, S. (2019). A review of arsenic in crops, vegetables, animals and food products. *Food Chemistry, 276*, 608–618. https://doi.org/10.1016/j.foodchem.2018.10.069.

Ventura, M., Cardoso, C., Bandarra, N. M., Delgado, I., Coelho, I., Gueifão, S., Martins, M., Costa, M. H., & Castanheira, I. (2020). Effect of season and proximate composition on the Br, As, Cd and Pb contents in different kinds of key foods consumed in Portugal. *International Journal of Food Science & Technology, 55*(5), 2219–2231. https://doi.org/10.1111/ijfs.14475.

Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J., & Meharg, A. A. (2006). Increase in Rice Grain Arsenic for Regions of Bangladesh Irrigating Paddies with Elevated Arsenic in Groundwaters. *Environmental Science & Technology, 40*(16), 4903–4908. https://doi.org/10.1021/es060222i.s001.

Zhao, F.-J., Zhu, Y.-G., & Meharg, A. A. (2013). Methylated Arsenic Species in Rice: Geographical Variation, Origin, and Uptake Mechanisms. *Environmental Science & Technology, 47*(9), 3957–3966. https://doi.org/10.1021/es304295n.