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#### ARSENIC IN FISH AND SHELLFISH

The Food Standards Agency (FSA) has completed a survey of total and inorganic arsenic in fish and shellfish. Total and inorganic arsenic were measured in bulk (composite) samples of 42 species of fish and 8 species of shellfish, as well as in 75 individual samples of shellfish. Arsenic is present in food in various chemical forms, with inorganic forms being the most toxic. Most arsenic in the diet is present in the less harmful organic forms.

In the UK, fish is the main contributor of arsenic in the diet. The aim of this survey was to provide data on fish and shellfish on which we previously had limited or no information, and to allow a more accurate and detailed estimate of dietary intakes of arsenic by consumers of these products.

The key facts of this survey are:

- Total and inorganic arsenic was measured in 42 composite samples of fish, 8 samples
  of bulk shellfish and 75 samples of individual shellfish.
- Levels of total arsenic in all samples of fish and shellfish were comparable with the
  literature where available, with higher levels found in the composite samples of skate
  and lemon sole. There is no regulatory limit for total arsenic in fish and shellfish, as the
  arsenic is predominantly in a less toxic (organic) form.
- The levels of inorganic arsenic were generally higher in shellfish samples but the
  percentage of inorganic arsenic was low in all samples. The maximum intake of
  inorganic arsenic was below 5 per cent of the safety guideline set previously by the
  World Health Organisation, although this guideline is due to be reviewed.

# **Background**

#### Arsenic in Food

Certain elements present in food are of concern because of their possible adverse health effects. Some, such as arsenic, have no known beneficial biological function and long-term exposure may be harmful to health. Arsenic in its inorganic form can damage DNA and is known to cause cancer. However, most arsenic in food is present in less harmful (organic) forms. Inorganic arsenic species found in food typically account for no more than 1 to 3 percent of the total arsenic present.

Metals and other elements enter food from a wide range of environmental sources. Arsenic is present in the environment from natural sources, such as rocks and sediments, and as a result of human activities such as coal burning, copper smelting and the processing of mineral ores. Levels of arsenic are higher in the aquatic environment than in most areas of land as it is fairly water-soluble and may be washed out of arsenic-bearing rocks.

A survey of total and inorganic arsenic in the 1999 Total Diet Study found fish to be the main source of both total arsenic (all forms of arsenic) and inorganic arsenic in the UK diet.<sup>2</sup> The average concentrations of total and inorganic arsenic in fish were 3214 micrograms/kilogram and 16 micrograms/kilogram respectively, whilst total arsenic concentrations in other food groups were considerably lower - the second highest level of 73 micrograms/kilogram was found in poultry. Inorganic arsenic was only detectable in two other food groups, "miscellaneous cereals" (cereals other than bread, for example, rice and breakfast cereals) and poultry (11.6 and 12.5 micrograms/kilogram respectively).

There is no Europe-wide regulation of arsenic in food. In the UK, the Arsenic in Food Regulations (SI 1959 no. 831) as amended lay down a general limit of 1 milligram/kilogram for total arsenic in food.<sup>3</sup> However, this does not apply to fish and edible seaweed, which mainly contain two forms of arsenic that are not considered to be a significant risk to health, arsenobetaine and arsenocholine.

## **Brand Names**

In accordance with the Food Standards Agency policy for the release of brand names when reporting the results of food chemical surveillance, details about the individual retail shellfish samples are given in full in Annex 2. It should be noted that the absence of any particular brand from this survey means only that the brand was not included in the survey. No further meaning should be read into the absence of any brand from this Food Survey Information Sheet.

The location of shellfish beds from which samples were taken are given in Annex 4. All of the sampled beds were classified as either A, B or C, that is, the shellfish were intended for human consumption. Category A beds can produce shellfish that may be sold direct for human consumption while shellfish from Category B and C beds must be subject to purification or heat treatment before entering the food chain.

Since the fish samples were composites of several different sources of the same species of fish, retail outlets and brands have not been named.

# Methodology

# <u>Sampling and preparation – fish and shellfish composite samples</u>

Composite fish and shellfish samples were obtained from the Food Standards Agency 2004 survey of PCBs and Dioxins in Fish and Shellfish (C02034). For the survey of PCBs and dioxins, 50 types of fish/shellfish were chosen and 60 samples of each type were purchased from various outlets, homogenised and the bulked sample analysed. For Mackerel, Herring, Salmon (Atlantic Wild), Farmed Rainbow Trout, Farmed Salmon, megrim and skate, 30 samples were homogenised and analysed as a bulk. Sampling was undertaken by the University of Bristol and Direct Laboratories. Samples analysed in this survey included fresh sea-fish and shellfish, canned and processed fish and shellfish, farmed sea-fish and farmed fresh-water trout. For the larger fish species steaks or fillets were obtained as far as possible. Full details of the fish and shellfish species are reported in Table 1.

Samples for each species were collected from England (49), Wales (3), Scotland (6) and Northern Ireland (2), the number of samples being proportional to the population. Sampling was further partitioned between the major retailers, according to their market share within each country, and other outlets such as market stalls and high street fishmongers.

Sampling was further broken down by season, for all but the seasonally available samples and the canned and processed samples, in order to encompass any seasonal changes in levels of contamination that might occur due to fluctuations in body oil, body weight, intake, etc.

The edible portions of the individual fish of each species were homogenised individually, and portions of each homogenate were then further homogenised into single composite samples for the analysis of each species.

# <u>Sampling and preparation – individual shellfish samples</u>

Samples were collected to obtain commercial species from many locations throughout Great Britain. The sample collection in England and Wales was undertaken in conjunction with environmental health officers, located in the relevant Local Authorities. In Scotland, samples were collected in conjunction with the FSA and the Fisheries Research Services.

The distribution of the collection of the harvested samples and thirty retail samples across the UK was as follows; East England (3), North West England (9), South England (5), South West England (27), South East England (37), North Scotland (6), West Scotland (44), and Wales (24). Retail samples were purchased from a number of supermarket chains, as well as several independent retailers and market stalls.

The harvested samples were collected between January and August 2004. For several species, samples were taken before and after spawning to determine if this caused changes in arsenic levels. The collection of the pre spawning samples took place between January and March, and the post spawning samples between June and August. The initial thirty retail samples were collected between June and August 2004.

Annex 1 shows details of all the retail samples collected and Annex 2 shows details of all the harvested samples collected.

Each sample collected consisted of a number of individual shellfish that were bulked to provide a sample; the number being collected in each case depending on the size of the individual shellfish. In general, for the harvested shellfish the sample sizes were fifty mussels or cockles or twelve clams or oysters, and for the retail samples at least three

packages of each product were purchased to make up an approximate sample weight of one kilogram (see Annexes 1 and 2).

Edible portions of the samples were prepared by the Centre for the Environment Fisheries and Aquaculture Science (CEFAS). The edible tissue was removed and the portions of the combined shellfish constituting each sample were then homogenised using an Ultra Turrax<sup>TM</sup> mixer. The process was repeated for each bulked sample and then samples were refrozen at minus 20°C until analysis. Edible tissue from at least three of the retail packages was combined to form a bulk sample. The sample contents were removed and, where excess storage medium, oil or saline solution was found, this was discarded if not considered part of the edible content. The whole net weight and sample weight were recorded.

# **Analysis**

All samples were analysed for total and inorganic arsenic at the Central Science Laboratory (CSL). Measurement uncertainty figures are shown in Annex 3.

## Total Arsenic

Samples were digested in concentrated nitric acid using a microwave-assisted digestion procedure. Total arsenic was measured using inductively coupled plasma-mass spectrometry (ICP-MS).

## Inorganic Arsenic

Following dissolution of the samples in concentrated hydrochloric acid and conversion of the inorganic arsenic species to As(III), the As(III) was converted into a covalent halide and then extracted into chloroform. The arsenic was back extracted from the chloroform into dilute hydrochloric acid and then quantified using ICP-high resolution-MS, operating at a resolution of 10,000.<sup>4</sup>

#### **Quality Control**

The method used by CSL for the determination of total arsenic is accredited by the United Kingdom Accreditation Service (UKAS) to ISO17025. At the time of analysis the method for inorganic arsenic analysis at CSL was not accredited but accreditation was achieved

shortly after. Throughout the duration of the study CSL performed satisfactorily in proficiency testing exercises for both total and inorganic arsenic.

- The quality assurance and quality control data obtained during this survey were as follows; mean recovery values for total arsenic (n=9); BCR278r = 112%, DORM-2 = 108%, BCR627 = 100% and BCR422 = 101%. Recovery of analyte from a spike procedural bland was 103%.
- There are no CRMs available for inorganic arsenic but BCR627 'Arsenic in Tuna Fish' reference material provides data for total arsenic, arsenobetaine and DMA, allowing a calculation of the 'inorganic' portion, to be made. DORM-2 was also used in the survey because an indicative value has been derived through a collaborative trial involving CSL and several other laboratories, and has been used in previous studies.
- The quality assurance and quality control data obtained during the measurement of inorganic arsenic in this survey's samples were as follows; mean recovery values for (n=9); DORM-2 = 107% and BCR627 = 101%. Recovery of analyte from a spiked 'procedural blank' was 101%.

# **Arsenic Speciation Stability Trial**

Some of the fish in the composite samples had to be stored for some time before analysis. To ensure that the relative proportion of inorganic arsenic to total arsenic did not change during storage, an arsenic speciation storage stability study was set up. Two large fish (Megrim and Huss) were purchased, filleted and the flesh cubed (2 cm x 2 cm). Each fish sample was then sub-divided into four portions, two of which were homogenised using a Büchi Mixer (B-400) and two left cubed. One cubed and one homogenised subsample was subjected to freeze drying, and the other equivalent samples stored at -18°C. Ten subsamples, representative of the four preparation/storage approaches were produced, and stored frozen, in similar conditions to the samples in the main survey, until required for analysis.

Sub-samples were analysed at various time points over a nine-month period beginning 10 days after being landed. A second experiment was carried out to look at more rapid changes, using a sample of plaice that had been caught less than 24 hours prior to being

delivered to the laboratory. The fish was treated in exactly the same way as the Huss and Megrim samples except for the fact that the time between landing and analysis had been reduced to 3 days.

#### Results

A summary of the results for the composite fish samples is given in Table 2, the composite shellfish samples in Table 3, and the individual shellfish samples in Table 4. Total arsenic, mean inorganic arsenic and percentage of inorganic arsenic are shown. The mean inorganic arsenic content was calculated for those samples that were analysed in duplicate. Calculation of percent inorganic arsenic was based on lower-bound values, that is, where levels of inorganic arsenic were below the limit of detection (LOD), the value was set at zero. This prevented anomalous percentage results occurring where total arsenic was low and the inorganic arsenic was below the LOD. For the individual shellfish samples, the mean minimum and maximum values for each type of shellfish are shown. The percentage inorganic arsenic is calculated using the mean values.

#### COMPOSITE FISH AND SHELLFISH SAMPLES

#### Total arsenic

The highest levels of total arsenic were found in lemon sole composite (19.29 mg/kg) and skate composite (20.17 mg/kg). According to other results<sup>6</sup>, the levels of total arsenic in skate are typically high, with a range of 14.4 – 61.5 mg/kg.

The third highest level of total arsenic was found in fresh crab composite (9.16 mg/kg) and is approximately half of the two highest levels. Three further samples had levels that were relatively similar to the fresh crab composite: dogfish composite (7.96 mg/kg), shark composite (8.65 mg/kg), and plaice composite (8.06 mg/kg). In comparison to the literature, where available, some of these levels are typical for the species. Fresh crab total arsenic levels have a range of 7.9-9.6 mg/kg<sup>7</sup> and plaice has reported mean levels above 10 mg/kg<sup>8</sup>.

#### Inorganic arsenic

The highest levels of inorganic arsenic were found in the fresh crab composite sample (0.08 mg/kg) and the dogfish and sardine composite samples (both 0.06 mg/kg). However, the percentage of inorganic arsenic was below 3% for all samples. Levels in the composite fish samples were relatively low with four samples being below the limit of detection.

#### INDIVIDUAL SHELLFISH SAMPLES

#### Total arsenic

The highest level of total arsenic was found in a single retail sample of whelks (15.42 mg/kg). This level is significantly higher than the other concentrations found in the shellfish samples measured in this survey. However, the percentage of inorganic arsenic for this sample was below 1 percent (0.26%) so this is not likely to pose a significant food safety risk. It has been reported before that whelks appear to contain elevated concentrations of arsenic while other common shellfish contain levels similar to the average fish group. All other levels of total arsenic in shellfish are comparable to the average level found in the fish group of the Total Diet Study (TDS fish group average 3.4 mg/kg fresh weight). No difference was observed between total arsenic levels in pre-spawning and post-spawning shellfish.

# Inorganic arsenic

The highest level of inorganic arsenic was found in a sample of pre spawning mussels (0.45 mg/kg) and the highest percentage of inorganic arsenic was found in a retail sample of cockles (13.27%). In general, the levels and percentages of inorganic arsenic were higher in the shellfish samples than in the composite fish samples.

#### ARSENIC SPECIATION STABILITY TRIAL

The results for the stability trials are shown in Table 9 for the four differently treated samples of megrim and Table 10 for the plaice. There is a general decrease in the inorganic arsenic content of all samples, most markedly in the early stages of the trial. The proportion of inorganic arsenic varies from 1.26 to 0.34 percent, confirming that most of the arsenic present is in the less toxic organic form and that extended storage does not significantly affect the relative amount of inorganic and organic arsenic present. The plaice samples show that in general, the inorganic arsenic content would have fallen in the initial days of storage. The results confirm the validity of the data on inorganic arsenic presented for the main survey of fish which include samples that had been stored for some time before analysis.

# **Estimation of Dietary Exposures**

# Composite fish and shellfish samples

Dietary exposure to total and inorganic arsenic was estimated for adults and toddlers for the following fish group composites, for which there is reliable consumption data from the National Diet and Nutrition Survey (NDNS)<sup>10,11</sup>: canned tuna, fresh trout, lemon sole, fresh mackerel, fresh salmon and canned salmon. The consumption data are summarised in Table 5. For toddlers there was not enough reliable consumption data available for the individual fish groups, so an average portion size was used. The lemon sole composite contained the second highest level of total arsenic (19.29 mg/kg) and the canned salmon one of the lowest levels (0.36mg/kg) and so a good range of dietary exposure was obtained. These estimates are summarised in Table 6.

To obtain a worst case estimate of dietary exposure to inorganic arsenic, estimations were made using the composite samples that contained the three highest levels of inorganic arsenic (fresh crab, sardines and dogfish). As these fish had insufficient consumption data it was not possible to estimate dietary exposure on the above basis. For these fish, the average inorganic arsenic intake from eating one portion of fish a day was estimated. The portion size was taken to be the average amount of fresh fish (including the types of fish measured in this survey only) that an adult or toddler consumer would consume at a single setting. To reflect the intake by consumers of fresh/prepared fish from the UK, recipes, i.e. composite foods that contain fish as part of the ingredients, were not included in the estimate. This was calculated for both a mean and high-level adult consumer. Data were only available for a mean level toddler consumer. Levels have been compared to the Joint Expert Committee in Food Additives' provisional tolerable weekly intake (JECFA PTWI) for inorganic arsenic<sup>12</sup> (equivalent to 2.14 μg/kg bw/day) although the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) concluded that there are currently no appropriate safety guidelines and that intakes should be as low as reasonably practicable<sup>13</sup>. All intakes of inorganic arsenic were below 5 % of the PTWI. These estimates are summarised in Table 7.

## Individual Shellfish Samples

Since limited consumption data exists for most of the shellfish groups analysed in this survey, it was not possible to calculate dietary exposures for specific shellfish consumers. Instead, a consumption value was derived from the NDNS based on consumers of one or more of the shellfish in this survey. To reflect the intake by consumers of fresh/prepared shellfish from the UK, recipes, i.e. composite foods that contain shellfish as part of the ingredients, were not included in the estimate. Estimates for total and inorganic arsenic are summarised in table 8. Inorganic arsenic intakes were compared to the PTWI, and all values were below 7 % of the value.

#### **Conclusions**

Shellfish tended to accumulate more of the more toxic inorganic form of arsenic than the composite fish samples, but the levels of inorganic arsenic were low and comparable to results previously published for specific species, where available. The maximum intake of inorganic arsenic was below 5 per cent of the safety guideline set previously by the World Health Organisation, although the guideline is due to be reviewed. Many samples were comparable to the range of levels of total arsenic found in the fish group of the 2000 TDS. These data indicate that exposure is as low as reasonably practicable.

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http://www.food.gov.uk/science/ouradvisors/toxicity/statements/cotstatements2003/arsenic statement

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A copy of the final report of this survey has been placed in the FSA Library – address details above. If you wish to consult a copy, please contact the library for an appointment giving at least 24 hours notice or, alternatively, copies can be obtained from the Library: a charge will be made to cover photocopying and postage.

Table 1: Fish and shellfish species analysed in this survey

Samples from FSA survey of PCBs and Dioxins							
	(analysed as compo		and Miscellaneous				
Anchovy (Canned)	Pallohius virens	Crab (Canned)					
Cod	Gaddus morhua	Crab (Carried)	Cancer pagurus				
		Fish Paste	labelled as crab, sardine, salmon, tuna,				
Coley	Pallohius virens		bloater and fish paste/spread				
Dogfish	Squalus spp	Mussels	Mytilus edulis				
Eel	Anguilla spp	Oysters	Ostrea edulis and Crassostrea gigus				
Halibut	Hippoglossus hippoglossus	Prawns (Cold water)	Pandalid spp				
Halibut (Farmed)		Prawns (Warm water)	Penaeid spp				
Haddock	Melanogammus aeglefinus	Rollmops (Herring)	Clupea harengus				
Hake	Merluccius merluccius	Scallops	Pecten & Chlamys spp				
Herring	Clupea harengus	Scampi	Nephrops norvegicus				
Lemon Sole	Microstomus Kitt	Surimi	Ocean or Crab Sticks				
Mackerel	Scomber scombrus	Commiss obtai	and from ECA common of				
Mackerel (Canned)			ned from FSA survey of otins in shellfish				
Megrim (Farmed)	Lepidorhombus whiffiagonis		s individual samples)				
Pilchard (Canned)		(anim) com a					
Plaice	Pleuronectus platessa	Clams					
Red Snapper	Lutjanus spp	Clams (Baby)					
Salmon (Alaskan)	Oncorhynchus spp	Cockles					
Salmon (Atlantic)	Salmo salar	Mussels					
Salmon (Canned)		Oyster (Native)					
Salmon (Farmed)	Salmo salar	Oyster (Pacific)					
Sardines	Sardina pilchardus	Razor Shells					
Sardines (Canned)		Scallops					
Sea Bass	Dicentrarchus labrux	Scallops (King)					
Sea Bass (Farmed)	Dicentrarchus labrax	Scallops (Queen)					
Sea Bream (Farmed)	Sparus aurata	Whelks					
Sea Trout (Farmed)	Oncorhynchus mykiss	Winkles					
Shark	Various spp						
Skate	Raja spp						
Sprat	Sprattus sprattus						
Swordfish	Xiphias gladius and Istrophous spp						
Trout (Farmed)	Oncorhynchus mykiss						
Tuna	Thunnus & Katsuwonus spp						
Tuna (Canned)		1					
Turbot (Farmed)	Psetta maxima						
Turbot (Greenland)	Reinhardtius hippoglossoides	1					
Turbot (UK)	Psetta mixmia	1					
Whitebait	Juveniles of assorted species	1					
Whiting	Merlangius merlangus	1					

All samples composed of fresh and frozen samples unless otherwise stated.

Table 2. Summary of arsenic levels in bulk fish samples

Sample	Description	Total Arsenic	Mean inorganic arsenic (mg/kg),	% inorganic
code	2 cocinpaion	(mg/kg)	with <lod 0<="" at="" set="" td=""><td>70 morgamo</td></lod>	70 morgamo
Flat-fish		\ 3. 3/		
M3530	Halibut	3.57	0.02	0.56
M3973	Halibut (Farmed)	1.55	0.01	0.66
M3004	Lemon Sole	19.29	0.01	0.07
M3926	Megrim (Farmed)	4.62	0.01	0.19
M3281	Plaice	8.06	0.02	0.31
M4033	Skate	20.17	0.02	0.10
M3387	Turbot (Greenland)	4.36	0.02	0.53
M3279	Turbot (UK)	4.07	0.02	0.39
M3810	Turbot (Farmed)	2.07	0.00	0.16
Cod-type	·		-	511.5
M2887	Cod	3.57	0.01	0.21
M3638	Coley	1.89	0.01	0.36
M3160	Haddock	4.57	0.02	0.43
M3702	Hake	2.02	0.00	0.13
M3684	Whiting	3.12	0.01	0.23
Herring-ty		3112		5.25
M0032	Anchovy (Canned)	0.96	0.01	1.10
M0021	Herring	2.96	0.04	1.40
M0036	Pilchard (Canned)	1.75	0.02	1.11
M3642	Sardines	3.43	0.06	1.61
M0034	Sardines (Canned)	2.31	0.03	1.08
M2884	Sprats	2.96	0.03	0.86
M3787	Surimi	0.12	0.00	0.00
M3612	Whitebait	1.51	0.02	1.63
Mackerel-				
M3080	Mackerel	2.18	0.04	1.93
M0023	Mackerel (Canned)	1.72	0.00	0.00
M4032	Red Snapper	1.85	0.00	0.00
M3799	Sea Bass (Farmed)	0.91	0.01	1.20
M3280	Sea Bass	1.14	0.01	1.20
M3824	Sea Bream (Farmed)	2.11	0.01	0.67
M2886	Swordfish	1.12	0.01	0.71
M2885	Tuna	1.04	0.02	1.63
M0035	Tuna (Canned)	0.91	0.01	1.10
Salmon-ty		l.		
M3613	Salmon (Alaskan)	0.48	0.01	1.63
M0033	Salmon (Canned)	0.36	0.00	0.00
M3927	Salmon (Farmed)	1.95	0.01	0.44
M3643	Salmon	1.54	0.01	0.76
M3823	Sea Trout (Farmed)	2.68	0.01	0.40
M3812	Trout (Farmed)	2.48	0.01	0.56
Shark-typ	,	•	· · · · · · · · · · · · · · · · · · ·	
M3294	Dogfish	7.96	0.06	0.73
M3286	Shark	8.65	0.01	0.14
Other fish	1	•		
M3675	Eel	0.23	0.01	2.68
M0022	Fish paste	2.71	0.04	1.40
M3797	Rollmops (Herring)	1.58	0.04	2.42
L		•	<u>'</u>	

Table 3. Summary of arsenic levels in bulk shellfish samples

Sample code	Description	Total Arsenic (mg/kg)	Mean inorganic arsenic (mg/kg), with <lod 0<="" at="" set="" th=""><th>% inorganic</th></lod>	% inorganic
M3708	Warm Prawns Composite	0.66	0.01	1.78
M3712	Cold Prawns Composite	5.49	0.02	0.30
M3713	Scallops Composite	1.53	0.01	0.65
M3746	Mussels Composite	2.07	0.04	1.92
M3763	Oysters Composite	2.04	0.04	2.02
M3701	Crab	9.16	0.08	0.86
M0031	Crab (Canned)	1.35	0.03	2.30
M3703	Scampi	3.87	0.04	1.15

Table 4. Summary of arsenic levels in shellfish

Shellfish Type	Number of Samples	Sample Source1	Levels of total arsenic (mg/kg)2			Levels o	f inorganio (mg/kg)2	Percentage inorganic arsenic	
			Minimum	Maximum	Mean	Minimum	Maximum	Mean	
Clams	1	PR	2.51	2.51	2.51	0.06	0.06	0.06	2.39
Baby Clams	1	R	0.97	0.97	0.97	0.12	0.12	0.12	12.37
All clams	2		0.97	2.51	1.74	0.06	0.12	0.09	5.17
Cockles	6	PR	1.07	1.49	1.30	0.06	0.19	0.13	10.00
Cockles	1	PO	1.15	1.15	1.15	0.14	0.14	0.14	12.17
Cockles	1	R	1.13	1.13	1.13	0.15	0.15	0.15	13.27
All cockles	8		1.07	1.49	1.26	0.06	0.19	0.14	11.11
Scallops	2	PR	1.65	2.15	1.90	0.05	0.25	0.15	7.89
King Scallops	1	PR	2.25	2.25	2.25	0.02	0.02	0.02	0.89
Queen Scallops	1	PR	2.96	2.96	2.96	0.06	0.06	0.06	2.03
Scallops	1	PO	1.66	1.66	1.66	0.02	0.02	0.02	1.20
All scallops	5		1.65	2.96	2.13	0.02	0.25	0.08	3.76
Mussels		PR	1.42	4.16	2.31	0.02	0.45	0.10	4.33
Mussels	7	PO	1.30	2.14	1.84	0.02	0.24	0.08	4.35
Mussels	2	R	1.29	1.93	1.61	0.07	0.09	0.08	4.97
All mussels	34		1.29	4.16	2.17	0.02	0.45	0.09	4.15
Native Oysters	6	PR	1.16	1.76	1.46	0.04	0.05	0.04	2.74
Pacific Oysters	11	PR	1.02	3.28	1.97	0.04	0.10	0.06	3.05
Pacific Oysters	3	PO	1.52	2.33	1.85	0.01	0.05	0.03	1.62
Native Oysters	2	PO	1.51	1.89	1.70	0.07	0.07	0.07	4.12
Oysters	1	R	3.33	3.33	3.33	0.14	0.14	0.14	4.20
All oysters	23		1.02	3.33	1.86	0.01	0.14	0.05	2.69
Razor Shells		R	1.88	1.88	1.88	0.06	0.06	0.06	3.19
Whelks	1	R	15.42	15.42	15.42	0.04	0.04	0.04	0.26
Winkles	1	R	4.53	4.53	4.53	0.21	0.21	0.21	4.64
All Shellfish	75		0.97	15.42	2.17	0.01	0.45	0.08	3.69

<sup>&</sup>lt;sup>1</sup> Source of shellfish either directly from shellfish beds, pre-spawning (PR) or post-spawning (PO), or as a retail sample (R). <sup>2</sup> Values expressed in milligrams per kilogram wet weight

Table 5. Consumption data from NDNS for fish species in this survey

Species	No. of consumers	Consumer mean (g/adult/day)	97.5%ile consumer (g/adult/day) <sup>1</sup>
Cod	19	23.68	null
Coley	3	17.81	null
Halibut	3	36.03	null
Herring	8	15.37	null
Mackerel	49	21.04	48.67
Pilchards	4	21.54	null
Plaice	2	53.08	null
Salmon	245	21.27	66.76
Skate	1	24.29	null
Sole	21	22.04	46.52
Swordfish	9	24	null
Trout	37	23.55	51.6
Tuna	430	15.69	52.16
Toddlers		Consumer mean (g/toddler/day)	97.5%ile consumer (g/toddler/day) <sup>1</sup>
All Fish	209	9	24

<sup>&</sup>lt;sup>1.</sup> Where a value of null is entered, there was not a sufficient number of consumers to measure the 97.5%ile.

Table 6. Estimation of dietary exposure to total arsenic for composite fish samples with sufficient consumption data

Fish type	concentration total As (mg/kg)	no of consumers	Adult mean consumer (mg/adult/day)	Adult high- level consumer (mg/adult/day)	Toddler mean consumer (mg/toddler /day) <sup>1.</sup>	Toddler high-level consumer (mg/toddler/ day) <sup>1.</sup>
canned tuna	0.91	430	0.014	0.047	0.0082	0.0218
fresh trout	2.48	37	0.058	0.128	0.0223	0.0594
sole	19.29	21	0.425	0.897	0.1736	0.4629
canned mackerel	1.72	44	0.036	0.0847	0.0155	0.0412
fresh salmon	1.95	145	0.048	0.13	0.0176	0.0468
canned salmon	0.36	63	0.0045	0.013	0.0032	0.0086

<sup>&</sup>lt;sup>1.</sup> Toddler intakes estimated using average portion sizes (9 g/day for a mean consumer, 24 g/day for a high level consumer) for each fish type

Table 7. Estimation of dietary exposure to inorganic arsenic for highest three levels found in composite samples in 'fish' survey

Fish type	inorganic	consumer (mg/adult/day)	consumer (mg/adult/day	consumer (mg/toddler/d	Toddler high-level consumer (mg/toddler/ day)
Average portion size (g/consumer/day	)10	24	80	9	24
Fresh Crab composite	0.079	0.0019	0.0063	0.0007	0.0019
Dogfish Composite	0.058	0.0014	0.0047	0.0005	0.0014
Sardines Composite	0.055	0.0013	0.0044	0.0005	0.0013

Table 8. Estimation of dietary exposure to total and inorganic arsenic for shellfish consumers

	total are	senic	inorganic arsenic		
	Adult mean	Adult high-level	Adult mean	Adult high-level	
	consumer	consumer	consumer	consumer	
	(mg/adult/day)	(mg/adult/day)	(mg/adult/day)	(mg/adult/day)	
Average portion size (g/adult/day)	12	49	12	49	
Clams	0.021	0.085	0.001	0.004	
Cockles	0.015	0.062	0.002	0.007	
Scallops	0.026	0.104	0.001	0.004	
Mussels	0.026	0.106	0.001	0.004	
Oysters	0.022	0.091	0.001	0.002	
Razor Shells	0.023	0.092	0.001	0.003	
Whelks	0.185	0.756	0.000	0.002	
Winkles	0.054	0.222	0.003	0.010	
All shellfish	0.026	0.106	0.001	0.004	
Toddlers	Toddler mean	Toddler high-	Toddler mean	Toddler high-	
	consumer	level consumer	consumer	level consumer	
	(mg/toddler/day)	(mg/toddler/day)	(mg/toddler/day)	(mg/toddler/day)	
All shellfish	1.25	na	0.05	na	

Table 9. Results for Megrim arsenic speciation trial

Time (Week)	0	1	2	4	13	18	25
Sample preparation technique	Inorganic Arsenic content (percent)						
Cubed (wet)	0.71	0.59	0.88	0.37	0.78	0.6	0.83
Cubed (freeze dried)	1.26	1.02	0.71	0.48	0.56	0.64	0.58
Homogenised (wet)	0.81	0.46	0.44	0.42	0.34	0.63	0.63
Homogenised (freeze dried)	1.01	0.5	0.47	0.43	0.34	0.53	0.47

Table 10. Results for Plaice arsenic speciation trial

Time (Day)	2	6
Sample preparation technique	Inorganic Arsenic content (percent)	Inorganic Arsenic content (percent)
Cubed (wet)	0.8	0.5
Cubed (freeze-dried)	0.8	0.6
Homogenised (wet)	1.2	0.9
Homogenised (freeze-dried)	1.2	1.2

Annex 1: Retail shellfish samples collected June – August 2004

Store	Post Code	Species	Product Description	Brand	Pack Weight	Country of Origin	Purchase date	Sample code	Mean total arsenic (mg/kg) <sup>1</sup>	Mean inorganic arsenic (mg/kg) <sup>1</sup>
Sainsbury's	CO1 1LG	Baby Clams	Brine in Tin	John West	142g drained weight	Thailand	29-Jun-04	2004/6483	0.97	0.12
Tesco	SA1 3RA		Cooked & Pickled in Jar	Van Smirren	100g drained weight	Holland	09-Jul-04	2004/7138	1.13	0.15
Safeway	CM9 6GG	IIV/III ICCAIC	Cooked & Pickled in Jar	Van Smirren	100g drained weight	Holland	29-Jun-04	2004/6697	1.29	0.09
Asda	CO4 5TU	New Zealand Mussels	Frozen	Asda	200g	New Zealand	29-Jun-04	2004/6422	1.93	0.07
Sainsbury's	CO1 1LG	Oysters	Smoked in Sunflower Oil in Tin	John West	65g drained weight	Korea	29-Jun-04	2004/6494	3.33	0.14
Tuckers	Swansea Market	Razor Shells	Fresh			Scotland	09-Jul-04	2004/7003	1.88	0.06
The Food Company	CO6 1ED	IVVIDDIKE	Fresh – Shelled			Ireland	29-Jun-04	2004/6811	15.42	0.04
Estuary Fish Merchants		Winkles	Fresh			Leigh-on-Sea	16-Aug-04	2004/8252	4.53	0.21

<sup>&</sup>lt;sup>1</sup> Values expressed in milligrams per kilogram wet weight of edible portion. Empty entries indicate information was not available.

# **Annex 2: Harvested shellfish samples**

Local Authority	Sample Source <sup>1</sup>	Grid Reference	Bed Name	Species Sampled	Date Collected	Sample code	No. of samples bulked	Total meat weight (grams)	Mean total arsenic <sup>2</sup> (milligrams per kilogram)	Mean inorganic arsenic <sup>2</sup> (milligrams per kilogram)
Clams										
Canterbury CC	PR	TR082669	Pollard	Clam	18-Feb-04	2004/1975	10	163.5	2.51	0.06
Cockles										
Carmarthenshire CC	PO	SS48309960	North West	Cockles	19-Jul-04	2004/7645	50	75.5	1.15	0.14
Western Isles	PR	NF826435	Loch Carnan	Cockles	12-Jan-04	2004/0597	16	92.5	1.49	0.08
Western Isles	PR	NF705053	Traigh Mhor	Cockles	12-Jan-04	2004/0871	21	96.1	1.07	0.06
Carmarthenshire CC	PR	SS48309960	North West	Cockles	24-Feb-04	2004/2088	50	41.8	1.46	0.12
Thanet DC	PR	TR274697	Minnis Bay	Cockles	24-Feb-04	2004/4457	50	123.1	1.19	0.18
City and Council of Swansea	PR	SS505959	South side (East)	Cockles	10-Mar-04	2004/4578	50	75	1.29	0.19
Kings Lynn & W Norfolk BC	PR	TF586348	Daseleys/Gat The Wash	Cockles	09-Mar-04	2004/4679	50	143.4	1.32	0.16
Mussels	•	•			•		•			
Carmarthenshire CC	РО	SN357073	St Ishmaels	Mussels	19-Jul-04	2004/7696	50	221	2.03	0.05
Copeland DC	РО	SD08359610	Ravenglass 2	Mussels	26-Jul-04	2004/7798	50	80.7	1.81	0.04
Western Isles	РО	NB 373 249	Loch Leurbost	Mussels	05-Jul-04	2004/8793	50	178.3	2.12	0.04
Lochaber	РО	NN 038 783	Loch Eil	Mussels	20-Jul-04	2004/9008	50	87.4	1.56	0.02
Argyll and Bute	РО	NN 170 105	Loch Fyne	Mussels	05-Jul-04	2004/9059	50	21.5	1.30	0.06
North Ayrshire	PO	NS 198 542	Fairlie	Mussels	21-Jul-04	2004/9174	50	157.4	2.14	0.08
Allerdale DC	PR	NY076517	Silloth	Mussels	11-Feb-04	2004/0493	40	226.7	1.57	0.03
Western Isles	PR	NB373249	Loch Leurbost	Mussels	12-Jan-04	2004/0546	50	234.7	1.64	0.04
Lochaber	PR	NM636859	Loch nan Ceol	Mussels	20-Jan-04	2004/1034	39	138.3	1.80	0.03
Lochaber	PR	NN062773	Loch Eil	Mussels	20-Jan-04	2004/1220	50	257.9	1.95	0.02
Lochaber	PR	NN146616	Loch Leven	Mussels	20-Jan-04	2004/1322	50	212.3	1.79	0.03
North Ayrshire	PR	NS198542	Fairlie	Mussels	14-Jan-04	2004/1749	44	222.6	2.70	0.06
Barrow BC	PR	SD185706	Cocken Tunnel	Mussels	18-Feb-04	2004/1904	50	203.7	2.66	0.05
Carmarthenshire CC	PR	SN357073	St Ishmaels	Mussels	24-Feb-04	2004/2139	50	237.6	2.17	0.05
City Council of Swansea	PR	SS62908930	Swansea Bay S	Mussels	10-Mar-04	2004/2190	50	126.7	3.51	0.09
Conwy County BC	PR	SH761797	Morfa	Mussels	17-Feb-04	2004/3270	40	270.2	2.39	0.05
Falmouth PHA	PR	SW84093878	T Pontoon	Mussels	26-Feb-04	2004/3383	50	297.8	3.43	0.29

Local Authority	Sample Source <sup>1</sup>	Grid Reference	Bed Name	Species Sampled	Date Collected	Sample code	No. of samples bulked	Total meat weight (grams)	Mean total arsenic <sup>2</sup> (milligrams per kilogram)	Mean inorganic arsenic <sup>2</sup> (milligrams per kilogram)
North Cornwall DC	PR	SW939747	Gentle Jane	Mussels	26-Feb-04	2004/3684	43	478	1.67	0.07
Penwith DC	PR	SW53403880	Carrack Gladden	Mussels	26-Feb-04	2004/3939	50	152.6	3.25	0.45
Taw-Torridge DC	PR	SS460311	Appledore Lifeboat slip	Mussels	26-Feb-04	2004/4145	50	159.6	1.84	0.15
W. Lancs DC	PR	SD328259	Salters Bank	Mussels	18-Feb-04	2004/4347	50	281.7	1.42	0.06
Wirral BC	PR	SJ227837	Caldy Blacks	Mussels	25-Feb-04	2004/4398	50	152.6	1.99	0.10
Kings Lynn & W Norfolk BC	PR	TF802455	Norton Creek	Mussels	09-Mar-04	2004/4399	50	160	2.46	0.06
Teignbridge DC	PR	SX91417275	Gappa Bank	Mussels	19-Feb-04	2004/4456	40	391.8	1.91	0.08
Wyre BC	PR	SD33105190	Wyre End Scar	Mussels	01-Mar-04	2004/4730	50	123.4	1.69	0.14
Shetland	PR	HU378644	Olna Firth	Mussels	23-Feb-04	2004/4842	50	141.9	2.80	0.07
Western Isles	PR	NF897631	Clachan Burrival	Mussels	22-Feb-04	2004/5146	31	218	4.16	0.07
Copeland DC	PR	SD08359610	Ravenglass 2	Mussels	01-Mar-04	2004/5438	50	223.8	2.48	0.06
Argyll and Bute	PR	NS072772	Loch Striven	Mussels	02-Feb-04	2004/6107	50	295.2	2.51	0.05
Plymouth PHA	PR	SX407567	Lynher - Shillingham	Mussels	01-Mar-04	2004/6801	49	265.9	1.85	0.25
Western Isles	PR	NF798283	Loch Eynort	Mussels	03-Feb-04	2004/6806	50	162.5	2.19	0.05
Oysters	•									
Colchester BC	РО	TL99101260	Salcott	Native oyster	28-Jul-04	2004/7397	10	67.1	1.51	0.07
South Hams DC	РО	SX67254489	Hexdown Quay	Native oyster	06-Jul-04	2004/7459	10	314.6	1.89	0.07
Colchester BC	PR	TM00001270	Strood Channel	Native Oyster	01-Mar-04	2004/2961	10	53.5	1.69	0.04
Colchester BC	PR	TM062160	Pyefleet Spit	Native Oyster	01-Mar-04	2004/2972	5	93	1.76	0.04
Falmouth PHA	PR	SW85623321	Percuil	Native oyster	26-Feb-04	2004/3456	10	84.2	1.62	0.04
Portsmouth PHA	PR	SU60290411	Peewit Island W	Native oyster	26-Feb-04	2004/3960	10	67.4	1.27	0.05
South hams DC	PR	SX67254489	Hexdown Quay	Native oyster	23-Feb-04	2004/4072	10	157.7	1.29	0.04
Portsmouth PHA	PR	SZ62239847	Haslar Wall	Native oyster	26-Feb-04	2004/4453	10	48.6	1.16	0.05
South Hams DC	РО	SX7554148	Geese Quarries	Pacific Oyster	20-Jul-04	2004/7470	10	77	2.33	0.05
Maldon DC	РО	TL925077	Goldhanger	Pacific Oyster	23-Jun-04	2004/7911	10	220	1.52	0.01
Western Isles	PR	NF828469	South Ford	Pacific Oyster	13-Jan-04	2004/0668	10	87	3.21	0.10
Sutherland	PR	NC594593	Kyle of Tongue	Pacific Oyster	12-Jan-04	2004/0882	10	134.4	2.20	0.04
Lochaber	PR	NM633733	Loch Moidart	Pacific Oyster	20-Jan-04	2004/1167	7	181.4	2.14	0.04
Argyll and Bute	PR	NM764153	Seil Sound	Pacific Oyster	05-Jan-04	2004/1497	10	121.3	1.89	0.04
Argyll and Bute	PR	NR355903	Colonsay	Pacific Oyster	19-Jan-04	2004/1698	10	56.4	3.28	0.06
Canterbury CC	PR	TR082669	Pollard	Pacific oyster	18-Feb-04	2004/2037	10	113.6	1.02	0.05

Local Authority	Sample Source <sup>1</sup>	Grid Reference	Bed Name	Species Sampled	Date Collected	Sample code	No. of samples bulked	Total meat weight (grams)	Mean total arsenic <sup>2</sup> (milligrams per kilogram)	Mean inorganic arsenic <sup>2</sup> (milligrams per kilogram)
South hams DC	PR	SX7554148	Geese quarries	Pacific oyster	26-Feb-04	2004/4083	10	110.2	1.55	0.05
Suffolk Coastal DC	PR	TM397487	Butley Creek	Pacific oyster	03-Mar-04	2004/4094	10	205.4	2.22	0.07
Maldon DC	PR	TL925077	Goldhanger	Pacific oyster	24-Feb-04	2004/4452	10	145.9	1.08	0.05
Argyll and Bute	PR	NN170105	Loch Fyne	Pacific Oyster	03-Feb-04	2004/6056	10	74	1.77	0.04
Fowey PHA	PR	SX12605320	Wisemans	Pacific oyster	09-Mar-04	2004/6179	5	251.6	1.27	0.07
Sutherland	PO	NC 594 593	Kyle of Tongue	Pacific Oysters	22-Jul-04	2004/8855	10	177.3	1.71	0.02
Scallop										
Falmouth & Truro PHA	PO	EC34	Falmouth Bay	Scallop	20-Jul-04	2004/7543	10	302	1.66	0.02
Falmouth and Truro PHA	PR	SW813321	Falmouth Bay	Scallop	26-Feb-04	2004/4741	10	190.6	1.65	0.05
Plymouth PHA	PR	SX483542	EC63	Scallop	01-Mar-04	2004/6802	10	500.5	2.15	0.25
Ross and Cromerty	PR	NG852891	Loch Ewe	King Scallops	02-Feb-04	2004/5334	7	329.9	2.25	0.02
Argyll and Bute	PR	NR870720	Loch Fyne	Queen Scallop	23-Feb-04	2004/5994	10	175.1	2.96	0.06

<sup>&</sup>lt;sup>1</sup> Source of shellfish directly from shellfish beds, either pre-spawning (PR) or post-spawning (PO). <sup>2</sup> Values expressed in milligrams per kilogram wet weight of edible portion.

# **Annex 3 - Measurement uncertainty**

Measurement uncertainty was estimated from the results obtained from various batches and is summarised below. A measure of the combined standard uncertainty was gained by combining the observed between batch uncertainty (standard deviation) with the standard uncertainty associated with factors that did not change between batches, and the standard uncertainty associated with correcting for bias.

The highlighted values in the table represent the measurement of uncertainty at the LOD and LOQ obtained during the Fish and Shellfish survey.

Concentration	Measurement uncertainty (95%)	R.S.D.		
(mg/kg)	(± mg/kg)	(%)		
100	15.0	15		
10	1.5	15		
1	0.16	16		
0.5	0.078	16		
0.2	0.034	17		
0.1	0.020	20		
0.05	0.015	31		
LOQ = 0.033	<u>0.014</u>	<u>43</u>		
0.02	0.014	68		
LOD = 0.01	0.013	<u>133</u>		