Arsenic levels in cod, flounder and shrimp caught in Belgian coastal waters (1984-1988)

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UDC-nr. *639.22:544 (493)*

Keywords *Arsenic, cod, flounder, shrimp*

Summary

Arsenic was determined in cod (*Gadus morhua*), flounder (*Platichthys flesus*) and brown shrimp (*Crangon crangon*) during a five years' period (1984-1988). Cod and flounder were divided into five length categories; 25 specimens were analyzed individually. For shrimp, a bulked sample of 100 cooked and peeled animals was taken.

In cod, arsenic levels did not appear to be influenced by the length (age) of the fish, whereas in flounder, the content clearly increased with length. Average values of both fish species were quite similar, ranging from 2.5 to 5.4 mg/kg in cod and 2.4 to 4.1 mg/kg in flounder. No clear temporal trend could be observed. Individual variations were large.

Arsenic concentrations in shrimp (4 to 10 mg/kg on average) were higher than in the two fish species with greater yearly variations. No significant temporal trend was noted. High values which were recorded in some fishery products, especially in flatfish, were not found during the present investigations. No problems are likely to occur with respect to human consumption. For the purpose of monitoring arsenic levels in the marine environment, shrimp with their higher concentration appear to be more appropriate than fish.

1. **Introduction**

Arsenic is present in marine organisms at much higher concentrations than in terrestrial animals (Chapman et al., 1926; Doyle et al., 1978). The major arsenicals however have been shown to be water soluble organic compounds which are much less toxic than the inorganic salts (Westöö et al., 1972; Shinagawa et al., 1983). In 1977 Edmonds et al. isolated and characterized arsenobetaine (trimethylarsoniumacetate) in rock lobster. Further investigations showed this compound to represent more than 70 % of the total arsenic concentration in most marine organisms (Kurosama et al., 1980; Edmonds et al., 1981a; Luten et al., 1983; Shiomi et al., 1983, 1984). Arsenobetaine is quite stable and is considered to be non toxic (Penrose, 1974). The major part of the organic arsenic ingested via fishery products is rapidly excreted unchanged (Freeman et al., 1979). A genotoxicity study of arsenobetaine did not show any effect of this compound (Jongen et al., 1985).

Inorganic arsenic compounds on the other hand are highly toxic and show a carcinogenic effect. For this reason the Joint Expert Committee of the FAO/WHO (1983) recommends an acceptable daily intake of 2 µg inorganic arsenic per kg body weight. The levels of inorganic arsenicals however seldom exceed 0.1 mg per kg wet weight. (Lunde, 1973; Brooke et al., 1981; Flanjak, 1982; Shinagawa et al., 1983). It is further known that marine biota in lower trophic level (bacteria, plankton) can transform inorganic arsenicals into organic ones while these in higher trophic levels can not (Shiomi et al., 1984). These marine animals do not take up organic arsenicals from sea water but from their baits. Excretion of organic arsenic however is quick and no accumulation in the food chain with increasing trophic level was observed (Penthreath, 1977; Wrench et al., 1979; Edmonds et al., 1981b). Arsenic in marine biota appears to be mainly of natural origin (Penrose, 1974; Andrea, 1978; Edmonds et al., 1981a). However in some areas such as estuaries anthropogenic inputs can increase the arsenic

levels significantly (De Groot et al., 1976; Michel, 1987).
Within the framework of the Belgian monitoring programme on trace contaminants, the analysis of arsenic in cod (*Gadus morhua*), flounder (*Platichthys flesus*) and brown shrimp (*Crangon crangon*) was included from 1984 onwards. This paper reports results for the five years' period 1984-1988.

2. Material and methods

2.1. Samples

Cod, flounder and shrimp were caught off the Belgian coast by trawling. According to

Table 1 Average arsenic content in cod (mg/kg wet weight)(a)

Length category (mm)	1984	1985	1986	1987	1988
< 261	7.8 (24.7)	—	—	—	—
261-300	3.0 (42.0)	—	—	—	—
301-340	—	—	2.8 (65.7)	3.3 (19.7)	—
341-380	4.6 (32.7)	4.3 (26.4)	2.0 (31.7)	3.2 (19.4)	3.4 (53.4)
381-420	—	—	2.9 (42.9)	4.2 (29.0)	—
421-460	—	5.2 (55.4)	2.2 (22.5)	3.8 (35.6)	3.2 (36.1)
461-500	—	5.1 (32.6)	2.6 (47.8)	4.1 (24.3)	3.0 (59.3)
500-540	—	—	—	—	2.8 (46.6)
541-580	3.2 (29.6)	7.5 (20.8)	—	—	3.1 (14.7)
> 580	5.4 (20.6)	4.9 (44.9)	—	—	—
Total	4.8 (38.0)	5.4 (40.6)	2.5 (48.0)	3.7 (24.8)	3.1 (45.2)

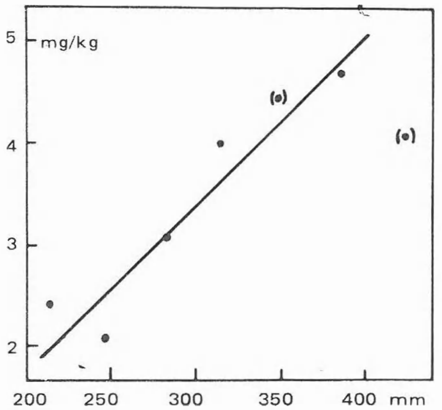
(a) Coefficient of variation (%) in brackets

Table 2 Average arsenic content in flounder (mg/kg wet weight)(a)

Length category (mm)	1984	1985	1986	1987	1988
< 231	1.8 (131.0)	2.6 (73.4)	—	3.5 (33.9)	1.7 (106.2)
231-265	2.2 (58.6)	1.9 (72.5)	—	3.1 30.8)	1.1 (101.9)
266-300	4.4 (16.3)	3.2 (25.8)	1.9 (35.4)	3.8 (48.9)	1.9 (59.3)
301-335	5.6 22.2)	3.4 (33.9)	3.3 (35.4)	4.7 (81.3)	2.9 (30.5)
336-370	—	—	4.3 (13.0)	—	—
371-405	4.2 (6.6)	3.8 (16.5)	5.3 (47.7)	5.4 (70.6)	4.5 (68.0)
> 405	—	—	4.0 (35.8)	—	—
Total	3.7 (36.0)	3.0 (44.1)	3.8 (55.0)	4.1 (62.4)	2.4 (72.9)

(a) Coefficient of variation (%) in brackets the guidelines of the International Council for the Exploration of the Sea (ICES, 1983) the fish specimens were divided into five length categories with 35 and 40 mm ranges for flounder and cod respectively (tables 1 and 2). It was however not possible to maintain the same categories over the five years' period, due to changes in the composition of the catches. A total of 25 specimens of both fish species were assessed individually. One bulked sample of 100 cooked and peeled shrimps was analysed.

Figure 1 Relationship between length and average arsenic content in flounder



(.) Values of 1986 not taken into account for the calculation of the linear regression

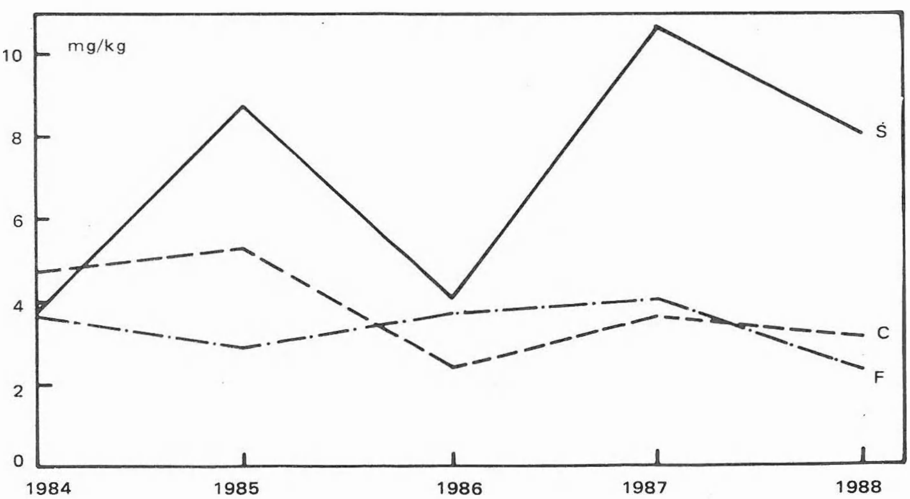
2.2. Determination of arsenic

One g of fish is weighed in a digestion bomb with Teflon liner (Parr 4746). After addition of 2 ml concentrated nitric acid, the bomb is placed in an oven and heated at 150° C for 1 1/2 hr. After cooling, 8 ml of bidistilled water is added. Determination is carried out by graphite furnace atomic absorption spectrometry (Varian SpectrAA 400 ZEEMAN). The furnace is equipped with a graphite tube with platform. A matrix modifier (Pd 0.04 % + Ni 0.1 %) is added. The ashing temperature is 1400° C, the atomizing temperature 2600° C. A standard curve is prepared using 3, 6 and 9 μl of a standard solution containing 50 μg/l arsenic (Van Hoeyweghen et al., 1985; Hoenig et al., 1986).

3. Results and discussion

The average arsenic concentrations in cod and flounder are reported in tables 1 and 2 respectively. In cod, arsenic levels did not appear to be influenced by the length (age) of the fish, whereas in flounder, the content clearly increased with length. Fig. 1 shows the regression between mean arsenic concentrations and length categories. The two classes 336-370 and > 405 mm (1986) were

Figure 2 Evolution of the average arsenic concentrations in shrimp, cod and flounder during the period 1984-1988



S: shrimp; C: cod; F: flounder

Table 3 **Arsenic levels in cod, flounder and shrimp from other areas (mg/kg wet weight)**

Species	Area	Mean	Min.-Max.	Reference
Cod	Newfoundland waters	0.8	0.4-1.5	Kennedy 1976
	NW-Atlantic	3.5 ± 1.7(a)	—	Zook et al. 1976
	Icelandic waters	0.8 ± 0.4(a)	—	id
	Norwegian waters	3.1	—	Anon. 1977
	Scottish waters	1.3	0.4-2.8	Falconer et al. 1983
	North Sea	4.3	1.0-8.2	Vos et al. 1986
Flounder	North Sea	3.7	0.45-6.8	Luten et al. 1983
Shrimp	North Sea	3.8	2.0-6.8	Vos et al. 1986

(a) Standard deviation

not taken into account for the calculation of the linear regression because only one figure was available. They are however shown in fig. 1. An increase in arsenic levels with age or weight of fish was also observed in the related species plaice (*Pleuronectes platessa*) (Shepherd et al., 1977).
The total average values of both fish species were quite similar, ranging form 2.5 to 5.4 mg/kg in cod and 2.4 to 4.1 mg/kg in flounder. No clear temporal trend could be observed (fig. 2).
The large variations in arsenic content should be stressed. This was also reported for other marine organisms and is probably due to variations in the arsenic concentrations of their preys (Zook et al., 1976; Pentreath, 1977; Michel, 1987). In general round fish, which feed primarily on small fish contain less arsenic than flat fish whose food consists of bottom living invertebrates, small crustaceans, molluscs and worms (Shepherd et al., 1977; Michel, 1987). This was not confirmed for cod during the present investigations but it should be remarked that cod caught off the Belgian coast are young fish (mainly 1-2 years old) which prey especially on benthic organisms, before leaving for deeper waters.
The arsenic levels in shrimp were higher than in the two fish species. It is known that crustaceans and molluscs generally contain higher amounts of arsenic than fish (Zook et al., 1976; Michel, 1987). Yearly variations also appeared to be more important than in cod and flounder. For this reason the apparant slight increase of the arsenic level over the five years' period was not statistically significant when a linear time trend (regression) was calculated. Arsenic levels reported in other areas are mentioned in table 3. Cod and flounder compare quite well with Dutch data from the North Sea. Concentrations in shrimp were somewhat higher.
On the other hand, high values (e.g. more than 50 mg/kg) which were recorded in some fishery products, especially flat fish, were not found during this study (Luten et al., 1982; Falconer et al., 1983).

Conclusions

No problems related to arsenic are likely to occur with respect to human consumption.
For the purpose of monitoring arsenic levels in the marine environment, shrimp with their higher concentration appear to be more appropriate than fish.

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Samenvatting

Arseengehalten in kabeljauw, bot en garnaal gevangen in Belgische kustwateren

Arseen komt in mariene organismen in sterkere koncentraties dan in landdieren voor. Meer dan 70 % bestaat echter uit arsenobetaine, dat niet toxisch blijkt te zijn. Anorganisch arseen daarentegen is zeer toxisch en carcinogeen.

In het kader van het Belgisch monitoringprogramma van kontaminanten werd de dosering van arseen in kabeljauw (*Gadus morhua*), bot (*Platichthys flesus*) en garnaal (*Crangon crangon*) vanaf 1984 uitgevoerd. De resultaten van de periode van 1984-1988 worden hier gerapporteerd.

Kabeljauw en bot werden in vijf lengtekategorieën ingedeeld. Van iedere soort werden 25 specimens individueel ontleed.

Voor garnaal betrof het een mengmonster van 100 gekookte en gepelde dieren.

In kabeljauw werd het arseengehalte niet door de lengte (leeftijd) van de vis beïnvloed. In bot echter steeg de koncentratie duidelijk met de lengte. De gemiddelde arseengehalten waren voor beide vissoorten vrij gelijk, variërend van 2,5 tot 5,4 mg/kg in kabeljauw en 2,4 tot 4,1 mg/kg in bot. Een duidelijke trend kon niet worden vastgesteld.

De individuele arseenkoncentraties schommelden sterk. Dit is vermoedelijk te wijten aan de variaties in de arseenniveau's van de prooien, de enige mogelijkheid voor de vissen om arseen op te nemen.

Het arseengehalte in garnalen (gemiddeld 4 tot 10 mg/kg) was hoger dan in de twee vissoorten, hetgeen door andere onderzoekers eveneens werd vastgesteld. De jaarlijkse schommelingen waren eveneens groter. Voor dit schaaldier werd evenmin een signifikante trend vastgesteld.

De gevonden arseenkoncentraties komen vrij goed met deze van de literatuur overeen. Hoge waarden zoals genoteerd in bepaalde

vissoorten, vooral platvissen, werden niet aangetroffen. In verband met de konsumptie van vis stellen de arseengehalten geen probleem. Wat betreft het monitoringprogramma van arseen in het mariene milieu, blijken garnalen met hun hoger gehalte beter geschikt dan vissen te zijn.

Résumé

Les taux d'arsénic dans le cabillaud, le flet et la crevette pêchés dans les eaux côtières belges

L'arsénic est présent dans les organismes marins à des taux nettement plus élevés que dans les animaux terrestres. Plus de 70 % cependant se compose d'arsénobétaïne, qui ne semble pas avoir d'effets toxiques. L'arsénic inorganique par contre est très toxique et cancérigène.

Dans le cadre du programme belge de surveillance des contaminants, le dosage de l'arsénic dans le cabillaud (*Gadus morhua*), le flet (*Platichthys flesus*) et la crevette (*Crangon crangon*) a été effectué à partir de 1984. Les résultats de la période 1984-1988 sont publiés ici. Le cabillaud et le flet étaient classés en cinq catégories basées sur la longueur; 25 spécimens de chaque espèce étaient analysés. Dans le cabillaud, le taux d'arsénic n'était pas influencé par la longueur (âge) du poisson. Dans le flet, par contre, la concentration augmentait avec la longueur.

Les taux moyens d'arsénic étaient assez semblables pour les deux espèces de poisson, variant de 2,5 à 5,4 mg/kg dans le cabillaud et de 2,4 à 4,1 mg/kg dans le flet. Aucune évolution dans le temps n'était constatée. Les concentrations individuelles d'arsénic variaient fortement. Ceci est probablement dû aux niveaux d'arsénic fluctuants dans les proies, seule possibilité pour les poissons d'ingérer de l'arsénic.

Le taux d'arsénic dans la crevette (4 à 10 mg/kg en moyenne) était plus élevé que dans les deux espèces de poissons, ce qui a également été noté par d'autres chercheurs. Les fluctuations annuelles étaient également plus fortes. Aucune évolution significative dans le temps n'était par ailleurs constatée dans ce crustacé.

Les concentrations d'arsénic trouvées concordent bien avec les données de la littérature. Des valeurs élevées, notées pour certaines espèces surtout de poissons plats n'ont pas été enregistrées dans la présente étude. Les taux d'arsénic ne posent aucun problême en ce qui concerne la consommation de poisson. Quant au programme de surveillance de l'arsénic dans le milieu marin, la crevette, avec son niveau plus élevé semble être un meilleur indicateur que les poissons.