Selenium assessment and its relation to mercury levels in fish, shrimp and mussels from Belgian continental shelf waters

Guns M.
Van Hoeyweghen P.

Ministerie van Landbouw
Bestuur voor Landbouwkundig Onderzoek
Instituut voor Scheikundig Onderzoek
Leuvensesteenweg 17
B - 3080 Tervuren

Vyncke W.
De Clerck R.

Ministerie van Landbouw
Bestuur voor Landbouwkundig Onderzoek
Centrum voor Landbouwkundig Onderzoek - Gent
Rijksstation voor Zeevisserij
Ankerstraat 1
B - 8400 Oostende

UDC-nr *639.3 : 597*

Keywords *Selenium, cod, flounder, shrimp, mussel*

Summary
Selenium and mercury were determined in cod (*Gadus morhua*), flounder (*Platichthys flesus*), spotted dogfish (*Scyliorhinus canicula*), brown shrimp (*Crangon crangon*) and blue mussel (*Mytilus edulis*) during the period 1985-1990.
For mercury, there was a positive correlation with length in cod and flounder. This was not so for selenium, indicating a different accumulation behaviour.
For none of the species analyzed a clear temporal trend neither for selenium nor for mercury could be noticed. The three fish species showed similar selenium concentrations (0.36-0.40 mg/kg on average). Mercury concentrations on the other hand were significantly different, averaging 0.11 mg/kg in cod, 0.22 mg/kg in flounder and 0.87 mg/kg in dogfish.
Selenium levels were higher in shrimp (0.85 mg/kg on average) than in fish. Mercury concentrations were low (0.10 mg/kg on average).
In mussels, the selenium content was length dependent. This was not the case for mercury. Average concentrations were 2.61 and 0.14 mg/kg dry weight for selenium and mercury respectively. Mussels from the middle and eastern parts of the coast showed significantly higher selenium concentrations (ca 30 %) suggesting the main input source to be the river Scheldt.
No significant correlation could be found between mercury and selenium concentrations neither in fish nor in shellfish.
Except in spotted dogfish, where 12 % of the ratios Se/Hg was below 1, selenium was stoichiometrically always in excess of mercury, indicating an effective antagonistic action against this toxic contaminant.
Selenium levels in the fish and shellfish species studied do not present a health hazard. On the contrary, they contribute to the supply of this essential dietary element.

1. Introduction

Selenium is an essential dietary micronutrient for humans and animals (WHO, 1986). Selenium deficiency, for example, may be associated with an increased incidence of certain forms of cancer (Diplock, 1984). It is also claimed to exert an antagonistic effect to mercury poisoning (Spallholz et al., 1981). At elevated levels however, selenium is toxic (Schroeder et al., 1971).

Selenium in marine animals seems to be predominantly associated with soluble proteins (up to 80 %) and not to be present as characterizable inorganic selenium compounds (Maher, 1985).

Selenium enters the atmosphere during the combustion of fossil fuels (Bertine et al., 1971) and is considered to be a potential marine pollutant (Fowler et al., 1976). Within the framework of the Belgian monitoring programme on trace contaminants, the analysis of selenium in the indicator species cod (*Gadus morhua*), flounder (*Platichthys flesus*), brown shrimp (*Crangon crangon*) and blue mussel (*Mytilus edulis*) was included from 1985 onwards. In 1987 an additional assessment on spotted dogfish (*Scyliorhinus canicula*) was carried out. This paper reports results for the period 1985-1990. For 1985, only data on flounder are available.

2. Material and methods

2.1. Samples

Cod, flounder and shrimp were caught in Belgian coastal waters (up to 12 miles) and dogfish in the northern part of the Belgian continental shelf (about 35 miles) by trawling in the period November-December.
A total of 25 specimens of the three fish species were assessed individually per year. The length of the fish varied from 30 to 90 cm for cod, 20 to 45 cm for flounder and 55 to 70 cm for dogfish.
One bulked sample of 100 cooked and peeled shrimp was analyzed per year.
Mussels were collected in September from three jetties along the coast situated at Nieuwpoort (west), Oostende (middle), and Blankenberge (east). They were divided into four length categories : 2.0-2.9 cm, 3.0-3.9 cm, 4.0-4.9 cm and 5.0-5.9 cm. From each category 40 to 50 specimens were taken. They were kept for 24 hrs in running sea water to eliminate impurities. The mussel flesh was removed from the shell, drained and homogenized. The average dry matter content was 26.0 % in 1986, 28.6 % in 1988, 27.3 % in 1989 and 25.9 % in 1990. All samples were kept at -28°C until analysis.

2.2. Analysis of selenium and mercury

Selenium was determined by atomic absorption spectrometry with graphite furnace, Zeeman background correction and Pd modifier.
Mineralization procedure : 1 g of fresh tissue is placed into a high pressure teflon lined acid digestion bomb, Parr 4746. After the addition of 2 ml HNO_3 the bomb is heated in the oven at 150°C for 1 hour. After cooling, clear solutions are diluted with water to 10 ml.
Mercury was determined by cold vapour atomic absorption spectrometry after digestion of the samples with sulphuric acid and hydrogen peroxide (De Clerck et al., 1988).

3. Results and discussion

The mean selenium and mercury concentrations per length interval in cod and flounder are reported in table 1. For mercury there was a positive and significant correlation with length, both in cod and flounder. This is the case for most fish species (GESAMP, 1988; ICES, 1989). Selenium concentrations on the other hand were not linked to the length of the fish, indicating a different accumulation behaviour. The apparent increase in cod was not statistically significant.
Table 2 shows the mean selenium and mercury contents per year in cod, flounder and shrimp. The molar Se/Hg ratios are also reported.
For none of the species analyzed a clear temporal trend neither for selenium nor for mercury could be noticed. Cod and flounder showed similar selenium concentrations. Mercury levels were about twice as high in flounder as in cod. This was also found during previous investigations (De Clerck et al., 1984).
This different accumulation pattern is also reflected in the Se/Hg ratio of flounder, which averaged less than half the value of cod. The selenium content of shrimp and the Se/Hg ratio were higher than in fish. It is known that shellfish contain more selenium than fish species (GESAMP, 1988).

Table 1 Average selenium and mercury concentrations in cod and flounder per length interval (mg/kg wet weight)

Species	Length interval (mm)	Se	Hg
Cod	301-380	0.34	0.09
	381-460	0.33	0.10
	461-540	0.42	0.10
	541-680	0.42	0.15
	681-760	0.44	0.20
	761-900	0.44	0.32
Flounder	201-230	0.38	0.15
	231-265	0.40	0.13
	266-300	0.38	0.19
	301-335	0.39	0.21
	336-370	0.32	0.26
	371-405	0.32	0.28
	406-450	0.36	0.28

Table 2 **Selenium and mercury concentrations in cod, flounder and shrimp (mg/kg wet weight) (*)**

Species	Parameter	1985	1986	1987	1988	1989	1990	Average
Cod	Se	–	0.26 (33.8)	0.36 (18.1)	0.51 (23.0)	0.35 (14.8)	0.42 (20.0)	0.38 (22.9)
	Hg	–	0.09 (33.0)	0.11 (39.8)	0.09 (28.5)	0.09 (37.8)	0.17 (64.9)	0.11 (42.7)
	Se/Hg	–	7.3	8.5	14.2	9.9	6.2	9.2
Flounder	Se	0.46 (4.5)	0.33 (42.1)	0.39 (27.8)	0.28 (47.1)	0.36 (30.4)	0.35 (36.9)	0.36 (37.1)
	Hg	0.23 (46.6)	0.19 (46.8)	0.21 (57.1)	0.18 (45.7)	0.27 (42.1)	0.22 (41.4)	0.22 (46.9)
	Se/Hg	4.9	4.4	4.7	3.9	3.4	4.0	4.2
Shrimp	Se	–	0.34	0.46	0.62	0.81	0.69	0.58 (32.1)
	Hg	–	0.08	0.13	0.14	0.09	0.08	0.10 (28.8)
	Se/Hg	–	10.8	9.0	11.2	22.9	21.9	15.2

(*) Coefficient of variation in brackets

In 1987, an additional set of analyses was made on spotted dogfish, a fish with a known higher concentration of mercury (Guns et al., 1985). The results were :
mercury : 0.87 mg/kg (range : 0.22-1.88 mg/kg)
selenium : 0.40 mg/kg (range : 0.24-0.60 mg/kg)
Se/Hg : 2.1 (range : 0.4-3.5)
Selenium was at the same level of cod and flounder resulting in a much lower Se/Hg ratio due to higher Hg-concentrations; 52 % of the values were below 1 (see further).
This would indicate that most fish species accumulate selenium to the same extent and confirms findings of other authors that the concentrations in the muscle tissue of marine fish appear to fall mostly in the range 0.2-1.0 mg/kg wet weight (GESAMP, 1988).
Table 3 summarizes selenium and mercury concentrations on dry weight basis in blue mussels together with the Se/Hg ratios. For comparative purposes, average data on wet weight basis were also included. Preliminary analysis of the data showed the selenium content to be length dependent. The average concentrations in mg/kg dry weight for the three sampling points were : 2.0-2.9 cm : 3.15; 3.0-3.9 cm : 2.68; 4.0-4.9 cm : 2.31 and 5.0-5.9 cm : 2.29. The correlation coefficient for n = 48 was - 0.471 and significant at the 99 % level. The regression equation was $y = 0.294 x + 3.78$ where y = selenium concentration and x = length of mussels.
An increase in the explanatory power of statistical analyses may thus be achieved by taking the length category 2.0-2.9 cm which shows the highest concentrations.
From table 3 it appears that there was no clear temporal trend neither for selenium nor for mercury.
There was however a spatial difference. Analysis of variance performed on the 2.0-2.9 cm category showed that the selenium levels at Nieuwpoort (western part of the Belgian coast) were significantly lower (ca 30 %) than at Oostende and Blankenberge (p = 95 %). There was no significant difference between the two latter locations. This strongly suggests that the main input source of selenium is the river Scheldt, Oostende and Blankenberge being

Table 3 Selenium and mercury concentrations in blue mussels (mg/kg dry weight) (a) (b)

Sampling point	Parameter	1986	1988	1989	1990	Average
Nieuwpoort	Se	1.31	2.56	2.53	2.43	2.21
	Hg	0.07	0.17	0.18	0.08	0.13
	Se/Hg	46.2	37.8	35.9	75.3	48.8
Oostende	Se	3.46	3.13	2.53	2.39	2.88
	Hg	0.09	0.18	0.17	0.16	0.15
	Se/Hg	97.6	44.4	37.6	37.7	54.3
Blankenberge	Se	2.41	3.31	3.00	2.24	2.74
	Hg	0.11	0.17	0.18	0.11	0.14
	Se/Hg	56.2	48.3	41.9	50.8	49.3
Total mean	Se	2.39 (44.9)	3.00 (20.4)	2.69 (16.9)	2.35 (13.4)	2.61
	Hg	0.09 (32.0)	0.17 (16.1)	0.18 (12.5)	0.12 (35.8)	0.14
	Se/Hg	67.5	43.5	38.6	50.6	50.0
Total mean (on wet weight)	Se	0.62	0.86	0.73	0.61	0.71
	Hg	0.02	0.05	0.05	0.03	0.04

(a) except last two lines
(b) coefficient of variation in brackets

situated in the gyratory mixing area of the estuary, which is not the case for Nieuwpoort (Nihoul, 1975).
For mercury, no spatial difference was noted. Selenium levels in South Wales also showed clearly more intersite variation than mercury (Micallef et al., 1989).
On a wet weight basis, selenium concentrations in mussels were higher than in fish and of about the same level as in brown shrimp. This confirms the findings that shellfish contain more selenium than fish muscle (GESAMP, 1988). Due to very low mercury contents the Se/Hg ratios were very high (50 on average) compared with fish and even shrimp.

Selenium concentrations reported in the present paper are in good agreement with levels assessed for the same species in other areas. Values of 0.22 to 0.32 and 0.17-0.39 mg/kg were assessed in cod from the Dutch coast (Vos et al., 1986; Akkerman, 1990) and the northeast Atlantic (Oehlenschläger, 1990) respectively.
Samples of flounder from Danish coastal waters showed an average of 0.25 mg/kg (Andersen, 1986). For mussels and shrimp from the Dutch coast selenium concentrations varied between 0.26-0.57 and 0.30-0.77 mg/kg wet weight respectively (Vos et al., 1986; Akkerman, 1990). In South Wales, mussels contained between 2.96 and 5.76

mg/kg dry weight selenium (Micallef et al., 1989).

No significant correlation could be found between the mercury and selenium concentrations in the muscles of the fish and shellfish species studied here. Our data confirm similar findings by other authors (Luten et al., 1980; Cappon et al., 1982; Barghigiani et al., 1991).

The observation that in fish muscle the concentrations of Hg and Se are independent of each other is not surprising since most of the Se is water soluble and does not form stable complexes with mercury which is mostly in the organic form (GESAMP, 1988). On the other hand, positive correlations have been observed in fish livers (Takeda et al., 1978; Luten et al., 1980). This suggests that also in marine organisms a Hg-Se relation as a protective effect is to be searched in the liver as for other detoxification mechanisms (Barghigiani et al., 1991).

Although the antagonistic action of selenium against mercury is complex and its mechanism only partially understood, the stoichiometric Se/Hg ratio seems to play a role. The antagonistic action of selenium is presumed to be effective when this ratio exceeds 1 (Vos et al., 1986; GESAMP, 1988). Except to some extent in spotted dogfish, where 52 % of the specimens were below 1, selenium was stoichiometrically always in excess of mercury. This was also noticed by other authors who reported similar ratios for different fish species (Luten et al., 1980; Cappon et al., 1981; Vos et al., 1986). Many fresh water fish on the other hand show Se/Hg ratios below 1 (Vos et al., 1986).

Seafood is considered to be a source of nutritionally desirable selenium levels. The World Health Organization recommends a minimum daily intake of 30 μg (WHO, 1986). The US Food and Nutrition Board (1980) has estimated that the safe and adequate range of dietary selenium intake is 50-200 μg per day. In Belgium, 125 μg per day is recommended (Anon., 1990). On the other hand, the threshold limit for adverse health effects is at least 700 μg Se per day. Even exceptionally excessive consumption of seafood with high selenium concentration does not bring intake into this region (WHO, 1986).

In Belgium the average daily seafood consumption is 25 g. With an average selenium concentration of 0.4 mg/kg, the daily intake is about 10 μg. Regular consumption of fish thus contributes to attain the desirable dietary selenium level.

Conclusion

Selenium levels in the representative fish and shellfish species cod, flounder, spotted dogfish, brown shrimp and blue mussel do not present a health hazard. On the contrary, they contribute to the supply of this essential dietary element.

Further monitoring of selenium in fishery products is not recommended.

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Samenvatting

Bepaling van selenium en zijn verhouding tot de kwikconcentraties in vis, garnaal en mosselen van de wateren van het Belgisch Continentaal Plat

Selenium en kwik werden in kabeljauw (*Gadus morhua*), bot (*Platichthys flesus*), hondshaai (*Scyliorhinus canicula*), garnaal (*Crangon crangon*) en mossel (*Mytilus edulis*) gedurende de periode 1985-90 bepaald.
Kwik vertoonde een positieve correlatie met de lengte van kabeljauw en bot. Dit was niet het geval voor selenium, hetgeen wijst op een verschillend accumulatiepatroon.
Bij geen enkele soort werd noch voor kwik noch voor selenium een duidelijke evolutie in de tijd waargenomen. De drie vissoorten vertoonden gelijklopende seleniumconcentraties (gemiddeld 0,36-0,40 mg/kg). De kwikgehalten daarentegen verschilden wezenlijk. met een gemiddelde van 0,11 mg/kg in kabeljauw, 0,22 mg/kg in bot en 0,87 mg/kg in hondshaai. De seleniumconcentraties in garnaal (gemiddeld 0,85 mg/kg) waren hoger dan in vis. De kwikgehalten waren laag (gemiddeld 0,10 mg/kg).
In mosselen bleek het seleniumgehalte van de lengte af te hangen. Dit was niet het geval voor kwik.
De gemiddelde concentraties bedroegen 2,61 en 0,14 mg/kg droog gewicht respectievelijk voor selenium en kwik.
Mosselen van de midden- en oostkust vertoonden significant hogere seleniumwaarden (ca 30 %) hetgeen er zou op wijzen dat de Schelde de voornaamste inputbron is.
Tussen de kwik- en seleniumgehalten van de onderzochte species werden geen significante correlaties gevonden. Uitgenomen in hondshaai, waar in 12 % van de gevallen de verhouding Se/Hg beneden 1 lag was er stoichiometrisch altijd een overmaat aan selenium t.o.v. kwik. Dit wijst op een effectieve antagonistische werking van selenium t.o.v. dit toxisch element. Seleniumconcentraties in de bestudeerde soorten stellen geen problemen voor de volksgezondheid. Integendeel, zij dragen bij tot de toevoer van dit voor het dieet essentieel micro-element.

Résumé

Dosage du sélénium et sa relation avec le mercure dans les poissons, crevettes et moules des eaux du plateau continental belge

Le sélénium et le mercure ont été dosés dans le cabillaud (*Gadus morhua*), le flet (*Platichthys flesus*), la roussette (*Scyliorhinus canicula*), la crevette grise (*Crangon crangon*) et la moule (*Mytilus edulis*) pendant la période 1985-1990.
Pour le mercure, une corrélation positive avec la longueur du cabillaud et du flet a été trouvée. Ceci n'était pas le cas pour le sélénium, ce qui indique un mode d'accumulation différent.
Avec aucune des espèces analysées, une évolution claire des concentrations de mercure et de sélénium dans le temps n'a pu être démontrée.
Les taux de sélénium dans les trois espèces de poisson étaient similaires (0,36 à 0,40 mg/kg en moyenne). Les concentrations de mercure, d'autre part, étaient nettement différentes avec en moyenne 0,11 mg/kg dans le cabillaud, 0,22 mg/kg dans le flet et 0,87 mg/kg dans la roussette. Les taux de sélénium dans la crevette (en moyenne 0,85 mg/kg) étaient plus élevés que dans les poissons. Les teneurs en mercure étaient faibles (0,10 mg/kg en moyenne).
Dans la moule, le taux de sélénium dépendait de la longueur. Ceci n'était pas le cas pour le mercure.
Les valeurs moyennes pour le sélénium et le mercure étaient respectivement de 2,61 et de 0,14 mg/kg (poids sec).
Les moules de la partie centrale et orientale de la côte contenaient nettement plus de sélénium (environ 30 %), ce qui suggère que la source principale des apports est l'Escaut.
Dans aucune des espèces étudiées, une corrélation significative entre le mercure et le sélénium n'a été constatée. A l'exception de la roussette où dans 12 % des cas le rapport Se/Hg se situait en dessous de 1, le sélénium était du point de vue stoechiométrique tou-

jours en excès par rapport au mercure. Ceci indique une action antagoniste effective du sélénium vis-à-vis de cet élément toxique. Les taux de sélénium dans les espèces marines étudiées ne présentent pas de problèmes pour la santé publique. Au contraire, ils contribuent à l'apport de cet oligo-élément essentiel du point de vue diététique.