Trace metals in squid *Illex argentinus*

Jerzy Falandysz

Veterinary Hygiene Research Station, ul. Kartuska 249, PL-80-125 Gdańsk, Poland

Spurenmetalle in Tintenfisch (Illex argentinus)

Zusammenfassung. Cadmium, Silber, Blei, Kupfer, Zink, Mangan, Eisen und Quecksilber wurden in den eßbaren und nichteßbaren Geweben von Tintenfisch *(Illex argentinus)*, gefangen 1986 in dem Continental Shelf of Argentina, bestimmt. Die Meßmethoden wurden für Cd, Ag, Pb, Cu, Zn, Mn und Fe durch Flammen-Atomabsorption und für Quecksilber durch Kaltdampf-Atomabsorption bestimmt. Die Mittelwerte waren für die eßbaren Teile, auf Naßgewicht (mg/kg) berechnet – für den hautlosen Mantel und Arme: 0,067 und 0,053 für Cd, bzw. 0,07 und 0,07 für Ag, 0,11 und 0,15 für Pb, 1,7 und 3,4 für Cu, 12 und 19 für Zn, 0,14 und 0,12 für Mn, 1,0 und 1,2 für Fe, und 0,012 für Hg (Mantel allein). Höhere Werte der Metalle wurden in Leber, Eingeweide, Haut, Augen und in der tintenähnlichen Flüssigkeit gefunden.

Summary. The determination of the cadmium, silver, lead, copper, zinc, manganese, iron and mercury levels is reported in edible and inedible tissues of the squid species *Illex argentinus*, caught in the region of the Continental Shelf of Argentina in 1986.

The methods of determination were flame AAS for Cd, Ag, Pb, Cu, Zn, Mn, and Fe and cold-vapour AAS for Hg. The mean values obtained were related to the wet weight (mg/kg). Th edible parts of the squid (skinless mantle and arms/crone) were 0.067 and 0.053 for Cd, 0.07 and 0.07 for Ag, 0.11 and 0.15 for Pb, 1.7 and 3.4 for Cu, 12 and 19 for Zn, 0.14 and 0.12 for Mn, 1.0 and 1.2 for Fe, and 0.012 for Hg (mantle only). Much higher levels of the metals investigated have been found in the liver, intestines, skin, eyes, arrow and the ink like liquid of the squid.

Introduction

Cephalopods (squid, octopus and sepias) are marine organisms which are important human food sources in some parts of the world. In Japan, for instance, a nation which traditionally consumes cephalopods the annual consumption of squid amounts to approximately 5 kg per capita.

In recent years, because of the significant decrease in the yields of traditional sea food due to overfishing and at a time when exclusive economic zones of coastal states cover most of the traditional fishing grounds, there has been an interest in some countries in the new or not previously used edible marine organisms like cephalopods or krill. Those parts of the squid's body which are unfit for human consumption can be used as a protein source in animal feeding.

The present study is solely concerned with the investigation of the levels of Cd, Ag, Pb, Cu, Zn, Mn, Fe and Hg in the edible and inedible tissues of the squid *Illex argentinus*.

Materials and methods

I. argentinus were caught during the commercial fishing period, in autumn 1986, in the waters of the south-western part of the Atlantic Ocean (region of the Continental Shelf of Argentina). Sample of deep-frozen (−25 °C) squid approx. 10 kg were delivered to the laboratory. The samples were carefully thawed and dissected, and the livers, in the frozen state were separated from the remaining tissues. The separation of the livers in the frozen state, has to be as fast as possible, in order to avoid leaking and thus contamination of the other tissues. A 5–20 g sample of the tissues was taken, when the squid was partly thawed and immediately weighed in a quartz vessel. Then samples were dried at 105 °C for 24 h and carefully ashed at 420 °C. Subsequently, concentrated nitric acid (≤ 0.5 ml) was added to make the ashed residue white. The resulting "white" residue was dissolved in a 1 *N*-solution of nitric acid. Ag, Mn and Fe were determined directly from the solution, Cu and Zn were determined after sample dilution and Cd and Pb were extracted with methyl isobutyl ketone. Each sample was analysed in duplicate using a Pye Unicam SP 9 atomic absorption spectrophotometer and air-acetylene flame.

For the determination of Hg a 5-g subsample of the skinless mantle was wet-decomposed with concentrated nitric acid, and the Hg content was determined by cold vapour atomic absorption using a UV Mercury Monitor LDC/Milton Roy.

Results and discussion

The contents of toxic metals such as Cd, Ag, Pb and Hg, and typical trace metals like Cu, Zn, Mn and Fe levels in the skinless mantle, arms/crone, liver, ink-like

Offprint requests to: J. Falandysz

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Table 1. Contents of cadmium, silver, lead, copper, zinc, manganese, iron, and mercury in the tissues of the squid species *Illex argentinus* (in mg/kg) on a wet-weight basis; arithmetic mean, standard deviation and range

Sample	*n*	Cadmium	Silver	Lead	Copper	Zinc	Manganese	Iron	Mercury
Skinless mantle	10	0.067±0.082 0.026–0.30	0.07±0.04 <0.07–0.16	0.11±0.05 0.06–0.22	1.7±0.7 1.1–3.2	12 ± 7 2.7–30	0.14±0.02 0.10–0.17	1.0 ±0.2 0.80–1.4	0.012±0.005 0.006–0.027
Arms/crone	10	0.053±0.020 0.033–4.5[a]	0.07±0.02 0.08–0.09	0.15±0.06 0.07–0.26	3.4±1.5 1.4–5.3	11 ± 3 5.0–14	0.12 ±0.05 0.089–0.24	1.2 ±0.8 0.65–3.2	n.a.
Liver	10	36±19 13–70	0.60±0.41 0.14–1.2	0.24±0.17 0.08–0.34	24 ± 25 6.8– 71	33±22 11–80	0.73±0.26 0.46–1.3	8.1± 3.7 5.3–17	n.a.
	9	38±19 16–74	0.30±0.18 0.08–0.57	0.60±0.88 0.1 –2.9	54 ± 50 11 –140	47±22 17–75	1.1 ±0.3 0.76–1.7	n.a.	n.a.
Ink-like liquid	3	2.2±0.4 1.9–2.7	3.6±0.2 3.4–3.7	34±20 12–52	36±14 20–44	150±130 23–280	6.0±1.6 4.4–7.5	n.a.	n.a.
Intestines[b]	10	0.38 ±0.50 0.076–1.7	0.10± 0.06 0.05– <0.50	0.30±0.36 0.07–1.3	21 ±10 5.7–56	27±14 12–62	0.87±0.24 0.51–1.1	3.2±1.7 1.8–7.4	n.a.
Skin	5 (10)[c]	0.15±0.08 0.10–0.29	0.18±0.09 <0.17–0.30	0.38±0.17 0.26–0.67	2.8 ±2.0 0.97–6.1	6.2±1.6 3.8–8.1	0.20±0.05 0.16–0.28	2.4±0.7 1.6–3.5	n.a.
Eyes	6	0.30 ±0.54 0.037–1.4	0.20±0.16 0.06–0.50	0.29±0.12 0.14–0.42	9.8± 6.6 2.1–18	10 ± 4 4.5–14	0.17 ±0.11 0.090–0.36	2.2 ±2.0 0.82–5.2	n.a.
Arrow	1 (10)	0.97	0.50	0.67	4.8	85	1.4	3.5	n.a.

[a] The value of 4.5 mg/kg was omitted
[b] Without liver
[c] Number of samples and number of squid in parentheses
n.a. Not analysed

liquid, intestines, skin, eyes and arrow of the squid species *I. argentinus* are given in Table 1. Some other squid species, e.g. *I. illecebrosus, Ommastrephes bartrami, Symplectoteuthis ovalaniensis*, and *Loligo ssp.* have been investigated for the content of trace metals [1–3]. However, we have not found available data for the species *i. argentinus.*

It is known that hemocyanin, a blood pigment of squid, contains copper. Easily absorbed Cd seems to be much more retained in liver of squid than other trace metals. In our study higher levels of Cu, Zn, Ag, Pb, and Mn, but not Cd, have been found in the ink-like liquid than in the liver (the ink-like liquid was taken from three specimens and analysed individually, Table 1). Because of the specific Cu requirement, and the increased co-absorption and accumulation of Cd, the muscle tissue of squid will potentially contain much higher levels of this toxic metal than, for example, the muscle tissue of marine fish.

The mean Cd content of the edible skinless mantle and arms/crone of the squid analysed ranged between 0.053 and 0.067 mg/kg (total range up to 0.30 mg/kg). Much higher levels of Cd had been reported in the mantle of the specie *I. illecebrosus*, taken from the north-western region of the Atlantic Ocean (from 0.040–0.92) [3], or from the Continental Shelf of Western Africa (0.42–1.1 mg/kg).[1]

The level of Cd in the liver and other inedible parts of squid is much higher than in the mantle or arms/crone (Table 1). A relatively high level of Cd (up to 200 mg/kg) were also found in the liver of other species of squid [1]. It was pointed out that improper sample preparation or storage can easily lead to the contamination of the edible parts of squid, with the trace metals contained in the liver or ink [1]. The contamined samples may be the cause of the high levels of Cd noted in the skinless mantle of squid as cited by other authors [3].

The values given for the levels of Ag in the edible parts (Table 1) are comparable with those found in the skinless mantle of *I. illecebrosus* (0.010–0.25 mg/kg) [3]. However, much higher levels have been found in the livers of other species (0.81–15 mg/kg) [1].

In the case of Pb, a particulary high level has been found in the ink-like liquid of the squid, e.g. 12–52 mg/kg, while in the edible parts the level was between 0.06 and 0.26 mg/kg (Table 1). Quite high levels of Pb were found in the skinless mantle of *I. illecebrosus* (0.15–2.0, and 0.41–0.52 respectively) while for unspecified squid the values were between 0.4 and 1.8 mg/kg [3–4].

The Hg content was found only in the skinless mantle and the noted values were quite low (0.006–0.027 mg/kg). Low level of Hg have also been reported in the mantle of *I. illecebrosus*. The mean value was 0.060 with a range from 0.0 to 0.40 mg/kg [2, 3].

Cu, Zn, Mu and Fe are essential trace elements which are generally found in much higher level in the liver of squid than in the muscle tissue [1]. The levels of Cu, Zn, Mn, and Fe found in the different tissues of *I. argentinus*, seemed to be typical (Table 1) and are comparable with those found in the tissues of other

[1] P. Szefer (personal communciation)

squid species, e.g. *I. illecebrosus, Symphectoteuthis ovalaniensis, Ommastrephes bartrami*, of *Loligo spp.*, and an unspecified squid [1–4].

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