Introduction

The German Mud Flats are located in the North Sea, surrounding the estuaries of the rivers Ems, Weser, Elbe and Eider. As the sludge of these rivers deposits in this area, it serves as a large natural sewage purification plant. Due to the predominant current, an additional load of pollutants carried by the river Rhine is discharged there [1]. Other sources of pollution are dump into the ocean and pollution by air. The mud flats are typically shallow and characterized by a very slow renewal of their water body taking about 36 months. The area of slowest water renewal is geographically congruent with the area of high discharge. The heavy metals cadmium (Cd), lead (Pb) and mercury (Hg), predominantly carried by the rivers and finally left in the sediments, are subject to cyclic rise and deposition in biological cycles in the shallow layers of the mud flats. Bacterial remobilisation takes place particularly with mercury.

Mainly due to industrialisation, the concentrations of the above-mentioned heavy metals in the upper layers of the sediment rose ten- (Pb) seven- (Cd) and eightfold (Hg) over the last 200 years. Along with this enrichment heavy metal accumulation in the animals of the habitat, e.g. shellfish, took

SUMMARY

Cadmium, lead and mercury contents of common shrimp (Crangon crangon L.) from the German Mud Flats in the North Sea were investigated by means of atomic absorption spectrometry. The heavy metal contents of the 48 samples were low. Thus, 0.037 ± 0.023 mg cadmium, 0.022 ± 0.012 mg lead and 0.023 ± 0.020 mg mercury (mean ± std) per kg wet weight were found. All of the samples contained lower amounts of the investigated elements than the official levels of concern of the Federal Institute for Health Protection of Consumers and Veterinary Medicine (BgVV) of 0.5 mg Pb/kg, 0.1 mg Cd/kg and 0.5 mg Hg/kg wet weight; the prevailing part of the samples showed significantly lower levels of contamination. Therefore, no risk for the consumer arises from the cadmium, lead and mercury contents of the shrimp caught in this environment. The main reasons for the overall low levels of contamination might be the short period of feeding of the shrimp and, in lead, an active mechanism of secretion. Over this, the heavy metal burden of the shrimp was different in the fishing seasons November resp. May. Compared to earlier investigations, samples recently taken showed reduced Cd and Hg burdens.

KEY-WORDS : heavy metals - residues - shrimp - risk assessment.

RÉSUMÉ

Les teneurs en plomb, mercure et cadmium des plages de vase du Nord de l’Allemagne (Wattenmeer) n’altèrent pas la qualité des crevettes communes. Par B. BRUNNER, H. MARX et A. STOLLE.

Les contenus en cadmium, plomb et mercure de la crevette commune (Crangon crangon L.) provenant des plages de vase allemandes en mer du Nord ont été analysés en spectrométrie d’absorption atomique. Les contenus en métaux lourds de 48 échantillons étaient bas. Ainsi, des teneurs de 0.037 ± 0.023 mg de cadmium, 0.022 ± 0.012 mg de plomb et 0.023 ± 0.020 mg de mercure (moyenne ± écart-type) par kg de poids vif ont été trouvées. Tous les échantillons contenaient des niveaux inférieurs aux limites fixées par l’Institut Fédéral de Protection de la Santé des Consommateurs et de Médecine Vétérinaire (BgVV) c’est-à-dire 0,5 mg Pb/kg, 0,1 mg Cd/kg et 0,5 mg Hg/kg de poids vif ; ces valeurs indiquent que les teneurs en cadmium, plomb et mercure trouvées dans les crevettes capturées dans cet environnement ne présentent pas de risque pour le consommateur. La raison principale de ces niveaux de contamination globalement faibles pourrait être due à la courte période de prise de nourriture des crevettes et, pour le plomb, à un mécanisme actif d’élimination. Par ailleurs, le niveau résiduel en métaux lourds est différent selon les périodes de pêche (Novembre par rapport à Mai). Les échantillons prélevés dans le cadre de cette étude ont des teneurs en cadmium et mercure réduite en comparaison des études plus anciennes.

MOTS-CLÉS : métaux lourds - résidus - crevette - évaluation du risque.
place [2]. Adequate measurements to protect this ecosystem against further pollution were disapproved by some countries bordering the North Sea for a long time 1.

Facing this situation, the development of the lead, cadmium and mercury burden of North Sea Shrimp (*Crangon crangon*) from the mud flats used for human consumption is under question.

**Material**

48 samples of North Sea Shrimp (English: common shrimp; German: Krabben, Granat, Sandgarnelen; *Crangon crangon* L. 1758) hauled in equal shares in 1995, 1996 and 2001 by different cutters in the mud flats north of Wremen harbour, situated in the Weser estuary, were investigated for their lead, cadmium and mercury content at the Institute for Hygiene and Technology of Food of Animal Origin (Munich, Germany). The samples were obtained during two hauling seasons: two thirds of the shrimp were caught in November, one third in May. The shrimp were fished in ground nets with small crab cutters, presorted and cooked in kettles. After cooking they were cooled, peeled, and packed in plastic bags, 500 g per sample, on board of the ships. After landing, the chilled samples were sent to our institute and stored frozen (-18 °C) until they were analysed.

**Methods**

After thawing the samples were ground in a soft tissue blender equipped with a plastic container and titan blades. The samples were digested with nitric acid under pressure at 140°C for 10 hours. Analysis was performed according to the following scheme. All measurements were carried out by atomic absorption spectroscopy. Cadmium and lead contents were determined via flameless atomic absorption spectroscopy with a graphite tube atomizer with L’vov platforms. Total mercury content was analysed against aqueous standards using cold vapour atomic absorption with amalgamation and revolatilisation by heating in a batch process. Tin chloride solution (10 %) was used as reducing agent. Results were verified with reference material DOLT-2 (Pb, Cd, dogfish liver, certified reference materials for trace metals, National Research Council, Ottawa, Canada) and Peach Leaves (Hg, National Institute of Standards and Technology NIST, Gaithersburg, Maryland, USA). The limits of determination of the analytical system used were 5 µg/kg in lead, 2 µg/kg in mercury and 1 µg/kg in cadmium. Data analysis was performed with SPSS software (SPSS, Chicago, USA). The T-test for independent samples was used to determine significant differences.

**Results and discussion**

1) **LEAD**

The investigated samples showed a mean lead contamination of 0.022 mg/kg wet weight (Median: 0.020 mg/kg). The lowest value detected was below the limit of determination, the highest 0.059 mg/kg. Using the official level of concern of the «Zentrale Erfassungs- und Bewertungsstelle für Umweltchemikalien» (ZEBS) [3] of 0.5 mg Pb/kg wet

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*Figure 1.* Heavy metal content of shrimp compared to the German levels of concern.  
*Figure 1.* Teneur des crevettes en métaux lourds par rapport au valeurs seuils allemandes.
weight for shellfish as reference value, one can see that the highest value detected (0.059 mg/kg) makes up less than 12% of this guideline (Fig. 1). Annual publishing of this national guideline was terminated in December 2000 favoring a European solution based on current data [4]. This European regulation is still to come. Investigations from 1983 [5] on the trace element content of *Crangon crangon* revealed an average lead burden of 0.052 mg/kg in raw muscle tissue (n = 16), which is slightly above the present values. The low overall contamination with lead might be attributed to the ability of decapodes to actively release both copper and lead into the environment. This phenomenon was described for giant tiger prawn, *Penaeus monodon*, a species that is widespread in the Indopacific Ocean [6]. The principle of this mechanism is apocrine secretion of lead into the thoracic extensions of the antennal gland followed by excretion with the urine. On the other hand, lead and mercury contents of prawns higher than the recommended values are also reported [7].

2) CADMIUM

An average cadmium burden of 0.037 mg/kg wet weight (Median : 0.024 mg/kg) was found in the samples. The lowest value detected was 0.014 mg Cd/kg wet weight. The samples with the highest contamination contained 0.091 mg Cd/kg, 0.088 mg Cd/kg and 0.077 mg Cd/kg wet weight. They were all from the autumn haul in 1995. The research already cited [4] claims for muscle tissue of North Sea shrimp a cadmium content within the same range, but somewhat lower (0.015 mg/kg).

The mean cadmium concentration in the edible parts of commercially caught marine fish generally seems to be lower than in crustaceans. In this type of material, cadmium contents below the limits of detection of 0.002 mg/kg [8] and 0.004 mg/kg [9] respectively, and mean values below 0.008 mg Cd/kg wet weight mostly were found [10, 11, 12, 13, 14]. In relation to the ZEBS-values for shellfish, 0.1 mg Cd/kg and 0.5 mg Pb/kg [3], the investigated common shrimp from the North Sea showed higher cadmium than lead values (Fig. 1). A possible explanation according to literature [15, 16] is cadmium accumulation taking place in common North Sea Shrimp as well as in fresh water prawns. Mechanisms of regulation similar to those described for lead and copper were not found.

In comparison to squid (molluscan shellfish), known as accumulator organism for cadmium and containing up to mean levels of 1.72 mg Cd/kg and 0.32 mg Cd per kg wet weight in the edible parts [17, 18], the content of the investigated shrimp samples is significantly lower. A very short period of active food consumption in connection with a dramatic growth rate seems to be a reason for the low cadmium burden of this species. Sufficient food supply provided, the shrimp grow to harvest size within several weeks. Even in a highly contaminated habitat, the cadmium intake via plankton, algae and sludge is not sufficient for the accumulation of relevant levels of cadmium in the tissues.

3) MERCURY

The North sea shrimp were contaminated with a mean level of 0.024 mg Hg per kg wet weight and a maximum of 0.076 mg/kg. The latter value makes up 15.2 % of the ZEBS index for shellfish (0.5 mg Hg/kg, Fig. 1). The mean level was only slightly above limit of determination. WHO surveys (Alexandrian coastline ; Belgium ; Netherlands ; [19] indicate that all types of shellfish generally show low levels of mercury contamination (Table I).

According to this source, mean values of mercury contamination found in shrimp are below 0.2 mg/kg. In contrast to this, the mercury burden of seafish is partly on a high level (shark : 1.8 mg/kg ; tuna and swordfish : 1.5 mg/kg).

Compared to data on the contamination of shrimp from other habitats (Table I), the investigated samples showed low values of contamination. This fact might also be due to the short period of food consumption and growth prior to the catch of the North Sea Shrimp.

<table>
<thead>
<tr>
<th>Area/Country</th>
<th>Name/Product</th>
<th>Hg [mg/kg] mean / min. - max.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgian coastline</td>
<td>shrimp</td>
<td>0.10 / n.g.</td>
<td>[20]</td>
</tr>
<tr>
<td>Alexandrian coastline</td>
<td>deep water shrimp</td>
<td>n.g. / 0.15 - 1.65</td>
<td>[18]</td>
</tr>
<tr>
<td>Persian Gulf</td>
<td>shrimp</td>
<td>0.24 / 0.08 - 0.88</td>
<td>[21]</td>
</tr>
<tr>
<td>USA, Mexico, Libya, India, Ecuador</td>
<td>shrimp</td>
<td>n.g. / 0.00 - 0.47</td>
<td>[22]</td>
</tr>
<tr>
<td>Malaysia</td>
<td>canned shrimp</td>
<td>0.13 / n.g.</td>
<td>[23]</td>
</tr>
<tr>
<td>Belgium</td>
<td>cooked brown shrimp</td>
<td>0.15 / n.g.</td>
<td>[19]</td>
</tr>
<tr>
<td>Netherlands</td>
<td>fresh common shrimp</td>
<td>0.05 / n.g.</td>
<td>[19]</td>
</tr>
<tr>
<td>Calcutta</td>
<td>prawn</td>
<td>n.g. / 0.00-0.042</td>
<td>[24]</td>
</tr>
</tbody>
</table>


\(^n.g. = \text{not given}\)

Table I. — Mercury burden of shrimp.

*Tableau I. — Teneur en mercure des crevettes.*
4) FOOD PROCESSING

Boiling or blanching of shellfish, two common methods for preparing seafood can reduce the mercury burden by up to 27% of the initial contamination [25]. The investigated samples were already subjected to this food processing step on board of the cutters. So it can be assumed that the initial mercury contamination was reduced by the above-mentioned treatment. This fact only partially explains the low overall mercury contamination of the investigated common shrimp.

5) INFLUENCE OF THE PERIOD OF THE CATCH

Shrimp from two subsequent fishing periods, November 1995 and May 1996 were investigated. In lead and cadmium, a comparison of these two periods always yielded higher mean values in the more aged shrimp caught in November. (Table II).

The difference between the two groups subsequently hauled groups in 1995 and 1996 was highly significant in the case of lead and cadmium (level of significance : 0.01) and significant (level : 0.05) concerning mercury. In addition to the length of the feeding period, the age of the shrimp seemed to play some role in the levels of heavy metal contamination. In contrast to this, [4] could not detect any seasonal difference in cadmium contamination of North Sea Shrimp. According to the research cited, lead values of shrimp caught in spring were even higher than those from autumn hauls.

6) LONG TERM CONSIDERATIONS

Comparing autumn hauls only, one can see similar lead and somewhat lower mercury and cadmium values in recently fished shrimp. This is only a small aspect in a complex system, but it might indicate that heavy metal contamination of food from this ecosystem is already past peak levels.

Acknowledgements

The authors are greatly indebted to Dr. K. PRIEBE, LmTVet Bremerhaven, for his help in providing the sample material.

Table II. Influence of the age of the shrimp resp. the season of the catch.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Season</th>
<th>n</th>
<th>mean [mg/kg]</th>
<th>SD [mg/kg]</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>May 96</td>
<td>16</td>
<td>0.013</td>
<td>0.0104</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Nov. 95</td>
<td>16</td>
<td>0.024</td>
<td>0.0077</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>May 96</td>
<td>16</td>
<td>0.019</td>
<td>0.0027</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td></td>
<td>Nov. 95</td>
<td>16</td>
<td>0.067</td>
<td>0.0127</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>May 96</td>
<td>16</td>
<td>0.025</td>
<td>0.0039</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>Nov. 95</td>
<td>16</td>
<td>0.040</td>
<td>0.0199</td>
<td></td>
</tr>
</tbody>
</table>

1 Students t-test for independent samples

Literature cited
