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Concentrations of nickel (Ni) in some coastal Baltic fishes

Heinz-Rudolf Voigt

In order to reveal the present situation regarding nickel (Ni) in the coastal Baltic Sea environment, four suitable fish species for coastal environment monitoring; Baltic herring, smelt, eelpout, flounder, from various parts of the Baltic Sea, were chosen. Ni was analyzed from various tissues and organs (mainly muscle tissue and liver). In some cases also the corresponding bottom sediment, was analyzed. With few exceptions the concentrations of Ni in the liver in most cases by far, exceeded the concentrations in muscle tissue, as in other observed organs (gonads). The mean values (mg kg$^{-1}$ d wt) for concentrations of Ni in the liver were: 0.12–1.2, e.g. Baltic herring; 0.12–0.20, smelt: 0.14–0.85, eelpout 0.39–1.2, flounder: 0.12–0.76. High concentrations in both liver and muscle tissue were recorded from fishes sampled from areas regarded contaminated, e.g. Tvärminne and the river mouth area of Kokemäenjoki/Kumoälv, respectively, underlining the suitability of these fish species, for environmental monitoring also regarding Ni. The lack of recommendations regarding Ni in fish as food for human consumption, deteriorate the interpretation of the obtained results.

Introduction

Investigations regarding concentrations of nickel (Ni) in the marine environment and biota of the Baltic Sea are very scarce (e.g. Szefer 2002), despite the constant inflow of the metal into the sea from numerous industrial plant, and greater urban centers, located within the drainage area of the Baltic Sea (e.g. Gupta 1972, Rühling et al. 1992, HELCOM 1993, Buse et al. 2003). Additionally there is a regular outfall of Ni from the atmosphere (e.g. HELCOM 1991, 1998, Rühling et al. 1996, Melanen et al. 1999, Jalkanen 2000), all contributing to a constant contamination by Ni of the Baltic Sea and its biota.

Although low levels of Ni, in some cases, are considered essential to maintain health in animals, elevated exposure may produce toxic effects (NRCC 1981) causing e.g. deformity, as teratogenicity in frogs (Hopfer et al. 1991), allergic reactions (Rühling et al. 1992), mutagenity (Fletcher et al. 1994), and even cancer, in man (Aitio & Tomatis 1991). Thus Ni and its compounds, generally are regarded hazardous (ATSDR 2005), wherefore the contamination by Ni in the marine environment of the Baltic Sea, is of interest when evaluating the quality of fish as food for human consumption and the usage of fishes for environmental monitoring, besides evaluating the state of the environment of this great sensitive brackish water reservoir of estuarine character.

Material and methods

Based on previous experience on coastal environmental monitoring concerning heavy metals (especially Hg and Cd), the four fish species Baltic herring, *Clupea harengus membras* L., smelt, *Osmerus eperlanus* L., eelpout, *Zoarces viviparus* L.,
and flounder *Platichthys flesus* L. (Voigt 2004a), were chosen for this investigation. Besides the four main sampling areas: Archipelago Sea–Åland (AS-A); Peimari/Pernar (AS) and Lemland–Näto (Å), Hanko/Hangö-peninsula (H-Tv); Tvärminne, Bay of Muuga (MB), Kieler Förde (KF); Laboe and Schventing, additional sampling was made off the river mouth area of Koke-
mänsjoki/Kumo River (KR), W-Estonia (M-VV); Matsalu and Väike Väin, Gulf of Riga (GR-R); Roja (Fig. 1.). Of the seven sampling areas chosen, only two are regarded unpolluted by heavy metals: Archipelago Sea–Åland (AS-A), W-Estonia (M-VV), Grimás et al. 1991, Astok & Suursaar 1991, meanwhile the other five: Kokemänsjoki/Kumo river mouth area (KR), Hanko/ Hangö-peninsula (H-Tv), Muuga (MB), Gulf of Riga (GR-R), Kieler Förde (KF) may be considered more or less contaminated by heavy metals (Luotamo & Luotamo 1977, Häkkilä 1985, Enckell-Sarkola et al. 1989, Astok & Suursaar 1991, Lahermo et al. 1996, Leivuori et al. 2000, EEIC 2001, HELCOM 2002, 2003, Voigt 2003a, Pohl & al. 2005). In addition to fish, bottom sediments were collected from two of the sampling areas: the open water body Tvärminne Storfjord (N 59° 51.3 18' 16.9), off the iron and steel plant at Koverhar, Hanko/ Hangö peninsula, at the inlet from the northern Baltic Proper into the Gulf of Finland (H-Tv), and the coastal waters off the biological field station of the Societas pro Fauna et Flora Fennica at Näto, Åland Islands; Näto Biological Station (N 60° 02.9 E 19° 58.7), bordering to the Baltic Proper (Å), respectively, were analyzed. The former station is characterized by the constant outflow of various heavy metals from the steel plant (Luotamo & Luotamo 1977, Lahermo et al. 1996) while the latter has been assumed notably less polluted, at least regarding heavy metals (Grimás et al. 1991, Voigt 1991, 2002). The sampling stations around the Baltic Sea are shown in Fig. 1.

The fishes were caught either by trawling, cages, or by gillnets, and the sediment samples were taken, either by a box corer sampler (Andersin & Sandler 1986), from Tvärminne (H-Tv), or by an Ekman-Birge corer sampler, from Lemland–Näto (Å), respectively.

Prior to analyses of muscle tissue and liver, and in some cases also gonads, the fishes were measured, weighed and gutted, where after they were stored in –20 °C along with the dried sediment samples. After treatment by acids (HNO₃ and H₂SO₄) the samples were analyzed by the AAS-technique; Varian-SpectrAA 400, equipped with a graphite furnace; GTA-96, ETAAS (Voigt 2007a, b). With the exception of the herring samples from Matsaltr–Väike Väin (M-VV), and the smelt samples from the Kieler Förde (KF), which both samples were analyzed pooled, all the other fishes were analyzed individually.

All samples were analyzed in duplicate, and the accuracy was assessed by using blanks (5 per each sequence of 40 samples), and reference materials; NIST 8704 Buffalo River sediment (NIST 2000), and CRM-422 cod muscle (Quevauviller et al. 1993), respectively. All results are expressed in Ni mg kg⁻¹ d wt (dry weight).

### Results

The certified and obtained values for the reference materials were: Ni certified 42.9±3.7, and Ni obtained 40.0±1.5, and 41.7±2.7 mg kg⁻¹ d wt (dry weight), respectively.
Table 1. Mean concentrations of Ni (mg kg\(^{-1}\) d wt ± SD), in muscle tissue (M), of Baltic herring (Clupea harengus membras), smelt (Osmerus eperlanus L.), eelpout (Zoarces viviparus L.), flounder (Platichthys flesus L.), from coastal waters around the Baltic Sea.

<table>
<thead>
<tr>
<th>Sampling station</th>
<th>Clupea harengus M (N)</th>
<th>Osmerus eperlanus M (N)</th>
<th>Zoarces viviparus M (N)</th>
<th>Platichthys flesus M (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS-Å</td>
<td>0.10±0.03 (12)</td>
<td>0.06±0.02 (17)</td>
<td>0.30±0.24 (12)</td>
<td>0.55±1.66 (29)</td>
</tr>
<tr>
<td>H-Två</td>
<td>0.14±0.06 (10)</td>
<td>0.25±0.19 (14)</td>
<td>0.28±0.33 (23)</td>
<td>0.26±0.21 (23)</td>
</tr>
<tr>
<td>MB</td>
<td>-</td>
<td>-</td>
<td>0.15±0.11 (10)</td>
<td>-</td>
</tr>
<tr>
<td>KR</td>
<td>-</td>
<td>0.15 (10)</td>
<td>0.27±0.27 (40)</td>
<td>0.12±0.12 (28)</td>
</tr>
<tr>
<td>M-VV</td>
<td>0.10 (10)</td>
<td>0.19±0.09 (17)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GR-R</td>
<td>-</td>
<td>-</td>
<td>0.05±0.01 (16)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Mean concentrations of Ni (mg kg\(^{-1}\) d wt±SD), in liver (L), of Baltic herring (Clupea harengus membras), smelt (Osmerus eperlanus L.), eelpout (Zoarces viviparus L.), flounder (Platichthys flesus L.), from coastal waters around the Baltic Sea.

<table>
<thead>
<tr>
<th>Sampling station</th>
<th>Clupea harengus L (N)</th>
<th>Osmerus eperlanus L (N)</th>
<th>Zoarces viviparus L (N)</th>
<th>Platichthys flesus L (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS-Å</td>
<td>0.12±0.05 (10)</td>
<td>0.14±0.20 (17)</td>
<td>-</td>
<td>0.56±1.07 (29)</td>
</tr>
<tr>
<td>H-Två</td>
<td>0.20±0.50 (6)</td>
<td>0.60±0.65 (14)</td>
<td>1.20±1.16 (17)</td>
<td>0.76±0.74 (23)</td>
</tr>
<tr>
<td>MB</td>
<td>-</td>
<td>-</td>
<td>0.66±0.27 (10)</td>
<td>-</td>
</tr>
<tr>
<td>KR</td>
<td>-</td>
<td>0.85 (10)</td>
<td>0.41±0.83 (36)</td>
<td>0.12±0.11 (28)</td>
</tr>
<tr>
<td>M-VV</td>
<td>0.20 (10)</td>
<td>0.25±0.10 (17)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GR-R</td>
<td>-</td>
<td>-</td>
<td>0.39±0.46 (15)</td>
<td>-</td>
</tr>
</tbody>
</table>

The mean concentrations of Ni in muscle tissue and liver (mg kg\(^{-1}\) d wt) are presented in Tables 1 and 2.

In all cases the concentrations of Ni in the muscle tissue of the fishes, are exceeded by the corresponding concentrations in liver, as observed previously also for several other heavy metals (e.g. Hofer and Lackner 1995, Voigt 1999). This difference however, was diminutive and insignificant for herring from the Archipelago Sea (AS), smelt from both Kokemäenjoki/Kumo (KR) and Matsalu–Väike Vään areas (M-VV), as for flounder from Lemland–Nätö (Å), and Kieler Förde (KF), as well.

### Baltic herring and smelt

The concentrations of Ni in herring were modest and the mean values varied between 0.10–0.20 mg kg\(^{-1}\) d wt (muscle) and 0.12–0.20 (liver), meanwhile for smelt the variations were considerably greater: 0.06–0.30 mg kg\(^{-1}\) d wt (muscle) and 0.14–0.85 mg kg\(^{-1}\) d wt (liver), respectively. The lowest mean concentrations of Ni, in both muscle tissue and liver, were found in herring and smelt from the Archipelago Sea (AS) and the West-Estonian coastal waters (M-VV). With exception for the pooled sample from Kieler Förde (liver of smelt), the highest mean concentrations of Ni, in both muscle tissue and liver, were calculated for herring from Tvärminne, and for smelts from the river mouth area of Kokemäenjoki/Kumoälav and Tvärminne. With exception of the Archipelago Sea, smelt from the other sampling areas were more contaminated than herring, though without statistical significance (Wilcoxon rank sum test).

Additionally the calculated mean concentrations of Ni (mg kg\(^{-1}\) d wt) in the gonads of smelt were; 0.14 ± 0.06 (M-VV), 0.08 ± 0.05 (KR), 0.06 ± 0.03 (AS). The mean values for Ni in both muscle tissue and the gonads were of the same order of magnitude for smelt from the Archipelago Sea, in contrast to the situation in western Estonia and the
river mouth area of Kokemäenjoki/Kumoäläv, where the mean concentrations of Ni in muscle tissue exceeded the calculated mean values of the gonads.

**Eelpout and flounder**

The mean concentration of Ni in muscle tissue of eelpout was lower than for flounder varying between 0.05–0.30 mg kg$^{-1}$ d wt, in contrast to 0.12–0.55 mg kg$^{-1}$ d wt, for flounder. In liver, however, higher mean concentrations of Ni were calculated for eelpout, varying between 0.39–1.2 mg kg$^{-1}$ d wt, than for flounder, varying between 0.12–0.76 mg kg$^{-1}$ d wt. The lowest mean concentrations of Ni in both muscle tissue and in liver, were calculated for eelpouts from the Gulf of Riga, meanwhile the lowest corresponding means for flounder were calculated from the Kieler Förde. The highest mean values for concentrations of Ni in muscle tissue of eelpouts were calculated from the Archipelago Sea, Tvärminne and Kieler Förde, all of the same order of magnitude. In liver the highest corresponding mean was calculated from eelpouts from Tvärminne. The highest mean concentration of Ni in muscle tissue of flounder was calculated from Lemland–Näto, while the highest mean concentration of Ni in liver, however, was calculated for flounder from Tvärminne.

The mean concentrations of Ni (mg kg$^{-1}$ d wt) in the gonads of eelpout were; 0.52 ± 0.71 (KF), 0.29 ± 0.33 (MB), and of flounder; 0.41 ± 0.65 (Å), 0.35 ± 0.19 (H-Tv), 0.11 ± 0.12 (KF), respectively. The mean concentrations of Ni in the gonads of eelpout from both Muuga Bay and the Kieler Förde exceeded the corresponding concentrations in muscle tissue at both sampling areas, as for the gonads of flounder from Tvärminne. In the flounder from Kieler Förde the mean concentrations of Ni in the gonads and the muscle tissue were of the same order of magnitude. For flounder from Lemland–Näto, the mean concentration of Ni in muscle tissue exceeded the concentration in the gonads.

**Sediments**

In the bottom sediments from Tvärminne Stor-fjärd, the mean concentration of Ni was calculated to 35 mg kg$^{-1}$ d wt (SD 7.1), in contrast to the mean 20.5 mg kg$^{-1}$ d wt (SD 7.8), calculated for the sediments off the Biological station at Näto.

**Discussion**

**Herring and smelt**

The differences in both available food, and especially in food habits, between herring and smelt, may explain the observed differences in Ni contamination, as heavy metals mainly concentrate in fish through their food (e.g. Reichenbach-Klinke 1978, Hofer & Lackner 1995). Pelagic herring mainly feed on zooplankton (e.g. Flinkman et al. 1992) when migrating over vast areas (Aro 1989), in contrast to the mainly stationary pelagic smelt, feeding on bottom organisms, although both species also compete on the same food, as vertically diurnally migrating opossum-shrimps (Mysis sp.), when dwelling in near shore coastal waters (e.g. Rajasila 1992, Voigt 2004a).

The comparatively low concentrations of Ni, in both muscle tissue and liver, of both herring and smelt from the Archipelago Sea, may be explained by the fact, that this area is not known to be polluted by heavy metals (Grimäs et al. 1991), in contrast to Tvärminne, where the effects of the constant metal emissions from the iron and steel plant at Koverhar may be observed also in the marine biota of the area (e.g. Luotamo & Luotamo 1979, Voigt 2003a, 2007b, c). The equally lower concentrations of Ni in smelts from both Matsalu and Väike Väin may support the assumption, as neither Estonian locality is known for any metal pollution (Astok & Suursaar 1991), in contrast to the river-mouth area of Kokemäenjoki/Kumoäläv (Enckell-Sarkola et al. 1989, Voigt 2004b) and the inner part of the Kieler Förde (e.g. Theede et al. 1979, Pohl et al. 2005).

**Eelpout and flounder**

Though, both species are abundant in same coastal areas in the Baltic Sea, and though they feed
mainly on benthic organisms, as mussels, crustaceans and worms, information about food competition between eelpout and flounder is scarce. Around Åland, in the Archipelago Sea (AS-Å) and at Tvärminne (H-Tv), the mussels *Macoma balthica* L., and *Mytilus edulis* L., are included in the diet of both species (e.g. Voigt 1997, 2001), while eelpout from the Gulf of Riga, mainly prefer crustaceans, as *Monoporeia* sp, and *Saduria entomon* L. (Urtans 1990). At Muuga Bay (MB) crustaceans also are included in the diet of eelpout (authors unpublished data), while in the Kieler Förde (KF), both eelpout and flounder prefer worms (*Polychaeta*), though also mussels are included in their diet (Arnitz 1978, and present authors unpublished data). Corresponding recent data from both western Estonian sampling areas (M-VV); Matlasu and Väike Väin, are lacking.

The comparatively high concentrations of Ni in muscle tissue, in the liver and in the gonads of flounder from Lemland-Nitto (Å) are confusing, bearing in mind that the whole archipelago of Åland is regarded unpolluted and even recommended, as reference area for coastal monitoring of the northern Baltic Sea (Leppäkoski et al. 1986). Similar, unexpected high concentrations of the toxic heavy metal cadmium (Cd), have however, previously been analyzed from flounder from the same area (Voigt 2002). The source for the presence of both Cd and Ni in this area is still not known, and therefore regarded local, as there are no emissions worth mentioning, of neither metal into the environment on the Åland Islands. Thus the present sample of flounder from Lemland-Nitto (Å) may be excluded in the further discussion, regarding polluted and non-polluted areas (AS-Å), leaving only Peimari/Pernarn in the Archipelago Sea (AS), in this respect unpolluted. The comparatively high concentrations of Ni in muscle and liver of both eelpout, and flounder from Tvärminne (H-Tv) may, as for smelt, be explained by the activity of the iron- and steel-plant in Koverhar. The construction work of a new port for the city of Tallinn at Muuga (EEIC 2001) may contribute to an explanation for the intermediate concentrations of Ni, that where calculated from the liver of the eelpouts from the same region. No doubt the high concentrations of Ni in muscle tissue of flounder from the river-mouth area of Kokemäenjoki/Kumoölvi (KR) originate from the polluting industry in the region (Häkkilä 1985, Enckell-Sarkola et al. 1989).

At Roja (GR-R), the mean concentrations of Ni in both muscle tissue and in liver of the eelpouts were considerably lower comparing to both Tvärminne (H-Tv) and Muuga (MB), indicating lesser contaminated food organisms here, than at Tvärminne and Muuga. Though compared to the mean concentrations of Ni in eelpouts from Kieler Förde (KF) the concentrations of Ni in muscle tissue still was lower, but in liver they were of the same order of magnitude for both sampling areas. The obtained present concentrations of Ni in liver of eelpouts from Roja (GR-R), mean 0.39 mg kg$^{-1}$ d wt, are however, considerably higher than the corresponding value calculated for eelpouts from the Gulf of Riga, in the 1970:s, mean ca. 0.16 mg kg$^{-1}$ d wt (Sejsumaa et al. 1984).

The modest concentrations of Ni in both muscle tissue and liver of flounder from the Kieler Förde (KF) may confuse, as they fall below the corresponding values for the eelpouts from the same area. This difference between the two species, may however, be explained by their different migrating- and food habits; eelpouts being extremely stationary (Schmidt 1917), in contrast to the seasonally migrating flounder (Aro 1989). Furthermore both species depend mainly on benthic invertebrates, such as mussels and polychaet worms, organisms that may be more contaminated, by e.g. heavy metals (as Ni), inside the Kieler Förde, compared to the situation in the more open Kieler Bucht (Bay of Kiel) and the southern Baltic Sea, outside the Kieler Förde. In contrast to the situation in the southern Baltic Sea, flounder in the northern part of the Baltic Sea, as around Åland, in the Archipelago Sea, and in the Gulf of Finland, are regarded less migrating (Aro & Sjöblom 1983), thus reflecting the situation in their environment considering e.g. metal contamination more effectively (e.g. Voigt 2003b).

**Sediments**

The mean concentration of Ni in the bottom sediments of Lemland–Näätö (20.5 mg kg$^{-1}$ d wt) corresponds to the value for “uncontaminated sediment”; 0–20 mg kg$^{-1}$ d wt” (Stokes 1981), while the corresponding value of Tvärminne Storjjärd
(35 mg kg\(^{-1}\) d wt), may be characterized as "slightly contaminated" (Fitchko & Hutchinson 1975). As the mean concentrations of Ni in the surface sediments of the northern Baltic Sea: 33 mg kg\(^{-1}\) d wt, SD 9 (Niemisto and Tervo 1978), and the Gulf of Finland; 42 mg kg\(^{-1}\) d wt (Leivuori 1998), both are of the same order of magnitude, as for Tvärminne, it may indicate an comparatively even contamination by Ni of the inlet area of the northern Baltic Sea into the Gulf of Finland. Compared to reported corresponding data for the Gulf of Riga; mean 41 mg kg\(^{-1}\) d wt, range 14–57 mg kg\(^{-1}\) d wt (Leivuori et al. 2000), the order of magnitude remains the same. In the surface sediments of the Kieler Bucht the corresponding concentrations of Ni are remarkably higher; ca 100 mg kg\(^{-1}\) d wt, range = 87–138 mg kg\(^{-1}\) d wt (Erlenkeuser et al. 1974), which may indicate concentrations of the same order of magnitude also in the Kieler Förde. In such a situation also the benthic fauna may be contaminated, which partly could explain the obtained concentrations of Ni in smelt and eelpout from the area. Correspondingly the migration behavior of the flounder may explain the considerably lower concentrations obtained (see above). Whether this is the case remains unclear, due to missing essential information regarding the presence of Ni in the Kieler Förde.

Conclusions

Due to missing relevant recent data for both benthic fauna and sediments, from other sampling stations, except Tvärminne and partly Lemland–Nätö, only the results of the investigated fishes may be used for evaluation. In this respect the results regarding the concentrations of Ni in the liver are most reliable, Ni, as most heavy metals, mainly concentrating in liver, and kidneys (e.g. Hofer & Lackner 1995). According to the obtained results all fish species at Tvärminne (H-Tv), smelt and eelpout at Kieler Förde (KF), seem contaminated by Ni, in contrast to fish from the sampling stations in the Archipelago Sea (AS) and along the Estonian western coast (M-VV), which appear to be the less contaminated. At Nätö–Lemland the obtained concentrations of Ni in flounder were considerably high in relation to the assumed non-polluted environment (Grímáš et al. 1991, Voigt 1991) in contrast to Kieler Förde, where the obtained concentrations of Ni from both eelpout and flounder were low in relation to the environmental situation (Theede et al. 1979, Pohl et al. 2005). Further investigations no doubt are required in order to reveal the true state of the environment at the sampling stations in question. As the considerably high concentrations of Ni in flounder from Lemland–Nätö however indicate a local contamination of the area, at least this area has to be rejected from those regarded as non-polluted around the Åland Islands.

Whether the revealed concentrations of Ni in the edible parts of the fishes (mainly muscle tissue) constitute a risk for humans remains open for discussion, as recommendations regarding allowed maximum levels of Ni in food, are still lacking (EUROPEAN COMMISSION 2006). The obtained concentrations, however, contribute to the total intake of Ni for consumers of fish all around the Baltic Sea.

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