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Heavy metal concentrations in four-horn sculpin *Triglopsis quadricornis* (L.) (Pisces), its main food organism *Saduria entomon* L. (Crustacea), and in bottom sediments in the Archipelago Sea and the Gulf of Finland (Baltic Sea)

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Abstract. Adult four-horn sculpin (*Triglopsis quadricornis*), its main food item, the isopod *Saduria entomon*, and surface sediments from three selected areas on the Finnish (Archipelago Sea, Western Gulf of Finland) and Estonian (Central Gulf of Finland) coasts were investigated for heavy metal (Fe, Mn, Zn, Cu, Cd, Pb, Ni, Hg) concentrations in order to find out eventual relationships between the contamination of the two species and their environment. The concentrations of metals in the liver of four-horn sculpin correlate with the concentrations of metals in the whole animal of *S. entomon*. Cadmium concentrations may have a significant negative effect upon the condition of the sculpins, amplified by iron and zinc. The broad variations of the metal concentrations analysed from the isopod *S. entomon* indicate a great tolerance towards harmful substances of the species even in continuously loaded areas. Additionally a “tolerance factor” (TF) is introduced.

Key words: heavy metals, *Triglopsis quadricornis*, *Saduria entomon*, sediments, Archipelago Sea, Gulf of Finland.

INTRODUCTION

The bottom-dwelling teleost, four-horn sculpin (*Triglopsis quadricornis* (L.)), and its main invertebrate food organisms the isopod *Saduria entomon* L., the amphipods *Monoporeia* and *Pontoporeia* spp., and the mysid shrimps *Mysis mixta* (Lilljeborg) and *M. relicta* (Lovén) are all regarded to be glacial relicts of the Baltic Sea, originating from arctic waters (e.g. Ekman, 1953; Segerstråle, 1982). All these animals prefer the muddy cold-water basins of the Northern Baltic Sea, and they are abundant in the soft bottom depths of the Archipelago Sea, SW Finland, as well as in the depths of the Gulf of Finland (e.g. Andersin et al., 1978; Seire, 1988; Mattila, 1993; HELCOM, 2002).

Belonging to the earliest postglacial inhabitants of the Baltic Sea and thus being well adapted to changing conditions of their environment these species may show an ability of tolerance to contamination by harmful substances, e.g. certain heavy metals, mainly of anthropogenic origin.

MATERIAL AND METHODS

Three sites (Fig. 1.) differing in environmental conditions were chosen for the sampling of the material:

- The open waters of Tvärminne Storfjärden (Tvä-1) off the Hanko-Hangö Peninsula, NW Gulf of Finland. This area is known to be continuously loaded by various heavy metals (e.g. Fe, Mn, Zn, Cu, Cd, Pb, Ni), emitted from the iron and steel plant at Koverhar in the vicinity since the early 1960s (Luotamo & Luotamo, 1976; Lahermo et al., 1996; Voigt, 2003a), but not otherwise loaded by other pollutants, as e.g. either nutrients or organic substances (e.g. Kauppila & Bäck, 2001). Additionally the area is influenced by the constant outflow of fresh water from large Pohja-Pojo Bay (e.g. Sarvala, 1985) and affected by surface and especially bottom currents, mainly from the eastern and southern directions (Palmén, 1930).
- The inner coastal waters at Airisto-Erstan (AS-2) of the central Archipelago Sea, SW Finland. This area is known to be continuously loaded by nutrients, but not to be otherwise polluted, especially not by heavy metals (e.g. Pitkänen et al., 1988; HELCOM, 1991; Kauppila et al., 2001). Other characteristics of the area are numerous smaller and larger islands, including reefs and depths of great variation, and strong main and local currents influencing the whole area (e.g. Tulkki, 1960).
- Käsmu Bay (Kä-3) on the open coast of northern Estonia, central Southern Gulf of Finland. According to the present author's interpretation of the data and the maps in *State of Environment in Estonia on the Threshold of 21st Century* (EEIC, 2001), this area is assumed to be least affected by any of the pollutants mentioned above. However, it is influenced by dominant western currents (Talpsepp, 1993), which include water transportation from the locally polluted area of Tallinn Bay (Astok & Suursaar, 1991; Suursaar, 1992; EEIC, 2001).

In the years 2000–2005 surface sediments and benthic animals from the major depth (35 m) at Tvärminne Storfjärden, Tvä-1, were sampled together using a 0.04 m^2 box-corer for sampling soft bottom macrozoobenthos (Andersin & Sandler, 1986). The sediment was scooped out from the samples with plastic tools, frozen (–20 °C), and stored before analysing. The rest of the sample was strained and sieved under water flow (Karjala & Lassig, 1985) in order to detect the animals. The corresponding benthic data for the two other fish sampling stations originate

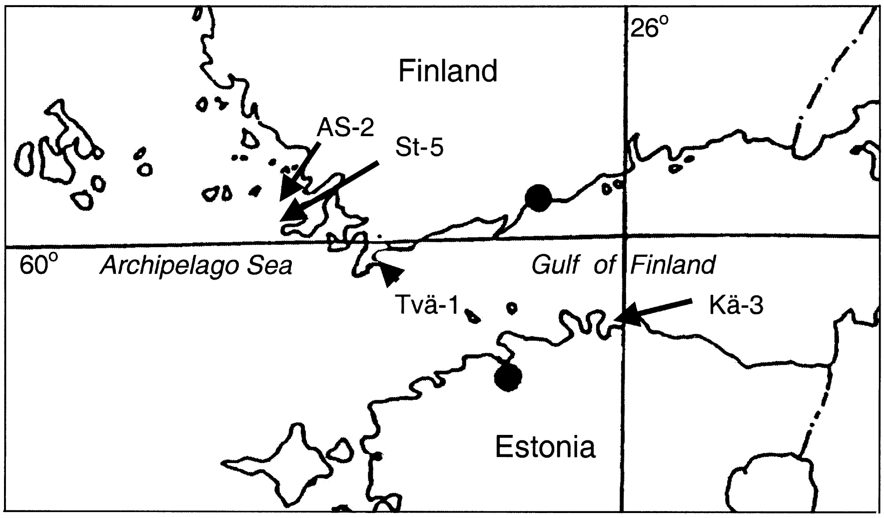

Fig. 1. Sampling sites of sediments, *Saduria entomon* L., and *Triglopsis quadricornis* (L.) from the Archipelago Sea and the Gulf of Finland. Tvä-1 – Tvärminne Storfjärden, Western Gulf of Finland; AS-2 – Airisto-Erstan, Archipelago Sea; St-5 – Seili-Själö, Archipelago Sea; Kä-3 – Käsmu Bay, Central Gulf of Finland.

from the literature: Müller's "Station 5" (Müller, 1999), at Seili-Själö in the vicinity of AS-2, ("St-5"), and from Käsmu Bay, respectively. The Hg data originate from Ott & Jankovski (1980), and the data on the other metals, from Jankovski et al. (1996), Pachel et al. (2001), and Simm & Roots (2003).

Regardless of sex, the size of the *Saduria entomon* accepted for comparisons between the sampling stations varied between 4 and 5 cm. This size, besides being recommended for Baltic monitoring (HELCOM, 1988), also is that of isopods preferred as food by adult four-horn sculpin (larger than 20 cm) at all three investigated areas, as shown by the present author's unpublished data and previously for the Swedish coast in the Bothnian Sea by Leonardsson et al. (1988).

The adult fish were caught either by bottom-trawling (Tvä-1, 1998–2005) or with gillnets (AS-2, 1998; Kä-3, 1998), weighed, and measured fresh before freezing (–20 °C), as were the isopods. In the laboratory the samples of liver and dorsal muscle tissue from the fish and the isopods were prepared for the analyses of Fe, Mn, Zn, Cu, Cd, Pb, and Ni content by electrothermal atomic absorption spectrometry (ETAAS; Varian SpectrAA400) and Hg by cold vapour atomic absorption spectro-photometry (CVAAS; Perkin Elmer MAS-50B), see Voigt, 2004. Additionally the sediment samples were dehydrated in an oven at 110 °C for 24 h before acid treatment (HNO_3 and H_2SO_4) prior to the analyses of Fe, Mn, Zn, Cu, Cd, Pb, Ni, in contrast to the analyses of Hg, for which the samples were dried in the oven, also for 24 h, but at 40 °C only, prior to acid treatment. The acid treated samples were analysed together with five blanks added to each set of

40 samples (Voigt, 2000; Tervahattu et al., 2001; Lodenius et al., 2002). All samples were analysed in duplicate and the accuracy was assessed by using blanks and reference materials (NIST SRM 1573a tomato leaves and CRM 422 cod muscle, respectively). The results for Fe, Mn, Zn, Cu, Cd, Pb, and Ni are all expressed in mg kg^{-1} d wt (dry weight), and so is Hg, though only for the sediment samples. For the fish and *S. entomon* samples the results regarding Hg are all expressed in mg kg^{-1} f wt (fresh weight).

RESULTS

The calculated mean concentrations of Fe, Mn, Zn, Cu, Cd, Pb, and Hg in the surface sediments from the main depth of Tvärminne Storfjärden (35 m), Tvä-1, in the isopod *S. entomon* (4–5 cm) analysed *in toto* from the same depth, and the liver of *T. quadricornis* caught by trawling from the same site are presented in Table 1.

The broad variations of the concentrations of the metals in the sediments are indicated by the value of SD for each metal in question. For Zn, Cu, Cd, and especially for Hg, the variations appear to be moderate in contrast to Fe, Mn, and Pb. For Hg the same is valid only for the metal concentrations of *S. entomon*. The mean concentration of Fe in *S. entomon* constitutes a tenth of the concentration in the sediment, in contrast to Mn, for which the mean concentration in the isopod is twice as high as in the sediment. The mean concentrations of Zn and Cu in the isopod and in the sediment are of the same order of magnitude, though showing a broader variation for *S. entomon*. The Cd and especially Pb and Ni concentrations are considerably lower in the isopod *S. entomon* (Ni = 2.3 mg kg^{-1} d wt) than in the sediments (Ni = 35 mg kg^{-1} d wt). With the exception of Hg, all the calculated mean concentrations of the metals in the liver of *T. quadricornis* are considerably lower compared to the isopod *S. entomon*. A similar distinction is even more pro-

Table 1. Mean concentrations of Fe, Mn, Zn, Cu, Cd, Pb, and Hg (mg kg^{-1} d wt) from the surface sediments of the main deep (35 m) of Tvärminne Storfjärden (Tvä-1, 2000–2005), the isopod *Saduria entomon* (4–5 cm, analysed *in toto*) from the same depth (2000–2005), and in the liver of *Triglopsis quadricornis* trawled from the same site (1998–2005)

Sample Years	Fe (SD)	Mn (SD)	Zn (SD)	Cu (SD)	Cd (SD)	Pb (SD)	Hg (SD)	N
Sediment	40000	380	175	45	0.85	55	0.07	20
2000–2005	(1540)	(75)	(15)	(3.2)	(0.15)	(4.9)	(0.01)	
S. entomon	4890	720	160	53	0.23	1.3	0.02*	15
2000–2005	(470)	(74)	(230)	(15.5)	(0.16)	(1.5)	(0.01)	
T. quadr.	154	1.2	80	15.8	0.08	–	0.11*	30
1998–2005	(99)	(1.0)	(43)	(13.8)	(0.04)		(0.07)	

* The Hg values for *S. entomon* and the liver of *T. quadricornis* are expressed in mg kg^{-1} f wt.

nounced regarding the concentrations of metals in the liver of the fish compared to the surface sediments of the same area (the fresh weight value of 0.11 mg kg^{-1} f wt Hg in Table 1 corresponds roughly to 0.30 mg kg^{-1} d wt Hg). The variations however are notably high: for Fe, Mn, and Cu the concentrations vary twice in contrast to Zn, Cd, and Hg, in which the variation is only half as high.

As to the sediment data from St-5 (Müller, 1999), the concentrations of Fe there are even higher compared to Tvä-1: 54 500 mg kg^{-1} d wt in contrast to 40 000 mg kg^{-1} d wt. Also for Zn the concentrations at St-5 are considerably higher: 240 mg kg^{-1} d wt in contrast to 180 mg kg^{-1} d wt. The corresponding values for Cu vary slightly: 55 mg kg^{-1} d wt in contrast to 45 mg kg^{-1} d wt. For Pb the concentrations are more or less of the same order of magnitude: 50 mg kg^{-1} d wt and 53 mg kg^{-1} d wt. However, for Cd (0.30 mg kg^{-1} d wt in contrast to 0.85 mg kg^{-1} d wt) and for Ni (55 mg kg^{-1} d wt in contrast to 35 mg kg^{-1} d wt) the difference is large.

Compared to the available corresponding sediment data from Kä-3 (for Hg, from Ott & Jankovski, 1980; for Cu and Cd, from Jankovski & Põder, 1980; Jankovski et al., 1987), the concentrations of Cu are about half of the corresponding concentrations calculated for both St-5 and Tvä-1: 25 mg kg^{-1} d wt in contrast to 55 and 45 mg kg^{-1} d wt, respectively. Also for Cd the value at Kä-3 is lower than at both St-5 and Tvä-1: 0.25 mg kg^{-1} d wt in contrast to 0.30 and 0.86 mg kg^{-1} d wt, respectively. For both Kä-3 and St-5 the values of Cd are of the same order of magnitude. The value for Hg is considerably lower at Kä-3 than at Tvä-1: 0.02 mg kg^{-1} d wt in contrast to 0.07 mg kg^{-1} d wt.

Comparison of the calculated mean values of metal concentrations in the whole animal of 4–5 cm individuals of *S. entomon* from Tvä-1 (Table 1) with available metal data for *S. entomon* from Seili-Själö (Miettinen & Verta, 1978) shows that the concentrations of Zn in 1974 were roughly half of the value for Tvä-1 today: 67 mg kg^{-1} d wt in contrast to 160 mg kg^{-1} d wt. For Cu the situation was the opposite: 186 mg kg^{-1} d wt in contrast to 53 mg kg^{-1} d wt. For Cd this difference is more than eightfold: 1.91 mg kg^{-1} d wt in contrast to 0.23 mg kg^{-1} d wt, but for Pb the values are of the same order of magnitude: 1.43 mg kg^{-1} d wt and 1.3 mg kg^{-1} d wt. For Hg the calculated mean value was lower at Seili-Själö compared to Tvä-1: 0.01 mg kg^{-1} f wt in contrast to 0.02 mg kg^{-1} f wt.

Comparison of recent Estonian data from Käsmu Bay (Simm & Roots, 2003) with corresponding metal means for the isopod *S. entomon* from Tvä-1 (Table 1) reveals a lower value for Zn (100 mg kg^{-1} d wt in contrast to 160 mg kg^{-1} d wt) at Tvä-1. For Cu, Cd, and Pb, however, the values at Käsmu are higher than at Tvä-1: 131 mg kg^{-1} d wt in contrast to 53 mg kg^{-1} d wt, 1.0 mg kg^{-1} d wt in contrast to 0.23 mg kg^{-1} d wt, and 2.6 mg kg^{-1} d wt in contrast to 1.3 mg kg^{-1} d wt, respectively. For Fe, Mn, and Hg corresponding data are missing, but for Hg the mean value corresponding to 0.01 mg kg^{-1} f wt has been presented for *S. entomon* from the Estonian Gulf of Finland (Roots et al., 2001; Simm & Roots, 2003).

The mean concentrations of the metals analysed from the liver of *T. quadricornis* from AS-2, Tvä-1, and Kä-3 are presented in Table 2.

Table 2. Concentrations of some heavy metals (Fe, Mn, Zn, Cu, Cd (mg kg^{-1} d wt) and Hg (mg kg^{-1} f wt)) from the liver of *Triglopsis quadricornis* from Airisto-Erstan in the Archipelago Sea (AS-2), Tvärminne Storfjärden, Western Gulf of Finland (Tvä-1), and Käsmu Bay, Central Gulf of Finland (Kä-3)

Sampling site Year(s)	Fe (SD)	Mn (SD)	Zn (SD)	Cu (SD)	Cd (SD)	Hg (SD)	N
AS-2 1998	470	4.8	130	5.7	0.55	0.06	17
	(330)	(3.0)	(54)	(1.7)	(0.40)	(0.03)	
Tvä-1	154	1.2	80	15.8	0.08	0.11	30
2000–2005	(100)	(1.0)	(40)	(13.8)	(0.04)	(0.07)	
Kä-3 1998	84	4.4	105	29	0.10	0.11	10
	(40)	(1.5)	(20)	(16)	(0.09)	(0.02)	

With the exception of Cd and Hg in the liver of the four-horn sculpin from Käsmu Bay in 1998 (Voigt, 2003b), all data in the table are original for the present study. The calculated high mean value for Fe in the liver of *T. quadricornis* from AS-2 is notable, as is the corresponding value for Cd, all in contrast to the corresponding values from the other two sites. Also for Mn and Zn these values were higher at AS-2 compared to Tvä-1 and Kä-3, respectively. Only for Cu and Hg significantly lower means were calculated for AS-2. The lowest means for Mn, Zn, Cu, and Cd were all calculated for the liver of *T. quadricornis* from Tvä-1. The lowest mean for Fe in the liver of the investigated fish was calculated from Kä-3. Regarding the concentrations of Hg in the liver of the fish the decreasing order is Kä-3–Tvä-1–AS-2; the order for the concentrations of Hg in the muscle tissue is the same: Kä-3 0.21 (SD 0.17), Tvä-1 0.19 (SD 0.10), AS-2 0.10 (SD 0.06) Hg mg kg^{-1} f wt.

The condition factor (CF; Suworow, 1959) of the investigated sculpins (Table 2) was calculated as well: AS-2 1.12 (♀♀ 1.19, ♂♂ 1.02), Tvä-1 1.29 (♀♀ 1.29, ♂♂ 1.28), Kä-3 1.31 (♀♀ 1.35, ♂♂ 1.22).

DISCUSSION

Sediments

With the exception for Fe, the higher concentrations of the metals Zn, Cu, and Ni at St-5 compared to Tvä-1 are confusing, especially as they by far exceed the values reported as background levels for Northern and Central Baltic sediments (for Zn 100, Cu 40, Pb 25, Ni 30, and for Hg 0.03 mg kg^{-1} d wt, respectively; Perttilä & Brügmann, 1992). Moreover, the Archipelago Sea is considered not to be polluted in this respect (HELCOM, 1991; Grimås et al., 1993). For the high value of Fe the explanation may be related to the oxic condition of the area in question (Brügmann, 1987). In addition the high values of Cu and Cd may be explained by the effects of increased eutrophication of the area, leading to increased deposition of both metals in the sediments due to the oxygen depletion associated with eutrophication (HELCOM 2002, 2003). The high concentrations of various metals in the sediments from St-5 may, however, also indicate only some unknown local pollution, instead of being representative for the depths in the Archipelago Sea.

The high values of Fe, Pb, and especially Cd in the sediments from Tvä-1 (Table 1) are all due to the activity of the iron and steel plant at Koverhar in the vicinity (Louekari et al., 1991; Voigt, 2004). Besides, the annual accumulations of Cd and Pb into the sediments are clearly higher in the Gulf of Finland than in the Gulf of Bothnia (Vallius & Leivuori, 1999), of which the Archipelago Sea constitutes a part. As Hg is not included in any of the processes at Koverhar (Voigt, 2003a), the obtained value of 0.07 is confusing, as is the low value of Ni, which is only slightly higher than the background level (see above). For Mn background level data of the sediments in the Baltic Sea are still lacking.

The reported concentrations of both Cu and Hg at Käsmu are lower compared to Tvä-1, while only Cu is lower than at St-5. Regarding other metals, such as Fe, Zn, Pb, and Ni information is lacking. However, for Mn, Zn, Pb, and Ni corresponding data from some unspecified depth(s) in the Estonian southern part of the Gulf of Finland are available: 200–11 000 mg kg^{-1} d wt for Mn, 18–1500 mg kg^{-1} d wt for Zn, 7–30 mg kg^{-1} d wt for Pb, and 8–36 mg kg^{-1} d wt for Ni (Pustelnikov & Jankovski, 1980, quoted in Brügmann, 1987). Compared to the corresponding background values (see above), the reported values in the sediments in the depths of the Estonian coast support the perception of Kä-3 as a relatively non-polluted area, regarding at least Cu, Cd, and Hg.

Saduria entomon

The high concentrations of Fe from *S. entomon* at Tvä-1 (Table 1) no doubt originate from the iron and steel plant at Koverhar, as do the concentrations of Mn. Iron concentrations of the same order of magnitude were also reported in the same species in the 1970s from several sampling stations outside the river mouth of the Kokemäenjoki-Kumoälv (Häkkilä, 1980). This area is regarded to be the most polluted coastal area in the Finnish part of the Bothnian Sea as far as metals are concerned (Häkkilä, 1985; Enckell-Sarkola et al., 1989). The comparatively high concentrations of Zn in the species support the assumption in contrast to the notably low concentrations of Cu. The means for Cd show a broad variation both in time (see comment below) and between the sampling stations, though for Pb the variation is even higher. Like for Mn, corresponding data for Ni are lacking. The highest recorded means of Hg concentrations in *S. entomon* (0.13 mg kg^{-1} f wt) originate from samples from locally polluted coastal zones in the Bothnian Sea in the 1970s (Voipio et al., 1977; Häkkilä, 1980), in contrast to the presently obtained comparatively low concentrations, which may indicate a moderately low concentration of the metal in the environment at present.

The regrettable lack of recent information regarding heavy metal concentrations in the isopod *S. entomon* from Airisto-Erstan in the Archipelago Sea is replaced by old data from Seili-Själö in the same area, as St-5, but originating from 1974 (Miettinen & Verta, 1978). Keeping in mind that these data originate from the 1970s, when also the analytical procedure was less exact than at present, it may be said with some reservations that both Cd and Pb decreased notably, along with Hg, all over the Baltic Sea since the 1970s (HELCOM, 1998). Compared to other corresponding old (1980s) data from the Gulf of Bothnia (Sandler, 1986) they mostly are, however, of the same order of magnitude for e.g. Zn, Cu, and Hg, contrary to Cd and Pb, for which the values at Seili-Själö were five and two times as high as the earlier concentrations. When Cd is concerned, the high mean value of 1.91 mg kg^{-1} d wt obtained at Seili-Själö in 1974 (Miettinen & Verta, 1978) was however exceeded at Tvärminne in 1975, when I. Luotamo calculated a mean as high as 2.13 mg kg^{-1} d wt for *S. entomon* in the vicinity of the iron and steel plant at Koverhar (Voigt, 2006). At the present time mean values exceeding 1 mgCd kg^{-1} d wt in *S. entomon* have been reported only from Estonian bays of the Gulf of Finland – Klooga, Kakumäe, Käsmu, Kunda, and Sillamäe (Volož et al., 1990; Jankovski et al., 1996; Pachel et al., 2001; Roots et al., 2001; Simm & Roots, 2003). In addition, the obtained means for both Cu and Pb from Käsmu exceed the corresponding values from Tvärminne notably, indicating some contamination of the area, by at least the three metals in question, Cd, Cu, and Pb.

Background levels of metals for *S. entomon* are not known, but some values of all the calculated means of metal concentrations obtained from the isopod from various parts of the Baltic Sea may be close to such levels. A relation between such a low level and the highest calculated mean thus may, in some way, describe the tolerance of *S. entomon* to each metal separately. In this case the lowest calculated mean for Fe in *S. entomon* (4–5 cm) from Finnish and Estonian waters is 181 mg kg^{-1} d wt (Bothnian Sea; Sandler, 1983). The highest calculated corresponding mean – 4890 mg kg^{-1} d wt – originates from Tvä-1 (Table 1). This value may be divided with the value of the lowest mean (see above) to obtain the ratio; 27 (Table 3). Corresponding ratios, or "factors of tolerance" (TF), between the calculated lowest known means of metal concentrations in *S. entomon* and the corresponding calculated highest mean metal concentrations are presented in Table 3.

Despite the lack of experiments, the broad variation between the calculated means suggests a high tolerance of the isopod *S. entomon* towards the analysed metals. Besides, *S. entomon* is known to survive in low oxygen conditions (Kangas & Lappalainen, 1978) and to tolerate even high concentrations of various phenol compounds (Oksama & Kristoffersson, 1979, 1980), all underlining the general high tolerance of the species.

In future studies, attention should be paid to both the size and especially to the sex of investigated *S. entomon* individuals, as males grow considerably bigger than females (Haahtela, 1990) and as males accumulate higher amounts of Cu than females (Simm et al., 1994). Whether the same is valid also for other metals

Table 3. The ratio between the calculated highest mean and the calculated lowest mean (tolerance factor, TF) of Fe, Zn, Cu, Cd, Pb (mg kg^{-1} d wt), and Hg (mg kg^{-1} f wt) analysed from the isopod *Saduria entomon* L. from Finnish and Estonian waters

Metal	Highest mean	Source	Lowest mean	Source	Ratio (TF)
Fe	4890	Voigt, 2006	181	Sandler, 1983	27
Zn	960	Luotamo & Luotamo, 1977	51	Sandler, 1983	19
Cu	233	Voipio et al., 1977	10	Luotamo & Luotamo, 1977	23
Cd	2.38	Miettinen & Verta, 1978	0.12	Sandler, 1983	20
Pb	2.90	Miettinen & Verta, 1978	0.15	Sandler, 1983	19
Hg	0.13	Voipio et al., 1977	0.01	Roots et al., 2001	13

has not been investigated, but regarding fish, a similar distinction between the sexes, though contradictory, has been observed for several metals analysed from some abundant Baltic fish species (Protasowicki, 1986; Voigt, 2004).

Four-horn sculpin

The comparatively high concentrations of Fe in the liver of the four-horn sculpins from the Archipelago Sea, which is unpolluted regarding metals (Grimås et al., 1993), may be explained by the high Fe concentrations in the sediments (Müller, 1999), though for Mn the explanation is open for discussion – especially because the concentrations of this metal are of the same order of magnitude also at Käsmu – all in contrast to the moderate concentration of Mn in the liver of four-horn sculpins from Tvä-1, the Tvärminne area being continuously contaminated especially by Fe and Mn (Voigt, 2003a; Table 1). Also for Zn the same peculiar discrepancy may be noted. For Cu the higher concentrations at Kä-3 are somewhat confusing, though the corresponding high concentrations (131–139 mg kg^{-1} d wt) of the main food item, the isopod *S. entomon* (Volož et al., 1990; Jankovski et al., 1996; Simm & Roots, 2003) may contribute to the explanation. The high concentrations of Cd in four-horn sculpin from AS-2 (Table 2) correspond to the concentration obtained from the main food item *S. entomon* (1.91 mg kg^{-1} d wt) from the same area (Miettinen & Verta, 1978). As for the concentrations of Hg in the liver of four-horn sculpin, they all are more or less of the same order of magnitude as are the concentrations of the main food item, *S. entomon* (Miettinen & Verta, 1978; Roots et al., 2001; Voigt, 2006), in opposite, however, to the concentrations in the sediments (Ott & Jankovski, 1980; Voigt, 2003a; Table 1).

With the exception of Hg, all other metals analysed concentrate in the liver and kidneys of fish (e.g. Hofer & Lackner, 1995). In contrast, Hg is mainly concentrated and accumulated in the muscle tissue of four-horn sculpin (Voigt, 2003b). Thus muscle concentrations are of higher significance than the concentrations obtained from the liver. The descending order of the mean concentrations of Hg in the muscle tissue of the four-horn sculpins is in accordance with the corresponding descending order of Hg found in their main food item, the isopod *S. entomon* (Miettinen & Verta, 1978; Roots et al., 2001; Voigt, 2006), though not statistically significant. The results may also support an indication of higher concentrations of Hg in the environments at Käsmu and Tvärminne compared to Airisto-Erstan, though neither is significantly proved. The mean calculated Hg muscle concentration for *T. quadricornis* from AS-2 is of the same order of magnitude as the mean (0.13 mg kg^{-1} f wt) reported in the 1970s for four-horn sculpins from "an unpolluted area" at Bromarf in the vicinity (Nuorteva & Häsänen, 1975). Also the present mean for Hg in the muscle tissue of sculpins from Tvärminne (see above) is (still) of the same order of magnitude as in the 1970s (0.22 mg kg^{-1} f wt; Voigt, unpubl. data).

Whether the observed main metal concentrations in the muscle tissue (Hg) or liver (Fe, Mn, Zn, Cu, Cd) have an influence on the condition of the fish, as described by the condition factor, CF = 100 × weight of fish, g/(length of fish, cm)^3 (Suworow, 1959), was simply tested by either the Spearman rank or the Pearson correlations tests (Statistix 7, 2000) for each metal separately (Voigt, 2004). The tests resulted in no significant correlations between Hg and Mn, on the one hand, and the CF, on the other, at either study area. Significant negative correlations, however, were calculated between CF and Fe at AS-2 (–0.63), CF and Zn at AS-2 (–0.65) and at Tvä-1 (–0.83), and between CF and Cd at AS-2 (–0.65), all indicating some negative relation between the metals in question and the fish studied (Voigt, 2004). The lowest mean CF was calculated for the four-horn sculpins from AS-2 (1.12), where also the highest mean for Cd in the liver was calculated (0.55), contrary to the equally higher mean CF for the fish of Tvä-1 and Kä-3 (1.20 and 1.31, respectively) and lower means for Cd (0.08 and 0.10 mg kg^{-1} d wt, respectively).

The moderate concentrations of Hg found in the sculpins apparently have no major influence on the condition, neither do the modest concentrations of the comparably harmless metals Fe, Mn, Zn, and Cu, but for the harmful metal Cd (Eisler, 1985) some influence may be expected. Among the effects of Cd that on the growth of fish should be mentioned (Hofer & Lackner, 1995), which directly affects the CF. This may explain the calculated lower CF for the four-horn sculpins from AS-2 compared to the CF of the fish from Tvä-1 and Kä-3, and probably even the observed negative correlations of Fe and Zn, both of which were analysed in higher concentrations from AS-2 compared to the two other study areas.

CONCLUDING REMARKS

Despite the scarce information concerning the present state of the environment of the study areas, especially regarding the contamination of the sediments with metals, there are indications of contaminations by e.g. Fe, Zn, and Ni of the unpolluted central Archipelago Sea compared to the locally polluted Tvärminne area in the NW Gulf of Finland. Consequently, higher concentrations of Cd have been recorded from the sediments of Tvärminne compared to both the central Archipelago Sea and Käsmu Bay. Regarding Cu, Cd, and Hg, the recorded low mean concentrations support the perception of Käsmu Bay as an area not polluted by metals. Contradictorily, however, the mean concentrations of Cu, Cd, and Pb in *S. entomon* from Käsmu are higher than from Tvärminne.

Similar differences are even more pronounced in four-horn sculpin, as the highest concentrations of Fe, Mn, Zn, and Cd were all recorded from the liver of sculpins from Airisto-Erstan in the Archipelago Sea. On the contrary, the highest concentrations of Cu were recorded from the liver of sculpins from Käsmu, where the corresponding concentrations of Fe were the lowest. Furthermore, also the highest concentrations of Hg were recorded in the muscle tissue of the sculpins from Käsmu. The concentrations of Hg in the muscle tissue at all stations exceeded the corresponding concentrations in the liver. Paradoxically the concentrations of all metals analysed from the sculpins at Tvä-1 lay between the corresponding values for AS-2 or Kä-3, the Tvärminne area being continuously contaminated by metals, aberrant from the other two, considered un- or less polluted areas. The need for further investigations of the areas in question is thus obvious in this respect.

In spite of the regrettable lack of present and complete data regarding heavy metal concentrations in *S. entomon*, particularly from the Archipelago Sea, and in part, Käsmu Bay, the reported and obtained results indicate a positive relation between the isopod and its predator, the four-horn sculpin, especially as the concentrations of the metals analysed in the liver of four-horn sculpin correspond stronger to the concentrations of their main food organism, the isopod *S. entomon*, than to the sediments of the area in question.

As to possible physiological effects of the analysed metals on the observed isopods and fish, which were not the main object of the study, only some suggestions can be made. However, for some of the metals, e.g. Fe, Zn, and mainly Cd, sublethal effects, like e.g. restricted growth, may be included in the evaluation of the condition of fish, considering that the higher the metal contamination in the fish, the lower the value of CF.

Assuming in addition a limited migration of both the benthic invertebrate in question and its predator, the four-horn sculpin, the environmental situation and the differences between the sampling stations may be reflected by the organisms in one way or another. Both species however seem to tolerate the present metal pollution of their environment without drastic effects, though they seem to be more exposed to more “natural” changes like oxygen deficiency (Andersin & Sandler, 1991), changes in both salinity and hydrogen sulphide conditions (Laine et al., 1997), increased eutrophication, food shortage, and mass predation, by e.g. the Baltic cod, *Gadus morhua callaris* L. (Voigt, 2006).

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Raskmetallide sisaldused Soome saarestikumere ning Soome lahe (Läänemeri) põhjasetetes ja merihärja *Triglopsis quadricornis* (L.) (Pisces) ning merikilgi *Saduria entomon* L. (Crustacea) organismis

Heinz-Rudolf Voigt

Raskmetallide sisaldusi on analüüsitud Soome ja Eesti rannikumere kolmes eri piirkonnas. On uuritud raskmetallide sisaldusi merihärja *Triglopsis quadricornis* (L.) ja tema põhitoidu merikilgi *Saduria entomon* L. organismis ning põhjasetetes eesmärgiga leida kemikaalide ülekande seaduspärasusi. Kaadmiumi sisalduste negatiivset mõju kaladele võimendavad lisaks kaadmiumile organismis sisalduvad raud ja tsink. Raskmetallide sisaldused merikilgi organismis erinevad piirkonniti ja isegi reostunud rannikumere aladel.