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HEAVY METAL AND ORGANOCHLORINE LEVELS IN COASTAL FISHES FROM THE VÄIKE VÄIN STRAIT, WESTERN ESTONIA, IN HIGH SUMMERS OF 1993–94

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Abstract. Heavy metals (Hg, Fe, Mn, Zn, Cu, Cd, Pb, Ni) and organochlorine compounds (HCHs, HCB, DDTs, PCBs) were analysed from muscle tissue and livers of Baltic herring (*Clupea harengus membras* L.), sprat (*Sprattus sprattus balticus* L.), smelt (*Osmerus eperlanus* L.), pike (*Esox lucius* L.), bleak (*Alburnus alburnus* L.), roach (*Rutilus rutilus* L.), ruffe (*Gymnocephalus cernua* L.), perch (*Perca fluviatilis* L.), and garpike (*Belone belone* L.) from the Väike Väin Strait during high summers of 1993–94. Mercury concentrations were higher in the muscle tissue than liver for both smelt and perch. For perch both these concentrations were higher than they were for smelt. In the muscle tissue of all predatory fishes (pike, perch, ruffe, garpike) the concentrations of mercury were higher than for the nonpredatory species (herring, sprat, smelt, bleak, roach). The concentrations of mercury were higher in the coastal inshore species (pike, perch, roach, smelt) than in open-sea fishes (garpike, herring, sprat). For metals other than mercury the values of manganese tended to be higher in smelt than in the two clupeids but for copper the opposite was observed. For cadmium and nickel the values measured for sprat, smelt, and bleak tended to be higher than they were from the same species from comparable Finnish coastal waters. The same is true for lead from herring, smelt, and bleak. For iron and zinc no such differences were observed. For both the organochlorine pesticides and PCBs, the concentrations were higher in the homogenates of migrating pelagic partly open-sea species (herring, sprat, garpike) than in the homogenates of less migrating coastal species (smelt, pike, perch). The food safety levels in Estonia or Finland for either metals or organochlorine compounds were exceeded in no cases.

Key words: heavy metals, organochlorine pesticides, PCBs, Baltic coastal fish, Väike Väin.

INTRODUCTION

There are numerous studies and reports regarding monitoring of harmful substances in Baltic open sea fishes, e.g., herring, cod, and flounder (Dybern, 1972; HELCOM, 1987; Protasowicki, 1987; Naturvårdsverket, 1988; ICES, 1991). However, only a few deal with common coastal and inshore species, e.g., smelt, pike, bleak, roach, perch, and ruffe (Nuorteva & Häsänen, 1975; Linko et al., 1979; Ott et al., 1982), although they could be expected to reflect the eventual pollution situation of their environment as well as the chosen monitoring species herring, cod, and flounder do for their environment.

The investigation reported here was included in the project "Ecological Studies in the Aquatic Environment of Väike Väin Strait in West Estonia" in 1993, but continued as an independent project "Harmful Substances in the Fish from Väike Väin Strait" in 1994. Preliminary results were published in 1994 (Voigt, 1994a). The checked final results give some more information on the situation regarding coastal fishes from the Väike Väin Strait, between the islands of Saaremaa and Muhu on the western coast of Estonia, during the high summer periods of 1993–94. High summer was chosen as the sampling season in order to avoid possible variations connected with the seasons of the year.

MATERIAL AND METHODS

The material for the analysis of heavy metals and organochlorine compounds consisted of 11 species including a total of 66 specimens partly also included in the material treated and presented by Saat & Vetemaa (1993) and Saat & Eschbaum (1995). The species sampled from the Väike Väin Strait were Baltic herring (*Clupea harengus membras* L.), sprat (*Sprattus sprattus balticus* L.), smelt (*Osmerus eperlanus* L.), pike (*Esox lucius* L.), bleak (*Alburnus alburnus* L.), roach (*Rutilus rutilus* L.), ruffe (*Gymnocephalus cernua* L.), perch (*Perca fluviatilis* L.), and garpike (*Belone belone* L.). In addition only mercury analysis from one sturgeon (*Acipenser sturio* L.) and one whitefish (*Coregonus lavaretus* L.) was made.

Atomic absorbtion spectrometry (metals) and gas chromatography (organochlorine compounds) were applied for the analyses as presented previously (Voigt, 1994b). Metals in fish were analysed individually but for organochlorine analysis homogenates of 2–5 specimens were used.

The metals analysed were mercury, iron, manganese, zinc, copper, cadmium, lead, and nickel. The organochloric compounds included pesticides HCHs (α-, β- and γ-HCH), HCB, and DDT, and also a selection of some essential PCB congeners.

RESULTS

Complete and checked results of all the analyses from the fish sampled from the waters of the Väike Väin Strait in 1993–94 are presented in Tables 1–5.

For smelt and perch only mercury analyses were made from both muscle tissue and liver. The results presented in Table 1 indicate the concentrations of mercury (fresh weight) to be higher in the predatory perch than the benthic–pelagic feeding smelt. For both species the concentration of mercury was considerably higher in the muscle tissue than in the liver. The ratio of mercury for muscle/liver was for smelt 1.4 and for perch 2.4.

Table 1. Concentrations of mercury (mg/kg, fresh weight) in the muscle tissue and liver of smelt and perch from the Väike Väin Strait in the high summers of 1993–94

Species	Muscle		Liver		Age of fish, years		*N*
	Mean	Range	Mean	Range	Mean	Range	
Smelt	0.07	0.04–0.14	0.05	0.03–0.11	3.8	3–5	10
Perch	0.30	0.17–0.37	0.13	0.07–0.20	6.1	2–8	8

The mean concentrations of mercury in the muscle tissue of the nonpredatory herring, sprat, bleak, and roach and the predatory ruffe, pike, and garpike are presented in Table 2.

Table 2. Concentrations of mercury (mg/kg, fresh weight) in the muscle tissue of nonpredatory and predatory fishes from the Väike Väin Strait during the high summers of 1993–94

Nonpredatory fish				Predatory fish			
Species	Mean	Range	*N*	Species	Mean	Range	*N*
Herring	0.06	0.03–0.13	12	Ruffe	0.21	0.14–0.27	4
Sprat	0.04	0.02–0.06	10	Pike	0.33	0.18–0.44	6
Bleak	0.04	0.02–0.05	6	Garpike	0.12	0.10–0.13	2
Roach	0.16	0.10–0.21	6				

Not surprisingly, the mean values of mercury in the muscle tissue of predatory fishes exceeded those for nonpredatory species, as also shown since the 1960s by e.g. Westöö (1967), Johnels et al. (1967), Häsänen & Sjöblom (1968), and Sjöblom (1969). There also seems to be a difference between the pelagic open-sea species herring, sprat, and garpike and the inshore species smelt, roach, ruffe, perch, and pike. The inshore fishes, with the exception of the shortlived small bleak, contained more mercury in their muscle tissue than the open-sea species. The size of the samples, however, was too small for meaningful statistical treatment.

For one female planktivorous whitefish, 45 cm in total length, a concentration of 0.06 mg/kg Hg in the muscle tissue was measured. For a female sturgeon, 2.9 m in total length and a weight of 136 kg, aged 45 years, caught from the same waters in May 1995 ("Maria"), the concentrations were 0.27 mg/kg Hg in the muscle tissue and 0.13 mg/kg Hg in the liver.

The concentrations of other heavy metals besides mercury in the muscle tissue of some of these fishes are presented in Table 3.

Table 3. Mean concentrations of heavy metals (mg/kg, dry weight) in the muscle tissue of fishes from the Väike Väin Strait during the high summers of 1993–94

Species	Fe	Mn	Zn	Cu	Cd	Pb	Ni	*N*
Herring	34	2.8	103	3.9	0.02	0.3	0.2	7
Sprat	42	4.4	36	4.2	0.04	0.1	0.2	6
Smelt	26	5.6	54	3.1	0.04	0.3	0.2	10
Bleak	37	2.3	98	2.8	0.04	0.4	0.2	5

The values for cadmium, lead, and nickel were slightly higher than they are in fish from relatively unpolluted Finnish coastal waters. The results only indicate trends for some metals such as manganese for smelt and copper for herring (found also for smelt and herring in Finnish waters; Voigt, 1998a).

The organochlorine compounds were analysed from homogenates of 2–5 fish. The values for pesticide compounds are given in Table 4.

Table 4. Organochlorine pesticides from homogenates of fishes (extractable fat, mg/kg) from the Väike Väin Strait in the high summers of 1993–94

Species	Tot-HCH	HCB	p,p´-DDE	p,p´-DDD	p, p´-DDT	Tot-DDT
Herring	0.43	0.01	0.20	0.14	0.10	0.44
Sprat	0.17	0.03	0.47	0.28	0.08	0.83
Smelt	<0.005	0.02	0.10	<0.005	0.005	0.11
Pike	0.01	0.01	0.01	0.04	0.03	0.08
Perch	0.01	<0.005	0.12	<0.005	0.01	0.13
Garpike	0.34	0.03	0.13	0.04	0.10	0.27

The concentrations of total HCH and DDTs were considerably higher in the migrating open sea species sprat, herring, and garpike than in the more stationary local inshore species smelt, pike, and perch.

The corresponding values for only the most frequent congeners of PCBs and the total PCB mg/kg of the fishes are presented in Table 5.

Table 5. Concentrations of some frequent PCB congeners and total PCB from homogenates of fishes (extractable fat, mg/kg) from the Väike Väin Strait in the high summers of 1993–94

Species	PCB-49	PCB-52	PCB-87/115	PCB-123/149	PCB-153	Tot-PCB
Herring	0.02	0.09	0.24	0.22	0.34	1.79
Sprat	0.06	0.19	0.67	0.14	0.27	2.01
Smelt	0.02	0.03	0.03	0.06	0.10	0.51
Pike	0.005	0.008	0.02	0.02	0.02	0.28
Perch	0.008	0.04	0.005	0.04	0.02	0.33
Garpike	0.11	0.63	0.19	0.49	0.55	3.17

Other PCB congeners included in the value for total PCB were PCB-82/151, PCB-90/101, PCB-105/132, PCB-118, PCB-146, PCB-137/176, PCB-138/158, and PCB-180.

Also the concentrations for the congeners of PCB were higher in the migrating open sea species garpike, sprat, and herring as compared to the more local and stationary inshore species smelt, pike, and perch.

DISCUSSION AND CONCLUSIONS

Compared to previous investigations in adjacent Estonian coastal waters, Matsalu Bay (Ott et al., 1982), the results for mercury levels in muscle tissues are of the same order of magnitude for sprat (0.04 mg/kg), perch (0.32 mg/kg), and pike (0.31 mg/kg) but considerably lower for herring (0.02 mg/kg) and smelt (0.04 mg/kg). From comparable SW Finnish coastal waters and during the same period (1993–95) these mean values were for herring 0.12, sprat 0.05, smelt 0.07, pike 0.37, and perch 0.24 mg/kg (Voigt, 1998b). For herring and pike caught from the Gulf of Finland in 1978 Miettinen et al. (1985) recorded values of 0.06 and 0.22 mg/kg fresh weight, respectively.

Mercury comparisons of this kind, however, are made difficult by evident local differences within the species as shown by Haahti (1991) for Finnish open-sea herring, for which means of 0.02–0.07 mg/kg fresh weight were measured during the period 1979–88.

The concentrations of mercury were considerably higher in predatory fishes than in nonpredatory fishes. However, regardless of predatory status the concentrations of mercury were higher in the more inshore coastal species than in the open-sea species. The concentrations of cadmium in the muscle tissue of sprat, smelt, and bleak were slightly higher than the values found in the same species in comparable Finnish coastal waters where means of 0.01–0.03 mg/kg dry weight were measured (Voigt, 1998b). Therefore, they may together with the corresponding values of lead and nickel (for which values in fish from unpolluted Finnish coastal waters seldom exceed 0.2 mg/kg for both metals; Voigt, 1998b) indicate some local burden of metal pollution in the Väike Väin Strait.

The relatively high concentrations of HCBs and DDTs (p,p′-DDE, p,p′-DDD and p,p′-DDT) from herring and especially sprat as compared to smelt may partly be explained by the higher fat content of the former species. For pike and perch the low fat content then also partly explains the low concentrations of these fat soluble pesticides. The concentrations of DDTs were of the same order of magnitude with the corresponding values for perch from the waters off southern Hiiumaa, north of the Väike Väin Strait, where Blomkvist et al. (1993) in 1992 measured 0.06 mg/kg extractable fat for p,p′-DDE, 0.02 for both p,p′-DDD and p,p′-DDT, and 0.09 for total DDT.

For the pesticides HCB, p,p′-DDE, p,p′-DDD, p,p′-DDT, and sum-DDT Roots & Aps (1993) give for Eastern Baltic open-sea herring in 1991 0.14, 0.84, 0.65, 0.38, and 1.87 mg/kg extractable fat and for sprat 0.08, 0.52, 0.72, 0.32, and 1.55 mg/kg extractable fat, which are all considerably higher than the values found in these fishes from the Väike Väin Strait.

For herring from the Gulf of Riga Roots (1996a) reports however a lower mean value of total DDT – 0.28 mg/kg extractable fat – and therefore he states that the Gulf of Riga is a high class reference area due to the low concentrations found there compared with the concentrations found elsewhere along and off the Estonian coast. This finding and the values of total DDT for herring from the Gulf of Bothnia and the Finnish part of the Gulf of Finland of 0.3–0.7 mg/kg extractable fat (Haahti & Perttilä, 1988) make the values for herring from the Väike Väin Strait intermediate to those for herring from the open sea and the inner parts of the Baltic Sea. Miettinen et al. (1985) however recorded considerably higher concentrations of total DDT in both herring (1.6 mg/kg extractable fat) and pike (2.9 mg/kg extractable fat) from the coastal waters of the Gulf of Finland reflecting the pollution situation of the waters at the time of sampling in 1978. The concentrations of total DDT for herring from the Väike Väin Strait are of the same order of magnitude as the values given by Luckas et al. (1980) for herring caught in the second half of the 1970s from the Gotland basin, but for sprat from the same area they are almost twice as high. For garpike from the waters around Rügen Island in the southern Baltic Luckas et al. (1980) found total DDT concentrations of the same order of magnitude as the values measured for garpike from the Väike Väin Strait.

The high concentrations of PCBs in herring, sprat, and especially garpike may partly be explained by the high fat content of these fishes. For some congeners an indication for accumulation in some species may be imaginable, e.g. for PCB-52 and PCB-153 in garpike and PCB-87/115 in sprat. For garpike the high value of total PCB is confusing. The material analysed however is far to small for drawing conclusions. In herring from the Gulf of Finland a total PCB of 2.80 mg/kg extractable fat was calculated for the same period, 1992 (Himberg et al., 1993), and in previous observations from coastal waters of the Gulf of Finland a mean of 3.6 mg/kg extractable fat was recorded for herring, and of 16 mg/kg extractable fat for pike (Miettinen et al., 1985).

The high concentrations of DDTs and PCBs in the planktonic organisms in the open Baltic Sea (Jankovski & Simm, 1984, 1985) off the Estonian west coast compared to more inshore coastal waters (Jankovski et al., 1984) may partly also explain the higher concentrations of these compounds in the planktivorous pelagic species herring and sprat. Both species also inhabit open waters like their predator the garpike before they migrate into the coastal waters. Roots (1984) also states that there is a clear tendency for the open-sea herring to contain more PCB and DDT than the Gulf of Riga herring does.

In all inshore species, smelt, pike, and perch, the concentrations of the pesticides and PCBs were considerably lower than in herring, sprat, and garpike, which for some periods of their life cycles stay in the open-sea waters of the Baltic Sea before migrating towards the coast.

In full agreement with Roots (1995), who argues that at present it is very difficult to compare the results of the analyses of chlororganic compounds, further comparisons have been avoided.

Calculated on the basis of fresh weight for metals other than mercury and organochloric compounds the stipulated safety levels for fish as human food were exceeded in no case either in Estonia or in Finland (European Commission, 1993; Roots, 1996b; Tahvonen & Kumpulainen, 1998). However, the levels indicate slight pollution of the Väike Väin Strait and the open Baltic Sea off the Estonian coast as they are higher than the levels found elsewhere in nonpolluted areas on the Estonian coast. In this respect these levels should be noted as early warning signals.

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RASKMETALLIDE JA KLOORORGAANILISTE ÜHENDITE TASE VÄIKESE VÄINA KALADES 1993. JA 1994. AASTA SUVEL

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On uuritud raskmetallide (Hg, Fe, Mn, Zn, Cu, Cd, Pb, Ni) ja kloororgaaniliste ühendite (HCH, HCB, DDT, PCB) sisaldust Väikeses väinas elutseva räime (*Clupea harengus membras* L.), kilu (*Sprattus sprattus balticus* L.), tindi (*Osmerus eperlanus* L.), haugi (*Esox lucius* L.), viidika (*Alburnus alburnus* L.), särje (*Rutilus rutilus* L.), kiisa (*Gymnocephalus cernua* L.), ahvena (*Perca fluviatilis* L.) ja tuulehaugi (*Belone belone* L.) lihaskoes ja maksas 1993. ja 1994. aasta suvel. Nii tindi kui ka ahvena lihaskoes oli elavhõbeda kontsentratsioon kõrgem kui maksas. Elavhõbeda sisaldus ahvena lihaskoes ja maksas oli suurem kui tindil. Röövtoiduliste kalade, nagu haugi, ahvena, kiisa ja tuulehaugi lihaskoes oli elavhõbedat ohtramalt kui mitteröövtoiduliste kalade, nagu räime, kilu, tindi, viidika ja särje lihaskoes. Avamerekalad – tuulehaug, räim ja kilu – sisaldasid vähem elavhõbedat kui rannavetes elutsevad haug, ahven, särg ja tint. Mangaani oli tindis rohkem kui räimes ja kilus, vase puhul oli olukord vastupidine. Väikese väina kilus, tindis ja viidikas mõõdetud kaadmiumi ja nikli kontsentratsioon oli kõrgem kui Soome rannikumeres elutsevatel sama liigi esindajatel. See kehtib ka plii kontsentratsiooni kohta räimes, tindis ja viidikas. Raua ja tsingi puhul niisugust erinevust ei täheldatud. Kloororgaaniliste pestitsiidide ja PCB kontsentratsioon oli rändeid tegevas avamere räimes, kilus ja tuulehaugis suurem kui ranniku lähedal elutsevas tindis, haugis ja ahvenas. Raskmetallide ja kloororgaaniliste ühendite kontsentratsioon kalades ei ületanud ühelgi juhul Eestis ja Soomes toiduainetele kehtestatud vastavaid piirväärtusi.