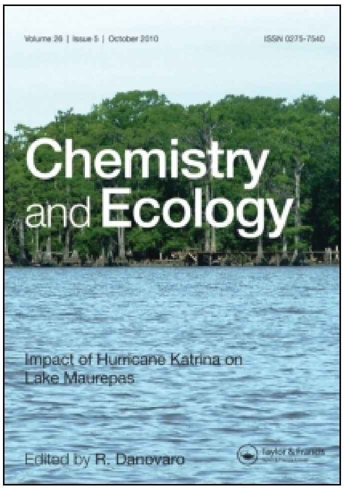

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METALS IN ZOOPLANKTON FROM THE BALTIC SEA, 1980–84

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Between 1980 and 1984, plankton was collected for metal analysis during four expeditions in the Baltic Sea. For comparison, samples from adjacent areas of the northeastern Atlantic Ocean were also taken. The mixed net-plankton samples were analyzed by AAS for metals (Al, Cd, Co, Cr, Cu. Fe, Mn, Ni, Pb, and Zn). The results are discussed with regard to spatial and temporal trends and for comparison with data from other authors. Correlations among the contents of the different metals and between the metal contents and 'external factors' including salinity, season, percentage of co-collected phytoplankton, and concentration of dissolved and particulate metals in the water are considered.

There is a tendency for higher metal contents in plankton from the brackish Baltic Sea (Al, Mn and Hg), while other metals (e.g. Cd) show higher levels in samples taken from the marine environment. Except for mercury, no clear correlations could be found between the metal content in plankton and the dissolved concentration of the same metal in the ambient water. Otherwise, the contents of aluminium, iron, manganese and zinc in the suspended particulate matter and in the plankton seem to be partly related to each other.

KEY WORDS: trace metals, plankton, Baltic Sea, trends.

INTRODUCTION

By sampling from different ecosystem compartments, e.g. water, sediments or biota, temporal and spatial trends of the heavy metal contamination of the marine environment can be investigated. In general, plankton bioconcentrates metals up to 10^3 or even 10^5 times. Compared to studies on water samples, this reduces the risk of analytical errors caused by contamination of the samples during sampling and further treatment. In contrast to studies using sediment samples, plankton investigations are also more closely relevant to human health aspects because the plankton serves directly as food for several economically important fish species. On the other hand, the zooplankton, through production of faecal pellets, may be important in the formation and composition of pelagic sediments (Boström *et al.*, 1974; Li, 1981).

Unfortunately, information gained on metal contents in mixed zoo-/phyto-plankton samples may be very much reduced in its usefulness. This is because

(a) the metal content between different species may vary over a rather broad range (Martin and Knauer, 1973; Pohl, 1989; Weber *et al.*, 1992),

(b) some zooplankton species may accumulate the metals depending on their life stage and age (Diaz and Fernandez-Puelles, 1988),

(c) some metals seem to be well regulated by the zooplankton,

(d) non-biogenic material of natural or anthropogenic origin adheres easily to phytoplankton agglomerates or becomes incorporated into the zooplankton (e.g. rust particles, paint chips, clay particles) and may result in higher metal contents of the zooplankton samples, and

(e) there is no clear cut-off possible between phyto- and zooplankton using different mesh sizes of the nets (Martin and Knauer, 1973), i.e. a higher percentage of phytoplankton in the samples (Boström *et al.*, 1974) may result in higher metal contents.

Nonetheless, zooplankton has already been used frequently to study metal contamination in the marine environment (Phillips, 1980). It may be at least a valuable tool for the identification of pollution hot spots (V.-Balogh, 1988).

In the present paper we investigate whether or not information on spatial and/or temporal trends of metals in the Baltic Sea can be obtained from analysis of mixed net-plankton samples collected over four subsequent years. In addition, we looked for possible correlations between the metal content of the plankton and the concentration of dissolved and particulate metals in the ambient water.

EXPERIMENTAL PROCEDURES

The samples were taken during four expeditions with RV "A. v. Humboldt" in the Baltic Sea in September 1980, May/June 1981, June/July 1983 and November/December 1984. The stations visited (Fig. 1a, showing as an example the distribution of cadmium in "zooplankton", Nov-Dec, 1984) were those agreed for the "Baltic Monitoring Programme" (BMP) of the HELCOM (Helsinki Commission). These expeditions aimed to perform complex field studies on the degree of contamination within the Baltic Sea environment, including the search for possible spatial gradients extending to adjacent sea areas. Therefore, in 1981 and 1983 the cruise routes were extended to the North Sea and further out to parts of the northeastern Atlantic Ocean (Fig. 1b).

Details of the method used and the results obtained for dissolved (Brügmann *et al.*, 1983; 1985a, b; 1987) and particulate (> 0.4 μm) metal contents (Bernard *et al.*, 1989; Brügmann, 1986; Brügmann *et al.*, 1992) in the water body have been reported earlier.

Sampling of the zooplankton was performed using a standard UNESCO-WP2 nylon net (mesh size 0.2 mm) equipped with a PTFE beaker. This net is commonly used for collecting small mesozooplankton; in fact, in most cases the sample was comprised predominantly by different zooplankton species. In the following text this collected material is referred to as "zooplankton" although some phytoplankton may be included. At stations with water depths below 100 m, for all areas investigated, vertical sampling was started about 3 m above sea bottom. At stations with greater depths, samples were collected above 100 m only. To avoid contamination of the samples by the uncontrolled collection of particles released by the research vessel, as for instance abraded paint chips and other debris, the net was closed 5 to 7 m below the sea surface. In very rough weather with a fast drifting ship, the hauls were extended up to the

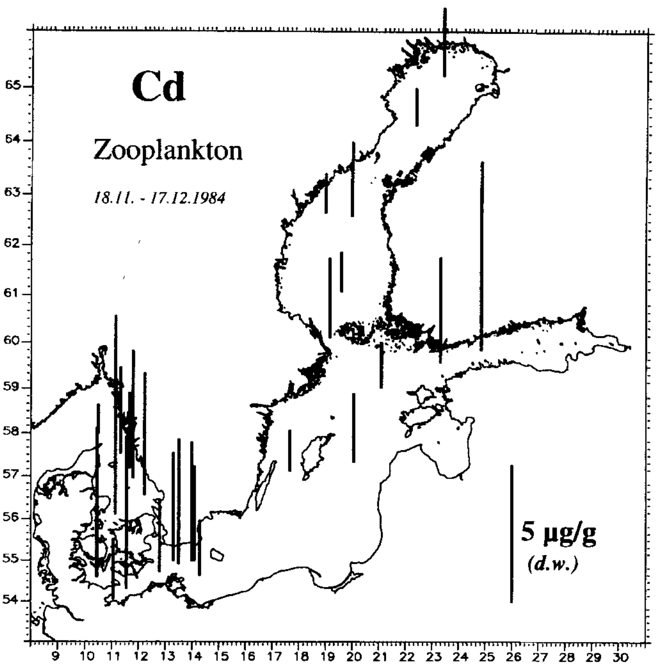

Figure 1a Cd in "zooplankton" from the Baltic Sea, 1984 (The sampling sites being identical with the origin of the vertical bars represent the Cd contents)

surface. In addition to these precautions, the collected material was carefully inspected for any contaminating matter (e.g. paint chips, rust particles). Following flushing with de-ionized water the plankton was deep-frozen in plastic bags. Before analysis, the samples were freeze-dried, checked again with a teflon coated magnet for metal particles (Martin and Knauer, 1973) and homogenized in an agate mortar.

About 50 mg sample of the dried material was digested in PTFE pressure multi-bombs with 1 ml sub-boiling quartz distilled nitric acid at 170 °C for 2 hours. The digests were made up to 10 ml in stoppered polypropylene vials and analyzed by flameless and flame-injection AAS techniques using a "Perkin Elmer 4000" machine. Deuterium background correction was applied for all measurements. In the flameless AAS mode, glassy carbon platforms in pyrolytically coated tubes together with matrix modifiers provided reliable STPF (stabilized-temperature-platform-furnace) conditions (Slavin and Manning, 1981).

For the determination of mercury, pressure digestion was performed for only one hour at 160 °C using 50 to 200 mg of dried sample. The digest was made up to about 20 ml and further oxidized for at least 2 hours by adding 1 ml saturated solution of potassium permanganate. Following further dilution to about 80 ml, the excess of the permanganate was reduced with 0.1 ml saturated hydroxylamine hydrochloride solution and made up to 100 ml with de-ionized "MilliQ" water. In aliquots of this solution the mercury ions were reduced to the elemental state with Sn(II). The elemental mercury was analyzed by the AAS 'cold-vapour' technique in an open system

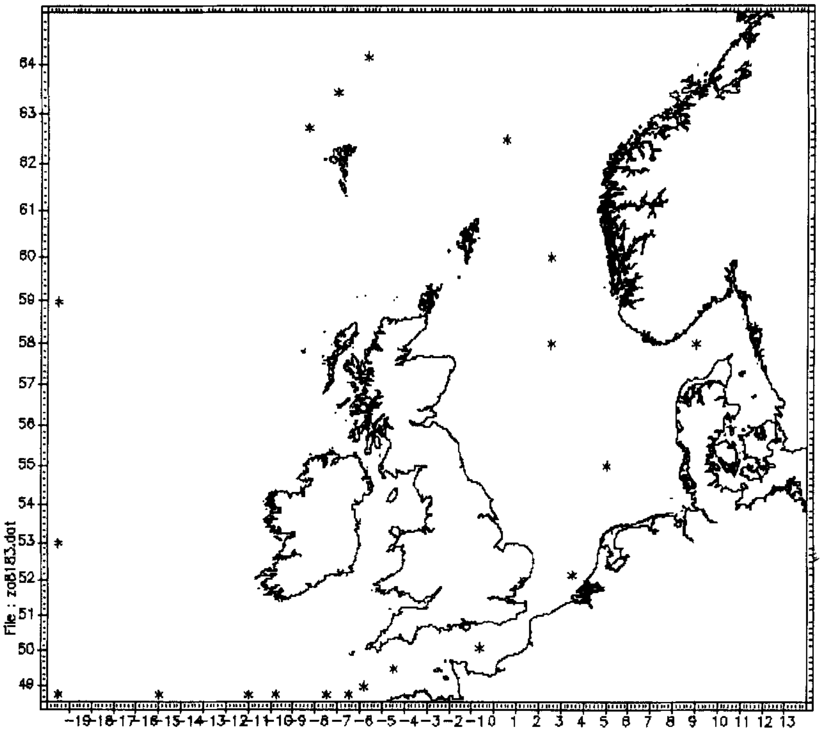

Figure 1b Reference sampling sites for "zooplankton" 1981 and 1983 (Stations indicated by a '*')

with argon as the carrier gas. Before finally passing the absorption cell, the Hg(0) was accumulated, and thereby also separated from other substances absorbing in the UV range, by amalgamation onto gold-coated silica wool. The mercury content was recorded with a Coleman MAS 50 Mercury Analyzer.

In two of the four sets of samples cobalt and chromium were not analyzed. The content of selenium was determined only in samples collected in 1984.

The relative standard deviation (RSD) of the procedures used for determination of mercury and of the other metals in the plankton samples was dependent on the elements analyzed. Except for selenium (RSD ± 18%), the SD values were less than ± 10%. As reference material for the analytical quality assurance IAEA's "MAA-1" copepod homogenate was run in parallel to the samples. The results obtained for this material were within 2 SD of the certified contents.

Data on dissolved and particulate metal concentrations in the water measured in parallel had to be processed before being used for comparison with the metal contents in plankton. This manipulation is needed to take account of the procedure used for sampling. Typically, several water samples for analysis were taken from different depths of the column drawn through by the plankton net. This water column was separated into different layers characterized by their salinities and/or temperature (densities), and the mean values for these columns weighted for the thickness (volume) of the layers. Metal concentrations obtained for the interface with the atmosphere (surface microlayer) and for samples taken very close to the bottom were excluded from the calculation of a mean value over the plankton sampling column.

RESULTS AND DISCUSSION

The results of the analyses of the plankton samples are reported on a dry weight basis (Table I, Figures 2 and 3). The data set was separated into four geographically defined categories comprising the "Baltic Sea" where the majority of the samples was taken, the "Kattegat" as the Baltic transient area to the North Sea, the "North Sea" including the Skagerrak and the English Channel, and the "NE Atlantic Ocean" summarizing data obtained from the Norwegian Sea, from the Atlantic Ocean west of the Faerøe Islands and Great Britain, and from the Bay of Biscay. Five samples with exceptionally high metal contents were excluded from the descriptive statistics and correlation computations. Three were found obviously enriched in phytoplankton, while in the other two samples, the presence of small-sized inorganic metal-rich but not iron based debris is assumed.

As a major factor for variation of metal contents in plankton samples, the species composition must be taken into consideration. For instance, Martin and Knauer (1973) found strontium-concentrating radiolarians to be primarily responsible for elevated levels of lead, mercury, copper, iron, and zinc in mixed zooplankton samples. In addition, it has been shown that, even within the copepods, different percentages of selected species may cause wide variations of the metal contents. From the data of Weber *et al.* (1991) it appears that *Acartia* spp., compared to *Calanus* spp., have about twice the level of copper and 3 times higher zinc content. In contrast, *Calanus* spp. may have up to three times higher cadmium. A high ratio of fish larvae in the samples may 'dilute' the metal contents introduced by other zooplankton species, while amphipods may have a higher overall content of cadmium and *Temora* spp. could be responsible for higher zinc values.

The percentage of zooplankton faecal pellets in the collected samples may also influence the metal content of the analyzed material. The content of metals in the pellets is about 200(Al), 100(Mn), 33(Fe), 20(Cu), 10(Cd), 7(Co), 5(Zn), 4(Cr), and 3(Hg, Ni, Pb) times higher than in the zooplankton itself (Savenko, 1988). To avoid much of the variation introduced by different zooplankton species composition and by variations in the percentage of phytoplankton present in the samples, it would seem obvious to pick out single animals for analysis. However, while for zooplankton from more saline and marine waters (Haarich *et al.*, 1992; Pohl, 1989; Weber *et al.*, 1991) single zooplankton specimens may be separated easily for metal studies, this is impracticable for plankton from the brackish Baltic Sea, where the size of the different species is much lower than in the ocean.

Zooplankton from the Baltic Sea consists mainly of herbivorous copepods. Typically for the post-spring bloom "summer conditions", copepods constitute more than 80% of the zooplankton biomass, dominated by *Acartia* spp. (50–60%) and *Pseudocalanus* spp. (20–30%) (Schulz, 1985).

Within the present studies, for the four expeditions in the Baltic Sea, a mean zooplankton (dry) biomass of 34 (2–239) mg m^{-3} was found. This value was comparable to that

Table I Mean (bold) and median (underlined) values -in μg g^{-1} dry weight-, and relative standard deviations (RSD—in ± %—italics) for metal contents in plankton of the Baltic Sea and adjacent areas, 1980–84

	Al	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Baltic Sea			*Sept 1980* (*n* = 13)								
	180	**3.7**	**0.61**	**2.0**	**23**	**570**	**0.19**	**90**	**5.7**	**8.3**	**42**
	67	*39*	*37*	*101*	*58*	*86*	*49*	*167*	*32*	*96*	*38*
	210	3.5	0.61	1.7	19	510	0.16	30	6.2	6.6	44
			May–June 1981 (*n* = 18)								
	200	**1.3**	**0.86**	**4.0**	**15**	**900**	**0.06**	**30**	**5.7**	**14.3**	**94**
	95	*59*	*25*	*61*	*30*	*114*	*32*	*100*	*35*	*156*	*95*
	140	1.2	0.85	3.8	14	570	0.06	20	5.4	4.6	61
			June–July 1983 (*n* = 20)								
	50	**3.9**			**13**	**500**	**0.05**	**30**	**4.6**	**2.5**	**320**
	60	*60*			*37*	*130*	*29*	*67*	*26*	*139*	*53*
	40	3.4			12	160	0.04	20	4.5	0.9	259
			Nov–Dec 1984 (*n* = 21)								
	600	**5.4**	**0.34**	**8.3**	**29**	**2640**	**0.37**	**40**	**10.8**	**19.7**	**573**
	162	*194*	*71*	*116*	*46*	*95*	*62*	*75*	*68*	*141*	*62*
	290	2.7	0.28	3.5	27	2090	0.36	30	8.4	6.3	466
Kattegat			*May–June 1981* (*n* = 5)								
	70	**0.8**	**0.80**	**1.8**	**9**	**320**	**0.07**	**20**	**2.2**	**4.2**	**36**
	43	*38*	*7*	*76*	*31*	*94*	*42*	*50*	*35*	*61*	*24*
	80	0.6	0.80	1.3	9	180	0.05	20	2.0	3.5	40
			June–July 1983 (*n* = 5)								
	220	**2.0**			**13**	**680**	**0.05**	**50**	**4.8**	**4.1**	**228**
	41	*14*			*24*	*66*	*40*	*40*	*53*	*57*	*22*
	240	1.9			11	510	0.05	60	3.9	3.9	
			Nov–Dec 1984 (*n* = 6)								
	600	**3.9**	**0.59**	**8.1**	**73**	**1960**	**0.65**	**50**	**4.8**	**10.8**	**673**
	47	*54*	*26*	*61*	*116*	*58*	*27*	*60*	*34*	*64*	*67*
	550	3.9	0.60	7.2	31	2010	0.64	50	5.5	8.7	577

North Sea			*May–June 1981* ($n = 5$)								
	90	**2.0**	**0.77**	**3.9**	**18**	**1450**	**0.06**	**10**	**2.8**	**6.1**	**42**
	89	*72*	*24*	*90*	*62*	*90*	*36*	*100*	*69*	*69*	*14*
	40	1.8	0.85	2.0	14	1610	0.06	10	2.2	6.9	42
			June–July 1983 ($n = 4$)								
	690	**1.8**			**18**	**1760**	**0.07**	**50**	**6.0**	**9.4**	**408**
	117	*15*			*35*	*81*	*55*	*120*	*42*	*54*	*45*
	400	1.8			16	1560	0.06	30	5.0	9.0	405
NE Atlantic Ocean			*May–June 1981* ($n = 9$)								
	10	**7.1**	**0.62**	**3.8**	**11**	**310**	**0.02**	**4**	**5.5**	**5.9**	**40**
	89	*63*	*38*	*113*	*48*	*123*	*30*	*65*	*101*	*143*	*53*
	10	4.9	0.58	2.1	10	110	0.02	4	3.3	3.5	42
			June–July 1983 ($n = 5$)								
	130	**4.5**			**13**	**960**	**0.05**	**20**	**5.9**	**6.2**	**468**
	46	*22*			*70*	*42*	*47*	*19*	*44*	*62*	*77*
	110	4.0			11	600	0.04	20	6.1	4.5	342

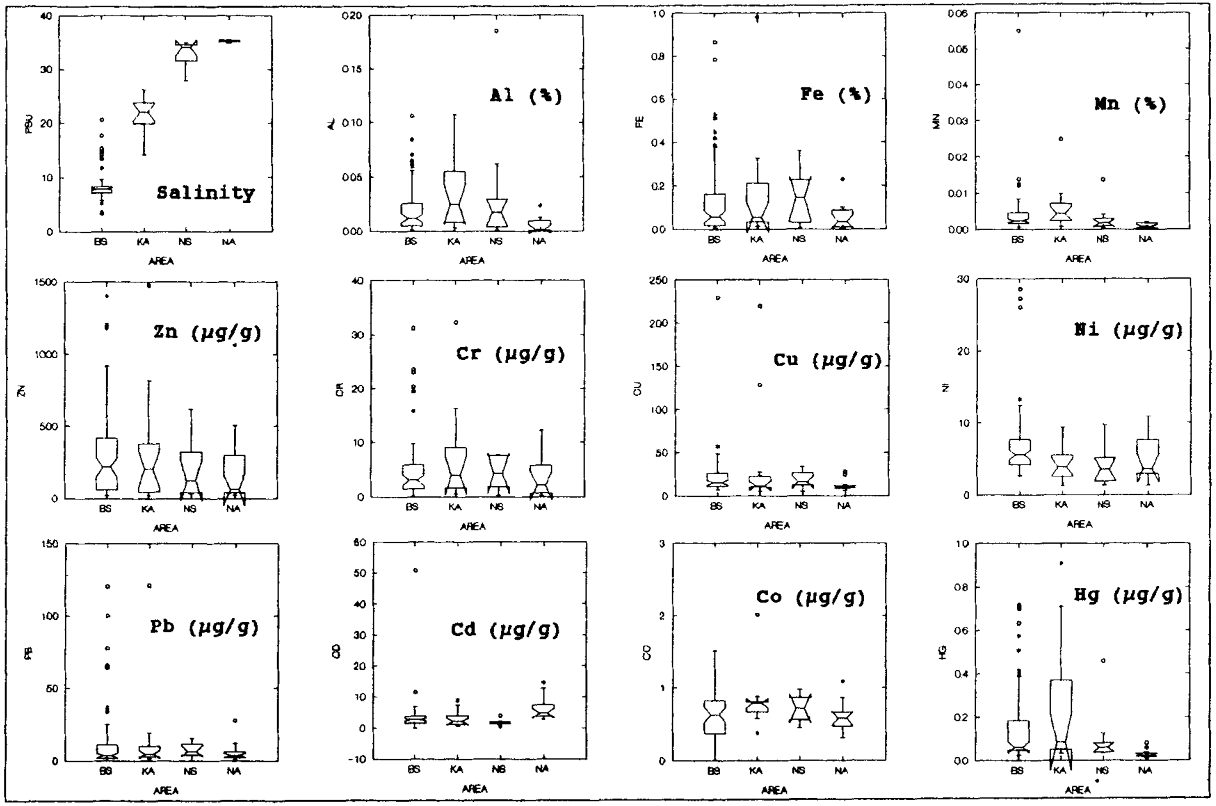

Figure 2 Multiple notched box- and-whisker plots for the different data sets on metal contents in zooplankton and on salinity (‰), 1980–84, (*BS* – Baltic Sea, *KA* – Kattegat, *NS* – North Sea, *NA* – NE Atlantic Ocean. (*central line: median, central box: 50% of the data, notch: confidence interval for the median, whiskers: extending to the minimum and maximum, separate points: outliers exceeding 1.5 times the interquartile range*)

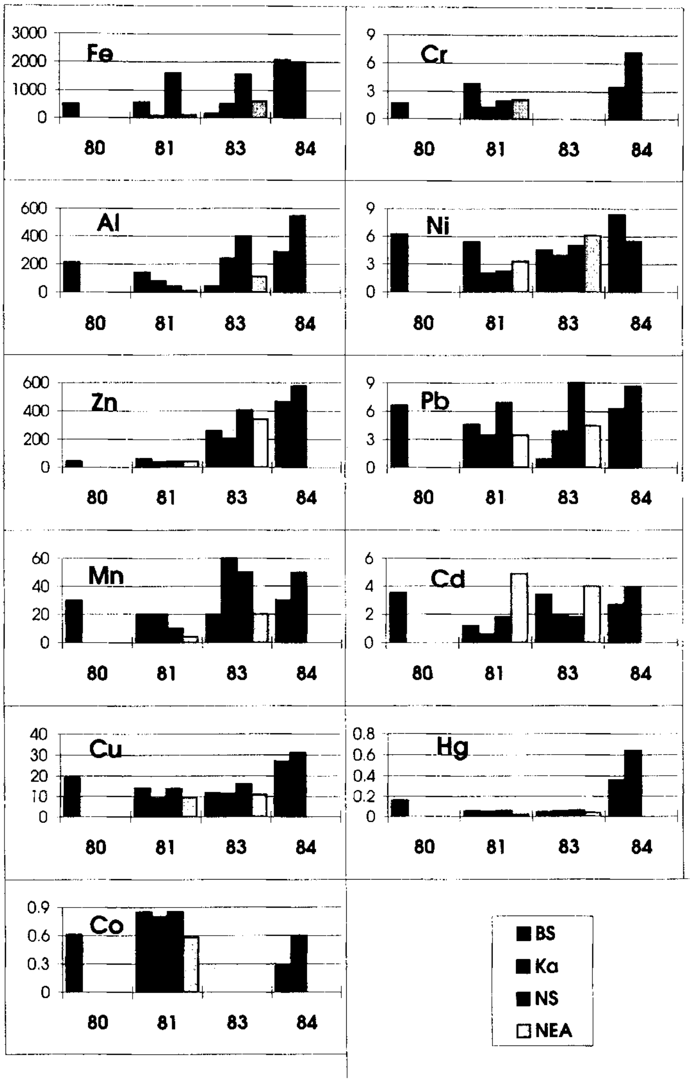

Figure 3 Median values in $\mu g\,g^{-1}$ dry weight of metal contents in zooplankton, 1980–84. (Sampling: *IX-1980*; *V/VI-1981*; *VI/VII-1983*; *XI/XII-1984*. *BS*: Baltic Sea; *Ka*: Kattegat; *NS*: North Sea; *NEA*: NE Atlantic Ocean)

obtained for the North Sea (38 mg m^{-3}) and for the NE Atlantic Ocean (33 mg m^{-3}). However, within the Baltic Sea the means for the four years differed significantly, from only 9 mg m^{-3} (Nov./Dec. 1984), to 18 mg m^{-3} (May/June 1981) and 63 mg m^{-3} (Sept. 1980, June/July 1983). This is assumed to be caused by both seasonal and spatial effects.

In Table II, our data are listed together with those published by other authors for copepods and mixed "zooplankton" samples taken from different sea areas. The arithmetic means given for metals in mixed "zooplankton" samples may be misleading

Table II Metal content in zooplankton (in $\mu g\,g^{-1}$ dry weight) from different areas including means (bold), ranges: (italics), medians (underlined), year of sampling, mesh size of the used plankton net (in mm), number and type of the sample

Ref.	this work	[1]	[1]	[1]	[2]	this work	this work	[3]	[4]	this work	[5]	[6]	[7]
Area	Baltic Sea	Baltic Proper	Gulf of Finland	Gulf of Riga	southern Baltic	Kattegat	North Sea	North Sea	North Sea	NE Atlantic	NE Atlantic	Arctic & Atlantic	Pacific
Year	1880–84	1979–82	1979–82	1979–82	1980	1981–84	1981–83	1991	1990	1981–83	1974	1989–90	1970
mm	0.2	0,1–0.2	0.1–0.2	0.1–0.2	0.2, 0.33	0.2	0.2	0.3	0.3	0.2	0.2	0.33	0.36
No.	72	233	303	39	20	16	10	230		14	49	101	14
Type	mixed ZP	mixed ZP	mixed ZP	mixed ZP	mixed ZP	mixed ZP	mixed ZP	mixed ZP	*Calanus*	mixed ZP	mixed ZP	*Calanus*	mixed ZP
Al	**200** *20–1070* 120					**360** *30–1070* 250	**350** *10–1860* 170			**50** *10–240* 20			**17** *9–31* 15
Cd	**3.6** *0.5–51* 2.7	**1.4** 0.5–1.0	**1.3** 0.5–1.0	**6.3**	**1.7** *<0.2–4.6*	**2.9** *0.6–8.9* 2.0	**1.8** *0.6–4.1* 1.7	**0.2–51**	**5.9** *2.7–13.1* 4.4	**6.1** *2.8–14.6* 4.7	**9.4** *0.5–28.5*	**2.0–8.9** *0.8–15.7* 2.3	**2.4** *1.9–3.5*
Co	**0.62** *0.01–1.52* 0.63				*<0.1–1.3*	**0.83** *0.38–2.02* 0.79	**0.72** *0.45–0.98* 0.72			**0.62** *0.31–1.09* 0.58			
Cr	**5.3** *0.2–31.3* 3.1					**7.5** *0.6–32.4* 4.0	**4.4** *0.3–7.8* 4.4			**3.8** *0.3–12.3* 2.1			*<1.0–137*
Cu	**22** *7–230* 15	**21** 10–15	**25** 10–15	**16**	**30** *5–78*	**46** *5–220* 12	**19** *5–34* 16	**2–34**	**7.5** *4.4–12.4* 7.4	**12** *7–29* 10	**24** *2–230*	**3.9–8.4** *2.1–15.9*	**15** *6–58* 12
Fe	**1270** *70–8670* 600				**1780** *300–6800*	**1580** *130–9840* 540	**1560** *70–3610* 1450			**540** *40–2310* 350		**59–207** *10–271*	**490** 90–1720 100

Hg	**0.16** *0.02 -0.72* 0.06					**0.24** *0.03–0.91* 0.09	**0.10** *0.03–0.46* 0.06			**0.03** *0.01–0.08* 0.03			**0.14** *0.04–0.45* 0.11
Mn	**40** *10–550* 20				**29** *5–120*	**60** *10–250* 40	**30** *10–140* 20			**10** *5–20* 10			**4.5** *2.9–7.1* 4.3
Ni	**6.9** *2.6–28.6* 5.6				**8.6** *1.0–16.6*	**4.0** *1.3–9.4* 3.9	**4.0** *1.3–9.7* 3.6		**2.4** *1–5.5* 1.9	**5.7** *1.3–18.3* 3.6		*0.4–9.6*	**98** *5–608* 8.4
Pb	**12** *0.3–120* 3.9	**18** 5–10	**17** 5–10	**8**	**27** *1–120*	**14** *2–122* 4.7	**7.4** *0.5–15.4* 6.7		**1.1** *0.4–2.3* 1.0	**6.0** *1.0–28.1* 3.8	**44** *1–480*	**0.4–2.0** *0.06–6.4*	**7.2** *1.5–14.4* 2.1
Se	**1.4** *0.2–3.2* 1.1					**2.8** *2.6–3.2* 2.8	**2.0**						
Zn	**308** *2.3–1410* 218	**320** 250–300	**340** 200–250	**130**	**1170** *40–4800*	**330** *23–1480* 206	**213** *36–621* 124	**45–520**	**115** *55–171* 114	**199** *25–1070* 63	**174** *36–1390*	*33–271*	**264** *50–750* 180

[1] Davidan and Savchuk, 1989 (including citations of other papers published in the Russian literature)
[2] Szefer *et al.*, 1985 (Gdansk Bay and Slup Furrow; samples dominated by *Pseudocalanus elongatus*)
[3] Weber *et al.*, 1991 (8 zooplankton species analyzed separately; 165 of the 230 samples from 3 cruises represented copepods)
[4] Haarich *et al.*, 1992 (samples from one cruise in autumn 1990 covering 7 transects with 47 stations)
[5] Brügmann, 1978 (measurements performed by anodic stripping voltammetry)
[6] Pohl, 1992 (samples from 2 expeditions into the Arctic Ocean and from one transect Capetown-Bremerhaven)
[7] Martin and Knauer, 1973 (samples taken 10 miles offshore-water depth 1000 m- and from a transect Monterey Bay - Hawaii)

because the results could be biased by a high content of metal-rich phytoplankton or other suspended particulate matter. Therefore, we preferred as other authors (Boström *et al.*, 1974; Martin and Knauer, 1973) to rely mainly on the geometric means. Because of the many variables involved in the sampling (area, season, mesh-size of the net, precautions against co-collection of non-zooplanktonic material), all of which may cause significant variations in the metal contents of the so-called "zooplankton" samples finally analyzed, it does not make much sense to try an in-depth comparison between the different sets of data summarized in Table II. For nearly all metals investigated, the contents in "zooplankton" seem to fall into the same order of magnitude, and obvious differences could be explained by spatial effects or different sampling procedures. Other data published for the Baltic Sea (Davidan and Savchuk, 1989; Szefer *et al.*, 1985) agree reasonably well with our results, especially for Cd, Cu, Fe, Mn, Ni, Pb, and Zn.

The main objective of our studies was to obtain information on possible contaminant distribution patterns within the Baltic Sea. These patterns should be supported by and related to contaminants in adjacent sea areas. In general, this resulted in a less dense station network and, because of higher costs for fuel and ship-time, in a lower sampling frequency for the North Sea and the north-eastern Atlantic Ocean. Therefore, for those areas, the results listed in Tables I and II may not be very representative.

Whereas for dissolved and particulate metals in the water, the expected gradients of decreasing concentrations from the Baltic Sea towards the Atlantic Ocean could be clearly shown (Brugmann, 1986, 1992), this was not the case for the elemental composition of mixed "zooplankton" samples.

In addition to calcium and magnesium in "zooplankton", which clearly increased from the brackish Baltic waters towards the more saline waters of the Kattegat, North Sea and the ocean, for the metals discussed in the present paper only manganese, aluminium and mercury seem to reflect clear gradients of successively decreasing contents when approaching Atlantic waters. Both manganese and aluminium in the zooplankton from the Baltic Sea were significantly correlated with the particulate metal concentrations. This could simply reflect the co-collection of such suspensions. Because of the high river input, the high primary production and the low average depth favouring resuspension of fine-grained deposits, the suspended particulate matter present in the Baltic Sea is about ten times higher than in the investigated oceanic areas. The ingestion of manganese and aluminium-rich material, and the adsorption of dissolved species, for example on to chitin surfaces of copepods, could further contribute to their accumulation by the zooplankton.

The changes in the mercury content in Baltic "zooplankton" between 1980 and 1984 (Fig. 3) were also reflected by the total mercury concentrations in the water. This could be due to seasonal effects. In November/December 1984, significantly higher mercury concentrations in the water and the highest mercury contents in the "zooplankton" were registered. With selenium, only analyzed in samples taken in 1984, mercury was negatively (99% probability) correlated (Table III). This may due to the antagonistic behaviour between these elements in marine biota.

For lead and chromium, spatial trends would probably also have been apparent, provided that samples had been rigorously "cleaned" from phytoplankton agglom-

Table III Spearman's correlation matrix for the metal content of zooplankton from the Baltic Sea, 1980–84 ($n = 71$)

	Al	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Zn
Cd												
Co		–										
Cr	+++	+										
Cu	+++	+++	––	+++								
Fe	+++			+++	+++							
Hg	+++		–––	––	+++	+++						
Mn	+++		++	+	++	+++						
Ni	+++			++	+++	+++	++	+				
Pb	+++		+	+++	+++	+++	++	+++	+++			
Se		+++		+++			–––	+		+		
Zn		++	––	+++	++	+++			++	+	+	
Me_{cont}	+++					+++	0	+			0	+++
Me_{conc}	+++					+++	0	+++			0	+++
Me_{diss}	0	–	+++	0			+++	0			0	+
Salin.			++	++		++	–			+		+

$Me_{cont.}$ Metal content of the suspended particulate matter ($> 0.4\,\mu m$; in $\mu g\,g^{-1}$ or % of dry matter)
$Me_{conc.}$ Concentration of particulate metals in the water during sampling (in $nmol\,l^{-1}$)
$Me_{diss.}$ Concentration of dissolved (for Hg total) metals in the water during sampling (in $nmol\,l^{-1}$)

	probability
–, +	>90%
––, ++	>95%
–––, +++	>99%
0	no data

erates and other non-zooplankton material prior to analysis, or if only selected specimens had been picked out for analysis. The lead contents in the "zooplankton" samples covered a very wide range. This may reflect mainly the percentage of phytoplankton and detrital particles in the samples which effectively adsorb dissolved and agglomerate the particulate lead. Consequently, in both particulate matter $> 0.4\,\mu m$ and in phytoplankton from the Baltic Sea between 100 and 300 $\mu g\,Pb\,g^{-1}$ was found (Brügmann, 1986; Davidan and Savchuk, 1989). Zooplankton may take up lead by ingestion of particles and by adsorption. For lead in North Sea zooplankton, Haarich *et al.* (1992) found a positive correlation with the lead content of suspended particulate matter.

The cobalt contents show only small variations with a tendency to higher values for the Kattegat samples. This is in agreement with the significantly higher dissolved and particulate cobalt concentrations found by us in that area for the period 1980–91 (Brügmann, 1992). Other authors (Granéli and Haraldsson, 1993) speculated on a relationship between higher cobalt inputs from the surrounding Swedish catchment area, higher cobalt concentrations in Kattegat waters and the repeated occurrence of toxic dinoflagellate (*Chrysochromulina polylepis*) blooms.

Zinc contents in Baltic "zooplankton" increased over the investigated period by more than 10-fold, i.e., from a median value of 44 $\mu g\,g^{-1}$ in 1980 to 466 $\mu g\,g^{-1}$ in 1984. This is still in the range of zinc values reported by other authors for the Baltic Sea and related areas. The increase can hardly be interpreted as a real temporal trend caused by increasing contamination of the marine environment. It is known that the plankton animals may well regulate their zinc content (Pohl, 1992); this may change widely depending on season and the species composition of the samples (Weber *et al.*, 1991). On the other hand, zinc contents in the "zooplankton" were positively correlated with the concentration of particulate zinc in the water, and with the zinc content of suspended particulate matter. The observed differences in zinc contents in "zooplankton" could thus be caused and accompanied by corresponding differences in the zinc content of the food organisms. Direct sampling of zinc-rich suspended matter including phytoplankton cells with the 0.2 mm net may have contributed to this effect. Between 1980 and 1984, a tendency to higher dissolved zinc concentrations in the water was also noticed (Brügmann, 1992). Unfortunately, the existing data base on zinc and other trace metals in different compartments of the Baltic ecosystem is insufficient to take account of seasonal variations.

The concentrations of dissolved and particulate cadmium in the water decreased from the Baltic Sea to the NE Atlantic Ocean via the North Sea. Cadmium content in zooplankton did not follow this trend; indeed median values showed higher concentrations towards the ocean. Similar results were obtained by Weber *et al.* (1991) who observed lower cadmium in zooplankton from the more strongly contaminated parts of the North Sea than in the less impacted open ocean. Cadmium is taken up by the zooplankton mainly via the food chain and cannot be regulated. The Baltic Sea and parts of the North Sea are strongly contaminated with metals, including cadmium, but even more so with nutrients. This "nutrification" is the main cause of the higher primary production (eutrophication). Biologically available cadmium species will be taken up by the often excessive growth of phytoplankton. However, even in the "hot-spot" areas of severe heavy metal contamination, there may be a higher potential to "dilute" the cadmium within a greater phytoplankton biomass. In eutrophic areas of many parts of the Baltic and the North Sea, herbivorous zooplankton during most of the year can easily find food that is scarcely higher in cadmium than phytoplankton from the open ocean. Furthermore, in the Baltic Sea, zooplankton does not need so much food to compensate for energy lost in the search for food or for energy lost for osmotic regulation in more saline waters or due to lower temperatures such as found in polar regions. Consequently, the necessarily higher feeding rate in oceanic and especially polar regions may, together with speciation of dissolved cadmium, be one of the main reasons for its higher accumulation in zooplankton there, compared with waters with higher levels of dissolved cadmium.

Pohl (1992) analyzed copepods from the Arctic and Atlantic Oceans and found cadmium contents between 0.8 and 15.7 $\mu g\,g^{-1}$. The lowest contents were observed before the phytoplankton bloom and in mainly carnivorous animals from greater depths. The maximum values (mean 12 $\mu g\,g^{-1}$) were recorded for *Pontellidae* from the Atlantic Ocean which feed continuously in the uppermost part of the euphotic layer. A significantly positive correlation between the cadmium content of *Calanus* and of suspended particulate matter of samples from the North Sea was reported by Haarich *et al.* (1992).

Aside from a few exceptionally high values, there was no statistically significant gradient but only a weak decreasing tendency in the copper content of "zooplankton" from the Baltic Sea to the ocean. Copper is considered to belong to the group of biologically regulated trace elements. This would affect its correlation, as for zinc, with the metal content of suspended particulate matter (Haarich *et al.*, 1992). With dissolved copper, however, those authors found a negative relationship.

For nickel, the lowest variability within the zooplankton metal data was seen. Except for higher nickel values in samples taken during November/December 1984 in the Baltic Sea, there is no clear gradient between the data from different areas. This is in agreement with the finding that the Baltic Sea has no particular nickel contamination problem. Nickel concentrations in the water column occur predominantly in dissolved forms. The concentration patterns are only to a minor degree influenced by inputs from industry, rivers, sediments and atmosphere, or by uptake by phytoplankton and or by major changes in the redox properties of the water, including anoxic conditions. Nevertheless, there is, as for cadmium, a clear decrease in nickel concentrations in samples from the Baltic Sea towards the ocean which inversely follows the salinity increase. Provided that nickel accumulation by phytoplankton is diluted, as for cadmium as discussed above, in a greater biomass, the nickel content in "zooplankton" need not necessarily be physiologically regulated to compensate for the higher nickel concentrations in brackish and freshwater areas. On the other hand, as for copper, the speciation of nickel in Baltic waters is characterized by a very high content of organically complexed forms which may not be bioavailable. Because of the lower 'standing stock' of potential chelators in oceanic waters, the bioavailable concentrations of copper and nickel may be similar to those in the Baltic Sea. As yet there are not enough reliable data available on nickel contents of phytoplankton and zooplankton together, nor for nickel concentrations in the water of these areas, to check the alternative explanations discussed above. For the North Sea, Haarich *et al.* (1992) found a relationship of nickel content in *Calanus* significantly positive with that in suspended particulate matter but negatively correlated with dissolved nickel in the water.

The iron content of Baltic zooplankton samples varies over a rather broad range, with lowest values for a typical summer zooplankton community (median: 160 $\mu g\, g^{-1}$, June/July 1983), intermediate values for the period following the spring and late summer blooms (510 and 570 $\mu g\, g^{-1}$, September 1980 and May/June 1981) and a maximum value in winter (2090 $\mu g\, g^{-1}$, November/December 1984). As for aluminium, zinc and partly also for manganese, the iron content in Baltic "zooplankton" is significantly (99%) positively correlated with concentrations of particulate iron and with the iron content of suspended particulate matter. Towards the North Sea, the iron content of "zooplankton" increases. This follows closely the gradients found for both the dissolved and suspended iron concentrations in those waters and the iron content in suspended particulate matter (Brügmann,1986). The iron content of "zooplankton" collected from oceanic areas is lower. The oceanic data obtained in 1981 represent samples from the more northern parts of the Atlantic. They fall into the range found by Pohl (1992) for the Arctic and Atlantic Oceans. In 1983, all our oceanic "zooplankton" samples were taken from the Bay of Biscay. The iron levels of these samples compare well with those given by Fowler (1986) for the Mediterranean Sea.

As can be seen from Table III, many of the metals analyzed in the Baltic "zooplanton" are significantly correlated with each other. This is especially true for those elements which are essential for the zooplankton and are regulated or controlled (Cu, Zn, Fe, Ni). In part, these metals are correlated with their dissolved (Co, Hg) and particulate (Al, Fe, Mn, Zn) concentrations in the water. This may reflect both causal or random relationships.

Diaz and Fernandez-Puelles (1988) analyzed mixed zooplankton samples taken around the Canary Islands for seven metals. They found highly significant correlations between the contents of iron and copper, iron and nickel, and nickel and copper. These three metals were accumulated increasingly with the size (age) of zooplankton organisms, whereas zinc seemed to be regulated efficiently. For the Baltic Sea, using nets of different mesh sizes (0.09–0.17 mm) for "zooplankton" sampling, Davidan and Savchuk (1989) observed no significant correlations between the size of the animals, which varied between about 0.1 and 2 mm, and their metal (Cd, Cu, Pb, Zn) contents.

CONCLUSIONS

Not surprisingly, the use of "zooplankton" as a monitoring tool to detect spatial and temporal trends in the Baltic Sea showed several drawbacks. The sampling frequency and the number of samples taken for the present study could not be adjusted to the broad range of variations introduced by different hydrographic conditions, seasons and species composition. Consequently, from the resulting data sets on metal contents in mixed net-zooplankton covering four years, no significant conclusions can be drawn regarding possible temporal trends within the Baltic Sea during that period. For the detection of such trends, it is premature to increase the sampling frequency and monitoring should continue for a longer time span during which the sampling methods should not be changed. However, the sampling frequency should cover at least two typical stages in zooplankton development in the Baltic Sea, i.e. the low production winter period and the post-spring bloom situation. Sampling for "zooplankton" during the bloom may result in a 90% phytoplankton catch within the collected sample (Weber *et al.*, 1991). The number of sampling stations chosen for the present study may be sufficient for future work. Biological investigations of species composition in duplicate samples should be mandatory.

For only a few of the metals analyzed in "zooplankton" the spatial distribution patterns in the Baltic Sea and their gradients towards adjacent seas seem to follow the same patterns as the dissolved metal concentrations in the water, which are lowest in the open ocean and highest in the brackish Baltic Sea. On the other hand, significant correlations were found between metals in zooplankton and in suspended particulate matter. Therefore, complex investigations, including measurements of metals in dissolved and particulate forms, should be continued. In addition, to obtain reliable baseline data on biotic and abiotic metal transformations and cycles in the Baltic Sea ecosystem, metal investigations on phytoplankton should also be carried out. This kind of information is needed urgently to improve current estimates of fluxes and mass balances.

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