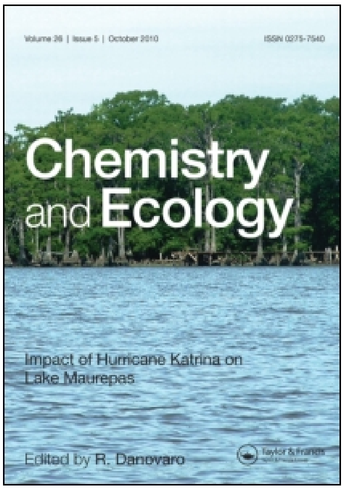

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Trace Metal Studies on the Starfish *Asterias rubens L.* From the Western Baltic Sea

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In 1984, 115 samples of the starfish *Asterias rubens L.* collected in the south-eastern part of Cadet Trench (Mecklenburg Bay/Western Baltic Sea) were analyzed for their contents of a few major (calcium, magnesium) and trace elements (cadmium, copper, iron, mercury, manganese, nickel, lead, selenium and zinc). Distinct differences were found between starfish from different stations, and these are attributed to the composition of the sediments acting as a substrate for their prey (mussels, snails). Except for cadmium, the concentrations of the elements studied all correlated negatively with the diameter and weight of the starfish.

Parallel analyses of starfish arms and the central discs of the same animals showed that iron, zinc, copper and mercury levels were 16 to 30% higher, and selenium, manganese, magnesium, calcium and lead were 4 to 9% higher in the arms. Cadmium concentrations were 20% higher in the central discs than in the arms.

Stock estimations (about 52,000 tons fresh weight) show that starfish play a significant role in the benthic ecosystem of the western Baltic Sea. They can consume up to 200,000 tons of mussels and clams (*Mytilus edulis, Macoma baltica*) a year and may therefore represent a notable factor in the trace metal balance of the region.

INTRODUCTION

The starfish *Asterias rubens L.* plays an important role in the benthic ecosystem of the western Baltic Sea. It reaches considerable population densities, for instance, up to 800 individuals per square metre in mobile algal carpets in Lübeck Bay (Anger *et al.*, 1977). According to Nauen (1978) this species consumes around 1%, and according to Anger *et al.* (1977) between 1.9 and 11.4%, of its weight per day as food. In the western Baltic Sea, *Asterias rubens* can achieve diameters of up to 30 cm (Arndt, 1969), and its growth rate is reported to be 20 to 100 mm annually (Milliman, 1974). In the Baltic Sea the growth rate reaches its maximum of about 0.6 mm per day during the "log phase" in summer, but growth of the calcareous exoskeleton drops to less than a tenth of this value during the "waiting phase" (Nauen and Böhm, 1979). The eastern distribution limit for this species in the Baltic Sea is usually given as Darss Sill (Arndt, 1964, 1969; Nauen, 1978). Although capable of tolerating salinities down to 10‰, 14.5 to 15‰ are necessary for reproduction and normal development. In Mecklenburg Bay and the Cadet Trench, starfish are therefore generally found at depths greater then 10 m, but in Kiel Bay they are also present in shallow water.

The starfish stock in Kiel Bay is estimated to be 32,000 tons fresh weight. Feeding mainly on small snails (*Hydrobia ulvae*), mussels (*Mytilus edulis* and *Macoma baltica*) and their spawn, they can consume up to two mussels in three days (Anger *et al.*, 1977). This corresponds to an annual food intake of around 120,000 tons of food organisms in Kiel Bay alone (Nauen, 1978) and illustrates both the economic importance of starfish, for instance as a potential threat to mussel banks, and also their possible importance as contaminant accumulators in the bio-geochemical flux of matter in the sea.

The available data pool concerning levels of contaminants such as heavy metals, chlorinated and petroleum hydrocarbons, radionuclides, etc., in *Mytilus edulis,* one of the most important food sources for the starfish, has reached almost unmanageable dimensions, partly as a result of "mussel-watch" programmes (Goldberg, 1975), but there are virtually no comparable data concerning starfish. The few data available are restricted to alkali elements (sodium, potassium), alkaline earth elements (magnesium, calcium, strontium) (Binyon, 1978; Nauen and Böhm, 1979), phosphorus and silicon (Milliman, 1974) and a few chlorinated hydrocarbons (Riley and Wahby, 1977). The purpose of the studies described here was to close, at least partially, the obvious gap in our knowledge regarding trace metal levels in these macrobenthic marine animals.

MATERIAL AND METHODS

The starfish for our studies were collected by divers at three stations with different depths and bottom types in the southeastern part of Cadet Trench (Mecklenburg Bay/Western Baltic Sea) (Table I). They were washed in sea water, placed in plastic bags and frozen. After defreezing at the laboratory, the animals were sorted by size (i.e. diameter) in a dust-free environment, thoroughly flushed with deionized water and, after surplus water had drained off, accurately measured and weighed. The starfish were weighed again after freeze-drying and then digested with nitric acid in quartz vessels. As a rule each animal was treated separately, but occasionally where the diameter was less than 4 cm several animals were pooled to form a single sample. In addition, the arms of 17 animals were analyzed separately from the central discs.

The dried weights of the samples varied between 0.06 and 1.8 g. A total of 15 ml of sub-boiling distilled nitric acid was used for digestion. The samples were left overnight with 10 ml of HNO_3,

TABLE I
Sampling stations for starfish in Cadet Trench

Station No.	365–6	365–7	385–4
Position	54°30.6′N/ 12°16.5′E	54°29.8′N/ 12°18.2′E	54°27.5′N/ 12°18.5′E
Date	12.04.1984	12.04.1984	15.04.1984
Depth (m)	19.5	21.3	15.5
Salinity (‰)	>18	>18	ca. 15
Temperature (°C)	<2.5	<2.5	2.6
Samples (n)	46	53	16

Remarks:

[a] Station 365–6: Substrate is marl, partly covered by a thin layer of medium and coarse sand. Stones up to a diameter of 0.4 m were often observed and were colonized by *Mytilus edulis*. Numerous individuals of the seastar were present, some of them with diameters of more than 20 cm.

[b] Station 365–7: Substrate is muddy fine sand with medium sand fractions. The substrate layer is about 1 m thick and only sporadically overgrown.

[c] Station 385–4: Substrate is medium sand with coarse sand fractions. Frequently, pebbles colonized by *Mytilus edulis* were observed. Starfish densities were 15 to 16 specimens per square metre.

whereupon they were heated to 73°C, slowly concentrated by evaporation, oxidized again with 5 ml nitric acid solution and made up to the desired volume in 25 ml quartz measuring flasks.

Metal concentrations in the digestion solution were measured by modified atomic absorption spectroscopic methods (AAS). AAS with an air acetylene flame was used for the quantitative determination of calcium, magnesium (after 1:50 dilution in each case), zinc, manganese, iron and copper. These measurements were made with a PE 4000 (Perkin–Elmer) unit. The same unit with HGA 400 tubular graphite cuvettes and an AS 40 automatic pipette was used for the flameless AAS determination of cadmium, nickel, lead and selenium. The stabilized temperature platform furnace method of Slavin *et al.* (1981) was used for these measurements. The aim of this is to achieve atomization with the cuvette temperature in a state of relative equilibrium through interruption of the inert gas flow, extremely high electrothermic heating rates and the use of substances to modify the matrix. The pyrolytically coated graphite tubes were equipped with glassy carbon platforms (both from VEB Elektrokohle Lichtenberg, Berlin). A 1.6% $NH_4H_2PO_4$ matrix modifier was used and added to the analyte on the platform in a volume ratio of 1:1. The solution was prepared from a chemical of reagent grade and further purified by solvent extraction with freon following addition of a complexing agent (APDC). (Slavin and Manning, 1979). Selenium concentrations were measured using the method described by Welz *et al.* (1984) in the presence of a mixed magnesium nitrate and Cu^{II} solution. Mercury analysis was performed by flameless "cold vapour" AAS using the Sn^{II} reduction/ventilation method. Intermediate concentration on quartz wool, on which gold had been deposited by evaporation, helped to increase the sensitivity of the method and to reduce interference phenomena.

The accuracy of the measurements was checked by parallel analysis of reference samples such as IAEA standard samples MAA-1 (copepod homogenate) and MAA-2 (fish flesh) containing certified amounts of the elements under analysis. The values obtained for these standard samples lay within acceptable limits, i.e. within twice the standard deviation of their certified contents. The relative standard deviation for the methods used was checked against the same standards and differed from element to element, but was below ±10% except for selenium (±18%).

RESULTS AND DISCUSSION

To avoid the risk of contamination associated with the use of mechanical homogenizers, the freeze-dried samples were cut only into fairly large pieces before digestion. To find out whether this affected the analytical results on the distribution of the metals in the different samples, several parallel analyses were performed, for instance on different arms of the same starfish or on the halves of the central discs. The differences between the value pairs yielded by these experiments were quite small within the constraints set by the standard deviation for our analytical procedures. It can therefore be assumed that the differences between metal concentrations in the arms and central discs of starfish, and the variations of these concentrations between collection sites are significant.

Table II presents a statistical review of the results. It is immediately evident that copper, iron and selenium levels, and to a smaller degree also zinc, manganese, lead, nickel, mercury and cadmium levels, are higher in starfish from station 365–7 than in those from the other two sampling sites. The copper and iron concentrations are found to be twice as high, for example. Positive deviations of the mean metal concentrations in these animals from those of starfish collected at station 365–6, which was only about one nautical mile away, were 140% for iron, 108% for copper, 60% for selenium, 42% for lead, 31% for manganese, 22% for zinc, 18% for mercury, 13% for cadmium. If the quotient of the mean dry weight and diameter per size class of the samples is taken as a parameter *F*, of feeding and growth conditions, there were no significant differences between these two stations ($F = 0.27$ and $0.25\,\mathrm{g\,cm^{-1}}$ respectively). It is therefore assumed that the concentration differences must be attributed to the quality of the sea bed at the two sites. Our experience from studies on the metal content of sediments taken in the western Baltic has shown that metal concentrations in the muddy fine sand at station 365–7 can be orders of magnitude higher than in clean coarse or moderately fine sand or marl (Brügmann and Lange, pers comm). Mussels, which were quite common at all stations (Table I), are the main food source of the starfish. Being filter feeders, they can accumulate metals from the sediment both through direct contact with bottom waters and by the ingestion of suspended matter. Owing to the remobilization processes associated with the initial stages of diagenesis, the pore water of muddy sediments, which is in a state of constant exchange with the near-bottom water through diffusion, compaction, bioturbation and turbulent mixing, much higher metal concentrations were found close to the starfish area than in the pore water of clean sand and marl. The higher metal uptake by starfish at station 365–7 could therefore take place both via the food web or directly from the pore water.

Further investigations regarding the metal contents of the different sediments, their pore water and the organisms inhibiting both the sediment and the water immediately above it could help confirm our interpretation of the data.

Histograms of the measured metal concentrations (Figure 1) also illustrate the differences between the stations. Taking all values into account, the most frequent concentrations are 9–12% (calcium), 1.3–1.4% (magnesium), 280–320 $\mu g \cdot g^{-1}$ (zinc), 25–30 $\mu g \cdot g^{-1}$ (manganese), 15–20 $\mu g \cdot g^{-1}$ (iron), 8–10 $\mu g \cdot g^{-1}$ (nickel), 0.3–0.45 $\mu g \cdot g^{-1}$ (cadmium and lead), 0.2–0.3 $\mu g \cdot g^{-1}$ (selenium) and 45–60 $ng \cdot g^{-1}$ (mercury) (Table II).

Since these "geometric" means either contain or are close to the arithmetic means except in the case of copper (Table II), one criterion for normally distributed data populations is fulfilled in most cases. Figure 1 shows that the maximum of the data subpopulation from station 365–7 is further to the right on the concentration axis towards higher values for several elements than the other two stations. The differences between stations 365–7 and 385–4 can be explained in terms of different hydrographic conditions, including water depth and salinity (differences: about 6 m and 3‰ respectively), and the corresponding differences in growth and metal accumulation conditions, but stations 365–6 and 365–7 obviously differ only with respect to sediment quality.

Due to a lack of comparable data for the starfish, a literature search was performed on published trace metal contents in other echinoderms. Investigations on sea-urchins (*Echinocardium*

TABLE II
Metal contents in starfish of 3 stations in Cadet Trench (concentrations given on dry weight basis)

	Station 365–6 (19.5 m, $n = 35$)	Station 385–4 (15.5 m, $n = 21$)	Station 365–7 (21.3 m, $n = 48$)	Mean ($n = 104$)
	$\bar{x} \pm \sigma$ (Range)	$\bar{x} \pm \sigma$ (Range)	$\bar{x} \pm \sigma$ (Range)	$\bar{x} \pm \sigma$ (Range)
Maximum diameter (cm)	8.8 ± 4.9 (1.5 – 18.0)	10.0 ± 2.0 (5.5 – 14.0)	6.5 ± 2.4 (3.1 – 10.5)	8.0 ± 3.6 (1.5 – 18.0)
Dry weight/ animal (g)	6.35 ± 7.63 (0.07 – 24.37)	5.13 ± 3.12 (0.81 – 14.37)	1.63 ± 1.45 (0.06 – 4.39)	3.93 ± 5.18 (0.06 – 24.37)
Ca (%)	11.8 ± 4.6 (4.4 – 25.0)	9.5 ± 2.3 (6.4 – 15.3)	12.1 ± 3.2 (6.0 – 20.1)	11.5 ± 3.7 (4.4 – 25.0)
Mg (%)	1.3 ± 0.2 (0.7 – 1.6)	1.2 ± 0.2 (0.9 – 1.5)	1.4 ± 0.2 (1.0 – 1.7)	1.3 ± 0.2 (0.7 – 1.7)
Zn ($\mu g \cdot g^{-1}$)	247 ± 52 (158 – 355)	215 ± 61 (180 – 307)	302 ± 57 (177 – 460)	268 ± 61 (158 – 460)
Mn ($\mu g \cdot g^{-1}$)	26 ± 5 (13 – 40)	22 ± 4 (15 – 31)	34 ± 7 (22 – 51)	29 ± 8 (13 – 51)
Fe ($\mu g \cdot g^{-1}$)	15 ± 6 (2 – 29)	18 ± 4 (11 – 26)	36 ± 10 (16 – 61)	25 ± 13 (2 – 61)
Ni ($\mu g \cdot g^{-1}$)	9.6 ± 3.5 (4.2 – 18.1)	8.4 ± 1.0 (6.6 – 11.6)	10.1 ± 1.8 (7.3 – 18.5)	9.6 ± 2.3 (4.2 – 18.5)
Cu ($\mu g \cdot g^{-1}$)	5.0 ± 2.4 (1.8 – 9.9)	3.3 ± 0.7 (1.9 – 5.1)	10.4 ± 6.4 (3.1 – 33.7)	7.1 ± 5.5 (1.8 – 33.7)
Pb ($\mu g \cdot g^{-1}$)	0.38 ± 0.20 (0.18 – 1.01)	0.33 ± 0.13 (0.12 – 0.62)	0.54 ± 0.31 (0.16 – 1.32)	0.45 ± 0.26 (0.12 – 1.32)
Cd ($\mu g \cdot g^{-1}$)	0.39 ± 0.18 (0.14 – 1.12)	0.42 ± 0.08 (0.28 – 0.54)	0.44 ± 0.22 (0.10 – 1.03)	0.42 ± 0.18 (0.10 – 1.12)
Se ($\mu g \cdot g^{-1}$)	0.25 ± 0.15 (0.07 – 0.64)	0.26 ± 0.07 (0.07 – 0.35)	0.40 ± 0.13 (0.20 – 0.75)	0.32 ± 0.15 (0.07 – 0.75)
Hg ($ng \cdot g^{-1}$)	56 ± 26 (17 – 163)	53 ± 17 (28 – 92)	66 ± 20 (29 – 124)	60 ± 22 (17 – 163)

cordatum, Strongylocentrotus drobachiensis) from the Sound showed comparable levels of copper and zinc (Bagge, 1972, unpublished data, cited from Anonymous, 1978). However, other trace metal contents were considerably higher, lead about twenty times, cadmium more than ten times, mercury three times and nickel two times. The different feeding behaviour of starfish and of a single sea-urchin do not justify further speculation with regard to the observed differences. A comprehensive study—14 stations with 4 samples each—was carried out by Kröncke (1987) in the North Sea on the lead and cadmium content of *Echinocardium cordatum.*

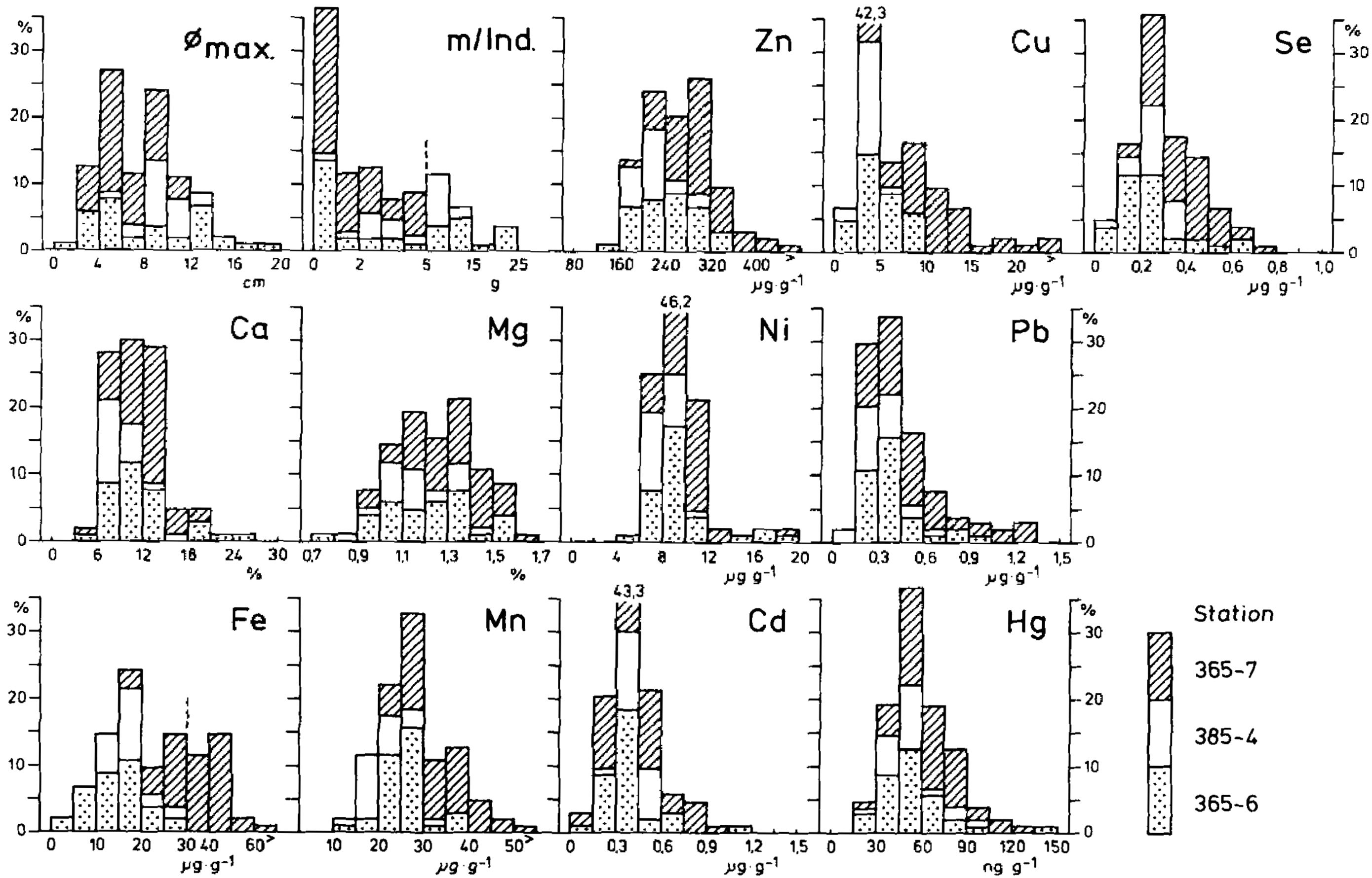

FIGURE 1 Histograms of the maximum diameter ("$\varnothing_{max}$"), mass ("m/Ind.") and metal content (Zn, Cu, Se, Ca, Mg, Ni, Pb, Fe, Mn, Cd, Hg) of the investigated starfish.

Again, the lead content (5–69 $\mu g \cdot g^{-1}$) exceeded that of the starfish by more than ten times. The cadmium level of the sea-urchin (0.1–0.5 $\mu g \cdot g^{-1}$) was comparable. Other studies in the northern Small Belt (Eichner and Forchammer, 1977, cited from Anonymous, 1978) on the trace metal content of the central disc of more than 300 snake-stars (*Ophiura albida*) showed significantly lower levels for several metals. The zinc content was only about 20%, the cadmium and nickel contents 50% and the copper content 75% in relation to those of the starfish. However, the lead values were more than ten times higher. Possibly, these differences could be due to the different location and bottom type. Another major reason would be the different feeding behaviour of both animals. In contrast to the starfish, *Ophiura albida* directly ingests the organic constituents of the sediment and the "detritus rain." Mussels and their spawn which have accumulated metals already, are seldom consumed (Arndt, 1969).

Compared with mussels taken from the Öresund (Phillips, 1979) and various locations on the Scottish and US coasts as part of "mussel-watch" projects (Davies and Pirie, 1980; Farrington *et al.*, 1983; Goldberg *et al.*, 1978, 1983), our starfish show lower mercury, cadmium, lead and iron levels, about the same levels of copper, and higher nickel, zinc and manganese levels. Mussels collected at five stations (GDR 030, 121, 160, 162, P 38) in the GDR fishery zone between the Mecklenburg and Oder Bays in 1981 had a mean mercury content of 150 $ng \cdot g^{-1}$ dry weight (69–233 $ng \cdot g^{-1}$; $n = 10$) in the freeze-dried and homogenized soft material (Manthey and Brügmann, unpublished data). The lower starfish concentrations shown in Table II suggest that mercury concentrations decrease along the food chain in a similar way to cadmium, lead and iron. This mercury "decumulation" is possibly a result of partial dilution of the metal inside the organism by the rapidly growing skeleton of the starfish, which consists of about 87% $CaCO_3$ (calcite) and about 7% magnesium admixtures (Nauen and Böhm, 1979; Milliman, 1974). According to Binyon (1978) about 80% of the fresh weight of starfish is water, 10% is (magnesium) calcite and the remainder consists of salts and organic matter. Nauen and Böhm (1979), on the other hand, found that in starfish from the western Baltic Sea the dry weight was only about 13% of the fresh weight. After maceration with hypochlorite solution, on average the remaining skeleton accounted for 35% of the dry weight. Nauen (1978) found that the mean dry weight of 179 samples was 17% of the fresh weight and that organic matter accounted for 49% of the dry weight. In the animals we analyzed, the dry weight relative to fresh weight was $24.4 \pm 6.7\%$ ($16.4 - 65\%$), the highest values being found in animals with a diameter of 3 cm or less and the majority of the values being between 20 and 30%.

To check our working hypothesis that certain elements are deposited mainly with the magnesium calcite in the skeleton, while others are accumulated primarily in the organic matter, metal concentrations of the arms of starfish which probably contain more skeletal substance were compared with those of the central discs where the digestive organs are situated (Table III). Significant differences were found in the case of mercury, copper, zinc and

TABLE III
Differences between mean metal contents of central discs ("M") and arms ("A") of the starfish (concentrations given on a dry weight basis)

		Stat. 365–6	Stat. 385–4	Stat. 365–7	Mean	A/M
Ca (%)	M	9.8	8.9	9.3	9.3	1.08
	A	10.3	9.4	10.3	10.0	
Mg (%)	M	1.2	1.2	1.2	1.2	1.08
	A	1.3	1.2	1.3	1.3	
Zn ($\mu g \cdot g^{-1}$)	M	206	216	269	223	1.27
	A	298	233	315	282	
Mn ($\mu g \cdot g^{-1}$)	M	24	21	27	24	1.04
	A	28	20	28	25	
Fe ($\mu g \cdot g^{-1}$)	M	14	17	31	19	1.16
	A	19	16	31	22	
Ni ($\mu g \cdot g^{-1}$)	M	8.2	8.1	9.4	8.4	1.00
	A	8.8	8.3	8.2	8.4	
Cu ($\mu g \cdot g^{-1}$)	M	3.8	3.2	4.7	3.7	1.30
	A	5.8	3.5	4.9	4.8	
Pb ($\mu g \cdot g^{-1}$)	M	0.38	0.30	0.28	0.33	1.09
	A	0.28	0.35	0.42	0.36	
Cd ($\mu g \cdot g^{-1}$)	M	0.39	0.40	0.46	0.41	0.80
	A	0.29	0.45	0.28	0.33	
Se ($\mu g \cdot g^{-1}$)	M	0.18	0.29	0.31	0.25	1.04
	A	0.20	0.24	0.33	0.26	
Hg ($ng \cdot g^{-1}$)	M	46	46	61	49	1.33
	A	55	68	73	65	

iron, the concentrations of these elements in the arms being respectively 33, 30, 27 and 16% higher than in the central disc. The cadmium concentration of the arms, however, was 20% lower, showing that much of this element is accumulated in the storage organs in the central disc, analogous to its accumulation in the kidneys of mammals and fish. The other positive deviations of the metal concentrations (lead, calcium, magnesium, manganese, selenium) in the arms relative to those of the central disc lay between 9 and 4% and must be regarded as insignificant at least in the case of lead, manganese and selenium, lying within the analytical error, and since this situation was reversed at some stations (Table III). The two sample types did not differ with respect to mean nickel concentrations.

In relation to their concentrations in the bottom water layer in Mecklenburg Bay/Cadet Trench, the trace metals we studied are accumulated several orders of magnitude more rapidly relative to the fresh weight of the animals than are the main constituents of sea salt such as calcium and magnesium (Table IV). Order of magnitude differences between the solubility products of the metal carbonates i.e., about 10^{-5} for magnesium, $5 \cdot 10^{-9}$ for calcium,

TABLE IV
Accumulation coefficient "A" for metals in seastars of Cadet Trench ($\mu g_{Me} \cdot g^{-1}$ seastar (fresh weight)/$\mu g_{Me} \cdot g^{-1}$ water[a])

Element	"A"
Zn	33,000
Ni	3,000
Pb	2,300
Cu	2,200
Cd	2,100
Ca	130
Mg	5

[a] Mean values from measurements carried out between 1980 and 1985 at station "GDR 030"/18 m (north eastern part of Cadet Trench).

$1.4 \cdot 10^{-10}$ for copper, $6 \cdot 10^{-11}$ for zinc, $1.5 \cdot 10^{-13}$ for lead and $2.5 \cdot 10^{-14}$ for cadmium, could possibly explain the different accumulation behaviour of trace and major elements. Zinc as an essential element accumulates fastest, whereas the accumulation coefficients for cadmium, copper and lead are practically identical. No accumulation coefficients were calculated for iron and manganese because their concentrations in the water fluctuate considerably with changes in the redox potential.

There are numerous significant positive correlations between the concentrations of the different metals (significance level: 99%, see Table V). This applies particularly to the correlation of elements other than iron with the main constituent calcium, and the less significant correlation of elements other than mercury, selenium, copper and iron with magnesium.

This may be linked to the incorporation of trace metals, particularly of nickel, lead and manganese, into the magnesium calcite. But significant positive correlations were also found between different trace metals. Most of them were correlated with manganese, but the element pairs lead–nickel, lead–selenium and lead–cadmium should also be mentioned. It is very unlikely that all of these correlations indicate causal relationships. Animal size (dry weight, age) is obviously a factor that has a great influence on the variance of metal concentrations. Except for cadmium, all elements studied were linked by a significant negative correlation (95% level for mercury, otherwise 99%) to dry weight per animal and, with even higher significance, with maximum diameter.

Similar negative correlations were obtained by Williamson (1980) in the case of lead, zinc and cadmium in snails and by Cossa *et al.* (1980) in the case of cadmium, copper, iron, manganese, nickel and zinc in *Mytilus edulis*. The phenomenon is attributed to specific metabolic features and to age-related changes in the animals' ability to control internal metal concentrations, for instance, by metal-binding protein synthesis, formation and breakdown of intra- and extracellular metal particles, adsorption, desorption, excretion, etc. Since calcium and magnesium seem to act in the same way as trace metals, this may indicate that in small animals, skeletal substance accounts for a larger proportion of the biomass than muscle and internal organs, in which case trace metals that are bound predominantly in the magnesium calcite would be accumulated accord-

TABLE V

Correlation matrix ($n = 104$; significant correlations ≥99% underlined)

	Ø[b]	Ca	Mg	Fe	Mn	Zn	Cu	Ni	Pb	Cd	Hg	Se
d.w.[a]	−0.44	−0.47	−0.52	−0.44	−0.52	−0.45	−0.45	−0.47	−0.30	−0.02	−0.25	−0.22
Ø[b]		−0.68	−0.56	−0.36	−0.64	−0.50	−0.57	−0.65	−0.46	−0.13	−0.24	−0.28
Ca			0.82	0.08	0.66	0.35	0.28	0.87	0.69	0.43	0.27	0.41
Mg				0.22	0.62	0.37	0.21	0.66	0.46	0.32	0.09	0.21
Fe					0.46	0.43	0.50	0.14	0.18	−0.01	0.22	0.31
Mn						0.51	0.58	0.52	0.65	0.35	0.24	0.52
Zn							0.39	0.31	0.29	0.17	0.39	0.45
Cu								0.29	0.42	0.07	0.28	0.43
Ni									0.58	0.36	0.24	0.42
Pb										0.53	0.24	0.55
Cd											0.14	0.47
Hg												0.29

[a] d.w. = dry weight in g(per animal).
[b] Ø = maximum diameter.

ingly. The special status of cadmium, which correlates significantly with neither the size nor weight of the animals is consistent with this interpretation.

The negative correlation between size (weight) and metal content might also be linked with the feeding habits of *Asterias rubens,* however, Anger *et al.* (1977) analysed the gut contents of starfish of various sizes taken from Lübeck Bay finding that the small animals living on the sediment feed mainly on snails (*Hydrobia ulvae*) and mussel spawn, whereas larger ones prefer whole mussels and clams (*Mytilus edulis, Macoma baltica*). Since, however, no data are available concerning metal concentrations in snails or mussel spawn, and *Asterias rubens* responds very flexibly to changes in food availability, it is not possible to discuss this question here.

Figure II shows the lines of regression between metal concentration (logarithmic scale) and maximum animal diameter for calcium, magnesium, copper, nickel, manganese and zinc. The different kinds of sample are also identified (T = whole animal, M = central disc(s), A = arm(s)).

Anger *et al.* (1977) and Nauen (1978), as a result of their stock estimations and studies regarding the feeding habits of *Asterias rubens,* came to the conclusion that at least in summer this starfish competes seriously with demersal fish such as cod for benthic food resources. Here we shall estimate roughly the importance of starfish as a factor influencing the metal flux in the western Baltic Sea. The part of the Baltic Sea to which starfish are restricted by salinity includes the Öresund, the Belt Sea (including Mecklenburg Bay up to a line running through Darss Ort and Gedser, Kiel Bay and the Great and Small Belts), and the eastern and western parts of the Kattegat. According to Ehlin *et al.* (1974) it has an area of about 42,400 km^2. From this we have to subtract the typical muddy regions, which also include areas of great depth where, according to Anger *et al.* (1977) and Nauen (1978), very few starfish are found on the bottoms, owing to low food availability and occasional periods of suboxic or anoxic conditions. According to Pheiffer Madsen and Larsen (1986) this applies to an area of 16,400 km^2 at the most, so that the potential area for colonization by starfish is about 26,000 km^2. Assuming a mean biomass of 2 g dry weight per square metre, this gives a total starfish stock of 52,000 tons containing, on the basis of our measurements, 14 tons of zinc, 1.5

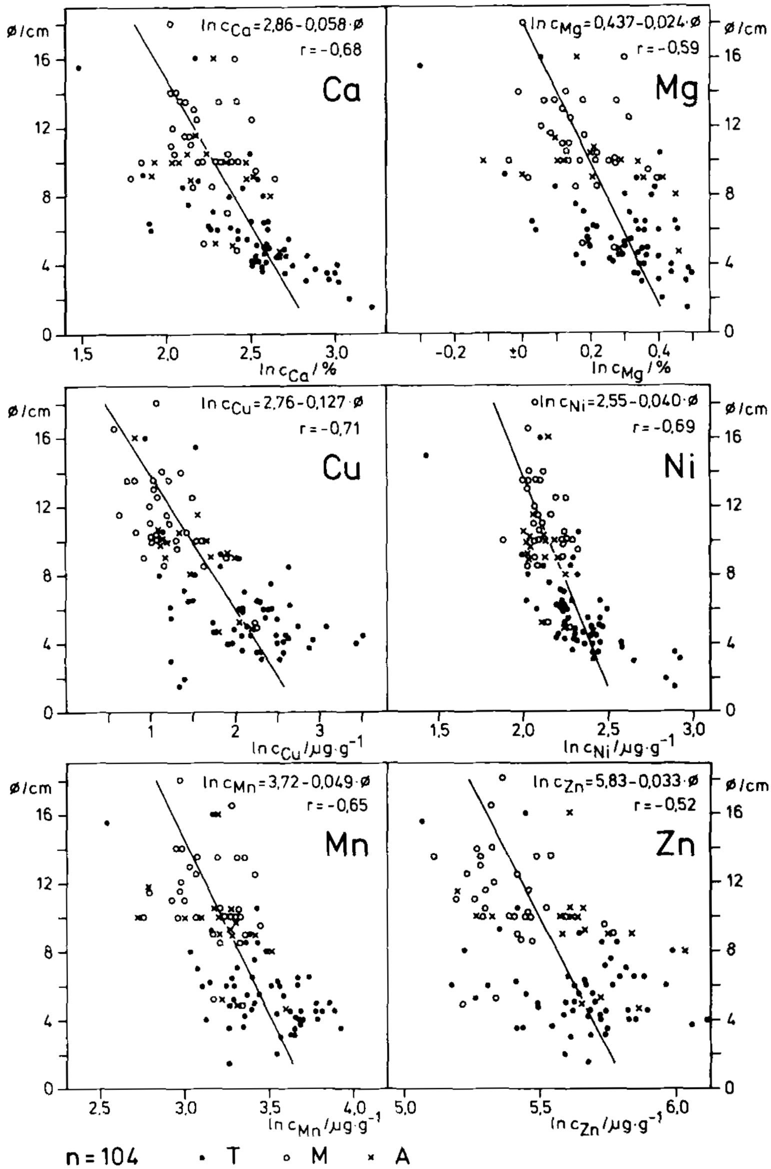

FIGURE 2 Lines of regression between maximum animal diameter and the contents of Ca, Mg, Cu, Ni, Mn and Zn (logarithmic scale).

tons of manganese, 1.3 tons of iron, 0.5 tons of nickel, 0.37 tons of copper, 23 kg of lead, 22 kg of cadmium, 17 kg of selenium and 3 kg of mercury.

However, in the case of elements such as cadmium, lead and mercury, which are of toxicologic relevance, the annual metal turnover of starfish is higher by more than an order of magnitude, because not only do starfish consume around four times their own weight each year as food, but also their potential food sources such as mussels contain far higher trace metal concentrations. Hence, at least in the case of cadmium flux, starfish are a factor of the same order of magnitude as, for instance, shipping or the discharge of industrial waste water into the area concerned.

Finally, we would like to mention that attempts to obtain additional starfish and mussel samples from the three stations in 1986 and 1987 ended with an unpleasant surprise: macrobenthos had completely vanished from this part of Cadet Trench, presumably owing to anoxic conditions. This phenomenon, hitherto observed only in late summer or early autumn, affects the bottom water in the deepest parts of the western Baltic Sea, and its frequency has possibly increased in recent years.

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