BALTIC SEA ENVIRONMENT PROCEEDINGS

No. 24

PROGRESS REPORTS ON CADMIUM, MERCURY, COPPER AND ZINC

BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION
— HELSINKI COMMISSION —

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December 1987

For bibliographic purposes this document should be cited as:
Baltic Marine Environment Protection Commission
— Helsinki Commission —
1987
Progress Reports on Cadmium, Mercury, Copper and Zinc
Baltic Sea Environment Proceedings No. 24

ISSN 0357-2994

Helsinki 1987 — Government Printing Centre

PROGRESS REPORTS ON CADMIUM, MERCURY, COPPER AND ZINC

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II PROGRESS REPORT ON MERCURY;
prepared by the Union of Soviet Socialist Republics

PREFACE

The Helsinki Commission initiated during its interim period (1974-1980) activities focused on preparation of relevant Recommendations regarding reduction and elimination of harmful substances discharged to the Baltic Sea, mentioned in the Annexes of the Convention (CONVENTION ON THE PROTECTION OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA, 1974 (HELSINKI CONVENTION)). The first Recommendations in this field were adopted by the Commission in 1982. The collection of relevant information from all Baltic Sea States has been a current activity since early 1980s based on the "Lead Country" principle. Each of the seven countries has undertaken the responsibility to collect relevant information on at least one of the harmful substances.

This publication consists of three first Progress reports on the harmful substances as follows:

PROGRESS REPORT ON CADMIUM; prepared by Sweden

PROGRESS REPORT ON MERCURY; prepared by the Union of Soviet Socialist Republics

PROGRESS REPORT ON COPPER AND ZINC; prepared by the German Democratic Republic

There are differences in the origin and the age of the data from country to country and substance by substance. The values are often very preliminary and rough, and therefore, it is obvious that the values should be used with great caution. Due to effective measures taken in the Baltic Sea States the amounts of harmful substances discharged vary from year to year. In some cases more recent data might be available in open literature and the users are advised to study also other sources of information.

The compilations prepared by the Lead Countries (for this publication Sweden, the USSR and the German Democratic Republic) are based on national information submitted by the Baltic Sea States within the framework of the Helsinki Commission. However, the responsibility of the Progress Reports is not on the Commission, but the Lead Country concerned.

PROGRESS REPORT ON CADMIUM;
prepared by Sweden

PREFACE

To the 6th Meeting of the Ad hoc Working Group on Criteria and Standards for Discharges of Harmful Substances into the Baltic Sea Area (WGS) in 1983, Sweden submitted a first Progress Report on Cadmium. The report includes, i.a. information on sources, discharges of cadmium from these sources and effects of cadmium observed in the marine environment of the Baltic Sea as well as proposals for possible measures aiming at the reduction of discharges of cadmium from various sources.

Comments were made and additional data given during and after the WGS meetings in 1983 and 1984. In accordance, parts of the document were revised in October 1984.

Sweden has, as Lead Country, further revised the document during the summer of 1987 in order to be able to give some more recent data. Sweden has also added some Lead Country comments for 1987.

1. INPUT OF CADMIUM TO THE BALTIC SEA

1.1 Airborne load

Different estimates of the airborne load on the Baltic are available. Poland reports an annual airborne load into the Gdansk Basin of an estimated 38 tonnes. Finland has submitted information on the rate of direct deposition in the Gulf of Bothnia and the western part of the Gulf of Finland, 0.17 mg/m^2 year and 0.31 mg/m^2 year respectively. (Ruoho 1981, The Finnish Meteorological Institute 1981). This indicates an airborne load of circa 20 tonnes/year to the Gulf of Finland. Rhode et al present in a Swedish report from 1980 an estimated deposition of circa 80 tonnes/year for the whole of the Baltic Sea (range 20-300) of which 20-25 tonnes reach the Baltic Proper, and circa 10 tonnes the Rattegat and the Belt Sea. The atmospheric fallout on Danish marine areas is estimated to be 8.8 tonnes/year by precipitation rate of 0.20 mg/m^2 year (Jensen and Møhlenberg 1980). The proportion of dry deposition to wet deposition is very different in the Swedish report mentioned above when compared to the data of the Polish National Report (10/70 and 22.8/14.6) but it must be pointed out that deposition data can be very uncertain.

According to a compilation made by the Commission in 1986, the airborne load on the Baltic Sea is about 80 tonnes/year. This is probably the best estimate presently available.

Concentrations of cadmium in the air are reported by the Federal Republic of Germany. Average concentrations vary considerably, from circa 1 ng/m^3 in areas with unpolluted air and 2-3 ng/m^3 in rural areas, via 5-15 ng/m^3 and 15-25 ng/m^3 in urban areas without and with specific emission sources, to 60 ng/m^3 in the direct proximity to emission sources. Measurements in Copenhagen and in rural areas of Denmark have shown levels of 2 ng/m^3 and 1 ng/m^3 respectively. These concentrations come close to the detection limit.

1.2 River load

The estimates of the river input of cadmium to the Baltic are very uncertain due to cadmium levels in the water near or below the detection limit. Finland has reported an input from seven rivers of between 2.2 and 9 tonnes/year. The estimate from Denmark is 1.3 tonnes/year. Sweden reported earlier 14 tonnes/year, but more recent monitoring indicates a considerably lower flow of cadmium, around 3 tonnes/year. The cadmium load of the Vistula River in Poland is estimated at 10.4 tonnes/year. The Soviet Union reports 21.6 tonnes/year to the Gulf of Finland. The input by Warnow River in the German Democratic Republic has been calculated on basis of analyses to 0.088 tonnes/year. The major rivers of the Federal Republic of Germany do not empty into the Baltic.

According to the compilation made by the Commission in 1986, the river load is about 60 tonnes/year. This is probably the best estimate presently available.

1.3 Direct discharges

Data have been obtained from three of the member states. Finland estimates the direct municipal emissions at 0.15 tonnes/year from approximate cadmium concentrations in the effluents from municipal waste water plants (0.5 mg/m^3). The industrial emissions are circa 0.12 tonnes/year. Denmark discharges circa 2.8 tonnes/year in sewage to marine areas. Swedish emissions from municipal sources are circa 0.2

tonnes/year. The emissions from industrial sources were circa 1 tonne in 1985 but have been larger, the figures from the main source, the Rönnskär smelter, having shown a considerable variation. The USSR reports 0.4 tonnes/year to the Baltic Proper.

No other data regarding the discharge of cadmium to the Baltic have been submitted. It is thus impossible to assess the absolute amounts discharged, but from the information available it can be concluded that the direct discharges are of a lower magnitude than the river load, except perhaps in Denmark.

2. CADMIUM IN TEE AQUATIC ENVIRONMENT

An assessment of the reported cadmium levels in the Baltic environment must be done with great care. First, we know hardly anything about the seasonal variations in the cadmium levels of water and biota. Reports from the different areas consisting of materials sampled at different times cannot be put together for an estimation of the regional variations. Secondly, there have been several intercalibration exercises which show that the agreement of the cadmium analyses between the participating laboratories is rather poor (see for instance Baltic Sea Expert Meeting 1974, Report of the Baltic Intercalibration Workshop 1977, ICES Cooperative Report 1977, Joanny et al 1980).

The general conclusion must be that a reliable regional estimate of the cadmium levels in the Baltic environment must be based on better knowledge of seasonal variations in the various subareas and intensified intercalibration exercises.

2.1 Concentrations in the water

Several regional cruises have been done in the Baltic Proper to investigate the cadmium concentrations in the water. Filtered and unfiltered water have been analysed with atomic absorption spectophotometry (AAS) and anodic stripping voltammetry (ASV) techniques. Some of the results are listed in Table 1. Since at least 90 % of the total cadmium in the water appears in soluble form the various results can be compared directly. The absolute cadmium levels differ by almost one order of magnitude between the older and the more recent reports. The latter probably better represent the actual situation, a result of more accurate sampling and analysis.

A regional variation in the cadmium concentrations of the surface water was found in only one of the six cruises (Briigmann 1977): Briigmann found the highest values in the south-western Baltic, south of Öland, in the Gdansk Basin and in the Gulf of Finland.

Both Kremling (1973) and Gustavsson (1981) consider their values to be at the same levels as in open ocean waters. The range of concentrations reported is 0.03-0.07 µg/l (Westerlund 1980, Koroleff 1980, Gustavsson 1981).

Table 1 Average cadmium concentrations in unfiltered and filtered water from the Baltic

Unfiltered water from different cruises (all depths)

	Date of sampling	µg/l	± sd%	Range µg/l
Kremling (1973)	Sept 1971	0.17	71	0.03 - 0.49
Briigmann (1977)	1972-1975	0.29	168	0.01 - 8.79
Koroleff (1980)	1980			0.03 - 0.07
Magnusson & Westerlund (1980)	March 1980	0.03	0.05	0.02 - 0.07
Briigmann 1981*				0.03 - 0.07

* Compiled from various reports

Filtered water from different cruises (all depths)

	Date of sampling	µg/1	± sd%	range µg/l
Kremling (1973)	April 1972	0.22	46	0.08 -0.53
Gustavsson (1981)	July 1979	0.043	28	0.029-0.053
	Nov 1979	0.035	81	0.03 -0.122

Recent investigations in the Danish marine areas of the Baltic have shown cadmium concentrations between 0.025-0.06 (Magnusson and Rasmussen, 1981). In the Little Belt an average of 0.025 µg/l (standard deviation 0.004 µg/l) has been found (Rasmussen, 1981).

Average cadmium concentration of 0.261 µg/l and 0.277 µg/l in filtered and unfiltered water from the Polish economic zone of the Baltic have been reported by Poland. These values are rather high and might reflect a strong coastal influence.

Vertical variations in the cadmium concentrations in the water have only been reported occasionally. Kremling (1978) found increased dissolved cadmium concentrations in the upper layer during the BOSEX expedition in the southern central Baltic. This was suggested to be due to uptake of cadmium by plankton in the surface water and regeneration in the deeper layers. Gustavsson (1981) found low cadmium concentrations in some deep water samples, which was suggested to be due to precipitation of CdS.

Of the total cadmium concentrations in the Baltic sea water only 2-3 % seem to be in particulate form (Kremling and Petersen 1978, Danielsson and Westerlund 1978). However, calculations by Kremling (1978) indicate that the particulate fraction of cadmium can be substantially higher during spring and summer.

To summarize, in general the cadmium concentrations in the Baltic sea water seem to be rather stable regionally and independent of water depth. According to recent analyses, the concentration is about 0.03 µg/l. The older values are probably too high. Improvement in sampling and analysing techniques might reduce the variations and even decrease the mean values.

2.2 Concentrations in plankton and particulate matter

Cadmium in seston has been reported by **Weigler** (1975) and kremling and Petersen (1978). Weigler found 1-5 mg Cd/kg dw in seston from the Gotland Deep and the Bornholm Basin, while the levels in the Gulf of Finland were higher, 5-10 mg Cd/kg dw. Kremling and Petersen found 3.2-5.6 mg Cd/kg dw in the Bornholm Sea. The cadmium content was correlated with iron content but not with particulate carbon. Gustavsson and Notter (1978) reported 1-4 mg Cd/kg dw in the Bothnian Bay. Brügmann (1977) has reported 5.4 mg Cd/kg dw in blue green algae from the Bornholm Basin. Lithner (1981) made a survey at two occasions of the cadmium content in zooplankton from the Bothnian Bay, the Bothnian Sea and the Baltic Proper (see Table 2).

From Poland is reported 14.5 mg Cd/kg dw in suspended material and values of 1.04 mg Cd/kg dw in zoo- and phytoplankton from the Polish economic zone.

Table 2 Cadmium concentrations in zooplankton in May/June 1975 and 1979. After Lithner 1981

		mg Cd/kg dw	± sd	n
Bothnian Bay	1975	2.1	0.4	7
	1979	1.6	0.6	5
Bothnian Sea	1975	2.6	0.6	16
	1979	3.8	2.2	10
Åland Sea	1975	3.2		2
Baltic Proper	1979	3.4	1.0	3

It is difficult to draw any reliable conclusions on the regional variation from these few reports. Furthermore, the composition of plankton and seston varies in time and space, which might influence the cadmium content. The only rough conclusion that can be drawn is that the cadmium content of particulate matter in the Baltic is at the ppm-level.

2.3 Concentrations in the sediments

Several investigations of sediment chemistry have been performed in the Baltic and some of them are listed in Table 3, where the cadmium and carbon contents in the surface sediments are given. The cadmium content of the surface sediment of the Baltic-is generally rather high. Thus, the variability between the different basins probably does not depend on bad analytical precision.

Niemistö and Voipio (1979) found indications of differences in the sedimentation processes between different basins. The scavenging agent for heavy metals was assumed to be iron in the Bothnian Sea and organic carbon in the Gulf of Finland and the Baltic Proper. This means that basins with different sedimentation environments, for instance including both anoxic and oxidized sediments, cannot be compared. In Table 3 there are indications that a covariation might exist between the carbon and the cadmium content in the surface sediments (r circa 0.9).

The organic accumulation bottoms in some of the deep basins of the Baltic might be a result of a transport of organic matter from the coastal areas. Since cadmium seems to be associated with organic carbon this would result in a high cadmium content in these bottoms. However, Olausson et al (1977) found almost no differences when comparing cadmium and carbon contents in surface sediment from near shore and off shore localities (see Table 3). In an overview of cadmium in the marine environment (ICES Coop. Res. Report 1982) it is noted that the atmospheric deposition of cadmium is comparable to the riverine input of the.element. A very large portion of the cadmium brought down to the ocean in wet and dry atmospheric precipitation is solubilized in the oceanic surface waters. The distribution and transport in the ocean is greatly influenced by marine biological activity.

Suess and Erlenkeuser (1975) made calculations of the zinc fluxes to the bottoms of three different basins in the Baltic Proper. The zinc concentrations in the surface sediments varied by a factor 2, while the fluxes expressed as mg Zn/m^2 year were the same. This type of calculation for cadmium has been tried by Jensen (1980), when the natural background of cadmium was known only for two cores of six, which permitted rather few conclusions. In the future, calculations of this kind might give more reliable information about the differences between the basins of the Baltic. However, the methods for determining the sedimentation rate and the importance of diagenesis, bioturbation, and resuspension need further consideration.

The cadmium concentrations in sediment cores increase generally towards the sediment surface, about tenfold, due to anthropogenic influences. By dating the sediment cores, the time for the increase can be estimated. By the profiles by Niemistö and Voipio (1979) it can be concluded that the increase of cadmium in sediment cores from the Gotland Deep started at the beginning of this century, and slightly later in the northern Baltic Sea. Jensen (1980) found that the increase of cadmium in the sediments from the Arcona Basin and to the west of Bornholm started at the beginning of the last century.

Some of the cadmium concentrations reported in Table 3, notably from the Gotland Deep and the Northern Baltic, are remarkably high, almost on the same level as concentrations in the top layer from polluted areas.

Table 3 Cadmium and organic carbon in surface sediments from the Baltic

Area	mg Cd/kg dw	%C dw	Reference
Gulf of Bothnia	4.1 ± 1.3		Hallberg 1979
	0.2*	2*	Niemistö & Voipio 1979
Gulf of Finland	1.5*	5*	-"-
Baltic Proper			
near shore	1.1 ± 0.2	4.5 f0.4	Olausson et al 1977
off shore	0.7 ± 0.1	4.0 ± 0.3	-"-
Northern Baltic	5.7*	10	Niemistö & Voipio 1979
Gotland Deep	6.5	8.5*	-"-
Bornholm Basin	2.2	5.1	Suess & Erlenkeuser 1975
Southern Central	5.5-6.3	8.9-10.5	Niemistö & Tervo 1978
Kieler Bucht	1.9	5.5	Erlenkeuser et al 1974
West Bornholm	0.7		Jensen 1980
Arkona	0.9	4**	-"-
The Sound	1.6	5**	-"-

* Estimated from diagrams

** Estimated from diagrams on the loss of ignition and calculated by a formula given by Jensen, 1980

A marked increase in the surface layers of sediment cores has been observed in samples taken in the vicinity of an iron and steel factory in Finland (Luotamo and Luotamo 1979). Most levels in the top layer were between 1 and 2 mg/kg dw but at some points the level rose to 6-7 mg/kg dw. Häkkilä (1980) found cadmium concentrations significantly exceeding the natural background level in the surface sediments of Pihlavanlahti situated at the mouth of the river Kokemäenjoki. The results from this and adjacent sampling sites are shown in Table 4. Remarkably high concentrations of cadmium in surface sediments, 9 mg/kg dw, have been measured outside the harbour of a fertilizer plant off Uusikaupunki (Häkkilä 1980 a). The explanation is probably handling of raw materials in the harbour and discharges to water from the plant.

Table 4 Average cadmium concentrations in surface layer (O-2 cm) and in older layers of bottom sediments in the sea area off Pori on the west coast of Finland (Häkkilä 1980)

Station		Concentration of Cd mg/kg dw
Pihlavanlahti		
160	o - 2	11
	12 - 14	2.0
161	o - 2	7.1
	9 - 10	0.4
162	o - 2	6.2
	8 -9	0.4
Ahlainen		
163	o - 2	1.3
	6 -7	0.2
164	0 -2	2.2
	8 -9	0.2
Surroundings of Reposaari		
2	o - 2	1.6
	6 -7	0.5
9	o - 2	0.6
	8 -7	0.3
Kaijakari-Tahkoluoto		
22	o - 2	0.9
	10 - 11	1.0
26	o - 2	0.9
	9 - 10	1.1
16	o - 2	lil
	9 - 10	0.6
Discharge area		
49	o - 2	0.2
	2 - 4	0.2
Open sea area		
90	0 - 1,6	0.53
	2.4 - 4	0.27
91	0 - 1.6	0.39
	2.4 - 4	0.13
92	0 - 1.6	0.21
	2.4 - 4	0.14
93	0 - 1.6	0.15
	2.4 - 4	0.07

In the assessment of todays situation (ICES 1982) the rates at which cadmium is being mobilized through industrial activity are comparable with the natural fluxes of the element through the atmosphere and runoff.

The total cadmium input to the Baltic Sea is about 140 tonnes/year. The input is one order of magnitude greater than the output through the Sound and the Danish straits. It must be assumed, then, that about 140 tonnes of cadmium are accumulated yearly in the sediments of the Baltic Sea.

This figure may be related to sediment concentration as follows.

The sediment load on the accumulation bottoms of the Baltic is about 40 million tonnes of dry matter per year. Most of this originates from transport bottoms and some of it is of river origin. The cadmium input will accumulate in the sediments, rising the cadmium concentration by an average 140/40 = 4 mg/kg. This corresponds rather well to concentrations obtained by analysis of deep bottom sediments (3-9 mg/kg).

Analysis and a simple budget calculation thus indicate that cadmium concentrations in recent Baltic Sea sediments are about ten times higher than background concentrations (about 0.3 mg/kg).

2.4 Biological availability

There is no evidence that cadmium is biologically essential to any organism, but its toxicity is well documented in the literature. Cadmium has a high affinity for sulfhydryl groups, and also for hydroxyl groups and ligands containing nitrogen (Nilsson 1970). Thus, binding to such groups in essential enzymes or enzyme systems might affect various basic biochemical and physiological processes and thereby interfere with and adversely disturb central functions of the organism, even at very low cadmium concentrations (Larsson et al 1976). Furthermore, the low excretion rate of accumulated cadmium makes even a minor cadmium contribution to the environment a potential risk in a more long-term perspective.

Due to complexation with chloride in saline waters, data on uptake and toxicity in fresh water are not applicable to the situation in the Baltic. The toxicity and the bioaccumulation potential of cadmium are lower in this environment. Some evidence for this statement is given below.

Within the ecological range of the Baltic, the sensitivity to cadmium increases with higher temperatures and lower salinities (Scholz et al 1978, Voyer et al 1977). Engel and Fowler (1979) have demonstrated that the toxicity of cadmium to estuarine shrimp and larval fish is a function of the free cadmium ion concentration, which in turn is controlled by the chloride concentration. The concentration of free cadmium ion decreases relative to total dissolved metal, due to its complexation with chloride ions.

Accordingly, Bengtsson (1977) demonstrated a strong negative correlation between salinity and the accumulation of cadmium from the water in minnow (Ph. phoxinus) and common goby (Pomatoschistus minutus).

Studies on Clava multicornis have shown, however, that the pronounced dependence of toxicity on temperature and salinity may be reduced in long-term experiments (Fig. 1, Theede 1980). This indicates that chronic toxicity is less dependent of these factors.

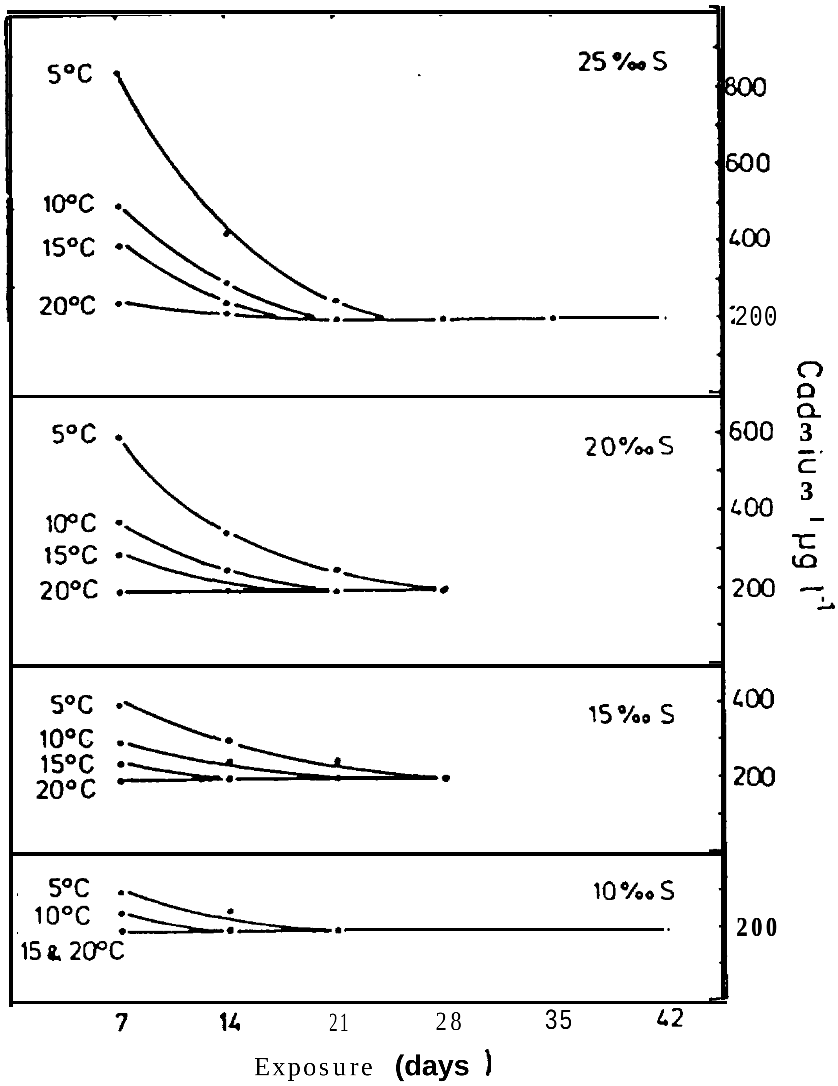


Fig. 1 . <u>Clava multicornis</u>. Changes of the modifying effects of temperature and salinity during transition from acute to chronic toxicity of cadmium. The graph indicates the limits of Cd concentrations at which feeding responses occurred (in Theede 1980).

The toxicity of cadmium in soluble form also depends upon its degree of chelation. Less complexed forms seem to accumulate more easily in ciliate cells and are the most toxic ones (Houba and Remacle 1982). Organic complexing agents, such as NTA (Sunda et al 19781, EDTA (Hung 1982, Bengtsson, unpubl. obs.) and humus (Musani et al 1980) are effective in reducing the toxicity. This further supports the opinion that the cadmium ion is the most toxic species. Bengtsson and Granmo (1977) have, in laboratory experiments, also demonstrated that increased salinity and EDTA concentrations reduce the uptake of cadmium in mussels (M. edulis). Further, Gjessing (1981) has shown that the toxicity of cadmium to fish and algae is considerably reduced when humus is present. To some degree, there appears to be a relationship between the reduction of toxicity and the concentration of humus. The linkage between humus and cadmium is, however, very weak, compared with copper and lead. Musani et al (1980) suggest that the amount of chelating material (i.e. humic material) dissolved in the open sea is too small to contribute significantly to the chelation of cadmium, while, in estuarine waters, their role might be more important. This latter situation might be applicable to the Baltic.

Marine polychaete worms (Nereis japonica) accumulated cadmium from the sediment in laboratory experiments, but it was also concluded that accumulation from water was a much more important way of contamination (Ueda et al 1976).

Experiments performed by Bengtsson et al (1983) in brackish water (salinity 3.5 o/oo) have shown that cadmium in the sediments is biologically available to a certain extent. Tubifex sp. that were living in and feeding on a sediment contaminated with 7.5 mg Cd/kg dw increased their body burden of cadmium from 0.7 to 2.1 µg/g dw after several weeks. Juveline fourhorn sculpin (Myoxocephalus quadricornis), which fed on the contaminated Tubifex during four months, demonstrated an increase of cadmium concentrations.

From experiments with marine invertebrates McLeese (1981) concludes that bioavailability and bioaccumulation of cadmium depends largely on the concentration of cadmium leached from the sediment to water, which, in turn, depends on organic carbon content and cation-exchange capacity of the sediment. Studies of the release of metals from contaminated sediments, for example in the Bight of Skellefteå, have shown that cadmium relatively easily passes from sediments to water (Edgren et al 1978). The lack, or slow rate, of excretion indicates that accumulation of cadmium in the organisms is practically irreversible. Cadmium in sediments should therefore be considered a potential risk to marine life.

From an experimental marine ecosystem, run with mussels and plaice (Pleuronectes platessa) for 300 days, it was concluded that the mussel was the most sensitive indicator of elevated cadmium concentrations (Westernhagen 1978). Many molluscs are able to accumulate large quantities of cadmium without any signs of physical damage (Scholz et al 1978). The authors suggest the existence of special cadmium-binding proteins as the main reason for the high tolerance of M. edulis to cadmium. Such a protein has also been identified in oysters (Engel and Fowler 1979) and in fish (Beattie and Pascoe 1979, Marafante 1976, Overnell and Coombs 1979, Woodworth and Pascoe 1983). The role of these proteins in eventually reducing the cadmium toxicity is yet not fully understood.

2.5 Concentrations in the biota

Phillips (1977 a) studied cadmium in whole soft parts of the blue mussel, Mytilus edulis, from the Baltic Proper, the Sound, the Kattegat, and the Skagerack, sampled from April to June 1976. He found higher cadmium levels in mussels from water of low salinity than in those from relatively high-saline water (see Table 5). The same pattern could be seen in an investigation in June 1977 covering the regions of the Sound (Phillips 1979).

Cadmium concentrations in Mytilus edulis from the Sound and other Danish coastal areas are also shown in Table 6. These variations in the mussels were believed to be dependent on the trace metal concentrations of the food, which in turn probably were dependent on the salinity. However, the concentrations of cadmium in the tips of Fucus vesiculosus from the regions of the Sound did not show any differences between localities (see Table 7). The disagreement between mussels and seaweed was suggested to be due to an uptake of particulate cadmium by the mussels and by direct uptake of cadmium in solution by the seaweeds.

Results from an investigation of Mytilus edulis from the coastal waters of the Federal Republic of Germany are given in Table 8a (Theede et al 1979). The locations are shown in Figure 2. The concentrations were higher in the Western Baltic than in the North Sea and highest in the inner parts of the Kiel Fjord (20-40 mg/kg dw). Small mussels had in general higher concentrations than bigger ones. The concentrations in mussels from pier timbers were considerably lower than in specimens from the sediments near by.

Cadmium levels in Macoma balthica collected near an iron and steel plant near Tvärminne Zoological Station in Finland have been determined by Luotamo and Luotamo (1976). Near the discharge from the plant, cadmium concentrations in small mussels were between 1.5 and 5 mg/kg ww. In bigger mussels and all mussels outside the direct influence of the discharge the concentrations were lower, 0.5-1.2 mg. In the earlier mentioned study on heavy metals in sediments and bottom fauna in the sea off Pori, Finland (Häkkilä 1980), an area affected by the river Kokemäenjoki and water discharges from a titanium dioxide plant, cadmium concentrations in Macoma balthica and Mesidothea entomon were published. The concentrations in Macoma balthica varied between 0.9 and 5.0 mg/kg dw depending on the proximity to the mouth of the river, with an average of 2.1 mg/kg. The corresponding variation for Mesidothea entomon was 1.3-1.8 mg/kg and the average 1.6 mg/kg dw.

Table 5 Concentrations (mean ± standard deviations, µg/g dry weight) of cadmium in whole soft parts of *Mytilus edulis* from 53 locations in Scandinavia. After Phillips 1977.

Location	Mean	sd	Location	Mean	sd
Gulf of Finland			Great Belt		
Helsinki	5.3	0.82	Svinö	1.2	0.82
Kopparnhs	4.2	1.26	Nyborg	0.6	0.19
			Korsör	1.1	0.28
Åland Sea			Bogense	0.7	0.20
Saggö	6.0	1.05	Svallerup	0.8	0.17
Finbo	9.3	3.78	Gylling Nhss	1.2	0.31
öregrund	4.0	0.83	Århus	0.8	0.11
			Ebeltoft	0.5	0.06
Baltic					
Edöfjorden	2.8	0.88	Kattegatt		
Grissleholmen	3.6	0.9	Risö	1.0	0.16
Korsholmen	9.5	2.58	Nyrup	0.5	0.09
Rånö	11.7	4.55	Kullen	1.9	0.44
Landsort	5.3	0.98	Steninge	0.8	0.14
Sävösund	5.6	2.16	Klosterfjorden	0.7	0.23
Risö	4.2	0.97	Ringhals	0.6	0.18
Utterholmen	1.7	0.42	Onsala	0.6	0.10
Oxelösund	4.8	1.60	Lbngholmen	1.0	0.31
Nävekvarn	1.8	0.49	Rivö	0.9	0.22
Isö	1.3	0.46	Göteborg	1.5	0.38
Simpevarp	5.8	1.34			
Öland	4.7	1.64	Skagerrak		
Torhamn	2.6	0.52	Stenungsön	0.7	0.12
			Stenungsund	0.8	0.24
The Sound			St. Askerön	0.7	0.09
Fakse Ladeplads	2.4	0.52	Flatholmen	0.5	0.13
Mosede	2.5	0.28	Brofjorden	0.4	0.05
Köbenhavn	0.8	0.15			
Barsebäck	4.2	0.96	Oslo Fjord		
Taarbaek	1.5	0.52	Steilene	0.9	0.14
Niverod	1.9	0.62	Ostöya	0.8	0.12
Helsingör	0.7	0.10	Malmöykalven	0.9	0.13
			Hovedöya	1.2	0.27

Table 6 Concentrations of cadmium in Mytilus edulis from Danish coastal areas (mg Cd/kg dry tissue)

Area	year	mean	max.	min.	No. of samples
Limfjorden (whole area)	1975	3.0	8.6	0.5	14
Ebeltoft Vig	1976	0.5			10
Århus Bugt		0.8			10
Gylling Näs	1974	1.1	1.9	0.25	2
Gylling Näs	1976	1.2			10
Nyborg Fjord	1976	0.6			10
Båring Vig	1976	0.7			10
Roskilde Fjord	1976	1.0			10
Nyrup Bugt	1976	0.5			10
Jammerland Bugt	1976	0.8			10
Korsör Nor	1976	1.1			10
Fakse Bugt	1976	2.4			10
Öresund (ved Stevns)	1977	3.3			10
Köge Bugt	1976-77	2.3			20
	1977	6.3	9.2	3.6	10
Öresund (ved Dragör)	1977	5.0			10
(ved Korgedybet)	1976	2.4	3.6	1.9	10
(ved København)	1976-77	0.8			20
(ved Skovshoved)	1972	4.3	8.5	1.2	14
(ved Tårbaek)	1976-77	1.3			20
Nivå Bugt	1976-77	2.0			20
Öresund (ved Helsingör)	1976-77	0.9			20
Kattegatt (ved Gilleleje)	1977	1.5			10
Östersoen (ved Rönne)	1975	6.0	6.4	5.5	2

Table 7 Concentrations (means ± standard deviations, µg/g dry weight) of cadmium in whole soft parts of Mytilus edulis from 19 locations and growing tips of Fucus vesiculosus from 9 locations in the region of the Sound. Swedish, Danish and Mid-Sound locations are quoted in separate groups, from south to north in each case. (After Phillips 1979)

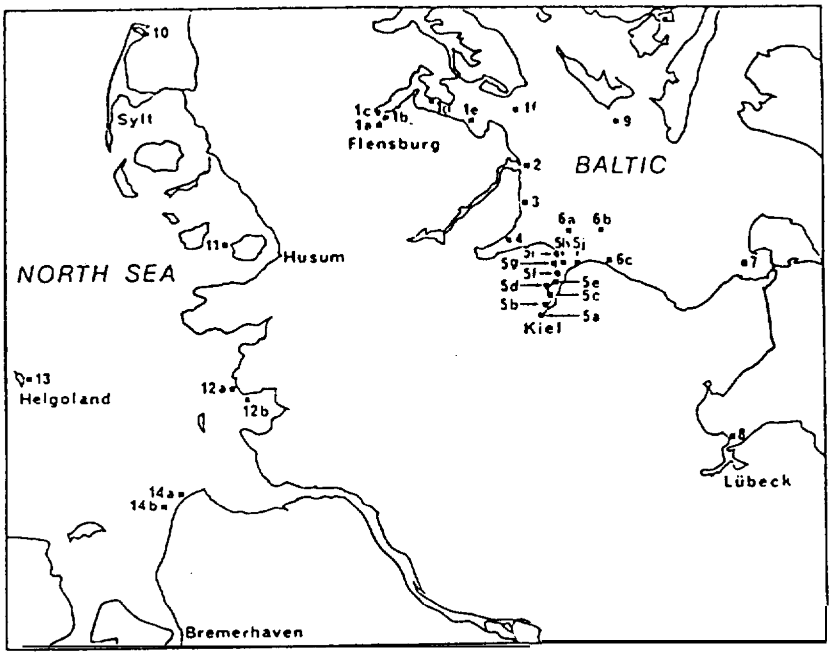
Location	Mytilus edulis		Fucus vesiculosus	
	Mean	sd	Mean	sd
SWEDEN				
Smygehuk	7.6	2.50	2.1	0.41
Fredshög				
Falsterbo kanal	2.4	0.25		
Barsebäck	2.3	0.62		
Saxtorp	5.0	1.50		
Fortuna	0.9	0.15	2.0	0.30
Viken	0.9	0.19	1.9	0.42
Kullen	0.7	0.13	3.2	0.68
Ripagården	0.6	0.10	2.5	0.51
Haverdalsstrand	1.2	0.40	3.9	0.85
DENMARK				
Højerup	3.3	0.80		
Mosede	2.1	0.44		
Dragør	5.0	1.12		
København	0.8	0.32		
Taarbaek	1.1	0.35	2.4	0.69
Niverod	2.0	0.70		
Helsingør	1.0	0.31	2.7	0.45
Gilleleje	1.5	0.63	1.9	0.55
MID-SOUND				
Saltholm	3.3	1.06		
Ven 0.9	0.15			

Table 8a. Mytilus edulis. Cadmium content in **mussels** from locations on the German coasts of the North Sea and the Baltic (from Theede et al 1979).

Position No	Area	Shell-length cm	Fresh weight of soft parts g	Dry weight of soft parts g	Cd-content µg/g dry weight	Number of individuals n
1 a*	Flensbg. Fjord	1.66 ± 0.Cb	0.15 ± 0.01	0.04 ± 0.01	3.90 ± 0.37	10
1a*	"	3.50 ± 0.14	1.16 ± 0.17	0.29 ± 0.04	2.74 ± 0.32	9
1 b	"	3.79 ± 0.10	1.19 ± 0.10	0.29 ± 0.02	6.62 ± 0.47	9
1 c	"	4.26 ± 0.14	2.36 ± 0.24	0.49 ± 0.05	2.94 ± 0.28	10
1 d	"	2.31 ± 0.07	0.24 ± 0.03	0.05 ± 0.01	4.29 ± 0.10	10
1 d	"	4.26 ± 0.15	1.57 ± 0.10	0.32 ± 0.02	4.86 ± 0.19	10
1 d	"	6.11 ± 0.15	6.00 ± 0.60	1.07 ± 0.14	3.59 ± 0.31	9
1e	"	4.90 ± 0.14	4.00 ± 0.32	0.81 ± 0.0s	2.63 ± 0.16	9
1 e	"	6.51 ± 0.19	7.23 ± 0.49	1.29 ± 0.11	4.04 ± 0.16	9
1f	"	2.12 ± 0.10	0.50 ± 0.06	0.12 ± 0.02	2.66 ± 0.23	9
1f	"	4.54 ± 0.07	4.54 ± 0.08	0.67 ± 0.08	4.11 ± 0.50	8
1f	"	7.33 ± 0.17	11.50 ± 0.52	2.44 ± 0.09	3.91 ± 0.29	13
2	Schleimünde	2.27 ± 0.09	0.44 ± 0.06	0.12 ± 0.02	4.19 ± 0.45	9
2	"	4.37 ± 0.12	2.57 ± 0.36	0.65 ± 0.09	4.93 ± 0.33	9
3	Damp	7.74 ± 0.15	11.50 ± 0.71	2.04 ± 0.17	8.34 ± 0.52	9
4	Bight of	2.56 ± 0.14	0.61 ± 0.09	0.13 ± 0.02	3.78 ± 0.18	11
4	Eckernförde	4.35 ± 0.18	2.54 ± 0.24	0.53 ± 0.05	3.00 ± 0.13	11
4	"	7.06 ± 0.09	9.38 ± 0.11	1.72 ± 0.10	3.55 ± 0.40	4
4	"	8.36 ± 0.18	12.32 ± 0.75	2.38 ± 3.16	4.81 ± 0.41	8
5 a*	Kiel Fjord	1.75 ± 0.05	0.19 ± 0.02	0.04 ± 0.00	34.10 ± 1.54	10
5 a*	"	3.23 ± 0.10	1.40 ± 0.17	0.29 ± 0.03	25.90 ± 1.27	12
5 b*	"	1.65 ± 0.41	0.13 ± 0.01	0.03 ± 0.00	12.30 ± 1.35	10
5 b	"	2.04 ± 0.04	0.23 ± 0.02	0.04 ± 0.00	10.60 ± 0.23	8
5 b*	"	3.01 ± 0.06	1.06 ± 0.08	0.22 ± 0.02	8.40 ± 0.60	9
5 b*	"	4.21 ± 0.06	2.52 ± 0.20	0.48 ± 0.05	9.60 ± 1.03	6
5 c*	"	2.74 ± 0.07	0.83 ± 0.07	0.19 ± 0.02	2.70 ± 0.17	10
5 d*	"	3.22 ± 0.13	1.27 ± 0.15	0.24 ± 0.04	2.30 ± 0.16	10
5 e	"	3.23 ± 0.12	1.25 ± 0.1'	0.20 ± 0.02	6.80 ± 0.70	8
5 f*	"	2.94 ± 0.05	1.11 ± 0.0s	0.26 ± 0.02	1.78 ± 0.11	10
5 g*	"	2.41 ± 0.05	0.52 ± 0.03	0.12 ± 0.01	1.40 ± 0.09	10
5 h	"	2.86 ± 0.12	1.08 ± 0.16	0.20 ± 0.03	3.04 ± 0.14	8
5 h	"	6.23 ± 0.07	9.01 ± 0.80	1.68 ± 0.17	5.90 ± 0.43	8
5 i*	"	2.32 ± 0.09	0.29 ± 0.02	0.04 ± 0.00	2.40 ± 0.19	10
5 i*	"	3.07 ± 0.08	0.73 ± 0.11	0.10 ± 0.02	2.90 ± 0.38	9
5 i*	"	4.65 ± 0.11	2.13 ± 0.19	0.24 ± 0.01	3.00 ± 0.61	9
5 j	"	3.45 ± 0.16	1.86 ± 0.24	0.38 ± 3.05	3.10 ± 0.31	10
6 a	Kiel Bight	1.64 ± 0.07	0.23 ± 3.03	0.05 ± 0.01	2.97 ± 0.31	10
6 a	"	4.07 ± 0.17	2.34 ± 0.31	0.51 ± 0.08	2.81 ± 0.12	8
6 a	"	6.57 ± 0.17	9.21 ± 0.55	1.92 ± 0.12	3.85 ± 0.22	10
6 b	"	2.02 ± 0.03	0.42 ± 0.02	0.59 ± 0.01	3.69 ± 0.22	10
6b	"	2.64 ± 0.0s	0.90 ± 0.07	0.20 ± 0.02	1.99 ± 0.11	10
6c	"	2.96 ± 0.10	1.04 ± 0.10	0.22 ± 0.02	3.86 ± 0.44	9
6c	"	5.91 ± 0.57	9.82 ± 2.60	2.X ± 0.61	4.05 ± 0.73	6
7	Fehmarn Sound	7.28 ± 0.09	It.15 ± 0.74	2.13 ± 0.17	7.51 ± 0.59	10
8*	Lübeck Bay	2.08 ± 0.03	0.19 ± 0.03	0.03 ± 0.00	6.15 ± 0.66	9
8*	"	4.57 ± 0.10	2.49 ± 0.19	0.38 ± 0.03	5.89 ± 0.57	8
9	Western Baltic	7.75 ± 0.13	11.40 ± 1.08	1.99 ± 0.22	5.94 ± C.49	9
10*	Isle of Sylt	7.92 ± 0.16	1.13 ± 0.20	0.24 ± 0.04	1.56 ± 0.05	8
10	"	3.17 ± 0.11	1.01 ± 0.05	0.23 ± 0.01	1.85 ± 0.11	9
11	Isle of	3.08 ± 0.1:	0.94 ± c.13	0.19 ± 3.03	1.10 ± 0.39	14
11	Nordstrand	5.21 ± 0.13	4.03 ± 0.24	0.89 ± 0.07	1.13 ± 0.13	10
12 a	Büsum	3.55 ± 0.06	1.42 ± 0.12	0.27 ± 0.03	2.62 ± 5.17	8
12 b	"	3.85 ± 0.12	1.65 ± 0.20	0.32 ± 0.05	2.93 ± 0.19	8
13	Isle of	2.74 ± 0.08	0.39 ± 0.02	0.07 ± 0.01	2.62 ± 0.09	7
13	Helgoland	3.34 ± 0.11	1.19 ± 0.14	0.26 ± 0.04	2.79 ± 3.13	9
13	"	5.94 ± 0.12	b.CO ± 0.31	1.48 ± 0.09	2.92 ± 0.24	10
14 a	Cuxhaven	3.55 ± 0.10	1.52 ± 0.10	0.25 ± 0.02	2.74 ± 0.14	8
14 b	"	3.25 ± c.11	0.98 ± 0.10	0.1-l ± 0.01	2.61 ± 0.09	9

* From piles.

Fig. 2. Locations of Mytilus edulis from German Coasts of the North Sea and the Baltic (from Theede et al 1979).



Examples of cadmium levels in <u>Mesidothea entomon</u> and <u>Macoma balthica</u> from different parts of the Baltic Sea are shown in Table 8b (data from Tervo et al 1980 and the National Report of Poland 1981).

Table 8b. Cadmium in some invertebrates

Species	Area	mg Cd/kg ww	mg Cd/kg dw
<u>Mesidothea entomon</u>	Bothnian Bay*	0.253	1.15
	Bothnian Sea*	0.156	0.74
<u>Macoma balthica</u>	Gulf of Finland*	0.132	0.70
	Gdansk Bight**		0.58
	Pomeranian Bight**		0.07

* Tervo et al 1980

** National Report of Poland 1981

Cadmium concentrations in the liver of cod, Gadus morhua (Engberg 1976, Table 9) and of Baltic herring, Clupea harengus (Table 10, Edgren unpublished) indicate again a dependence on the salinity and/or differences in the bioavailability of cadmium in the different hydrographic regions. Other examples, see Tables 11 and 12.

Table 9 Cadmium in the liver of cod from Denmark collected 1973-1975 (Engberg 1976)

Area	mg Cd/kg dw	± 95% conf	n
The Baltic	0.11	0.05	9
The Sound	0.12	0.04	15
Kattegat	0.08	0.04	12
North Sea	0.06	0.04	13

Table 10 Cadmium in the liver of herring from Sweden collected in the autumn of 1980 (Edgren 1981

Area	mg Cd/kg dw	± s.d.	n
The Bothnian Bay	3.49	2.19	20
The Bothnian Sea	1.43	1.26	20
Northern Baltic	2.69	1.19	17
Southern Baltic	1.37	0.55	20
Kattegat	0.62	0.48	20

Table 11 Cadmium in the liver of cod from Finland collected 1979 (Tervo et al 1980)

Area	mg Cd/kg ww	± s.d.	n
Vaasa	0.016	0.005	28
Pori	0.012	0.004	4
Hanko	0.056	0.056	27
Kotka	0.065	0.049	21

Table 12 Cadmium in the dorso-lateral muscle of Baltic herring (homogenate of 20 specimens) collected 1979 (Tervo et al 1980)

Area	mg Cd/kg ww
Gulf of Bothnia	
Kalajoki	0.007
Gulf of Finland	
Hanko	0.007
Kaunissaari-Haapasaari	0.006

Analyses of cadmium in the liver of flounder from Danish areas, caught in 1979 and 1980, show an average cadmium concentration of 0.11 mg/kg ww (Table 13, Jensen 1981). This is a little lower than what was found in 1973/76, but the difference could be explained by analytical divergence.

Table 13 Levels of cadmium in liver of fish and in Mytilus edulis 1979/80 (mg Cd kg dry weight: mg Cd/kg wet weight). Number in brackets is the number of analysed fish.

	Flounder		Dab		M. edulis[1])	
	1979	1980	1979	1980	1979	1980
The Sound Nivaa Bight	0.27:0.084 (19)	0.27:0.01 (19)				
Great Belt Halskov	0.23:0.066 (19)	0.28:0.096 (20)	0.12:0.050 (5)	-	1.7	1.7
Sjaellands Odde	-			0.24:0.10 (19)	1.9	1.9
Laesø	0.65:0.202 (20)	-			0.80	-

[1]) The sample is an aggregate sample of 40-50 mussels

The cadmium concentrations in fish muscles are about one order of magnitude lower than in fish liver (ICES 1977, Tervo et al 1980). An example is given in Table 14, concerning five coastal fish species from the area of the Bothnian Sea.

Table 14 Concentrations of cadmium in tissues of fish from the brackish water area near Tvärminne Zoological Station. All values are expressed as ppm fresh weight. Figures represent mean + s.d. (Kristoffersson and Oksama, unpublished).

Species/tissue	Mean	s.d.	n
<u>Perca fluvialis</u>			
Perch, muscle	0.031	0.018	28
liver	0.57	0.27	26
<u>Esox lucius</u>			
Pike, muscle	0.021	0.017	15
liver	0.10	0.05	14
<u>Leuciscus rutilus</u>			
Roach, muscle	0.017	0.003	9
liver	0.21	0.09	9
<u>Myoxocephalus quadricornis</u>			
Sculpin, muscle	0.019	0.009	8
liver	0.16	0.06	7
<u>Zoarces viviparus</u>			
Eelpout, muscle	0.028	0.024	19
liver	0.77	0.42	8

Cadmium concentrations in fish from the Bothnian Bay, near the Rönnskär smelter in Sweden, are determined regularly. Levels in liver of fourhorn sculpin and in liver and muscles of whitefish and pike are summarized in Table 15 and 16 (Andersson 1980). A tendency to seasonal variations reflecting the concentrations in the water can be discerned in the liver of fourhorn sculpin, where the levels are building up during the time of the year when the water is frozen to a maximum in May. Differences between the three sampling sites (Byske circa 30 km north of Rönnskär, Rönnskär and Skallön circa 15 km south-east of Rönnskär) can be seen in liver of fourhorned sculpin but not in liver and muscles of whitefish. The concentrations in pike are relatively low.

Table 15 Cadmium concentrations in liver of fourhorn sculpin from Rönnskär.

	May 1979	October 1979	January 1979
Average concentration (mg/kg ww)	0.70	0.52	0.41

Table 16 Cadmium concentrations in liver and muscles of different kinds of fish from the Rönnskär area (mg/kg ww).

Species	Sampling station Byske	Rönnskär	Skallön
Fourhorn sculpin			
liver	0.30	0.52	0.30
Whitefish			
muscle	0.003	0.02	0.008
liver	0.18	0.19	0.18
Pike			
muscle		0.01	
liver		0.021	

The determination of the low cadmium levels in organisms is still a difficult analytical problem. However, cadmium pollution does not seem to increase the levels in fish muscle, which is believed to be due to internal regulations by the organisms (Eustace 1974, Phillips 1977b, Chernoff and Dooley 1979). This is supported by laboratory tests (Row and Massaro 1974, Benoit et al 1976, Edgren and Notter 1980).

The problems concerning the analytical precision at the low levels in biota make it difficult to compare todays data with older material. The measurements of cadmium in benthic invertebrates and fish in the Gulf of Bothnia and the Gulf of Finland in 1979 (Tervo et al 1980) indicate, however, that the concentrations have not increased in these areas when compared with the Baltic Baseline Studies in 1974/1975 (ICES 1977).

The sediment is obviously polluted by cadmium throughout the Baltic. The higher levels, especially in recent deposits, point to an anthropogenic influence. With the exception of locally polluted areas along the coasts, the levels of cadmium in biota seem to be mainly salinity dependent. A gradient of decreasing concentrations with increasing salinity can be demonstrated in invertebrates and fish liver. The levels of cadmium in fish muscle are low and no correlation can be demonstrated with cadmium pollution.

Salinity thus seems to be of great importance to the bioavailability of cadmium, but it is not evident for all organisms. Differences in ways of exposure could influence the uptake. Size and age of individual organisms sampled are factors which also must be considered. Concerning the blue mussel, for example, the size decreases with the salinity, which partly might explain the effect of salinity on cadmium levels.

2.6 Indications of toxic effects in the Baltic

As already mentioned, cadmium is less toxic in saline waters, and fresh water data are not applicable to the situation in the Baltic. The mussel, for instance, has higher concentrations of cadmium in aeras of low salinity than in high salinity areas, 'which has been demonstrated by Phillips (1977a). His studies were based on offshore material, and he concluded that the situation in the Baltic should cause some concern, especially as these waters are known to be polluted by several other compounds as well. In this context, it deserves to be mentioned that the perhaps most critical area, the Bothnian Bay, was not covered by his survey, due to the fact that M. edulis can not survive in such low salinities.

Cadmium levels in liver of herring, caught in the Bothnian Bay and Northern Baltic (Edgren 1981, Table 10) are rather high, i.e. 3.5 and 2.7 mg Cd/kg dw respectively. Larsson and Haux (1982) have found in laboratory experiments that rainbow trout, with comparable levels of cadmium in the liver, show increased blood glucose levels and decreased levels of glycogen in muscle. Larsson (1975) suggested that this kind of response might be a result of a combination of reduced insulin secretion and a stimulated gluconeogenesis in cadmium-exposed fish. It is different to evaluate the ecological significance of the observed response, but it might lead to serious consequences for the general body metabolism and the energetic economy of the fish.

Other sensitive reactions of brackish water fish to cadmium have been reported by Johansson-Sjöbeck and Larsson (1978) and Larsson et al (1981). Flounders, exposed to cadmium in laboratory experiments, developed reductions in hematocrit, hemaglobin and red blood cell counts. An increase of the number of lymphocytes was also noted, indicating an action on the immunological defence of the fish. Further, cadmium caused ionic and neuromuscular disturbances.

Recent data from fourhorn sculpin (Myoxocephalus quadricornis), caught up to 3 km east of the Rönnskärsverken smelter, have demonstrated high concentrations of cadmium in the liver (Johansson-Sjöbeck et al 1983). Thus, a mean concentration of 5.2 ± 1.2 mg Cd/kg dw was reported. In unpolluted areas the concentration is usually below 1 mg/kg. The material was also investigated for sublethal effects and a variety of physiological disturbances was recorded. It is uncertain, however, whether the effects can be related only to cadmium, as several other metals were present in the water.

In conclusion, there is reason for some concern about the present (and future) cadmium situation in low salinity areas of the Baltic. Some fish populations may already be severly affected, or are very close to a critical level. A more systematic search for sublethal effects in field populations of fish is therefore recommended for the future.

2.7 Cadmium in human food and in man

In the National Report of Finland on cadmium, information is presented from a project concerning, amongst others, mineral composition of foods, initiated in 1975 and completed in 1978. The samples of sea fish were collected from Helsinki fish harbour, where fish from different areas are available (Gulf of Finland, Gulf of Bothnia, Northern Baltic Sea). Some results of the study are given in Table 17. The estimated per capita intake due to ingestion of fish products is 0.4 µg Cd/d.

Cadmium in fish from the open market in Sweden has been reported by the Swedish National Food Administration. A selection of potential species from the brackish waters is given in Table 18. The cadmium concentration in fish muscle varies within the range of l-72 µg/kg ww and the mean value of herring, known to be caught in the Baltic, is 20 µg/kg ww.

The daily intake of cadmium for an average Dane is circa 30 µg/day of which only a few per cent comes from food of marine origin. Most of the cadmium intake can be assigned to agricultural products such as potatoes, cereals, vegetables and meat and intestines from animals. Different cadmium levels can be seen in products from different areas, but the modern distribution systems for food and the variety in the normal diet reduces the potential differences in intake. Special diets or consumption of garden vegetables grown in particularly polluted areas may, however, lead to a higher daily intake (Miljøministeriet 1980).

Table 17 Concentrations of Cd per 1 kg/wet weight (means and range) in fish and fish products

Species	Cd µg mean	range
Perch (*Perca fluviatilis*)	5	
Pikeperch (*Lucioperca luciop.*)	5	
Baltic Herring filets (*Clupea harengus membras*)	5	2-10
Baltic Herring with bones (*Cl. har. membr.*)	10	5-10
Sprat (*Sprattus sprattus*)	10	10-20
Salmon (*Salmo salar*)	5	2- 5
Rainbow trout (*Salmo gairdnerii*)	5	2- 5
Whitefish (*Coregonus sp.*)	5	l-20
Vendace filets (*Coregonus albula*)	10	5-20
Vendace with bones (*Cor. alb.*)	20	l-20
Roach (*Rutilus rutilus*)	5	1-10
Ide (*Idus idus*)	5	1- 5
Bream (*Abramis sp.*)	5	1- 5
Pike (*Esox lucius*)	5	1- 5
Eel (*Anguilla sp.*)	50	30-60
Cod (*Gadus morhua*)	5	
Burbot (*Lota lota*)	5	1-5
Flounder (*Platichtys flesus*)	5	2-5
Roe, perch	5	
Roe, vendance	5	1-5
Baltic herring, smoked	20	10-20

Information from the National Report on'cadmium, Finland 1981.

Table 18 Concentrations of cadmium, µg/kg wet weight, in muscles of some selected fish species from the open market in Sweden.

Species	Cd µg/kg ww Mean	range	n
Pike (*Esox lucius*)	1	1-2	11
Pike-perch (*Lucioperca luciop.*)	1	1-2	3
Burbot (*Lota lota*)	1		1
Salmon (*Salmo salar*)	1	1-3	8
Whitefish (*Coregonus sp.*)	3		1
Flounder (*Platichtys flesus*)	20	15-24	4
Baltic herring (*Clupea harengus*)	20	3-72	23
Cod (*Gadus morrhua*)	6	1-18	40

Studies of cadmium levels in humans living near or working at the Rönnskär smelter in Sweden showed a slight but not statistically significant tendency towards higher levels (Blinder et al 1978). An increase in the concentrations in food from the areas near the smelter has also been seen (Kjellström 1973, Pettersson 1976). Elinder and Piscator (1978) analyzed cadmium in the renal cortex from horses and found high levels in horses from the Rönnskär area. Similar studies of liver and kidney from cattle in the same area did not show any significant changes in cadmium concentrations when compared to results from other investigations.

A net accumulation of cadmium in Danish soils, caused mainly by atmospheric fallout and the use of fertilizers, has been observed. This will likely involve increasing levels in agricultural products, leading to a higher intake of cadmium by man. The differences in daily intake and retention by the organism has led to the statistically based estimate that between 1 000 and 30 000 Danes could be expected to have increased protein concentrations in their urine, due to elevated cadmium renal contex concentrations (Miljøministeriet 1980).

3. USES AND EMISSIONS OF CADMIUM

3.1 The use of cadmium

An unambiguous definition of the national use of cadmium for different applications has not been given, and the amounts reported do not always correspond to the same concept of use. The use of cadmium in pigments, for example, can thus imply the amounts of cadmium incorporated in pigments produced in the country, but also the industrial use of cadmium pigments, imported or domestic, or even the total amounts of cadmium in pigments consumed in the country both industrially and in imported goods. The cadmium content of imported products is often not well known, and the use of cadmium can be difficult to assess with accuracy. Many of the figures presented in Tables 19 and 21 are very approximate. Neither are they complete as data are lacking from the USSR and the German Democratic Republic. Some of the information is moreover referrinq to the situation a decade ago.

A very rough estimate of the "final" cadmium cunsumption may, however, be made as follows.

World production is about 18 000 tonnes/year. Most of this is consumed in the USA, the USSR, Europe and Japan with a total population of 1100 million. The average per-capita cunsumption, thus, is about 16 q/year. The final Swedish cadmium consumption (8 million people) could thus be estimated at 150 tonnes/year. (The Swedish cadmium regulations have, however, resulted in a markedly lower consumption; probably less than 100 tonnes/year in 1985.)

According to Swedish estimates, Sweden has accumulated (in various products) some 5 000 tonnes of cadmium within its technosphere. The final fate of this cadmium is uncertain. It must be assumed, however, that some of it will eventually reach the biosphere. The magnitude of this potential pollution problem may be illustrated by the fact that 5 000 tonnes of cadmium corresponds to the natural cadmium content of the uppermost 5 centimeters of all Swedish land. Similar estimates may, of course, be made for other countries.

Intentional use

Considerable amounts of cadmium are thus spread with products. There is, however, a tendency towards a more restricted use of cadmium in several European countries in consideration of the health and environmental hazards associated with cadmium. Finland and Sweden report, for example, decreasing amounts of cadmium used for plating, in plastics, and for electrical purposes. Substitutes for cadmium in different applications exist or are being developed. In some countries, voluntary measures are considered sufficient, while in others legal actions are discussed or realized. The Swedish ban on cadmium, comprising the use of cadmium for electroplating and in stabilizers and pigments, is aiming at a reduction of the cadmium cunsumption to only those applications where cadmium is absolutely necessary. Similar actions have been taken in Denmark and are considered in Finland, while measures to reduce cadmium use in the Federal Republic of Germany are taken case-by-case and mainly on a voluntary basis. Very stringent emission limits can also have the effect that the use of cadmium decreases, which has been seen, for example, in electroplating. Examples of measures to limit the use of cadmium are listed in Table 20.

Table 19 Intentional use of cadmium in tonnes/year (no data submitted by USSR and GDR)

		Finland (1980)	FRG (1977)[1]	Denmark (1977/78)	Sweden (1980)	Poland (1983)
Accumulators and batteries	production	-	238		170	
	use	7		4.2	38	
Paints and pigments		0.022	572	27.2[3]	8[4]	
Stabilizers		14	366	133	75	
Alloys	production			47	40	> 333
	use			6		
Surface treatment		1	397	1.16	l-27	
Electric and electronic products		2	6			
Glass			15			

1 No specifications of the uses given.

2 In production of Ti02 pigments. Circa 4 tonnes of pigments are imported for industrial use.

3 Imports in products included but probably under-estimated.

4 Used in domestic manufacture. Circa 60 tonnes imported in goods.

5 Used in domestic manufacture. Circa 36 tonnes imported in goods.

6 Imports not taken into account.

7 Plus circa 40 tonnes in imported goods.

The use of Ni/Cd cells, on the other hand, has rapidly increased during the 1970's. The larger, open cells are less widely used and easier to collect and recycle than the small, sealed cells, found in, for example, calculators, photographic equipment and industrial applications. Collection systems for batteries exist or are being discussed in several countries, and there is no doubt that the environment could be spared considerable quantities of cadmium this way. As an example could be mentioned a newly constructed plant in Sweden for the recovery of 40 tonnes of cadmium per year from open cells.

Table 20 Measures to reduce the use of cadmium.

- Shift to cadmium-free pigments, stabilizers and solders.
- Plating with zink instead of cadmium.
- Restrictive use of nickel-cadmium batteries.

Cadmium as contamination

Examples of the quantities of cadmium as impurity handled in different industrial fields are presented in Table 21. Most of the cadmium appear in metallurgical activities such as mining and metal production. Sulfur dioxide occurring as a by-product from processing and refining of non-ferrous metals, contains cadmium which can be emitted directly or during the conversion of sulfur dioxide to sulfuric acid. Some cadmium follows the acid. The emissions from the production of TiO_2 pigments in Finland are entirely due to the cadmium content of the sulfuric acid used in the process.

The quantities of cadmium handled in the phosphate-based industry vary depending on the cadmium level of the raw phosphate. As a good deal of the phosphoric acid produced goes to fertilizer production, some of the cadmium will end up in the fertilizers. Gypsum waste from this production also contains cadmium and is considered an important source of emissions to water in some European countries.

Fossil fuels hold small amounts of cadmium, which are released to the atmosphere during combustion. The growing use of coal, which contains more cadmium than oil, could result in increasing emissions from energy production.

The figures in Table 21 show that the quantities of cadmium in uses where cadmium appears as an impurity are very important. They cannot easily be restricted. Actions are taken to reduce the distribution of cadmium to the environment through emission control and, in some cases, selection of less cadmium-rich raw materials. Cadmium is usually not the only heavy metal from these sources.

Tabell 21 Quantities of cadmium handled as contamination in tonnes/year (data not submitted by Poland, USSR and GDR)

	Finland* (1980)	FRG (1977)	Denmark (1977/78)	Sweden (1985)
Mining industry	175			40
Smelters, iron and steel	596		6	50-100
Production of fertilizers and phosphoric acid	26		8.1	3-14
Energy production	(2)		8.7	2-3
Production of sulfuric acid	9			
Cadmium in zinc		52	3.4	10-40
Cadmium in slags		18		
Others		121	5.1	

* Quantities potentially affecting the Baltic Sea, figure in paranthesis valid for the whole of Finland

3.2 Emissions of cadmium

The emissions of cadmium in tonnes/year to air and water are shown in Tables 22 and 23. They include emissions from all sources within the country and not only those which might affect the Baltic Sea. A comparison between the two tables shows that the emissions to air are larger than the emissions to water. This observation is supported by data, reported by e.g. Denmark and Sweden, on the atmospheric fallout versus the direct input of cadmium to the aquatic environment. It seems reasonable to suppose that much of the airborne cadmium finally reaches the sea. This points to the importance of controlling cadmium emissions to the air as well as direct discharges to water.

Table 22 Emissions of cadmium to air in tonnes/year (no data submitted by the USSR and the German Democratic Republic)

	Finland	FRG (1979)	Denmark (1977/78)	Sweden (1985)	Poland (1983)
Mining			No mining	0.2	
Smelters, iron and steel industry	2	21.1	0.2	5	14,2
Manufacture of accumulators and batteries		0.3	No prod.	0.06	
Incineration of municipal waste	0.26	2.9	2.2	0.4	
Other handling of municipal waste					
Pigments		0.3			
Stabilizers		0.1			
Energy production	0.3-0.7	9.6	1.4	0.35	
Others		5 (glass)	1.2	0.5 (cable incineration)	

Table 23 Emissions of cadmium to water in tonnes/year (no data submitted by the USSR and the German Democratic Republic)

	Finland	FRG (1978/80)	Denmark (1977/78)	Sweden (1985)	Poland (1983)
Mining	0.02	-	-	0.4	
Abandoned mines				1.0	
Smelters, iron and steel	0.2	8-18	Very small	0.5	6,2
Electroplating		0.8	0.1	0.05	
Manufacture of accumulators and batteries	-	3	-	0.01	
Fertilizer and phosphoric acid industry		0.7	0.7	0.1	
Sulphuric acid manufacture	0.3			0.1"	
Municipal sewage	0.15		2.8	0.2	
Pigments	0.02	1.2			

* Except sulfuric acid as by-product from smelting of sulfide ores

3.3 Methods for reducing cadmium emissions

Cadmium often occurs together with other heavy metals in discharges to air and water. Conventional methods for reducing metal emissions, such as electrostatic precipitators or bag filters on dust are therefore naturally also applied to cadmium. Examples of water pollution control are precipitation, ion exchange and electrolytical removal.

Specific measures justified by the presence of cadmium might, however, sometimes be necessary. Cadmium in process gas or flue gas preferably absorbs on to or forms small particles, which put higher demands on removal efficiency. Finland reports that cadmium until recently escaped with the ejector water from jet condensers in a sulfuric acid plant. Drop separators have now been installed which, together with some process modifications, are expected to lead to a substantial reduction in the emissions of cadmium from this plant. Scrubber water from an iron and steel mill in Finland will be treated and recycled in a closed system. The Federal Republic of Germany reports that dry methods for dust control are preferred within the iron and steel industry. Dust from different metal production processes is recycled. Process water and run-off is collected and recycled or treated.

A facility in Sweden producing copper-cadmium alloys is currently testing an improved filtering technique, a so-called absolute filter, for capturing dust.

Wastewater containing cadmium should be treated apart from other water streams for the best result. Chemical treatment is common and recycling of process water reduces cadmium emissions even further.

Emissions from incineration of domestic waste can be tackled in two ways: through installation and improvement of emission control devices or through partial elimination of cadmium from the waste. Examples from Denmark and Sweden show that while larger facilities for incineration of waste are often equipped with sufficient emission control, smaller facilities seldom have emission control equipment or use very rudimentary control systems. The greater importance of refuse as a source of energy can in the future result in increasing emissions. Actions to reduce the use of cadmium in consumers products would counteract this tendency.

A summary of the different methods reported to reduce cadmium emissions are presented in Table 24.

Table 24 Measures to control cadmium pollution (proposed or actually applied)

Recycling of process water in ore concentrating plants.

Condensation of cadmium fumes in zinc production.

Precipitation and flocculation of cadmium in waste water and scrubber water.

Process gas treatment (electrostatic precipitators, bag filters, scrubbers).

Drop separators in sulfuric acid production.

Recycling of scrubber water from gas treatment in iron and steel production.

Manual or mechanical separation of cadmium from scrap (cars and cables) and domestic refuse (plastics and batteries).

Collection of open and sealed Ni/Cd cells and recovery of their cadmium content.

3.4 **National standards**

Emission standards

Three principal constructions of the legislative basis for emission control can be seen:

- General emission standards.
- Permit systems with individual prescriptions and emission limits.
- Emission limits as a function of environmental quality criteria.

Emission standard combined with a permit system exist in the Federal Republic of Germany. The rules of the Technische

Anleitung zur Reinhaltung der Luft (TA-Luft), which is an ordinance to be used by the permit-issuing authorities and a complement to the Bundes-Immissionsschutzgesetz, limit the concentration of cadmium and its soluble compounds in emissions to air to 20 mg/m^3 provided that the emission rate is 0.1 kg/h or more.

Directives concerning limit values for water discharges have been adopted by the Commission of the European Communities. The emission limits are set individually for different kinds of industrial sources, both as a maximum concentration in the effluent and a maximum amount of cadmium discharged per kg of cadmium handled (see Table 25). These are the maximum emission limits, stricter provisions may thus be prescribed. The directives also state that, in the case of new plants, the emission standards shall be set in accordance with the best technical means available.

Denmark has to date no emission standards for cadmium. The water quality criteria can be used for control of emissions to marine areas. The standpoint of the environmental authorities is that the emissions of cadmium to the whole environment should be reduced as much as possible.

Neither Finland nor Sweden apply general standards for emissions, but limit values are set case by case. Anyone planning to handle cadmium industrially in Finland must, not later than six months in advance, notify the National Board of Waters and present, <u>inter alia</u>, an estimate of the effects, preventive measures and a monitoring programme. A supervision rule of the 1970's sets the maximum concentrations in effluents from surface treatment plants to 2-3 mg/l. There are also draft standards for the influent to municipal sewage treatment plants. 0.01 mg/l if only treatment process is considered 0.005 mg/l if the sludge is to be used for fertilization.

Table 25 Emission standards of the Commission of the European Communities (from the official Journal of the European Communities 1983)

I. Limit values and time limits

Industrial sector (1)	Unit of measurement	limit values which must be complied with as from	
		I. I. 1986	I. I. 1989 (2)
1. Zinc mining, lead and zinc refining, cadmium metal and non-ferrous metal industry	Milligrams of cadmium per litre of discharge	0,3 (3)	0,2 (3)
2. Manufacture of cadmium compounds	Milligrams of cadmium per litre of discharge	0,5 (3)	0,2 (3)
	Grams of cadmium discharged per kilogram of cadmium handled,	0,5 (4)	(5)
3. Manufacture of pigments	Milligrams of cadmium per litre of discharge	0,5 (3)	0,2 (3)
	Grams of cadmium discharged per kilogram of cadmium handled	0,3 (4)	(5)
4. Manufacture of stabilizers	Milligrams of cadmium per litre of discharge	0,5 (3)	0,2 (3)
	Grams of cadmium discharged per kilogram of cadmium handled	0,5 (4)	(5)
5. Manufacture of primary and secondary batteries	Milligrams of cadmium per litre of discharge	0,5 (3)	0,2 (3)
	Grams of cadmium discharged per kilogram of cadmium handled	-1,5 (4)	(5)
6. Electroplating (6)	Milligrams of cadmium per litre of discharge	0,5 (3)	0,2 (3)
	Grams of cadmium discharged per kilogram of cadmium handled	0,3 (4)	(5)
7. Manufacture of phosphoric acid and/or phosphatic fertilizer from phosphatic rock (7)		—	—

(1) Limit values for industrial sectors not mentioned in this table will, if necessary, be fixed by the Council at a later stage. In the meantime the Member States will fix emission standards **for cadmium discharges autonomously** in accordance with Directive 76/464/EEC. Such standards must take into account the best technical means available and must not be less stringent than the most nearly comparable limit value in this Annex.

(2) On the basis of experience gained in implementing this Directive, the Commission will. pursuant to Article 5 (3), submit in due course to the Council proposals for fixing more restrictive limit values with a view to their coming into force by 1992.

(3) Monthly flow-weighted average concentration of total cadmium.

(4) Monthly average.

(5) It is impossible for the moment to fix limit values expressed as load. If need be, these values will be fixed by the Council in accordance with Article 5 (3) of this Directive. If the Council does not fix any limit values, the values expressed as load given in column '1. 1. 1986' will be kept.

(6) Member States may suspend application of the limit values until I January 1989 in the case of plants which discharge less than IO kg of cadmium a year and in which the total volume of the electroplating tanks is less than 1,5 m^3, if technical or administrative considerations make such a step absolutely necessary.

(7) At present there arc *no* economically feasible technical methods for systematically extracting cadmium from discharges arising from the production of phosphoric acid and/or phosphatic fertilizers from phosphatic rock. No limit values have therefore been fixed for such discharges. The absence of such limit values does not release the Member States from their obligation under Directive 76/464/EEC to fix emission standards for these discharges.

2. Limit values expressed as concentrations which in principle must not be exceeded arc given in the above table for the industrial sectors in sections 2, 3, 4, 5 and 6. In no instance may limit values expressed as maximum concentrations be greater than those expressed as maximum quantities divided by water requirements per kilogram of cadmium handled. However, because the concentration of cadmium in effluents depends on the volume of water involved. which differs for different processes and plants, the limit values. expressed in terms of the quantity of cadmium discharged in relation to the quantity of cadmium handled, given in the above table must be complied with in all cases.

3. The daily average limit values arc twice the corresponding monthly average limit values given in the above table.

4. A monitoring procedure must be instituted to check whether the discharges comply with the emission standards which have been fixed in accordance with the limit values laid down in this Annex.

   This procedure must provide for the taking and analysis of samples and for measurement of the flow of the discharge and the quantity of cadmium handled.

   Should the quantity of cadmium handled be impossible to determine. the monitoring procedure may be based on the quantity of cadmium that may be used in the light of the production capacity on which the authorization was based.

5. A sample representative of the discharge over a period of 24 hours will be taken. The quantity of cadmium discharged over a month must be calculated on the basis of the daily quantities of cadmium discharged.

   However, a simplified monitoring procedure may be instituted in the case of industrial plants which do not discharge more than IO kg of cadmium per annum. In the case of industrial electroplating plants, a simplified monitoring procedure may only bc instituted if the total volume of the electroplating tanks is less than 1,5 m^3.

Sweden applies a permit system where emission limits, necessary precautions, emission control equipment etc. are established by the National Franchise Board or the County Administration Boards with consideration of the risks of effects in the environment, the best available technology and economic means.

Polish legislation does not involve emission standards but regulates discharges with the help of environmental quality standards. Water discharged to the municipal sewage systems should not contain more than 0.1 mg Cd/l.

Standards of environmental qualitv

The adopted directives of the Commission of the European Communities include limit values for fresh water and salt water as well as certain constraints regarding cadmium levels in sediments and organisms (see Table 26).

Table 26 Environmental aualitv objectives of the CEC (Official Journal of the European Communities, 1983).

For those **Member States which apply the exception referred to in Article** 6 (3) **of Directive 76/464/EEC, the emission** standards which Member States must establish and ensure are applied, pursuant to Article 5 of that Directive. will be fixed so that the appropriate quality objective or objectives from among those listed below is or are complied with in the area affected by discharges of cadmium. The competent authority shall determine tbe area affected in each case and shall select from among the quality objectives listed in paragraph 1 the objective *or* objectives that it deems appropriate having regard to the intended use of the area affected, while taking account of the fact that the purpose of **this Directive is to eliminate all pollution.**

1. The following quality objectives [1], which will be measured sufficiently close to the point of discharge, are fixed, with the object of eliminating pollution within the meaning of Directive 76/464/EEC and pursuant to Article 2 of that Directive [2]:

1.1. The total cadmium concentration in inland surface waters affected by discharges must not exceed 5 µg/litre. -

1.2. The concentration of dissolved cadmium in estuary waters affected by discharges must not exceed 5 µg/litre.

1.3. The concentration of dissolved cadmium in territorial waters and in internal coastal waters other than estuary waters affected by discharges must not exceed 2.5 µg/litre.

1.4. In the case of waters used for the abstraction of drinking water, the cadmium content must conform to the requirements of Directive 75/440/EEC [3].

2. In addition to the above requirements, cadmium concentrations must be determined by the national network referred to in Article 5 and the results compared with the following concentrations [2]:

2.1. In the case of inland surface waters, a total cadmium concentration of 1 µg/litre.

2.2. In the case of estuary waters, a dissolved cadmium concentration of 1 &litre.

2.3. In the case of territorial and internal coastal waters, other than estuary waters. a dissolved cadmium concentration of 0,5 µg/litre.

If these concentrations arc not complied with at any one of the points on the national network, the reasons **must be reported to the Commission.**

3. The concentration of cadmium in sediments and/or shellfish, if possible of the species Mytilus edulis, must not increase significantly with time.

4. Where several quality objectives are supplied to waters in an area, the quality of the waters must bc sufficient to comply with each of those objectives.

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(1) 'The cadmium concentrations indicated in 1.1, 1.2 and 1.3 are the minimum requirements necessary to protect aquatio life.

(2) With the exception of quality objective 1.4, all concentrations relate to the arithmetic mean of the results obtained over one year.

(3) Directive 75/440/EEC concerns the quality required of surface water intended for the abstraction of drinking water in the Member States (OJ No L 194. 25. 7. 1975, p. 26). It provides for a mandatory cadmium value of 5 µg/litre on the basis of 95 % of the samples taken.

The environmental quality standards in Poland follow different water areas and purity classes. The maximum admissible cadmium concentration in harbour basins and interval sea water is 5 µg/l. Surface fresh waters are divided into three purity classes, each with its environmental quality standard:

I Drinking water, water for cultivation of salmonide fish. Cadmium limit 5 µg/l.

II Water for cultivation for other kinds of fish, drinking water for farm animals, bathing, recreation and water sports. Cadmium limit 30 µg/l.

III Water for industrial purposes (where water of higher quality is not required), irrigation of agricultural land used for horticulture and in greenhouses. Cadmium limit 100 µg/l.

A similar classification of water bodies exists in Finland. Five different classes are defined by physical and chemical parameters: I (excellent), II (good), III (satisfactory), IV (passing), V (poor). Cadmium concentrations higher than 10 µg/l puts the water in question in the classes IV-V and it can then only be used for cooling, power production and transportation. The maximum cadmium concentration in water for domestic use is 5 µg/l.

Standards for the maximum concentration of cadmium in waters of the USSR are
10 µg/l as a standard related to human health,
5 µg/l as a standard for fishing waters.

Standards of environmental quality do not exist yet in Sweden, but standards for cadmium in fresh water are being discussed. In the proximity of point sources, cadmium levels are below 0.5 µg/l, with the exception of one industry, outside which levels around 1.5 µg/l have been measured, and the normal level is considerably lower. A Swedish standard of environmental quality will probably be set much below 1 µg/l.

4. PROPOSALS FOR FURTHER ACTIONS

4.1 Actions reported by the Contracting Parties

Some of the member states have submitted information on national strategies, proposed'or implemented, to reduce the use and emissions of cadmium.

Finland. A working group with the task to study these matters has been formed. Finland would also like to emphasize the need for taking every practicable measure to eliminate cadmium discharges, but does not recommend insertion of cadmium into Annex I with the motivation that Annex I should be reserved for synthetic hazardous substances.

Denmark.
Considering
that cadmium is extremely toxic to man and animals,
that an increasing occurrence of cadmium in our environment, especially the soil, can be observed,
that cadmium is accumulated in human kidneys,
that these tendencies can be expected to persist if counter-measures are not taken,
national and international shift to the use of cadmium-free products should be endeavoured and an improved control of cadmium discharges to the environment should be realized. The following concrete actions have been reported to the Paris Commission:

1. Pigments: restrict the use of cadmium to few, strictly necessary areas.
2. PVC-stabilizers: shift to cadmium-free stabilizers.
3. Surface coating: restrict the use of cadmium to few, necessary areas.

4. Soldering: restrict the use of cadmium to few, necessary areas.
5. Ni-Cd accumulators: consider marking and recycling.
6. Coal: investigate the possibilities to improve emission control equipment on power plants.
7. Refuse and sewage sludge: improve emission control equipment on incinerators.
8. Fertilizers: investigate the possibilities to reduce the cadmium content.
9. Local emissions: specific actions.

By the end of 1982 actions had been taken on items 1, 2 and 3 by way of drafting a statutory order to ban cadmium, with some exceptions, for these three areas of use, which supposingly would reduce the cadmium burden by 60-70 %. The order was passed in 1983 (Miljøministeriets bekendtgørelse nr. 196 af 26. juli 1983) and bans all use of cadmium for cadmiation and as pigments and stabilizers from 1989, 1987 and 1988 (for other plastics than PVC, 1987) respectively with a few exceptions.

A number of studies and monitoring programmes related to cadmium are also running. Among these can be mentioned plant uptake of cadmium from fertilizers, mobility of cadmium in soil and ground water, import of cadmium in plastics and coated products, and monitoring of cadmium deposition and levels in human kidneys.

Regarding insertion of cadmium to Annex I, Denmark would like to await the final report on cadmium.

<u>The Federal Republic of Germany</u>. In a report to the Technical Working Group of the Paris Convention (1983), the Federal Republic of Germany stresses emission control at major sources as being the most cost-effective way of reducing cadmium pollution.

The contribution from a few industrial sources to the overall cadmium emissions, especially to water, seems rather important, and elsewhere has been reported that non-ferrous metal works and remelting installations contribute almost 90 % of the emissions to water.

The recommendations of the Federal Minister of the Interior and the Federation Panel on Environmental Chemicals can be summarized as follows:

1. Revision of the TA-Luft. Is there need for more, specific emission limits?

2. Further research in the field of
   - substitutes for cadmium pigments (exception for high process temperatures)
   - substitutes for cadmium stabilizers (exception for high process temperatures)
   - substitutes for cadmium as protective coating (replacement by aluminium and other metals possible in some applications)
   - possibilities of reuse and recycling of Ni/Cd batteries, and plastics containing cadmium stabilizers and pigments, which have been proven to be technically feasible
   - no-effluent electroplating processes.

3. Limitations of indirect discharges to municipal sewage plants.

4. Ordinance on dredged material.

5. Identification of polluted agricultural soils.

6. Monitoring stations for specific ecosystems.

7. Ground water control.

8. Protection of non-productive soils.

9. Surveillance of levels in food.

10. Epidemiological studies.

11. Improvement of analytical methods.

Sweden. Measures should be taken in accordance with the following principles:

1. Cadmium in pigments, stabilizers and cadmium for surface treatment: all use of cadmium should be prohibited where it is not absolutely necessary.

2. Cadmium in batteries: the use of cadmium should be permitted, but complete marking, collecting of used batteries and recycling should be endeavoured.

3. Cadmium in fertilizers: development of methods to eliminate cadmium should be promoted.

4. Cadmium from industrial sources, combustion of fossil fuels and incineration of domestic waste: the best available technology for reducing cadmium emissions should be used, determined on a case-by-case basis.

Actions on items 1, 3 and 4 were taken in 1983 or earlier. In 1987 the Government decided that cadmium batteries should be marked and collected for recovery or safe disposal. A pilot plant for low-cadmium phosphate fertilizers will be built with Government support.

4.2 Summary and Lead Country recommendations as by May 1983[1])

It is evident from what has been reported on measures and activities in different countries that cadmium pollution is considered a serious hazard to human health and to the environment. The importance of'the cadmium flow to the Baltic Sea from anthropogenic sources is reflected in the cadmium levels of the sediments. Dating of the sediment layers reveal an increase, about tenfold, since the last century or the beginning of this century. The concentrations in invertebrates and fish do not constitute an immediate threat to human health in general, but certain risk groups might need closer attention. The human intake of cadmium is mainly a function of cadmium levels in other parts of the diet than food of marine origin. However, the concentrations in the Baltic are such that local fish populations might be affected, especially in areas of low salinity where cadmium toxicity is higher.

Routes of input to the Baltic Sea are deposition of airborne cadmium, river load and direct discharges from coastal sources. The annual load of airborne cadmium seems to be as large, if not larger, than the collected discharges to water. Controlling cadmium emissions to the air is thus just as relevant to the situation of the Baltic as limiting direct cadmium discharges to the Baltic itself or its tributaries.

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[1]) These are the original recommendations made by Sweden in 1983. They are repeated here, in spite of the fact that some of them are no longer up to date (1987).

The strategy of cadmium pollution abatement follows three principal lines:

Restriction of the use of cadmium in products.
Reuse and recovery of cadmium-containing products and materials.
Control of emissions to air and water from point sources.

Cadmium in products is an important future source of cadmium pollution. The consumption for intentional use has been, and still is, decreasing in many fields of application as a result of national regulations or voluntary action. Equivalent substitutes are available for much of the cadmium used as stabilizers, pigments, solders, and for metal plating, and the development of processes and products will probably further reduce the number of applications. There is, however, probably still much cadmium incorporated in products for reasons of routine, costs or lack of information, which easily could be omitted.

The Contracting Parties are recommended to take every opportunity to eliminate or reduce the use of cadmium in products to only strictly necessary applications.

The following fields of applications should be considered specifically:
- electroplating
- stabilizers
- pigments
- solders
- fertilizers
- alloys.

It is also recommended that measures taken and planned be presented to the Commission, at latest to the meeting of the WGS in 1984.

Recovery of Ni/Cd cells is technically feasible, and collection systems exist or are being arranged in several European states. Labelling of the batteries is of vital importance, and should be effected on an international level.

The Contracting Parties are recommended to see to that labelling, collection and recovery of batteries containing cadmium be accomplished as soon as possible or latest by January 1, 1986. The Parties are also recommended to report to the Commission on actions taken, the amount of batteries collected, the final destination etc.

Emissions to air and water from many point sources have decreased substantially with the development and introduction of emission control techniques, but, according to the National Reports, much remains to be done. The Contracting Parties are recommended to take all available measures to reduce cadmium emissions as far as possible. Tangible plans for how and when emissions to air and water will be limited on the national level, together with complementary data on the emitted amounts of cadmium and emission rates/concentrations from different sources, should be presented to the meeting of the WGS in 1984.

An emission standard for discharges to water of 0.1 mg/l as a monthly average is suggested. Too little information on current emission rates and standards is available today for a proposal regarding standards for emissions to air to be made. The Contracting Parties are requested to submit such information to the meeting of the WGS in 1984.

Only one statement concerning transfer of cadmium from Annex II to Annex I has been submitted. Finland is of the opinion that Annex I should be reserved for synthetic pollutants, which cadmium is not. Sweden does not, on the other hand, see any formal hindrance for inserting cadmium in to Annex

I, which would, in fact, facilitate an agreement on actions to prevent discharges and environmental effects of cadmium. As the Lead Country, Sweden therefore recommends that cadmium be inserted into Annex I.

The cadmium levels in the Baltic Sea are generally within the range of 0.02-0.03 µg/l according to recent investigations. Higher values can be found in areas directly influenced by rivers or coastal discharges. Threshold values between 0.5 and 1.0 µg/l for toxic effects on fish in fresh water have been reported. Reproduction of certain invertebrates is disturbed already at levels below 0.2 µg/l in fresh water and changes in the composition of fresh water plankton communities occur at 0.2-0.3 µg/l. The toxicity of cadmium decreases with increasing salinity, but the difference between toxic levels and levels common in the environment is relatively small, especially in low salinity areas of the Baltic.

Sweden proposes that the following water quality objectives for the Baltic Sea be adopted by the Contracting Parties:

- the concentration of cadmium in the coastal zones of the Baltic Sea should not exceed 0.10 µg/l,

- in general, an increase in the cadmium concentration of more than 25-30 % of the background level should not be permitted.

Environmental quality objectives regarding cadmium concentrations in biota, e.g. Mytilus edulis, could be a valuable complement to the water quality criteria. However, such objectives have not been suggested in this report. More information is needed on background levels in indicator organisms, taking into consideration variations due to analysis, locality, season, and phenomena such as the influence of the salinity on development and cadmium uptake of the organism. A method to overcome several of these difficulties has been suggested by Fischer (1983 and 1984). The body burden of soft parts is related to shell weight, which is considered a more precise way of monitoring, especially for detection of slightly elevated levels.

Regarding the sediment, a general recommendation, similar to the environmental quality objectives of the European Communities, that an increase over time in cadmium concentration not be permitted, is suggested.

4.3 Comments on the first progress report

The additional information from the Contracting Parties to the technical och scientific review in this report confirmed the general conclusions drawn on basis of the former version of the document, namely that

- Deposition of airborne cadmium followed in importance by river input are the main routes of cadmium to the Baltic Sea.

- In certain areas the level of contamination is such that the marine environment is endangered.

- The flow of cadmium to the Baltic must be reduced as far as possible.

Written comments to the lead country proposals on water quality objectives and on methods to reduce cadmium pollution were received from the USSR, the German Democratic Republic and Finland.

The USSR accepts the recommendations to

- take every opportunity to eliminate or reduce the use of cadmium in different applications and to report on the measures adopted and planned,

- to consider the possibilities to label, collect and recover cadmium-containing batteries at the latest January 1, 1986, and to inform the Commission about the actions undertaken,

- to take all opportunities to reduce the emissions of cadmium and to submit specific proposals on national planning of appropriate measures as well as data on quantities and concentrations of emissions from different sources,

- to submit proposals concerning standards for emissions to air,

- to prevent an increase in the cadmium levels of bottom sediments.

These recommendations agree in all essentials with the corresponding Swedish proposals.

Regarding the recommended standards for water quality, the USSR has objection to the proposed maximum allowable concentrations in water, 0.1 µg/l. It is pointed out that this is many times lower than the hygienic and fishery freshwater criteria in the Soviet Union and several other countries. A more precise evaluation of the effects of cadmium on the marine environment is necessary. Such low concentrations are also practically impossible to measure. A definition of the concept "coastal zone" is needed. If an increase of more than 25-30 % of the background concentration is not to be permitted, what level should then be accepted as background level? The USSR finds no reason to transfer cadmium from Annex II to Annex I with the motivation that cadmium is a natural element of the sea.

The German Democratic Republic states that lowest measurable concentration is 0.2 µg/l.

The response from Finland also'deals with the analytical difficulties connected with the proposed standards. Resources should be allocated to establish reliable techniques for monitoring cadmium concentrations in water, marine organisms and sediments. It might also, according to Finland, be difficult to reach 0.1 µg/l near an effluent outfall even when the concentration in the effluent is very low. The criteria should therefore include instructions as to where and how far from discharges the cadmium concentrations shall be measured.

Comments were also made to the proposed standard for emissions to water. The USSR considers it hardly possible to establish just one standard for emissions independent of the water quality criteria and local conditions. Finland can in principle accept the lead country proposal, which should, however, be complemented by recommendations regarding dilution. Finland also recommends an adjustment of the limit to each kind of industrial source and proposes that a small working group be established to study the possibilities for such a differentiation.

Lead Country Comments (1987)

Recent investigations of cadmium in the Baltic water show that the concentrations lie well under 0.1 µg/l, mostly in the range 0.02-0.03 (-0.05) µg/l. Few regional variations can be seen. This level, low as it may seem, may well be elevated over the natural background level since the present cadmium input is at least ten times larger than the natural input. Levels around the proposed water quality objective of

0.1 µg/l constitute a considerable increase over the present level and of the amount available to the marine environment. The basic principle must be that only a slight augmentation of the background level can be permitted. This means that circa 0.1 µg/l would be the upper limit for acceptable cadmium concentrations. At levels from 0.1 µg/l there are strong reasons to believe that ecological effects on the marine environment can occur. These must be the main factors to take into consideration when establishing a quality objective for water.

Sweden is of the opinion that measurement of such low concentrations is feasible but realizes that it presents many practical difficulties. A certain time for improvement of analytical methods should therefore be allowed.

The concentrations in sediments and living organisms reflect water quality. Analysis of cadmium in sediments and living organisms can be of help when water analysis is uncertain. Concentrations in sediments and biota also give more relevant information about the degree of pollution from a toxicological-ecological point of view. Sediment data also provide valuable information about the variation in cadmium concentrations over time. Sweden is of the opinion that water quality objectives should be complemented by objectives for sediments and biota.

Selection of indicator organisms and determination of maximum permissible concentrations are complicated by the variations in salinity between different areas of the Baltic. The common mussel (Mytilus edulis) is generally considered a suitable indicator organism but does not exist in the northern parts. It would be advisable that one or several complementary species be chosen. An interesting possibility could be perch liver, where cadmium concentrations have shown a correlation with the concentrations in the surrounding water. This, however, needs further consideration.

However, a draft recommendation document regarding primary products and emission control is being prepared and will be presented to the WGS.

4.4 Proposed recommendations **(WGS 1984)**

At the 7th meeting of the WGS in 1984, Sweden submitted a draft proposal for recommendations to reduce the emissions of cadmium to the environment from a number of industrial sources and from the handling of cadmium containing batteries. Sweden also proposed environmental quality objectives for water and, in a rather general form, for sediments and mussels:

(i) in general a maximum elevation of the background level in water of 30 %,

(ii) in water of the coastal zones a maximum concentration of 0.1 µg/l from 1. 1.1987. Monitoring and analysis methodology will be defnied later.

(iii) no significant increase of cadmium concentrations with time in sediments and shellfish should be permitted. Standards for maximum levels of cadmium in sediments and marine organisms based on health assessments and ecological aspects will be established later.

The meeting was of the opinion that priority should be given to recommendations aiming at reduction of use and emissions of cadmium and that the environmental quality objectives can be considered at a later stage. Two proposals for recommendations were adopted, one for safe handling of used mercury- and cadmium-containing batteries and one regarding limitation of cadmium discharges from landbased sources. They appear here in the form adopted by the Helsinki Commission (see pages 118-120).

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PROGRESS REPORT ON MERCURY;
prepared by the Union of Soviet Socialist Republics

1. INTRODUCTION

The main chemical contaminant of the environment is considered mercury and mercury compounds. Different from pesticides, detergents and other toxicants of anthropogenic origin mercury and its compounds occur in all parts of the environment and in all living organisms. In the process of geochemical cycle mercury is released to the environment. Unfavourable ecological effects are caused by elevated concentrations of mercury.

In this report an attempt is made to generalize the materials submitted by the Baltic Sea States to the Helsinki Convention concerning the occurrence of mercury in natural systems, the use of mercury in various sectors of economy and emissions of mercury to the environment.

The Baltic Sea States are aware of the actual and potential problems which can be caused by mercury pollution. The environmental protection efforts are concentrated on a number of counter-measures. Much is already been done both at national levels and within the Helsinki Convention to reduce the levels of mercury entering the marine environment. However, the national governments recognise that continuing actions need to be taken in order to ensure that the sea is kept free from pollution.

2. MERCURY IN THE ENVIRONMENT OF THE BALTIC SEA

2.1 Mercury in the environment and the toxicity of mercury compounds

The mercury contamination of the environment was established as the main cause of an unknown desease in Japan during which hundred of people died. Since that time, increasing scientific interest has been devoted to mercury as an environmental contaminant. Studies are concentrated on the effects of mercury on organisms and on the behaviour of mercury in the aquatic environment. Mercury and its compounds are toxic, bioaccumulative and persistent.

The elemental mercury although chemically comparatively inert possesses a high ionization and oxidizing potential. In aqueous medium the metallic mercury is oxidized to mercurousions (Hg_2^{2+}) which have a high affinity to sediments and which are easily transformed to mercuric ions (Hg^{2+}) that are often very soluble in water. In bottom sediments under the vital activity of bacteria the inorganic mercury compounds are converted to organic compounds. Characteristic to mercury is the formation of organic mercury compounds of the type R_2Hg and $RHgX$ (R - organic radical. X - residue of inorganic or organic acid). The reaction ability is largely depending on the nature of R and X. Under the prolonged influence of air, light and warmth the organic mercury compounds are decomposed by free radical mechanism to free radical and elemental mercury. The elemental and inorganic forms are prevailing in the atmosphere. The environmental cycle of mercury is shown in Figure 1.

Mercury compounds belong to thiolic poisons. When entering the organism ions of mercury react on the carboxyl and amino groups of the proteins. Mercury spreads relatively fast to all tissues of the organism, especially to those rich in lipoids, including the brain. As a result changes appear in the vegetative nervous system as well as in the heart, organs of respiration, stomach, liver, kidneys etc. Methyl mercury is considerably more toxic than other organic and inorganic compounds. This can be explained by the pecularities of its metabolism. The biological half-life period of methyl mercury in an organism lasts for about two years.

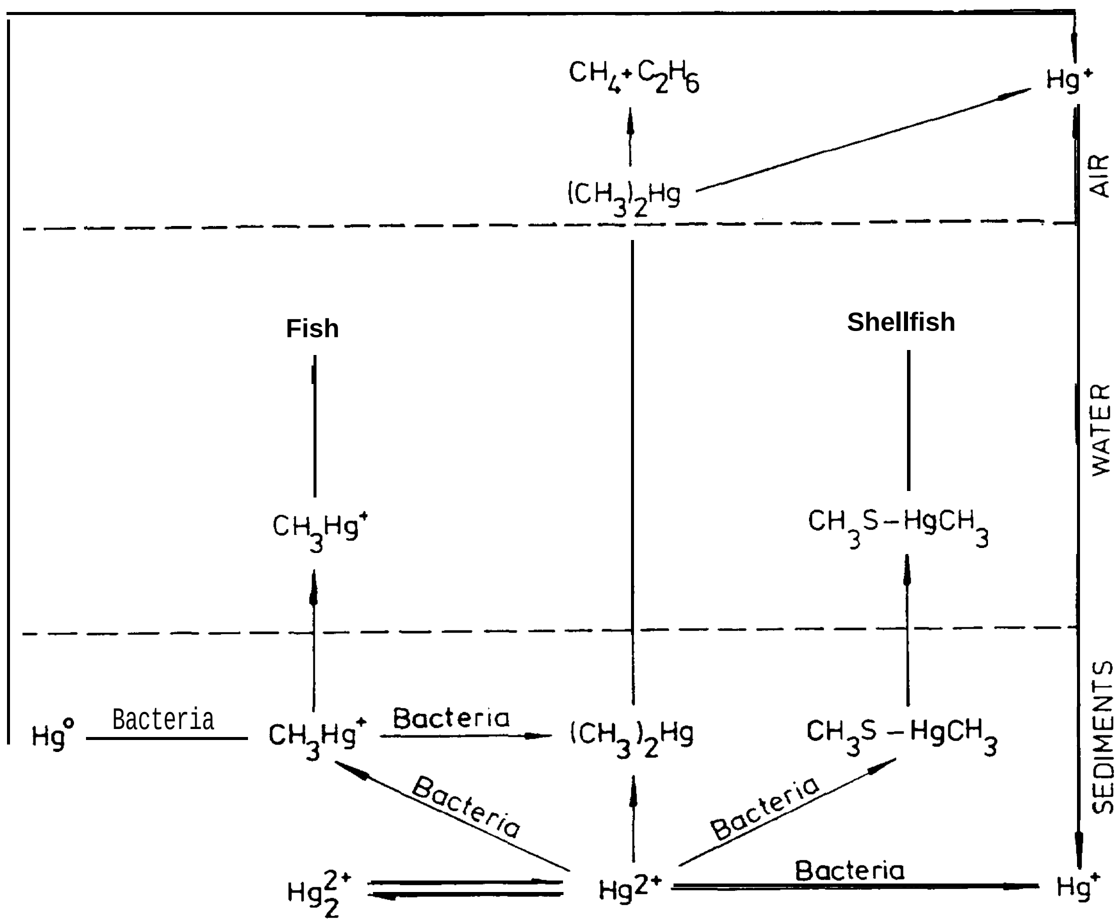

Fig. 1. The biological cycle of mercury
(Figure taken from Wood and Goldberg, 1977)

2.2 Mercury in the water

Pesticides, radionuclides, hydrocarbons and mercury are considered the most dangerous contaminants of the marine environment. Single determinations of mercury concentration in natural waters (sea water included) and hydrobionts have been made in the early 50-ies. Investigations in this field have expanded in the last decade, but the development of analytical techniques for determining mercury in the environment has evidently been unsufficient. The analysis of the data has indicated an interesting law-governed process: the content of mercury in the environment is continuously decreasing despite of the increasing anthropogenic input. Up to date there has been no confidence in the reliability of the obtained values of the concentration of mercury, although the sensitivity and selectivity of techniques used for determining the levels of mercury in environmental samples has improved. Results obtained only recently can be trusted. The obtained data are presented in Table 1.

Table 1. Mercury content in the Baltic Sea water (µg/l)

Area	Mercury content
Central Baltic	0.007 – 0.217
Gulf of Finland	0.01 – 0.14
Gulf of Bothnia	0.002 – 0.04
Gulf of Riga	0.01 – 0.04
Bay of Gdansk	0.277 – 0.63
Bay of Tallinn	0.005 – 0.14
Bay of Narva	0.01 – 0.14
Bay of Pärnu	0.01 – 0.04
Bay of Matsalu	0.005 – 0.13

These findings demonstrate an uneven distribution of mercury within the aquatory of the sea. Uneven distribution is also observed in the North Atlantic. Evidently this phenomenon is characteristic for all surface layers of the seas and oceans thus being determined by hydrochemical and hydrological processes proceeding more intensely in the upper layers of the water column. Along the vertical the content of mercury is decreased. The vertical distribution of mercury in the water column, based on the data of the I Soviet-Swedish complex cruise in the Landsort Deep is shown in Figure 2.

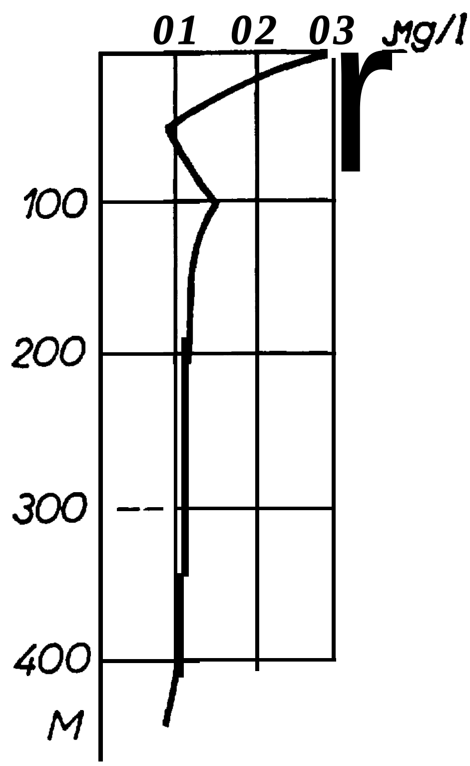

Fig. 2. Changes in the content of mercury along the vertical

Investigations carried out in the Matsalu Bay in 1982-1983 have indicated a seasonal dynamics in the content of mercury in the near-shore water of the Baltic Sea. In the winter the mercury concentration was 0.01 µg/l, in the spring 0.08 µg/l and in the summer 0.12 µg/l.

Experimental results are in agreement with published data. It may be assumed that seasonal dynamics of the content of mercury in the Baltic Sea water is influenced by hydro-biological processes.

2.3 Mercury in the hydrobionts

Information on the levels of mercury content in the hydrobionts of Baltic Sea is rather scanty. Due to the variety in the sampling, preparation and storage procedures as well as analytical methods used the comparison of available data on the content of the mercury is rather difficult. The concentration of mercury in hydrobionts depends on several factors, such as individual, sexual, specific differences, on growth and seasonal dynamics. A relationship exists between the levels of mercury concentration in the water and hydrobionts, the accumulation of mercury is influenced by several environmental factors, such as temperature, salinity and pH. In every concrete case the influence of the above-mentioned factors is exposed in various ranges or may not occur.

The following hydrobionts - plankton, benthos, fish - are examined. The content of mercury in hydrobionts of the Baltic Sea is listed in Tables 2, 3, 4.

Table 2. The content of mercury in plankton (mg/kg dry weight)

Area	Mercury content
Gulf of Finland	1.08 - 1.24
Central part of the Baltic Sea	0.16 - 0.81
Bay of Matsalu	0.1

Table 3. The content of mercury in benthos (mg/kg wet weight)

Area	Macoma baltica	Mytilus edulis
Gulf of Finland	0.07	
Central part of the Baltic Sea		0.003 - 0.017
Coastal waters of Finland	0.013 - 0.35	
Coastal waters of FRG		0.07 - 0.09
Bay of Tallinn	0.05 - 0.18	0.02 - 0.09
Coastal waters of PPR	0.04	0.01 - 0.04

Data presented in Table 3 do not serve as immediate basis for conclusions on the regional changeability of the concentration of mercury molluscs. The reason being the structural heterogeneity of selection (difference in age) and the scantiness of comparable results in several parts of the Baltic Sea.

Table 4. The content of mercury in fish (mg/kg wet weight)

Fish species	Kind of feeding	Content of mercury
Herring	planktonophag	0.007 - 0.073
Sprat	"	0.00 - 0.079
Flounder	benthophag	0.003 - 1.50
Cod	predatory fish	0.01 - 0.21

Average content of mercury in fish (mg/kg)

- Planktonophag 0.05
- Benthophag 0.05
- Predatory fish 0.48

As seen, the content of mercury in predatory fish is higher than in planktonophages and benthophages. The content of mercury in the marine environment is regularly growing along the food chain and achieves maximum values in predatory fish.

2.4 Mercury in the bottom sediments

The data on the content of mercury in bottom sediments is rather scanty.

Table 5. Content of mercury in bottom sediments (mg/kg dry sample)

Area	Content of mercury
Economic zone of PPR	0.02 - 0.67
Northern part of the Baltic Sea	0.01 - 0.68
Bay of Tallinn	0.01 - 1.22
Baltic Sea Oulu district	1.3 - 9.8
Baltic Sea Pori district	0.1 - 3.7
Bay of Matsalu	0.02 - 0.44
Central part of the Baltic Sea	0.02 - 0.48

The content of mercury in bottom sediments is influenced by the nature of deposits (mineralogical and granulometric). Sandy deposits are characterized by lower content of mercury in comparison with clayey muds, which indicates on the sorbtion ability of the bottom sediments. The content of mercury less than 1 mg/kg points to the satisfactory state of the bottom sediments. Elevated concentrations of mercury in bottom sediments are recorded in the areas affected by mercury-containing discharges.

Figure 3 demonstrates the distribution of mercury between the links of the ecosystem of the Baltic Sea.

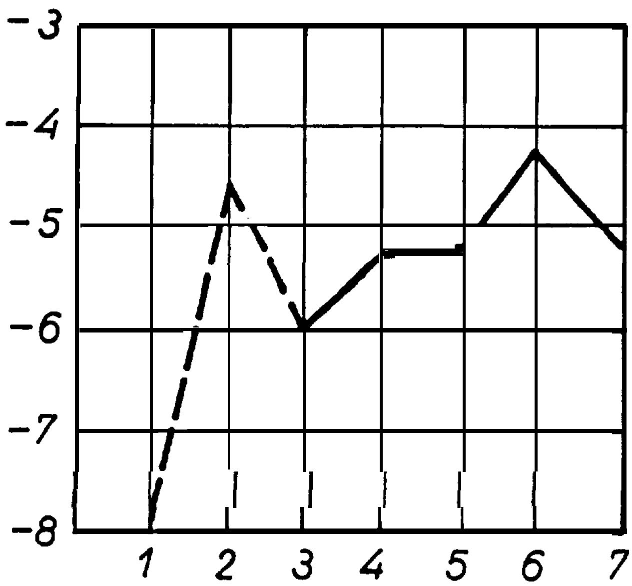

Fig. 3. Distribution of mean concentration of mercury in the main components of the ecosystem of the Baltic Sea

At the ordinate axis are the logarithms of mean concentrations of mercury in per cent of wet weight, the abscissa axis represents the components of the ecosystem: 1 - water, 2 - suspended solids, 3 - phytoplankton, 4 - zooplankton, 5 - planktonophagic fish, 6 - predatory fish, 7 - bottom sediments.
The dotted line represents the assumed mean concentration of mercury in the water and suspended solids.

3. PRODUCTION AND USE OF MERCURY AND SOURCES OF MERCURY POLLUTION

3.1 Production and use of mercury

In this chapter the materials of the Contracting Parties of the Helsinki Convention concerning the production and use of mercury in various branches of economy are reviewed. The balance of mercury between production, use and losses to the environment is imprecise, since the reports reflect the approach and point of view of the separate states to the problem of environmental protection. In the reports of Denmark, Finland and the Polish People's Republic the main attention is focused on the use of mercury in separate branches of economy. Considerably less attention is paid to the load on the sea via river systems and point sources. The specification of the load of mercury to the Baltic Sea is not possible on the basis of presented data, as the materials reflect the discharge of mercury from industrial plants to the aquatic environment, whereby the amounts of mercury entering the Baltic Sea are not defined. In the Soviet Union main consideration is given to the control of the state of the environment.

The annual production of mercury in the Baltic Sea states, listed in Table 6, is of the same order of magnitude as the use in these countries.

Table 6. Production of mercury in the Baltic Sea States (t/y)

State	Production
Finland (1980)	75
Federal Republic of Germany (1982)	48 (primarly)
	126 (recycling)
Polish People's Republic (1976)	357
Sweden (1976)	130

No mercury processing industries are in Denmark and in the Baltic Soviet Socialist Republics. Data on the production and use of mercury in the German Democratic Republic are missing.

Mercury and its compounds are used in a large number of fields. The use of mercury in'various branches of economy in the Baltic Sea States is shown in Table 7. The main consumers of mercury are chlor-alkali industry, dentistries, manufacturing of batteries.

Studies performed have shown that mercury is also used in various other industries a.o. the metallurgic, tanning, plastic, textile and paint industries. For centuries mercury and mercury compounds have been used for medical treatment of some deseases. To-day mercury-containing medicine is used to a very limited extent for antiseptic, chemo-terapeutic and preservation purposes.

A lot of investigations have shown that various types of laboratories a.o. educational, research, development and service laboratories use metallic mercury in equipment, and mercury compounds are used as analytical reagents.

In agriculture mercury compounds are used in limited quantities for the treatment of agricultural seeds. Extensive research into substitutes for mercury-containing pesticides is being carried on.

The figures presented in Table 7 are rather imprecise. Some of the information is referring to the situation 7-8 years ago. The degree to which the industries in the Baltic Sea catchment area do in fact use mercury is rather difficult to estimate, since the Federal Republic of Germany, the Polish People's Republic and the USSR are only partly located in the catchment area of the Baltic Sea.

Table 7. The use of mercury in the Baltic Sea States (t/y)

	Branch of economy	Denmark 1977	Finland 1980	Federal Republic of Germany 1982	Poland 1979	Sweden 1976	USSR**
1.	Chlor-alkali industry		3-4.4	46.3	66.7	39.0	-
2.	Dentistry and pharmacy	4.2	3.4	23.6		9.4-10.9	10
3.	Manufacturing and use of batteries	6.0	1.8	56.8	10.0	6.5	4
4.	Laboratories	2.0	3.0	-	-	1.4	2
5.	Control measuring apparatus (thermometers, manometers etc.) and processing of electro-technical equipment	5.0	0.8	15.0	45.5*	13.9	2
6.	Production and consumption of paint	0.5		3.8	5.4	0.1	
7.	Other chemical industry			53.9	100		
8.	Agriculture	2.3	2.3	4.1		1.4	
9.	Uninvestigated use	4.0					
10.	Other kinds of industry	6.0		5.2		8.4	

* The value presented includes amounts of mercury used in pharmacy, dentistry and laboratories

** Expert estimations

3.2 Sources of mercury pollution

Mercury compounds are emitted in the atmosphere by biological and physical processes. The main natural sources are rocks, volcanoes and soil-forming minerals. Mercury is released into the soil environment due to weathering and as a result of vital activity of micro-organisms. Volcanic emissions, evaporation of gaseous mercury from oceans and other water-bodies contribute to the inflow of mercury and its compounds to the atmosphere. Mercury emissions to water-bodies are originated by river discharges and atmospheric fall-out.

Anthropogenic emissions of mercury to the environment are ensued i.a. from mining and smelting, burning of fossil fuel, industrial production processes, agriculture and consumption-related discharges.

The amounts of mercury contained in the atmosphere have been established between 1.10^{-9} and 1.10^{-a} g/m^3. Mercury is introduced to the atmosphere by such human activities as the burning of fossil fuel, from chlor-alkali factories emitting mercury vapours and from land-based incineration plants for solid wastes.

Deposition of mercury from the atmosphere to land and sea surface can take place either by precipitation or by direct uptake at the surface. Up to now there is little information about the level of mercury content in the atmospheric precipitation within the aquatory of the Baltic Sea. The determination of the input of air-borne mercury is based either on the atmospheric precipitation over West Europe or on global estimates. According to literature data the deposition of mercury in the Baltic Sea is estimated in the ranges of 4 to 29 tons per year. The analysis of data presented by the Baltic Sea states does not allow to make a precise estimation of the load of mercury on the Baltic Sea.

Studies on the losses of mercury to the air from several branches of industry have been performed in Denmark and Sweden. Mercury emissions to the atmosphere based on Danish data are listed in Table 8.

Table 8. Mercury emissions'to the atmosphere (kg/y)

Pollution source	Emission to the atmosphere
Cement and lime production	300
Dentistry	900
Fossil fuel	1000
Refined oil products	340
Combustion of waste in Copenhagen	1000 - 1500
Production processes	500
Electrical supplies	4000
Electrical equipment	500
Paint	400
Thermometers	1000
Measurement and control equipment	500
Laboratories	1000

The annual emission of mercury to the air amounts to about 12 tons. The greatest discharges originate from consumed batteries (4 t/y), waste incineration (1.0 - 1.5 t/y) and from combustion of fossil fuel. In Denmark the discharge of mercury to the atmosphere constitutes 30% from the total mercury used.

In Sweden the discharge of mercury to the atmosphere is estimated to be from 6.1 to 6.9 t/y. The main contamination source is the chlor-alkali industry. The input to atmosphere (2.16 t/y) constitutes approximately 6% from the total quantity of mercury used in industry. The modifying or changing of production processes and the improvement of waste treatment methods have resulted in considerable reduction of mercury emissions from chlor-alkali industry. At present the main contamination source is considered the energy production, the emissions of which are estimated at 1.3 t/y. The other substantial sources of mercury emissions are mining and processing of metals, elimination of wastes and consumer goods.

In the Polish People's Republic the discharges of mercury to the atmosphere from chlor-alkali industry amount to about 8 t/y. In the Federal Republic of Germany the discharges of mercury from chlor-alkali industry to the atmosphere amount to 9.5 t/y (1982). But it should be born in mind that the mentioned industry is located outside the catchment area of the Baltic Sea.

In the Baltic region of the USSR the main source of mercury pollution is the combustion of solid fuels (oil shale, peat briquette). The discharge of mercury to the atmosphere is estimated at 5.5 t/y.

The mercury emissions to the atmosphere from the Baltic Sea states amount to about 50 t/y. But it must be emphasized that the submitted data are incomplete and inapplicable for the determination of the amount of mercury entering the Baltic Sea via atmosphere. On the grounds of the presented data it may be concluded that more than half of the mercury emitted to the atmosphere is originated from chlor-alkali industry.

The main pathways through which mercury enters the marine environment are river discharges, direct discharges from towns and industrial plants and atmospheric precipitation.

The mean content of mercury in river water fluctuates from 0.02 to 0.10 μg/l and the total load on the Baltic Sea ranges from 8 t/y to 43.5 t/y. About 3.7 t/y of mercury is transported to the Baltic Sea from the territory of the USSR via rivers. The discharge of river water constitutes about 20% from the total balance of the Baltic Sea.

The load of mercury on the Baltic Sea cannot be revised on the basis of presented data, since the materials reflect the total mercury discharges from the industries to the aquatic environment, whereby the proportion of mercury entering the Baltic Sea is not defined.

According to Swedish data the emission of mercury to the aquatic environment are 0.11 t/y (50% are emitted to the atmosphere). The main sources of mercury pollution of the aqueous media are dentistries (3.4-4.0 t/y), about 30-35% from the mercury used is thrown to sewage water. An analogous situation is observed in Denmark. The other sources of mercury pollution are of less importance.

The presented documents give no evidence about the amounts of untreated and treated effluents entering the sea or rivers as well as the amounts of mercury deposited in rivers.

Municipal discharges to which mercury is supplied from dentistries, laboratories and enterprises are important sources of the pollution of the marine environment. In Poland the observed maximum concentration of mercury in municipal effluents is 0.01 µg/l, in Tallinn and Kohtla-Järve the mean concentrations are 0.54 and 0.11 µg/l, respectively. The efficiency of biological purification is 75-85%. As the data of other municipal discharges are missing, it is not possible, however, to estimate the amounts of mercury carried to the Baltic Sea by municipal discharges.

3.3 National requirements for discharges

The protection and control system of the environment is based on principally differing systems of standardization:

standards for discharge (emission standards)

standards for environmental quality (immission standards)

Very often a combined standardization and control system is used. The system first mentioned is applied in Denmark, the Federal Republic of Germany and Finland. There exist, however, some normative indices for the estimation of the state of the environment. The emission standards referred to are concerned with chlor-alkali industry. In Finland the content of mercury in effluents from chlor-alkali industry was not to exceed 0.2 g/t Cl produced, according to a target set by the national water authorities. The target has been later set by the Water Court at 0.3 g/t Cl produced. Mercury emissions in ventilation air are restricted by requirements set for in-plant air quality: in practice mercury content of 3-5 g/t Cl produced has been reached. As for mercury content in hydrogen gas the limit aimed at is 1 g/t Cl produced. The content of mercury in alkali has been kept by the industry in the range of 0.2-0.5 mg/l.

In Sweden the following requirements for existing enterprises are set:

the total mercury emission in ventilation air must not exceed 5 g/t produced chlorine;

the maximum emission of mercury in hydrogen gas must not exceed 1 g/t produced chlorine.

Limit values for mercury discharges from chlor-alkali industry binding for the Federal Republic of Germany are set in the corresponding Commission for the European Community (EEC) Council directives.

Table 9 depictures the emission standards, time limits and monitoring procedures.

3.4 Environmental quality standards

The environmental quality objective approach is used in various countries. In the Soviet Union limiting permissible concentrations for pollutants in the water of a water-body depending on the kind of water use have been established. Water-bodies are divided into two groups according to the kind of water use:

water-bodies for fishery,
water-bodies for municipal drinking water supply.

The limiting permissible discharge of pollutants, depending on the kind of water use and hydrological and hydrochemical characteristics are determined so that the pollution concentration at the site of water use should not exceed the prescribed concentration norms.

The limiting permissible concentrations of mercury in the water-bodies and waste effluents to be converted to the treatment plant in the Soviet Union are as follows:

for municipal drinking water supply 5 µg/l in fresh water;

for fishery 1 µg/l in sea water;

for effluents to be converted to the treatment plant 10 µg/l.

Table 9. Limit values, time limits and monitoring procedures for mercury-containing discharges

Industrial sector	Limit values which must be compiled as from 1 July 1986/	1 July 1989	Unit of measurement
1. Chemical industries using mercury catalysts			
(a) in the production of vinyl chloride	0.1	0.05	mg/l effluent*
	0.2	0.1	g/t vinyl chloride production capacity
(b) in other processes	0.1	0.05	mg/l effluent
	10	5	g/kg Hg processed
2. Manufacture of mercury catalysts used in the production of vinyl chloride	0.1	0.05	mg/l effluent
	1.4	0.7	g/kg Hg processed
3. Manufacture of organic and non-organic mercury compounds (except for products referred to in point 2)	0.1	0.05	mg/l effluent
	0.1	0.05	g/kg Hg processed
4. Manufacture of primary batteries containing mercury	0.1	0.05	mg/l effluent
	0.05	0.03	g/kg Hg processed
5. Non-ferrous metal industry **			
5.1 Mercury recovery plants	0.1	0.05	mg/l effluent
5.2 Extraction and refining of non-ferrous metals	0.1	0.05	mg/l effluent
6. Plants for the treatment of toxic wastes containing mercury	0.1	0.05	mg/l effluent

* Limit values for industrial sectors other than the chlor-alkali electrolysis industry which are not mentioned in the table such as the paper and steel industries or coal-fired power stations, will, if necessary, be fixed by the Council at a later stage. In the meantime, the Member Stations will fix emission standards for mercury discharges autonomously in accordance with Directive 76/464/EEC. Such standards must take into account the best technical means available and must not be less stringent than the most nearly comparable limit values in this Annex.

** On the basis of experience gained in the implementation of this Directive the Commission will, pursuant to Article 6(3), submit to the Council proposals for more stringent limit values to be introduced ten years after the notification of this Directive.

In the Polish People's Republic the environmental quality standards establish the following permissible concentrations of mercury in the aquatic environment:

harbour basins and internal sea waters	1 μg/l
surface fresh water	
I purity class (drinking water, water for economic need, fish farming)	1 μg/l
II purity class (recreational use)	5 μg/l
III purity class (water for agricultural irrigation and industrial water supply)	10 μg/l
effluents to be converted to municipal sewage plants, mercury content must not exceed	500 μg/l

In the Federal Republic of Germany measures to prevent land-based pollution are based on the Federal Water Act; one of its objective is to prescribe emission standards designed to keep quantity and noxiousness of waste water as low as possible when applying the appropriate methods in accordance with the generally accepted rules of technology. The established minimum standards must be compiled with irrespective of the given water quality. Stricter standards will be imposed on a case-by-case basis if required in view of the water quality of the receiving body of water. Nevertheless, quality objectives set by the EEC are respected by the Federal Republic of Germany, so in EEC Directives quality objectives for mercury content are set to river water which is directly used as drinking water as well as fishing grounds. The content of mercury in these waters must no exceed 0.5 μg/l.

The national Board of Health of Finland has set limits for mercury content in drinking water at 2 μg/l. Also the limit for mercury content in raw water used for preparing potable water has been brought down to 2 µg/l. According to the general water use classification a water-body is classified as passing or poor if the content of mercury in water is above 5 µg/l. A new general classification of waters is under development.

On the basis of the above review it may be concluded that the setting of emission and immission standards for various kinds of water uses is an important step in solving water protection problems and in the abatement of environmental pollution. Emission standards provide the minimum well founded technological discharges of mercury to the environment, while the immission standards elaborated for receiving water-bodies affected by discharges of mercury enable to check up the efficiency of elaborated emission standards.

3.5 Proposals concerning reduction of mercury emissions to the environment.

3.5.1 Measures applied in the Baltic Sea states for reducing mercury emissions to the environment

The proposals by the Contracting Parties of the Helsinki Convention concerning the use and discharges of mercury and measures to be taken to reduce the discharges of mercury to the environment are discussed.

Denmark

On the basis of results of investigations and gained experience the Working Group of the National Agency of Environmental Protection has proposed to reduce mercury discharges and to control the use of mercury in the following branches of **economy**:

- mercury batteries
- clinics, hospitals and dentistries
- mercury-containing paint.

The limiting of mercury use in other economic fields is foreseen in the nearest future on the basis of new knowledge. It will be possible within a 5 year period to reduce the mercury pollution by a total of approximate 8 tons or 30% of the present estimated total release.

Finland

According to Finnish water legislation the discharge of certain harmful substances, among them mercury, is prohibited in quantities which would cause pollution of the waters. To guarantee the purity of water-bodies the National Board of Waters elaborates case by case requirements, usually incorporated in Water Court permits, for discharges from different enterprises.

In chlor-alkali industry following measures aiming at reduction of mercury discharges are applied:
Separate sewerage is used for mercury-containing waste water. These waste waters undergo advanced treatment.
A reduction in the amount of mercury released into the atmosphere has been achieved e.g. by the application of special anodes.

The Federal Republic of Germany

Limit values for mercury discharges from chlor-alkali industry are in force in the Member States of the EEC from 1 July 1983. The EEC Council Directives 82/176/EEC and 4964/84 are binding for the Federal Republic of Germany. Tables 10 and 11 present data on mercury discharges, time limits and monitoring procedure.

Table 10. The maximum permissible discharges from chlor-alkali industry

Kind of enterprise, unit of measurement	Monthly mean from 1 July 1983	1986	Remarks
All kinds of chlor-alkali industry			Applicable to all kinds of mercury-containing wastes
Micrograms of mercury per litre	75	50	

The limit values expressed as maximum concentrations may not be greater than those expressed as maximum quantities divided by water requirements per ton of installed chlorine production capacity. Taking into consideration that the limit values of mercury in effluents depend on the technology of processing it were expedient to express the limit values in terms of quantity of mercury in relation to a unit of production.

Table 11. The maximum permissible discharge of mercury per ton chlorine depending on the applied technology

Industry and unit of measurement	Monthly average limit values not to be exceeded from 1 July 1983	1986	Remarks
Recycled brine Grams of mercury per ton of installed chlorine production capacity	0.5	0.5	Applicable to the mercury present in effluent discharged from chlorine production unit.
	1.5	1.0	Applicable to the total quantity of mercury present in all mercury-containing waters discharged from the site of industrial plant.
Lost brine Grams of mercury per ton of installed chlorine production capacity	8.5	5.0	Applicable to the total quantity of mercury present in all mercury-containing waste discharged from the site of the industrial plant.

Sweden

No emission or immission standards to control the discharges of mercury to the environment are there in Sweden. Some measures are taken to reduce the mercury emissions to the environment. Among others are the following:

immediate collection of discharged mercury from industrial effluents

the cooling of reactors before opening

collection and redistillation of mercury-containing wastes

floor coatings of easily cleaned materials

the cooling and cleaning of hydrogen gas on activated carbon filters

collection and treatment of all mercury-containing effluents in central purification plants.

Several modifications of chemical-mechanical purification have been used in effluent treatment.

Alkali is filtered through activated carbon. The content of mercury in alkali is reduced to 0.1 mg/l corresponding to 0.2 per ton chlorine produced.

3.5.2 Proposals of measures aimed at the reduction of discharges of mercury

The proposed measures and time limits dealt with in national reports point the importance of the problem. Investigations carried out in the area of the Baltic Sea have indicated an increase in the content of mercury in the biota and bottom sediments in zones influenced by the activity of man. The elevated concentrations of mercury in flora and fish at present do not create danger for man, but the risk factor requires attention.

The main sources of mercury emissions are industrial plants (chlor-alkali, chemical industry), dentistries, electrical batteries, liquid and solid fuel, raw material for cement and lime processing etc. Mercury is released to the Baltic Sea from atmosphere, via river discharges or discharges from industries and towns.

To eliminate the discharges of mercury to the environment it would be necessary:

to reduce the industrial use of mercury

to collect and reproduce mercury-containing goods

to control discharges of mercury to the air and to aquatic environment.

Recommendations concerning measures for reducing mercury discharges from main pollution sources have been submitted by the Contracting Parties of the Helsinki Convention. Preliminary recommendations presented in documents WGS 5/2d/rev.1 and WGS 6/12/3 are revised in the light of subjected correlations. The proposed technical measures are replaced by more general requirements, which enable industry and local authorities to solve technical details and to take necessary decisions based on the best economical possibilities. Attention is paid towards the presentation of concrete numerical values for mercury discharges per unit of installed production capacity. The presented recommendations are foreseen for industries located in the catchment area of the Baltic Sea. The countries of the Helsinki Convention partly located outside the boundaries of the catchment area of the Baltic Sea (Federal Republic of Germany, Polish People's Republic, USSR) are bound to agreements of other international conventions. The authorities are responsible for the implementation of measures for reducing mercury-containing wastes from dentistries and consumed batteries.

Recommendations of measures aimed at the reduction of discharges of mercury related to chlor-alkali industry, dentistry and the use of batteries are enclosed.

4. INSERTION OF MERCURY TO ANNEX 1 OF THE HELSINKI CONVENTION

The main responsibility of the Convention is the prevention of the pollution of the Baltic Sea. The term "pollution" is defined in Article 2 as follows: "Pollution" means introduction by man, directly or indirectly, of substances or energy into the marine environment, including estuaries, resulting in such deterious effect as hazard to human health, harm to living resources and marine life, hindrance to legitimate uses of the sea including fishing, impairment of the quality for use of sea water, and reduction of amenities. According to Article 5 the Contracting Parties undertake to conteract the introduction, whether airborne, waterborne or otherwise, into the Baltic Sea Area hazardous substances as specified in Annex 1 of the presented Convention.

In Article 6 are sited the principles and obligations concerning land-based pollution. According to Article 2 the Contracting Parties are obligated to take all appropriate measures to prevent and abate pollution with noxious substances and materials listed in Annex 2 of the Helsinki Convention. In accordance with paragraph 5 of the mentioned Article the Contracting Parties shall endeavour to establish and adopt criteria for issuing permits for discharges. In Annex 1 are listed hazardous substances which discharge to the Baltic Sea is prohibited.

The Contracting Parties shall take all appropriate measures to control and strictly limit pollution by noxious substances and material in accordance with Annex 2 of the Convention. Mercury is a natural element and is constituent of many rocks, from which it is released in natural geo-chemical processes and as a result of the activity of man. The use of mercury in various branches of economy is well known. At present mercury is used in chlor-alkali industry, in control measuring instruments, dentistry, in manufacturing batteries etc. The use of mercury in pulp and paper mills and agriculture is prohibited due to the toxicity of mercury and its compounds. In many sectors of the economy extensive research into less harmful subsitutes for mercury is carried out. In recent years a reduction in the mercury emissions to the environment has been recorded. The recommended measures for reducing mercury discharges to the Baltic Sea, when applied in the Baltic Sea states may serve as a basis in a step-by-step reduction of the use of mercury in the economy.

In view of the above-said the leading country is of the opinion that mercury should not be inserted into Annex 1 of the Helsinki Convention.

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PROGRESS REPORT ON COPPER AND ZINC;
prepared by the German Democratic Republic

1. GENERAL

This report was prepared on the basis of the information and comments received from the Contracting Parties to the Helsinki Convention to the questionnaire relating to copper and zinc (WGS 4/8, Annex 16).

2. COPPER AND ZINC IN THE MARINE ENVIRONMENT

Among a number of heavy metals, which are to be considered to be highly toxic (e.g. mercury and cadmium) and those to be less toxic (e.g. arsenic, antimony, bismuth, thallium and nickel) to the marine environment, copper and zinc besides selenium, vanadium, and cobalt are the most essential trace elements for the living food resources, if the respective critical limit values are not exceeded. It is unlikely and not to be expected that copper and zinc will affect the human organism through the marine environment.

Since comparative data from the past are missing, it is, presently, impossible to assess the trend of advancement of quantity of copper and zinc contained in water and biological material of the marine environment of the Baltic Sea.

Summary No. 1 shows the present quality situation with respect to the copper and zinc content of water, sediment and organisms of the Convention area.

Summary No. 1.
Copper and Zinc Content of the Convention Area

	Water ($\mu g/m^3$)	Sediment (mg/kg) dry weight	Organisms (mg/kg) wet weight
Copper	0.3 - 52	1 - 210	0.08 - 16
Zinc	1 - 120	6 - 640	1.2 - 110

Below concentration intervals are mentioned for the central part of the Baltic Sea. This can be considered to be a normal basic load:

copper 0.3 - 3 $\mu g/dm^3$
zinc 1 - 7 $\mu g/dm^3$

The highest concentration levels were measured in the regions below:

	Water	Sediment
Copper	Kattegat, Øresund, Belts, Bay of Kiel	Gotland Deep
Zinc	Gulf of Finland	Gotland Deep

The highest contents of copper and zinc found in organisms were measured in shells.

Copper and zinc are mainly discharged into the Baltic Sea area from rivers and atmosphere. A first assessment of the pollution effects on natural resources of the Baltic Sea (1980) revealed that about 50 - 80 p.c. are discharged from the atmosphere into the Baltic Sea and 53 - 83 p.c. of zinc from rivers. Domestic sewage contributes to the load by heavy metals for about 1 - 6 p.c. only.

Discharges from the industry significantly contribute to an increase of the content of trace metals in relatively closed regions of the Baltic Sea.

Swedish investigations prove that discharges of copper and zinc into the marine environment lead to concentrations which possibly may endanger the biotop of the appropriate marine area. To characterize the quality situation near the discharge places of the Rönnskär smeltery (RS) at the Swedish coast, results of long-term investigations were published, out of which some are given below:

Water	Copper (µg/l)	Zinc (µg/l)
basic values	2	3
Baltic Sea	0.6 - 1.0	1.5 - 3.5
0.5 km southwards of RS	15	50
10-100 km southwards of RS	2	1
1976/77 >3 km of RS	<0.6 - 8	0.4 - 20
1978 >3 km of RS	7.4	3.4
1979 >3 km of RS	2.7	10
during ice cover	18 - 22	66 - 110

Particular fractions (Pore width 0.4 µm)	Copper (mg/kg of dry weight)	Zinc
basic value		
30 km NE of RS	90	
< 5 km of RS	2800 - 300	3700 - 400
<15 km of RS	400 - 200	630 - 170

Sediment	Copper (mg/kg of dry weight)	Zinc
Near RS	4300	3500
about 5 km southwards of RS	100 - 600	200 - 600

Algae (Diatomeen)	Copper	Zinc
	(mg/kg of dry weight)	
3 km southwards of RS	400 - 600	500 - 900
30 km southwards of RS	20 - 30	250
100 km southwards of RS	15	300
10 km northwards of RS	60	250
20 km northwards of RS	3	60

Invertebraten (Lymnea sp.)	Copper	Zinc
	(mg/kg of dry weight)	
2 km southwards of RS	1400 - 1100	1100 - 800
20 km northwards of RS	92 - 60	130 - 100

To study the effect of copper and zinc on the marine environment of the Baltic Sea area, several organisms were exposed by Swedish investigators to the influence of these heavy metals. The most important results of these tests are reflected in Summary No. 2.

Summary No. 2

Species	Effects of	
	Copper	Zinc
Ephemerella mucronata (larvae)	significant increase in mortality	no effect
Salmo trutta	significant increase in mortality	no effect
Fontinalis dalecarlia	enrichment: 20fold	enrichment: 3fold
Ephemerella ignita	significant changes of mortality and of breeding behaviour	no effect
Salmo gairdneri	Liver: 40-90 mg/kg of fresh weight	no tendency to enrichment liver: 20-35 mg/kg of fresh weight

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Species	Effect of Copper	Effect of Zinc
Mytilus edulis	increased mortality near smeltery 20 mg/kg of fresh weight	increased mortality near smeltery 20-50 mg/kg of fresh weight
Algae	enrichment: 5-10fold near smeltery	enrichment: 2-3fold near smeltery
Phoxinus phoxinus		1)

1) - With advancing age and size of the fish increase in resistance (96 hours LC 50 3,2 mg for adult fish).

Interference with reproduction in case of rise of zinc concentration from 0.05 mg (control value) to 0.13 resp. 0.20 mg (decrease in number of eggs per female for 17 p.c. - 21 p.c.).

Mortality of fry for 100 p.c. at 0.26 mg.

After 270 days rate of mortality of fish was 50 p.c. at 0.3 mg, 70 p.c. of vertebrates were attacked (below 0.2 mg, vertebrates were not attacked).

Only 18.4 mg caused mortality of 100 p.c. after one day. Attack of vertebrates could not be detected during this short time.

3. NATIONAL QUALITY STANDARDS FOR ENVIRONMENT

The load of marine environment of the Baltic Sea area caused by copper and zinc is regulated by the Contracting States by means of emission limits fixed to keep discharges of noxious substances into the marine environment as low as possible.

Binding fixed limit values are being applied in Denmark, the German Democratic Republic, the Polish People's Republic and the Union of Soviet Socialist Republics.

Sweden, Finland and the Federal Republic of Germany fix their limit values for discharges in each case. In doing so, they fix different quality goals for taking into account the sometimes rather complex utilization of waters and sections of waters. In particular, Sweden and Finland orientate to a gradual reduction of the load of waters caused by copper and zinc up to 1984 resp. 1986. In practice below emission values are of importance:

	Denmark	GDR	FRG	PPR	USSR
copper (mg/dm^3)	0.1/0.5	0.005	0.05	0.01	0.001/0.005
zinc (mg/dm^3)	0.5/1.0	0.01	1.0	0.01	0.01 /0.05

To limit discharges of copper and zinc from sewage emission some of the Contracting States apply limit values for emissions, which regulate load capacity of the waters concerned. They may be combined in below concentration intervals:

copper: 0.1 - 3.0 mg/l
zinc: 0.5 - 10.0 mg/l

Presently, the Baltic coastal states apply below limitations of copper and zinc discharges from main pollution sources into the marine environment of the Baltic Sea area, vide Summary No. 3:

Summary No. 3.

Limitations of copper and zinc discharges

Zinc	Sweden	Finland')	PPR	FRG	GDR
Mining	<0.5 mg/l				
Iron and steel industry		120 kg/d+ 30 kg/d* 3 kg/d**	-	4 mg/l	-
Smelteries	0.58 kg/t Cu	40 kg/d			-
Textile industry	350 kg/d 150 kg/d*			3 mg/l	-
Zinc and cobalt production		60 t/a 40 t/a* 20 t/a**			
Titanium dioxide industry		3.5 t/t TiO_2	-	-	
Copper processing	-	6 kg/d	-	-	-
Galvanic industry	-	-		5 mg/l	0.7 t/a
Discharge of industrial waste water into sewage treatment plants		5.0 mg/l 0.7 mg/l*** (proposed limit values)	2 mg/l	-	2 mg/l

Copper	Sweden	Finland 1)	PPR	FRG	GDR
Smelteries	0.63 kg/t Cu	20 kg/d 1)	-		
Cobalt production		10 t/a			
Textile industry		-		1 mg/l	
Copper processing	-	20 kg/d			
Galvanic industry				2 mg/l	0.2 t/a
Discharge of industrial waste water into sewage treatment plants	-	1.5 mg/l 0.5 mg/l*** (proposed limit values)	0.2 mg/l	-	0.5 mg/l

1) proposals for limit values used
\+ plant 1
* 1984, plant 2
** 1986, plant 2
*** in case of utlization of sludge

4. DISCHARGE OF COPPER AND ZINC INTO THE MARINE ENVIRONMENT

The figures yet submitted by the Contracting Parties on copper and zinc discharged into the marine environment of the Baltic Sea area are subdivided according to major loads in Tables 1 and 2. Although the reports show some non-uniformity, what is obviously due to the age of the measured values based on calculations, the assessments prepared by Denmark, Sweden and the Polish People's Republic prove a relatively high airborne load caused by copper and zinc. In comparison therewith as well as with the discharges of copper and zinc from rivers, load of the marine environment in consequence of direct discharge of domestic and industrial sewage can be assessed to be rather low.

The data presently available make it very difficult to prove total load of marine environment of the Baltic Sea area on the basis of discharge values from all Contracting States.

Table 1. Discharge of Copper into the Marine Environment (tons/year)

from	Denmark	Finland	GDR	PPR	Sweden	USSR
1	50	2.3*	-	-	20	55
2		42*	-	48.2	10	
3	66			2742	1200	-
4					35	-
5			1.8	781	1890	320

1 - domestic sewage
2 - industrial sewage
3 - airborne
4 - diffuse sources
5 - rivers

* Helsinki and Turku

Table 2. Discharge of Zinc into the Marine Environment (tons/year)

from	Denmark	Finland	GDR	PPR	Sweden	USSR
1	300	18*	-	-	60	110
2		318*	-	1439	50	-
3	660			682	5000	-
4					70	-
5			8.7	1139	3140	645

1 - domestic sewage
2 - industrial sewage
3 - airborne
4 - diffuse sources
5 - rivers

* Helsinki and Turku

5. MONITORING OF COPPER AND ZINC DISCHARGED INTO MARINE ENVIRONMENT

To check discharge of copper and zinc into the marine environment of the Baltic Sea area the Baltic coastal states conduct quite different monitoring activites aiming at preparation of basic material for gradual limitation of discharges of noxious substances and - within the Baltic Sea Monitoring Programme - being also of increasing importance. Sweden and Denmark reported on results of investigations:

	Sweden		Denmark	
	copper	zinc	copper	zinc
- fish (mg/kg if wet weight)	0.3-6.9	4.5-34	0.24-10.5	5-124
- mytilus edulis (mg/kg of dry weight)	1.5-6.9	7-21	1.1 -410	63-574

	Sweden		Denmark	
	copper	zinc	copper	zinc
- sediment (mg/kg of dry matter)	12-129	45-319	0.04-220	3-1050
- Baltic Sea water (µg/l)	0.6-1.0	1.3-1.5	0.6 -1.0	1.5-3

The summary shows that the quality situation of the Baltic Sea water is not coming up to values, which differ from the known "normal" condition. In contrast thereto, the maximum values for biological material and sediment show high rates of accumulation, what mainly prove the results of the Danish investigations.

For fundamentally assessing discharges of copper and zinc into marine environment of the Baltic Sea area and developing therefrom an effective limitation based on appropriate measures, it will be necessary to use the results of investigations of all the Baltic Sea states in future time.

6. RECOMMENDATIONS FOR LIMITATION OF DISCHARGES OF COPPER AND ZINC

To limit discharges of copper and zinc we recommend as follows:

Reduction of emissions and discharges;

Preparation of instructions for standards of quality for environment and emissions;

Monitoring of discharge;

Monitoring of effects of copper and zinc on the marine environment.

7. REFERENCES

The metal concentrations have been taken from "Assessment of the effects of pollution on the natural resources of the Baltic Sea, 1980".

Water:	page 205
Sediments:	page 207
Organisms:	page 209
Basic load:	page 206

IV HELCOM RECOMMENDATIONS CONCERNING CADMIUM AND MERCURY, adopted by the Commission in 1985 as Recommendations

HELCOM RECOMMENDATION 6/3:
Recommendation concerning measures aimed at the reduction of discharges of mercury from chloralkali industry

HELCOM RECOMMENDATION 6/4:
Recommendation concerning measures aimed at the reduction of mercury resulting from dentistry

HELCOM RECOMMENDATION 6/5:
Recommendation concerning safe handling of used mercury- and cadmium-containing batteries

HELCOM RECOMMENDATION 6/6:
Recommendation concerning limitation of discharges of cadmium from land-based sources

CONVENTION ON THE PROTECTION OF THE MARINE
ENVIRONMENT OF THE BALTIC SEA AREA

BALTIC MARINE ENVIRONMENT PROTECTION
COMMISSION - HELSINKI COMMISSION -

HELCOM 6/16
Annex 6

Sixth Meeting
Helsinki 12-15 March 1985

HELCOM RECOMMENDATION 6/3

adopted 13 March 1985, having regard
to Article 13, Paragraph b) of
the Helsinki Convention

RECOMMENDATION CONCERNING MEASURES AIMED AT THE REDUCTION OF DISCHARGES OF MERCURY FROM CHLORALKALI INDUSTRY

THE COMMISSION,

RECALLING that according to Article 6 of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1974, (Helsinki Convention), the Contracting Parties shall take all appropriate measures to control and strictly limit pollution by noxious substances,

RECALLING ALSO that Annex II of the Helsinki Convention defines mercury as a noxious substance for the purposes of Article 6 of the Convention,

RECOGNIZING that chloralkali industry is one of the main sources of pollution by mercury,

BEING MINDFUL of the pollution caused by chloralkali industry,

DESIRING to limit this pollution by accomplishing the treatment of chloralkali industry effluents corresponding to modern technology,

RECOMMENDS to the Governments of the Contracting Parties to the Helsinki Convention that:

a) best technical means should be used in industrial plants to be constructed after 1986 to minimize pollution by mercury; and

b) the existing industrial plants in operation should meet the following requirements:

- the total quantity of mercury in all water discharged from the site of the industrial plant should not exceed the monthly average of 1 g per ton chlorine production capacity from 1986;

- technology should be developed and high-effective vacuum equipment in departments should be put into operation before 1987 so that the losses in ventilation air are less than 5 g per ton.chlorine production capacity, and less than 2 g per ton chlorine production capacity as target for 1990;

- the annual average mercury concentration in alkali should be reduced to 0.5 mg/l before 1987 and to 0.3 mg/l by 1990;

- the monthly average amount of mercury in hydrogen **gas** should be reduced to 1 g per ton chlorine produced by the end of 1986 and to 0.2 g per ton chlorine produced by 1990.

RECOMMENDS ALSO that measures taken in accordance with this Recommendation and the analyses and estimation methods used should be reported to the Commission one year after the adoption of this Recommendation and thereafter every 3 years,

RECOMMENDS FURTHER that the Contractig Parties, whenever possible, apply even more stringent measures than stated above aimed at the reduction of mercury from chloralkali industry.

CONVENTION ON THE PROTECTION OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA

BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION - HELSINKI COMMISSION -

Sixth Meeting
Helsinki 12-15 March 1985

HELCOM 6/16
Annex 7

HELCOM RECOMMENDATION 6/4

adopted 13 March 1985, having regard to Article 13, Paragraph b) of the Helsinki Convention

RECOMMENDATION CONCERNING MEASURES AIMED AT THE REDUCTION OF MERCURY RESULTING FROM DENTISTRY

THE COMMISSION,

RECALLING that according to Article 6 of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1974, (Helsinki Convention), the Contracting Parties shall take all appropriate measures to control and strictly limit pollution by noxious substances,

RECALLING ALSO that Annex II of the Helsinki Convention defines mercury as a noxious substance for the purposes of Article 6 of the Convention,

RECOGNIZING the relative importance of dentistry as the source of pollution by mercury,

BEING MINDFUL of the pollution caused by emissions of mercury resulting from dentistry,

DESIRING to limit this pollution by reducing mercury emissions from dental clinics, laboratories and surgeries,

RECOMMENDS to the Governments of the Contracting Parties to the Helsinki Convention that arrangements for collection of waste containing mercury from dental clinics, laboratories and surgeries should be established for such undertakings that start operating after the end of 1986 and for those already in operation before that date not later than the end of 1988,

RECOMMENDS ALSO that elaborating new mercury-free materials for tooth fillings should be encouraged and the use of mercury-containing materials for this purpose should, whenever possible, be abandoned,

RECOMMENDS FURTHER that the Contracting Parties report to the Commission data on the existing and available technique one year after the adoption of this Recommendation.

CONVENTION ON THE PROTECTION OF THE MARINE
ENVIRONMENT OF THE BALTIC SEA AREA

BALTIC MARINE ENVIRONMENT PROTECTION
COMMISSION - HELSINKI COMMISSION -

Sixth Meeting
Helsinki 12-15 March 1985

HELCOM 6/16

Annex 8

HELCOM RECOMMENDATION 6/5

adopted 13 March 1985, having regard
to Article 13, Paragraph b) of
the Helsinki Convention

RECOMMENDATION CONCERNING SAFE HANDLING OF USED MERCURY- AND CADMIUM-CONTAINING BATTERIES

THE COMMISSION,

RECALLING that according to Article 6 of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1974, (Helsinki Convention), the Contracting Parties shall take all appropriate measures to control and strictly limit pollution by noxious substances,

RECALLING ALSO that Annex II of the Helsinki Convention defines mercury and cadmium as noxious substances for the purposes of Article 6 of the Convention,

RECOGNIZING the pollution caused by the introduction of mercury and cadmium from used batteries to the marine environment of the Baltic Sea Area,

DESIRING to limit this pollution by a safe handling of such batteries,

RECOMMENDS to the Governments of the Contracting Parties to the Helsinki Convention that:

a) batteries containing appreciable amounts of mercury or cadmium be labelled;

b) such spent batteries be collected;

c) recovery or safe disposal of the metal content of such spent batteries be applied in order to avoid contamination of the environment; and

d) research into less harmful substitutes in batteries containing even small quantities of cadmium and mercury should be encouraged,

RECOMMENDS FURTHER that the actions taken by the Contracting Parties in accordance with Paragraphs c) - d) above should be reported to the Commission by 1 July 1986 and subsequently at three years' intervals.

CONVENTION ON THE PROTECTION OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA

BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION - HELSINKI COMMISSION -

HELCOM 6/16
Annex 9

Sixth Meeting
Helsinki 12-15 March 1985

HELCOM RECOMMENDATION 6/6

adopted 13 March 1985, having regard to Article 13, Paragraph b) of the Helsinki Convention

RECOMMENDATION CONCERNING LIMITATION OF DISCHARGES OF CADMIUM FROM LAND-BASED SOURCES

THE COMMISSION,

RECALLING that according to Article 6 of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1974, (Helsinki Convention), the Contracting Parties shall take all appropriate measures to control and strictly limit pollution by noxious substances,

RECALLING ALSO that Annex II of the Helsinki Convention defines cadmium as a noxious substance for the purposes of Article 6 of the Convention,

NOTING the existing risk of pollution of the marine environment of the Baltic Sea Area by cadmium caused by discharges of this substance from various sources,

RECOGNIZING that the concentration of cadmium in effluents from industrial sources directly after treatment can be kept below 0.1 mg/l by the use of common wastewater treatment technology (e.g. precipitation, ion exchange),

DESIRING to limit cadmium pollution of the Baltic Sea Area by accomplishing special measures concerned,

RECOMMENDS to the Governments of the Contracting Parties to the Helsinki Convention that:

a) national regulations for the limitation of the use of cadmium to a strict minimum be established within the following applications:

   (i) electroplating;
   (ii) pigments; and
   (iii) stabilizers;

b) the following measures be taken to reduce discharges of cadmium from industrial sources:

(i) recycling of cadmium-containing wastewater, or otherwise limitation of the use of water in processes where cadmium is handled;

(ii) strict separation of cadmium-containing wastewater from all other effluents; and

(iii) effective treatment of wastewater containing cadmium by the use of common or other advanced technology so that the concentration and quantity of cadmium in effluents from various industrial sources as monthly averages should not exceed the following values measured at the point where the effluent leaves the plant:

	from 1986	from 1989
Electroplating	0.5 mg/l	0.2 mg/l
gjkg Cd handled	0.3*)	
Manufacture of pigments	0.5 mg/l	0.2 mg/l
gjkg Cd handled	0.3	
Manufact. of stabilizers	0.5 mg/l	0.2 mg/l
g/kg Cd handled	0.5	
Manufact. of batteries	0.5 mg/l	0.2 mg/l
g/kg Cd handled	1.5	
Manufact. of Cd compounds	0.5 mg/l	0.2 mg/l
g/kg Cd handled	0.5	
Zinc mining	0.3 mg/l	0.2 mg/l

c) the development of methods to reduce the cadmium content in phosphatic fertilizers and discharges from fertilizer production be urged, and national regulations to this matter be adopted when such methods are available,

RECOMMENDS FURTHER that regular reports on national measures taken in accordance with Paragraphs a) (i)-(iii) be submitted to the Commission by 1 July 1986 and subsequently at three years' intervals.

*) application of the limit value may be suspended until 1988 in the case of plants which discharge less than 10 kg of cadmium a year and in which the total volume of electroplating tanks is less than 1.5 m^3.

V

BALTIC SEA ENVIRONMENT PROCEEDINGS

No. 1 JOINT ACTIVITIES OF THE BALTIC SEA STATES WITHIN THE FRAMEWORK OF THE CONVENTION ON THE PROTECTION OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA 1974-1978
(1979)*

No. 2 REPORT OF THE INTERIM COMMISSION (IC) TO THE BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION
(1981)

No. 3 ACTIVITIES OF THE COMMISSION 1980
- Report on the activities of the Baltic Marine Environment Protection Commission during 1980
- HELCOM Recommendations passed during 1980
(1981)

No. 4 BALTIC MARINE ENVIRONMENT BIBLIOGRAPHY 1970-1979
(1981)

No. 5A ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980
PART A-1: OVERALL CONCLUSIONS
(1981)*

No. 5B ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980
PART A-1: OVERALL CONCLUSIONS
PART A-2: SUMMARY OF RESULTS
PART B: SCIENTIFIC MATERIAL
(1981)

No. 6 WORKSHOP ON THE ANALYSIS OF HYDROCARBONS IN SEAWATER
Institut für Meereskunde an der Universität Kiel, Department of Marine Chemistry, March 23 - April 3, 1981
(1982)

No. 7 ACTIVITIES OF THE COMMISSION 1981
- Report of the activities of the Baltic Marine Environment Protection Commission during 1981 including the Third Meeting of the Commission held in Helsinki 16-19 February 1982
- HELCOM Recommendations passed during 1981 and 1982
(1982)

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* out of print

No. 16 WATER BALANCE OF THE BALTIC SEA
A Regional Cooperation Project of the Baltic Sea States; International Summary Report
(1986)

No. 17A FIRST PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA, 1980-1985; GENERAL CONCLUSIONS
(1986)

No. 17B FIRST PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA, 1980-1985; BACKGROUND DOCUMENT
(1987)

No. 18 ACTIVITIES OF THE COMMISSION 1985
- Report on the activities of the Baltic Marine Environment Protection Commission during 1985 including the Seventh Meeting of the Commission held in Helsinki 11-14 February 1986
- HELCOM Recommendations passed during 1986
(1986)*

No. 19 BALTIC SEA MONITORING SYMPOSIUM
Tallinn, USSR, 10-15 March 1986
(1986)

No. 20 FIRST BALTIC SEA POLLUTION LOAD COMPILATION
(1987)

No. 21 SEMINAR ON REGULATIONS CONTAINED IN ANNEX II OF MARPOL 73/78 AND REGULATION 5 OF ANNEX IV OF THE HELSINKI CONVENTION
National Swedish Administration of Shipping and Navigation; 17-18 November 1986, Norrköping, Sweden
(1987)

No. 22 SEMINAR ON OIL PULLUTION QUESTIONS
19-20 November 1986, Norrköping, Sweden
(1987)

No. 23 ACTIVITIES OF THE COMMISSION 1986
- Report on the activities of the Baltic Marine Environment Protection Commission during 1986 including the Eighth Meeting of the Commission held in Helsinki 24-27 February 1987
- HELCOM Recommendations passed during 1987
(1987) *

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* out of print

Baltic Marine Environment Protection Commission
— Helsinki Commission —
Mannerheimintie 12 A
SF-00 100 Helsinki

ISSN 0357-2994

Helsinki 1987 Government Printing Centre