

# Heavy Metals Contamination in the Polish Zone of Southern Baltic

K. KORZENIEWSKI and E. NEUGEBAUER

Department of Marine Chemistry and Marine Environmental Protection, University of Gdansk, Czolgistow 46, 81-378 Gdynia, Poland

This paper contains additional results from the baseline study of the level of contaminating heavy metals in abiotic (e.g. water, suspended matter, sediments) and biotic (plankton, fish) components of Baltic ecosystem in Polish zone. Materials for investigation were collected every year from 1980 to 1985. Investigations concerning different compartments of the coastal environment showed an increased concentration level of cadmium and lead (input via atmosphere), copper and zinc (river input) in coastal waters and Gulf of Gdansk. Enrichment factors in suspended matter varied from  $10^4$ - $10^6$ , in sediments from  $10^3$ - $10^5$ , in plankton from  $10^4$ - $10^5$ . The content of heavy metals in fish did not exceed the national and international standards.

This paper contains additional results from the baseline study of: i) the level of contaminating trace metals in abiotic (e.g. water, suspended particulate matter, sediments) and biotic (plankton, fish) components of Baltic ecosystem in Polish zone; ii) ecological consequence of the trace metals pollution of the South Baltic; iii) accumulation of trace metals in the biota.

## Trace metal balances for the Baltic Sea

According to a compilation made in 1986 by the HELCOM (1987), Paris Commission (1986) and recent information from Sweden (Wallgren 1988) and GDR (Brügmann and Hennings 1984), trace metals budget for the Baltic Sea are preliminary elaborated (Fig.1). Estimates of the amounts of the five metals in the water column have been obtained by multiplying the volume of the Baltic Sea (22,000 km<sup>3</sup>) by representative values for their total concentrations in the water column. The annual outflow of water through Öresund and the Danish Straits corresponds to about 3% of the Baltic's water volume. In one assumes, in order to simplify, that the net outflow of metals corresponds to 3% of the metal content of the water column. The accumulation bottoms of the Baltic receive annually about 40 million tons of dry matter. The deposition of metals causes on increase of metals concentrations in the deposited material.

## Materials and methods

Materials for investigations were taken during seasonal cruises of the r/v "Professor Siedlecki" and "Dr Lubecki" from 1980 to 1985. Water samples for chemical analysis were taken at 100 sampling stations, in high-density polythene acid washed bottles (Fig.2). Determination of Cu, Cd, Pb and Zn in water required sometimes the previous concentration by chelation (APDC, NaDDC, PAR) and solvent extraction (MIBK). The methods has been described in detail by Angino and Slavin (1968), Bruland et. al (1979), Kinrade and VanLoon (1974), Grasshoff et. al. (1983). Measurements were made on Varian AA-1200 atomic absorption spectrophotometer.

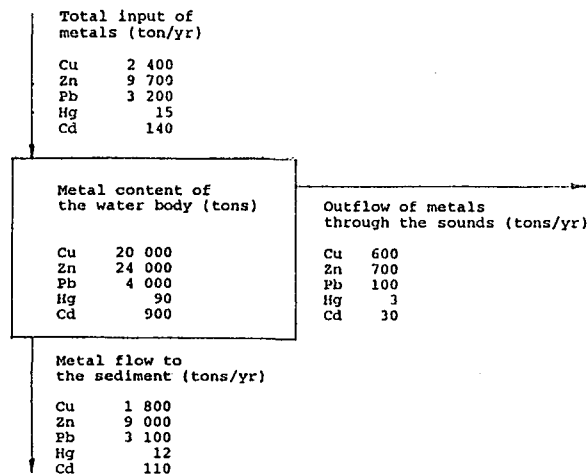


Fig.1 Metal balances for the Baltic Sea

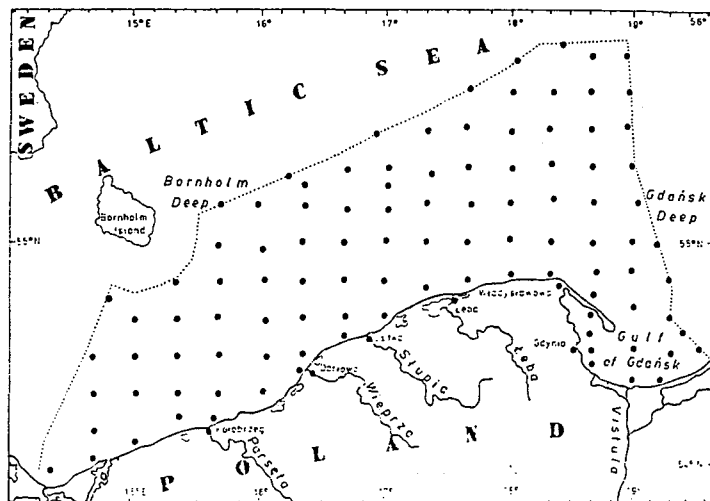


Fig.2. Location of the sampling stations in Polish zone of the Southern Baltic

**Results**

The concentration of copper in the water samples collected from Southern Baltic ranged from  $0.52-2.02 \mu\text{g}\cdot\text{dm}^{-3}$  (Fig.3), and cadmium from  $0.07-1.15 \mu\text{g}\cdot\text{dm}^{-3}$ . Lead concentration ranged from  $0.27-1.09 \mu\text{g}\cdot\text{dm}^{-3}$  and those of zinc from  $3.49-13.7 \mu\text{g}\cdot\text{dm}^{-3}$ . The heavy metals levels seemed relatively stable throughout the collecting area. In the Southern Baltic the highest different between the heavy metals concentration in surface and near-bottom waters show cadmium (Enrichment factor  $E_f=6.2$ ) then copper ( $E_f=2.2$ ), lead ( $E_f=1.5$ ) and zinc ( $E_f=1.2$ ). The contaminant levels of noxious heavy metals in the water samples collected from the Gulf of Gdansk are generally higher. The concentration of copper ranged from  $1.35-2.37 \mu\text{g}\cdot\text{dm}^{-3}$  and cadmium from  $0.14-1.04 \mu\text{g}\cdot\text{dm}^{-3}$ . Lead concentration ranged from  $0.40-0.95 \mu\text{g}\cdot\text{dm}^{-3}$  and those of zinc from  $6.40-10.0 \mu\text{g}\cdot\text{dm}^{-3}$ . In the Gulf of Gdansk no apparent great difference between the heavy metals concentration in surface and near-bottom waters. The highest concentration of heavy metals were in the sediments determined from the loam and sandy-loam (Cu  $38.4 \mu\text{g}\cdot\text{g}^{-1}$ , Cd  $3.7 \mu\text{g}\cdot\text{g}^{-1}$ , Pb  $29.8 \mu\text{g}\cdot\text{g}^{-1}$ , Zn  $171.6 \mu\text{g}\cdot\text{g}^{-1}$ ). The lower concentration were investigated from the sandy sediments (Cu  $8.1 \mu\text{g}\cdot\text{g}^{-1}$ , Cd  $1.4 \mu\text{g}\cdot\text{g}^{-1}$ , Pb  $7.2 \mu\text{g}\cdot\text{g}^{-1}$ , Zn  $31.4 \mu\text{g}\cdot\text{g}^{-1}$ ). The highest concentration levels were measured from the sediment of Vistula estuarium, Gulf of Gdansk, Puck Bay, Gdansk Deep and Bornholm Deep. The mean level of heavy metals in suspended particulate matter from the Gulf of Gdansk are as

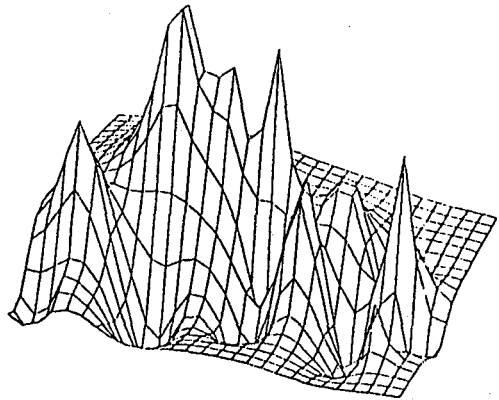
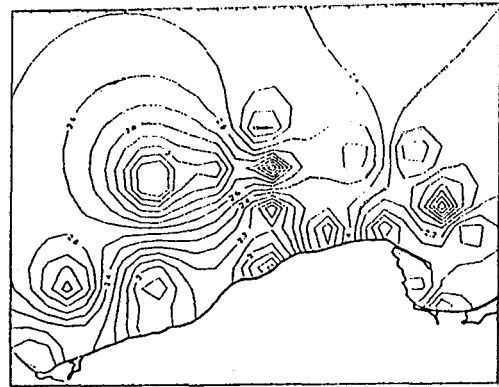


Fig.3. Concentrations ( $\mu\text{g}\cdot\text{dm}^{-3}$ ) of dissolved Cu in off-shore Baltic surface waters (Sept./Oct. 1983)

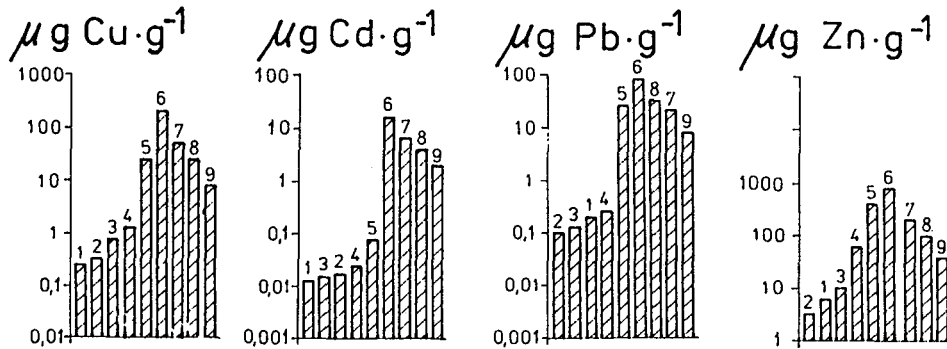


Fig.4. Contaminant levels of noxious heavy metals in the components of Southern Baltic ecosystem. 1-flounder, 2-cod, 3-heering, 4-sprat, 5-plankton, 6-suspended matter, 7-loam, 8-sandy-loam, 9-sandy sediment

follows: Cu  $82.9-365 \mu\text{g}\cdot\text{g}^{-1}$ , Cd  $12.5-116 \mu\text{g}\cdot\text{g}^{-1}$ , Pb  $51.8-211 \mu\text{g}\cdot\text{g}^{-1}$ , Zn  $546-6292 \mu\text{g}\cdot\text{g}^{-1}$  (Fig.4). The mean level of trace metals in plankton from Southern Baltic are as follows: Cu  $25.86 \mu\text{g}\cdot\text{g}^{-1}$ , Cd  $4.46 \mu\text{g}\cdot\text{g}^{-1}$ , Pb  $21.34 \mu\text{g}\cdot\text{g}^{-1}$  and Zn  $339.7 \mu\text{g}\cdot\text{g}^{-1}$  (Fig.4).

**Discussion**

The Baltic Sea States are aware of the actual and potential problems which can be caused by heavy metals pollution. 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. As, Sb, Bi, Ni) to the marine environment, copper and zinc are the most essential trace elements for the living food sources, 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 (HELCOM 1987). The concentration factors (Fig.5) of heavy metals in suspended particulate matter ranging from  $10^4$  to  $10^6$  and reduce in rank  $\text{Pb} > \text{Cd} > \text{Zn} > \text{Cu}$  in surface waters and in rank  $\text{Pb} > \text{Zn} > \text{Cd} > \text{Cu}$  in near-bottom waters. The concentration factors of heavy metals in sediments ranging from  $10^3$  to  $10^5$  and reduce in rank:

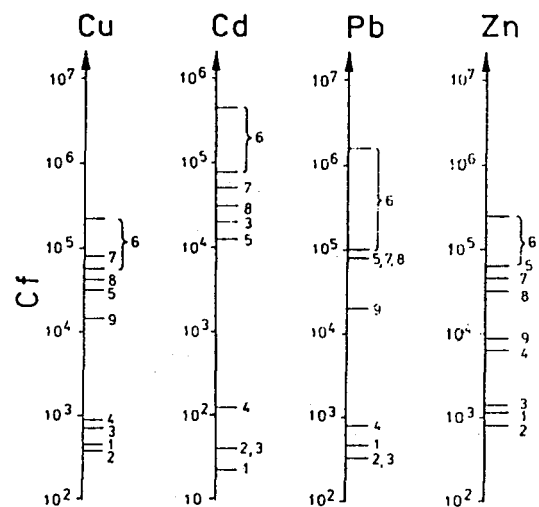


Fig.5. Concentration factors (Cf) of Cu, Cd, Pb and Zn in Southern Baltic ecosystem (1-9 as in Fig.4)

loam > sandy loam > sand. The concentration factors of heavy metals in plankton are rather lower than in suspended matter and reduced in rank  $Pb > Zn > Cu > Cd$ . The maximum values for biological materials show high rates of accumulation:

- in the meat of fish  $Zn > Cu > Pb > Cd$

- in the liver of cod  $Cu > Zn > Pb > Cd$ .

The content of trace metals in fish caught during the years 1980-1985 in the Polish Baltic fishery zone did not exceed the national and international standards. Sprat were found to contain the higher concentration of all heavy metals.

### References

- Angino E., Slavin W. 1968. Atomic absorption spectroscopy. Interscience, New York, 246.
- Bruland K.W., Franks R.P., Knauer G.A., Martin J.M. 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc and nickel at the nanogram per liter level in seawater. *Anal. Chem. Acta*, 99, 275-282.
- Brügmann L., Hennings V. 1984. Trace metal budget and fluxes for the Baltic Sea. Proc. of the XIV Conf. of the Baltic Oceanogr., Gdynia 28 Sept.-2 Oct. 1984, 465-489.
- Grasshoff K., Ehrhardt M., Kremling K. 1983. Methods of seawater analysis. Sec. Ed. Verlag Chemie, Weinheim.
- Helsinki Commission 1987. Progress Reports on Cadmium, Mercury, Copper and Zinc. *Baltic Sea Environment Proc.*, No 24.
- Kinrade J.D., Van Loon J.C. 1974. Solvent extraction for use with flame atomic absorption spectrometry. *Anal. Chem.* 46, 13, 1894-1898.
- Paris Commission 1986. Convention for the Protection of Marine Pollution from Land-Based Sources. Report from the Fourth Meeting of the Working Group on the Atmospheric Input of Pollutants to Convention Waters. Oslo, 28-30 Oct., Annex 7.
- Wallgren B. 1988. Heavy metals budget for the Baltic Sea. National Environmental Protection Board, Sweden 1-8 (typescript).