Sediment and Stream Water Quality in a Changing Environment: Trends and Explanation
(Proceedings of the Vienna Symposium, August 1991) IAHS Publ. no. 203, 1991.

EXCHANGE OF HEAVY METALS BETWEEN SEDIMENT AND WATER IN THE WLOCLAWEK RESERVOIR ON THE VISTULA RIVER

J.R. DOJLIDO & B. TABORYSKA
Institute of Meteorology and Water Management, Podlesna 61, 01-693 Warsaw, Poland

ABSTRACT The exchange of heavy metals between water and sediments was studied. The average accumulation coefficients in sediments were: zinc 2800, lead 7100, copper 14200 and chromium 33700. Accumulation of metals in sediment depended on the concentration of organic matter in the sediment. The desorption of metals from sediment was studied with the following parameters changing: organic matter content in sediment, time of contact and salinity of water. The average percentage of metals liberated was chromium 2.3%, zinc 6.1%, copper 7.2% and lead 7.2%.

INTRODUCTION

In the impoundments on the Vistula river situated upstream of the city of Wloclawek large amounts of sediment have accumulated. Water flowing to the reservoir is heavily polluted by organic and inorganic substances, including heavy metals. The bottom sediment has accumulated large amounts of metals that create a great danger for the aquatic environment.

A study of the accumulation and liberation of metals from the bottom sediments of Wloclawek reservoir therefore has been undertaken.

DESCRIPTION OF THE WLOCLAWEK IMPOUNDMENT

The dam on the Vistula river at Wloclawek (674 km) constructed in 1970, created a water reservoir of rheolimnical type (Fig. 1). The characteristics of the reservoir are as follows

- capacity 408 $m^3 \times 10^6$
- surface 70 km^2
- length ca. 60 km
- average width 1210 m
- max. width 2500 m
- average depth 5.5 m
- max. depth (at the dam) 15 m
- theoretical water exchange time at the mean flow ca. 12 days.

SOURCES OF POLLUTION

Sewage from the city of Plock and wastewater from the petrochemical plant in Plock are discharged directly into the Wloclawek impoundment (Fig. 1). In spite of some treatment they contain a great pollution load. The polluted water of the Vistula river also flows into

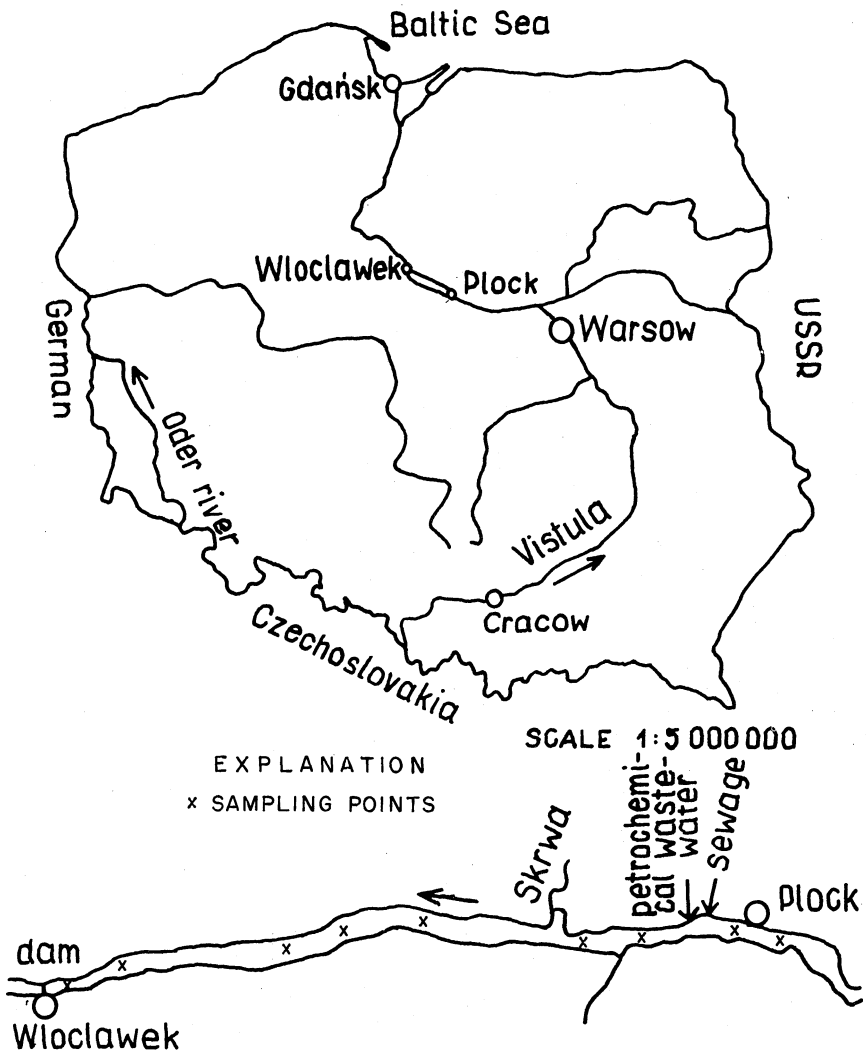

FIG. 1. Location of the Wloclawek reservoir.

the reservoir. The main reasons for pollution of the Vistula are untreated sewage from Warsaw and discharges of wastewater from Silesia and the Cracow region.

SEDIMENTATION IN THE IMPOUNDMENT

The decrease of flow velocity in the impoundment causes sedimentation of suspended solids. In addition, sediment moving along the river bed is transported into the impoundment. From 1400 to 2000 thousand tons of sediment are transported annually to the reservoir.

The sediments comprise both sandy sediment of average diameter (d_{50}) 0.08 - 0.3 mm and fine sediment of 0.01 - 0.05 mm size. Sandy sediments are found at the head of the im-

poundment and on the areas close to the banks (erosion). Fine sediments cover the majority of the reservoir bottom and they are mainly generated by sedimentation of suspended solids. The thickness of the bottom sediments varies. At the head of the impoundment, below the city of Plock, the thickness of sediment is from 80 to 90 cm. The thickness decreases along the river course and is usually less than 35 cm on the old river bed and up to 70 cm over the inundated area.

METHODS OF INVESTIGATION

The research was undertaken in 1986 and 1987. Along the reservoir 9 sampling points for water and sediment were selected (Fig. 1). In some cross-sections bottom sediment samples were taken at three different points. The following parameters were determined in the water: temperature, pH, dissolved oxygen, COD-$K_2Cr_2O_7$, ether extract, suspended solids, dissolved solids, conductivity and heavy metals (Pb, Zn, Cu, Cr, Co).

Fine bottom sediments samples were taken in vertical profiles up to 15 cm in depth and sectioned at 5 cm intervals. Sandy sediments were sampled up to 5 cm in depth. Sediments were air dried at room temperature, then at 105°C and digested in a mixture of HCl and HNO_3. The following parameters were determined in the sediment: concentration of organic matter as volatile substances at 600°C, ether extract and heavy metals: Pb, Zn, Cu, Cr, Co. The metals were determined by Pye-Unicam ASA spectrophotometer.

WATER QUALITY IN THE WLOCLAWEK RESERVOIR

- Aeration of water was good. Concentrations of dissolved oxygen ranged from 4 to 13 mg l^{-1} O_2.
- pH ranged from 7.7 to 8.7.
- Total suspended solids concentrations varied with season, from low values, 1 mg l^{-1}, in winter up to the highest value, 20 mg l^{-1}, during spring. Along the river the concentration of suspended sediment decreased from 30 to 50% of their initial concentrations. This confirms the intensive sedimentation processes occurring in the impoundment.
- Organic pollution characterized by COD was in the range 21 to 73 mg l^{-1}. The highest values were observed in summer time.
- Mineral pollution characterized by electrical conductivity varied from 410 to 560 µS cm^{-1}. The concentration of dissolved solids was in the range 350 - 650 mg l^{-1}.
- The concentrations of heavy metals are shown in Table 1.

In comparison with permissible values of water for municipal supply, rather high concentrations of zinc were observed. The concentrations of copper also were higher than the recommended limit. Concentrations of chromium and lead were within the permissible range. Concentrations of cobalt were in the range usually observed in surface waters.

THE CHARACTER OF THE BOTTOM SEDIMENT

The bottom sediments contained large amounts of organic matter. The average concentration of organic matter was ca 10%. The sediments from the head of the reservoir and from close to the dam contained the highest concentrations of organic substances. The range of

heavy metal contents in sediment are shown in Table 2. The highest values were observed for chromium, then for zinc and the lowest values for cobalt.

TABLE 1 Concentration of heavy metals in the water of the Wloclawek impoundment, 1986 -1987; values are in mg l^{-1}.

Metal	Minimum	Average	Maximum
Zn	0.1	0.26	1.1
Co	0.002	0.006	0.014
Cr	0.001	0.009	0.036
Cu	0.007	0.018	0.059
Pb	0.004	0.023	0.084

TABLE 2 Properties of the bottom sediment (calculated for dry mass).

	Minimum	Average	Maximum
Ether extract (g kg^{-1})	4	9	28
Organic matter (g kg^{-1})	4	103	164
Zn (mg kg^{-1})	20	620	990
Co (mg kg^{-1})	1	25	93
Cr (mg kg^{-1})	90	750	2800
Cu (mg kg^{-1})	20	190	460
Pb (mg kg^{-1})	20	100	240

TABLE 3 Data characterixing exhcange of metals between water and sediment.

	Zn	Cr	Cu	Pb
Water, average value mg l^{-1}	0.26	0.009	0.018	0.023
Sediment, average value mg kg^{-1}	620	750	190	100
Accumulation coefficient (mg kg^{-1}) (mg l^{-1})$^{-1}$	2800	33700	14200	7100

Very high variation of the metal content of the sediments was observed. This depended on the type of sediment, the location and the season of the year. The highest concentrations of metals were found in fine sediments containing high levels of organic matter.

TABLE 4 Liberation of metals from bottom sediments with differenct organic matter content.

Organic matter content, %	Desorption of metals, %			
	Zn	Cr	Cu	Pb
2.5	8.5	3.1	7.2	7.7
11.5	3.8	1.4	7.1	6.7

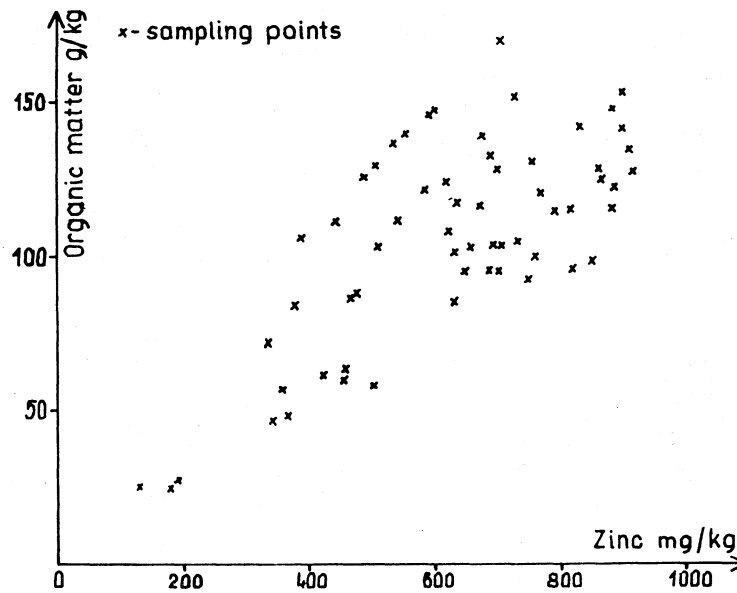

FIG. 2 Relationship between the concentration of organic matter and the concentration of zinc in bottom sediment.

ACCUMULATION OF METALS IN BOTTOM SEDIMENTS

Accumulation coeffecients were calculated as the quotient of the metal concentration in sediment in mg/kg of dry mass and the concentration of metal in water in mg l^{-1}(Table 3). The values of the accumulation coefficient were lowest for zinc and lead. The accuulation of metalshighly depended on organic matter content in the sediments. The high correlation between the content of metals in the sediment and the concentration of organic matter in sediment occurred for zinc (Fig. 2) and lead. For copper, chromium and cobalt the relationship was less clear, but always found in the fine sediment with high concentration of organic matter A similar relationship, although not so clear, was observed between organic matter concentration in sediments and the accumulation coefficient.

LABORATORY INVESTIGATION OF METAL DESORPTION FROM SEDIMENT TO WATER

A sample consisting of 100 g of natural watered sediment was placed in a glass container, providing a layer of sediment ca 5 cm thick, and 1 l of water was added. The sediment and water were mixed with a velocity of ca 35 rotations min^{-1}. The concentration of metals in the sediments and the water was monitored. The rate of metal liberation was studied as a function of the following parameters: concentration of organic matter in sediment, time of sediment contact with water, pH and salinity of water.

- Time. The results up to 32 hours did not show any change in the concentration of metals in water Equilibrium of metal concentration between sediment and water was established after 1 hour.
- Salinity. Change of salinity from 800 uS cm^{-1} (actual salinity of Vistula water) to 2500 uS cm^{-1} did not influence the desorption process.
- pH of water was changed form 4 to 9. The highest desorption for chromium and copper appeared at pH 7-8, and for lead at pH 5-6.
- Organic matter. The influence of organic matter content of sediment on desorption processes was observed for zinc and chromium. The desorption was two times lower for sediments rich in organic substances (Table 4). This relationship was not found for copper and lead.

CONCLUSIONS

In the bottom sediments of the Wloclawek reservoir the highest concentrations and the highest accumulation coefficients were observed for chromium. Concentrations of zinc were also high, but the accumulation coefficient for zinc comparatively low.

The large amounts of heavy metals accumulating in the Wloclawek reservoir, especially chromium, zinc and lead, represent a great danger for the aquatic environment in the event of a rapid change of river water quality entering the impoundment.