# USE OF ENRICHMENT, AND CONTAMINATION FACTORS TOGETHER WITH GEOACCUMULATION INDEXES TO EVALUATE THE CONTENT OF Cd, Cu, AND Ni IN THE RYBNIK WATER RESERVOIR IN POLAND

#### KRZYSZTOF LOSKA<sup>1</sup>, JAN CEBULA<sup>1</sup>, JACEK PELCZAR<sup>1</sup>, DANUTA WIECHUŁA<sup>2</sup> and JERZY KWAPULIŃSKI<sup>2</sup> <sup>1</sup> Institute of Engineering of Water and Wastewater, Silesian Technical University <sup>2</sup> Department of Toxicology, Silesian Medical Academy

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Abstract. In this paper, the contamination degree of the Rybnik Reservoir with cadmium, copper and nickel was analyzed. Quality of the water from the reservoir was determined by drawing comparisons between the metal content in the water and both the officially permitted levels (contamination factor) and levels of metals occurring in the water of non-contaminated areas (enrichment factor). Contamination of bottom sediment with chosen metals was analyzed with reference to the metal content in mudstone (geoaccumulation index, enrichment factor, contamination factor). Trends towards changing the metal content in the bottom sediment was analyzed by determining the enrichment factor of the surface layer of the bottom sediments in relation to a deeper layer. Enrichment of the bottom sediments with metals coming from the water was also determined.

Key words: reservoir of heated water, contamination, cadmium, copper, nickel, sediment, water, enrichment factor, geoaccumulation index, contamination factor

### 1. Introduction

While evaluating reservoirs in terms of chemoecology, apart from determining the content of metals in water it is very often determined in bottom sediment. The content of metals in water may be subject to considerable sudden changes, resulting from e.g. increased inflow of sewage, increased flow from fields, dilution or elution of pollution by heavy rains etc. Thus, the evaluation of the contamination degree of a reservoir may be distorted as a result of such episodic, single cases. Nevertheless, it is possible to avoid mistakes and erroneous conclusions by applying a longterm research conducted on adequately positioned sampling sites on the reservoir, although it is very often costly and time-consuming.

Determination of the metal content in the bottom sediment is an easier, deprived of random errors, method. Researches on bottom sediments, which accumulate most pollutants that get into the reservoir, enable us to gain an integrated picture of the contamination, because the level of metals in bottom sediments is the result of prolonged sedimentation processes and does not undergo sudden changes because of altering external conditions. Additionally, by distinguishing separate layers of the bottom sediment, it is possible to evaluate the trends towards changing the metal content in terms of time, which is rather impossible at present, taking the metal contamination of water as the basis for the evaluation.

The use of bottom sediment as a contamination indicator of water reservoirs let us establish several factors which, by means of certain mathematical equations, enabled an unmistakable evaluation.

Some of the most often used indicators of contamination in the sediment are: geoaccumulation index, enrichment factor, degree and factor of contamination.

### 1.1. ENRICHMENT FACTOR

The enrichment factor (EF) was used in ecotoxicological and chemoecological evaluations by Buat-Menard (1979).

The EF can be defined as follows:

$$EF = \frac{Me_i}{Me_c}$$

where:

 $Me_i$  = metal concentration in the sediment fraction <63  $\mu$ m,

 $Me_c$  = mean metal content present in the fraction of mudstone.

In order to calculate the enrichment factor in the complete fraction of bottom sediments, it is advisable to standardize their content in relation to the reference element. Thus, the enrichment factor takes the following form:

$$\mathsf{EF} = \frac{\frac{c_1 \mathsf{M} \mathsf{e}^{+n}}{c_{1n}}}{\frac{c_2 \mathsf{M} \mathsf{e}^{+n}}{c_{2n}}}$$

where:

 $c_1 Me^{+n} = \text{content of the examined element in the examined environment,}$  $c_2 Me^{+n} = \text{content of the examined element in the reference environment,}$ 

 $c_{In}$  = content of the reference element in the examined environment,

 $c_{2n}$  = content of the reference element in the reference environment.

The reference element is assumed to have little variability of occurrence, and is present in trace concentration in the examined environment. It is also possible to use a geochemically characteristic element which is present in the environment in large concentration, but is characterized by none of these effects i.e. synergism or antagonism towards the examined element. Elements which are most often used as reference ones are: Sc, Mn, Al, Fe (Buat-Menard and Chesselet, 1979; Martin and Meybeck, 1979; Li, 1981; Tomza *et al.*, 1982; Szefer and Szefer, 1986) and Ti (Quevauviller *et al.*, 1989; Pacyna and Winchester, 1990).

Enrichment factor may also be used to evaluate the metal enrichment of one element of the environment caused by another e.g. sediment by water, surface layer sediment by deeper layers of sediment (Lo and Fung, 1992; Müller and Irion, 1984; Szefer and Skwarzec, 1988; Kwapuliński *et al.*, 1993b), bottom sediment by bed-rock or soil (Baumann, 1984; Matschullat and Wyrobek, 1933; Zhang *et al.*, 1994), bottom sediment by rainfall (Kwapuliński *et al.*, 1993a).

# 1.2. GEOACCUMULATION INDEX

Geoaccumulation index allows to determine the contamination of the examined sediment with organic and inorganic substances by comparing present concentrations with pre-industrial levels. Concentrations of geochemical background are multiplied each time by the constant 1.5 in order to allow content fluctuations of a given substance in the environment as well as very small anthropogenic influences. Values of the geoaccumulation index can be defined as follows:

$$I_{\text{geo}} = \log_2 \frac{c_n}{1/5B_n}$$

where:

 $c_n =$  concentration of the examined element in the examined bottom sediment

 $B_n$  = geochemical background of a given element in mudstone.

Müller (1981) has distinguished 6 classes of the geoaccumulation index:

class value quality of sediment;

| 0 | $I_{\rm geo} \leq 0$     | unpolluted;                        |
|---|--------------------------|------------------------------------|
| 1 | $0 < I_{geo} < 1$        | unpolluted to moderately polluted; |
| 2 | $1 < I_{geo} < 2$        | moderately polluted;               |
| 3 | $2 < I_{\text{geo}} < 3$ | moderately to strongly polluted;   |
| 4 | $3 < I_{geo} < 4$        | strongly polluted;                 |
| 5 | $4 < I_{geo} < 5$        | strongly to extremely polluted;    |
| 6 | $5 < I_{\rm geo}$        | extremely polluted.                |
|   |                          |                                    |

The class 6 is an open class and comprises all values of the geoaccumulation index higher than 5.

# 1.3. CONTAMINATION FACTOR

The following equation (Hakanson, 1980) is a measure of the contamination factor:

$$c_f^i = \frac{c_{0-1}^i}{c_n^i}$$

where:

- $C_{0-1}^{i}$  = mean content of metals in the bottom sediment taken from at least 5 sampling sites ( $\mu g/g \, dw$ ),
  - $C_n^i$  = pre-industrial concentration of metal.

Values of the contamination factor are characterized as follows:  $C_f^i < 1$  – low contamination factor indicating low contamination of the sediment with the examined substance,  $1 \le C_f^i < 3$  – moderate contamination factor,  $3 \le C_f^i < 6$  considerable contamination factor,  $6 \le C_f^i$  very high contamination factor.

Contamination factor is used to evaluate the pollution of the environment by single substances. The sum of contamination factors expresses the value of contamination degree which describes the contamination of the environment by all examined substances. The degree of contamination defines the quality of the environment in the following way:  $C_d < 8$  low degree of contamination,  $8 \le C_d < 16$  moderate degree of contamination,  $16 \le C_d < 32$  considerable degree of contamination degree may be utilized in characterizing the role of a given element in the global contamination of the reservoir by determining the proportion of a given element in the contamination (Hakanson, 1980; Hakanson, 1984; Hakanson and Jansson, 1983).

The above-mentioned factors were applied to the evaluation of the Rybnik Reservoir pollution with cadmium, copper and nickel.

# 2. Materials and Methods

# 2.1. CHARACTERISTICS OF THE RESERVOIR

The dam reservoir, built on the Ruda River, is used for surface cooling of the water from the condensers in the Rybnik Power Station. It is a shallow, non-freezing reservoir of heated water, characterized by a high degree of eutrophication. Its total, usable and stable capacities are 24.3 mln m<sup>3</sup>, 4.3 mln m<sup>3</sup> and 18.2 mln m<sup>3</sup> respectively (Kozłowski *et al.*, 1981). The reservoir is approximately 4.5 km long. Its total area is 555 ha, 444 ha of which is used for cooling (main reservoir). The mean depth of the reservoir is about 4.5 m while the maximum depth in the area close to the dam is 10 m. Apart from the surface inflow of water, the reservoir is supplied with water from the Ruda River, partly treated sewage from a sewagetreatment plant and with periodic overflows of the strongly polluted Nacyna River.

# 2.2. MATERIALS

The research dealt with the samples of bottom sediments and water from the Rybnik Reservoir collected in 1991 and 1992 at 7 sites – Figure 1. Sites 2, 8, 9 were situated in the area close to the dam, 10 and 12 in the middle of the reservoir and sites 7 and 11 in the area of shallow water, close to the backwater.



Figure 1. Rybnik Reservoir with sampling stations.

# 2.3. Methods

Water samples, collected by a transmission measuring set "Toń-2", were filtered through 0.45  $\mu$ m membrane filters (cellulose nitrate) and acidified to get pH lower than 2 (spectrally pure nitric acid).

Metals dissolved in water were measured by atomic absorption spectrophotometry, using electrothermal activation technique. In the research, the AAS-30 atomic absorption spectrophotometer made in Carl-Zeis-Jena and HCL lamps were applied.

5 cm layers of the bottom sediment were taken with an Ekman-Birge apparatus to a depth of 20 cm. Concentrations of metals in the sediments were measured by flame atomic absorption spectrophotometry using deuterium and halogen background correction after wet mineralization with nitric and perchloric acid (8:1).

The enrichment factors of the mean metal content in the water were measured in reference to the metal content in the water coming from non-contaminated regions (Kabata-Pendias and Pendias, 1993). Manganese was the reference metal. The contamination factor of the minimum, mean and maximum metal content in the water were measured in relation to permissible standards (Dz. U., 1977).

The enrichment factors of metal content in the bottom sediment of the reservoir were also calculated. The metal content in clumps constituted the reference environment (Turekian and Wedepohl, 1961). The enrichment factor was also applied in order to evaluate the enrichment of the surface layer of the bottom sediment in relation to the water as well as the bottom sediment taken at the depth of 20 cm. Manganese was the reference element here too.

Geoaccumulation index value of mean and maximum metal content in the bottom sediment of the Rybnik Reservoir were measured with reference to the metal content in clumps (Turekian and Wedepohl, 1961).

Contamination factor of the bottom sediment with metals was measured to achieve the mean value of metal content in the surface layer of the bottom sediment in relation to metal level in clumps (Turekian and Wedepohl, 1961).

# 3. Results

Arithmetic mean content and standard deviation of metals in the water and bottom sediment of the Rybnik Reservoir are presented in Tables I and II.

# 3.1. CADMIUM

In general, the mean cadmium content in the water of the reservoir was within permissible standards. Only site 2 in 1991, situated close to the dam, was an exception because the mean contamination factor there was higher than 1. The contamination factor value of maximum cadmium content in the water was also

| Table I<br>The occurre | nce of metals in w        | vater in the Rybnik Re | servoir $[\mu g/dm^3]$ |                   |                     |                   |
|------------------------|---------------------------|------------------------|------------------------|-------------------|---------------------|-------------------|
|                        | 1661                      |                        |                        | 1992              |                     |                   |
| Station                | Cd                        | Cu                     | Ż                      | Cd                | Cu                  | Ni                |
| C1                     | 6.526±5.655               | 26.836±14.236          | 9.037±4.938            | 1.429±1.154       | 23.349±11.601       | 7.421±5.645       |
| 7                      | 4.120土4.212               | 25.860±16.822          | 8.713±4.826            | 1.968±1.751       | 18.876±6.604        | 9.626±10.264      |
| 8                      | 2.477±2.139               | 23.995±14.696          | 6.623±3.717            | $1.863 \pm 1.989$ | 22.896±11.240       | 7.0873.945        |
| 6                      | 2.388±1.408               | 23.341±11.542          | 7.049±3.416            | 1.644±1.528       | 22.242±10.243       | 7.488±5.250       |
| 10                     | $2.160\pm1.526$           | 24.334±10.901          | $6.294 \pm 2.088$      | 1.659±1.732       | 21.604±9.973        | 7.677±8.833       |
| 11                     | 2.146±1.232               | 19.819±5.107           | 8.168±2.782            | 1.731±1.343       | 23.632±15.071       | 8.058±3.818       |
| 12                     | 2.015±1.707               | 20.492±5.846           | 7.128±3.109            | $1.292 \pm 1.019$ | 19.596±5.346        | 7.047±3.539       |
| TABLE I<br>The occu    | II<br>rrence of metals in | n bottom sediment in I | the Rybnik Reservoir [ | [8/87]            |                     |                   |
|                        | 1991                      |                        |                        | 1992              |                     |                   |
| Station                | Cd                        | Cu                     | Ni                     | Cd                | Cu                  | Ż                 |
| 2                      | 20.48±7.03                | 604.05±185.96          | 72.48±24.87            | 22.26±7.17        | 460.91±195.37       | 63.75±19.82       |
| 7                      | $33.10 \pm 8.03$          | 166.76±192.28          | 110.38±17.82           | $39.38 \pm 10.10$ | $122.37\pm 15.02$   | 95.25±13.55       |
| 8                      | 24.38±5.18                | 671.77±226.85          | 86.38±17.71            | 22.29±7.88        | 414.93±222.97       | 58.89±23.57       |
| 6                      | 23.56±4.43                | $601.23\pm202.06$      | 81.39±15.53            | 23.46±11.69       | 356.21±214.84       | 51.87±22.30       |
| 10                     | 27.46±7.65                | 548.70±222.13          | 78.30±19.66            | 27.70±16.11       | 352.38±172.25       | $53.86 \pm 20.29$ |
| 11                     | 44.56±9.31                | 206.57±40.37           | 117.08±17.34           | 51.07±13.14       | $205.21\pm66.04$    | 88.13±20.45       |
| 12                     | 43.39土6.88                | 399.53±144.57          | $112.76 \pm 19.10$     | 43.97±21.56       | $370.09 \pm 145.92$ | 74.60±16.05       |

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Figure 2a. Contamination factor of water with cadmium.

Table III

Enrichment factor of water with metals compared to the water from noncontaminated regions (Kabata-Pendias, 1993)

|         | 1991 year |        |        | 1992 year |        |        |
|---------|-----------|--------|--------|-----------|--------|--------|
| Station | Cadmium   | Copper | Nickel | Cadmium   | Copper | Nickel |
| 2       | 18.84     | 0.26   | 0.52   | 2.49      | 0.14   | 0.26   |
| 7       | 16.40     | 0.34   | 0.69   | 4.96      | 0.16   | 0.48   |
| 8       | 10.49     | 0.34   | 0.56   | 3.18      | 0.13   | 0.24   |
| 9       | 9.29      | 0.30   | 0.55   | 3.12      | 0.14   | 0.28   |
| 10      | 7.54      | 0.28   | 0.44   | 3.52      | 0.15   | 0.33   |
| 11      | 7.17      | 0.22   | 0.55   | 4.30      | 0.20   | 0.40   |
| 12      | 6.00      | 0.20   | 0.42   | 2.21      | 0.11   | 0.24   |

the highest at this site -5.77. The maximum cadmium content in samples taken at all remaining sites were higher than the permissible standards (Figure 2a).

Although the loading of the water from the reservoir with cadmium is very slight, it is possible to notice that the cadmium content in the reservoir is higher compared to its natural content in the water of unpolluted regions – Table III. Enrichment factor values of the water from the reservoir compared to the values of



Figure 2b. Contamination factor of water with copper.

| Enrichment factor of water in relation to the bottom sediment from the bottom layer |           |        |        |           |        |        |  |  |  |
|---|-----------|--------|--------|-----------|--------|--------|--|--|--|
|   | 1991 year |        |        | 1992 year |        |        |  |  |  |
| Station   | Cadmium   | Copper | Nickel | Cadmium   | Copper | Nickel |  |  |  |
| 2   | 5.91      | 0.74   | 2.06   | 0.58      | 0.36   | 0.96   |  |  |  |
| 7   | 2.87      | 2.01   | 1.54   | 0.37      | 1.24   | 0.83   |  |  |  |
| 8   | 4.26      | 1.11   | 2.88   | 0.75      | 0.41   | 1.00   |  |  |  |
| 9   | 3.11      | 0.93   | 2.39   | 0.89      | 0.60   | 1.53   |  |  |  |
| 10  | 2.84      | 1.21   | 2.47   | 1.03      | 0.75   | 2.03   |  |  |  |
| 11  | 0.87      | 1.40   | 1.11   | 0.31      | 0.87   | 0.73   |  |  |  |
| 12  | 0.79      | 0.66   | 1.02   | 0.29      | 0.37   | 0.71   |  |  |  |

 Table IV

 Enrichment factor of water in relation to the bottom sediment from the bottom layer

the water from unpolluted regions ranged from 2.21 to 18.84 and were much higher in 1991 than in 1992. These changes of cadmium contamination are confirmed by the enrichment factors obtained from the examined relation: bottom water – bottom sediment – Table IV. The values of these factors, generally smaller than 1 in 1992, show weak enrichment of the water from the bottom layer with metals accumulated in the bottom sediment due to an exceptionally large number of sunny, windless



Figure 2c. Contamination factor of water with nickel.

days and a slight wavy motion of the reservoir. The enrichment factor value of water by the bottom sediment in 1991 was much higher, especially at sites 2, 8 and 9 from the deep area of the reservoir – Table IV. Calculation of values of enrichment factors for the reversed system i.e. enrichment of bottom sediment with metals coming from water unmistakably confirms this direction of metal shift between the sediment and water (Table V). Low values of this factor in 1991 confirm a trend of metals to stay in water that year. Next year, 1992, the value of enrichment factors is much higher as a result of metal accumulation in the bottom sediment.

Next, a contamination degree of the bottom sediment in the Rybnik Reservoir was analyzed. Figures 3 and 4 present contamination characteristics of the bottom sediment based on the value of geoaccumulation index. The analysis of the obtained data allows to evaluate the bottom sediment as extremely contaminated with cadmium. All values of mean cadmium content in the bottom sediment belonged to class 6.

A similar conclusion may be drawn while analyzing the values of the enrichment factor of the bottom sediment in relation to the pre-industrial content – Tables VI, VII. The contamination degree of the bottom sediment was particularly high in the backwater area of the reservoir, at sites 7 and 11, where the obtained values of the enrichment factor ranged from 53.91 to 306.15. However, a trend to increase the

# USE OF ENRICHMENT AND CONTAMINATION FACTORS Table V

|         | 1991 year |        |        | 1992 year |        |       |
|---------|-----------|--------|--------|-----------|--------|-------|
| Station | Cadmium   | Copper | Nickel | Cadmium   | Copper | Nicke |
| 2       | 0.76      | 7.48   | 1.40   | 6.79      | 18.02  | 3.37  |
| 7       | 0.43      | 1.13   | 1.14   | 4.12      | 1.48   | 1.39  |
| 8       | 0.64      | 2.50   | 0.47   | 5.91      | 14.91  | 3.44  |
| 9       | 0.65      | 2.57   | 1.01   | 4.76      | 9.23   | 2.39  |
| 10      | 1.38      | 3.44   | 1.24   | 3.63      | 6.93   | 2.04  |
| 11      | 1.78      | 1.34   | 1.59   | 4.93      | 2.27   | 2.49  |
| 12      | 1.85      | 2.62   | 1.52   | 8.58      | 8.22   | 3.29  |



Figure 3. Geoaccumulation index of metal content in bottom sediment in 1991.

cadmium content in the bottom sediment was not observed – Table VIII. Enrichment factors describing the relation between the cadmium content in the surface layer and the deepest examined layer of the bottom sediment – 15-20 cm, was lower than 1 at almost all sites.



Figure 4. Geoaccumulation index of metal content in bottom sediment in 1992.

Extreme contamination of the bottom sediment with cadmium is also confirmed by the value of contamination factor which amounts to 75.60 in 1991 and 102.16 in 1992. Cadmium takes a leading role in the global contamination of the reservoir with metals which is best presented by the analysis of the value of contamination degree – Figure 5.

# 3.2. COPPER

Contamination factor of the mean copper content was always lower than 1, usually about 0.5 – Figure 2b. Also the maximum copper content only slightly exceeded the permissible standards; but the value of contamination factor was not higher than 2.

The mean copper content in the water of the reservoir was also lower than the average copper content in the water of unpolluted regions – Table III. Very low values of obtained enrichment factors in both examined years connected with contamination factors indicate the copper impoverishment of the water from the reservoir, which is explained by the specific role of copper in physiology of bluegreen algae which are the cause of blooming in the reservoir.

| T | ab | le | ٧ | I |
|---|----|----|---|---|
|   |    |    |   |   |

| Station | Layer    | Cadmium | Copper | Nickel |
|---------|----------|---------|--------|--------|
| 2       | 0–5 cm   | 30.12   | 6.63   | 0.53   |
|         | 5–10 cm  | 30.71   | 6.29   | 0.51   |
|         | 10-15 cm | 31.83   | 5.69   | 0.46   |
|         | 15–20cm  | 41.40   | 6.29   | 0.47   |
| 7       | 0–5 cm   | 53.91   | 3.23   | 0.94   |
|         | 5–10 cm  | 64.32   | 1.93   | 1.00   |
|         | 10–15 cm | 101.44  | 2.00   | 1.33   |
|         | 15–20cm  | 102.25  | 1.98   | 1.25   |
| 8       | 0–5 cm   | 23.24   | 5.77   | 0.41   |
|         | 5–10 cm  | 30.59   | 5.03   | 0.47   |
|         | 10–15 cm | 34.32   | 5.57   | 0.51   |
|         | 15–20cm  | 46.50   | 7.70   | 0.69   |
| 9       | 0–5 cm   | 28.19   | 6.14   | 0.48   |
|         | 5–10 cm  | 33.36   | 5.83   | 0.52   |
|         | 10-15 cm | 39.03   | 5.91   | 0.54   |
|         | 15–20cm  | 52.74   | 6.36   | 0.74   |
| 10      | 0–5 cm   | 25.07   | 4,41   | 0.37   |
|         | 5–10 cm  | 32.80   | 4.47   | 0.40   |
|         | 10–15 cm | 34.09   | 3.66   | 0.38   |
|         | 15–20cm  | 49.64   | 5.51   | 0.62   |
| 11      | 0–5 cm   | 78.23   | 2.97   | 1.02   |
|         | 5–10 cm  | 108.25  | 3.25   | 1.21   |
|         | 10–15 cm | 120.31  | 3.18   | 1.20   |
|         | 15–20cm  | 111.72  | 3.30   | 1.44   |
| 12      | 0–5 cm   | 71.84   | 5.86   | 0.87   |
|         | 5–10 cm  | 85.28   | 5.81   | 1.05   |
|         | 10–15 cm | 107.65  | 5.83   | 1.18   |
|         | 15–20cm  | 138.76  | 6.14   | 1.46   |

Enrichment factor of bottom sediment with metals in relation to pre-industrial level (Turekian and Wedepohl, 1961) in 1991

Low content of Cu in the water also results, to a great extent, from its trends to occur in a suspended matter and the ability of bottom sediments to adsorb it fast and easy. The bottom sediment is enriched with copper coming from water to a much greater extent than with cadmium – Table V. The values of enrichment factor were slightly lower – 1.13 and 1.48 at sites 7, and 1.34 and 2.27 at site 11, only in the backwater area, where the mixing of the bottom sediment under the influence of an intensified wavy motion of water is more intense. A considerable enrichment of the bottom sediment with copper in comparison to geochemical level has also been observed – Figures 3, 4, Tables VI, VII. The values of geoaccumulation index of mean copper content ranged from 0.68 to 3.59. The bottom sediment

#### Table VII

| Station | Layer    | Cadmium | Copper | Nickel |
|---------|----------|---------|--------|--------|
| 2       | 0–5 cm   | 40.28   | 7.20   | 0.56   |
|         | 5–10 cm  | 50.43   | 7.18   | 0.69   |
|         | 10–15 cm | 50.17   | 6.60   | 0.62   |
|         | 15–20cm  | 62.05   | 5.46   | 0.61   |
| 7       | 0–5 cm   | 127.27  | 2.40   | 1.22   |
|         | 5–10 cm  | 103.56  | 2.25   | 1.15   |
|         | 10-15 cm | 89.21   | 1.98   | 1.03   |
|         | 15–20cm  | 111.22  | 2.36   | 1.25   |
| 8       | 0–5 cm   | 39.78   | 6.06   | 0.50   |
|         | 5–10 cm  | 47.22   | 6.08   | 0.58   |
|         | 10–15 cm | 39.46   | 4.60   | 0.45   |
|         | 15-20cm  | 65.10   | 5.22   | 0.62   |
| 9       | 0–5 cm   | 33.17   | 4.46   | 0.39   |
|         | 5–10 cm  | 39.35   | 4.29   | 0.41   |
|         | 10–15 cm | 41.17   | 4.02   | 0.40   |
|         | 15–20cm  | 59.83   | 3.50   | 0.42   |
| 10      | 0–5 cm   | 32.32   | 3.85   | 0.33   |
|         | 5–10 cm  | 48.37   | 4.09   | 0.42   |
|         | 10–15 cm | 58.10   | 4.06   | 0.44   |
|         | 15–20cm  | 77.00   | 3.93   | 0.52   |
| 11      | 0–5 cm   | 130.85  | 4.25   | 1.15   |
|         | 5–10 cm  | 173.99  | 4.90   | 1.41   |
|         | 10–15 cm | 287.12  | 5.94   | 1.77   |
|         | 15–20cm  | 306.15  | 6.19   | 1.87   |
| 12      | 0–5 cm   | 73.30   | 5.68   | 0.71   |
|         | 5–10 cm  | 87.79   | 5.50   | 0.71   |
|         | 10–15 cm | 106.08  | 5.12   | 0.71   |
|         | 15–20cm  | 156.75  | 4.78   | 0.78   |

Enrichment factor o bottom sediment with metals in relation to pre-industrial level (Turekian and Wedepohl, 1961) in 1992

from the backwater area may be evaluated as slightly polluted. In 1991, in the area close to the dam, values expressed strong pollution whereas the remaining values showed moderate pollution of the bottom sediment with copper. The values of geoaccumulation index calculated for maximum copper content in the bottom sediment were usually higher by one class. The enrichment of the bottom sediment with copper in relation to pre-industrial values was described by enrichment factors which ranged from 1.93 to 7.70 in 1991 and from 1.98 to 9.20 in 1992. In 1992, a small trend towards the increase of copper content in the surface layer of the bottom sediment in comparison to a 15–20 cm deeper layer was observed – Table VIII.

Enrichment factor of surface layer of bottom sediment in relation to a 15-20 cm layer

|         | 1991 year |        |        | 1992 year |        |        |
|---------|-----------|--------|--------|-----------|--------|--------|
| Station | Cadmium   | Copper | Nickel | Cadmium   | Copper | Nickel |
| 2       | 0.73      | 1.05   | 1.12   | 0.65      | 1.32   | 0.92   |
| 7       | 0.53      | 1.63   | 0.75   | 1.14      | 1.02   | 0.97   |
| 8       | 0.50      | 0.75   | 0.59   | 0.61      | 1.16   | 0.81   |
| 9       | 0.53      | 0.97   | 0.65   | 0.55      | 1.27   | 0.92   |
| 10      | 0.50      | 0.80   | 0.60   | 0.42      | 0.98   | 0.64   |
| 11      | 0.70      | 0.90   | 0.71   | 0.43      | 0.69   | 0.61   |
| 12      | 0.52      | 0.95   | 0.59   | 0.47      | 1.19   | 0.90   |



Figure 5. Proportion of heavy metals in the contamination of bottom sediment of the reservoir.

The following values of contamination factor: 9.60 in 1991 and 7.75 in 1992 show a considerable contamination of the bottom sediment with copper; Cu is third among metals which contaminate bottom sediments – Figure 5.

#### 3.3. NICKEL

Contamination factors of the mean nickel content in the water of the reservoir were very low, about 0.25 – Figure 2c. The maximum nickel content in the water slightly exceeded the permissible standards at some sampling sites (site 2 in both years and site 7 and 10 in 1992).

Comparison of nickel content in the water of the reservoir to the levels of this metal occurring in non-contaminated areas also allows to describe the reservoir as unpolluted with nickel - Table III. Nickel, like most metals, is precipitated relatively fast - Table V. Geoaccumulation index of the mean nickel content in the bottom sediment classifies the sediment as slightly polluted only at site 7 and 11 in the backwater area in 1991. At the remaining areas, the obtained values belonged to class 0 which showed a lack of contamination of the bottom sediment with this metal in both examined years Figures 3, 4. Value analysis of enrichment factor of the bottom sediment with nickel in relation to pre-industrial level leads to a similar conclusion. Maximum values of enrichment factor, not higher than value 2, occurred only in the backwater area whereas in the remaining area the values were lower that 1 – Tables VI, VII. The increase in the content of nickel was not observed in the surface layer of the bottom sediment - Table VIII. It presents an equal proportion of nickel in vertical section in relation to the layer of the bottom sediment collected at a depth of 20 cm and representing a much earlier era of the reservoir. To a certain extent, it also shows chemical equilibrium among individual layers (0-5 cm and 15-20 cm) as a result of big movements of water and mixing of organic gases realasing from sediment in anaerobic conditions (e.g. methane).

Contamination factor of the bottom sediment with the value of 1.24 in 1991 and 1.06 in 1992 shows a slight contamination of the bottom sediment with nickel and classifies it, together with iron, as the last among metals which contaminate bottom sediments – Figure 5.

#### 4. Discussion

Authors who use enrichment factors in evaluating contamination degrees of bottom sediments of a reservoir most often use, as a reference material, sediment from deeper layers, which exemplifies the reservoir as it was several or tens years ago. Obtained values of cadmium enrichment factor are usually quite high: 13 in the bottom sediment from Hebe Haven (Lo and Fung, 1992), 3.38 in the bottom sediments from the southern Baltic (Pempkowiak and Widrowski, 1988), 1.9 in the bottom sediments from the North Sea (Müller and Irion, 1984). The comparison

of literature data, concerning copper content of the surface and deeper layers of bottom sediments also leads to the conclusion that the contamination of bottom sediments has increased for the last few years. The copper enrichment factor in the sediments from Hebe Haven amounted to 5.2 (Lo and Fung, 1992), and it ranged from 1.1 to 1.8 in the Gdańsk Basin (Skwarzec *et al.*, 1985). Such regularity has not been observed in the Rybnik Reservoir, which is very young in geochemical terms, and its accumulated sediments are influenced anthropogenicly. Thus, the layer of bottom sediments with its specific composition, characteristic of reservoirs which has existed for a long time, is not found here.

Analysis of enrichment factor which presents the relation between a present content of a given metal in bottom sediments and its pre-industrial one, confirms our results that the loading of bottom sediment with cadmium is considerably higher than with copper or nickel. The enrichment factor of these metals in certain European lakes are as follows: cadmium 2.6, copper 1.2, nickel 0.8 in Lake Varnen (Hakanson, 1977); cadmium 2.9, copper 1.1, nickel 0.9 in Lake Constance (Förstner and Müller, 1974); cadmium 4.6, copper 2.7, nickel 1.0 in Lake Geneva (Vernet, 1976). Higher values of enrichment factor have been obtained for the Baltic and North Sea – cadmium 7.5, copper 2.0 and 1.8, nickel 1.6 and 1.3, respectively (Erlenkeuser *et al.*, 1974; Förstner and Reineck, 1974) as well as for Lake Erie : Cd - 7.3, Cu - 3.7 and Ni – 2.1 (Walers *et al.*, 1974).

According to various researches, cadmium belonged to the group of metals which contaminated most German rivers. The obtained values of geoaccumulation index belonged to classes 3-6 and classified bottom sediments of the rivers as strongly to extremely polluted with cadmium (Salomons and Förstner, 1984; Müller, 1979; Müller, 1980; Müller, 1985). The loading level of bottom sediment was also high in the case of Cauvery Basin - class 4 of geoaccumulation index (Vaithiyanathan et al., 1993) and Lake Fertö, where the value of geoaccumulation index ranged from 2.5 to 3,4 at individual sampling sites, while the values of other examined metals were minus and belonged to the class 0. It exemplified the lack of loading of bottom sediment (Horváth and Pannonhalmi, 1989). Contamination of German rivers with cadmium, examined by Müller (1979, 1980, 1985), Salomons and Förstner (1984) may be described as average; the obtained values of geoaccumulation index usually belonged to class 2. The geoaccumulation index value of copper presented by Colley (1988) and concerning the Austrian part of the Danube; ranged from -0.24 to -0.83 and shows a lack of copper loading in this part of the river.

#### 5. Conclusions

1. The content of cadmium, nickel and copper in the water of the Rybnik Reservoir in most cases, did not exceed permissible standards, however, it was

possible to observe a considerable enrichment of water with cadmium in comparison to the content of this metal in the water of non-contaminated regions.

- 2. The content of cadmium in the global contamination of the bottom sediment with examined metals amounted to 72%.
- 3. Pollution evaluation of a water reservoir may be successfully made by means of contamination factor, enrichment factor and geoaccumulation index.

#### References

- Baumann, A.: 1984, 'Extreme Heavy Metal Concentrations in Sediments of the Oker-a River Draining an Old Mining and Smelting Area in the Harz Mountains Germany', in J. Nriagu (ed.), *Environmental Impacts of Smelters* 15, 579.
- Buat-Menard, P.: 1979, Influence de la retombée atmosphérique sur la chimie des métaux en trace dans la matière en suspension de l'Atlantique Nord. Thesis, Univ. Paris VI, 434.
- Buat-Menard, P. and Chesselet, R.: 1979, Earth Planet. Sci. Lett. 42, 398.
- Colley, R.: 1988, Acta Hydrochim. Hydrobiol. 16, 4, 407.
- Erlenkeuser, H., Suess, E. and Willkomm, H.: 1974, Geochim. Cosmochim. Acta 38, 823.
- Förstner, U. and Müller, G.: 1974, Schwermetalle in Flüssen und Seen als Ausdruck der Umweltverschmutzung, Springer-Verlag, Berlin, p. 225.
- Förstner, U. and Reineck, H. E.: 1974, Senckenberg Marit 6, 175.
- Hakanson, L.: 1977, Naturvardsverkets Limnol. Undersok. 92, 155.
- Hakanson, L.: 1980, Water Res. 14, 975.
- Hakanson, L.: 1984, Arch. Hydrobiol. 101, 373.
- Hakanson, L. and Jansson, M.: 1983, Principales of Lake Sedimentology, Springer-Verlag, Berlin, 280–281.
- Horváth, L. and Pannonhalmi, M.: 1989, 'Heavy Metal Pollution in the Sediment of Lake Fertö', *Hidrológial Közlöny* 69, 220–222 (in Hungarian).
- Kabata-Pendias, A. and Pendias, H.: 1993, *Biochemics of Trace Elements*, PWN, Warszawa (in Polish).
- Kozłowski, W., Karaś, M. and Fiedler, K.: 1981, *The Monograph of Rybnik Reservoir*, Wydawnictwo Komunikacji i Łączności, Warszawa (in Polish).
- Kwapuliński, J., Bazgier-Antoniak, M., Wiechuła, D., Górka, P., Wydra, M. and Loska, K.: 1993a, *Acta Hydrobiol.* **35**, 87.
- Kwapuliński, J., Wiechuła, D., Anders, B., Loska, K. and Szilman, E.: 1993b, The pollution of the water and bottom sediment in dam reservoir Goczałkowice by nickel. Chrom, nikiel i glin w środowisku – problemy ekologiczne i metodyczne, Ossolineum, pp. 185–187 (in Polish).
- Li, Y. H.: 1981, Geochim. Cosmochim. Acta 45, 2073.
- Lo, C. K. and Fung, Y. S.: 1992, Wat. Res. 26(12), 1605.
- Martin, J. M. and Meybeck, M.: 1979, Mar. Chem. 7, 173.
- Matschullat, J. and Wyrobek, M.: 1993, Water, Air, and Soil Pollut. 69, 393.
- Müller, G.: 1979, Umschau 79, 778.
- Müller, G.: 1980, Naturwiss 67, 560.
- Müller, G.: 1981, Chemiker-Zeitung 105, 157.
- Müller, G.: 1985, 'Heavy metal concentration in sediment of major rivers within the Federal Republic of Germany: 1972 and 1985', International Conference *Heavy metals in the Environment*, Athens, Vol. 1, pp. 110–112.
- Müller, G. and Irion, G.: 1984, Mitt. Geol. Paläont. Inst. 56, 413.
- Pacyna, J. M. and Winchester, J. W.: 1990, Palaeogeography, Palaeoclimatology, Palaeoecology 82, 149.
- Pempkowiak, J. and Widrowski, H.: 1988, 'The Pollution of Surface Bottom Sediment of Southern Baltic Sea by Heavy Metals', Arch. Ochr. Środ. 1–2, 55–66 (in Polish).
- Quevauviller, P., Lavigne, R. and Cortez, L.: 1989, Environ. Pollut. 59, 267.

- Decree Minister of Health and Social Welfare from day 31 May 1977 (Dz. U. nr 18, poz. 72) ( in Polish).
- Salomons, W. and Förstner, U.: 1984, Metals in the Hydrocycle. Springer-Verlag, Berlin, p. 81.
- Skwarzec, B., Bojanowski, R. and Bolałek, J.: 1985, 'Distribution of Chemical Elements in Selected Basins of the Southern Baltic', Studia i Materiały Oceanologiczne PAN KBM 48, 69–84 (in Polish).
- Szefer, P. and Skwarzec, B.: 1988, Mar. Chem. 23, 109.
- Szefer, P. and Szefer, K.: 1986, Sci. Total Environ. 57, 79.
- Tomza, U., Maenhaut, W. and Cafmeyer, J.: 1982, 'Trace Elements in Atmospheric Aerosols at Katowice, Poland', in D. D. Hemphill (ed.), *Trace Substances in Environmental Health-XVI*, Univ. Missouri, Columbia, pp. 105–115.
- Turekian, K. K. and Wedepohl, K. H.: 1961, Bull. Geol. Soc. Am. 72, 175.
- Vaithiyanathan, P., Ramanathan, Al. and Subramanian, V.: 1993, *Water, Air, and Soil Pollut.* **71**, 393. Vernet, J. P.: 1976, Etude de la Pollution des Sediments du Leman et du Bassin du Rhone. Comm.
- Inter. pour la Protection des Eaux du Lac Leman contre la Pollution. Geneva, pp. 247–321.
- Walters, L. J., jr, Wolery, T. J. and Myser, R. D.: 1974, Occurrence of As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Sb and Zn in Lake Erie sediments, Proc. 17th Conf. Great Lakes Res., pp. 219–234.
- Zhang, J., Huang, W. W., Liu, M. G. and Cui, J. Z.: 1994, Water Res. 28(3), 609.