

## Heavy metal contamination of waters in reservoirs in an urban agglomeration

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### Abstract

The aim of the study was to estimate the degree of heavy metal pollution in water reservoirs in the city of Poznań as well as that in supply and outlet waters. The experimental data were compared with the results of mathematical analyses based on mathematical equations of linear regression that were derived. No considerable discrepancies were noted for zinc, cadmium, or copper in the 2004-2005 period.

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The metal concentrations in the analyzed water reservoirs were affected by the neighboring agglomeration and land development in the catchment area. The lowest concentrations of analyzed metals in inflowing waters ranged from  $0.013 \mu\text{g dm}^{-3}$  for cadmium to  $454 \mu\text{g dm}^{-3}$  for zinc. The application of simple mathematical models may considerably facilitate forecasting adverse changes that occur in aquatic ecosystems.

## INTRODUCTION

Municipal areas belong to the most transformed natural areas of the environment, and the quality of life of their inhabitants is affected by numerous factors such as location and the resulting natural conditions of the area, its economic standing, and municipal structure, including the size of municipal green areas (Bretzel et al. 1997). Urban green areas, frequently referred to as the natural wealth of a city, consist not only of varied terrestrial vegetation but also of both emerged and submerged aquatic vegetation that inhabit reservoirs of different sizes.

In urban systems, which, in a spatial sense, are functionally anthropogenic units, water reservoirs (both small water bodies and larger reservoirs) and natural and artificial lakes constitute a characteristic element of the urban landscape.

The role of water reservoirs in the modification of the environment has been recognized for a long time. Water bodies modify the level of ground water, affect both the microclimate and the biodiversity of the landscape, and provide specific habitat conditions for plant and animal species that are frequently protected by strict regulations. Small water bodies located in municipal areas are also areas of everyday leisure for inhabitants, and larger reservoirs located in the vicinity of cities provide suitable conditions for outdoor recreation (Szpakowska et al. 2005).

The constant pressure of civilization-related factors results in the decreased resistance of water reservoirs to degradation. Water reservoirs located within cities are most frequently small and shallow and are often characterized by oxygen deficits that lead to the generation of reduction conditions in the bottom layers. In the summertime these release methane and hydrogen sulfide, which are the end products of metabolic processes.

Environmental protection programs for reservoir waters stipulate steps to be taken which aim at preventing further water degradation by reducing or eliminating the inflow of noxious substances, among which heavy metals play a considerable role. The presence of these elements in waters and other structural units of ecosystems are analyzed extensively by naturalists. The results of such analyses make it possible to determine the degree of ecosystem pollution. Mathematical analyses and models are of great use in such assessments as they

facilitate forecasting phenomena and trends occurring in the natural environment (Hrehoruk et al. 1991, Lindström 2001).

The aim of the study was to assess the degree of heavy metal pollution (zinc, lead, copper, cadmium) of several water reservoirs in the city of Poznań including supply and outlet waters. Moreover, experimental data were compared with the results of mathematical analyses based on mathematical equations that were derived.

## MATERIALS AND METHODS

Metal concentrations were analyzed in the waters of two natural postglacial lakes: Lake Kierskie (LK) and Lake Strzeszyńskie (LS), as well as in those of three artificial reservoirs: Lake Rusałka (LR), Lake Maltańskie (LM), Sołacki Pond (SP). Selected morphometric parameters of these reservoirs are presented in Table 1. Water samples were collected in different places at a depth of 0.2 m in the reservoirs and supply and outlet waters in accordance with Polish norm PN-74 C-04620/02.

**Table 1**

Morphometric parameters of the analyzed water reservoirs

| Water reservoir    | Water table surface [ha] | Capacity [thousand m <sup>3</sup> ] | Mean depth [m] | Littoral area [%] |
|--------------------|--------------------------|-------------------------------------|----------------|-------------------|
| Lake Kierskie      | 285.6                    | 28 858                              | 10.1           | 10.3              |
| Lake Strzeszyńskie | 34.9                     | 2 847                               | 8.2            | 11.7              |
| Lake Rusałka       | 36.7                     | 701                                 | 1.9            | 1.74              |
| Lake Maltańskie    | 64.0                     | 2000                                | 3.13           | 0.76              |
| Sołacki Pond       | 0.255                    | 2.2                                 | 0.85           | 1.52              |

Concentrations of zinc, lead, copper, and cadmium in the waters of these reservoirs, including both supply and outlet waters, were determined during the vegetation season, i.e., in spring, summer and fall of 2004 and 2005. These metals were assayed with atomic absorption spectrometry using a Varian Spectra AA 200 spectrophotometer coupled with an automatic sample port. Zinc concentration was assayed using flame atomic absorption spectrometry (FAAS), while concentrations of the other three metals were assayed using electrothermal atomization (ETAAS). The results were used to derive mathematical equations of linear regression  $y = ax + b$ .

## RESULTS AND DISCUSSION

### *Concentrations of heavy metals in waters of reservoirs under varying anthropogenic pressure*

Results from previous studies (Karlik et al. 2003, Wojtkowska 2003, Szpakowska et al. 2004) on the occurrence of heavy metals in waters of reservoirs located in areas subjected to different types and degrees of pressure indicate that mean metal concentrations are ranked according to decreasing concentration values and are noted most frequently in water ecosystems in the following order: zinc > lead > copper > cadmium (Table 2).

**Table 2**

Mean metal concentrations in waters of reservoirs located in areas with anthropogenic factors of varying intensity

| Metal   | Metal concentrations in reservoirs in areas used for:<br>[ $\mu\text{g dm}^{-3}$ ] |              |            |
|---------|--|--------------|------------|
|         | recreation   | agriculture* | industry** |
| Zinc    | 98.2   | 92.6         | 78         |
| Lead    | 21.6   | 10.3         | 43.0       |
| Copper  | 5.35   | 8.2          | 16.0       |
| Cadmium | 0.037  | 0.22         | 3.6        |

\* - Karlik and Szpakowska (1999); \*\* - Barankiewicz et al. (1999)

The occurrence of heavy metals in the analyzed waters is connected with the effect of abiotic and biotic factors. Anthropogenic pressure factors connected with industry and agriculture increase the inflow of metals into waters, whereas vegetation growing in reservoirs, as one of the structural elements of aquatic ecosystems, is a biotic factor that decreases their content (Karlik et al. 2003). The concentrations of metals determined in the waters of reservoirs may also depend on their location within a city (Table 3). Four of the analyzed reservoirs are located in the left-bank part of the city of Poznań, which

**Table 3**

Mean concentrations of metals in waters of the analyzed reservoirs in 2004 (a) and 2005 (b)

| Metal   | Year of study | Metal concentration<br>[ $\mu\text{g dm}^{-3}$ ] |       |       |       |       |
|---------|---------------|--|-------|-------|-------|-------|
|         |               | LK   | LR    | LS    | SP    | LM    |
| Zinc    | a             | 87.8   | 119.1 | 102.0 | 121.3 | 111.8 |
|         | b             | 137.5  | 185.4 | 141.7 | 179.2 | 171.7 |
| Lead    | a             | 18.0   | 18.4  | 15.2  | 25.4  | 30.1  |
|         | b             | 12.5   | 9.9   | 5.9   | 12.3  | 16.2  |
| Copper  | a             | 5.45   | 6.60  | 6.37  | 7.04  | 5.99  |
|         | b             | 4.2  | 4.4   | 4.7   | 4.1   | 8.9   |
| Cadmium | a             | 0.021  | 0.060 | 0.023 | 0.023 | 0.040 |
|         | b             | 0.046  | 0.070 | 0.065 | 0.072 | 0.098 |

is divided by the Warta River, while the fifth reservoir analyzed, Lake Maltańskie, is situated in the right-bank part of the city. Of the reservoirs studied in this location, the four in the left-bank part of the city had metal concentrations as follows: the lowest concentrations were noted in the waters of Lake Kierskie (i.e., the reservoir situated the farthest from the city center), while the highest were in Sołacki Pond, which is located in a municipal park in the central part of Poznań near roads with heavy traffic.

#### *Analysis of metal concentrations in reservoir supply and outflow waters*

The lowest concentrations of metals determined in supply waters ranged from 0.013  $\mu\text{g dm}^{-3}$  for cadmium to 454  $\mu\text{g dm}^{-3}$  for zinc. The lowest concentration values of the metals determined (except for zinc) were higher in the outflow waters than in the supply waters. In turn, the highest concentrations in outflow waters were lower (except for copper) in comparison with the highest concentrations of metals determined in supply waters (Table 4).

**Table 4**

Comparison of the lowest (L) and highest (H) concentrations of heavy metals in supply and outflow waters of flow reservoirs determined in the period of the study (2004 – 2005)

| Metal   | Metal concentration [ $\mu\text{g dm}^{-3}$ ] |                  |                   |
|---------|---|------------------|-------------------|
|         | Type of concentration                         | In supply waters | In outflow waters |
| Zinc    | L   | 6.5              | 6.2               |
|         | H   | 454.1            | 378.3             |
| Cadmium | L   | 0.013            | 0.017             |
|         | H   | 0.104            | 0.086             |
| Lead    | L   | 1.7              | 4.2               |
|         | H   | 54.0             | 42.5              |
| Copper  | L   | 0.9              | 1.37              |
|         | H   | 6.5              | 7.0               |

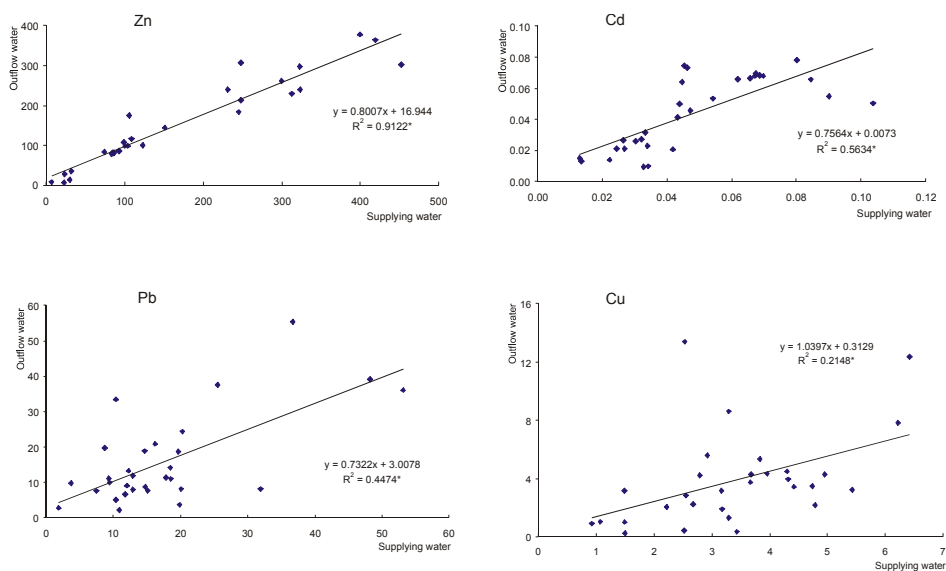
Experimental data obtained in 2004 and 2005 (three seasons in each year) on the metal concentrations in reservoir waters and the supply and outflow waters made it possible to derive linear equations (Fig. 1).

The values of metal concentrations in outflow waters from the reservoirs were calculated using these equations of linear regression and were compared with data measured experimentally (Table 5). No considerable discrepancies were found for zinc, cadmium, or copper in either of the years analyzed. Only in 2005 did the lead concentration calculated with the linear regression equation differ considerably from the concentration of this metal measured experimentally.

Table 5

Comparison of metal concentrations determined analytically with calculated values in outflow waters in 2004 (a) - 2005 (b)

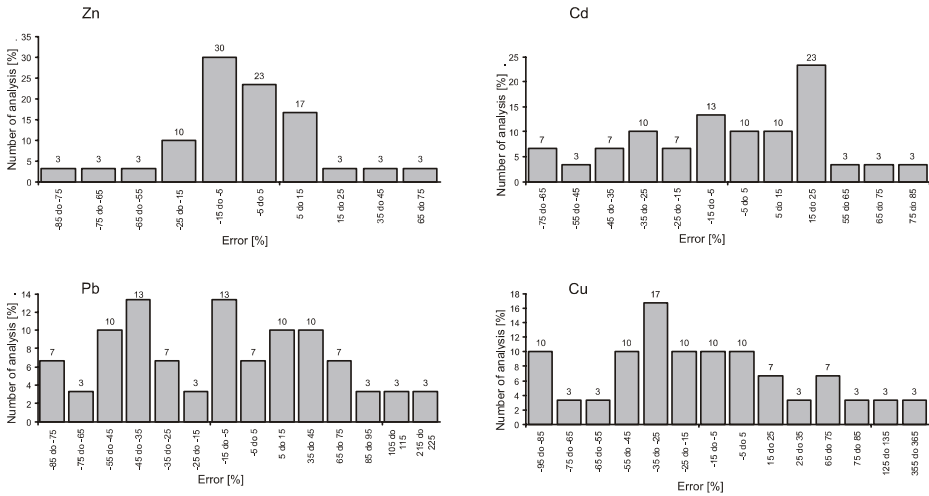
| Metal   | Metal concentration [ $\mu\text{g dm}^{-3}$ ] |                       |                           |                                       |       |
|---------|---|-----------------------|---------------------------|---------------------------------------|-------|
|         | Determined analytically                       |                       | Calculated from equations | Difference in concentration [A] – [E] |       |
|         | In supply waters                              | In outflow waters [A] | In outflow waters [E]     |                                       |       |
| Zinc    | a   | 87.3                  | 89.3                      | 86.8                                  | 2.5   |
|         | b   | 246.5                 | 211.9                     | 214.3                                 | -2.4  |
| Cadmium | a   | 0.030                 | 0.035                     | 0.029                                 | 0.006 |
|         | b   | 0.074                 | 0.071                     | 0.063                                 | 0.008 |
| Lead    | a   | 22.3                  | 21.2                      | 19.3                                  | 1.9   |
|         | b   | 12.7                  | 10.4                      | 16.5                                  | -5.9  |
| Copper  | a   | 2.97                  | 4.65                      | 3.39                                  | -1.26 |
|         | b   | 3.81                  | 3.02                      | 3.78                                  | 0.76  |



**Fig. 1.** Dependence between concentrations of analyzed heavy metals in supply and outflow waters of the reservoirs.

Based on the results obtained, the distribution of error between the measured and calculated values was analyzed, taking into consideration the number of analyses and the error range expressed in % (Fig. 2).

In the error range of  $\pm 5\%$  the highest consistency (23%) between measured and calculated values was found for zinc, while the lowest was for lead (7%). In the same error range for cadmium and copper the calculated and experimentally determined values were consistent at 10%. In the error range of  $\pm 15\%$



**Fig. 2.** Distribution of error between the values of measured and calculated concentrations [%].

consistency between metal concentrations determined experimentally and those calculated with equations was 70% for zinc, 33% for cadmium, 30% for lead and 27% for copper.

The deteriorating quality of urban reservoirs requires regular monitoring of the degree of pollution in them. When assessing the degree of water degradation, especially in flow reservoirs, it is necessary to monitor pollution not only in the reservoir waters, but also in the supply and outflow waters. The application of simple mathematical models may considerably facilitate forecasting adverse changes occurring in aquatic ecosystems. As indicated by the current study, using mathematical analyses based solely on metal concentrations in waters produces a consistency between experimental and calculated results that is far from satisfactory. Better consistency might be obtained after taking into consideration not only metal concentrations in waters, but also several other parameters such as reservoir morphometry and metal distribution in different structural elements of aquatic ecosystems.

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