

Toxic Metals in Urban Reservoirs in the Prague Metropolitan Area (Czech Republic)

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Abstract: Levels of selected toxic metals (Cd, Cu, Cr, Ni, Pb, Zn, Mn, Fe and Al) were determined in water, sediment and different species of fish in twelve reservoirs of the Prague metropolitan area. These reservoirs are affected by different types of urban drainage systems, which alter the level and fate (properties, availability, accumulation, toxicity) of toxic metals in the aquatic environment. Measurements of toxic metals were complemented by analysis of basic water quality parameters. Environmental quality standards (EQS) were exceeded in more than 50% of the studied reservoirs for the following chemical parameters: total organic carbon (TOC), chemical oxygen demand (COD) and phosphate (PO_4^{3-}). These parameters indicate a significant organic pollution and a high eutrophication level. Copper was identified as the most hazardous pollutant among the selected toxic metals in water. Other metals (Zn, Fe, Mn) exceeded the EQS only exceptionally. High concentrations of copper and zinc resulting in exceeded EQS were also identified in the sediment of most reservoirs. In a few cases increased concentrations of chromium, cadmium and lead were exceeded the EQS. A high variability of metal levels was detected in fish species, according to their age and food habits. The highest levels of toxic metals were found in the Kyjský reservoir (Zn, Cu, Ni, Cd and Pb), Strnad reservoir (Zn, Cu, Cr and Fe) and the retention reservoirs Stodůlecký N3 (Zn, Cu and Cr) and Hájecký RN3 (Zn, Cu, Cr and Pb). These reservoirs are highly affected by different anthropogenic activities, such as printing industry, traffic (Prague's ring road) and wastewater treatment plants.

Keywords: Toxic metals, fish, sediment, water, reservoirs, urban drainage.

INTRODUCTION

The contamination of fresh waters by toxic metals has become a matter of concern over the last few decades, dominantly in heavily industrialized and highly populated cities [1-4]. Toxic metals are typically released into aquatic ecosystems from domestic and industrial waste water and other human activities [5,6], and have devastating effects on the ecological balance of stream and the diversity of aquatic organisms [7-9]. The solubility, bioavailability and toxicity of toxic metals depend on physicochemical parameters such as pH, hardness, and the presence of organic matter [10, 11]. These parameters are influenced by the type of urban drainage such as combined sewer overflow, storm water drain, or waste water treatment plant [12]. Metals dissolve in water and are easily absorbed by fish and other aquatic organisms. The toxicity of metals causes negative biological effects on survival, activity, growth, metabolism, or reproduction of many species [13]. The load of aquatic ecosystems by toxic metals has been often assessed through analysis of fish species, considering their position on the top of the food chain [14, 15]. Numerous studies [16-18] carried out on different fish species have shown that toxic metals can change the physiological activities and biochemical parameters of the

fish body. A number of publications has also compiled the toxic effects of metals and their bioaccumulation in aquatic biota (fish and macrozoobentos) [19-21]. Symptoms of metal poisoning typically include hyperactivity followed by sluggishness before death, swimming at the surface, lethargic and uncoordinated movements, hemorrhaging at gills and base of fins, shed scales, and extensive body and gill mucous [22]. Elevated levels of toxic metals can alter the haematology [23], respiratory and cardiac physiology of fish species, and may also lead to retarded growth and inhibition of spawning [24, 25].

Small and shallow aquatic ecosystems such as urban reservoirs typically have a lower resilience compared to large and deep ones [26]. Particular attention has therefore to be paid to the assessment of the levels of toxic metals and other pollutants in reservoirs located in urban watersheds in agglomerations. This task has been frequently addressed in the past, however most of the previous works were focused separately on toxic metals in water, sediment or fish. This paper presents first complex study of toxic metals occurrence in Prague reservoirs. The main objectives of the study were to quantify the contamination in ecosystems of selected reservoirs with extensive fish farming in the Prague metropolitan area and assess the effect of various pollution sources and urban drainage systems. Three components (water, sediment and fish) of the ecosystem are expected to provide information on the current load, acute risk, long-term load, chronic risk and bioaccumulation (level to which the aquatic biota is loaded from the environment and food) of toxic metals.

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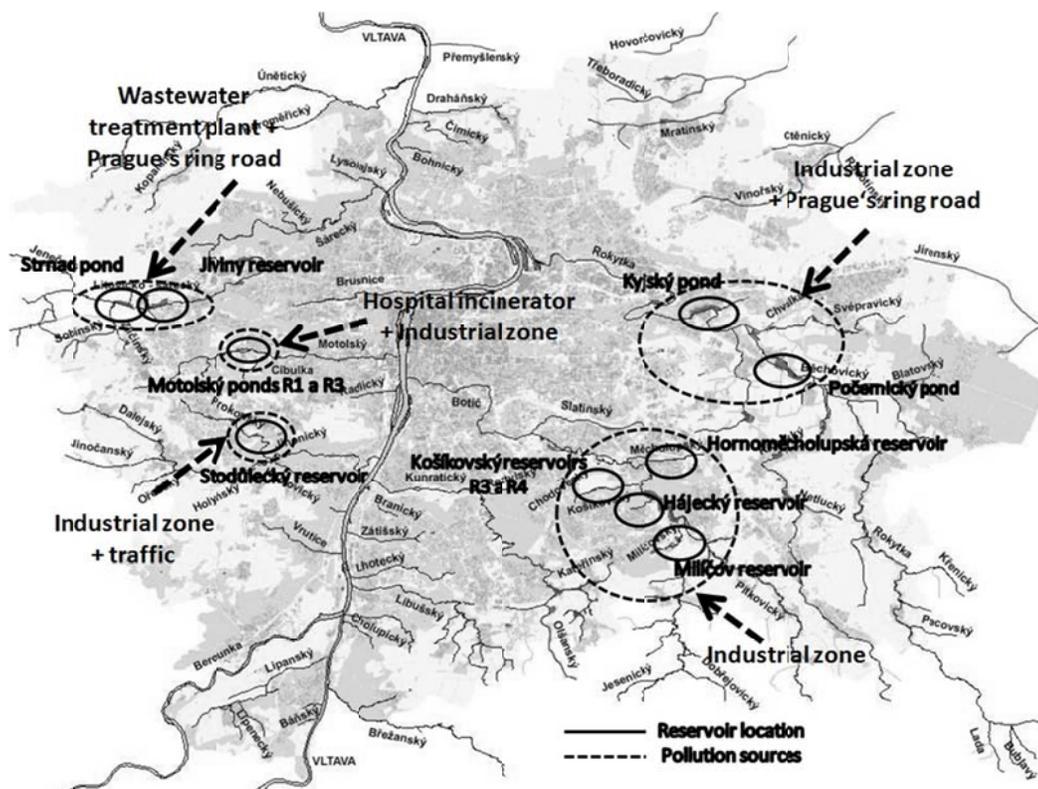


Fig. (1). Location of monitored reservoirs in the Prague agglomeration with identified main pollution sources.

Table 1. List of Monitored Reservoirs with their Basic Characteristics

| Reservoir | Main inflow to Reservoir | Function of Reservoir | Storage Volume (m ³) | Watershed Area (km ²) |
|----------------------------|--------------------------|-----------------------|----------------------------------|-----------------------------------|
| Kyjský reservoir | Rokytká creek | R, L, FF | 455 480 | 115.7 |
| Počernický reservoir | Rokytká creek | R, L, B, FF, | 310 000 | 102.5 |
| Jiviny reservoir | Litovicko-Šárecký creek | R, FF, B | 138 000 | 37.8 |
| Strnad reservoir | Litovicko-Šárecký creek | B, R, L | 114 015 | 34.5 |
| Stodůlky reservoir 3 | Prokopský creek | R, L, FF | 25 750 | 4.5 |
| Košikovský reservoir 3 | Košikovský creek | R, FF, L | 13 674 | 3.5 |
| Košikovský reservoir 4 | Košikovský creek | R, FF, L | 7 843 | 3.5 |
| Motolský reservoir 1 | Motolský creek | FF, L | 10 914 | 2.6 |
| Motolský reservoir 3 | Motolský creek | FF, L | 5 394 | 2.6 |
| Hornoměcholupský reservoir | Měcholupský creek | R, L | 6 760 | 2.5 |
| Miličův reservoir 3 | Miličůvský creek | R, FF | 29 507 | 1.9 |
| Hájecký reservoir 3 | Hájecký creek | R, L, FF | 16 000 | 0.5 |

Note: R – retention, FF – fish farming, L – landscaping, B – biological

METHODS

Field Monitoring and Sampling

Accumulation of toxic metals was monitored in fish farming ecosystems of twelve reservoirs in the Prague metropolitan area, which are affected by different types of urban drainage (Fig. 1). These reservoirs have small natural catchments, but much of the inflowing water is discharged from large impervious areas, stormwater channels and pipelines. A list of reservoirs with short characteristics is given in Table 1.

The reservoirs have a small surface area of a few hectares, and they are very shallow, with an average depth of 3-5 m or less. The surrounding urban watersheds therefore exert a strong influence on the water and sediment quality in the reservoirs.

Samples of water were collected 6 times throughout the years 2010 and 2011 to nontransparent 100ml bottles and processed immediately after returning to the laboratory. Conductivity, pH and dissolved oxygen were determined by combined probes (Hach) directly in the field. Samples of sediments were collected from several locations in the reser-

Table 2. Characteristics of the Studied Fish Species

| Fish Species | Fish Family | Food Habits | Pieces |
|--------------------------------|-------------|---|--------|
| <i>Cyprinus carpio</i> | Cyprinidae | aquatic plants, macroinvertebrates, benthic worms | 12 |
| <i>Carassius carassius</i> | Cyprinidae | aquatic plants, macroinvertebrates, benthic worms | 12 |
| <i>Gobio gobio</i> | Cyprinidae | aquatic plants, macroinvertebrates, benthic worms | 5 |
| <i>Alburnoides bipunctatus</i> | Cyprinidae | aquatic plants, macroinvertebrates, benthic worms | 30 |
| <i>Perca fluviatilis</i> | Percidae | macroinvertebrates, benthic worms, small fishes | 4 |
| <i>Rutilus rutilus</i> | Cyprinidae | plankton, macroinvertebrates, benthic worms, | 4 |
| <i>Tinca tinca</i> | Cyprinidae | aquatic plants, macroinvertebrates, benthic worms | 4 |
| <i>Blicca bjoerkna</i> | Cyprinidae | aquatic plants, macroinvertebrates, benthic worms | 2 |
| <i>Esox lucius</i> | Esocidae | fish, crayfish, frogs, mice, muskrats and young waterfowl | 4 |
| <i>Ctenopharyngodon idella</i> | Cyprinidae | aquatic plants, macroinvertebrates, benthic worms | 2 |

voirs in 2009, 2010 and 2011. A set of samples was always collected at the time of the autumn harvesting of fish, and additional samples were also collected 6 times in 2010 and 2011. Sediments were transferred with a plastic scoop into a plastic container to prevent undesirable secondary contamination by metals.

Fish bodies were obtained from fishermen during the autumn harvesting in 2009, 2010 and 2011. Principal characteristics of the studied fish species are summarized in Table 2.

Preparation and Analysis of Samples

All analyzes were carried out in the laboratory of the Department of Sanitary and Ecological Engineering of the Czech Technical University in Prague, unless stated otherwise. Laboratory analysis of water samples included toxic metals and other basic parameters of physical - chemical quality of water ($N-NH_4^+$, $N-NO_3^-$, $N-NO_2^-$, Cl^- , $P-PO_4^{3-}$, COD, and TOC). Water samples for determination of toxic metals (Cd, Pb, Zn, Cr, Ni, Cu and Al, Mn and Fe) were fixed by the addition of 1 ml HNO_3 and analyzed by the atomic absorption spectrometer SolaarS with graphite and flame atomization. Other parameters were determined in the laboratory by the cuvette tests (Hach - Lange).

Samples of sediments and fish were frozen and freeze-dried. Fish for analyses were dissected to separate parts and organs (meat, heads, skeletons, fins, scales, gills, air bladders, gall bladders, hearts, livers, kidneys, intestines and gonads – sperm and eggs). Samples of sediments were sieved to separate larger fractions ($>600 \mu m$), whereas the fraction $<600 \mu m$ was processed as the total sediments. Sediment and fish samples were microwave-digested in a mixture of 9 ml HNO_3 and 1 ml H_2O_2 [27, 28]. After the digestion (by ETHOS, Milestone) the sediment and fish samples were analysed for selected toxic metals (Cd, Pb, Zn, Cr, Ni, Cu and Al, Mn and Fe) by atomic absorption spectrometer (SolaarS, Thermo).

The amount of organic matter in sediment samples was identified as loss on ignition, and the proportion of total organic carbon was analysed by TOC instruments Analytik Jena multi N/C 2100 in the laboratory of the Department of Irrigation, Drainage and Landscape Engineering of the Czech Technical University in Prague. The level of metals in water was evaluated according to the Government regulation

of the Czech Republic No. 23/2011[29], and the level of metals in sediment was evaluated according to the US EPA benchmarks (TEC -Threshold effect concentration, PEC – Probable effect concentration) [30]. The level of metals in fish samples was evaluated according to the European Directive 466/2001 [31], which sets a maximum allowed concentration of various toxic metals in fresh biomass of fish for human consumption.

RESULTS AND DISCUSSION

Water Quality

Values of basic chemical and physical parameters are shown in Table 3. The Environmental quality standards (EQS) [29] on water quality were exceeded in more than 50% of the studied reservoirs for total organic carbon, chemical oxygen demand, phosphate, ammonium nitrogen and dissolved oxygen. These parameters indicate a high level of eutrophication and organic pollution of the respective reservoirs, indicating that organic pollution is a frequent problem in urban reservoirs [26]. Eutrophication contributes to fish mortality, loss of riparian habitat, death of beneficial aquatic insects and taste and odor problems. The concentrations of toxic metals in water (Table 4) occur in the order $Fe > Al > Cu > Mn > Zn > Cr > Ni > Pb > Cd$. The concentrations of copper in most observed reservoirs exceed the EQS and therefore cause in water a toxic stress for the fish population. For example, the sensitive species (rainbow trout) produce a physiological stress response, characterized by hyperactivity, increased blood levels of the stress hormone cortisol and synthesis of the metal detoxifying protein already in very low copper concentrations in water ($1.4 \mu g/l$) [33].

Copper also causes reduced sperm and egg production in many fish species, early hatching eggs, smaller fry and increased incidence of abnormalities and reduced survival in the fry [32,33]. The toxicity of copper also depends on the form of occurrence [34].

Sediment Quality

Levels of toxic metals in the sediment samples are presented in Table 5. Metal accumulation in sediment was found in the order $Fe > Al > Mn > Zn > Cu > Cr > Ni > Pb > Cd$.

Table 3. Basic Chemical and Physical Parameters of Water in the Studied Reservoirs

| Reservoir | | pH | Dissolved O ₂ (mg l ⁻¹) | Cond. (µScm ⁻¹) | N-NH ₄ ⁺ (mg l ⁻¹) | N-NO ₃ ⁻ (mg l ⁻¹) | N-NO ₂ ⁻ (mg l ⁻¹) | Cl ⁻ (mg l ⁻¹) | P-PO ₄ ³⁻ (mg l ⁻¹) | COD (mg l ⁻¹) | TOC (mg l ⁻¹) |
|---------------------------|------------|------------|--|-----------------------------|--|--|--|---------------------------------------|---|---------------------------|---------------------------|
| Hájecký reservoir 3 | <i>MAX</i> | 8.76 | 13.6 | 781 | 0.081 | 0.74 | 0.040 | 74.3 | 0.095 | 36.3 | 8.82 |
| | <i>AVE</i> | 8.49 | 10.2 | 452 | 0.075 | 0.61 | 0.032 | 61.8 | 0.061 | 21.7 | 7.68 |
| | <i>MIN</i> | 8.07 | 8.4 | 278 | 0.061 | 0.47 | 0.029 | 31.0 | 0.026 | 13.8 | 6.47 |
| Miličov reservoir | <i>MAX</i> | 7.92 | 7.9 | 395 | 0.189 | 0.59 | 0.056 | 32.8 | 0.139 | 46.0 | 13.5 |
| | <i>AVE</i> | 7.75 | 6.97 | 328 | 0.109 | 0.32 | 0.031 | 27.4 | 0.129 | 31.4 | 11.1 |
| | <i>MIN</i> | 7.46 | 5.6 | 267 | 0.044 | 0.19 | 0.017 | 18.2 | 0.120 | 21.7 | 10.2 |
| Počernický reservoir | <i>MAX</i> | 9.1 | 17.1 | 810 | 0.361 | 2.3 | 0.125 | 84.8 | 0.309 | 59.1 | 18.9 |
| | <i>AVE</i> | 8.97 | 15.7 | 741 | 0.210 | 1.8 | 0.114 | 71.2 | 0.247 | 43.9 | 15.6 |
| | <i>MIN</i> | 8.81 | 13.5 | 666 | 0.093 | 1.4 | 0.108 | 67.5 | 0.176 | 37.0 | 14.6 |
| Kyjský reservoir | <i>MAX</i> | 8.94 | 17.2 | 877 | 0.054 | 1.89 | 0.115 | 96.2 | 0.276 | 70.6 | 13.5 |
| | <i>AVE</i> | 8.64 | 12.8 | 724 | 0.051 | 1.62 | 0.101 | 88.3 | 0.178 | 42.1 | 12.7 |
| | <i>MIN</i> | 8.42 | 9.7 | 680 | 0.040 | 1.24 | 0.094 | 76.0 | 0.111 | 26.6 | 12.2 |
| Jiviny reservoir | <i>MAX</i> | 9.4 | 18.56 | 977 | 0.647 | 2.27 | 0.117 | 118.0 | 0.464 | 54.6 | 15.6 |
| | <i>AVE</i> | 8.98 | 12.9 | 821 | 0.321 | 1.57 | 0.067 | 97.4 | 0.341 | 50.1 | 11.6 |
| | <i>MIN</i> | 8.77 | 10.5 | 685 | 0.052 | 0.56 | 0.039 | 88.3 | 0.210 | 47.2 | 8.3 |
| Stodůlecký reservoir 3 | <i>MAX</i> | 8.55 | 10.11 | 1563 | 0.761 | 2.60 | 0.086 | 125.0 | 0.151 | 56.3 | 15.5 |
| | <i>AVE</i> | 7.97 | 9.12 | 874 | 0.401 | 1.68 | 0.070 | 108.1 | 0.68 | 31.2 | 12.5 |
| | <i>MIN</i> | 7.14 | 8.25 | 545 | 0.165 | 0.67 | 0.061 | 71.1 | 0.010 | 2.8 | 9.28 |
| Motolský reservoir 3 | <i>MAX</i> | 7.96 | 7.94 | 1306 | 0.158 | 1.17 | 0.017 | 238.0 | 0.078 | 27.3 | 36.2 |
| | <i>AVE</i> | 7.91 | 7.25 | 1210 | 0.098 | 0.84 | 0.010 | 201.9 | 0.060 | 24.7 | 14.8 |
| | <i>MIN</i> | 7.87 | 6.18 | 1140 | 0.031 | 0.29 | 0.008 | 161.0 | 0.042 | 19.1 | 5.02 |
| Košík reservoir 3 | <i>MAX</i> | 8.49 | 7.13 | 1545 | 0.334 | 1.93 | 0.137 | 91.5 | 0.407 | 37.7 | 12.8 |
| | <i>AVE</i> | 7.88 | 6.74 | 845 | 0.174 | 1.56 | 0.107 | 67.8 | 0.138 | 26.6 | 10.9 |
| | <i>MIN</i> | 6.86 | 5.91 | 330 | 0.096 | 1.14 | 0.075 | 44.5 | 0.021 | 9.2 | 8.5 |
| Košík reservoir 4 | <i>MAX</i> | 8.79 | 6.14 | 1633 | 0.552 | 1.16 | 0.108 | 88.7 | 0.325 | 73.2 | 12.3 |
| | <i>AVE</i> | 7.69 | 5.47 | 896 | 0.467 | 0.99 | 0.095 | 69.2 | 0.142 | 31.5 | 10.9 |
| | <i>MIN</i> | 6.89 | 3.61 | 370 | 0.399 | 0.77 | 0.076 | 49.8 | 0.020 | 5.8 | 7.28 |
| Strnad reservoir | <i>MAX</i> | 8.1 | 10.93 | 1037 | 2.980 | 2.79 | 0.236 | 111.2 | 0.692 | 59.7 | 16.3 |
| | <i>AVE</i> | 7.98 | 10.09 | 894 | 1.421 | 2.51 | 0.235 | 109.7 | 0.512 | 42.8 | 15.7 |
| | <i>MIN</i> | 7.84 | 9.4 | 859 | 0.807 | 2.17 | 0.233 | 94.4 | 0.416 | 38.0 | 13.1 |
| Hornoměřolupská reservoir | <i>MAX</i> | 7.81 | 8.56 | 598 | 0.254 | 1.46 | 0.116 | 45.4 | 0.193 | 64.3 | 11.8 |
| | <i>AVE</i> | 7.78 | 6.25 | 507 | 0.231 | 1.08 | 0.103 | 40.8 | 0.162 | 45.9 | 10.1 |
| | <i>MIN</i> | 7.32 | 3.06 | 395 | 0.211 | 0.631 | 0.092 | 31.8 | 0.113 | 35.9 | 8.5 |
| Motolský reservoir 1 | <i>MAX</i> | 8.07 | 7.45 | 1480 | 0.118 | 1.39 | 0.035 | 188 | 0.152 | 32.6 | 10.8 |
| | <i>AVE</i> | 7.54 | 6.87 | 947 | 0.094 | 0.94 | 0.032 | 168 | 0.94 | 17.4 | 9.2 |
| | <i>MIN</i> | 7.29 | 6.10 | 826 | 0.073 | 0.35 | 0.030 | 145 | 0.011 | 4.4 | 8.5 |
| EQS (NV 23/2011) [29] | | 6-9 | >9 | - | 0.23 | 5.4 | 0.14 | 150 | 0.15 | 26 | 10 |

Note: Values enhanced in bold and italic exceed the EQS [29]

Table 4. Concentration of Toxic Metals in Water in the Studied Reservoirs

| Reservoir | | Zn ($\mu\text{g l}^{-1}$) | Cu ($\mu\text{g l}^{-1}$) | Ni ($\mu\text{g l}^{-1}$) | Cd ($\mu\text{g l}^{-1}$) | Cr ($\mu\text{g l}^{-1}$) | Pb ($\mu\text{g l}^{-1}$) | Fe ($\mu\text{g l}^{-1}$) | Mn ($\mu\text{g l}^{-1}$) | Al ($\mu\text{g l}^{-1}$) |
|---------------------------|-----|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Hájecký reservoir 3 | MAX | 15.7 | 63.7 | 2.09 | 0.041 | 2.03 | 0.745 | 352.0 | 32.1 | 107.0 |
| | AVE | 13.4 | 57.2 | 1.54 | 0.025 | 1.84 | 0.612 | 274.4 | 24.1 | 98.5 |
| | MIN | 8.8 | 51.2 | 1.15 | 0.014 | 1.45 | 0.411 | 156.0 | 12.3 | 87.0 |
| Miličův reservoir | MAX | 15.6 | 72.9 | 3.07 | 0.042 | 6.12 | 1.45 | 1374.0 | 124.3 | 712.0 |
| | AVE | 13.4 | 66.4 | 2.74 | 0.019 | 5.32 | 1.24 | 1122.5 | 114.4 | 521.8 |
| | MIN | 9.4 | 42.1 | 1.61 | PMD | 4.72 | 0.94 | 1095.0 | 95.4 | 321.0 |
| Počernický reservoir | MAX | 19.8 | 65.1 | 5.212 | 0.067 | 5.103 | 0.704 | 432.0 | 354.0 | 282.0 |
| | AVE | 12.4 | 59.7 | 4.211 | 0.047 | 4.424 | 0.624 | 374.0 | 278.0 | 192.0 |
| | MIN | 6.3 | 55.1 | 3.647 | 0.032 | 3.653 | 0.508 | 314.0 | 206.0 | 102.0 |
| Kyjský reservoir | MAX | 10.5 | 63.7 | 5.367 | 0.012 | 5.641 | 0.727 | 151.0 | 150.1 | 126.0 |
| | AVE | 8.2 | 56.4 | 4.752 | 0.010 | 4.721 | 0.612 | 98.0 | 148.4 | 102.0 |
| | MIN | 4.7 | 47.4 | 4.095 | 0.007 | 3.452 | 0.478 | 74.0 | 147.1 | 74.0 |
| Jiviny reservoir | MAX | 8.5 | 67.4 | 5.241 | 0.012 | 1.113 | 0.314 | 372.0 | 68.5 | 124.0 |
| | AVE | 6.7 | 49.1 | 4.240 | 0.009 | 1.024 | 0.308 | 254.0 | 47.2 | 101.9 |
| | MIN | 4.3 | 25.8 | 3.386 | 0.004 | 0.941 | 0.288 | 124.0 | 24.9 | 82.0 |
| Stodůlecký reservoir 3 | MAX | 12.6 | 52.6 | 6.483 | 0.011 | 1.782 | 0.829 | 422.0 | 82.3 | 151.0 |
| | AVE | 10.1 | 38.1 | 5.120 | 0.007 | 1.245 | 0.621 | 307.0 | 61.4 | 142.0 |
| | MIN | 7.4 | 12.1 | 2.319 | 0.003 | 0.607 | 0.184 | 94.0 | 36.1 | 134.0 |
| Motolský reservoir 3 | MAX | 7.5 | 45.6 | 4.132 | 0.151 | 2.314 | 0.539 | 451.0 | 125.5 | 163.0 |
| | AVE | 5.2 | 29.7 | 3.841 | 0.112 | 1.945 | 0.421 | 320.0 | 117.0 | 139.0 |
| | MIN | 2.1 | 13.5 | 3.215 | 0.075 | 1.231 | 0.194 | 197.0 | 108.8 | 122.0 |
| Košík reservoir 3 | MAX | 22.9 | 59.9 | 2.647 | 0.011 | 2.745 | 2.117 | 508.0 | 141.1 | 350.0 |
| | AVE | 17.6 | 38.4 | 2.121 | 0.006 | 2.245 | 1.124 | 345.0 | 109.3 | 274.0 |
| | MIN | 11.3 | 11.2 | 1.777 | 0.002 | 1.834 | 0.529 | 245.0 | 69.1 | 158.0 |
| Košík reservoir 4 | MAX | 21.3 | 49.3 | 2.707 | 0.038 | 2.421 | 3.124 | 463.0 | 613.1 | 456.0 |
| | AVE | 17.9 | 37.2 | 2.302 | 0.025 | 1.948 | 2.415 | 297.0 | 534.1 | 345.0 |
| | MIN | 14.7 | 14.7 | 2.025 | 0.001 | 1.231 | 0.973 | 120.0 | 507.8 | 169.0 |
| Strnad reservoir | MAX | 28.9 | 61.6 | 6.105 | 0.032 | 3.124 | 0.641 | 1258.0 | 202.7 | 664.0 |
| | AVE | 19.8 | 45.1 | 5.978 | 0.027 | 2.994 | 0.478 | 1189.0 | 179.1 | 498.0 |
| | MIN | 13.9 | 23.4 | 5.214 | 0.019 | 2.856 | 0.384 | 1074.0 | 129.8 | 343.0 |
| Hornoměřolupská reservoir | MAX | 34.6 | 64.7 | 4.596 | 0.045 | 7.091 | 6.879 | 1918.0 | 229.1 | 1265.0 |
| | AVE | 27.5 | 49.2 | 3.784 | 0.029 | 6.647 | 5.684 | 1647.0 | 164.2 | 975.0 |
| | MIN | 19.7 | 31.5 | 3.014 | 0.008 | 6.214 | 4.215 | 1241.0 | 94.5 | 754.0 |
| Motolský reservoir 1 | MAX | 21.6 | 45.6 | 7.947 | 0.003 | 11.723 | 0.513 | 463.0 | 132.9 | 228.0 |
| | AVE | 18.2 | 29.4 | 6.512 | 0.002 | 10.245 | 0.410 | 294.0 | 109.2 | 119.0 |
| | MIN | 14.5 | 13.3 | 5.505 | 0.001 | 9.247 | 0.246 | 96.0 | 98.4 | 81.0 |
| EQS (NV 23/2011) [29] | | 92.0 | 14.0 | 20 | 0.3 | 18 | 7.2 | 1000.0 | 300.0 | 1000.0 |

Note: Values enhanced in bold and italic exceed the EQS [29]

Table 5. Content of Toxic Metals in Sediments of the Studied Reservoirs

| Reservoir | | Zn (mgkg ⁻¹) | Cu (mgkg ⁻¹) | Ni (mgkg ⁻¹) | Cd (mgkg ⁻¹) | Cr (mgkg ⁻¹) | Pb (mgkg ⁻¹) | Fe (gkg ⁻¹) | Mn (mgkg ⁻¹) | Al (mgkg ⁻¹) |
|-------------------------|------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|-----------------------------|-----------------------------|
| Hájecký reservoir 3 | <i>MAX</i> | 754 | 84 | 34 | 0.526 | 78 | 64 | 34 | 401 | 11.2 |
| | <i>AVE</i> | 671 | 72 | 28 | 0.460 | 52 | 56 | 29 | 384 | 7.8 |
| | <i>MIN</i> | 502 | 52 | 21 | 0.304 | 35 | 32 | 27 | 302 | 6.4 |
| Miličov reservoir | <i>MAX</i> | 310 | 87 | 27 | 0.412 | 54 | 55 | 45 | 420 | 8.6 |
| | <i>AVE</i> | 270 | 73 | 23 | 0.384 | 49 | 47 | 34 | 381 | 6.2 |
| | <i>MIN</i> | 198 | 65 | 18 | 0.351 | 43 | 43 | 29 | 256 | 4.5 |
| Počernický reservoir | <i>MAX</i> | 165 | 77 | 23 | 0.514 | 58 | 32 | 22 | 631 | 6.6 |
| | <i>AVE</i> | 148 | 63 | 17 | 0.455 | 51 | 28 | 19 | 551 | 4.7 |
| | <i>MIN</i> | 132 | 51 | 11 | 0.412 | 37 | 24 | 18 | 425 | 3.8 |
| Kyjský reservoir | <i>MAX</i> | 326 | 60 | 32 | 1.542 | 56 | 57 | 23 | 950 | 17.1 |
| | <i>AVE</i> | 226 | 55 | 28 | 1.084 | 49 | 48 | 17 | 849 | 14.2 |
| | <i>MIN</i> | 159 | 32 | 24 | 0.621 | 46 | 32 | 12 | 745 | 12.4 |
| Jiviny reservoir | <i>MAX</i> | 112 | 27 | 11 | 0.141 | 22 | 15 | 15 | 268 | 5.8 |
| | <i>AVE</i> | 87 | 24 | 10 | 0.131 | 18 | 14 | 12 | 176 | 4.2 |
| | <i>MIN</i> | 60 | 18 | 9.6 | 0.121 | 14 | 13 | 9 | 135 | 3.9 |
| Stodůlecký reservoir 3 | <i>MAX</i> | 448 | 76 | 36 | 0.335 | 60 | 33 | 26 | 310 | 11.2 |
| | <i>AVE</i> | 347 | 52 | 27 | 0.264 | 43 | 31 | 24 | 278 | 10.1 |
| | <i>MIN</i> | 221 | 36 | 21 | 0.201 | 20 | 29 | 21 | 256 | 9.4 |
| Motolský reservoir 3 | <i>MAX</i> | 154 | 83 | 34 | 0.405 | 39 | 34 | 27 | 611 | 8.8 |
| | <i>AVE</i> | 139 | 78 | 31 | 0.389 | 36 | 32 | 24 | 564 | 7.1 |
| | <i>MIN</i> | 121 | 75 | 29 | 0.378 | 31 | 31 | 21 | 485 | 6.9 |
| Košík reservoir 3 | <i>MAX</i> | 198 | 19 | 16 | 0.102 | 20 | 15 | 19 | 148 | 5.2 |
| | <i>AVE</i> | 124 | 17 | 14 | 0.074 | 17 | 13 | 18 | 121 | 4.1 |
| | <i>MIN</i> | 43 | 15 | 10 | 0.027 | 15 | 10 | 16 | 98 | 3.7 |
| Košík reservoir 4 | <i>MAX</i> | 194 | 33 | 17 | 0.348 | 25 | 26 | 20 | 233 | 13.1 |
| | <i>AVE</i> | 119 | 27 | 15 | 0.214 | 24 | 23 | 17 | 220 | 11.4 |
| | <i>MIN</i> | 49 | 16 | 14 | 0.164 | 23 | 22 | 14 | 201 | 9.8 |
| Strnad reservoir | <i>MAX</i> | 380 | 67 | 26 | 0.248 | 59 | 20 | 17 | 523 | 14.4 |
| | <i>AVE</i> | 224 | 59 | 20 | 0.194 | 36 | 18 | 15 | 481 | 12.8 |
| | <i>MIN</i> | 119 | 47 | 13 | 0.15 | 22 | 13 | 11 | 465 | 10.7 |
| Hornoměřolská reservoir | <i>MAX</i> | 173 | 61 | 34 | 0.372 | 38 | 47 | 10 | 216 | 6.9 |
| | <i>AVE</i> | 127 | 47 | 32 | 0.245 | 29 | 35 | 8 | 179 | 6.1 |
| | <i>MIN</i> | 85 | 24 | 31 | 0.097 | 16 | 18 | 6 | 154 | 5.2 |
| Motolský reservoir 1 | <i>MAX</i> | 185 | 35 | 28 | 0.197 | 34 | 17 | 24 | 363 | 13.3 |
| | <i>AVE</i> | 162 | 29 | 26 | 0.148 | 28 | 15 | 21 | 325 | 10.2 |
| | <i>MIN</i> | 128 | 25 | 25 | 0.125 | 25 | 13 | 16 | 301 | 8.4 |
| TEC (US EPA 1997) [27] | | 159 | 28 | 39.6 | 0.592 | 56 | 34.2 | - | - | - |
| PEC (US EPA 1997) [27] | | 1532 | 77.7 | 38.5 | 11.7 | 159 | 396 | - | - | 58 |

Note: Values enhanced in bold and italic exceed the EQS [27]

The average content of organic matter detected as ignition loss in the total bottom sediments was 9%, with sediments mainly composed of mineral substances. The mean total organic carbon content was 4.7%. The highest content of organic matter (OM) and the highest proportion of total organic carbon (TOC) were found in the Strnad reservoir,

whose total sediment has 23% OM and 14% TOC. As shown in Table 5, the levels of Zn and Cu exceed the US EPA benchmarkers in the majority of studied reservoirs. Levels of Cr, Cd and Pb exceed the critical values in at least one of the reservoirs. Although Zn, Cu and Ni are not highly toxic to humans, they can be highly toxic to some fish and many

Table 6. The Average Concentration of Toxic Metals in Muscle of *Cyprinus Carpio* and *Carassius Carassius* (Wet Weight Concentration)

| Reservoir | | Zn (mg-g ⁻¹) | Cu (mg-g ⁻¹) | Ni (mg-g ⁻¹) | Cd (mg-g ⁻¹) | Cr (mg-g ⁻¹) | Pb (mg-g ⁻¹) | Fe (mg-g ⁻¹) | Mn (mg-g ⁻¹) | Al (mg-g ⁻¹) |
|----------------------------------|------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Košík reservoir 4 | <i>Cyprinus</i> | 11.85 | 0.25 | 30.67 | 0.29 | 22.54 | 3.45 | 3.22 | 0.51 | 3.07 |
| | <i>Carassius</i> | 11.04 | 0.28 | 25.48 | 0.29 | 17.00 | 2.28 | 3.47 | 0.69 | 2.41 |
| Motolský reservoir 3 | <i>Cyprinus</i> | 10.61 | 0.23 | 17.58 | 0.69 | 2.75 | 1.24 | 12.48 | 3.14 | 2.15 |
| | <i>Carassius</i> | 11.77 | 0.24 | 22.81 | 0.65 | 2.39 | 2.15 | 15.42 | 4.08 | 2.96 |
| Kyjský reservoir | <i>Cyprinus</i> | 25.72 | 0.83 | 23.07 | 0.21 | 23.81 | 8.76 | 4.93 | 0.20 | 3.18 |
| | <i>Carassius</i> | 19.26 | 0.21 | 38.62 | 0.46 | 19.23 | 6.02 | 2.03 | 0.90 | 7.66 |
| Hornoměřolupská reservoir | <i>Cyprinus</i> | 12.78 | 0.40 | 37.30 | 0.20 | 25.32 | 4.31 | 0.57 | 0.41 | 3.35 |
| | <i>Carassius</i> | 17.99 | 0.22 | 57.80 | 0.25 | 18.42 | 2.44 | 1.85 | 0.79 | 1.70 |
| Stodůlecký reservoir 3 | <i>Cyprinus</i> | 8.73 | 0.22 | 125.1 | 0.25 | 19.62 | 11.6 | 2.27 | 0.74 | 2.98 |
| | <i>Carassius</i> | 8.44 | 0.75 | 159.7 | 0.37 | 17.42 | 17.59 | 2.87 | 0.85 | 2.74 |
| Strnad reservoir | <i>Cyprinus</i> | 29.90 | 1.77 | 50.49 | 0.21 | 32.57 | 35.96 | 1.82 | 6.12 | 1.96 |
| | <i>Carassius</i> | 11.98 | 1.82 | 71.89 | 0.51 | 34.45 | 30.12 | 2.68 | 6.96 | 3.21 |
| Počernický reservoir | <i>Cyprinus</i> | 11.52 | 0.44 | 87.71 | 0.18 | 19.22 | 14.63 | 2.62 | 2.83 | 0.91 |
| | <i>Carassius</i> | 18.30 | 0.43 | 121.3 | 0.25 | 23.35 | 22.69 | 3.26 | 6.97 | 1.12 |
| Hájecký reservoir 3 | <i>Cyprinus</i> | 15.24 | 0.58 | 23.25 | 0.12 | 18.08 | 3.77 | 2.60 | 2.95 | 1.5 |
| | <i>Carassius</i> | 11.42 | 0.47 | 19.41 | 0.24 | 16.71 | 2.54 | 1.87 | 3.12 | 1.97 |
| European Directive 466/2001 [31] | | - | - | - | 50 | - | 200 | - | - | - |

aquatic animals [34]. Elevated concentrations of Cr, Cd, Cu and Pb in sediment may cause a problem when accompanied by high concentrations of zinc and remobilized into water. Mixtures of zinc with copper, lead, cadmium and chromium are considered to have more than additive toxicity effects to a wide variety of aquatic organisms, including oyster larvae, marine fish, freshwater fish and amphipods [35]. The metals in the sediment of the studied reservoirs are also source of chronic hazard for the aquatic organisms, especially for those living in the bottom sediment.

Quality of Fish

Metal accumulation was found in the order Fe > Al > Zn > Mn > Cu > Ni > Pb > Cr > Cd for the whole fish bodies.

Metal accumulation levels in fish muscle never exceeded the maximum allowed [31] level of Cd and Pb in fresh biomass of fish for human consumption (Table 6).

The lowest levels of metals in fish was found in reservoirs located below other reservoirs which function as a pre-treatment (Košík reservoir 4, Motolský reservoir 3, Stodůlecký reservoir 3) where part of the metals is removed. The highest concentrations of metals in fish were found in Strnad reservoir, Kyjský reservoir and Počernický reservoir.

SUMMARY AND CONCLUSIONS

The study summarized loads of toxic metals and their accumulation in the water, bottom sediments and fish biomass in twelve reservoirs in the Prague metropolitan area. Basic chemical and physical parameters of water and sediment were also measured, because they may influence the behaviour and fate of toxic metals in the aquatic environment.

Measured values of water quality parameters and toxic metals in the monitored reservoirs were often exceeded the EQS, including total organic carbon, chemical oxygen demand, phosphate, ammonium nitrogen, dissolved oxygen and copper. Copper and zinc were evaluated as most hazardous metals in the studied reservoirs. The copper concentrations exceeded the EQS for water and sediment, and increased zinc concentrations were often found in sediment. Both metals are highly toxic to some fish and many aquatic animals. The lead ecological standards were exceeded in four reservoirs and cadmium standards in one reservoir.

The geographical assessment of the loads of metals has concluded that the highest concentrations in sediment were found in the reservoirs Kyjský, Počernický, Miličův and Hájecký. All of these four reservoirs are located near large industrial areas. The high metal load in the Kyjský and Počernický reservoir is probably caused by a significant storm water input from adjacent urbanized areas, including major polluters such as Prague Heating plant, Vltava-Labe Press (printing plant), Penguin CZ and IDEAL (laundry and dry cleaning of textile and fur products). Another significant source of pollution by toxic metals are the surface flow and exhalations from the busy roads E67 and E65 (R1-Prague ring road) near the Kyjský and Počernický reservoirs. The pollution by toxic metals may be present in a significant portion of combined sewer overflows and illegal wastewater pipelines connected to storm water drains or directly to the recipient - Rokyta creek [36, 37]. Hájecký reservoir and Miličův reservoir have the smallest watershed area of all reservoirs. Significantly smaller number of industrial polluters is located in their watersheds compared with watershed of Kyjský and Počernický reservoirs. The major polluters are five branches of Prague Heating plant – South City and ex-

halations from the busy roads E55 and E50 (R1-Prague ring road). Attention should be paid to Strnad reservoir where the EQS for following parameters were exceeded: N-NH_4^+ , N-NO_2^- , Cl^- , P-PO_4^{3-} , COD, TOC, Cu and Fe in water, and Cu, Zn and Cr in sediment. It can be concluded that the Strnad reservoir works like a biological purification pond for the wastewater treatment plant Hostovice. This hypothesis was supported by fishermen at fish harvests and also by significant content of organic matter in sediment.

The measured data in the reservoirs have indicated various types of pollution and eutrophication, and provide a rationale for a further continuous monitoring of the reservoir ecosystems, with particular emphasis on the most polluted reservoirs. It would allow to better evaluate the occurrence and movement of metals between water, sediment and fish. Special attention should be also paid to continuous monitoring and evaluation of the quality of fish, because fish from most of the reservoirs are used for human consumption. Although toxic metals in fish meat meet the valid legislation requirements, it is highly recommended to continue the complex monitoring of the pollutants in the entire system water-sediment-fish.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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