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Research Article

Accumulation of Mn, Cu, and Zn in Flowers and Leaves of *Catalpa bignonioides* in an Urban Area Under Climate Change Conditions

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Green areas are an important part of the urban landscape. Trees produce oxygen, provide shade, maintain soil moisture, and reduce the amounts of toxic gases and dust in the air. Due to the changing climate, species characteristic of other climatic zones, e.g. *Catalpa bignonioides*, are planted in urban parks in Poland, mainly due to the attractive appearance of the leaves and flowers. The aim of the study was to assess the content of Mn, Cu, and Zn in flowers and leaves of *C. bignonioides* in the urban park and to determine the value of bioconcentration coefficients (BCF) of these metals. The obtained results indicate that the flowers and leaves of *C. bignonioides* accumulate lesser amounts of manganese, copper, and zinc. It is a consequence of the limited bioavailability of these components in soils, due to too high pH values resulting from alkalinization of urban soils. The values of bioconcentration coefficients (BCF <1) confirm the low accumulation of Mn, Cu, and Zn in both leaves and flowers of *C. bignonioides*, due to the limited mobility of manganese, copper, and zinc compounds in the soils of the urban park and the low impact of falling dusts, which are the carriers of the analyzed components.

Keywords: urban park, trees, pollutions, heavy metals, bioconcentration coefficients

1 Introduction

Urban areas are ecosystems with a predominant human impact, in which the main elements are buildings and communication networks. In urban space, a prominent place is also occupied by vegetation, mainly anthropogenic, as well as the remains of natural systems, i.e. watercourses, water reservoirs or the fragments of forests. A critical issue in planning urban greenery, which performs significant natural functions, is the preservation of biodiversity. Vegetation, especially trees, in addition to the aesthetic function regulate the ambient temperature, increase air humidity, and facilitate water retention. Trees, and especially their leaves, improve air quality by reducing the concentration of toxic gases (SO_2, NO, NO_2) and dust (Aksoy et al., 2000; Islam et al., 2012). The leaves retain on their surface suspended dust particles with a diameter of less than 10 and 2.5 μm, which are carriers of many heavy metals (Pb, Cd, Zn, Cu, Ni and other), (Monaci et al., 2000; Kocić et al., 2014; Li et al., 2019). However, not all trees accumulate pollutants in equal amounts. Some species, i.e. ash, spruce or linden, have difficulty tolerating certain environmental pollutants. Literature data indicate that maples, poplars, and oaks (Gratani et al., 2008) are more resistant to atmospheric and soil pollution. In urban parks of Poland, in addition to lindens, maples, poplars, ash trees, birches, chestnut trees, and willows, occur species from other climatic zones, e.g. *Catalpa bignonioides* (Öztürk & Bozdoğan, 2015; Kurbaniyazov et al., 2021). This species was imported from North America. Currently, it is one of the popular ornamental trees. Due to its interesting silhouette, as well as the attractive appearance of leaves, flowers and fruits, it is eagerly planted in gardens and parks, especially in urban areas. Due to the relatively large size of the tree and its leaves, it should be expected that this species accumulates in its shoots, in addition to nutrients, significant amounts of impurities, e.g. heavy metals (Aksoy et al., 2000; Piczak et al., 2003; Islam et al., 2012; Öztürk & Bozdoğan, 2014, 2015). Pollution of the urban environment adversely affects the living condition of many plant species, worsening their conditions of growth and development (Neverova & Kolmogorova, 2002; Sawidis et al., 2011). Excessive accumulation of heavy metals in the leaves of woody plants results in a weakening of their life potential,

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which may lead to negative changes in the functioning of physiological processes and an overall weakening of their health condition (Brtnický et al., 2019; Kurbaniyazov et al., 2021; Hrynyova & Kryshtop, 2021). Sparse literature data indicate that *C. bignonioides* accumulates greater amounts of Cu in urban areas than other species of woody plants (Öztürk & Bozdoğan, 2015). The study of the content of heavy metals in the tree leaves allows to determine which species accumulate the greatest amount of pollution, which is important from the point of view of urban planning and species selection planning affecting the improvement of air quality in cities.

The aim of the research was to assess the content of manganese, copper, and zinc in the flowers and leaves of *C. bignonioides* in the urban park, to characterize the physicochemical properties of the soil collected under the crowns of these trees, to determine the value of bioconcentration coefficients (BCF) of Mn, Cu, and Zn in the leaves and flowers of *C. bignonioides*, and to assess the possibility of using this species for the qualitative assessment of the urban environment.

2 Materials and methods

The research was conducted in northern Poland, in the city park in Słupsk (54° 27′ 50″ N, 17° 1′ 43″ E). The *Catalpa bignonioides* trees selected for research were planted in order to increase the biodiversity of the species and decorate the park (Fig. 1). Ten *C. bignonioides* trees were selected for chemical research and the samples of flowers, leaves and soil from their rhizosphere (from a depth of 0–0.15 m) were taken. Samples of mature leaves, flowers, and soil were taken for testing in June, during the flowering of trees. In addition, after the growing season, old leaves were collected in October. Leaves and flowers were collected at a height of 2 m from four sides of the tree crowns (from the North, South, East, and West), then combined into one mixed sample, from each tree separately.

Before proceeding with the analyses, the samples were pre-treated. The soil, leaves and flowers were dried in paper bags in a forced-air dryer at 65 °C for 48h (PolEco). Subsequently, soil samples were rubbed in a mortar and sieved through a 1 mm mesh sieve. Plant samples were homogenized in a laboratory grinder (IKA, A11 basic). Until the analysis, the samples were stored in tightly closed string bags. During laboratory tests, a total of 40 samples (10 soil samples, 10 samples of mature leaves, 10 samples of old leaves and 10 samples of flowers) were analysed.

In soil samples, the content of organic matter was determined using the loss on ignition method, in the muffle furnace, at 550 °C and active acidity (pH in H_2O) in a weight ratio of 1 : 2.5 by potentiometric method (Kabała & Karczewska, 2017) using a pH meter (CPI 551 Elmetron). In order to determine the content of Mn, Cu, and Zn (0.5 g), samples of flowers, leaves and soil were mineralized in a mixture of 65% HNO_3 and 30% H_2O_2 in a microwave mineralizer (ETHOS EASY by MILESTONE) at 200 °C for 15 minutes. After mineralization, solutions of flower and leaf samples were made up to 50 ml with deionized water, and soil samples were made up to 25 ml after filtration. In the obtained solutions, the content of Mn, Cu, and Zn was determined by atomic absorption spectrometry (ASA), with the iCE3500 apparatus (Thermo Scientific), using flame technique (FAAS) in a mixture of acetylene and air. The original standard solutions of Zn, Cu, and Mn from Fluka with a concentration of 1 mg.1,000 ml^{-1} were used to calibrate the apparatus. Absorption measurements were performed at the following wavelengths: Mn at 279.5 nm, Cu at 324.8 nm, and Zn at 213.8 nm.

The obtained results are presented in tables and figures. In order to compare the content of Mn, Cu and Zn in flowers, mature leaves and old leaves, the non-parametric Wallis Kruskal test was used at p <0.05. The values of bioconcentration coefficients (BCF) for Mn, Cu and Zn in flowers and leaves of *C. bignonioides* were calculated in relation to their content in the soil. Mutual correlations between the metal content in the soil and in flowers and leaves were expressed in the form of Spearman correlation coefficients. Calculations and figures (Fig. 2) were made in Statistica 13.3.

3 Results and discussion

The soil samples taken directly under the crowns of C. It was shown that the pH values ranged from 5.4 to 6.5, and the coefficient of variation (CV) remained at 6.4%. The content of organic matter remained in the range of 8.3 to 14.2%, showing a variation of 17.5%.

The content of heavy metals in soil samples also varied and ranged from 183.7 to 360.9 mg.kg^{-1} Mn, from 14.9 to 46.3 mg.kg^{-1} Cu, and from 50.3 to 108.5 mg.kg^{-1} Zn (Table 1). The values of the coefficients of variation remained at the level from 20.9% for Mn to 35.2% for Cu.

The highest average Mn content was shown in mature leaves (52.9 mg.kg^{-1}) and old leaves (51.3 mg.kg^{-1}). Much lower amounts of Mn were found in flowers (27.0 mg.kg^{-1}) (Fig. 2). Slightly different results were obtained in the case of Cu, which dominated in flowers (on average 11.1 mg.kg^{-1}). The mature and old leaves contained 9.6 mg.kg^{-1} and 6.5 mg.kg^{-1} of Cu, respectively. The highest zinc content was found in old leaves

Figure 1 Trees (A), flowers (B), leaves (C), fruits and seeds (D) of *C. bignonioides*
(Foto: A. Yurchak)

Table 1 Physicochemical properties of soil from the rhizosphere of *C. bignonioides*.

Parameter	Mean ±sd	Range	CV (%)
pH	6.3* ±0.4	5.4–6.5	6.4
OM (%)	10.5 ±1.8	8.3–14.2	17.5
Mn (mg.kg^{-1})	270.3 ±56.6	183.7–360.9	20.9
Cu (mg.kg^{-1})	29.8 ±6.5	14.9–46.3	35.2
Zn (mg.kg^{-1})	75.6 ±21.0	50.3–108.5	27.8

* median, OM – organic matter, sd – standard deviation, CV – coefficient of variation

(35.2 mg.kg^{-1}) and flowers (33.6 mg.kg^{-1}). Both in the case of Mn, Cu, and Zn, statistically significant differences were found in the content of the tested metals in flowers, mature leaves, and old leaves (Mn at p <0.001, Cu and Zn at p <0.05).

The mutual relations between the physicochemical properties of the soil and the content of metallic elements in flowers and leaves of *C. bignonioides* are presented using bioconcentration coefficients (BCF) and Spearman's correlation coefficients (Tables 2 and 3). BCF values showed minor variation and took values from 0.10 to 0.21 for Mn, from 0.25 to 0.43 for Cu, and from 0.40 to 0.49 for Zn.

Positive values of correlation coefficients between pH and Cu and Zn content in mature leaves of *C. bignonioides* and in the case of soil organic matter content over Mn content in flowers, Cu in flowers and mature leaves and Zn in flowers, mature and old leaves (Table 3) were shown. Negative values of correlation coefficients were shown in the case of Mn contained in soil, and the content of Mn and Zn in flowers, and in the case of Cu and Zn contained in soil, and the concentration of Mn in flowers and mature leaves, respectively. Positive correlation coefficients were found in the case of Mn contained in the soil, and the content of Cu (in flowers) and Zn in mature and old leaves. Copper contained in the soil correlated with Cu in mature and old leaves and with Zn contained in old leaves. A positive correlation was also found in the case of Zn content in the soil and Zn content in old leaves.

Ecotoxicological studies indicate that plants selectively take elements from the surrounding environment (Wierzbicka, 2015). These components are used to build their own tissues and take part in many metabolic transformations. The growth and proper functioning of trees depends on the appropriate content and bioavailability of macro- and micronutrients in the soil. The bioavailability of the components is strictly dependent on the pH and the content of organic matter in the soil. Reaction is a particularly important soil feature that affects the absorption of nutrients by plants

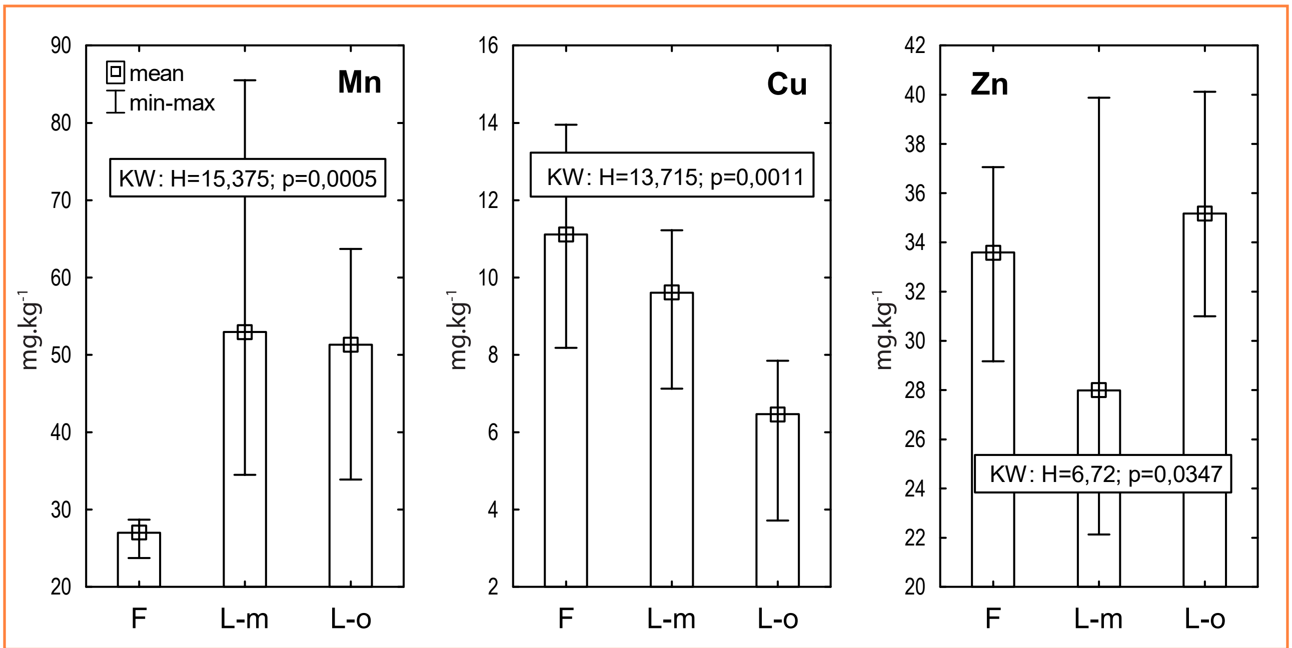

Figure 2 Changes in the content of Mn, Cu, and Zn in flowers and leaves *C. bignonioides* with Kruskal Wallis (KW) test results
F – flowers, L-m – mature leaves, L-o – old leaves

Table 2 Bioconcentration coefficients of Mn, Cu, and Zn in flowers and leaves of *C. bignonioides*

	Mn	Cu	Zn
Flowers/soil	0.10 ±0.03	0.43 ±0.12	0.47 ±0.13
Leaves-m/soil	0.21 ±0.08	0.35 ±0.11	0.40 ±0.17
Leaves-o/soil	0.20 ±0.07	0.25 ±0.08	0.49 ±0.12

Leaves-m – mature leaves, Leaves-o – old leaves

Table 3 Spearman correlation coefficients between soil, leaves, and flowers properties (n = 30, p <0.05, $r_{crit.}$ = 0.31)

		pH	OM	Mn	Cu	Zn
		soil				
Mn	flowers (■ red, □ red) mature leaves (■ green, □ green) old leaves (■ blue, □ blue)	–	■ blue	□ red	□ red	□ green
Cu		■ green	■ red, ■ green	■ red	■ green, ■ blue	–
Zn		■ green	■ red, ■ green, ■ blue	□, ■ green, ■ blue	■ blue	■ blue

■ red, ■ green, ■ blue – positive correlations, □ red, □ green, □ blue – negative correlations

(Ostrowska et al., 1991). Most metallic elements show increased mobility and bioavailability to plants in an acidic environment. Zinc and manganese are characterized by increased bioavailability at pH ≤6.0, and copper at pH ≤5.5 (Kabata-Pendias & Pendias, 1999). Manganese is additionally characterized by increased solubility in an alkaline environment (pH ~8). Significant amounts of it are associated with organic matter. The metallic elements contained in the soil migrate slowly and are among its most persistent pollutants. Their toxic effects on living organisms depend mainly on their concentration, the type of chemical substances with which they are associated, as well as the durability of these compounds under specific physicochemical conditions. The primary source of copper and zinc in soils are minerals, mainly sulphides, combined with other components (Ostrowska et al., 1991). Copper ions released in the weathering process form complexes with organic compounds. In weathering processes, zinc-containing minerals are easily decomposed. Zinc ions are bound into mineral compounds and can also be retained by soil organic matter (Parzych, 2022). According to literature data, the pH of urban soils most often takes values in the range of neutral or slightly alkaline. This is the result of alkaline dust fallout, mainly from the combustion of hard coal (Parzych & Jonczak, 2014) and sprinkling the roads and pavements with NaCl and $CaCl_2$ in winter.

The content of organic matter in the soil is shaped by the amount and quality of organic fallout, discharged by vegetation in the autumn (Ostrowska et al., 1991). However, in urban parks, organic fallout is systematically removed for orderly and aesthetic reasons, which limits the possibility of enriching the soil with components released from organic fall (Parzych, 2022).

Metallic elements bioaccumulate in plant tissues. The contents of the analyzed ingredients remained at a relatively low level in both flowers and leaves, not exceeding the limit values for plants (Kabata-Pendias & Pendias, 1999). The relatively low content of manganese, copper, and zinc in the flowers and leaves of *C. bignonioides* results from the low bioavailability of these components in the soils of the city park in Słupsk, which is a consequence of the alkalization of urban soils (Parzych, Jonczak 2014). Comparable amounts of zinc in the leaves of *C. bignonioides* were found in an urban area in Turkey – 25.5 $mg.kg^{-1}$ (Öztürk & Bozdoğan, 2015). The obtained values of bioconcentration coefficients confirm the small accumulation of Mn, Cu, and Zn in both leaves and flowers of *C. bignonioides* (Łaszewska et al., 2007). At the same time, BCF<1 values indicate limited bioavailability of manganese, copper, and zinc compounds for plants in urban park soils and a small impact of falling dusts, which are carriers of the analyzed components.

A number of statistically significant, positive and negative Spearman correlation coefficients indicate close relationships between the metals contained in flowers and leaves and pH and the content of organic matter, Mn, Cu and Zn in the soil. These dependencies indicate the possibility of using *C. bignonioides* for the qualitative assessment of the urban environment.

4 Conclusions

Soil samples taken under the crowns of *C. bignonioides* had a slightly acidic reaction, and the coefficient of variation remained at 6.4%. The organic matter content averaged 10.5%, showing a variation of 17.5%. The content of Mn, Cu and Zn in soil samples varied, but did not exceed the limit values for urban soils.

The Mn content in mature and old leaves was 52.9 $mg.kg^{-1}$ and 51.3 $mg.kg^{-1}$, respectively, and in flowers

27.0 mg.kg^{-1}. Copper predominated in flowers (11.1 mg.kg^{-1}), and the mature and old leaves contained 9.6 mg.kg^{-1} and 6.5 mg.kg^{-1} Cu, respectively. The highest zinc content was found in old leaves (35.2 mg.kg^{-1}) and flowers (33.6 mg.kg^{-1}). Statistically significant differences were found in the content of the tested metals in flowers, mature leaves, and old leaves (Mn at p <0.001, Cu and Zn at p <0.05).

BCF values showed minor variation. In the case of Mn, they took values from 0.10 to 0.21, from 0.25 to 0.43 for Cu, and from 0.40 to 0.49 for Zn, which confirms the low bioavailability of the analysed soil components for plants.

Statistically significant correlation coefficients between the analysed parameters in soil, flowers, and leaves confirm the possibility of using *C. bignonioides* for qualitative assessment of the urban environment.

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