

## THE IMPACT OF VARIED FERTILISATION ON THE CONCENTRATION OF CADMIUM AND COPPER IN ORGANS OF WILLOW TREES (*SALIX VIMINALIS*)

Aleksandra SIECIECHOWICZ<sup>1</sup>

University of Zielona Gora, Institute of Environmental Engineering, Poland

### Abstract

The paper presents the impact of varied fertilisation with sewage sludge on the concentration of cadmium and copper in willow organs during the first three years of cultivation. The lowest mean concentration of cadmium in *Salix viminalis* biomass was found in the plantation fertilised only with mineral fertilisers. The mean content of copper in the biomass of plants fertilised with mineral fertilisers was higher than the content of this metal in plants grown in non-fertilised soil by 23.4%.

It has been shown that the method of fertilisation does not have an impact on the cadmium allocation in different organs. The highest content of cadmium and copper in the willow biomass was found in the foliage (1,76 mg/kgd.m. and 12,73 mg/kgd.m. respectively).

Keywords: cadmium, copper, heavy metals, sewage sludge, *Salix viminalis*

### 1. INTRODUCTION

The far-reaching objective of the climatic and energy policy of the EU is the accomplishment of a minimum of 20% of the energy share from renewable sources by the year 2020. In this context, it is estimated that the demand for plant biomass grown for energy purposes will increase by almost 8,000,000 tonnes by the year 2020. It seems impossible to cover such a high demand by waste biomass alone, which creates prospects for the expansion of plantation areas intended for energy crops, in spite of the unstable financial support policy

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<sup>1</sup> Corresponding autor: University of Zielona Gora, Institute of Environmental Engineering, Szafrana st 15, 65-516 Zielona Gora, e-mail: a.sieciechowicz@iis.uz.zgora.pl, tel. +48683282574

with regards to the crops [1,10,18]. Therefore, the plantations of perennial energy crops (miscanthus, willow, sida hermaphrodita) have presently become a promising complement to the biomass supply on the energy market [16]. The willow has the capacity for the accumulation of heavy metals as well as nitrogen and phosphorus compounds. The particular use of this plant is related to the fast growth of biomass and the intensive ion exchange between the roots and soil, which is a consequence of it [9]. The main determinants of the yield include water, the soil conditions, the species and variety, as well as the appropriate fertilisation. Willow plantations may be fertilised with mineral fertilisers and sewage sludge [2,3,12,26,28]. The doses of the sewage sludge to be used for the purpose of fertilisation, depend also on their heavy metal concentration. However, for plant growth it is not the total concentration, but their easily soluble forms. Also, the intensity of the application of sewage sludge - on a one-off basis or gradually - is important. Heavy metals in raw sewage sludge occur in the dissolved form, that is, the form which is more accessible to the plants than after absorption by the soil [24,25]. Heavy metals include both, plant micronutrients and toxic elements. Thus cadmium and lead are harmful, zinc and copper only in excessive concentrations [1,7,17]. At present, a constant increase in the content of cadmium in the environment is observed, therefore, there the necessity arises to determine the impact of this element on, among other things, plants [14]. Despite the fact that cadmium is not necessary for the development of plants, it is taken up by them with exceptional ease and in proportion to the concentration in the solution or soil [5].

The plants take up cadmium through their root system and leaves. Cadmium causes disturbances in the process of photosynthesis and transpiration [18,19]. It also has a negative impact on the transformations of nitrogen compounds. In soils used for agricultural purposes, cadmium may occur in higher concentrations [14,15]. The reason for this is the use of phosphorus fertilisers, sewage sludge and industrial sewage used for soil liming. Cadmium mobility in the soils depends on the soil pH. Also as a result of the introduction of phosphorus into soil contaminated with cadmium, the number of its easily soluble forms is decreased. In fact, they convert to oxides and carbonates, and are partly bound to organic carbon [6,11].

Copper is introduced into the soil by certain organic and mineral fertilisers and accumulates in the soil surface, where it is strongly bound and does not move to deeper soil layers. The toxic effect of copper on the plants depends on the soil and the plant specific properties [11]. Cu accumulates in the roots of plants. Its excess leads to a growth reduction [4].

The aim of the study was to determine the effect of the fertilisation type on the cadmium and copper concentration in roots, stems and leaves of willow during the first three years of cultivation. The hypothesis was, that Cd and Cu applied in sewage sludge was not or poorly plant available (in contrast to the control or fertilisation with mineral fertilisers) and therefore poorly or not increased in willow organs. As an alternative the fertilisation with P was intended also to convert Cu and Cd in the stopsoil to less plant available phosphates.

## 2. OBJECT OF THE STUDIES AND METHODOLOGY

The programme of the utilisation of sewage sludge at the energy willow plantation has been implemented for over ten years. The dehydrated sewage sludge - after hygienisation with lime - was dosed on a one-off basis into the soil before the establishment of the crops. Properties of the surface layer of soil on the land before planting willow cutting were characterized in 2000 (Table 1).

Table 1. Properties of the surface layer of soil before planting willow cutting

Indicator	Unit	Value
pH <sub>KCl</sub>	-	6.90
P <sub>2</sub> O <sub>5</sub>	mg/100g d.m.	28.00
K <sub>2</sub> O	mg/100g d.m.	6.80
Pb <sup>2+</sup>	mg/kg d.m.	9.66
Cd <sup>2+</sup>	mg/kg d.m.	0.09
Cr <sup>2+</sup>	mg/kg d.m.	6.22
Cu <sup>+</sup>	mg/kg d.m.	7.21
Ni <sup>2+</sup>	mg/kg d.m.	4.02
Hg <sup>+</sup>	mg/kg d.m.	0.07
Zn <sup>2+</sup>	mg/kg d.m.	44.25

The preferential factors for determining the dose of sludge included its soil-forming properties, ensuring the multi-year productivity of the substrate in the area intended for the plantations of plants with high demands for nutrients and water [9]. The factors which limited the quantity of sludge introduced into the soil were the relationships of the content of heavy metals in the sewage sludge (especially the concentration of zinc, and to a lesser extent, the concentration of copper) and soil formations, and the strongly alkaline reaction of the hygienised sludge [9,21].

The sewage sludge was tested on a regular basis at the Laboratory of Water, Sewage and Waste of the Institute of Environment Engineering at the

University of Zielona Góra. The determined indices, test methodology and results of analyses of sewage sludge samples have been listed in table 3. In connection with this, the collection of samples and the laboratory tests were conducted in the years 2007-2009. Pursuant to the Regulation of the Minister of Environment of 1 August 2002 on municipal sewage sludge [23], the analyses of sewage sludge samples confirm their usefulness for natural utilisation in agriculture and for the reclamation of lands for agricultural and non-agricultural purposes. It must be emphasised that the Regulation of the Minister of Environment of 13 July 2010 on municipal sewage sludge [22] was not yet in force in the period of sample collection and laboratory tests (years 2007-2009).

Based on the performed tests [21], the doses of sewage sludge ranging between 88 and 94 tonnes of d.m./ha were established. The planting density amounted to 33,400 pcs./ha. Cuttings of the common osier of the Scandinavian varieties (Ulv and York varieties) from clones obtained in Marzęcin were 40cm long. The willow was planted in the year 2007 during the period of early spring. The whole area of cultivation of the willow was divided into three sections: with an addition of sewage sludge, with an addition of mineral fertilisers in the form of potassium salt at a dose of 0.12 tKCl/ha and superphosphate at a dose of 0.08 tP<sub>2</sub>O<sub>5</sub>/ha and the control section.

The plant samples were collected in summer of the years 2007, 2008 and 2009. The collection consisted of the careful digging up of the entire plant, cleaning of the root of any deposited soil and dividing of the plant into the root, stem and foliage. The air-dried samples - the stem and the root were treated into the form of chips, and the leaves were ground in to mortar. The analysed index (content of cadmium and copper) was determined by means of the reference method (atomic absorption spectrometry after mineralisation in aqua regia) pursuant to the Regulation of the Minister of Environment of 1 August 2002 on municipal sewage sludge [23]. The samples were collected during the summer - in the period of the first three years of cultivation.

### **3. RESULTS OF THE STUDY AND DISCUSSION**

The study concerning the uptake of trace elements by the plants as a consequence of the introduction of sewage sludge into the soils are inconclusive. On the other hand, an effect of fertilisation on the uptake and the content of copper and cadmium in the above-ground parts of the plants is noted [13,20].

In the biomass of the plants from the non-fertilised (control) plantation, the content of cadmium was the lowest (Figs. 1-3), and the highest concentration of this metal was observed in the soil fertilised with sewage sludge (Table 2).

According to the studies conducted by Mc Bride [14], there is not sufficient evidence that cadmium introduced into the soil together with sewage sludge is less phytoavailable than cadmium present in the soil. Although he emphasises that the organic matter introduced into the soil together with the sludge may limit the uptake of this element by the plants.

Table 2. Effect of fertilization on the average content of cadmium and copper in the soil

Combination of fertilization	Year of cultivation	Form marked in the 1M HCl	
		mgCd/kg	mg Cu/kg
Control	I	0.250	1.648
Control	II	0.350	1.649
Control	III	0.810	2.750
Sewage sludge	I	0.800	6.145
Sewage sludge	II	1.454	9.984
Sewage sludge	III	1.050	8.770
Mineral fertilizer	I	1.001	6.321
Mineral fertilizer	II	0.501	1.502
Mineral fertilizer	III	0.920	2.220

The tendencies to take up cadmium by the plants were related to the used fertilisers. In the biomass of the plants fertilised with mineral fertilisers, a smaller mean content of cadmium was observed (by about 4.9%) in relation to the plants grown with the addition of sewage sludge. The samples of biomass from the non-fertilised plantation were characterised by the highest content of this metal, that is, higher by about 6.7% than in the case of the plantation containing mineral fertilisers.

Numerous studies report that the degree and direction of movement of the respective elements in the plant is varied and depends on biological factors and specific properties of elements, which can be divided into:

- elements easily transported to above-ground parts: Mg, B, Ag, Li,
- medium mobile elements: Mn, Ni, Zn,
- poorly mobile elements (accumulation in the root): Cd, Co, Cu, Fe, Pb, Hg [1,24,27].

Regardless of the plant species, its roots constitute the main barrier that limits the movement of metals to sprouts, leaves and fruit. The content of metals in the plants decreases in the following order:

root > leaves > sprouts > underground organs collecting nutrients > fruit > seeds [17].

The results of the conducted studies (Figs. 1-3) show that during the three years of cultivation - irrespective of the type of fertilisation - the leaves and roots of

*Salix viminalis* were characterised by the highest content of cadmium, and the smallest amount of this metal was accumulated in the stem of the willow.

It must be emphasised that in the case of the plantation fertilised with mineral fertilisers and sewage sludge, during the first year of cultivation, the content of metal in the plant decreased in the following order: root > leaves > stem. Only in the case of the control plantation, the highest mean content of cadmium during the first year of the cultivation was observed in the leaves of the willow (1.37 mgCd/kg of d.m.), and the accumulation of this metal in the underground part of the plant was slightly lower and amounted to 1.30 mgCd/kg of d.m on average.

The high content of cadmium in the foliage of the energy willow can be explained by the fact that heavy metals are collected by the plants not only through the root system, but also through the above-ground parts, mainly leaves, on the surface of which they are deposited in the form of dust [8].

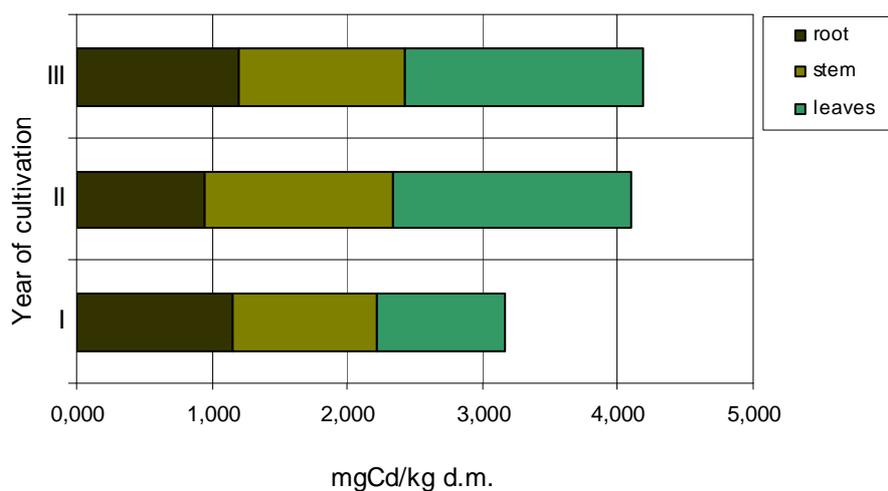


Fig. 1. Changes in the average content of cadmium in the biomass fertilized with sewage sludge



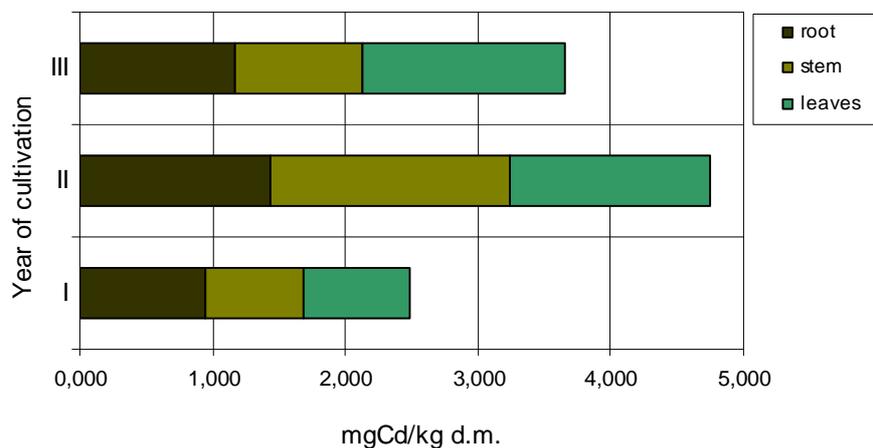


Fig. 2. Changes in the average content of cadmium in the biomass fertilized with mineral fertilisers

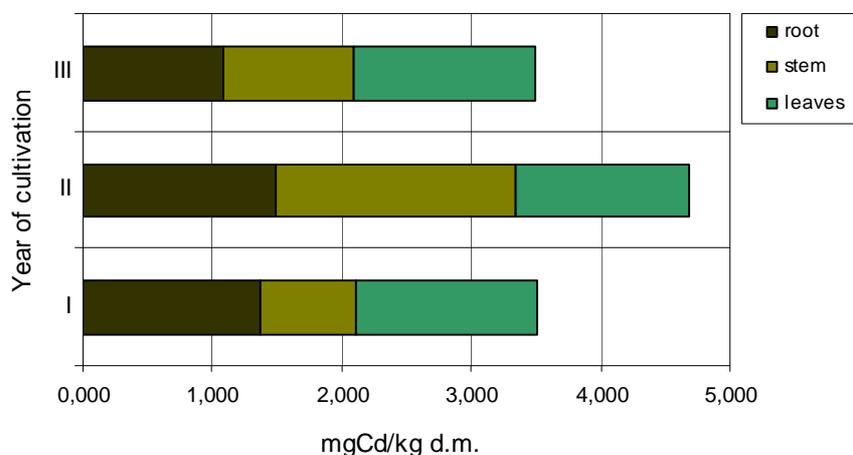


Fig. 3. Changes in average the content of cadmium in the biomass without fertilization

Just as is the case with cadmium, the accumulation of copper in plants depended on the type of fertilisation. The copper content in the biomass of the plants fertilised with mineral fertilisers was higher than the content in the plants cultivated on non-fertilised soil by about 23.36%. In the biomass of the plants fertilised with sewage sludge, a higher content of copper (by about 30.0%) was found in relation to the plants grown on control soils (Figs. 4-6).

It was observed that irrespective of the method of fertilisation, and the year of cultivation, the foliage was the part of the plant which accumulated copper to the greatest extent.

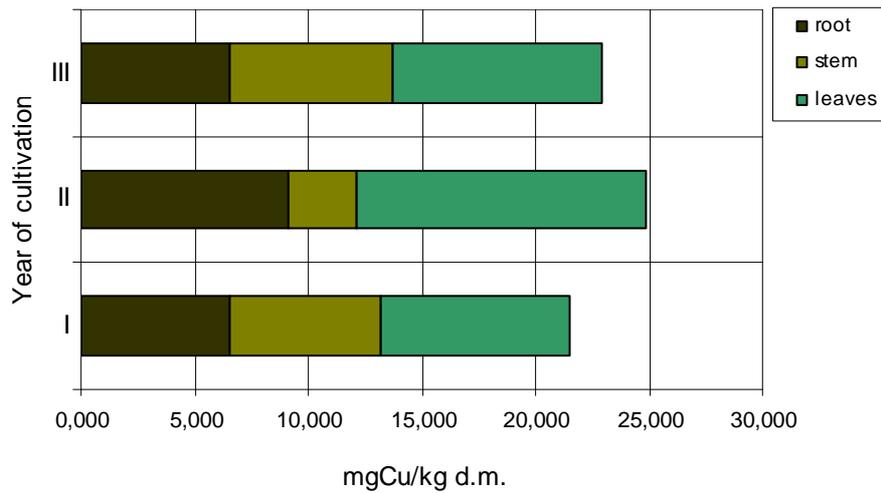


Fig. 4. Changes in the average content of copper in the biomass fertilized with sewage sludge

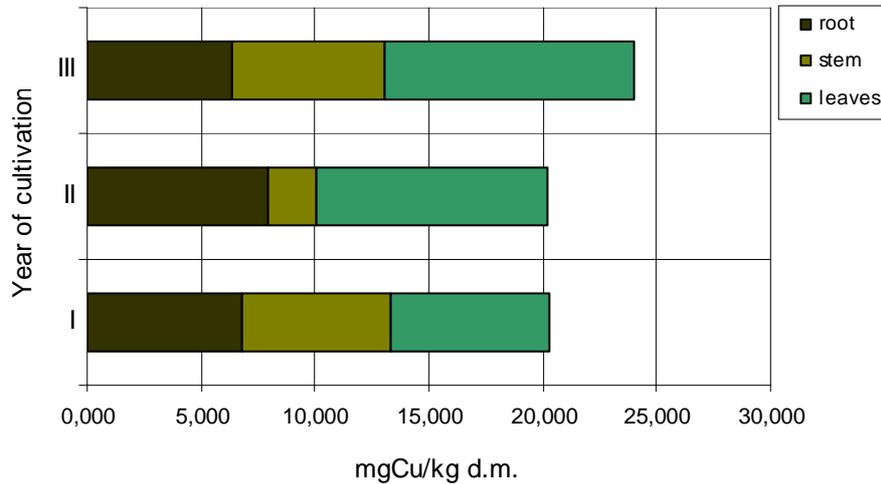


Fig. 5. Changes in the average content of copper in the biomass fertilized with mineral fertilisers

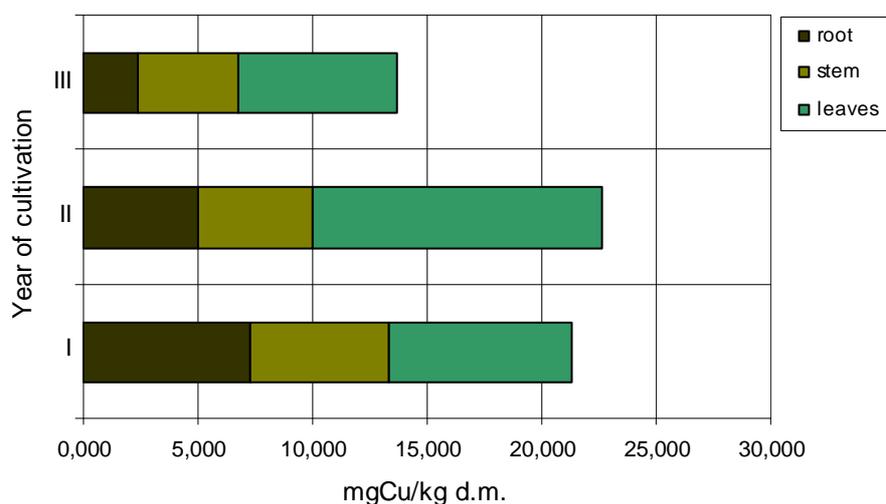


Fig. 6. Changes in the average content of cadmium in the biomass without fertilization

In the course of three years of cultivation, with regards to the plantation fertilised with sewage sludge, the highest mean content of copper was present in the samples of foliage (10.10 mgCu/kg of d.m.), and the smallest amount was accumulated in the stem (5.63 mgCu/kg of d.m.). A similar situation was observed in the plantation fertilised with mineral fertilisers, where the highest content of copper (9.33 mgCu/kg of d.m.) was present in the leaves of *Salix viminalis*. In the case of this plantation, the smallest amount of the metal was accumulated by the stem of *Salix viminalis* (5.13 mgCu/kg of d.m.). Thus, a similar sequence of copper accumulation was observed for all types of fertilisation: leaves > root > stem.

During the first year of cultivation, the highest content of copper - irrespective of the type of the fertilisation - was noted in the leaves of the willow. In the case of the plantation fertilised with sewage sludge, the mean content of copper in the foliage was higher than the content of the metal in the non-fertilised biomass by 8% and the difference in the content of copper in the foliage of the control plantation as well as the plantation fertilised with mineral fertilisers was insignificant and amounted to 1.4%.

The analysis of the results of the studies presented in figs. 4-6 shows that the degree of the accumulation of copper in the non-fertilised willow biomass decreased as time passed by. During the third year of the cultivation, the mean content of the metal in the *Salix viminalis* biomass was lower than the content of copper during the first year of the cultivation by 36%. On the other hand, in

the case of the two other plantations, the accumulation of copper in the above-ground and underground parts of the plant was the lowest in the first year of the cultivation. After the expiry of the period of 3 years, the metal content in the biomass fertilised with mineral fertilisers and sewage sludge was higher than the concentration of this metal during the first year of the cultivation by 42.9% and 40.3% respectively.

#### 4. CONCLUSIONS

The results of the studies show that the tendencies to collect copper and cadmium by the plants were related to the method of fertilisation of the soil. The smallest mean content of cadmium in the *Salix viminalis* biomass was observed in the case of the plantation fertilised with mineral fertilisers, and the highest quantity of the metal was accumulated by the biomass of the non-fertilised plantation.

The mean content of copper in the biomass of the plants fertilised with mineral fertilisers was higher than the content of this metal in the plants grown in the non-fertilised soil by about 23.4%. The biomass samples fertilised with sewage sludge were characterised by the highest content of copper, higher by about 30.0% than in the case of the plants grown on the control soils, .

It was demonstrated that the type of mineral used for fertilisation does not affect the site in which the cadmium is accumulated in the plant. For all types of fertilisation, the metal content decreased according to the following sequence: leaves > root > stem.

The highest content of cadmium in the foliage of the willow was related to the penetration of the mineral ingredients through the cuticle to the leaf. (in accordance with the principle of diffusion and ion exchange).

It was found that irrespective of the method of fertilisation and the year of cultivation, the foliage was the part of the plant which accumulated copper to the greatest extent. In reference to the plantation fertilised with sewage sludge, the mean content of copper in the foliage was higher than the content of the metal in the non-fertilised biomass by 8%, and the difference in the content of copper in the foliage of the control plantation fertilised with mineral fertilisers was insignificant and amounted to 1.4%.

#### ADDITIONAL INFORMATION

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#### WPLYW ZRÓZNICOWANEGO NAWOŻENIA NA ZAWARTOŚĆ KADMU I MIEDZI W WIERZBIE WICIOWEJ (*Salix viminalis*)

##### Streszczenie

W pracy określono wpływ zróżnicowanego nawożenia osadami ściekowymi na zmiany zawartości kadmu i miedzi w wierzbie wiciowej przez pierwsze trzy lata uprawy. Najmniejszą średnią zawartość kadmu w biomase *Salix viminalis* wykazano dla plantacji nawożonej mineralnie. Średnia zawartość miedzi w biomase roślin nawożonych mineralnie była o ok. 23,4% większa od zawartości tego metalu w roślinach uprawianych na glebie nienawożonej.

Wykazano, że sposób nawożenia nie wpływa na miejsce kumulowania się kadmu w roślinie. Najwyższe zawartości kadmu i miedzi odnotowano w próbkach listowia *Salix viminalis* (odpowiednio 1,76 mg/kgs.m. i 12,73 mg/kgs.m.).

Słowa kluczowe: kadm, miedź, metale ciężkie, osady ściekowe, *Salix viminalis*

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