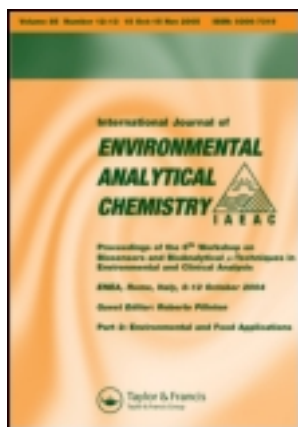


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## Heavy metals in *Phalaris arundinacea* growing in a constructed wetland treating municipal sewage

Jan Vymazal<sup>ab\*</sup>, Lenka Kröpfelová<sup>ab</sup>, Jaroslav Švehla<sup>c</sup> and Jana Němcová<sup>c</sup>

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Constructed wetlands with horizontal subsurface horizontal flow are commonly used for treatment of municipal sewage and are well monitored for removal of organics, suspended solids, nutrients and bacteria. However, the information on removal of heavy metals and their sequestration in plants growing there is very limited. The present study deals with sequestration of six heavy metals in *Phalaris arundinacea* growing in a constructed wetland treating municipal sewage in the Czech Republic during the period 2004–2008. The aboveground biomass of *Phalaris arundinacea* is higher than the average *Phalaris* biomass in other Czech constructed wetlands and also as compared to natural stands. Contrary to natural stands, the root to shoot (R/S) ratio is lower than 1.0 and varied between 0.34 and 0.68 with a mean value of 0.49. For all studied heavy metals the concentrations are the highest in the roots while in other parts, i.e. leaves, stems, rhizomes and flowers, the concentrations usually do not differ significantly. Because of low belowground biomass, the standing stocks are higher aboveground for Zn, Cd, Pb and Cu with copper standing stock being significantly higher than belowground. On the other hand, for Cr and Ni the belowground standing stocks were significantly higher than aboveground because of very high Cr and Ni concentrations in the roots. In most cases the concentrations found in our study are within the order of magnitude as compared to results from other constructed wetlands and natural stands. Heavy metal aboveground standing stocks represented between 1.6% (Cr) and 15.1% (Cd) of the annual metals inflow with an average value of 6.5%. The amount of heavy metals sequestered in the aboveground biomass accounted for between 3.7% (Zn) and 38.4% (Cd) of the heavy metal removal in the filtration beds with an average value of 13.2%.

**Keywords:** constructed wetlands; heavy metals; *Phalaris arundinacea*; wastewater

### 1. Introduction

Constructed wetlands with horizontal subsurface flow (HF CWs) are commonly designed for treatment of municipal sewage. These systems have extensively been monitored with respect to removal of organics, suspended solids, nitrogen, phosphorus and bacteria [1–3] but the information on the removal of heavy metals and their sequestration in plants growing in HF CWs is limited [4–10]. In addition, those results mostly deal with

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*Phragmites australis*, the most frequently used plant in HF CWs and there is only limited information on trace elements in *Phalaris arundinacea* (Reed canarygrass). Despite being a very common wetland macrophyte, there is also limited information on trace elements in *Phalaris arundinacea* growing in natural stands [11–13].

*Phalaris arundinacea* L. (Poaceae) (Reed canarygrass) is commonly used for HF CWs in the Czech Republic mainly because of its vigorous growth and easy planting [14]. It is a one to three metres tall long-lived perennial grass with a C3 photosynthetic pathway [15,16]. It produces dense crowns and prominent networks of vigorous roots and rhizomes, penetrating to a depth of about 30–40 cm, allowing for aggressive vegetative spread [17,18]. Studies have shown that *Phalaris* responds positively to nutrient enrichment. The controlled experiments of Green and Galatowitsch [19] (reported in 2001) and Maurer and Zedler (reported in 2002) [20] showed that high nutrient treatments increased biomass of *Phalaris* and increased allocation to aboveground growth. Also Kätterer and Andrén [18] reported that fertilisation decreased the amount of biomass allocated belowground as compared to aboveground biomass.

The objective of this study was to (a) evaluate above- and belowground biomass of *Phalaris arundinacea* growing in a constructed wetland treating municipal sewage, (b) evaluate the amount of heavy metals in the biomass and (c) compare heavy metal standing stocks with inflow loading.

## 2. Experimental

The study was carried out in a 100 PE (population equivalent) horizontal sub-surface flow constructed wetland Břehov in south Bohemia. The system was put in operation in October 2003 and it is designed to treat wastewaters from a combined sewer system, i.e. sewage and stormwater runoff. Total area of 504 m<sup>2</sup> is divided in two beds planted with *Phalaris arundinacea* and *Phragmites australis* in bands parallel to water flow.

The biomass was sampled during the period 2004–2008. Samples of above- and belowground biomass of *Phalaris arundinacea* were taken from the area of 0.25 m<sup>2</sup> in four replicates (two in the inflow zone and two in the outflow zone) during the peak standing crop in mid-July. The aboveground biomass was clipped at the ground level, divided into leaves including leaf sheaths, stems and inflorescence and dried at 70°C to a constant weight. Belowground biomass was completely dug out from the sampled area, divided into roots and rhizomes and thoroughly washed with pressure water. The washing was performed in a big jar in order to minimise loss of hairy roots. The sediments are very loosely attached to the roots and rhizomes and they are very easily washed out. The belowground biomass was dried under the same conditions as aboveground biomass. By washing in water heavy metals on the roots and rhizomes are probably lost but this is a common preparation in order to avoid any sediments in the belowground biomass sample. Therefore the concentrations are comparable with other literature data. The aboveground biomass was not washed as the water level is kept below the surface and shoots do not get in contact with water and/or sediments.

For heavy metals evaluation, 10 *Phalaris* stems were clipped next to each sampled square and also divided into leaves including leaf sheaths, stems and inflorescence. This method was used in order to make sure that all parts of the shoot are taken into analysis as it is known that concentrations of elements are not the same in all leaves or parts of the stem [21]. The biomass was dried at 70°C until constant weight and then

homogenised samples were mineralised in pressure microwave apparatus MARS-5 using  $\text{HNO}_3 + \text{H}_2\text{O}_2 + \text{HF} + \text{H}_3\text{BO}_3$  under high temperature and pressure [22]. Mineralised samples were analysed for Cd, Cr, Cu, Ni, Pb, and Zn using Inductively Coupled Plasma Mass Spectrometer PQ-ExCell (VG-Thermo Elemental, Winsford, Cheshire, UK). Samples of roots and rhizomes were taken from the biomass sample and processed according to the same procedure as aboveground biomass. In 2008, two samples of *Phalaris* above- and belowground biomass growing in the nearby ditch were taken for comparison and the samples were processed together with samples from the constructed wetland.

For all measurements presented, standard quality control (QC) was performed. Quality control samples consisted of triplicate samples and spiked samples. For the evaluation of measurement precision and accuracy the standard materials BCR-RM 060 *Lagarosiphon major* and BCR-RM 279 *Ulva lactuca* (European Commission, Community Bureau of Reference, Brussels, Belgium) were used. The reproducibilities expressed as a relative standard deviation of the QC samples were less than 5%. The recoveries between found and certified values were for all measurements in the range of 80–120%. In order to eliminate non-spectral interferences and drift of the analytical signal in ICP-MS technique internal standardisation was used.

### 3. Results and discussion

#### 3.1 Biomass

The aboveground biomass fluctuated between  $1263 \text{ g m}^{-2}$  in 2008 and  $2265 \text{ g m}^{-2}$  in 2005 and the belowground biomass varied between  $482 \text{ g m}^{-2}$  in 2004 and  $1232 \text{ g m}^{-2}$  in 2005 (Figure 1). The aboveground biomass is high as compared to other Czech constructed wetlands. Vymazal and Kröpfelová [23] reported the aboveground biomass of *Phalaris arundinacea* between  $345 \text{ g m}^{-2}$  and  $1902 \text{ g m}^{-2}$  with an average value of  $1286 \text{ g m}^{-2}$  for eight HF CWs. In constructed wetlands or natural stands affected by wastewater outside the Czech Republic the aboveground biomass has been reported in the range of

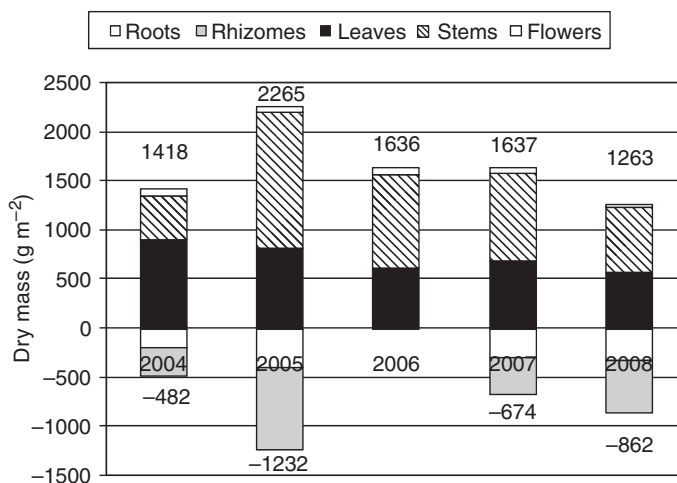


Figure 1. Biomass of *Phalaris arundinacea* growing in a constructed wetland at Břehov during the period 2004–2008.

831–1713 g m<sup>-2</sup> [11,24,25] similar to that found in the Czech Republic. Only Hurry and Bellinger [26] reported the value of 2458 g m<sup>-2</sup> for the overland flow in UK but this was achieved using a multiple harvest. The values of *Phalaris* aboveground biomass in natural stands usually does not exceed 1500 g m<sup>-2</sup> [27–30] and values above this level are not frequent [31].

The average biomass of individual plant parts were 720 g m<sup>-2</sup>, 871 g m<sup>-2</sup>, 53 g m<sup>-2</sup>, 303 g m<sup>-2</sup> and 510 g m<sup>-2</sup> for leaves, stems, flowers, root and rhizomes, respectively. The belowground to aboveground ratio (R/S, root to shoot) varied between 0.34 and 0.68 with a mean value of 0.49. This is a difference as compared to natural stands where R/S ratio is usually between 1 and 2 [2]. In constructed wetlands the supply of nutrients is very high and as mentioned before, high nutrient increases the aboveground growth. Similar values were also reported by Bernard and Lauve [11] and Behrends *et al.* [24].

## 3.2 Heavy metals in plant biomass

### 3.2.1 Zinc

Under aerobic conditions zinc is commonly associated with Fe and Mn oxides, hydroxides and oxyhydroxides [32,33]. Zinc is also retained in iron plaques on plant root surface [34]. Under anoxic/anaerobic conditions zinc forms very insoluble sulphides [35–37] and carbonates [33,38].

Concentrations of zinc in various parts of *Phalaris arundinacea* are shown in Figure 2a. The highest average concentration was found in roots (78.9 mg kg<sup>-1</sup>), followed by rhizomes (38.2 mg kg<sup>-1</sup>), flowers (25.7 mg kg<sup>-1</sup>), stems (16.1 mg kg<sup>-1</sup>) and leaves (11.3 mg kg<sup>-1</sup>). The average aboveground and belowground Zn concentrations in *Phalaris* were 15.2 mg kg<sup>-1</sup> and 48.4 mg kg<sup>-1</sup>, respectively. The concentrations of zinc in roots are slightly higher but comparable with other studies from HF CWs. Behrends *et al.* [24] reported the concentration of 48 mg kg<sup>-1</sup> in Alabama and Bernard and Lauve [11] found the concentration of 35 mg kg<sup>-1</sup> in a system treating landfill leachate in New York. Also average Zn concentration found in rhizomes is slightly higher than the concentration of 20 mg kg<sup>-1</sup> reported by Bernard and Lauve [11]. On the other hand, the average belowground Zn concentration is substantially lower as compared to the value of 119 mg kg<sup>-1</sup> reported by Vymazal and Krása [8] from another Czech HF CW at Nučice. The zinc concentrations in leaves and stems of *Phalaris* biomass were comparable with those reported by Behrends *et al.* [24] for leaves (20 mg kg<sup>-1</sup>) and stems (15 mg kg<sup>-1</sup>) but Vymazal and Krása [8] found Zn concentrations slightly higher (leaves 39 mg kg<sup>-1</sup>, stems 57 mg kg<sup>-1</sup>).

The information on zinc concentrations in *Phalaris* growing in natural stands is very limited. However, the available results indicate that zinc concentrations found in natural stands do not differ from those found in constructed wetlands for wastewater treatment. The concentrations found in *Phalaris* growing in the nearby ditch were 50.6 mg kg<sup>-1</sup>, 28.5 mg kg<sup>-1</sup>, 21.3 mg kg<sup>-1</sup>, 20.7 mg kg<sup>-1</sup> and 8.6 mg kg<sup>-1</sup> in roots, rhizomes, flowers, stems and leaves, respectively, indicating very little difference between constructed wetland and natural stand.

The average aboveground Zn concentration of 15.2 mg kg<sup>-1</sup> found in our study is comparable with Zn concentrations of 15 mg kg<sup>-1</sup> [11], 35 mg kg<sup>-1</sup> [12], and 19.5 mg kg<sup>-1</sup> [13] reported from the Czech Republic, USA and Poland, respectively. Also, Zn concentrations of 31 mg kg<sup>-1</sup> and 37 mg kg<sup>-1</sup> in roots and rhizomes, respectively, reported by Bernard and Lauve [11] from natural stands in New York State, are comparable with values reported from constructed wetlands.

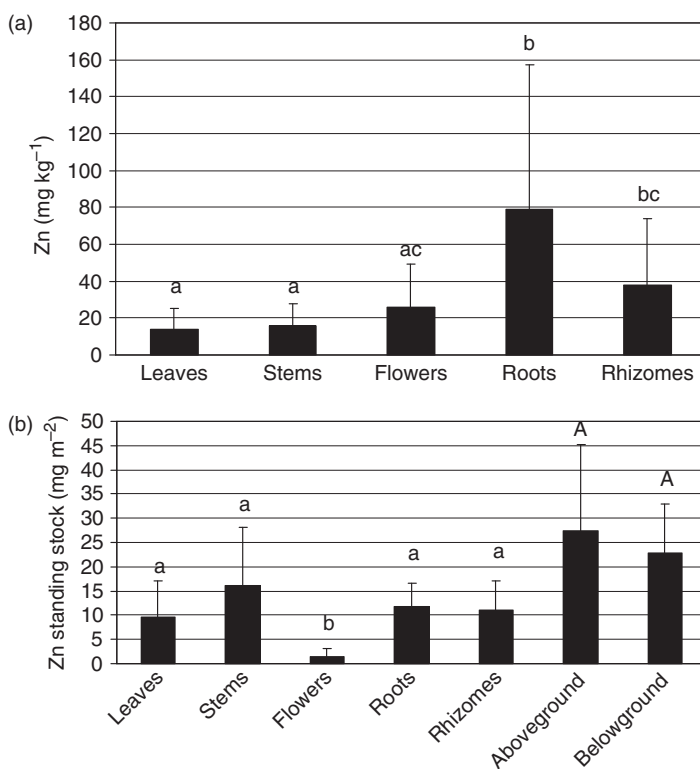


Figure 2. Average concentrations (a) and standing stocks (b) of zinc in leaves, stems, flowers, rhizomes and roots of *Phalaris arundinacea* growing in the constructed wetland at Břehov, Czech Republic. Standard deviations are also shown. For standing stocks, total aboveground and belowground values are added. Different letters indicate significant difference at  $\alpha = 0.05$  between the means.

Zinc standing stocks, i.e. the amount of zinc sequestered in the plant biomass, are shown in Figure 2b. Despite significant differences in concentrations in above- and belowground parts (Figure 2a) the standing stocks are comparable for aboveground ( $27.4 \text{ mg m}^{-2}$ ) and belowground ( $22.0 \text{ mg m}^{-2}$ ) parts because of the lower belowground biomass (Figure 1). Bernard and Lauve [11] reported aboveground Zn standing stocks of  $16.9 \text{ mg m}^{-2}$  and  $20.5 \text{ mg m}^{-2}$  for constructed wetland and unpolluted site. The respective values for belowground standing stocks amounted to  $10.8 \text{ mg m}^{-2}$  and  $9.6 \text{ mg m}^{-2}$ .

It has been suggested that the amount of heavy metals sequestered in the aboveground biomass and thus available for harvesting and removal, is very low as compared to inflow loading and usually does not exceed 5% of the inflow [2,5,8]. The results of our study are in a good agreement with this finding – on average, only 2.5% of the annual inflow zinc load was sequestered in the aboveground *Phalaris* biomass. This amount represents 3.7% of the total annual zinc removal.

### 3.2.2 Copper

Copper forms under anoxic conditions very insoluble compounds with sulphur, including both cupric and cuprous sulphides [36,37,39,40] and may also associate with pyrite [41].

These processes may restrict copper from being easily taken up by plants. Concentrations of copper in various parts of *Phalaris arundinacea* are shown in Figure 3a. The highest average concentration was found in roots ( $18.2 \text{ mg kg}^{-1}$ ), followed by leaves ( $9.0 \text{ mg kg}^{-1}$ ), stems ( $6.5 \text{ mg kg}^{-1}$ ), rhizomes ( $3.8 \text{ mg kg}^{-1}$ ) and flowers ( $3.1 \text{ mg kg}^{-1}$ ). The average aboveground and belowground Cu concentrations in *Phalaris* were  $6.6 \text{ mg kg}^{-1}$  and  $9.5 \text{ mg kg}^{-1}$ , respectively. The concentrations of copper in roots are higher than available data reported in the literature for *Phalaris arundinacea*. Behrends *et al.* [24] reported the concentration of  $5.0 \text{ mg kg}^{-1}$  in Alabama and Bernard and Lauve [11] found the concentration of  $4.8 \text{ mg kg}^{-1}$  in a system treating landfill leachate in New York. However, the Cu concentration in rhizomes was comparable with the concentration of  $2.7 \text{ mg kg}^{-1}$  reported by Bernard and Lauve [11]. The average belowground Cu concentration of  $9.5 \text{ mg kg}^{-1}$  was nearly identical with the value of  $9.9 \text{ mg kg}^{-1}$  reported by Vymazal and Krása [8] from another Czech HF CW at Nučice. The copper concentrations in leaves ( $9.0 \text{ mg kg}^{-1}$ ) and stems ( $6.5 \text{ mg kg}^{-1}$ ) in *Phalaris* biomass were higher as compared to literature data. Behrends *et al.* [24] reported the concentration of  $1.0 \text{ mg kg}^{-1}$  for both leaves and stems for leaves in HF CWS in Alabama while Vymazal and Krása [8] reported

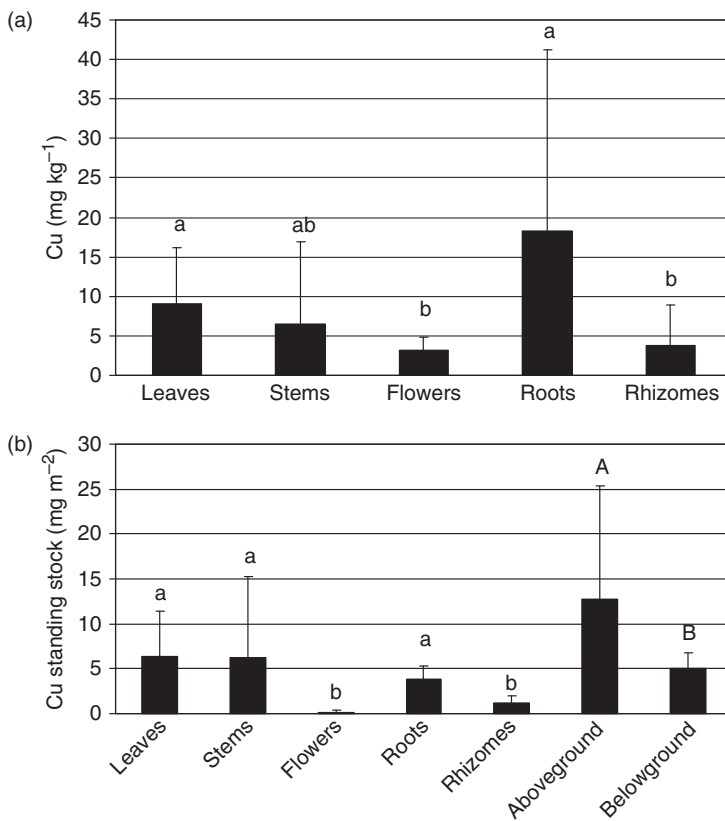


Figure 3. Average concentrations (a) and standing stocks (b) of copper in leaves, stems, flowers, rhizomes and roots of *Phalaris arundinacea* growing in the constructed wetland Břehov, Czech Republic. For details see Figure 2.



copper concentrations in leaves ( $3.0 \text{ mg kg}^{-1}$ ) and stems ( $4.6 \text{ mg kg}^{-1}$ ). Bernard and Lauve [11] reported lower total aboveground copper concentration of  $1.9 \text{ mg kg}^{-1}$ .

The copper concentrations found in *Phalaris* growing in the nearby ditch were  $4.5 \text{ mg kg}^{-1}$ ,  $2.6 \text{ mg kg}^{-1}$ ,  $1.3 \text{ mg kg}^{-1}$ ,  $10.7 \text{ mg kg}^{-1}$  and  $8.6 \text{ mg kg}^{-1}$  in roots, rhizomes, flowers, stems and leaves, respectively. These concentrations are very similar to those found in constructed wetland with the exception of roots where Cu concentration in constructed wetland was four times higher. The average aboveground copper concentration of  $6.6 \text{ mg kg}^{-1}$  found in our study is comparable with Cu concentrations of  $6.4 \text{ mg kg}^{-1}$  [13] found in *Phalaris* growing in two anthropogenic lakes in West Poland and with Cu concentration ( $5.1 \text{ mg kg}^{-1}$ ) in *Phalaris* growing in natural stands in the South Bohemia [12]. Copper concentrations of  $10 \text{ mg kg}^{-1}$  in both roots and rhizomes were reported by Bernard and Lauve [11] from natural stands in New York State. These data differ from data found in our study where Cu concentrations in roots were substantially higher than in rhizomes.

Copper standing stocks in *Phalaris* are shown in Figure 3b. The values are comparable in leaves, stems and roots while in flowers and rhizomes the standing stock is significantly lower. As a result, the total aboveground standing stock is significantly higher than belowground. Bernard and Lauve [11] reported aboveground Cu standing stocks of only  $3.2 \text{ mg m}^{-2}$  and  $3.6 \text{ mg m}^{-2}$  for constructed wetland and unpolluted site. These values are lower than the value of  $12.8 \text{ mg m}^{-2}$  found in our study. However, the total belowground Cu standing stock found in our study ( $5.1 \text{ mg m}^{-2}$ ) was similar to Cu belowground standing stocks of  $4.7 \text{ mg m}^{-2}$  and  $6.3 \text{ mg m}^{-2}$  reported by Bernard and Lauve [11] for constructed wetland receiving landfill leachate and natural stand, respectively. The Cu aboveground standing stock represented 7.1% of the average annual Cu inflow load and 9.8% of the average Cu removal.

### 3.2.3 Lead

Lead, like Zn and Cu, forms under anaerobic conditions discrete sulphide phases [35,42] and may also bind strongly to organic matter [43]. Also carbonates could be an effective sink for lead [44]. It has been shown that lead also strongly adsorbs to Fe/Mn oxides and it has been found in association with rhizosphere Fe(III) plaques [45].

Concentrations of lead in various parts of *Phalaris arundinacea* are shown in Figure 4a. The highest average concentration was found in roots ( $6.3 \text{ mg kg}^{-1}$ ), followed by leaves ( $2.3 \text{ mg kg}^{-1}$ ), stems ( $2.0 \text{ mg kg}^{-1}$ ), rhizomes and flowers (both  $1.4 \text{ mg kg}^{-1}$ ). The average aboveground and belowground Pb concentrations in *Phalaris* were  $1.85 \text{ mg kg}^{-1}$  and  $3.33 \text{ mg kg}^{-1}$ , respectively. The concentrations of copper in roots and rhizomes were substantially lower than the concentrations of  $28 \text{ mg kg}^{-1}$  and  $20 \text{ mg kg}^{-1}$  for roots and rhizomes, respectively, reported by Bernard and Lauve [11] from a system treating landfill leachate in New York. The average belowground Pb concentration of  $3.3 \text{ mg kg}^{-1}$  was lower than the concentration of  $17.8 \text{ mg kg}^{-1}$  reported by Vymazal and Krása [8] from another Czech HF CW at Nučice. The copper concentrations in leaves ( $2.3 \text{ mg kg}^{-1}$ ) and stems ( $2.0 \text{ mg kg}^{-1}$ ) in *Phalaris* biomass were lower as compared to respective concentrations of  $6.5 \text{ mg kg}^{-1}$  and  $9.1 \text{ mg kg}^{-1}$  reported by Vymazal and Krása [8].

Similarly to copper, the concentrations found in *Phalaris* growing in the nearby ditch were comparable with constructed wetland with the exception of lower concentration in roots ( $1.7 \text{ mg kg}^{-1}$ ,  $0.5 \text{ mg kg}^{-1}$ ,  $1.3 \text{ mg kg}^{-1}$ ,  $2.7 \text{ mg kg}^{-1}$  and  $2.6 \text{ mg kg}^{-1}$  in roots, rhizomes, flowers, stems and leaves, respectively). The average aboveground lead

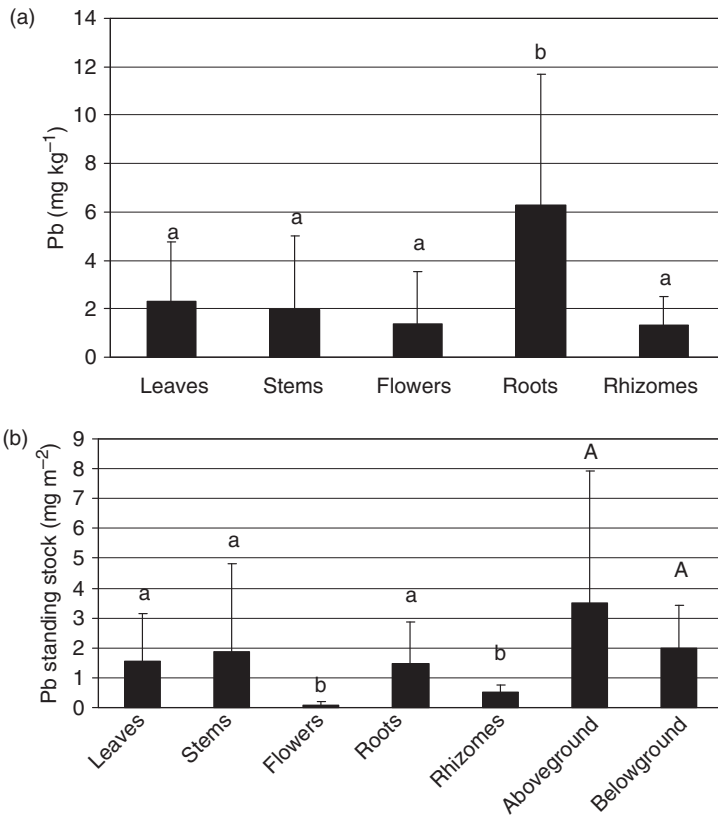


Figure 4. Average concentrations (a) and standing stocks (b) of lead in leaves, stems, flowers, rhizomes and roots of *Phalaris arundinacea* growing in the constructed wetland Břehov, Czech Republic. For details see Figure 2.

concentration of  $1.8 \text{ mg kg}^{-1}$  found in our study equals the aboveground concentration reported by Švehla *et al.* [12] for *Phalaris* growing in natural stands in South Bohemia. On the other hand, total aboveground lead concentration reported from a natural stand in New York [11] was slightly lower ( $0.8 \text{ mg kg}^{-1}$ ) and concentration of lead ( $12.6 \text{ mg kg}^{-1}$ ) reported from two anthropogenic lakes in Poland [13] was much higher. Lead concentrations of  $3.2 \text{ mg kg}^{-1}$  and  $2.1 \text{ mg kg}^{-1}$  in roots and rhizomes, respectively, reported by Bernard and Lauve [11] from natural stands in New York State were similar to concentrations found in our study.

Lead standing stocks in *Phalaris* are shown in Figure 4b. The values are comparable in leaves, stems and roots while in flowers and rhizomes the standing stock is significantly lower. As a result, the total aboveground standing stock is higher than belowground but the difference is not significant. Bernard and Lauve [11] reported aboveground Pb standing stocks of only  $0.2 \text{ mg m}^{-2}$  and  $0.1 \text{ mg m}^{-2}$  for constructed wetland and unpolluted site. These values are lower than the value of  $3.5 \text{ mg m}^{-2}$  found in our study. The total belowground Pb standing stock found in our study ( $2.0 \text{ mg m}^{-2}$ ) was similar to Pb belowground standing stocks of  $1.8 \text{ mg m}^{-2}$  at an unpolluted marsh but substantially lower than  $9.9 \text{ mg m}^{-2}$  reported by Bernard and Lauve [11] for constructed wetland

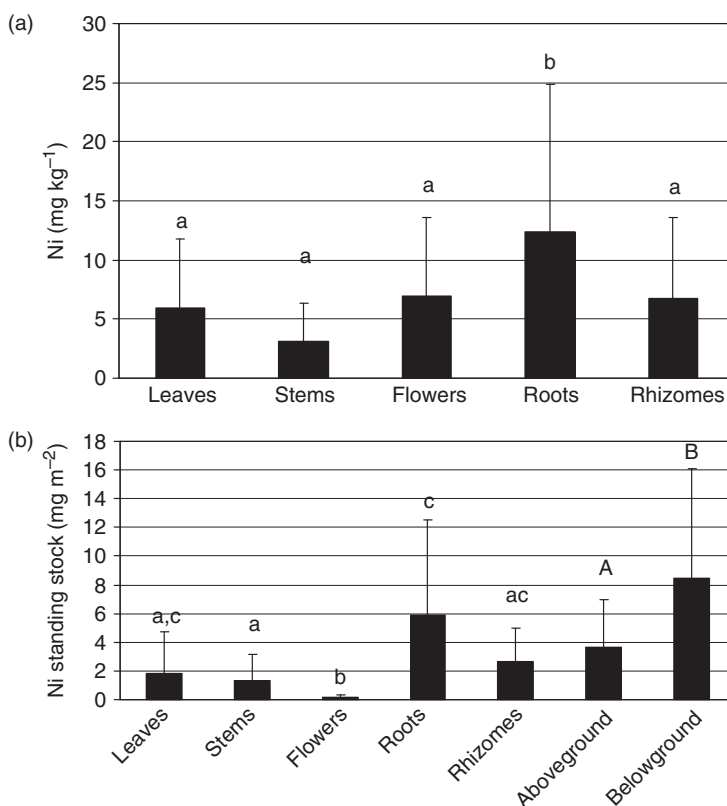


Figure 5. Average concentrations (a) and standing stocks (b) of nickel in leaves, stems, flowers, rhizomes and roots of *Phalaris arundinacea* growing in the constructed wetland Břehov, Czech Republic. For details see Figure 2.

receiving landfill leachate. The Pb aboveground standing stock represented 6.5% of the average annual lead inflow load and 14.1% of the average lead removal.

### 3.2.4 Nickel

Under oxic or suboxic conditions, Ni sorbs to Mn oxides and can substitute for Ni in the lattice of some Mn oxides [46,47]. Under anoxic/anaerobic conditions nickel forms insoluble sulphides [39,42] and is incorporated into pyrite [48]. Also carbonates could be an effective sink for nickel [44].

Concentrations of lead in various parts of *Phalaris arundinacea* are shown in Figure 5a. The highest average concentration was found in roots (12.4 mg kg<sup>-1</sup>), followed by leaves (6.0 mg kg<sup>-1</sup>), flowers (6.9 mg kg<sup>-1</sup>), rhizomes (6.8 mg kg<sup>-1</sup>) and stems (2.1 mg kg<sup>-1</sup>). The average aboveground and belowground concentrations were 3.8 mg kg<sup>-1</sup> and 8.5 mg kg<sup>-1</sup>, respectively. The only information on nickel concentration in *Phalaris* growing in a constructed wetland [8] indicates substantially higher concentrations: 20.7 mg kg<sup>-1</sup>, 42 mg kg<sup>-1</sup> and 86 mg kg<sup>-1</sup> in leaves, stems and belowground tissues.

Nickel concentrations in *Phalaris* growing in natural stands were comparable to those found in our study. Samecka-Cymerman and Kempers [8] reported average aboveground Ni concentration of  $4.4 \text{ mg kg}^{-1}$  in *Phalaris* growing in two anthropogenic lakes in Poland and Švehla *et al.* [12] reported the concentration of  $1.0 \text{ mg kg}^{-1}$  in *Phalaris* growing in natural stands in South Bohemia. The concentration of nickel in *Phalaris* growing in stands adjacent to the constructed wetland were very similar to concentrations found in constructed wetland ( $11.2 \text{ mg kg}^{-1}$ ,  $4.6 \text{ mg kg}^{-1}$ ,  $8.3 \text{ mg kg}^{-1}$ ,  $4.7 \text{ mg kg}^{-1}$  and  $2.6 \text{ mg kg}^{-1}$  in roots, rhizomes, flowers, leaves and stems, respectively).

Nickel standing stocks in *Phalaris* are shown in Figure 5b. The values are comparable in leaves, stems and rhizomes while in flowers and roots the standing stock is significantly lower and higher, respectively. As a result, the total belowground standing stock is significantly higher than aboveground standing stock. The Ni aboveground standing stock represented 6.1% of the average annual nickel inflow and 9.1% of the average nickel removal.

### 3.2.5 Chromium

Contrary to most heavy metals such as Zn, Cd, Pb or Ni chromium undergoes a change in oxidation state as a consequence of soil oxidation-reduction conditions [49]. These conditions play a major role in chromium speciation, solubility and mobility with reduction transformations being microbially mediated [50,51]. In anoxic sediments, reduced chromium is not readily incorporated into sulphides [41] but instead tends to associate with organic matter [52].

Concentrations of chromium in various parts of *Phalaris arundinacea* are shown in Figure 6a. The highest average concentration was found in roots ( $18.5 \text{ mg kg}^{-1}$ ), followed by rhizomes ( $3.3 \text{ mg kg}^{-1}$ ), leaves ( $1.3 \text{ mg kg}^{-1}$ ), stems and flowers (both  $0.8 \text{ mg kg}^{-1}$ ). The Cr concentration in roots was significantly higher than in all other plant compartments. The average aboveground and belowground Cr concentrations were  $0.95 \text{ mg kg}^{-1}$  and  $9.4 \text{ mg kg}^{-1}$ , respectively. We have not found any information on chromium concentration in *Phalaris* growing in constructed wetlands. Samecka-Cymerman and Kempers [8] reported average aboveground Ni concentration of  $4.6 \text{ mg kg}^{-1}$  in *Phalaris* growing in two anthropogenic lakes in Poland while Švehla *et al.* [12] reported comparable aboveground Cr concentration of  $0.84 \text{ mg kg}^{-1}$  in *Phalaris* growing in natural stands in South Bohemia. The concentration of chromium in *Phalaris* growing in stands adjacent to the constructed wetland were similar to concentrations found in constructed wetland with the exception of substantially lower Cr concentration in the roots ( $3.5 \text{ mg kg}^{-1}$ ,  $1.6 \text{ mg kg}^{-1}$ ,  $1.1 \text{ mg kg}^{-1}$ ,  $0.7 \text{ mg kg}^{-1}$  and  $0.5 \text{ mg kg}^{-1}$  in roots, rhizomes, flowers, leaves and stems, respectively).

Chromium standing stocks in *Phalaris* are shown in Figure 6b. The situation is the same as for nickel. The values are comparable in leaves, stems and rhizomes while in flowers and roots the standing stock is significantly lower and higher, respectively. As a result, the total belowground standing stock is significantly higher than aboveground standing stock. The Cr aboveground standing stock represented only 1.6% of the average annual chromium inflow and 4.1% of the average Cr removal.

### 3.2.6 Cadmium

Cadmium forms under anoxic conditions very insoluble compounds with sulphide ( $\text{CdS}$ ) [36,42] and under slightly reduced to oxidised conditions solid carbonate ( $\text{CdCO}_3$ )

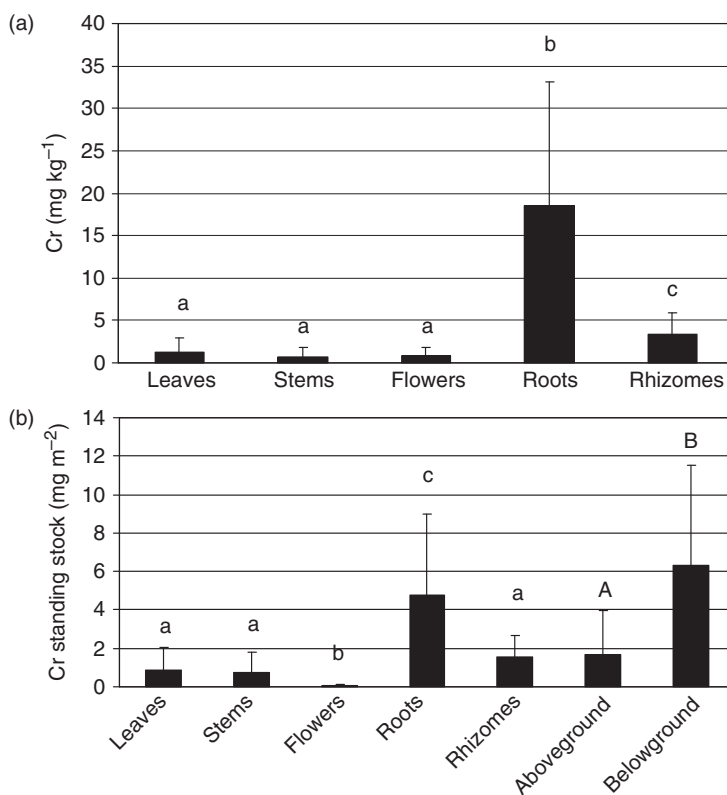


Figure 6. Average concentrations (a) and standing stocks (b) of chromium in leaves, stems, flowers, rhizomes and roots of *Phalaris arundinacea* growing in the constructed wetland Břehov, Czech Republic. For details see Figure 2.

is a major control mechanism for cadmium solubility [53]. Under aerobic conditions, cadmium could be adsorbed or co-precipitated with oxides, hydroxides, and hydrous oxides of Fe, Mn and possible Al [53]. Cadmium complexed with the organic fraction may be divided into chelated and organic bound. Chelated Cd is the fraction that is loosely attached to immediately mobile and easily decomposable organic material while organic-bound Cd is the fraction incorporated into the insoluble organic material and can be solubilised only after intense oxidation of the organic matter [53].

Concentrations of cadmium in various parts of *Phalaris arundinacea* are shown in Figure 7a. The highest average concentration was found in roots ( $0.31 \text{ mg kg}^{-1}$ ), followed by rhizomes and stems ( $0.08 \text{ mg kg}^{-1}$ ), flowers ( $0.07 \text{ mg kg}^{-1}$ ), and leaves ( $0.06 \text{ mg kg}^{-1}$ ). As for chromium, cadmium concentration in roots was significantly higher than in all other plant compartments. The average aboveground and belowground Cr concentrations were  $0.06 \text{ mg kg}^{-1}$  and  $0.16 \text{ mg kg}^{-1}$ , respectively. Vymazal and Krása [8] reported much higher Cd concentrations in *Phalaris* growing in HF CWs Nučice in the Czech Republic (leaves  $1.5 \text{ mg kg}^{-1}$ , stems  $2.2 \text{ mg kg}^{-1}$  and total belowground  $4.0 \text{ mg kg}^{-1}$ ). Samecka-Cymerman and Kempers [8] reported similar average aboveground Cd concentration of  $1.4 \text{ mg kg}^{-1}$  in *Phalaris* growing in two anthropogenic lakes in Poland while Švehla *et al.* [12] reported aboveground Cr concentration of  $0.25 \text{ mg kg}^{-1}$  in *Phalaris* growing in natural

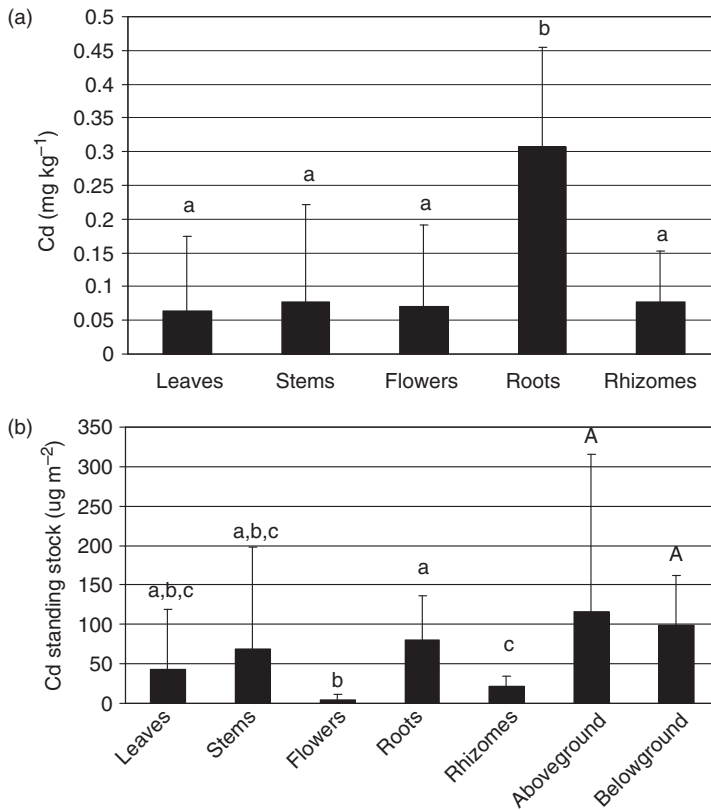


Figure 7. Average concentrations (a) and standing stocks (b) of cadmium in leaves, stems, flowers, rhizomes and roots of *Phalaris arundinacea* growing in the constructed wetland Břehov, Czech Republic. For details see Figure 2.

stands in South Bohemia. It seems that the Cd concentrations in our constructed wetland were quite low. The concentrations of cadmium in *Phalaris* growing in stands adjacent to the constructed wetland were below the detection limit with the exception of roots ( $0.15 \text{ mg kg}^{-1}$ ).

Cadmium standing stocks in *Phalaris* are shown in Figure 7b. Despite significant differences in concentrations in above- and belowground parts (Figure 7a) the standing stocks are comparable for aboveground ( $116 \mu\text{g m}^{-2}$ ) and belowground ( $99 \mu\text{g m}^{-2}$ ) parts because of the lower belowground biomass (Figure 1). The cadmium aboveground standing stock represented 15.1% of the average annual chromium inflow and 38.4% of the average Cr removal. These values are much higher as compared to other heavy metals but similar results were reported by Vymazal *et al.* [54]. The authors found 43.8% of the removed cadmium sequestered in the aboveground plant biomass composed of *Phalaris arundinacea* and *Phragmites australis*.

#### 4. Conclusions

The aboveground biomass of *Phalaris arundinacea* growing in a horizontal flow constructed wetland Břehov is higher than the average *Phalaris* biomass in other Czech

constructed wetlands and also as compared to natural stands. Contrary to natural stands, the root to shoot (R/S) ratio is lower than 1.0 and varied between 0.34 and 0.68 with a mean value of 0.49. However, this is a common feature in constructed wetlands for wastewater treatment.

For all studied heavy metals the concentrations are the highest in the roots while in other parts, i.e. leaves, stems, rhizomes and flowers, the concentrations usually do not differ significantly. Because of low belowground biomass, the standing stocks are higher aboveground for Zn, Cd, Pb and Cu with copper standing stock being significantly higher than belowground. On the other hand, for Cr and Ni the belowground standing stocks were significantly higher than aboveground because of very high Cr and Ni concentrations in the roots. In most cases the concentrations found in our study are within the order of magnitude as compared to results from other constructed wetlands and natural stands.

Heavy metal aboveground standing stocks represented between 1.6% (Cr) and 15.1% (Cd) of the annual metals inflow with an average value of 6.5%. The amount of heavy metals sequestered in the aboveground biomass accounted for between 3.7% (Zn) and 38.4% (Cd) of the heavy metal removal in the filtration beds with an average value of 13.2%.

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