CONTENT OF HEAVY METALS IN REED ASH AND POSSIBILITIES OF REED ASH UTILIZATION

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Abstract. Reed growths are important regulators of the content of heavy metals in water bodies and silt. While growing, reed captures heavy metals, therefore it can be considered that the extraction of reeds would facilitate removal of heavy metals from water bodies. However, after burning reeds, heavy metals would remain in a concentrated amount in reed ash. Reed ash could be disposed by incorporating them in the soil, but the content of heavy metals that would determine the maximum allowable dose of ash dispersion is not known. It raises the need for further studies on this issue. To determine the maximum 5-year dose of ash that can be dispersed in 1 hectare of soil, maximum values of heavy metal content in reed ash were chosen, by using limiting values of heavy metal content determined for sewage sludge. Analysis of heavy metal content was carried out in relation to chrome (Cr), copper (Cu), cadmium (Cd), nickel (Ni) and lead (Pb). The analysed reed samples were taken from 11 natural and artificial water bodies in Latvia, whose resources of reeds are considered to be significant. It was found that the main heavy metal in reed ash that limits the dose of ash dispersion in the soil is Cr, the maximum 5-year dose for reed ash dispersion in sandy, sandy clay soil constitutes 14.3 tons of ash per hectare, while in loam and clay soils it amounts to 16.6 tons, which is more than in wood ash. Therefore, it can be concluded that in case of burning crushed reed together with wood, maximum reed ash dispersion dose would be greater than the dose of wood ash, and thus it would require smaller soil areas for ash disposal.

Keywords: heavy metals, ash, Common reed (*Phragmites australis* (*Cav.*) *Trin. Ex Steud*).

Introduction

Up to now, potential of water plant biomass as an energy resource in Latvia has not been taken into account. Reed (*Phragmites australis* (*Cav.*) *Trin. Ex Steud*) growing in natural and artificial water bodies is one of the plants that could be used for energy generation in Latvian conditions [1-3]. Besides, studies carried out by foreign scientists have shown that reed can be used as a raw material for fuel production [4; 5]. Reed gives 40-60 $t\cdot ha^{-1}$ of green fodder or 7.5-13.0 $t\cdot ha^{-1}$ of dry matter [2; 6]. Foreign literature states that productivity of reed growths can amount to 30 $t\cdot ha^{-1}$ of dry matter when mowing reeds in winter period [5]. In reed growths that were used for waste water treatment in Estonia, dry reed mass ranged from 3 to 17.6 $t\cdot ha^{-1}$ [7]. The broad range of reed productivity in different studies carried out all around the world shows that it is different and depends on the growing place and conditions. Reed growths are considered to be an important regulator of heavy metal content in natural waters and silt [8]. Rapid growing of reeds in the spring leads to assimilation of heavy metals from water and soil [9; 10]. Heavy metal content in reed biomass varies depending on the time of harvesting [10; 11]. Changes of heavy metal concentration in reeds may be caused by a variety of reasons, such as variation of metal content in the water, interactions between heavy metals and other elements, or inflow of heavy metals with the influent water from rivers and streams. Heavy metal content in reed stalks is the highest in winter period [11].

Cadmium content in reed biomass increases during the growing process, it is the lowest in May and the highest in November. Pb concentration during the growing process does not change substantially, and it remains similar across the whole reed growing period. The highest bio-accumulation index is in reed roots as they accumulate the most of the heavy metals. Reed growths accumulate Cd much better, because it is much more mobile than Pb, therefore Cd content in nature is much lower than Pb (approximately 10 times lower). Heavy metal content in reed biomass is directly related to its concentration in sediments and water [10].

By burning reed biomass, heavy metals enter in to ash. Results of our research show that the mean ash content in reed biomass is 5 %. In order to prevent ash from entering landfills, it is needed to analyse possibilities of their utilization. There is no legislation for maximal reed ash dose on soil in Latvia. One of the possible ways of utilization is ash dispersion in agricultural soils, by application of requirements on incorporation of sewage sludge into the soil set out in the Cabinet Regulation No. 362 “Regulation on Utilisation, Monitoring and Control of Sewage Sludge and Compost thereof” [12]. The main factor determining dispersion in the soil is heavy metal content, hence arises the need for further studies on heavy metal content in reed ash.

Materials and Methods

Reed samples for burning were taken from 11 largest water bodies of Latgale region with reed growths of at least 50 ha: Lubanas lake, Kvapanu ponds, Idenas ponds, Raznas lake, Cirmas lake, Ludzas lake, Rusonas lake, Feimanu lake, Cirisa lake, Luknas lake and Sivera lake. The research was carried out in 2010, 2011 and 2012 in March, as the ice is then thickest, which allows for the reeds to be mechanically harvested, and the collected data can be used to establish the reed biomass characteristics for energy extraction. In each of the lakes after surveying the reeds, four reed plants were selected, which visually reflected the average characteristic parameters of the specific water reservoir. For each stand two sampling plots were investigated. From each sampling plot about 1kg of the common reed biomass was taken, which was used for the determination of the parameters in laboratory conditions. Analysis carried out in the chemistry laboratory of Rezekne Technologies Academy.

Samples for laboratory research were prepared by using the standard method CEN/TS 14780.

To determine the ash content, standard method CEN/TS 14775 was used. To determine the content of heavy metals in ash, mineralisation of samples through the respective methodology was carried out: 1.5 g of reed ash sample was weighted. Then, 15 ml of concentrated HNO_3 were added, the sample was heated at a temperature of 95 ^{0}C for 2 hours. Cooled sample was filtered through a filter that had previously been washed with 0.5 % HNO_3 and diluted with deionised water until 65 ml. The metal content in the solution was determined by optical plasma emission spectrometer *Perkin Elmer Optima 2100 DV*. Heavy metal concentration C per1 kg of reed biomass can be calculated by using the equation 1.

$$C = \frac{C_{el} \cdot V_{par} \cdot 1000}{m_b}\text{, mg}\cdot\text{kg}^{-1} \quad (1)$$

where C_{el} – element concentration, mg·l^{-1};
V_{par} – sample volume after mineralisation, l;
m_b – quantity of ashes, g.

The data gathered in the laboratory analysis was processed by using descriptive statistics and variance analysis methods [13]. For data and relationship visualization the authors have used figures and tables.

Results and Discussion

Ash content in the analysed samples varied within the limits of 2-8 % (Fig. 1).

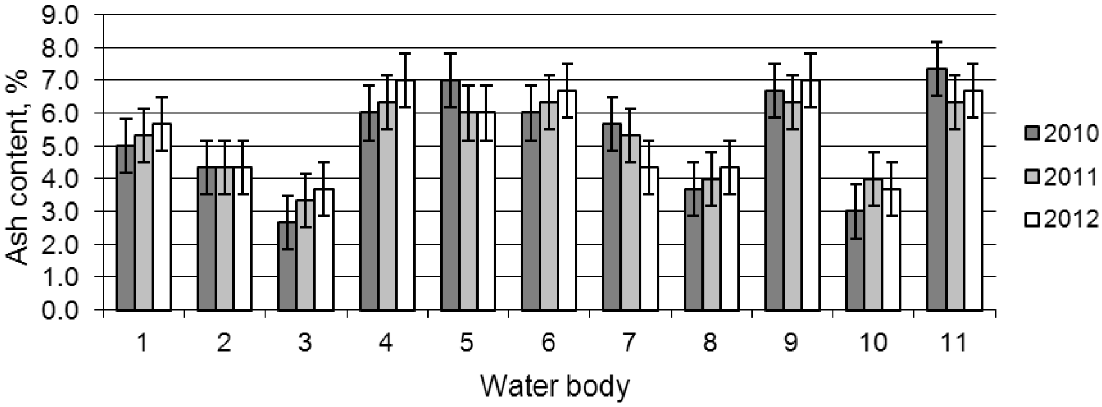

Fig. 1. **Mean values of ash content in winter for the reed biomass harvested above ice in the lakes of Latgale region:** 1 – Lubanas lake; 2 – Kvapanu ponds; 3 – Idenas ponds; 4 – Luknas lake; 5 – Cirisa lake; 6 – Sivera lake; 7 – Rusonas lake; 8 – Feimanu lake; 9 – Raznas lake; 10 – Cirmas lake; 11 – Big Ludzas lake

Mean value of ash content in reed biomass is 5 %, which is five times more than the average index of wood ash; it resembles the straw and canary seed ash content.

Consequently, burning of reeds results in significant quantities of ash that need to be utilized. Ash is classified as hazardous waste. An important indicator characterising ash utilization is heavy metal content in the ash. In order to analyse the possibilities of ash utilization, heavy metal content in ash of reed growing in 11 Latvia's water bodies was determined.

Chrome content in reed ash of the respective samples ranged from 21 to 63 $g \cdot t^{-1}$ (Fig. 2) and it was different within one water body over a several-year period.

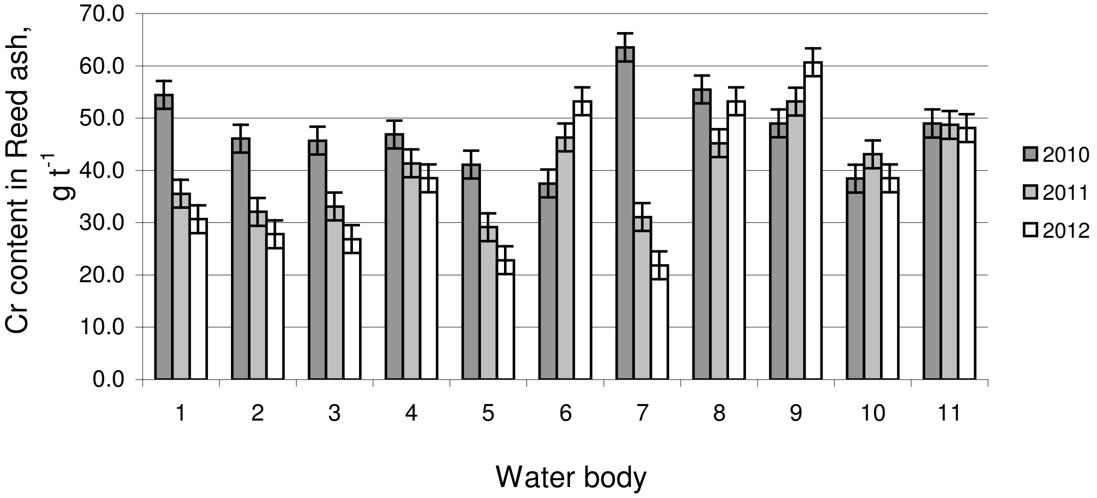

Fig. 2. **Mean values of Cr content in reed ash:** 1 – Lubanas lake; 2 – Kvapanu ponds; 3 – Idenas ponds; 4 – Luknas lake; 5 – Cirisa lake; 6 – Sivera lake; 7 – Rusonas lake; 8 – Feimanu lake; 9 – Raznas lake; 10 – Cirmas lake; 11 – Big Ludzas lake

Mean value of Cr content in the analysed samples from 11 water bodies of Latgale region over a three-year period amounted to approximately 42 $g \cdot t^{-1}$.

Copper content in reed ash of the studied samples varied from 20.5 to 55.2 $g \cdot t^{-1}$ (Fig. 3) and it differed significantly within one water body over a several-year period.

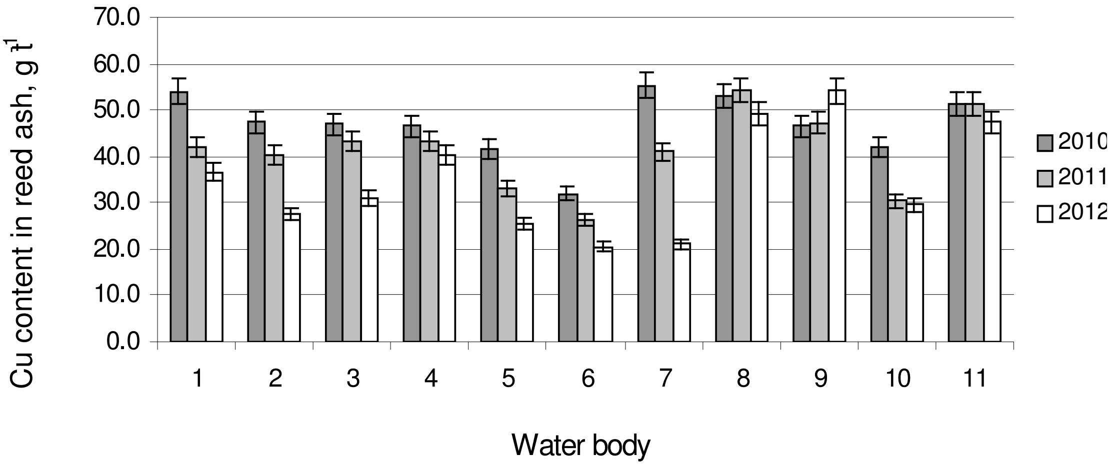

Fig. 3. **Mean values of Cu content in reed ash:** 1 – Lubanas lake; 2 – Kvapanu ponds; 3 – Idenas ponds; 4 – Luknas lake; 5 – Cirisa lake; 6 – Sivera lake; 7 – Rusonas lake; 8 – Feimanu lake; 9 – Raznas lake; 10 – Cirmas lake; 11 – Big Ludzas lake

Mean value of Cu content in the analysed samples taken from 11 water bodies of Latgale region over a three-year period amounted to approximately 41 $g \cdot t^{-1}$.

Lead content in reed ashes of the studied samples varied from 0 to 19 $g \cdot t^{-1}$ (Fig. 4) and it varied significantly within one water body over a several-year period.

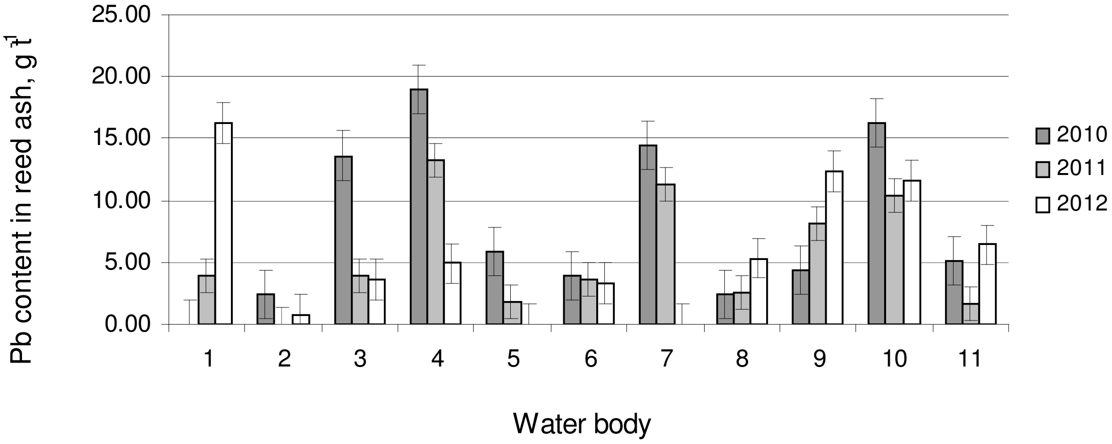

Fig. 4. **Mean values of Pb content in reed ash:** 1 – Lubanas lake; 2 – Kvapanu ponds; 3 – Idenas ponds; 4 – Luknas lake; 5 – Cirisa lake; 6 –Sivera lake; 7 – Rusonas lake; 8 – Feimanu lake; 9 – Raznas lake, 10 – Cirmas lake,11 – Big Ludzas lake

Average Pb content in the analysed samples taken from 11 water bodies of Latgale region over a three-year period amounted to approximately 6.5 $g \cdot t^{-1}$.

Nickel content in reed ash of the studied samples varied from 10.2 to 24 $g \cdot t^{-1}$ (Fig. 5) and it varied significantly within one water body over a several-year period.

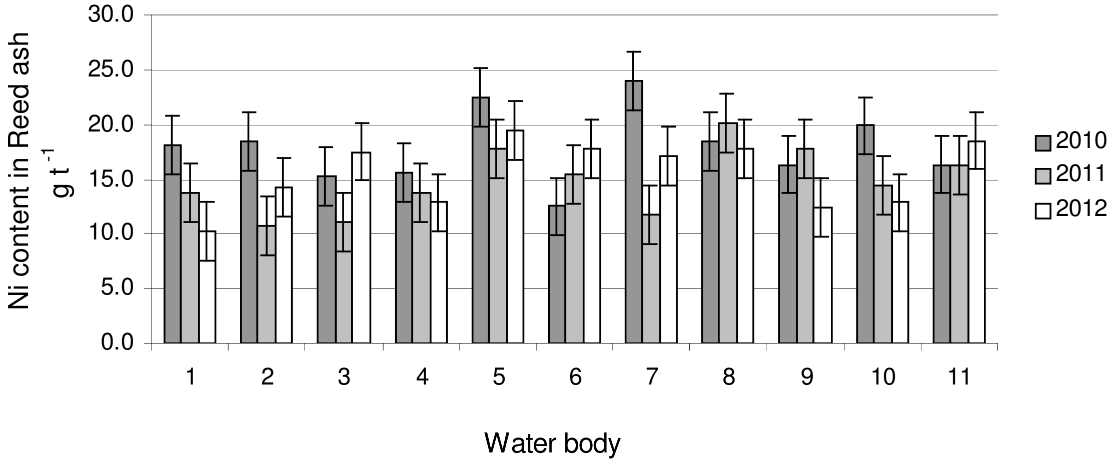

Fig. 5. **Mean values of Ni content in reed ash:** 1 – Lubanas lake; 2 – Kvapanu ponds; 3 – Idenas ponds; 4 – Luknas lake; 5 – Cirisa lake; 6 –Sivera lake; 7 – Rusonas lake; 8 – Feimanu lake; 9 – Raznas lake, 10 – Cirmas lake,11 – Big Ludzas lake

Mean value of Ni content in the analysed samples taken from 11 water bodies of Latgale region over a three-year period amounted to approximately 16 $g \cdot t^{-1}$.

It should be noted that no Cd was found in any of the analysed samples of reed ash. One of the most appropriate ways of biomass ash disposal is its incorporation into the soil.

The research has revealed maximum allowable reed ash doses for incorporation into the soil, by assessing Cd, Cu, Cr, Pb and Ni content in reed ash. Maximum allowable reed ash doses to be incorporated per unit of area of soil were evaluated in accordance with incorporation of the sewage sludge into the soil. Dose limitations were determined in accordance with the Cabinet Regulation No. 362 "Regulation on Utilisation, Monitoring and Control of Sewage Sludge and Compost thereof" (Table 1).

In order to determine the maximum five-year dose of ash that can be dispersed over 1 hectare of soil, average values of heavy metal content in reed ash were taken, by using limit values of heavy metal content in sewage sludge. The average heavy metal content in reed ash and maximum allowable dose of distribution over a five-year period by our calculations is shown in Table 2.

Table 1

Limit values of annual heavy metal emission in soils used in agriculture [12]

Element	Average for a five-year period, $g \cdot ha^{-1}$ per year	
	Sand, clayey sand	**Sandy loam, clay**
Cadmium (Cd)	30	35
Copper (Cu)	1000	1200
Nickel (Ni)	250	300
Chromium (Cr)	600	700
Lead (Pb)	300	350

Table 2

Mean values of heavy metal content in reed ashes and maximum allowable dose of ash dispersal

Limiting element	Mean value in reed ash, $g \cdot t^{-1}$	Maximum allowable (5-year period) dose of ash dispersal, $t \cdot ha^{-1}$	
		Sand, clayey sand	**Sandy loam, clay**
Chromium (Cr)	42	14.3	16.6
Copper (Cu)	41	24.4	29.3
Cadmium (Cd)	0	-	-
Nickel (Ni)	16	15.6	18.8
Lead (Pb)	6.5	46.2	53.9

Copper content in straw ash is 23.2 $g \cdot t^{-1}$, which is approximately two times less than in reed ash, while lead content is 7.7 $g \cdot t^{-1}$ [14], which is similar to the heavy metal content in reed ash.

It should be noted that straw ash contain 0.7 $g \cdot t^{-1}$ of Cd [14] that is much more dangerous in natural environment than other metals, but in reed ash Cd was not found.

The main of the studied heavy metals in reed ash that limits the dose of ash dispersal in the soil is Cr; maximum 5-year dose for reed ash dispersal in sand and clayey sand soil constitutes 14.3 tons of ash per hectare, while in sandy loam and clay soils it amount to 16.6 t which is more than wood ash. Thus, it can be concluded that, when burning chopped reeds together with wood, maximum ash dispersal dose would be larger than the dose of wood; besides, ash disposal would require smaller area of soil.

Conclusions

1. Mean value of reed biomass ash content is 5%, which is five times more than the average index in wood, but it resembles the straw and canary seed ash content.
2. In the analysed reed ash samples, mean value of Cr content amounted to 42 $g \cdot t^{-1}$, Cu content 41 $g \cdot t^{-1}$, Cd was not found. Average Ni content was 16 $g \cdot t^{-1}$ and Pb content was 6.5 $g \cdot t^{-1}$.
3. Reed ash can be utilised by incorporating them into the soil. Maximum 5-year dose of reed ash for incorporation into the soil constitutes 14.3 tons of ash per hectare of sandy soil and clayey sand soil, 16.6 tons in sandy loam and in clay. The main element that limits the reed ash dispersal dose is Cr.

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