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Website: www.aarf.asia Email : editor@aarf.asia , editoraarf@gmail.com

CONTENT OF HEAVY METALS IN REED BIOMASS AND FACTORS AFFECTING IT

Edgars Čubars

Institute for Regional Studies, Rezekne Technologies Academy, Latvia.

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.

On the other hand, these heavy metals are not desirable in fuels. Content of heavy metals in reed biomass is limited in different standards. This research contains analysis of the content of heavy metals in reed biomass and their suitability for fuel production. The author of the research has determined the content of Cu, Cd, Ni and Pb in reed dry matter and its changes depending on the water body where the reeds were obtained and on the harvest year, in order to see whether the content of heavy metals in reed dry matter is significantly affected by the harvest place and harvest year, which allows to assess if reeds from different places may be mixed together and used as a solid fuel. With a help of the method of two-factor dispersion analysis, the content of Cu, Cd, Ni, Pb in reed biomass was analysed within a three-year period (2009 - 2012) by using biomass samples taken from 11 lakes located in Latgale region.

Results of the research reveal that the content of heavy metals in reed meets the solid fuel production requirements; in none of the respective water bodies this content exceeded maximum permissible concentrations. The most significant differences in the content of heavy metals were found among reed samples taken in different water bodies. Content of heavy metals depends on individual reed growing conditions in each water body. Content of heavy metals in biomass depends on its content in water and sediments.

KEYWORDS- Reed beds, heavy metals, Common reed *(Phragmites australis (Cav.) Trin. Ex Steud)*, biomass, renewable energy resource.

1. INTRODUCTION

Up to this point in time, 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, 2, 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*ha^{-1} of green fodder or 7.5–13.0 t*ha^{-1} of dry matter [2, 6]. Foreign literature states that productivity of reed growths can amount to 30 t* 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*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.

One of the most important environmental achievements in removing reeds is the reduction in nitrogen and phosphorus levels of pollution in natural water, in addition the substitution of fossil energy resources by renewable energy resources. In the same way reeds absorb heavy metals very well [8,9] and therefore it can be said that reed extraction will help remove heavy metals from water reservoirs.

Reed growths are considered to be an important regulator of heavy metal content in natural waters and silt [10]. Rapid growing of reeds in the spring leads to assimilation of heavy metals from water and soil [11, 12]. Heavy metal content in reed biomass varies depending on the time of harvesting [12, 13]. 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 [13].

Cd 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 [12].

Reed growths are located in various Latvia's places and it is important to find out whether they can be gathered in one place and used for fuel production.

Content of heavy metals in reed biomass is an important factor defining its suitability for fuel production. It is limited in different standards. Our research reveals that it varies in different places and in biomass obtained in different years. The aim of the research is to study the content of heavy metals and the factors affecting it in reed biomass obtained in Latvia's water bodies, to analyse suitability of the biomass for fuel production, and to determine the possibilities of removing heavy metals from water bodies by harvesting reeds.

2.MATERIALS AND METHODS

The research determines the content of Cu, Cd, Ni and Pb in reed dry matter and its changes depending on the water body where the reeds were obtained and on the harvest year, in order to see whether the content of heavy metals in reed dry matter is significantly affected by the harvest place and harvest year.

Reed samples for research were taken in 3 years period from 11 largest water bodies of Latgale (Region in Latvia) 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 Sivers lake. Reeds were mowed above ice in winter and gathered (Figure 1).

1 Figure. Harvested reed, winter 2012.

Samples for laboratory research were prepared by using the standard method CEN/TS 14780. To determine the heavy metal content in the biomass the mineralization of the samples was carried out using the relevant methodology. The reed biomass was reduced in size by a milling process which produced bits <150 um, which were weighed as a 1,5g dry biomass sample. Then 15ml concentrated HN03 was added, the sample heated to 95 degrees C over 2 hours. The cooled sample was filtered, the filter having been washed with 0,5% HN03 and diluted with deionized water up to 65ml. The metal content in the solution was established with an optical plasma spectrometer Perkin Elmer optima 2100 DV. The data gathered in the trials and laboratory analysis was processed by using variance analysis method [14]. For data and relationship visualization the author has used figures and tables.

In the research two factors were analyzed which influenced Heavy metals content in reed biomass. It can be influenced by a wide spectrum of factors, to achieve their evaluation as regards materiality and intensity of influence the assessment factors were grouped in main categories:

1. Extraction year is characterized by the climatic conditions affecting Heavy metals content in reed biomass. The temperature in the growing phase, the rainfall amount, the wind effect and so on.
2. Extraction place is characterized by the growth differences within the boundaries of different water reservoirs – the various reed growing areas, the water depth, chemical condition of water and sediments, the proximity of cultivated land, river estuaries and sources and so on.

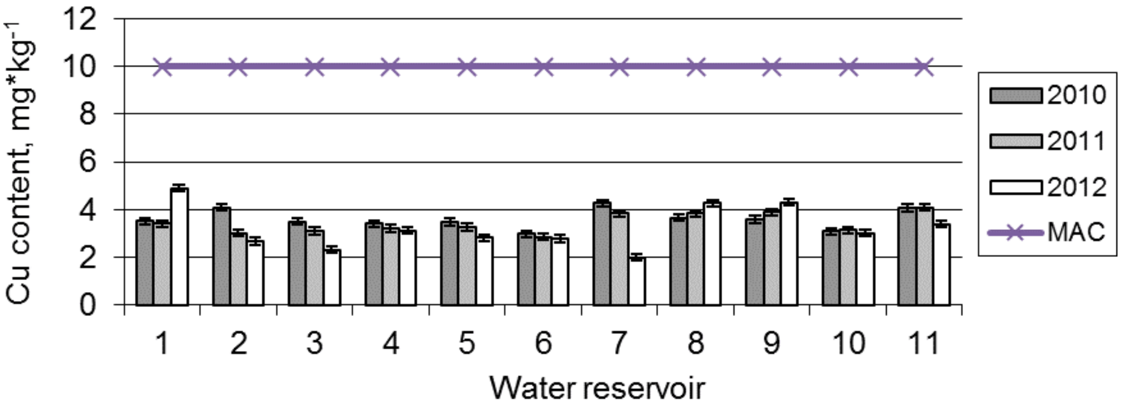
3.RESULTS AND DISCUSSION

The heavy metal content in the biomass, which is used for fuel production, is limited by various standards. The reed biomass suitability has been evaluated accordingly to the German standard DIN 5173, and EC standard prEN 14961 – 3, where the heavy metal maximal acceptable concentrations (MAC) in the solid biofuel are specified.

Cu content in the reed biomass varied within the limits of 1,98 – 4,98 mg*kg^{-1} which comprised up to 50% of the MAC biomass fuel. Cu content in forestry production waste comprises about 2 mg*kg^{-1} [15] which leads one to believe, that the reed biomass contains on average 1,5 times more Cu than the forestry production waste however it is still within the MAC limits. The reed plant Cu substance output comprised 1,38 – 3,48 mg*kg^{-1} which is about two times smaller, than that which has been established in the reed biomass of sewage treatment plants [16].

The ability of reeds to absorb Cu from natural water bodies and sediments is dependent on the Cu compound concentration in them. Harvesting 1ha of reeds from the water it is possible to remove 138 – 148g Cu. The Cu substance output level in other research [8], where the reed stalks were harvested, was shown as 570 g for 1ha, which shows that reed stalks have a good absorption capacity for Cu, which confirms the findings of previous research [17].

Cu compounds were noted in all the analyzed samples. In lakes Lukna, Sivers and Cirma, for the Cu content there were no significant differences between the samples taken over different years, in the other lakes the Cu content varied in the reed biomass according to the harvesting year, which shows high Cu mobility in natural waters, although in none of the research samples did the Cu content exceed the MAC (Figure 2).



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-L.Ludzas lake.

2 figure. Cu average content in winter in the reed biomass harvested in the lakes of Latvia

The results of 3years research for Cu content in the reed biomass show that by using a two-factor variance analysis, that the Cu content in the research samples fundamentally (p<0,001) is influenced by the extraction location and year and the interaction factor between the location and year (1 table).

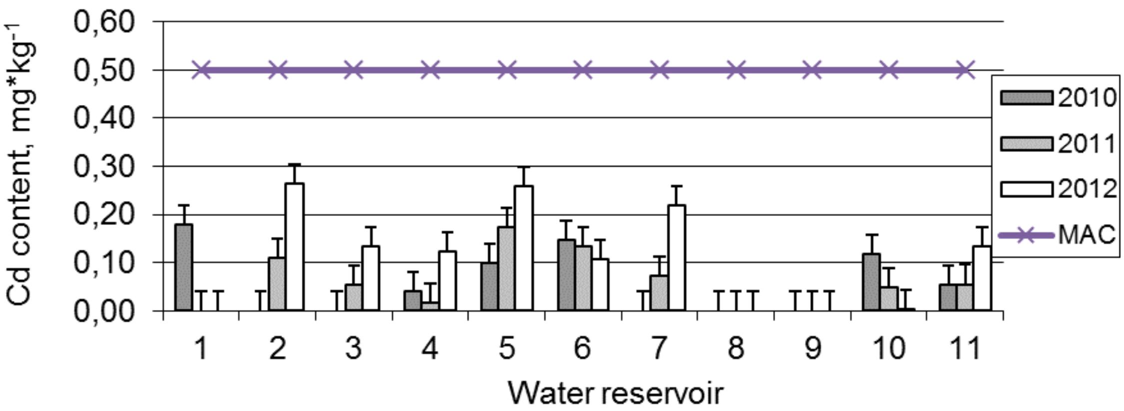
Table 1

The factors influencing the significant proportions of Cu content in the reed biomass, η %

Factor	p- value	η %
Extraction place (A)	<0,001	40,7
Extraction year (B)	<0,001	6,1
Interconnection (A×B)	<0,001	51,8

The highest significant factor proportion was the extraction place and year interconnection, the influencing intensity was high – 51,8%. The climatic condition influence on the heavy metal content in reed dry matter is weak, even though the influence of the harvesting year was significant ($p<0,001$) although it is eight times smaller than the interconnection of both factors – 6,1%. The extraction location factor significant proportion is 40,7%, which leads one to assume, that the Cu content in the reed biomass is dependent on the Cu content in the water and sediment of each water reservoir. Cu content is significantly different in the harvested reeds from different lakes, although it did not exceed MAC in any of the researched lakes, which leads one to assume, that the reeds extracted from various lakes can be mixed together and used as fuel.

Cd content in the reed biomass was relatively small and varied within limits 0 – 0,28 mg*kg^{-1}, which was below MAC in all the research lakes (3 Figure) Cd content in forestry production waste consists of 0,1 – 0,2 mg*kg^{-1} [15] which leads one to deduce that the Cd content is similar in reed biomass and fire wood. The Cd substance output from reeds comprised 0 – 0,20 mg*m^{-2}*year^{-1}, which was higher than from reeds in sewage treatment plants [16] where it consisted of 0,014 – 0,038 mg*m^{-2}*year^{-1}, which shows that Cd absorption in reed stalks is dependent on its content in water and sediment.



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-L. Ludzas lake.

3 Figure. Cd average content in winter in the reed biomass harvested in the lakes of Latvia

In all the researched water reservoirs, the Cd content in the reed biomass significantly changed according to the harvesting year, which shows a high Cd compound mobility in natural waters which has been described in other research [12, 17]. In lakes Feimanu and Raznas no traces of Cd were found in the reed biomass for the research years, in lake Lubanas Cd was found in 2010 in the reed biomass, but not 2011 or 2012. In the Kvapanu and Idenas ponds Cd was not found in 2010 in the reed biomass research samples, but was found in 2011 and 2012. In the other research lakes Cd was found in various concentrations every year, which shows a high Cd compound mobility in natural waters. The research results regarding Cd content in the reed biomass show by the two-factor variance analysis, that the Cd content in the research samples was significantly influenced ($p<0,001$) by the extraction location, extraction year and the interconnection factor between the two (table 2).

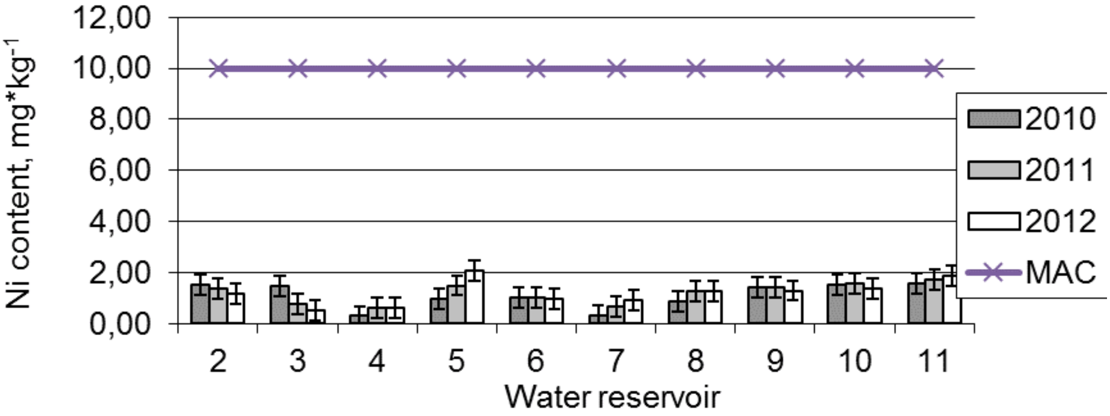
Table 2

The factors influencing the significant proportions of Cd content in the reed biomass, η %

Factor	**p- value**	**η %**
Extraction place (A)	<0,001	44,2
Extraction year (B)	<0,001	9,4
Interconnection (A×B)	<0,001	43,9

The greatest significant proportion factor was the interconnection of the extraction location and extraction year, as well as the extraction location factor, the influencing intensity was similar about 44%. Even though the influence of the extraction year was significant it was relatively small – 9,4%, which leads one to deduce that the Cd content in the reed biomass is largely influenced by the heavy metal content in the water and sediment in each water reservoir, rather than the extraction year. Cd content is significantly different in the harvested reeds from different lakes, although it did not exceed the MAC in the researched lakes, as a result one can assume that the reeds from different lakes can be mixed together as a fuel.

Ni content in the reed biomass varied within limits of 0,29 – 2,06 $mg*kg^{-1}$, in all the research water reservoirs it was about five times smaller than the MAC. Ni content in forestry production waste consists of about 0,5 $mg*kg^{-1}$ [15] which leads one to deduce, that the Ni content in the reed biomass is on average three times greater than the Ni content for fire wood, although it is smaller than the MAC. The reed Ni substance output consisted of 0,2 – 1,44 $mg*m^{-2}*year^{-1}$, which varied within a wider range, than for reeds, which were used in sewage treatment plants [16] where the Ni substance output consisted of 0,57 – 0,91 $mg*m^{-2}*year^{-1}$, Ni compounds were noted in all the analyzed samples. In Lubanas lake, the Idenas ponds and Cirisa lake significant differences were noted in the reed biomass for Ni content in the samples taken in different years. In the other researched lakes, Ni content in the reed biomass did not change significantly dependent on the harvesting year (Figure 4).



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-L.Ludzas lake.

Figure 4. Ni average content in winter in the reed biomass harvested in the lakes of Latvia

The Ni content in the research samples was significantly ($p<0,001$) influenced by the harvesting location and the interconnecting factor of the harvesting location and harvesting year but the harvesting year had no significant influence ($p<0,05$) on the Ni content in the reed biomass (Table 3).

Table 3

The factors influencing the proportions of Ni content in the reed biomass, η %

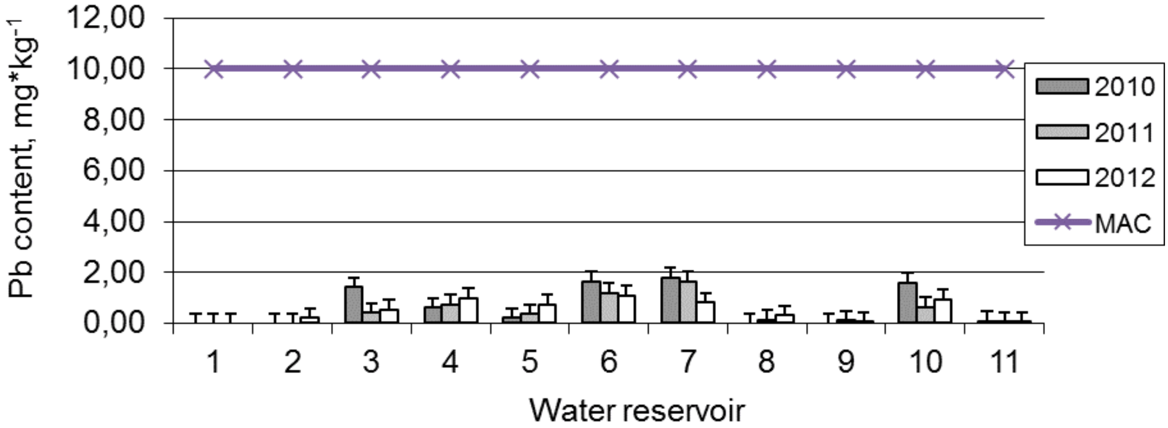
Factor	**p- value**	**η %**
Extraction place (A)	<0,001	57,9
Extraction year (B)	<0,001	0,0
Interconnection (A×B)	<0,001	25,6

The largest significant proportion influence was for the harvesting location, the intensity influence was high – 57,9%, therefore the Ni content in the reed stalks was influenced by the Ni content in water and sediment in each specific water reservoir. The climatic conditions do not influence the Ni content in the dry matter, the harvesting year influence was not significant and did not influence the Ni content, therefore Ni has a comparatively low mobility in natural waters. The harvesting location and harvesting year interconnection factor significant proportion is 25,6%. Ni content significantly varies between the reeds harvested in different lakes, however in none of the researched lakes did it exceed the MAC, therefore one can assume, that the reeds collected from various lakes can be mixed together and used for fuel.

Pb content in the reed biomass varied between the limits of 0 – 1,81 mg*kg^{-1} in none of the researched lakes did it exceed MAC. Pb content in forestry production waste consists of 2 – 5mg mg*kg^{-1} [15] which leads one to assume, that the Pb content in the reed biomass is lower than in the forestry production waste. The reed substance output for Pb in our research consisted of 0 – 1,27 mg*m^{-2}*year^{-1}, which varied over a wider range than for reeds which are used for sewage treatment plants [16] where the substance value for Pb consisted of 0,36 – 0,44 mg*m^{-2}*year^{-1}. In all the researched water reservoirs, except for lakes Luknas and Cirisa, the Pb content in the reed biomass significantly changed according to the harvesting year. In Lubanas lake Pb was not noted for any of the years in the reed biomass (5 Figure).

The research results for Pb content in the reed biomass in a two-factor variance analysis show, that the Pb content in the research samples was significantly influenced by the harvesting location, and the interconnection factor between the harvesting location and harvesting year. The harvesting year influence was also significant ($p<0,05$) (Table 4).

The greatest significant proportion influence was for the harvesting location, as well as the interconnecting factor for the harvesting location and year, respectively the intensity for both was 71,9% and 15,9%, Even though the harvesting year influence was significant, however the influencing proportion was comparatively small – 1,9%.



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-L. Ludzas lake.

Figure 5. Pb average content in winter in the reed biomass harvested in the lakes of Latvia

Table 4

The factors influencing the proportions of Pb content in the reed biomass, η %

Factor	p- value	η %
Extraction place (A)	<0,001	71,9
Extraction year (B)	<0,001	1,9
Interconnection (A×B)	<0,001	15,9

The Pb content in reed biomass is influenced little by the harvesting year in each of the water reservoir waters and sediments. The Pb content significantly varies between the reeds for the different lakes, even though it did not exceed the MAC in the researched lakes, and from that one can assume that the harvested reeds can be mixed together and used as fuel.

CONCLUSIONS

The most significant differences in the content of heavy metals were found among reed samples taken from different water bodies. Content of heavy metals in biomass depends on individual reed growing conditions in each water body.

Content of heavy metals in biomass depends on its content in water and sediments.

The content of the above-mentioned heavy metals in reed meets the solid fuel production requirements; in none of the respective water bodies this content exceeded maximum permissible concentrations. Reeds from different water bodies may be mixed together and used for fuel production.

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