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CARDOON (*CYNARA CARDUNCULUS* L.) AS A BIOFUEL CROP FOR PHYTOREMEDIATION OF HEAVY METAL CONTAMINATED SOIL

Violina ANGELOVA[1], Vanya ZAPRYANOVA[2]

[1]Agricultural University of Plovdiv, 12 Mendeleev Blvd, Plovdiv, Bulgaria
[2]Laboratory for Testing of solid biofuels and compost, Plovdiv, Bulgaria

Corresponding author email: vileriz@abv.bg

Abstract

There has been carried out comparative research, which allows determining the quantities and the depots of accumulation of heavy metals, macro, and micro elements in the vegetative organs of Cynara cardunculus L., efficacy for phytoremediation and quality of biomass as renewable energy sources for the combustion process. The field experiment was performed on an agricultural field contaminated by the Non-Ferrous-Metal Works (MFMW) near Plovdiv, Bulgaria. The experimental plots were situated at different distances (0.5, and 8 km) from the source of pollution. Macronutrients (N, P, K, Mg, Ca), micro elements (Fe, Mn, Cu) and heavy metal (Cd, Pb, Zn) concentrations in plant materials (roots, and leaves) were determined. Heating value, ultimate and proximate analyses were evaluated at the end of the second growing season. Cardoon is tolerant towards the heavy metals and can be grown on highly contaminated soils (2544.8 mg/kg of Zn, 2429.3 mg/kg of Pb and 51.5 mg/kg of Cd). The depot for accumulation follows the order: roots>leaves. The high concentration of heavy metals in the roots and the low translocation factor indicate the possibility of cardoon to be used in phytostabilization. The obtained results have shown that cardoon has potential to be a significant source of good quality raw material in the production of solids bio-fuels. The biomass is of good quality (carbon (39.3-43.0%), hydrogen (3.8-4.52%), nitrogen (0.72-0.877%), chlorine (4.7-6.8%), and sulphur (0.266-1.12%) content) and high energy potential (14.54-16.09 MJ/kg LHV). The degree of soil contamination did not have a significant influence on heating values, carbon, hydrogen, nitrogen, and sulphur contents but did influence on biomass heavy metal contents. The content of heavy metals in the biomass of cardoon grown on heavily contaminated soils is significantly higher and exceeds the limit values according to the standard ISO 17225-6:2014. Biomass of cardoon from highly contaminated soils could be used as a source of energy if the burning of biomass occurs in power plants equipped with purification systems to control dust emissions.

Key words: *biomass properties, cardoon, heavy metals, phytoremediation, polluted soils*

INTRODUCTION

Cynara is a genus of thistle-like perennial plants of the Asteraceae family. Cardoon (*Cynara cardunculus* L.) is a perennial C3 crop with an annual growth cycle, well adapted to the soil and climatic conditions of Southern Europe. The plant is found primarily in the Mediterranean region, located mainly in Spain, Italy, and Greece, with mild winters, hot, dry summers, and light rainfall, unevenly distributed throughout the year. Cardoon produces significant biomass in spring and summer (Danalatos et al., 2006) and develops again after the first rains in autumn. Dry biomass is harvested in July-August (with a plant moisture content of 15%).

C. cardunculus is a crop with various applications. The aboveground biomass (leaves and stems) can be used as animal feed, energy production (Mancini et al., 2019), and in the food industry. Cardoon, unlike artichoke, is a crop little known in Bulgaria. Cardoon is a crop that is not demanding in terms of soil and can be grown without irrigation because it withstands drought. The climatic conditions in southern Bulgaria are suitable for its cultivation.

The use of cardoon as an energy crop is associated with very low cultivation costs, high yields of dry biomass, low moisture content in the biomass at harvest, biomass composition mainly of lignocellulose type, and high calorific value. As a solid fuel, cardoon can be used to heat or generate energy (for example, co-combustion mixed with coal). The possibilities of using cardoon as a solid biofuel were studied by Fernandez et al. (1997), Piscioneri et al. (2000), Gherbin et al. (2001), and Dahl and Obernberger (2004). Crop management techniques can affect the characteristics of cardoon biomass as a fuel.

For example, the way the harvest is carried out can lead to contamination of the soil's biomass, which leads to a higher ash content and leads to slag problems. Similarly, fertilization with KCl can increase K and Cl's content in the biomass, which can lead to the formation of deposits in the boiler (Dahl and Obernberger, 2004).

Direct combustion is the most common way to extract energy from biomass, for which energy crops, agricultural residues, forest residues, industrial and other waste can be used (Elbehri, 2013). In terms of combustion, the most critical biomass properties include proximate analysis, ultimate analysis, heating value, lignocellulosic composition, and micro-and macro elements. The standard for solid fuels ISO 17225-6 (2014) specifies the values for different agricultural and forest biomass types when burned as bio-fuel.

Phytoremediation is an emerging technology, which should be considered for remediation of contaminated sites because of its cost-effectiveness, aesthetic advantages, and long-term applicability (Chaney et al., 1997). This technology can be defined as the efficient use of plants to remove, detoxify or immobilize environmental contaminants in soils, waters, or sediments through the natural, biological, chemical, or physical activities and processes of the plants (Ciura et al., 2005).

The use of bio-fuel crops for phytoremediation of heavy metal contaminated soils increases interest (Pidlisnyuk et al., 2013). The main reason for this is the increase in demand for biomass as an alternative energy source and the possibility of remediation of contaminated soils. Energy crops include fast-growing varieties of trees and annual and perennial grasses. The phytoremediation potential of cardoon (*Cynara carduncului* L.) has been studied in several studies (Papazoglou, 2011; Llugany et al., 2012; Pandey et al., 2016; Arena et al., 2017; Domínguez et al., 2017). Arena et al. (2017) and Sorrentino et al. (2018) found that cardoon is tolerant to Cd and Pb and has a significant ability to accumulate heavy metals in pot experiments. It has been found that cardoon does not get toxic metals in As contaminated soils and accumulates toxic metals in Cd or Pb contaminated soils (Papazoglou 2011; Sanchez-Pardo et al., 2015). Domínguez et al. (2017) found that soil contamination did not significantly affect the cardoon's biomass.

Insufficient is the information available on cardoon potential for accumulation of heavy metals and its potential for use for phytoremediation in field experiments. Most publications have focused on evaluating the use of cardoon seeds for biodiesel production. There is insufficient information on the chemical composition of the cardoon biomass and the quality of bio-fuel.

The purpose of this study is to conduct systematic research that will allow us to determine the quantities and the deposits for the accumulation of heavy metals, macro, and microelements in the vegetative organs of cardoon, the quality of cardoon biomass as a biofuel, as well as the possibilities to use the plant for phytoremediation of heavy metal contaminated soils

MATERIALS AND METHODS

The experiment was performed on agricultural fields contaminated by Zn, Pb, and Cd, situated at different distances (0.5 and 8.0 km) from the source of pollution, the NFMW near Plovdiv, Bulgaria.

The soils were slightly neutral to basic with moderate organic matter content and essential nutrients (N, P, and K), (data are not shown). The pseudo-total content of Zn, Pb, and Cd is high and exceeds the maximum permissible concentrations (MPC) in soil 1 (S1) (Table 1).

Table 1. Content of Pb, Zn and Cd in soils sampled from NFMW

Distance	pH	Pb x ± sd	Zn x ± sd	Cd x ± sd
Soil 1 (S1) 0.5 km	7.4	2509.1±6.5	2423.9±6.3	64.3±0.2
Soil 2 (S2) 8 km	7.5	49.4±0.2	172.7±2.1	1.0±0.1

x - average value (mg/kg) from 5 repetitions; sd - mean standard deviation; MPC (pH 6.0-7.4) - Pb - 100 mg/kg, Cd - 2.0 mg/kg, Zn - 320 mg/kg; MPC (pH > 7.4) - Pb - 100 mg/kg, Cd - 3.0 mg/kg, Zn - 400 mg/kg

The study included cardoon (*Cynara carduncului* L.), grown on areas located at different distances (0.5 km and 8.0 km) from the source of contamination NFMW Plovdiv. Cardoon seeds were sown to a depth of 3-4 cm; between row and within the row, distances were 70 and 30 cm, respectively. Cardoon is grown according to conventional technology. The analyses were made in the second year of the growing of the plants. Five plants of each of the areas were used for the analysis. The test plant was). On reaching commercial ripeness, the plants of cardoon were gathered.

The pseudo-total content of metals in soils was determined in accordance with ISO 11466. The available (mobile) heavy metals contents were extracted following ISO 14870 by a solution of DTPA. The contents of heavy metals, micro- and macro-elements in the plant material (roots and leaves) were determined by the microwave mineralization method. To determine the content in the plant and soil samples, an inductively coupled emission spectrometer (Jobin Yvon Horiba "ULTIMA 2", France) was used. Digestion and analytical efficiency of ICP were validated using a standard reference material of apple leaves (SRM 1515, National Institute of Standards and Technology, NIST).

Proximate analysis: The samples were characterized according to standard methods: moisture content (BDS EN ISO 18134-3:2015), ash (BDS EN ISO 18122:2015), fixed carbon (by difference), and volatile matter (BDS EN ISO 18123:2015).

Ultimate analysis: Total carbon, hydrogen, nitrogen, and sulfur were determined by dry combustion in a Vario Macro CHNS analyzer (Elementar GmbH, Germany) (BDS EN ISO 16948:2015). The O content was calculated by difference.

Heating value: The heating value was determined by the ISO method (BDS EN ISO 18125:2017) using an IKA C6000 oxygen bomb calorimeter (IKA Wercke GmbH, Germany).

RESULTS AND DISCUSSIONS

Soils

The results presented in Tables 1 and 2 show that in the soil samples S1 (taken from the area situated at the distance of 0.5 km from NFMW), the reported values for Pb were exceeding MPC approved for Bulgaria and reached 2509.1 mg/kg. In the area located at a distance of 8.0 km, the contents of Pb significantly reduce to 49.4 mg/kg. Similar results were obtained for Cd and Zn.

The results for the mobile forms of the metals extracted by DTPA show that the mobile forms of Cd in the contaminated soils are the most significant portion of its total content and reached 57,2%, followed by Pb with 33.8% and Zn with 9.8%.

In the soil located at a distance of 8.0 km from NFMW, the mobile forms of Cd are the most significant part of it.

Table 2. DTPA-extractable Pb, Zn and Cd (mg/kg) in soils sampled from NFMW

Soils	Pb		Cd		Zn	
	mg/kg	%*	mg/kg	%	mg/kg	%
S1	849.1	33.8	36.8	57.2	236.8	9.8
S2	21.5	43.5	0.7	70	38.9	22.5

*DTPA -extractable/total content

Content of trace metals in vegetative organs of cardoon

To clarify the issues of absorption, accumulation, and distribution of heavy metals in vegetative organs of cardoon were analyzed samples of roots and shoots. Table 3 presents the results obtained for the content of heavy metals in the vegetative organs of the study crop.

Table3. Content of heavy metals (mg/kg) in vegetative organs of cardoon, translocation factor (TF) and bioconcetration coefficients (BCF root, BCF shoot)

	Root	Leaves	TF	BCFroot	BCFshoot
Pb	520.2	213.0	0.41	0.21	0.09
Cd	27.8	13.4	0.48	0.43	0.21
Zn	531.9	166.2	0.31	0.22	0.07

$BCF_{root}=[Metal]_{root}/[Metal]_{soil}$, $TF=[Metal]_{shoot}/[Metal]_{root}$, $BCF_{shoot}=[Metal]_{shoot}/[Metal]_{soil}$

Considerably higher amounts were established in the roots of cardoon compared to the above ground parts. The content of Pb in the roots of cardoon grown at 0.5 km from NFMW reached 520.2 mg/kg, Zn - 531.9 mg/kg, and Cd - 27.8 mg/kg. This is explained by the fact that during the penetration of heavy metals in the plasma, there is inactivation and disposal of significant quantities of them due to the formation of slightly mobile compounds with the organic substance. The results are consistent with Capozzi et al. (2019) finding that a significant accumulation of heavy metals in the roots of cardoon in the cultivation of cardoon in the pot experiments.

The heavy metals contents in the cardoon shoots were considerably lower than those in the root system, which showed that their movement through the conductive system was strongly restricted. Pb content in the shoots of cardoon grown at 0.5 km from NFMW reached 213.0 mg/kg, Zn - 166.2 mg/kg, and Cd - 13.4 mg/kg.

The obtained results obtained show that the content of Pb in the aboveground parts of cardoon is low despite the moderate level of bioavailable forms of Pb in the soil.

The choice of plant species for phytoremediation purposes is usually based on assessing their ability to accumulate heavy metals and translocate them from the roots to the aboveground mass. Bioaccumulation coefficients (BCFroots and BCFshoots) and translocation factor (TF) were calculated to evaluate the potential of cardoon for phytoremediation (phytostabilization or phytoextraction). Knowledge of such coefficients can provide useful information on the potential for phytostabilization or phytoextraction of cardoon. The Translocation Factor (TF) provides information on plants' ability to uptake heavy metals through the roots and to translocate them to the aboveground mass (stems and leaves). TF values <1 indicate a higher concentration of heavy metals in the roots, typical for plants with phytostabilization potential, while TF> 1 shows a higher content in the aboveground mass, which is typical for plants with potential for phytoextraction. The obtained results show that, concerning Pb, plants' translocation factor reached 0.41, Cd - 0.48, and Zn - to 0.31. Pb, Cd, and Zn accumulate mainly in the roots and translocate poorly in the aboveground mass. Thie results are consistent with the results of other authors who found low TF coefficients for As, Ni, Pb, and Zn in cardoon (Papazoglou, 2011; Sánchez-Pardo et al., 2015; Arena et al., 2017; Sorrentino et al., 2018). According to Garau et al. (2021) cardoon plants show TF <1 (0.09-0.45) for all elements except Cd (TF = 2.93), and TF values follow the order: Cd> Zn> Cu> Pb> As > Sb.

The effectiveness of phytoremediation is also determined by the bioconcentration factor (BCF). BCFroot is a ratio of the content of heavy metals in plant roots to soil content (BCFroots=[Metal]roots/[Metal]soils).

The obtained results show that this ratio reached 0.21 for Pb, 0.43 for Cd, and 0.22 for Zn.

BCF shoot is defined as the ratio of the metal concentration in the aboveground mass of the plant (stems and leaves) and the soil (BCFshoots=[Metal]shoots/[Metal]soils) and is a measure of the plant's ability to digest and move the metals to the aboveground mass, which can be easily harvested. The obtained results show that, concerning Pb, the BCFshoot reached 0.09, for Cd and Zn to 0.31 and 0.07, respectively. The results are consistent with Garau et al. (2021) finding that BCF is quite low (0.01-0.57).

Cardoon accumulates heavy metals through its root system, and most of them are retained by the roots. The quantity of heavy metals in the shoots of the plants was considerably lower than the root system, which showed that their movement through the conductive system was strongly restricted. The results show that cardoon is a crop tolerant to heavy metals and can be successfully grown on highly contaminated soils.

The high concentration of heavy metals in the roots and the low translocation factor indicate the possibility of cardoon being used in phytostabilization.

Heating value, ultimate and proximate analysis

Heating value, ultimate and proximate analysis, the content of macro-and microelements are among the main parameters in the assessment of biomass in the process of direct combustion. Moisture content (MC), ash content (AC), volatile matter (VM), nitrogen (N), sulfur (S), and oxygen (O) are undesirable components in biomass. The higher levels of fixed carbon (FC), carbon (C), hydrogen (H), and lower heating value (LHV) improve the quality of the biomass when it comes to direct combustion.

The results obtained for the cardoon biomass grown at a different distance from NFMW are presented in Tables 4, 5, and 6. According to standard CEN/TS 14961, biomass for solid biofuel is divided into three main groups (wood biomass, grass biomass, and fruit biomass). Cardoon biomass belongs to the group of herbaceous biomass - agricultural and horticultural herbs (others). The values of the biomass's main parameters are compared with the requirements of the standard ISO 17225-6 for herbaceous biomass and the data from other authors for the analysis of the cardoon biomass grown in different countries.

The term calorific value refers to biomass's energy content and characterizes biomass as a possible fuel resource. Higher and lower heating values can express the calorific value. According to ISO 17225-6, the standard for solid fuels for LHV is 14.5 MJ/kg.

LHV is one of the essential parameters for assessing the potential of biomass as a biofuel. According to the literature, the lower heating values range from 15.08 MJ/kg to 18.2 MJ/kg (Table 4). This study shows that the combustion's net heat on a dry basis varies from 14.54 to 16.09 MJ/kg, with higher values reported for the biomass of cardoon grown on uncontaminated soil. According to this parameter in the standard ISO 17225-6, cardoon biomass is characterized as a valuable energy raw material suitable for use in the combustion process. Cardoon biomass can be used as a raw material for heat and energy production. It has a gross calorific value (HHV) between 14.9 and 20.3 MJ/kg (Dahl and Obernberger, 2004; Gravalos et al., 2005, Grammelis et al., 2008). Cardoon biomass has calorific values typical of grassy biomass, i.e., 18–22 MJ/kg HHV (Gominho et al., 2018).

Table 4. Proximate analyses and lower heating value of cardoon biomass

Parameter	S1	S2	Reference	ISO 17225-6
Moisture, %	4.66	4.23	5.72-13.2	≤12 -15
Ash, %	21.45	17.05	6.9-29.6	≤6-10
Fixed carbon, %	8.15	5.55	10.9-14.6	-
Volatile matter, %	70.4	77.4	59.5-75.0	-
LHV, MJ/kg	14.54	16.09	15.08-18.2	≥14.5

Heating values decrease with higher moisture content, with higher levels leading to lower combustion temperatures and affecting quality (Clarke and Preto, 2011). In general, moisture can vary considerably and is an undesirable ingredient in any fuel. The moisture content is influenced by the climatic conditions and the period of biomass harvesting.

This study shows that the moisture content varies from 4.23 to 4.66%, with higher values reported for the biomass of cardoon grown on contaminated soil, which is by the standard ISO 17225-6:2014 (≤12-15) (Table 4).

Based on the data presented in Table 4, the average moisture content of contaminated and uncontaminated soil is less to the values obtained by other authors (5.71-13.2%) (Grammelis et al., 2008).

The content of fixed carbon is considered a positive property of biomass, representing the amount of energy released from a certain amount of biomass. Higher fixed carbon values affect the quality of biomass due to the higher heating values (Clarke and Preto, 2011). The fixed carbon content is the mass remaining after the release of volatile matter, excluding ash and moisture. Fixed carbon leads to the formation of carbon and burns as a solid in the fuel system. ISO 17225-6 does not specify a value for fixed carbon.

This study shows that the fixed carbon varies from 5.55 to 8.15%, with higher values reported for the biomass of cardoon grown on contaminated soil. According to the literature, the fixed carbon in the cardoon biomass is between 10.9% and 14.6% (Grammelis et al., 2008). The obtained values for fixed carbon in the cardoon biomass from contaminated and uncontaminated soils are significantly lower than other authors' results (Table 5).

The ash content is one of the main factors determining the quality of biomass, as more significant amounts of ash reduce fuel quality. The non-combustible content of biomass is called ash content. The high ash content leads to pollution problems, especially if the ash has high metal chloride content. Biomass fuels from crops or residues have higher ash content (Clarke and Preto, 2011).

The results obtained show that the ash content varies from 17.05 to 21.45%. The lowest values are found for biomass grown in the uncontaminated soil (S2). According to the standard for solid fuels EN ISO 17225-6, the ash content for non-wood pellets can vary from 6 to 10%. The biomass from the contaminated (S1) and uncontaminated area (S2) exceeds the permissible value. A probable reason for the higher ash content in cardoon is the higher content of macroelements in plant biomass. According to the literature data, the ash content is between 6.9% and 29.6% (Table 4). High values of ash are characteristic of cardoon biomass (4-17%) (Fernandez et al., 2006; Aho et al., 2008). Significantly higher results were obtained by Bartolome et al. (2008), Damartzis et al. (2011) (15.1-29.6%), and Monti et al. (2008) (19.2-22.2%). Significant lower results were obtained by Toscano et al. (2016) (6.3%), Grammelis et al. (2008) (6.9-7.2%), and Cavalaglio et al. (2020) (9.12%).

The studied biomass from cardoon grown on contaminated soils has qualities suitable for direct combustion. About the solid fuel standard, the ash content is higher than the standard.

In the combustion process, biomass decomposes into volatile gases and solid residue. Volatile matters are the components released at high temperatures when the fuel is heated, without taking into account the moisture that is part of the combustible gases (CxHy gases, CO, or H_2) and non-combustible gases (CO_2, SO_2, or NOx) (Garcia et al., 2012). A high percentage of volatile matter is one of the characteristics of biomass reducing the energy value.

The volatile matter content in cardoon biomass ranges from 60% to 78% (Suarez-García et al., 2002; Bartolome et al., 2008; Grammelis et al., 2008; Damartzis et al., 2011; Abelha et al., 2013). EN ISO 17225-6 does not specify a volatile matter rate in cardoon. The results showed that volatile matters vary from 70.4% to 77.4%, with the higher values found in cardoon's biomass grown on uncontaminated soil. The values for volatile matters are in line with the other authors' biomass results (59.5-75.0%).

Table 5 presents the ultimate analysis of cardoon grown on contaminated and uncontaminated soils. The ultimate analysis values are compared with the requirements of the standard ISO 17225-6 and the data from other authors for the analysis of the cardoon biomass grown in different countries. The main components of solid biofuels are C, H, and O. C and H are oxidized during combustion in exothermic reactions, which leads to the formation of CO_2 and H_2O and affects the gross calorific value of the fuel (Clarke and Preto, 2011). Organically bound O provides the part of O required for the combustion process, and O must be added by air injection. Higher C and H content lead to higher HHV.

Carbon is the primary and most crucial element in all types of fuels, and its content determines their quality, i.e., higher carbon levels increase fuel quality.

The total carbon content varies from 39.3 to 43.0%, with the higher values found for cardoon biomass from uncontaminated soil. According to the literature, the carbon content ranges from 24.1 to 46.7% (Table 4).

The content of hydrogen varies from 3.8% in contaminated soil to 4.52% in uncontaminated soil. According to the literature, the hydrogen content varies widely (from 4.8 to 6.63) (Table 5).

The energy value is negatively affected by the oxygen content. The oxygen content varies from 33.59 to 34.31%.

There were no significant differences in the biomass's oxygen content between the tested plants from the contaminated and uncontaminated soils. According to the literature, O's content varies from 35.52% to 46.80% (Table 5).

From an environmental point of view, nitrogen and sulfur contribute to increased greenhouse gases and are considered unfavourable biomass elements. When biomass is burned, NOx and SO_2 are formed, and therefore the nitrogen and sulfur content of the biomass must be as low as possible. The amount of nitrogen in the biomass is the cause of NOx emissions from biomass combustion. The fuel's low nitrogen content leads to lower NOx emissions (Clarke and Preto, 2011). Sulfur is an element with a minor presence in biomass, but nitrogen is a critical element for the environment. The content of S in the biomass largely depends on the macromolecular composition. SOx are formed during combustion and lead to significant contamination with dust particles and acid rain. Also, S can indirectly contribute to increased corrosion (Clarke and Preto, 2011).

The nitrogen content varies from 0.72% in uncontaminated soil to 0.877% in contaminated soil, at a nitrogen rate of 1.5-2%. The sulfur content varies from 0.268% for contaminated soil (S1) to 1.12% for uncontaminated soil (S2), with a sulfur rate of 0.2-0.3%. The values obtained for contaminated soils are below the permissible values for the limit for solid fuels. According to the literature data, the sulfur content in biomass varies from 0.11 to 0.29% (Table 4). The low N content found increases the quality of biomass in terms of its use for combustion processes. The nitrogen content is much lower than the established values for plant biomass (0.55 to 2.63%) (Table 5) (Grammelis et al., 2008; Toscano et al., 2016; Gominho et al., 2018).

Table 5. Ultimate analysis of cardoon biomass

Parameter	S1	S2	Reference	ISO 17225-6
N,%	0.877	0.72	0.55-2.63	1.5-2
C, %	39,3	43.0	24.1-49.3	-
S, %	0.268	1.12	0.11-0.29	0.2-0.3
H, %	3.8	4,52	4.8-6.63	-
O, %	33.41	33.59	43.0-51.45	-
Cl, %	6.8	4.7	nd- 1.73	0.1-0.3

The chlorine content varies from 4.7% in uncontaminated soil to 6.8% in contaminated soil, at a chlorine rate of 0.1-0.3%. The values obtained for contaminated soils are higher than the permissible values for the limit for solid fuels.

The high content of chlorine and alkaline elements is the reason for the increased deposition of alkaline chlorides, which damage the superheaters and reduce the boilers' life (Aho et al., 2008; Abelha et al., 2013).

Table 6 presents the results for the content of heavy metals, micro and macro elements in the biomass of cardoon, grown on contaminated and uncontaminated soils, and typical values of EN ISO 17225-6 for solid fuels.

The content of Pb in the above ground mass of cardoon grown at a distance of 0.5 km from NFMW reaches 155.9 mg/kg, Zn - up to 166.9 mg/kg, Cd - up to 13.4 mg/kg, Cu - up to 37.9 mg/kg, Fe - up to 183.6 mg/kg, Mn - up to 1780.1 mg/kg, K - up to 15756 mg/kg, P - up to 1780 mg/kg, Mg - up to 1373.9 mg/kg and Ca - up to 12637.2 mg/kg.

Significantly lower values were established in the above ground mass of cardoon when grown on unpolluted soils. The content of Pb reaches 5.6 mg/kg, Zn - up to 28.9 mg/kg, Cd - up to 0.09 mg/kg, Cu - up to 4.8 mg/kg, Fe - up to 117.9 mg/kg, Mn - up to 7.5 mg/kg, K - up to 11596.9 mg/kg, P - up to 888.3 mg/kg, Mg - up to 3146.7 mg/kg and Ca - up to 3146.7 mg kg.

Significantly higher amounts of K (24000 mg/kg), Ca (26620 mg/kg), Mg (1910 mg/kg), Fe (230 mg/kg), and Mn (1910 mg/kg) were established by Petropoulos et al., 2018 in the cardoon leaves cultivated in southern Greece. Higher values for K (31700-34900 mg/kg), Mg (4500 mg/kg), and Ca (17000 mg/kg) in the leaves of hydroponically grown cardoon plants were also found by Rouphael et al. (2012) and Borgognone et al., (2014). Monti et al. (2008) found that the iron content reached to 655 mg/kg, Mg to 1876 mg/kg, K to 4711 mg/kg, Ca to 27802 mg/kg, P to 1459 mg/kg. The variation between results may be due to cultivation conditions (hydroponic, greenhouse, and field trials) and plant age differences. The above studies refer to young plants and 5-year-old plants (Petropoulos et al., 2018).

Table 6. Heavy metals, micro and macroelements (mg/kg) of cardoon biomass

	Biomass (S1)	Biomass (S2)	Reference	EN ISO 17225-6
Pb	213.0	5.7	5.7-552	<10
Cd	13.4	0.09	0.2-204.1	<0.5
Zn	166.2	28.9	11-640	<100
Cu	37.95	4.8	8.93-250	<20
Fe	183.6	117.9	122-655	-
Mn	16.7	7.5	16.0-1910	-
P	1780.0	888.3	819.0-1459	-
K	15756.3	11596.9	3490-4711	-
Ca	12637.2	11676.3	12606-27802	-
Mg	1373.9	3146.7	1320.0-2488.3	-

The return of ashes from the combustion of biomass to the soil is the most ecological and sustainable disposal method. In this way, a significant part of the plant's macro-and micronutrients returns to the soil, closing the circulation of minerals (Zajac et al., 2018).

The ashes' chemical composition was dominated by the macroelements Ca, Mg, K, and P, which suggests their agricultural use. Simultaneously, the high content of toxic elements, such as Pb and Cd, should be a limiting feature in their use. The ash of biomass must be thoroughly analyzed before its recommendation for fertilizing purposes.

Contaminated biomass has to be treated as a hazardous material, and its incineration has to be done in facilities equipped with filters for the capture of metal oxides.

Ash-forming elements such as Al, Si, Ca, Fe, K, Mg, Na, and P in the biomass are significant

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for any thermochemical conversion process. The relatively high content of alkaline elements can lead to lead to significant slagging and furnace corrosion.

Biomass used as fuel may contain different pollutants in different concentrations. The biomass data concentration on As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V, and Zn varies depending on the biomass type. In the biomass of agricultural origin, these elements may accumulate when grown on contaminated soils or the use of fertilizers. As a result, their biomass concentration varies depending on the type of pollutant, distance from the source, and plant age. Values in the range of 60 to 640 mg/kg for Zn and 0.1 to 6.6 mg/kg for Cd are determined (Kajda-Szczesniak, 2014).

A small part of the elements is retained in the bottom ash during combustion, while a more significant amount is carried away along with the volatile ash. Non-volatile elements such as Fe, Cr, Cu, and Al form stable oxides, which are retained by coarser ash particles. Combustible metals (Cd, Pb, and Zn) evaporate during combustion, controlled mainly by fine dust particles. As a result, a significant part of the heavy metals and the fine dust particles are carried away with the gases through the chimney. The chlorine present in the biomass leads to a higher evaporation rate of volatile metals, which forms chlorides and oxides. Cd and Pb form $CdCl_2$ and $PbCl_2$ during combustion. Zn can also evaporate as chloride, but a significant amount remains in the ash from combustion due to a stable oxide form formation. In the industrial combustion of biomass from fuel, heavy metal emissions are controlled mainly by minimizing dust emissions. Furthermore, steps have been proposed to use adsorbent materials, such as alumina, kaolinite, bauxite, etc., to inhibit heavy metals' evaporation and retention in the fuel ash.

CONCLUSIONS

Based on the results obtained, the following important conclusions can be made:

1. The cardoon is a tolerant plant to heavy metals and can be grown in heavy metal polluted soils (2671.6 mg/kg Zn, 2694.8 mg/kg Pb, and 84.5 mg/kg Cd) and can be successfully used in the phytoremediation of heavy metal polluted soils.
2. The heavy metals distribution has a selective character that in cardoon decreases in the following order: roots > leaves.
3. The studied biomass of cardoon grown on contaminated soils is of high quality (high content of carbon and hydrogen, and low content of ash, nitrogen, chlorine, and sulfur) and high energy potential.
4. The content of heavy metals in the biomass of cardoon grown on contaminated soils is significantly higher and exceeds the limit values according to the standard ISO 17225-6:2014. Biomass of cardoon from contaminated soils could be used as a source of energy if biomass burning occurs in power plants equipped with purification systems to control dust emissions.

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