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MISCANTHUS X GIGANTEUS AS A BIOFUEL CROP FOR PHYTOREMEDIATION OF HEAVY METAL CONTAMINATED SOILS

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Abstract

There has been carried out comparative research, which allows determining the quantities and the depots of accumulation of heavy metals, macro, and microelements in the vegetative organs of Miscanthus x giganteus, 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, 3.5, and 15 km) from the source of pollution. Macronutrients (N, P, K, Mg, Ca), microelements (Fe, Mn, Cu), and heavy metal (Cd, Pb, Zn) concentrations in plant materials (roots, rhizomes, stems, and leaves) were determined during the three-year research period, two harvest periods (autumn, spring) per year. Heating value, ultimate and proximate analyses were evaluated at the end of the second growing season. Miscanthus x giganteus is tolerant towards heavy metals and can be grown on highly contaminated soils (2671.6 mg/kg of Zn, 2694.8 mg/kg of Pb, and 84.8 mg/kg of Cd). The depot for accumulation follows the order: roots>stems>leaves>rhizomes. The high concentration of heavy metals in the roots and rhizomes and the low translocation factor indicate the possibility of Miscanthus x giganteus to be used in phytostabilization.
The obtained results have shown that Miscanthus x giganteus can be a significant source of good quality raw material in the production of solids biofuels. The biomass is of good quality (high carbon (47.85-49.92%) and hydrogen (5.37-5.59%) content, and low ash (3.18-3.26%), nitrogen (0.05-0.1%), chlorine (0.056-0.085%), and sulphur (0.006-0.048%) content and high energy potential (17.38-18.32 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 Miscanthus x giganteus grown on heavily contaminated soils is significantly higher and exceeds the limit values according to the standard ISO 17225-6:2014. Biomass of Miscanthus x giganteus 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, heavy metals, Miscanthus x giganteus, phytoremediation, polluted soils.*

INTRODUCTION

Miscanthus x giganteus is a perennial crop of the Poaceae family to which there has been considerable interest in recent years. *Miscanthus* x *giganteus* is a sterile hybrid between *M. sinensis* and *M. sacchariflorus*, propagating vegetatively through its rhizomes. It is grown as an ornamental and energy crop for biofuel production. In the United States (Colorado and California), it is mainly used for decorative purposes, while in Europe, it is grown as an energy crop and for biofuel. In Europe, the areas with *Miscanthus* are still small, and it is cultivated on 43,000 ha (ABIOM, 2016). Approximately 20,000 ha (Lewandowski et al., 2018) are located mainly in the United Kingdom, Germany, and France, with suitable conditions for Miscanthus growth.

The cultivation of *Miscanthus* in Bulgaria started 5-6 years ago with planting material, and a complete technology for propagation and cultivation has been developed.

The plant is characterized by high biomass production, cold tolerance, C4 photosynthesis, non-invasiveness, does not require fertilizers and herbicides, and is easy to harvest (Jorgensen, 2011; Robson et al., 2012). The *Miscanthus* x *giganteus* can be harvested from November (after the early frosts) until the next growing season (March - April). In general, early harvest increases the yield per hectare to maximum, while late harvest leads to a decrease (Lewandowski et al., 2003; Zub et al., 2011). Due to falling leaves and stems, yields decrease by an average of 33-38% from October to February (Dzeletovic et al., 2014). The main use of energy from *Miscanthus* biomass is for direct combustion, but the crop also has significant potential in producing second-generation biofuels (Bilandzija et al., 2017). 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 biofuel crops for phytoremediation of heavy metal contaminated soils is of increasing interest (Pidlisnyuk et al., 2013). The main reason for this is the increase in demand for biomass as an alternative energy source, as well as the possibility of remediation of contaminated soils. Energy crops include fast-growing varieties of trees and annual and perennial grasses. Among perennial grasses, *Miscanthus* is considered the most promising biofuel plant. Preliminary studies have shown that Miscanthus can be used for phytoremediation of contaminated land after the Chernobyl disaster in Ukraine and contaminated soils from mining in Slovakia (Hauptvogl et al., 2020). The use of *Miscanthus* biomass for energy production seems promising in terms of the costs for phytoremediation and can find actual application in practice compared to the use of expensive conventional methods. Studies have shown that the utilization of biomass obtained as a source of energy is profitable and can make the phytoremediation process profitable (Dornburg et al., 2005).

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 important properties of biomass include proximate analysis, ultimate analysis, heating value (Imam and Capareda, 2012), lignocellulosic composition, and content of micro and macroelements. The standards for solid fuels CEN/TS 14961(2005) and ISO 17225-6(2014) specify the values for Miscanthus x giganteus and other types of agricultural and forest biomass when burned as biofuel. The standards are based on studies conducted in Sweden, Finland, the Netherlands, and Germany. The characteristics of biomass are influenced by its origin, and there is a great variety in the properties of fuels (Garcia et al., 2012).

Insufficient is the information available on the potential of *Miscanthus* for accumulation of heavy metals and its potential for use for phytoremediation. There are no comprehensive studies on the relationship between the total content of heavy metals in the soil, their uptake by the *Miscanthus* biomass and quality of biomass as a biofuel when growing *Miscanthus* on soils with different degrees of heavy metal pollution.

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 *Miscanthus*, the quality of *Miscanthus* 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 an agricultural field contaminated by Zn, Pb, and Cd, situated at different distances (0.5, 3.5, and 15.0 km) from the source of pollution, the NFMW (Non-Ferrous Metal Works) near Plovdiv, Bulgaria. Characteristics of soils are shown in Table 1. The soils used in this experiment were slightly alkalic, with moderate content of organic matter and essential nutrients (N, P, and K). The pseudo-total content of Zn, Pb, and Cd are extremely high (2671.6 mg/kg Zn, 2694.8 mg/kg Pb, and 84.5 mg/kg Cd, respectively) and exceeds the maximum permissible concentrations (320 mg/kg Zn, 100 mg/kg Pb and 2.0 mg/kg Cd) in soil 1 (0.5 km from NFMW).

The rapidly-growing energy crop *Miscanthus × giganteus* was investigated. The field tests were set after the block method in four replications. The size of the test parcel was 100 m^2. The plants were grown using the conventional technology on areas located at different distances (0.5 km, 3.5 km, and 15 km) from the source of contamination - NFMW Plovdiv. Five plants from each replication were used in the analysis.

The harvest was carried out in autumn and spring when the plants were two years old. The plants were gathered, and the contents of heavy metals, macro, and microelements in their different parts - roots, rhizomes, stems, and leaves, were analysed separately at two harvest periods (autumn and spring). Samples from the rhizomes, roots, stems, and leaves were dried at room temperature to obtain an air-dry mass and then dried at 105°C.

The pseudo-total composition of metals in soils was determined in accordance with ISO 11466. The available (mobile) heavy metals contents were extracted by a DTPA solution (ISO 14780).

The plant samples were treated by the method of microwave mineralization. To determine the heavy metals, micro- and macro elements content in the plant and soil samples, an inductively coupled emission spectrometer (Jobin Yvon Horiba "ULTIMA 2", France) was used.

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 analyser (Elementar GmbH, Germany) (BDS EN ISO 16948:2015). The O content was calculated by difference.

Table 1. Characterization of the soils

Parameter	Soil 1 (0.5 km)	Soil 2 (3.5 km)	Soil 3 (15 km)
pH	7.6	7.6	7.5
Organic carbon, %	3.99	2.24	1.54
N Kjeldal, %	0.24	0.22	0.23
Pseudo-total P, mg/kg	617.2	655.9	1221.1
Pseudo-total K, mg/kg	6108,7	9165.3	9630.8
Pseudo-total Pb, mg/kg	2694.8	186.3	64.1
DTPA-extractable Pb, mg/kg	1088.2	40.5	27.7
Pseudo-total Zn, mg/kg	2671.6	308.3	141.1
DTPA-extractable Zn, mg/kg	249.0	27.4	8.8
Pseudo-total Cd, mg/kg	84.5	4.0	2.1
DTPA-extractable Cd, mg/kg	64.0	0.75	0.67

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

RESULTS AND DISCUSSIONS

Accumulation of heavy metals in vegetative organs of Miscanthus x giganteus

To clarify the issues of absorption, accumulation, and distribution of heavy metals in vegetative organs of *Miscanthus* x *giganteus* were analyzed samples of rhizomes, roots, stems, and leaves. Table 2 presents the results obtained for the content of heavy metals in the vegetative organs of the study crop at autumn harvest.

Considerably higher amounts were established in the roots of *Miscanthus* x *giganteus* compared to the aboveground parts. The content of Pb in the roots of *Miscanthus* grown at 0.5 km from NFMW reached to 232.7 mg/kg, Zn - 331.8 mg/kg and Cd - 66.9 mg/kg, whereas in the rhizomes Pb reached to 64.9 mg/kg, Zn - 74.0 mg/kg and Cd - 11.2 mg/kg.

Table 2. Content of heavy metals (mg/kg) in vegetative organs of Miscanthus x giganteus

Element	Rhizomes	Roots	Stems	Leaves
S1Pb	64.9	232.7	109.2	93.0
S1Cd	11.2	66.9	5.7	2.1
S1Zn	74.0	331.8	168.4	120.4
S2Pb	4.0	9.8	1.3	3.1
S2Cd	0.39	1.4	0.5	0.2
S2Zn	9.7	38.4	30.7	18.5
S3Pb	0.25	4.9	0.47	0.83
S3Cd	0.04	0.48	0.06	0.02
S3Zn	9.5	36.4	14.9	11.6

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. This is consistent with the results obtained by Fernando and Oliveira (2004), who found that metals accumulate primarily in the underground parts of *Miscanthus* x *giganteus* rather than in the aboveground parts.

The heavy metals contents in the stems and leaves of the *Miscanthus* were considerably lower than those in the root system, which showed that their movement through the conductive system was strongly restricted. The content of Pb in the stems of *Miscanthus* grown at 0.5 km from NFMW reached 109.2 mg/kg, Zn - 168.4 mg/kg, and Cd - 5.7 mg/kg. The content of Pb in the leaves of *Miscanthus* grown at 0.5 km from NFMW reached 93.0 mg/kg, Zn - 120.4 mg/kg, and Cd - 2.1 mg/kg.

The obtained results show that the content of Pb in the aboveground parts of *Miscanthus* x *giganteus* is low despite the moderate level of bioavailable forms of Pb in the soil. The studies of Pogrzeba et al. (2011, 2013) show that the uptake of metals strongly depends on the level of accessible forms. In the cultivation of *Miscanthus* x *giganteus*, 2 mg/kg Pb, 0.3 mg/kg Cd and 25 mg/kg Zn are accumulated on clean soils, while at cultivation on contaminated soils - up to 200 mg/kg Pb, 5 mg/kg Cd and 700 mg/kg Zn. Barbu et al. (2009, 2010) found that there is a correlation between the Pb content of the aboveground parts of *Miscanthus* x *giganteus* and the Pb content in the soil. Barbu et al., (2009, 2010) found that the number of accumulated metals in leaves and stems of *Miscanthus* x *giganteus*, when grown on contaminated soil (680 mg/kg Pb and 13 mg/kg Cd), is very low. Similar results are obtained by Nsanganwimana et al. (2015), who found that, despite the high content of Pb in the soil, plants accumulate moderate amounts of this element in their aboveground mass, which may be due to the accumulation of Pb in the roots of the plant.

The Translocation Factor (TF) provides information on the ability of plants to digest absorb heavy metals through the underground parts (roots and rhizomes) and to move them to the aboveground mass (stems and leaves). The obtained results show that, concerning Pb, plants' translocation factor varies from 0.25 to 0.68, for Cd from 0.10 to 0.39, and Zn from 0.58 to 1.02.

The effectiveness of phytoremediation is also determined by the bioconcentration factor (BCF), (McGrath and Zhao, 2003). BCF root is a ratio of the content of heavy metals in plant underground (rhizomes and roots) to soil content ($BCF_{underground}$ = $[Metal]_{underground}$ / $[Metal]_{soils}$). The obtained results show that this ratio varies from 0.07 to 0.11 for Pb, from 0.78 to 1.73 for Cd, and from 0.15 to 0.32 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 ($BCF_{aboveground}$=$[Metal]_{aboveground}$/$[Metal]_{soils}$) and is a measure of the plant's ability to digest and move the metals to the aboveground mass, which can be easily harvested. In hyperaccumulators, the BCF factor is higher than one, and in some cases, it may reach 50-100 (McGrath and Zhao, 2003).

The obtained results show that, concerning Pb, the bioconcentration factor for plants varies from 0.02 to 0.08, for Cd from 0.09 to 0.26, and Zn from 0.11 to 0.19. The results obtained show that BCF is higher for Zn and Cd than for Pb. Higher values for Zn and Cd are probably a consequence of these elements' more remarkable ability to accumulate in the aboveground mass than in the roots, which is consistent with the results of Korzeniowska et al. (2011) and Yoon et al. (2006). According to McGrath and Zhao (2003), the BCF value for the aboveground parts of the accumulator plants should be higher than that of the plant roots and should exceed 1. The study results show that *Miscanthus* x *giganteus* can be classified as an accumulator type for Cd. The $BCF_{underground}$ for Cd varies from 0.92 to 2.01, whereas BCF aboveground - from 0.09 to 0.78.

Table 3. Translocation factor (TF) and bioconcentration coefficients (BCF underground, BCF aboveground) of *Miscanthus* x *giganteus*

Soil	Coefficient	Pb	Cd	Zn
S1	TF	0.68	0.099	0.71
S1	BCF under	0.11	0.92	0.15
S1	BCF above	0.08	0.09	0.11
S2	TF	0.31	0.39	1.02
S2	BCF under	0.07	2.01	0.16
S2	BCF above	0.02	0.78	0.16
S3	TF	0.25	0.15	0.58
S3	BCF under	0.08	1.73	0.32
S3	BCF above	0.02	0.26	0.19

BCF_{under}=$[Metal]_{under}$/$[Metal]_{soil,}$ TF=$[Metal]_{above}$/$[Metal]_{under)}$,
BCF_{above}=$[Metal]_{shove}$/$[Metal]_{soil}$

There is a distinct feature in the accumulation of The *Miscanthus* x *giganteus* accumulates a moderate amount of heavy metals in the leaves and has a relatively lower potential for phytoextraction.

According to Pidlisnyuk et al. (2013) and Kocon et al. (2012), *Miscanthus* x *giganteus* can be grown on contaminated soils which are not contaminated with a high concentration of metals.

Miscanthus x *giganteus* accumulates heavy metals through its root system, and most of them are retained by the roots. The quantity of heavy metals in the stems and leaves 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 *Miscanthus* is a crop that is 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 *Miscanthus* x *giganteus* 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, as opposed to fixed carbon (FC), carbon (C), hydrogen (H) and lower heating value (LHV), the higher levels of which improve the quality of the biomass when it comes to direct combustion.

The results obtained for the *Miscanthus* x *giganteus* biomass grown at a different distance from NFMW at spring harvest are presented in Tables 4, 5, and 6. The values of the biomass's main parameters are compared with the requirements of the standards CEN/TS 14961 and ISO 17225-6 and the data from other authors for the analysis of the *Miscanthus* biomass grown in different countries.

The term calorific value refers to the energy content of biomass and characterizes biomass as a possible fuel resource. The calorific value can be expressed by higher and lower heating values (McKendry, 2002; Garcia et al., 2012). According to CEN/TS 14961, the standard for solid fuels for HHV and LHV is 19.8 MJ/kg and 18.4 MJ/kg, respectively.

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 15.31 MJ/kg (Serbia, Cvetkovic et al., 2016) to 17.25 MJ/kg (Croatia, Jurisic et al., 2014). This study shows that the net heat of combustion done on a dry basis varies from 17.45 to 18.32 MJ/kg. Soil contamination does not affect LHV, with the highest values being obtained for biomass grown on heavily contaminated soils that comply with the standard CEN/TS 14961. The obtained results are higher than the presented data for Serbia, Croatia, Spain, the United Kingdom and France (Table 4).

According to this parameter in the standard CEN/TS 14961, *Miscanthus* biomass is characterized as a valuable energy raw material suitable for use in the combustion process.

Table 4. Proximate analyses and lower heating value of *Miscanthus* x *giganteus* biomass

Parameter	Moisture, %	Ash, %	FC, %	VM, %	LHV, MJ/kg
S1	10.38	3.18	8.51	88.31	18.32
S2	8.21	3.26	11.49	85.25	17.38
S3	8.12	4.92	9.99	85.09	17.45
Reference	8.30-8.60	1.50 - 9.60	9.50 - 18.97	74.40-86.52	15.31-17.25
CEN / TS 14961	-	-	-	-	18.4
ISO 17225-6	≤10	≤4	-	-	-

Heating values decrease with higher moisture content, with higher levels leading to lower combustion temperatures and affecting quality (Garcia et al., 2012).

In general, moisture can vary considerably and is an undesirable ingredient in any fuel (Obernberger and Thek, 2004). The moisture content is influenced by the climatic conditions and the period of biomass harvesting. If the average moisture content of M x giganteus biomass is less than 20%, it is considered that the application of a technological process of drying is not necessary before harvesting. Lewandowski and Heinz (2003) and Borkowska and Molas (2013) determined that biomass harvested in the spring is associated with lower moisture content (57.43% - 64.11%) compared to the autumn harvest. The lower moisture content of the spring harvest shows the potential for storing the harvested biomass without the need for additional drying, which is favourable for the energy balance and the economic efficiency of biomass production.

The results from this study show that the moisture content at spring harvest varies from

8.12 to 10.38%, with higher values reported for the biomass of *Miscanthus* grown on contaminated soil, which is by the standard ISO 17225-6:2014 (≤10) (Table 4).

Based on the data presented in Table 4, can conclude that the average moisture content of slightly contaminated and uncontaminated soil is similar to the values obtained in Poland (8.60%) and Germany (8.30%) (Werle et al., 2018).

The content of fixed carbon is considered a positive property of biomass, representing the amount of energy released from a certain amount of biomass (Garcia et al., 2012; Jurisic et al., 2017). Higher fixed carbon values affect the quality of biomass due to the higher heating values (McKendry, 2002; Obernberger and Thek, 2004). 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 (McKendry et al., 2002; Khodier et al., 2012). CEN/TS 14961 and ISO 17225-6 do not specify a value for fixed carbon.

Studies by Bilandzija et al. (2017) show that fixed carbon is not significantly affected by the harvesting season or fertilization, and the average value of this parameter is 9.31%. According to the literature, the fixed carbon in the *M.* x *giganteus* biomass is between 9.5% and 14.0% (Vassilev et al., 2010; Jegurim, 2010; Howaniec and Smolinski, 2011). The results show that the fixed carbon varies from 8.51 to 11.49%, with the lowest values found in the biomass of *Miscanthus* grown on highly contaminated soil. The obtained values for fixed carbon in the *Miscanthus* biomass from slightly contaminated and uncontaminated soil are in accordance with the results from other authors. In contrast, its content in *Miscanthus* from heavily contaminated soils is lower.

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, 2011). Hodgson et al. (2010) and Baxter et al. (2014) determined that higher-quality biomass with lower ash content is obtained by growing *Miscanthus* without fertilization. Lewandowski and Heinz (2003) decided that harvest postponing from autumn to spring leads to reducing ash content.

The results obtained show that the ash content varies from 3.18 to 4.92%. The lowest values are found for biomass grown in the heavily contaminated soil (S1). According to CEN/TS 14961, the ash content of *Miscanthus* x *giganteus* biomass must be ≤ 4. According to the standard for solid fuels EN ISO 17225-6, the ash content for non-wood pellets can vary from 6 to 10%, while for non-wood pellets from *Miscanthus* it should not be higher than 4%. The biomass from the heavily contaminated (S1) and slightly contaminated area (S2) meets the standard, while from the uncontaminated area (S3), it slightly exceeds the permissible value. A probable reason for the higher ash content in *Miscanthus* from the uncontaminated soil is the higher content of macroelements in plant biomass. According to the literature data, the ash content is between 1.4% and 9.6% (Table 4).

Table 5. Ultimate analysis of *Miscanthus* x *giganteus* biomass

	N, %	C, %	S, %	H, %	O, %	Cl, %
S1	0.09	49.92	0.006	5.37	41.44	0.056
S2	0.05	48.27	0.03	5.59	42.83	0.085
S3	0.1	47.85	0.048	5.47	41.66	0.058
Ref.	0.10-2.15	45.40-48.75	0.07-0.2	3.92-7.32	41.69-46.76	-
CEN/TS 14961	0.7	49	0.2	6.4	44	-
ISO 17225-6	≤0.5	-	≤0.5	-	-	≤0.08

The studied biomass from *Miscanthus* grown on soils with different degrees of contamination has qualities suitable for direct combustion. With regard to the solid fuel standard, the ash content is within 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 (C_xH_y gases, CO, or H_2) and non-combustible gases (CO_2, SO_2, or NO_x) (Garcia et al., 2012). A high percentage of volatile matter is one of the characteristics of biomass (about 75%, which can reach 90%, Khan et al., 2009), reducing the energy value (Grubor et al., 2015; Quaak et al., 1999). It was found that the content of volatile matter is not affected by the harvesting season, as well as by fertilization, and the average value of volatile matter reaches 88.88%. Khodier et al. (2012) and Nhuchhen and Salam (2012) determined that the volatile matter content in *M.* x *giganteus* biomass ranges from 70.7% to 87.2%. CEN/TS 14961 and EN ISO 17225-6 do not specify a volatile matter rate in *M.* x *giganteus*. The results obtained show that volatile matters vary from 85.09% to 88.31%, with the highest values found in the biomass of *Miscanthus* grown on highly contaminated soil. The values for volatile matters are in line with the biomass results from Croatia (86.52%). A comparison with studies conducted in Spain, the United Kingdom, and France shows that *Miscanthus* x *giganteus* grown in Bulgaria has a higher volatile matter content.

Table 5 presents the ultimate analysis of *Miscanthus* x *giganteus* grown on soils with different degrees of heavy metal contamination in Bulgaria. The values of the ultimate analysis are compared with the requirements of the standards CEN/TS 14961 and ISO 17225-6 and the data from other authors for the analysis of the *Miscanthus* biomass grown in different countries. The energy value is negatively affected by the oxygen content. Jegurim et al. (2010), Howaniec and Smolinski (2011), and Bilandzija et al. (2017) examined the oxygen content of *Miscanthus* × *giganteus* biomass and determined values ranging from 31.3 to 49.3%. The established values for oxygen of 46.3% are within the previous studies. 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 (Obernberger et al., 2006). Organically bound O provides the part of O required for the combustion process, and O must be added by air injection (Mantineo et al., 2009). Higher C and H content lead to higher HHV. According to CEN/TS 14961 for solid fuels, the values for C, H, O are 49%, 6.4%, and 44%, respectively.

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 47.85 to 49.92%, with the highest values found for the biomass of *Miscanthus* from contaminated soil. According to the literature, the carbon content ranges from 45.40 to 48.75% (Table 5), this is in line with this study's results.

The content of total hydrogen varies from 5.37 in heavily contaminated soil to 5.59% in slightly contaminated soil. According to the literature, the hydrogen content varies widely (from 3.92 to 7.32) (Table 5). Similar results similar were determined in Ireland (5.38%, France (5.70%), United Kingdom (5.98%), higher in Serbia (6.11%) and Spain (6.30%), Poland (7.32%) and Germany (7.28%), and lower in Croatia (3.98%).

The oxygen content varies from 41.44 to 42.83%. Slight differences were found in the biomass's oxygen content between the tested plants from the areas with different degrees of contamination, as lower values were found for *Miscanthus* from the highly contaminated soil. According to the literature, O's content varies from 35.52% to 46.80% (Table 5). Similar results were determined in the United Kingdom (41.69%) and higher in France (44.80%), Poland (44.25%), Germany (45.17%) and Spain (46.42%) and Croatia (46.76%).

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 (Obernberger and Thek, 2004). Sulfur is the element with a minor presence in biomass, but nitrogen is a critical element for the environment (Garcia et al., 2012; Saez Angulo and Martínez García, 2001). 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, 1989; Obernberger et al, 2006). According to CEN/TS 14961, the limit for N is 0.7%, and for S is 0.2%.

The total nitrogen content varies from 0.05% in slightly contaminated soil to 0.09% in heavily contaminated soil and 0.1% in uncontaminated soil, at a nitrogen rate of 0.5%. The content of total sulfur varies from 0.006% for highly contaminated soil (S1) to 0.03% for slightly contaminated soil (S2) and 0.048% for uncontaminated soil (S3), with a sulfur rate of 0.05%. The values obtained are below the permissible values for the limit for solid fuels. According to the literature data, the sulfur content in biomass varies from 0.06% to 0.2% (Collura et al., 2006; Jeguirim et al., 2010). 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 (0.1% to 2.15%), (Table 5), (Jegurim et al., 2010; Garcia et al., 2012; Moss et al., 2013; Bilandzija et al., 2017). The results obtained are similar for sulphur. *Miscanthus* x *giganteus*, grown in Bulgaria, despite the soil contamination, has a lower content of nitrogen and sulphur than *Miscanthus*, produced in Spain (0.1%), Serbia (0.3%), Ireland (0.29%), Croatia (0.48%), France (1.1%), United Kingdom (1.11%), Poland (1.38%) and Germany (2.15%). It was found that the content of elements in biomass is influenced by the harvesting season and treatment of fertilizers. Postponing the harvesting season from autumn to spring had a positive effect on the quality of biomass due to the increased C content and lower content of O, N, and S. A higher C content in the later harvest was determined by Baxter et al. (2014). Lewandowski and Heinz (2003) also determined a positive effect of spring harvest on reducing N and S content. Spring harvest is associated with a higher H content compared to the autumn harvest. Fertilization has a negative effect on the fuel properties of biomass due to the lowest determined content of C and H. Studies by Baxter et al. (2014) show that the quality of biomass is reduced due to nitrogen fertilization.

Table 6 presents the results for the content of heavy metals, micro and macro elements in the biomass of *Miscanthus* x *giganteus* at spring harvest, grown on soils with different degrees of heavy metal contamination in Bulgaria and typical values of CEN/TS 14961 for solid fuels. Statistically significant differences were found when comparing heavy metal concentration in plant shoots harvested during autumn and spring. Spring harvest of *Miscanthus* causes increases in heavy metals content of the biomass. The spring lead concentration was about tenfold lower when compared to the autumn harvest. Cadmium and zinc concentrations were three and tenfold higher when compared to autumn harvest, respectively. 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 the possibility for 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 analysed 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 for any thermochemical conversion process. The relatively high content of alkaline elements can lead to serious technical problems when used as a raw material for energy production.

Alkali metals are generally thought to be the main cause of slagging, fouling and sintering (Cuiping et al., 2004). Suppose the values obtained for *Miscanthus* x *giganteus* grown in Bulgaria are compared with CEN/TS 14961 for solid fuels. In that case, it is established that the values for solid fuels, it is established that the values of iron, and calcium, are fully compatible with the limit; potassium, magnesium, nickel, and chromium are lower. At the same time, copper, zinc, lead, and cadmium are significantly higher.

Table 6. Heavy metals, micro and macro elements (mg/kg) of *Miscanthus* x *giganteus* biomass

	S1	S2	S3	Reference	Standard
Pb	1070.7	42.0	6.3	2-200	≤10*
Cd	15.7	0.76	0.05	0.1-6.6	≤0.5*
Zn	1182.5	115.9	20.3	20.1-700	≤100*
Cu	72.3	4.2	2.4	2.5-5.3	≤20*
Fe	309.9	76.6	330.3	221.9	40-400**
Mn	49.4	65.0	53.5	74.6-502	-
P	116.4	212.2	286.3	-	-
Cr	0.82	0.79	0.55	22.7-34.6	≤50*
Ni	0.79	0.70	0.77	10.2-12.5	≤10*
Ca	2768	2394	3004	1615-4508	900-3000**
Mg	163.2	218.2	429.0	479-703	300-900**
K	266.6	304.2	657.8	819-3700	1000-1100**
Al	90.2	51.0	183.0	-	-

*EN ISO 17225-6, **CEN/TS 14961

The combustion of biomass with higher macroelements content can lead to significant slagging and furnace corrosion (Bilandzija et al., 2017; Cassida et al., 2005).

Significantly lower results are obtained for macro elements in plant biomass from contaminated soils (S1) compared to slightly contaminated (S2) and uncontaminated soils (S3). The established values for contaminated and uncontaminated soils are by the results published by other authors. Bilandzija et al. (2017) found that the sodium content varies from 63.9 to 90.0 mg/kg, Mg from 467.7 to 482.3 mg/kg, K from 833.6 to 887.2 mg/kg, and Ca from 1802 to 1956 mg/kg depending on the time of harvesting. The differences in the content of the studied elements are probably due to the content of the elements in the soil and the time of harvesting.

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 (Krzyzak et al., 2017). 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. Volatile metals (Cd, Pb, and Zn) evaporate during combustion, mostly controlled 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 presence of chlorine 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 the formation of a stable oxide form. 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 *Miscanthus* x *giganteus* 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 *Miscanthus* x *giganteus* decreases in the following order: roots>stems>leaves>rhizomes.
3. The moisture content of biomass in *Miscanthus* is low and is within the standard.
4. Ash as an indicator of fuel quality is also low, emphasizing the studied biomass's excellent quality.
5. The studied biomass of *Miscanthus* x *giganteus* grown on contaminated soils is of high quality (high content of carbon and hydrogen, and low content of ash, nitrogen, chlorine, and sulphur) and high energy potential.
6. The content of heavy metals in the biomass of *Miscanthus* x *giganteus* grown on heavily contaminated soils is significantly higher and

exceeds the limit values according to the standard ISO 17225-6:2014. Biomass of *Miscanthus* x *giganteus* from highly 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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REFERENCES

AEBIOM (2016). European biomass association, Statistical report - European bioenergy outlook. Brussels, Belgium.

Barbu, C.H., Pavel, B.P., Sand, C., Pop, M.R. (2009). Miscanthus x giganteus sinensis giganteus' behavour on soil polluted with heavy metals. Metal Elements in Environment, Medicine and Biology, Cluj University Press (Proccedings of 9th International Symposium of Romanian AcademyBranch Cluj-Napoca, 2009, October 16-17, ClujNapoca, Romania, IX, 21.

Barbu, C.H.., Pavel, B.P., Sand, C., Grama, B., Barbu, M.H. (2010). *Miscanthus* x *giganteus sinensis* x *giganteus* Cultivated on Soils Polluted with Heavy Metals - A Valuable Replacement for Coal. Conference Summary Papers, Green Remediation Conference, June 15-17, 2010, University of Massachusetts Amherst, 2.

Baxter, X.C., Darvell, L.I., Jones, J.M., Barraclough, T., Yates, N.E., Shield, I. (2014). Miscanthus combustion properties and variations with Miscanthus agronomy, Fuel, 117 (A), 851-869.

BDS EN ISO 18134-3 (2015). Solid biofuels. Determination of moisture content. Oven dry method. Moisture in general analysis sample

BDS EN ISO 18122 (2015). Solid biofuels. Determination of ash content.

BDS EN ISO 18123 (2015). Solid biofuels.Determination of the content of volatile matter.

BDS EN ISO 16948 (2015). Solid biofuels. Determination of total content of carbon, hydrogen and nitrogen.

BDS EN ISO 18125 (2017). Solid biofuels. Determination of calorific value.

Bilandzija, N., Jurisic, V., Voca, N., Leto, J., Matin, A., Grubor, M., Kricka, T. (2017). Energy Valorization of Miscanthus X Giganteus biomass: A Case study in Croatia, Journal on Processing and Energy in Agriculture, 21(1), 32-36.

Borkowska, H., Molas, R. (2013). Yield comparison of four lignocellulosic perennial energy crop species, Biomass Bioenerg, 51, 145-153.

Cassida K.A., Muir J.P., Hussey M.A., Read J.C., Venuto B.C., Ocumpaugh W.R. (2005). Biofuel component concentrations and yields of switchgrass in South central US environments. Crop Sci., 45, 682-692.

CEN/TC 14961 (2005). Biomass standards - Fuel specifications and classes.

Chaney, R. L., Malik, M., Li, Y. M., Brown, S. L., Brewer, E. P., Angle, J. S. (1997). Phytoremediation of soils metals. Current Opinion in Biotechnology, 8, 279–284.

Ciura, J., Poniedzialek, M., Sekara, A., Jedrszezyk, E. (2005). The possibility of using crops as metal phytoremediants. Polish Journal of Environmental Studies, 14, 17-20.

Clarke, S., Preto, F. (2011). Biomass Burn Characteristics, Factsheet, ISSN 1989-712X.

Collura, S., Azambre, B., Finqueneisel, G., Zimny, T., Weber, J.V. (2006). Miscanthus × Giganteus straw and pellets as sustainable fuels - Combustion and emission tests. Enviro. Chem. Lett., 4 (2), 75-78.

Cvetkovic, O., Pivic, R., Dinic, Z., Maksimovic, J., Trifunovic, S., Dzeletovic, Z. (2016). Hemijska ispitivanja miskantusa gajenog u Srbiji - Potencijalni obnovljiv izvor energije. Zaštita Materijala, 57 (3), 412–417.

Cuiping, L., Chuangzhi, W., Yanyongjie, M., Haitao, H. (2004). Chemical elemental characteristics of biomass fuels in China. Biomass and Bioenergy, 27, 119–130.

Dornburg, V., Faaij, A.P.C. (2005). Cost and CO_2-emission reduction of biomass cascading: methodological aspects and case study of SRF poplar. Climate Change, 71, 373-408.

Dzeletovic, Z., Maksimovic, J., Zivanović I. (2014). Yield of Miscanthus × giganteus during crop establishment at two locations in Serbia. Journal on Processing and Energy in Agriculture, 18 (2), 62–64.

Elbehri, A., Segerstedt, A., Liu, P. (2013). Biofuels and the sustainability challenge: aglobal assessment of sustainability issues, trends and policies for biofuels and related feedstocks. Food and Agriculture Organization of the United Nations (FAO), Rome, Italy.

Fernando, A., Oliveira, J. S. (2004). Effects on growth, productivity and biomass quality of Miscanthus x giganteus of soils contaminated with heavy metals, 2nd World Conference on Biomass for Energy, Industry and Climate Protection, 10-14 May 2004, Rome, Italy, 387-390.

Garcia, R., Pizarro, C., Lavín, A.G., Bueno, J.L. (2012). Characterization of Spanish biomass wastes for energy use, Biore. Technol., 103(1), 249-258.

Grubor M., Kricka T., Voca N., Jurisic V., Bilandzija N., Antonović A., Matin A. (2015). Utilization of cereal straw for green energy production (in Croatian). Krmiva, 57, 63-68.

Hauptvogl, H., Kotrla, M., Prcik, M., Paukova, Z., Kovacik, M., Losak, T. (2020). Review Phytoremediation Potential of Fast-Growing Energy Plants: Challenges and Perspectives – a Review, Pol. J. Environ. Stud., 29 (1), 505-516.

Hodgson, E.M., Fahmi, R., Yates, N., Barraclough, T., Shield, I., Allison, G., Bridgwater, A.V., Donnison, I.S. (2010). Miscanthus as a feedstock for fast-pyrolysis: Does agronomic treatment affect quality?, Biore. Technol., 101(15), 6185-6191.

Howaniec N. and Smoliński A. (2011). Steam gasification of energy crops of high cultivation potential in Poland to hydrogen-rich gas. Int. J. Hydrogen. Energy, 36, 2038-2043.

Imam, T., Capareda, S. (2012). Characterization of bio-oil, syngas and bio-char from switchgrass pyrolysis at various temperatures. Journal of Analytical and Applied Pyrolysis, 93,170-177.

ISO 11466. (1995). Soil Quality-Extraction of Trace Elements Soluble in Aqua Regia.

ISO 14870. (2001). Soil Quality- Exxtraction of Trace Elements by Buffered DTPA Solution.

ISO 17225-6. (2014). Solid biofuels. Fuel specifications and classes. Part 6: Graded non-woody pellets.

Jeguirim, C., Dorge, S., Trouvé, G. (2010). Thermogravimetric analysis and emission characteristics of two energy crops in air atmosphere: Arundo donax and Miscanthus giganthus, Biore. Technol., 101(2), 788-793.

Jorgensen, U. (2011). Benefits versus risks of growing biofuel crops: the case of Miscanthus, Current Opinion in Environmental Sustainability, 3 (1-2), 24-30.

Jurisić V., Voća N., Bilandžija N., Krička T., Antonović A., Grubor M., Matin A., and Kontek M. (2017). Pyrolysis properties of major energy crops in Croatia (in Croatian). 51st Croatian and 11th Int. Symp. Agriculture, February 13-17, Dubrovnik, Croatia.

Jurisic, V., Bilandzija, N., Kricka, T., Leto, J., Matin, A., Kuze, I. (2014). Fuel properties' comparison of allochtonous Miscanthus x giganteus and autochtonous Arundo donax L.: a case study in Croatia, Agric. Conspec. Sci., 79(1), pp 7-11.

Kajda-Szczesniak, M. (2014). Characteristics of ashes from fireplace. Arch. Waste Manag. Environ. Protect. 2014, 16, 73–78.

Khan, A.A., de Jong, W., Jansens, P.J., Spliethoff, H. (2009). Biomass combustion in fluidized bed boilers: Potential problems and remedies, Fuel process technol., 90(1), 21-50.

Khodier, A.H.M., Hussain, T., Simms, N.J., Oakey, J.E., Kigallon, P.J. (2012). Deposit formation and emissions from co-firing Miscanthus with Daw Mill coal: Pilot plant experiments, Fuel, Vol. 101, 53-61.

Kocon, A., Matyka, M. (2012). Phytoextractive potential of Miscanthus giganteus and Sida hermaphrodita growing under moderate pollution of soil with Zn and Pb. Journal of Food, Agriculture and Environment, 10, 1253.

Korzeniowska, J., Stanislawska Glubiak, E., Igras, J. (2011). Applicability of energy crops for metal phytostabilization of soils moderately contaminated with copper, nickel and zinc. J Food Agric Environ, 9(3–4), 693.

Krzyzak, J., Pogrzeba, M., Rusinowski, S., John Clifton-Brown, J., McCalmont, J.P., Kiesel, A., Mangold, A., Mos, M. (2017). Heavy Metal Uptake by Novel Miscanthus Seed-Based Hybrids Cultivated in Heavy Metal Contaminated Soil. Civil and Environmental Engineering Reports, 26 (3), 121-132.

Lewandowski, I. (2018). Bioeconomy Shaping the Transition to a Sustainable, Biobased Economy, ISBN 978-3-319-68151-1,

Lewandowski, I., Clifton-Brown, J.C., Andersson, B., Basch, G., Christian, D.G., Jorgensen, U., Jones, M.B, Riche, A.B., Schwarz, K.U., Tayebi, K., Texerija, F. (2003). Enviroment and harvest time affect the combustion qualities of Miskantus genotypes. Agronomy Journal, 95, 1274–1280.

Lewandowski, I., Heinz, A. (2003). Delayed harvest of Miscanthus - influences on biomass quantity and quality and environmental impacts of energy production, Eur J Agro, 19(1), 45-63.

Mantineo, M., Agosta, G.M. D., Copani, V., Patane, C., Cosentino, S.L. (2009). Biomass yield and energy balance of three perennial crops for energy use in the semi-arid Mediterranean environment, Field Crop Res., 114(2), 204-213.

McGrath, S.P., Zhao, F.J. (2003). Phytoextraction of metals and metalloids from contaminated soils. Curr Opin Biotechnol, 14, 277.

McKendry, P. (2002). Energy production from biomass (part 1): overview of biomass, Bioresource Technol., 83(1), 37-46.

Meehan, P.G., Finnan, J.M., Mc Donnell, K.P. (2013). The effect of harvest date and harvest method on the combustion characteristics of Miscanthus × giganteus, Glob. Change Biol., 5(5), 487-496.

Mos, M., Banks, S.W., Nowakowski, D.J., Robson, P.R.H., Bridgwater, A.V., Donnison, I.S. (2013). Impact of Miscanthus x giganteus senescence times on fast pyrolysis bio-oil quality, Bioresource Technol., 129, No. C, 335-342.

Nhuchhen, D.R., Salam, P.A. (2012). Estimation of higher heating value of biomass from proximate analysis: A new approach, Fuel, 99, 55-63.

Nsanganwimanaa, F., Pourruta, B., Waterlota, C., Louvela, B., Bidara, G., Labidic, S., Fontainec, D. J., Muchemblede, J., Lounès-Hadj Sahraouic, A., Fourriera, H., Douaya, F. (2015). Metal Accumulation and Shoot Yield of Miscanthus x giganteus × Giganteus Growing in Contaminated Agricultural Soils: Insights into Agronomic Practices. Agriculture, Ecosystems and Environment, 213 (3-4), 61-71.

Obernberger, I., Brunner, T., Barnthaler, G. (2006). Chemical properties of solid biofuels - significance and impact: standarisation of solid siofuels in Europe. Biomass and Bioenergy, 30(11), 973-982

Obernberger, I, Thek, G. (2004). Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour, Biomass Bioenerg, 27(6), 653-669.

Pidlisnyuk, V., Erickson, L., Kharchenko, S., Stefanovska, T. (2013). Bioaccumulation in Crops on Fly Ash Disposal Site. J Environ Prot Ecol, 14 (3), 986.

Pogrzeba, M., Krzyzak, J., Sas-Nowosielska, A. (2013). Environmental hazards related to Miscanthus x giganteus cultivation on heavy metal contaminated soil, E3S Web of Conferences DOI: 10.1051, published by EDP Sciences, 2013, 2013012900 1 e3sconf 29006.

Pogrzeba, M., Krzyżak, J., Sas-Nowosielska, A., Majtkowski, W., Małkowski, E., Kita, A. (2011). A heavy metal environmental threat resulting from combustion of biofuels of plant origin. L.I. Simeonov, M. Kochubovski and B. Simeonova (eds.), Environmental Heavy Metal Pollution and Effects on Child Mental Development – Risk Assessment and Prevention Strategies, Springer Science+Business media B.V.

Quaak P., Knoef H., and Stassen H.E., 1999. Energy from biomass: a review of combustion and gasification technologies (23, 1-78). World Bank Publications.

Robson, P., Mos M., Clifton-Brown J., Donnison I. (2012). Phenotypic Variation in Senescence in Miscanthus: Towards Optimising Biomass Quality and Quantity. BioEnergy Research, 5, 95–105.

Saez Angulo, F., Martínez García, J.M., 2001. Emisiones en la combustión de biomasa y el medio ambiente. Energía, 161, 75–83.

Yoon, J., Cao, X., Zhou, Q., Ma, L.Q. (2006). Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Sci Total Environ 368,456-464.

Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G. (2010). An overview of the chemical composition of biomass, Fuel, 89(5), 913-933.

Werle, S., Tran, K., Magdziarz, A., L.ovas, T. (2019). Energy crops for sustainable phytoremediation. Fuel characterization. Energy Procedia, 158, 867-872.

Zajac, G., Szyszlak-Bargłowicz, J., Gołebiowski, W., Szczepanik, M. (2018). Chemical Characteristics of Biomass Ashes, Energies, 11, 2885.

Zub, H.W., Arnoult, S., Brancourt-Hulmel, M. (2011). Key traits for biomass production identified in different Miscanthus species at two harvest dates. Biomass and Bioenergy, 35, 637– 651.