Environmental Science and Pollution Research (2019) 26:2974–2986
https://doi.org/10.1007/s11356-018-3741-0

RESEARCH ARTICLE

The estimation of *Miscanthus×giganteus*' adaptive potential for cultivation on the mining and post-mining lands in Ukraine

Mykola Kharytonov[1] · Valentina Pidlisnyuk[2] · Tatyana Stefanovska[3] · Mykhailo Babenko[1] · Nadia Martynova[4] · Iryna Rula[1]

Received: 9 July 2018 / Accepted: 12 November 2018 / Published online: 30 November 2018

Abstract
The possibility of *Miscanthus×giganteus* cultivation as an energy crop on the different types of mining rocks was studied. It was revealed that a loess-like loam and red-brown clay with the added black soil were the most suitable for plant growing. The yield of dry above-ground biomass ranged from 4.3 to 6.8 t DM ha^{-1} after the first year of cultivation and from 8.9 to 9.7 t DM ha^{-1} after the second year while using these substrates. The application of amendments stimulated the growth and development of plants and increased productivity from 50 to 140%. *M.×giganteus* showed sufficient tolerance and good enough growth on the geochemically active dark-gray schist clay with yield from 2 to 3 t DM ha^{-1} after the first year of cultivation already. For plants grown on the different strata of dark-gray schist clay, the thermal decomposition of the biomass took place in four stages in the temperature range from 30 to 640 °C. The samples grown on stratum 0–20 cm showed the highest reactivity with a peak 30.6%/min at 290 °C. There were differences in the concentrations of determined heavy metals: iron, zinc, copper, and lead in the plant tissues depending on the layer depth of dark-gray schist clay from 0 to 20 cm to 40–60 cm. The relatively limited content of heavy metals in the above-ground biomass was due to the preferential accumulation in the roots.

Keywords *Miscanthus×giganteus* · Phytomeliorated mining rocks · Biologically active agents · Biometric parameters · Productivity · Thermolysis · Heavy metal

Introduction

The energy consumption is growing every year, and mineral reserves are rapidly declining. Anxiety is exacerbated not only by how such high demands can continue to be met by depleted resources, but also by increased greenhouse gas emissions from fossil fuel combustion. Obviously, there is a need for alternative energy sources (Hein 2005; Otepka 2014). Renewable energy, especially from perennial grasses and woody plants, can significantly contribute to the prevention of climate change and to the security of energy supply in the future (Sims et al. 2006; Karp and Sheid 2008; Gasparatosa et al. 2017).

Today bioenergy industry is developing rapidly and its share in the total volume of world primary energy supplies is about 13% (AEBIOM Report 2011). Unfortunately, the pace of bioenergy industry development in Ukraine is significantly behind the world and Europe. Currently, the share of biomass in the total supply of primary energy in the country is no more than 1%. Nevertheless, the prospects for the development of this energy sector are very large (Geletukha et al. 2015, 2016).

Among the fast-growing plants used for biomass production, the most preferable are those which do not require intensive cultivation technologies, are unpretentious to environmental conditions, and show good yield. In the last years among those crops, second-generation *Miscanthus* has become the leading plant in supplying cellulose-rich feedstock for energy production and chemical industry (Powlson et al.

Responsible editor: Elena Maestri

✉ Mykola Kharytonov
kharytonov.m.m@dsau.dp.ua

1 Dnipro State Agrarian and Economic University, Sergey Efremov str., 25, Dnipro 49600, Ukraine

2 Jan Evangelista Purkyne University in Ústí nad Labem, Ústí nad Labem, Czech Republic

3 National University of Life and Environmental Sciences, Kyiv, Ukraine

4 Oles Honchar Dnipro National University, Gagarin av., 72, Dnipro 49010, Ukraine

2005; Heaton et al. 2008; Brosse et al. 2012). The biomass yield of this plant can reach 25 t ha^{-1} after 2 or 3 years of cultivation, making it one of the most productive terrestrial plants in the temperate climate (Christian et al. 2008; Heaton et al. 2010). Recent studies have shown that in Ukraine, depending on climatic conditions, the average yield of dry biomass is some 16–25 t ha^{-1} (Nunn et al. 2017; Gumentyk and Kharytonov 2018), and its calorific values vary within the range of 17.5–18.0 MJ kg^{-1} (Nosko et al. 2015; Ivanyshyn et al. 2018).

Among the few species of the *Miscanthus* genus, Giant Miscanthus (*Miscanthus×giganteus* J.M.Greef et Deuter ex Hodk. et Renvoize) is the most frequently grown crop in bioenergetics plantations. It is a perennial grass with C4 photosynthesis type, triploid spontaneous hybrid between *Miscanthus sacchariflorus* (Maxim.) Hack. and *Miscanthus sinensis* Anderss. Since the hybrid is sterile, there is no threat of its invasion into the natural ecosystems. Reproduction is only vegetative with rhizomes and the vegetative mobility is medium. The plants form friable clumps, which become denser with age.

The culture of this plant requires low input as most of the key nutrients are translocated to the rhizome at the end of the growing season in order to support the next germination.

Miscanthus can be grown at different soil types. It is believed that the plant has the best productivity on well-drained soils with pH ranged between 5.5–7.5 with medium and high fertility levels and possesses a relatively small water demand, which corresponds to an annual precipitation of 600–700 mm. Nevertheless, as the amount of biomass increases, this demand can grow and the water scarcity can lead to lower yields. Biomass productivity also declines on heavy soils (Matyka and Kus 2016).

One of the innovative approaches in sustainable management of polluted soil is a combination of phytotechnology with production of biofuel crops (Pidlisnyuk et al. 2014a, 2016). This allows to restore polluted land and to meet demand for biomass production. One of the main interests of *Miscanthus* application to polluted sites is the restoration of soil diversity and functionality. *Miscanthus×giganteus* shows great promises for growing on contaminated and disturbed soils (Skousen et al. 2012; Wanat et al. 2013; Blanco-Canqu 2016). This plant is a metal tolerant crop which does not transfer much of the pollutants from contaminated soil to aerial parts. Specifically, this feature was demonstrated with respect to Cd, Cr, Cu, Ni, and Pb (Fernando and Oliveira 2004; Arduini et al. 2006; Kocoń and Jurga 2017). In addition, there are prospects for using *Miscanthus* live plants, dry biomass, and biochar obtained from it as an adsorbent for heavy metal removal from wastewaters and soils (Antonkiewicz et al. 2016; Kołodynska et al. 2017; Osman et al. 2017b). Cultivation of *Miscanthus* at the contaminated soils has an important economic benefit, as the biomass produced can be used for production of solid biofuel or bioethanol (Gomes 2012; Xie et al. 2014).

An important qualitative characteristic of biomass is its calorific capacity and efficiency of the combustion process. The study of the features of thermal degradation, reactivity, and kinetics of *Miscanthus* biomass is a major way to understand this process (Kok and Özgür 2013; Cortes and Bridgwater 2015). However, these parameters depend not only on the kind of biomass, but can vary according to the physical and chemical properties of the substrate and the presence of trace elements in it, including heavy metals (Werle et al. 2016; Osman et al. 2017a).

Considering the relative unpretentiousness of *Miscanthus* to environmental conditions, it is important to study the potential of this plant to be cultivated on the different types of mining and post-mining lands. In Ukraine, there are rather big areas of such lands located at the Eastern and South-Eastern industrial parts of the country, requiring revitalization (Eionet NRC Soil 2015). Exploration of the possibility to grow the second generation energy crop *M.×giganteus* on the different mining and post-mining lands with simultaneous production of biomass is very important from scientific and practical points of view.

Materials and methods

The research was carried out for 2 years (2016–2017) at Pokrov land reclamation station of Dnipro State Agrarian and Economic University (Fig. 1), standing at 47°39′N, 34°08′E, with an elevation of 60 m. The station is located in the Dnipropetrovsk region in the steppe zone of Ukraine with moderately continental climate: dry and hot summer and moderate winter. The average long-term air temperature is + 8.5 °C. The hottest month is July with the average temperature of + 22.0 °C, the coldest is January with the average temperature − 4.1 °C. However, during the last 30 years, a gradual increase in the average annual air temperature has been observed. The site is located in the zone of unstable water supply with often prolonged droughts in the summer. The annual rainfall is 465 mm, 274 mm of which belongs to the warm period (April–October) and 191 mm refers to the cold period (November–March).

Pokrov land reclamation station is located in the Nikopol manganese ore deposit. The rocks of this ore basin are presented the holocene, postpliocene, neogene and paleogene deposits (Table 1). These mining rocks are brought to the surface during process of manganese ore mining (Fig. 2). The soil mass was taken off, piled up, and heaped onto the land after the rock was replaced. Substrates formed in this way can be attributed to the category of Technosol, which are soils strongly influenced by human activities, and as a result, their properties and pedogenesis are dominated by technical origin (De Kimpe and Morel 2000).

The main minerals of rocks silty fraction consist of feldspar, calcite, illite, montmorillonite, chlorite, and kaolinite. The X-ray diffractograms of rocks used in the experiment are shown at Fig. 3. The analysis of the spectra indicates that researched rocks have many similarities; however, previous studies (Kharytonov and Resio Espejo 2013) detected differences in the content of two rocks: montmorillonite and illite and their bigger content causes a higher plasticity of green-gray and red-brown clays.

Three experiment variants were established: two model tests and one field test. In the model tests, the rhizomes of *M.×giganteus* were planted in lysimetric containers (Fig. 4). In the first model test, eight diverse rock substrates were used (Fig. 5): (1) loess-like loam (LLL), taken from the board of the quarry (0–150 cm); (2) a rocks mix (RM), which consists of loess-like loam and red-brown clay taken from the board of the quarry (0–150 cm); (3) red-brown clay (RBC) taken from the board of the quarry (0–150 cm); (4) green-gray clay (GGC) taken from the board of the quarry (0–150 cm); (5) black soil (BS) 0–50 cm+green-gray clay (50–150 cm); (6) black soil (0–50 cm)+red-brown clay (50–150 cm); (7) black soil (0–50 cm)+loess-like loam (50–150 cm); and (8) black soil (0–150 cm). The humus content in these substrates varied from 1.05 (RBC) to 1.25% (GGC) and 3.29% (BS). The ratio of humic and fulvic acids was 1.36 for BS and 0.62–0.69 for other substrates. The maximal hygroscopicity level was observed in green-gray clay (20.5%), and the minimal level was in red-brown clay (7.6%). The reserves of easily soluble phosphorus forms were limited.

The second model variant was established with geochemically active dark-gray schist clay (DGSC). The clay was taken from the experimental plot, which has been in the stage of natural overgrowing for four decades. The clay was collected at the three strata of the aeration zone: 0–20 cm, 20–40 cm, and 40–60 cm. Thereafter the clay was poured into the lysimetric containers with a layer of 60 cm, and the sand was the underlying substrate. DGSC is characterized by a certain degree of toxicity and deficiency of organic matter (humus content 0.8–0.9%).

The third experimental variant was about growing *M.× giganteus* in the experimental field plots. The soil in the field was a post-mining land consisted of the mixture of loess-like loam and red-brown clay passed through a long-term phytomelioration stage. The soil humus content was about 1.5%, and the ratio of humic and fulvic acids was 0.2–0.5, which indicates a weak humus accumulation and active destruction of the soil mineral part. In order to determine the impact of amendments to the growth and development parameters of *M.×giganteus*, different amendments were used: mineral fertilizer with a balance of nutrients N_{60}:P_{60}:K_{60} kg ha^{-1}; ash of sunflower husk and sewage sludge in amount 10 t ha^{-1}; mixture of ash and sewage sludge (10 t ha^{-1}); a double dose of sludge (20 t ha^{-1}). All amendments were put into the soil in a dry form once in spring.

For all three experimental variants the biometric parameters and biomass productivity of *Miscanthus* were studied at the end of vegetation season (second part of September). Plant height was measured with a measuring ruler. The stem diameter was determined by caliper at 15 cm height above the ground surface by clamping the caliper onto a random plant tiller. The number of stems per plant was counted as well. Then the above-ground biomass was manually cut till a stable height 10 cm from the land surface and weighed in a wet state. The wet biomass was dried at temperature 30 °C until a constant weight in order to estimate the above-ground dry matter yield.

Soil samples were collected from the lysimetric containers presented with the DGSC three strata of the aeration zone: 0–20 cm, 20–40 cm, and 40–60 cm. The samples were transferred into clean polyethylene bags and were then transported to the laboratory. At the laboratory, each soil sample was air dried at temperature 22–26 °C for several days. Organic debris and other unwanted large particles were handpicked from each

Fig. 1 Pokrov land reclamation station, Dnipropetrovsk region, Ukraine

Table 1 Rock deposits stratigraphy

Age	Depth, m	Name of substrate
Q	0–7	Soils, loess-like loam
N_1SQ	7–12	Red-brown loam and clay
N_1Srm_{2+1}	12–47	Green-gray clay
N_1Srm_1	47–63	Sand-clay deposits
Pg_1ch_1	63–71	Green montmorillonite clay
Pg_1ch_1	> 71	Manganese ore

Q quaternary, N_2 Pliocene, upper (late) Neogene, N_1 Miocene, lower (early) Neogene, Srm_1 lower Sarmat, Srm_2 middle Sarmat, Srm_3 upper Sarmat, Pg_3 Oligocene, upper Palaeogene

sample. The dried samples were homogenized with a mortar to pass through a 2-mm sieve. The samples were labeled appropriately, stored in sealed polythene bags for analysis. For the decomposition of samples, 1 g (dry weight) sample was dissolved with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_20_2) according to the USEPA method 3050B for the analysis of heavy metals and major ions (USEPA 1996). Ammonium-acetate buffer (pH 4.8) was used in appropriate proportion (5 g of soil sample and 50 ml of extractant) to estimate the concentration of mobile forms of heavy metals. After that, the mixtures were closed in flasks and shaken off for 1 h and then filtered. The concentration of mobile and total forms of heavy metals in the filtered solutions was determined using atomic-absorption spectrophotometer S-115 (Ukraine). Heavy metal concentrations in each soil sample were measured three times. Then mean values were calculated.

To determine the heavy metals in the above-ground biomass, dry samples were thoroughly crushed using a laboratory mill. Prior to analyses, the samples were stored in paper bags in a dry and aerated place. In the chemical analysis, certified standard materials were used. In order to determine the content of heavy metals, sample with a weight 2 g each was combusted in a muffle furnace at 450 °C by means of drying method and then dissolved in 5 ml of 6 N spectral purity hydrochloric acid. The content of elements in the obtained mineralized biological material was measured by spectrophotometric analysis at S115 (Ukraine). The received data represented the arithmetic means of three replicates of each sample, their ranges, and standard deviation values.

The calorific value of *Miscanthus* biomass was measured using thermogravimetric analysis. This analysis was carried out for biomass produced at the second experimental variant. The analysis was performed at derivatograph Q-1500D of the "F. Paulik-J. Paulik-L. Erdey" system. The weight of sample used for analysis was 100 mg. The differential mass loss and heating effects were recorded, and the results of the measurements were processed using software package supplied with the device. The samples of biomass were analyzed dynamically at a heating rate of 10 °C/min in an air atmosphere. The reference substance was aluminum oxide.

Data received in experiments accomplished were processed by statistical methods using the software package StatGraphics Plus5 with all tests of significance being made at a type 1 error rate of 5%.

Results and discussion

The experimental variant 1 with different rock substrates

The data received in that experiment showed that the type of rock substrate affects the biometric values *M.×giganteus*. After the first growing season, the difference in height was up to

Fig. 2 The manganese ore opencast mining quarry

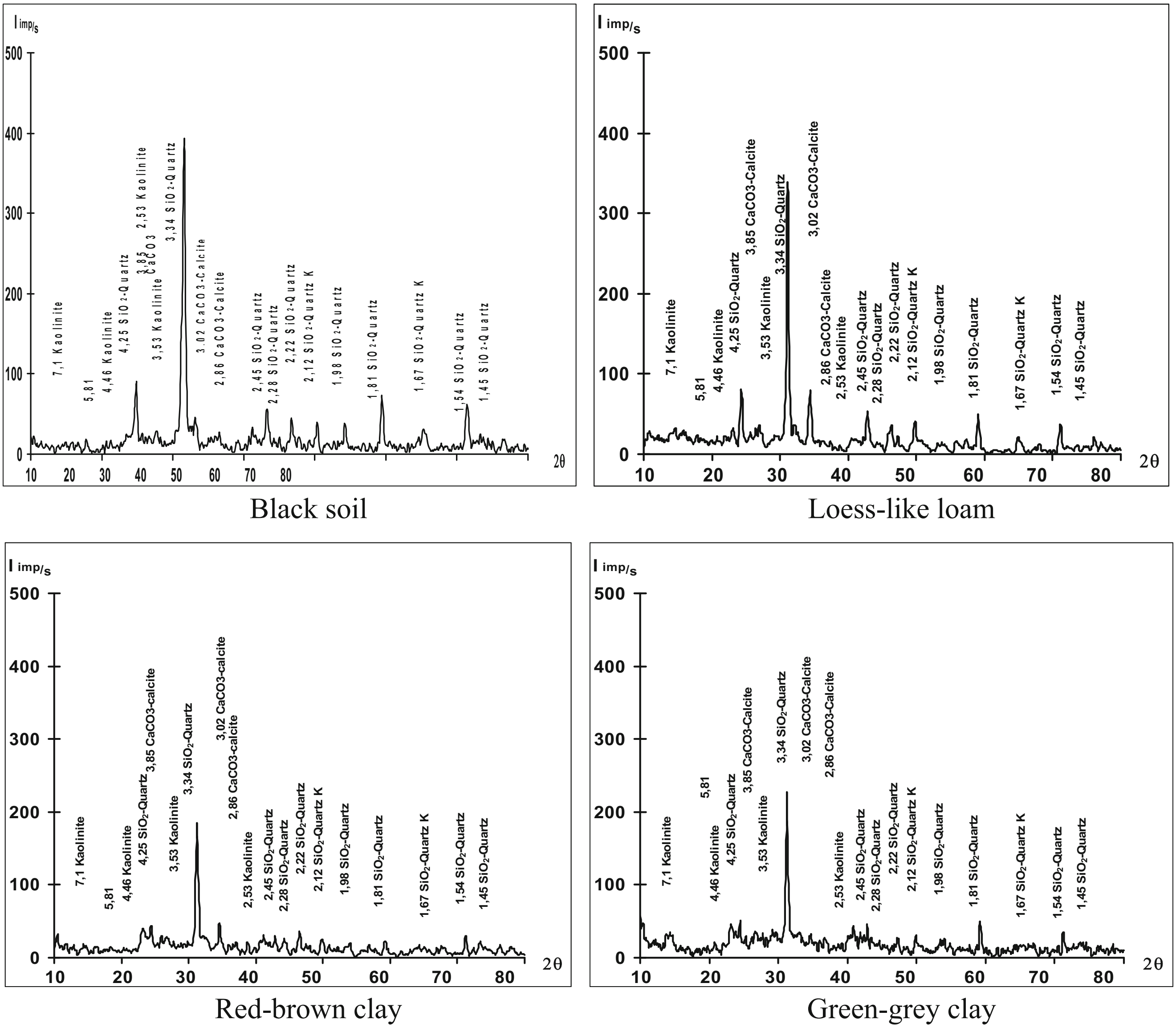


Fig. 3 X-ray diffractograms of majority rocks

Fig. 4 Model experiments with *Miscanthus* at Pokrov land reclamation station

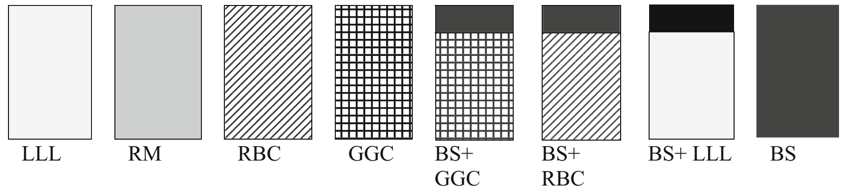


Fig. 5 Models of rock substrates in lysimeters

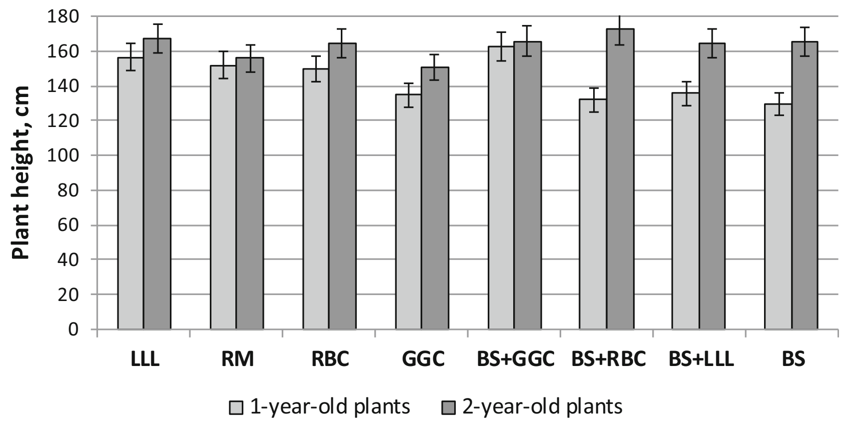


Fig. 6 *Miscanthus* plant height at the end of the first and second vegetation seasons while grown on the different substrates

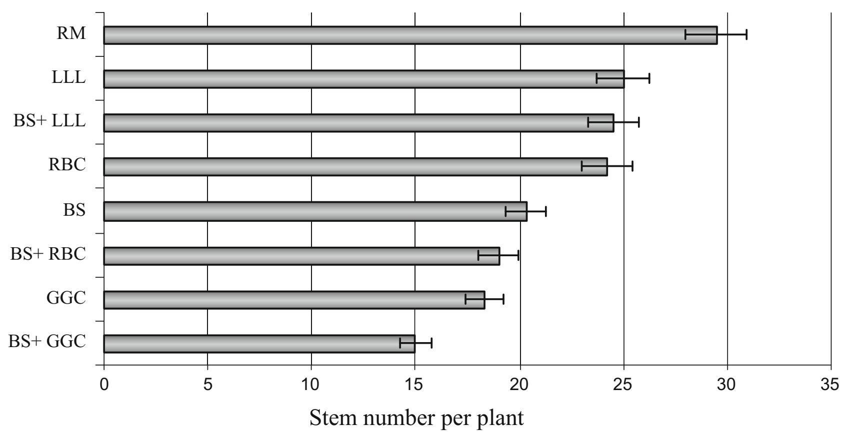


Fig. 7 Stem number for 2-year-old *Miscanthus* plants grown on the different rock substrates, second year of vegetation

33 cm depending on the substrates where the plants were grown, and the lowest value after the first growing season was noted for plants growing on the substrate BS (130 cm). After the second year of cultivation, this ratio was changed. The highest height was recorded for plants grown on the red-brown clay with the addition of black soil (172.5 cm), and the smallest in the variant with green-gray clay (150.8 cm). As shown in Fig. 6, with age, plants were added in growth from 2 to 3% (BS+ GGC and TM) to 20–30% (BS+ LLL, BS, and BS+ RBC).

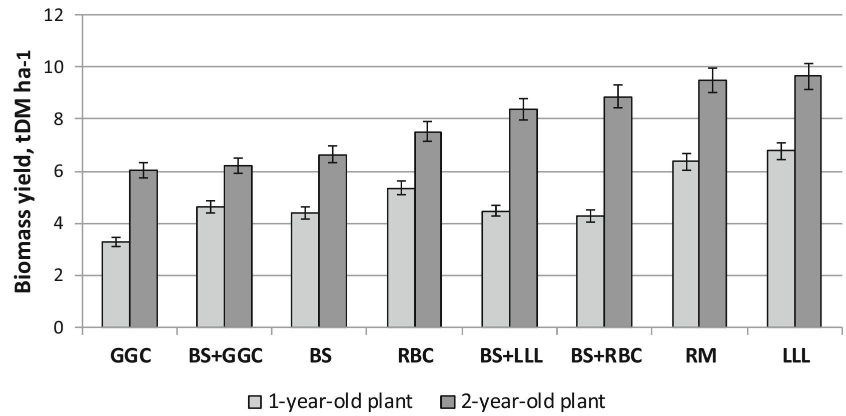
After the first year of cultivation, plants formed an average of 8–13 monocarpic shoots per clump, depending on the type of rock substrate on which they grew, and during the second vegetation season, the intensity of clump expansion was 70–120%. As a result, for 2-year-old plants, the stem numbers ranged from 15 to 30 pieces (Fig. 7).

Table 2 Monocarpic shoots diameter of *M.×giganteus* grown on different rock substrates (mm)

Models of substrate	Shoot diameter	Models of substrate	Shoot diameter
RM	9.40 ± 0.10	LLL	8.77 ± 0.14
RBC	8.35 ± 0.15	BS+GGC	8.26 ± 0.14
BS+RBC	7.75 ± 0.17	BS+LLL	7.52 ± 0.18
BS	7.33 ± 0.19	GGC	7.03 ± 0.12

RM rocks mix, *RBS* red-brown clay, *BS* black soil, *LLL* loess-like loam, *GGC* green-gray clay

Fig. 8 The *M.×giganteus* yield while grown on the different modeling substrates



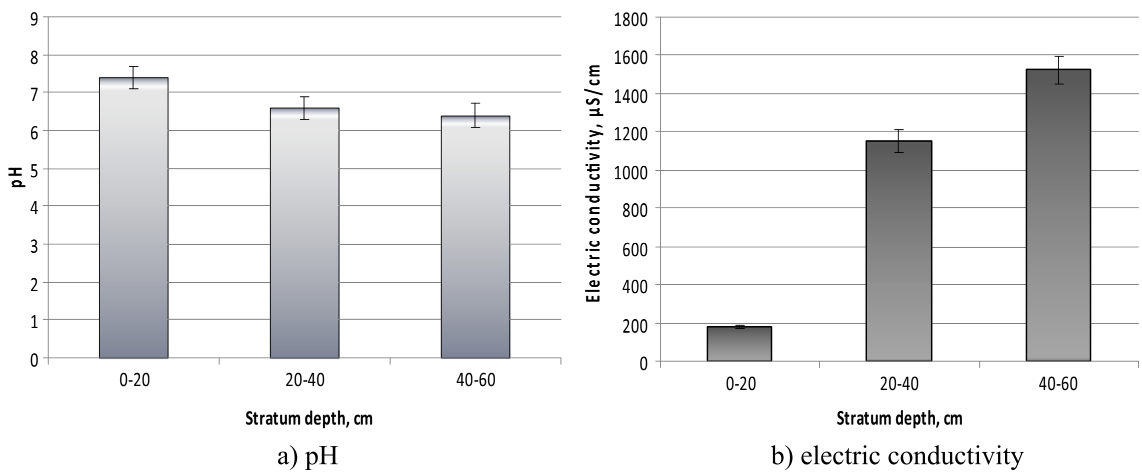
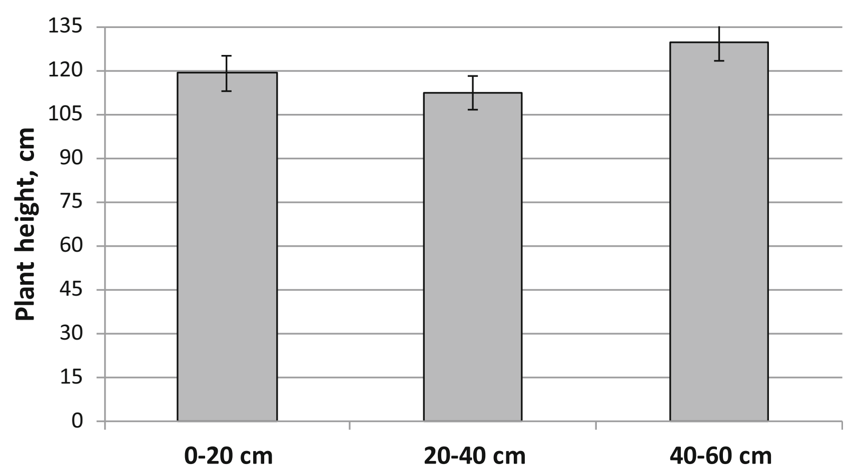


Fig. 9 The profile distribution of pH and electric conductivity on the different strata of DGSC

The diameter of a monocarpic shoot is a parameter that depends a little on the age of the plant, but environmental factors can influence its value significantly. Thus, in this experiment variant the variation of monocarpic shoots diameter was changed from 6.9 mm to 9.4 mm, depending on the substrate where the plants grew (Table 2). The thickest strong shoots of *Miscanthus* were produced on RM and LLL, and the weakest ones—on GGC.

Using data of dry *Miscanthus* biomass, the average weight of one plant was calculated and thereafter this value was converted to the dry biomass yield (DM) per hectare by means of planting density about 14,800 plants per ha (Kharytonov et al. 2017). Thus, the yield of plants in the first year of cultivation varied from 3.27 to 6.78 t DM ha^{-1}. The lowest productivity was shown by plants growing on GGC; the highest yield was recorded when *Miscanthus* was grown on LLL. At the end of

Fig. 10 *M.×giganteus* height at the end of the first vegetation seasons while grown on the DGSC



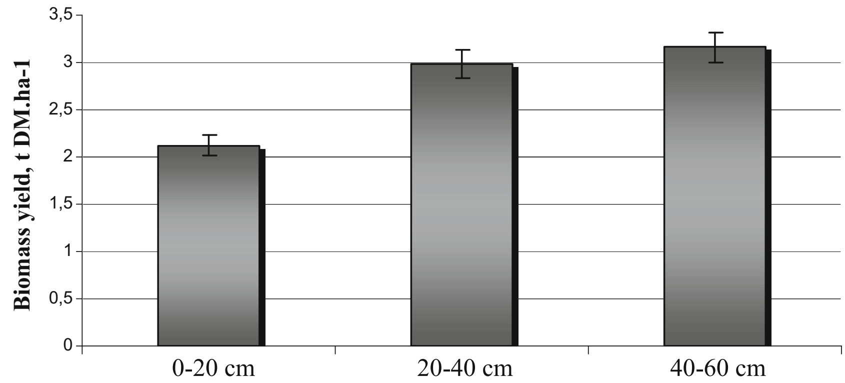


Fig. 11 The dry biomass yield of 1-year-old *Miscanthus* plants grown on three strata of the DGSC

the second year, the yield was increased from 42.0 to 87.9%, and the best result was shown when plants grew on LLL and RM (Fig. 8).

The data received for 1-year-old plants correspond to similar results reported for cultivation of *M.×giganteus* in Western Forest-Steppe region of Ukraine with a sufficiently high level of water supply (Gumentyk et al. 2013; Rakhmetov et al. 2015). The yield received for 2-year-old plants in our study was slightly lower than the reported ones which may be explained by oppressing of growth by soil quality and differences in precipitation regime. Since the most intensive growth of the vegetative mass occurs in May–July, the amount of water available to plants at this time is very important for the formation of the yield. In 2016, during this period, the amount of precipitation was 147 mm, and in 2017 it was only 101 mm. At that time, May and June were arid (19 mm and 7 mm, respectively). The more favorable conditions were in July (75 mm of precipitation). The average air temperature for both researched years was approximately the same.

The experimental variant 2 with the DGSC

The second experimental variant was focused on the possibility of *Miscanthus* to grow on the dark-gray schist clay (DGSC). Unlike other rocks, DGSC contains up to 1% pyrite. As a result of its oxidation in the presence of water, the ferrous form of iron and sulfuric acid are formed: $2FeS_2+2H_2O+7O_2 = 2FeSO_4+2H_2SO_4$. They, by-turn, acidify the soil solution, and detrimentally affect the growth and development of plants. During pyrite oxidation without access of water in reaction: $FeS_2+3O_2=FeSO_4+SO_2$ the sulphur oxide received, and this substance negatively affect the soil as well. These chemical processes are accompanied by the release of heat (spontaneous combustion), causing the dryness of rocks and scant content of organic matter. The reaction of the water extract in DGSC varies from alkaline or neutral to acidic; pH value is falling from 6.6–8.4 to 3.8–4.0. This leads to a rapid process of pyrite weathering in dark-gray schist clays. Thus, DGSC is harmful for most crop production and unsuitable to use for agricultural purpose without preliminary melioration. This clay was excavated to the earth surface of the reclamation site about 50 years ago being all those time under the influence of chemical and biological weathering. The electrical conductivity and pH of DGSC at three researched levels are presented at Fig. 9. One may see that at a depth of 20–60 cm the pH value varies from slightly alkaline to slightly acidic, and the lower layers are more salted. Thus, it may be concluded that the clay is still under the influence of oxidation-reduction processes in the aeration zone. All these features affected the growth and development of *M.×giganteus*.

Table 3 Data of thermal degradation of *M.×giganteus* biomass grown on the DGSC

Stratum depth, cm	Temperature interval, °C / Weight loss, %				The share of residual mass, %
0–20	20–160 9.0	160–270 19.8	270–380 33.4	380–580 25.8	12.0
20–40	30–180 8.6	180–280 19.8	280–390 33.2	390–640 25.8	12.6
40–60	30–170 8.0	170–280 18.8	280–380 29.2	380–640 30.8	13.2

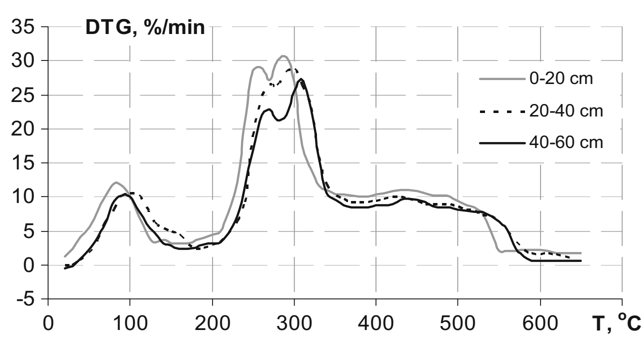


Fig. 12 DTG curves of *M.×giganteus* biomass depending on three strata where plants were grown

Table 4 Content of heavy metals in the DGSC

Stratum depth, cm	Total content of heavy metals in the substrate, mg/kg				
	Zn	Cu	Mn	Pb	Fe
0–20	84.08 ± 0.40	24.13 ± 0.46	297.41 ± 1.69	24.09 ± 0.28	44,445.66 ± 129.25
20–40	107.89 ± 0.53	30.89 ± 0.08	274.33 ± 0.78	30.09 ± 0.01	66,043.25 ± 130.11
40–60	94.35 ± 0.34	27.31 ± 0.06	145.47 ± 0.52	24.84 ± 0.20	60,871.89 ± 419.44
Permissible limit values	87.0	53.0	1500.0	32.0	–
	Mobile fraction content of heavy metals in the substrate, mg/kg				
	Zn	Cu	Mn	Pb	Fe
0–20	2.54 ± 0.01	1.0 ± 0.01	146.78 ± 2.35	6.85 ± 0.05	24.02 ± 0.13
20–40	3.14 ± 0.02	0.84 ± 0.03	98.11 ± 1.14	6.65 ± 0.13	42.44 ± 0.09
40–60	2.69 ± 0.01	1.20 ± 0.01	40.20 ± 0.86	8.19 ± 0.36	30.23 ± 0.14
Permissible limit values	23.0	3.0	140.0	6.0	–

Overall, the experiment showed that the growth and development of *Miscanthus* on this soil was oppressed in comparison with growth and development on the different modeling rock substrates (first experimental variant).

The maximum height of plants in the first year of cultivation did not exceed 125–130 cm, which is even slightly less than the lowest values obtained for plants grown on different models of rock substrates. The best values were noted for plants grown on the stratum 40–60 cm, the worst—on the stratum 20–40 cm (Fig. 10).

The intensity of monocarpic shoot formation was also low and by the end of the year varied from 4 (stratum 0–20 cm) to 9 shoots per plant (stratum 20–40 cm). As a result, the productivity of dry biomass was small. The average dry weight of one plant grown on 20–40 cm and 40–60 cm stratum was almost identical (201.8 ± 1.17 g and 213.4 ± 1.81 g respectively). Plant productivity on the 0–20 cm stratum was significantly lower (143.6 ± 1.30 g). Nevertheless, according to the calculation made *M.× giganteus* was able to produce a yield from 2 to 3 tons per hectare in the first vegetation season while grew on the DGSC (Fig. 11).

For *M.× giganteus* produced on three strata: 0–20 cm, 20–40 cm, and 40–60 cm, a study of the thermal stability was carried out based on the calorific value of the biomass. According to the obtained results, four temperature ranges could be distinguished with a variable rate of mass loss (Table 3). The entire process of biomass thermal destruction passed in the temperature range 20–30 °C–580–640 °C.

In the first stage of the thermolysis occurred in temperature interval 20–180 °C, endothermic processes took place, caused by water evaporation and the removal of volatile components. During this period the mass loss was insignificant and varied within 8.0–9.0%. The second stage occurred within the temperature range of 160–280 °C. At this period, along with the endothermic processes of dehydration and pyrolysis, the exothermic processes of the hemicellulose destruction were developed. The weight loss varied from 18.8 to 19.8%. Further loss of mass was associated with cellulose and lignin thermal degradation. The third stage of thermolysis (270–390 °C) was characterized by thermochemical active destructive processes and was accompanied by the highest rate of mass loss (29.2–33.4%). The biomass of plants grown on stratum 0–20 cm presented the highest reactivity with a peak 30.6%/min at 290 °C, which was clearly traceable to the DTG curves (Fig. 12). During the fourth stage of thermolysis (380–640 °C) thermal decomposition of cellulose and lignin completed the carbonated residue combusts as well. At this stage, the most pronounced exothermic effect was emerged. The weight loss varied from 25.8 to 30.8%. Results showed that the share of residual mass in studied samples varied from 12.0 to 13.2%. It has to be mentioned that overall, the biomass decomposition for plants grown on stratum 0–20 cm was faster and more completed than for plants which were grown on the deeper strata of the DGSC.

The feature of the DGSC is the rather high content of heavy metals, which is several times larger in comparison with the other substrates (Kharytonov 2008). The concentrations of Zn (total content), Mn (mobile forms), and Pb are almost equal to or exceed the permissible limit values (Table 4). The content of

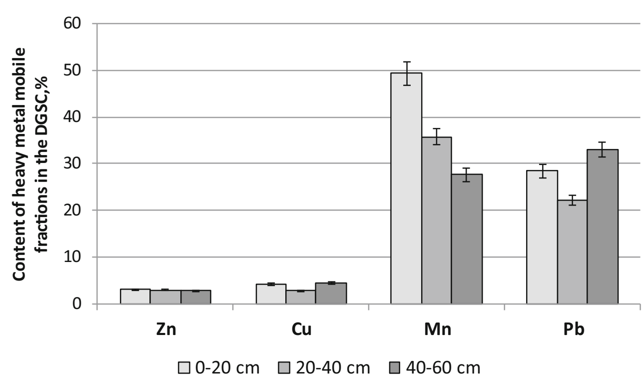


Fig. 13 The percentage of heavy metal mobile forms in the DGSC

Table 5 The heavy metals content in *M.×giganteus* above-ground biomass produced on three strata of the DGSC

	The heavy metal content in the biomass, mg/kg Biological accumulation coefficient				
Stratum depth, cm	Zn	Cu	Mn	Pb	Fe
0–20	19.89 ± 2.40 0.24	3.21 ± 0.30 0.13	30.53 ± 3.50 0.10	2.71 ± 0.12 0.11	369.86 ± 32.10 0.01
20–40	15.81 ± 1.20 0.15	2.44 ± 0.18 0.08	15.38 ± 1.90 0.06	1.67 ± 0.11 0.05	229.28 ± 22.05 0.003
40–60	13.26 ± 1.41 0.14	1.91 ± 0.20 0.07	30.11 ± 2.50 0.21	1.84 ± 0.14 0.07	134.45 ± 12.00 0.002

heavy metal mobile forms available to plants varies from 3 to 50% (Fig. 13). The available percentage of the Fe fraction is very small and does not exceed 0.05–0.06%.

Considering the high availability of some heavy metals for plants, the peculiarity of their accumulation in the *M.×giganteus* above-ground biomass produced on three strata of the DGSC was studied and biological accumulation coefficients (BAC) were calculated. Data are presented at Table 5. It may be seen that overall, the concentration of heavy metals in the above-ground biomass and BAC was rather small, which is in agreement with previously published results (Pidlisnyuk et al. 2014b, 2016) and is due to preferential accumulation of heavy metals occurred in the roots. Our study data showed that *M.×giganteus* is not a hyper accumulative plant. The level of the concentrations of heavy metals in the biomass was different depending on the stratum: the highest concentrations were detected at the stratum 0–20 cm, and the lowest results were observed at 40–60 cm. It has to be mentioned that those regularities were observed for all heavy metals researched. At the same time, the values of the BAC did not fully correspond to this pattern. The highest values of the BAC for Mn were observed on the stratum 40–60 cm, and the plants grown on the stratum 20–40 cm were characterized by the lowest biological accumulation coefficient of Pb.

Data on the uptake of heavy metals by above-ground biomass of *Miscanthus* grown on the DGSC are given in Fig. 14. The results illustrated that on stratum 0–20 cm, the maximum uptake by biomass was observed for Fe and Pb, on stratum 20–40 cm the maximum uptake was determined for Zn and Cu, and on stratum 40–60 cm the maximum uptake was detected for Mn.

The experimental variant 3: field test with amendments

The main task of the field experiment was to find out how different amendments influence the biometric parameters and productivity of *M.×giganteus* grown on the post-mining lands during two vegetation seasons.

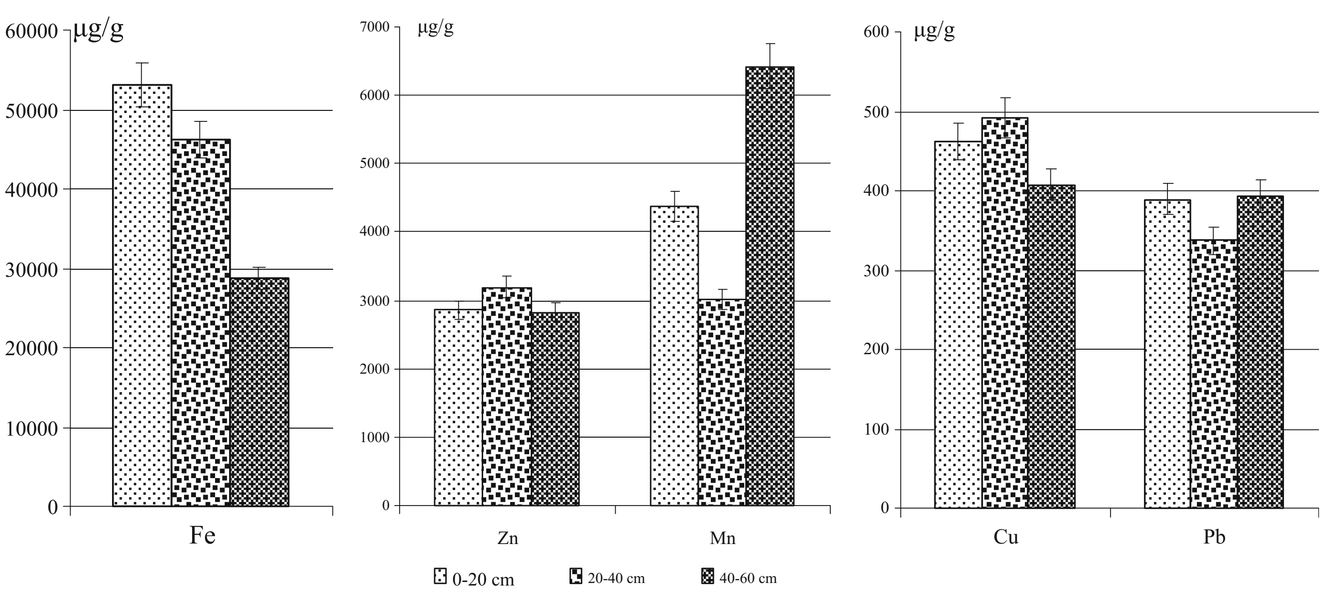


Fig. 14 Uptake of heavy metals by the above-ground biomass of *M.×giganteus* plants grown on different DGSC strata, µg/g

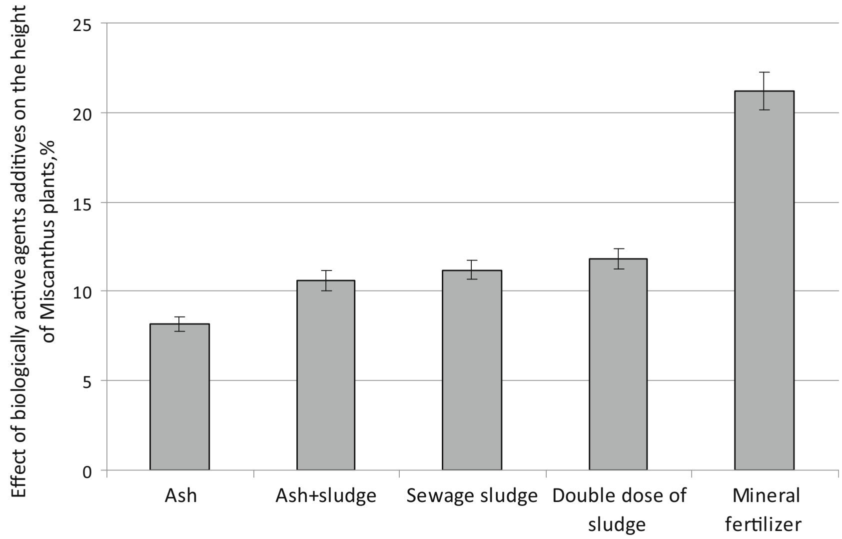


Fig. 15 Impact of soil amendments to the height of *Miscanthus* plants after the second year of cultivation, %

The results obtained in the field test showed that the application of amendments to the post-mining land (mixture of loess-like loam and red-brown clay) positively affected the growth parameters of *Miscanthus* (Fig. 15). The biggest effect was observed for plant growth on the soil amendment by adding of mineral fertilizers, while the application of ash showed the minimal increasing of the growth parameters.

In turn, the increase of the growth parameter promoted the enhancement of aboveground biomass yield, and the degree of this enhancement was in correlation with growth parameters. It has to be mentioned that the degree of this enhancement was different. In case of ash application, the yield increased by only 6.5% compared with the control, while the addition of mineral fertilizer and sewage sludge significantly increased the biomass yield by 2–2.3 times. As a result, the *Miscanthus* productivity in the second year of vegetation on these plots was 11.6 t DM ha^{-1} and 11.9 t DM ha^{-1}, respectively (Fig. 16). Thus, the current research confirms earlier reported data (An et al. 2011; Kołodziej et al. 2016) that sewage sludge is conducive to increasing the biomass *Miscanthus* yield.

Conclusion

The research results illustrated that different types of modeled rock substrates: loess-like loam (LLL), a rocks mix (RM), red-brown clay (RBC), green-gray clay (GGC), black soil (BS)+green-gray clay (GGC); black soil (BS)+red-brown clay (RBC); black soil (BS)+loess-like loam (LLM); and black soil (BS), were suitable for growing of *M.×giganteus* as raw material for renewable energy. From the substrates tested, the LLM, LLL+RBC, and RBC+BS showed the best growth of *Miscanthus* during two vegetation seasons. The plants growing on these modeled rock substrates showed a good development and formed annually a sufficiently large number of monocarpic strong shoots. In the first year of cultivation, the yield of dry biomass ranged from 4.3 to 6.8 t DM ha^{-1}, and in the second year that value varied from 8.9 to 9.7 t DM ha^{-1}. The lowest growth and development rates were obtained for plants grown on GGC, where the yield did not exceed 3.3 t DM ha^{-1} in the first year of cultivation and was 6.0 t DM ha^{-1} in the second

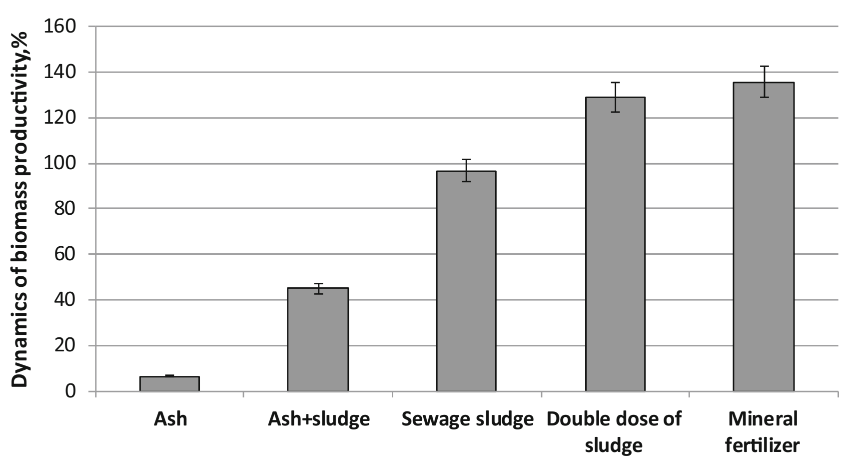


Fig. 16 *Miscanthus* biomass productivity (%) while growing on the post-mining soil with application of the different amendments

year. It was revealed that *M.×giganteus* showed a sufficient tolerance to the DGSC and can be cultivated on that contaminated mining land. Despite the fact that the growth, the intensity of the monocarpic shoot formation, and the diameter of shoots were small, the plant could produce a yield of 2 to 3 t DM ha^{-1} at the first year of cultivation. The biggest bioproductivity value was observed when *Miscantu*s was grown on the deeper DGSC stratum with pH 6.3–6.5.

The thermogravimetric analysis of *M.×giganteus* biomass produced at three strata of the DGSC showed that there were four stages of biomass thermal decomposition in the temperature range from 20 to 640 °C. The maximum rate of mass loss was occurred in the intervals of hemicellulose and cellulose thermal destruction. The biomass of plants grown on the DGSC stratum 0–20 cm showed the highest reactivity of decomposition with a peak 30.6%/min at 290 °C.

The concentrations of heavy metals at the above-ground biomass of *M.×giganteus* grown on the DGSC were rather small which was due to preferential accumulation of heavy metals in the roots, results ensured that the crop did not have a hyper accumulation feature. There were differences in heavy metal content in the above-ground biomass of *Miscanthus* depending on the DGSC stratum depth. All researched heavy metals: Fe, Zn, Cu, Pb, and Mn showed a similar character in decreasing the metal content in the above-ground biomass depending on the stratum where plants grew: from 0 to 20 cm to 40–60 cm. The results illustrated that the maximum uptake on stratum of 0–20 cm was observed for Fe and Pb; on stratum of 20–40 cm the maximum uptake was fixed for Zn and Cu, and on stratum 40–60 cm the maximum was detected for Mn.

It was revealed that application of different amendments to the soil post-mining soil (mixture of loess-like loam and red-brown clay) resulted in stimulation of *M.×giganteus* growth and development and, accordingly, increasing plant productivity from 50 to 140%. Thus, the results illustrated that application of amendments permitted to obtain the similar *Miscanthus* yields as at the arable lands. The special attention should be done to using of sewage sludge as a promising substitute of organic fertilizers while growing *M.×giganteus* on the post-mining lands.

Summarizing, it can be concluded that the adaptive potential of *M.×giganteus* to produce a stable yield at the mining and post-mining lands is essential. The small accumulation of heavy metals in the above-ground biomass showed a good prospect of this energy crop for cultivation on the phytomeliorated mining lands.

Funding information The research was partly supported by grant 0116U004738 from the Ministry of Education and Science of Ukraine and NATO SPS MYP G4687.

References

AEBIOM (2011) Annual Statistical Report on the contribution of biomass to the energy system in the EU 27. http://ru.scribd.com/doc/73012151/2011-AEBIOM-Annual-Statistical-Report

An G-H, Lee S, Koo B-C, Choi YH, Moon Y-H, Cha Y-L, Bark S-T, Kim J-K, Kim B-C, Kim S-P (2011) Effects of application of solidified sewage sludge on the growth of bioenergy crops in reclaimed land. Korean J Crop Sci 56(4):299–307. https://doi.org/10.7740/kjcs.2011.56.4.299

Antonkiewicz J, Kołodziej B, Bielinska EJ (2016) The use of reed canary grass and giant miscanthus in the phytoremediation of municipal sewage sludge. Environ Sci Pollut Res 23(10):9505–9517. https://doi.org/10.1007/s11356-016-6175-6

Arduini I, Masoni A, Ercoli L (2006) Effects of high chromium applications on Miscanthus during the period of maximum growth. Environ Exp Bot 58:234–243. https://doi.org/10.1016/j.envexpbot.2005.09.004

Blanco-Canqu H (2016) Growing dedicated energy crops on marginal lands and ecosystem services. Soil Sci Soc Am J 80(4):845–858. https://doi.org/10.2136/sssaj2016.03.0080

Brosse N, Dufour A, Meng GX, Sun Q, Ragauskas A (2012) Miscanthus: a fast-growing crop for biofuels and chemicals production. Review. Biofuels Bioprod Biorefin 6:580–598. https://doi.org/10.1002/bbb.1353

Christian DG, Riche AB, Yates NE (2008) Growth, yield and mineral content of Miscanthus ×giganteus grown as a biofuel for 14 successive harvests. Ind Crop Prod 28:320–327. https://doi.org/10.1016/j.indcrop.2008.02.009

Cortes AM, Bridgwater AV (2015) Kinetic study of the pyrolysis of Miscanthus and its acid hydrolysis residue by thermogravimetric analysis. Fuel Process Technol 138:184–193. https://doi.org/10.1016/j.fuproc.2015.05.013

De Kimpe CR, Morel J-L (2000) Urban soil management: a growing concern. Soil Sci 165(1):31–40. https://doi.org/10.1097/00010694-200001000-00005

Eionet NRC Soil (2015) Remediated sites and brownfields. Success stories in Europe. In: Perez A-P, Sanchez SP, Van Liedekerke M (eds) A report of the European Information and Observation Network's national reference centre for soil. https://doi.org/10.2788/01889

Fernando A, Oliveira JFS (2004) Effects on growth, productivity and biomass quality of *Miscanthus* x *giganteus* of soils contaminated with heavy metals. In: Van Swaaij WPM, Fjällström T, Helm P, Grassi A (eds) Biomass for energy, industry and climate protection - proceedings of the 2nd World Biomass Conference, 10–14 Maio 2004, pp 387–390. https://moodle.fct.unl.pt/pluginfile.php/92027/mod_resource/content/0/Fernando_e_Oliveira_2004.pdf

Gasparatosa A, Dollb CNH, Estebanc M, Tabitha AA, Olangc A (2017) Renewable energy and biodiversity: implications for transitioning to a green economy. Renew Sust Energ Rev 70:161–184. https://doi.org/10.1016/j.rser.2016.08.030

Geletukha G, Zheliezna T, Tryboi O (2015) Prospects for growing and use of energy crops in Ukraine. Part 2. Industrial Heat Engineering 37(5):58–67 http://ihe.nas.gov.ua/index.php/journal/article/view/122

Geletukha G, Zheliezna T, Tryboi O, Bashtovyi A (2016) Analysis of criteria for the sustainable development of bioenergy. UABio Position Paper 17:1–30 http://uabio.org/en/activity/uabio-analytics/3066-uabio-position-paper-17

Gomes E (2012) Phytoremediation for bioenergy: challenges and opportunities. Environ Technol Rev 1(1):59–66. https://doi.org/10.1080/09593330.2012.696715

Gumentyk M, Kharytonov M (2018) Development and assessment of technologies of Miscanthus and switchgrass growing in forest-steppe zone of Ukraine. Agriculture and Forestry 64(2):137–146. https://doi.org/10.17707/AgricultForest.64.2.10

Gumentyk M, Kwak V, Zamoyski O, Radejko B (2013) Biomass productivity of Miscanthus depending on the quality of planting material and growing conditions in the western forest-steppe region of Ukraine. Motrol 15(4):84–89 http://www.pan-ol.lublin.pl/wydawnictwa/Motrol15_4/motrol_15_4_2013.pdf

Heaton EA, Dohleman FG, Long SP (2008) Meeting us biofuel goals with less land: the potential of Miscanthus. Glob Chang Biol 14(9):2000–2014. https://doi.org/10.1111/j.1365-2486.2008.01662.x

Heaton EA, Dohleman FG, Miguez AF, Juvik JA, Lozovaya V, Widholm J, Zabotina OA, McIsaac GF, David MB, Voigt TB, Boersma NN, Long SP (2010) Miscanthus: a promising biomass crop. Adv Bot Res 56:76–137. https://doi.org/10.4236/eng.2011.34046

Hein K (2005) Future energy supply in Europe – challenge and chances. Fuel 84:1189–1194. https://doi.org/10.1016/j.fuel.2004.09.022

Ivanyshyn V, Nedilska U, Khomina V, Klymyshena R, Hryhoriev V, Ovcharuk O, Hutsol T, Mudryk K, Jewiarz M, Wróbel M, Dziedzic K (2018) Prospects of growing Miscanthus as alternative source of biofuel. In: Engineering, technology, innovation. Springer proceedings in energy, Springer, Cham, pp 801–812. https://doi.org/10.1007/978-3-319-72371-6_78

Karp A, Sheid I (2008) Bioenergy from plants and the sustainable yield challenge. New Phytol 179(1):15–32. https://doi.org/10.1111/j.1469-8137.2008.02432.x

Kharytonov M (2008) Geochemical assessment of reclaimed lands in the mining regions of Ukraine. In: NATO ARW soil chemical pollution, risk assessment, remediation and security. Springer, Netherlands, pp 57–60. https://doi.org/10.1007/978-1-4020-8257-3_16

Kharytonov MM, Resio Espejo JM (2013) Land reclamation in the manganese ore mining basin in Ukraine. VIII Reunión de Cuaternario Ibérico, La Rinconada- Sevilla, pp 150–152. http://tierra.rediris.es/aequa/doc/El_Cuaternario_Iberico_2013.pdf

Kharytonov M, Martynova N, Sitnyk S, Naumenko M, Pidlisnyuk V, Stefanovska T (2017) A productive potential estimation of five genotypes of the *Miscanthus* Anderss genus in the Ukrainian steppe zones conditions. INMATEH - Agricultural Engineering 52(2):129–136 http://www.inmateh.eu/INMATEH_2_2017/INMATEH-Agricultural_Engineering_52_2017.pdf

Kocoń A, Jurga B (2017) The evaluation of growth and phytoextraction potential of *Miscanthus x giganteus* and *Sida hermaphrodita* on soil contaminated simultaneously with Cd, Cu, Ni, Pb, and Zn. Environ Sci Pollut Res 24(5):4990–5000. https://doi.org/10.1007/s11356-016-8241-5

Kok MV, Özgür E (2013) Thermal analysis and kinetics of biomass samples. Fuel Process Technol 106:739–743. https://doi.org/10.1016/j.fuproc.2012.10.010

Kołodynska D, Krukowska J, Thomas P (2017) Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon. Chem Eng J 307:353–363. https://doi.org/10.1016/j.cej.2016.08.088

Kołodziej B, Antonkiewicz J, Sugier D (2016) Miscanthus × giganteus as a biomass feedstock grown on municipal sewage sludge. Ind Crop Prod 81:72–82. https://doi.org/10.1016/j.indcrop.2015.11.052

Matyka M, Kus J (2016) Influence of soil quality for yielding and biometric features of *Miscanthus × giganteus*. Pol J Environ Stud 25(1):213–219. https://doi.org/10.15244/pjoes/60108

Nosko VL, Boyko IE, Kamyshanov VV, Leshuk UI (2015) Perspective of energy crops in Ukraine. Scientific herald of NULES of Ukraine. Series: biology, biotechnology. Ecology 214:216–222 http://journals.nubip.edu.ua/index.php/Biologiya/article/view/6230

Nunn C, Hastings AFSJ, Kalinina O, Özgüven M, Schüle H, Tarakanov IG, Van Der Weijde T, Anisimov AA, Iqbal Y, Kiesel A, Khokhlov NF, Mc. Calmont JP, Meyer H, Mos M, Schwarz K-U, Trindade LM, Lewandowski I, Clifton-Brown JC (2017) Environmental influences on the growing season duration and ripening of diverse miscanthus germplasm grown in six countries. Front Plant Sci 8:907. https://doi.org/10.3389/fpls.2017.00907

Osman AI, Abdelkader A, Johnston CR, Morgan K, Rooney DW (2017a) Thermal investigation and kinetic modeling of lignocellulosic biomass combustion for energy production and other applications. Ind Eng Chem Res 56(42):12119–12130. https://doi.org/10.1021/acs.iecr.7b0347

Osman AI, Ahmed AT, Johnston CR, Rooneya DW (2017b) Physicochemical characterization of Miscanthus and its application in heavy metals removal from wastewaters. Environ Prog Sustain Energy 37:1058–1067. https://doi.org/10.1002/ep.12783

Otepka P (2014) Guidebook on local bioenergy supply based on woody biomass. Scientific & Academic Publishing, USA ISBN 978-1-938681-99-8

Pidlisnyuk V, Erickson L, Kharchenko S, Stefanovska T (2014a) Sustainable land management: growing Miscanthus in soils contaminated with heavy metals. J Environ Prot 5:723–730. https://doi.org/10.4236/jep.2014.58073

Pidlisnyuk V, Stefanovska T, Lewis EE, Erickson LE, Davis LE (2014b) Miscanthus as a productive crop for phytoremediation. Crit Rev Plant Sci 33(1):1–19

Pidlisnyuk V, Trogl J, Stefanovska T, Shapoval P, Erickson L (2016) Preliminary results on growing second generation biofuel crop Miscanthus x giganteus at the polluted military site in Ukraine. Nova Biotechnol Chim 15(1):77–84. https://doi.org/10.1515/nbec-2016-0008

Powlson DS, Riche AB, Shield I (2005) Biofuels and other approaches for decreasing fossil fuel emissions from agriculture. Ann Appl Biol 146:193–201. https://doi.org/10.1111/j.1744-7348.2005.040056.x

Rakhmetov DB, Shcherbakova TO, Rakhmetov SD (2015) Miscanthus in Ukraine: introduction, biology, bioenergetics. Phytosociocenter, Kiev

Sims R, Hastings A, Schlamadinger B, Taylor G, Smith P (2006) Energy crops: current status and future prospects. Glob Chang Biol 12:2054–2076. https://doi.org/10.1111/j.1365-2486.2006.01163.x

Skousen J, Keene T, Marra M, Gutta B (2012) Reclamation of mined land with switchgrass, miscanthus and arundo for biofuel production. J Am Soc Mining Recl 2(1):177–191. https://doi.org/10.21000/JASMR13010177

USEPA (1996) Test methods for evaluating solid waste. Physical/chemical methods. In: Method 3050B, acid digestion of sediment, sludges and soils, 3rd edn. USEPA, Washington, DC SW-846

Wanat N, Austruy A, Joussen E, Soubrant M, Hitmi A, Gauthier-Moussard C, Lenain JF, Vernay P, Munch JC, Pichon M (2013) Potential of Miscanthus x giganteus grown on highly contaminated Technosols. J Geochem Explor 126-127:78–84. https://doi.org/10.1016/j.gexplo.2013.01.001

Werle S, Bisorca D, Katelbach-Wozniak A, Pogrzeba M, Krzyzak J, Ratman-Kłosinska I, Burnete D (2016) Phytoremediation as an effective method to remove heavy metals from contaminated area – TG/FT-IR analysis results of the gasification of heavy metal contaminated energy crops. J Energy Inst 90:408–417. https://doi.org/10.1016/j.joei.2016.04.002

Xie J, Weng Q, Ye G, Luo S, Zhu R, Zhang A, Chen X, Lin C (2014) Bioethanol production from sugarcane grown in heavy metal-contaminated soils. BioResources 9(2):2509–2520. https://doi.org/10.15376/biores.9.2.2509-2520