Rys. 13. Przenośny monitor pyłu zawieszonego DustTrak DRX
Fig. 13. Personal Aerosol Monitor DustTrak DRX

Możliwości pomiarowe oraz elastyczność w dostosowaniu do różnorodnych warun-
ów pracy pyłomierzy DustTrak zostały wykorzystane przy doborze rozwiązania do kon-
'oli stopnia zapylenia powietrza miejskiego w nowopowstałym programie ochrony przed
egatywnymi skutkami smogu 'Krakowski Alarm Smogowy'. Idea pomiarów opiera się
a kilkudniowych ciągłych pomiarach zapylenia w poszczególnych dzielnicach miasta
bieżącym opracowywaniu wyników w oparciu o dane zarejestrowane w pamięci urzą-
zeń. O funkcjonalności mierników DustTrak świadczy również fakt, że pomyślnie prze-
zły również test porównawczy z pomiarami wykonywanymi przez pyłomierze referen-
yjne WIOŚ. Więcej informacji na temat projektu www.krakowskialarmsmogowy.pl

. Podsumowanie

Powyższe przekrojowo zaprezentowane w tej publikacji urządzenia i systemy po-
iarowe doskonale sprawdzają się w warunkach występujących w procesach gospoda-
›wania wszystkimi rodzajami odpadów, zarówno w trakcie ich transportu, składowania
ık i przekształcania. Zapewniają pracownikom pełną ochronę w trakcie uczestniczenia
tych działaniach, jak również monitorują czynniki niebezpieczne i toksyczne wydzie-
ıne do atmosfery w procesach przekształcania i utylizacji zgodnie z coraz bardziej za-
strzającymi się wymogami prawnymi.

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ASSESSMENT OF REMEDIATION POTENTIAL OF ENERGY CROPS CULTIVATED ON HEAVY METAL CONTAMINATED SITES - PROJEKT PHYTO2ENERGY

OCENA POTENCJAŁU REMEDIACYJNEGO ROŚLIN ENERGETYCZNYCH UPRAWIANYCH NA TERENACH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI – PROJEKT PHYTO2ENERGY

Zanieczyszczenie gleb metalami ciężkimi jest problemem występującym szeroko w Europie jak i w świecie. Obszary zanieczyszczone mogą stanowić zarówno miejsca dawnej działalności przemysłowej, jak i obszary rolnicze znajdujące się w ich sąsiedztwie. Obecność metali ciężkich w glebie w ilościach przekraczających dopuszczalne normy powoduje, iż obszary te zostają wyłączone z produkcji, przy jednoczesnym braku skutecznych metod ich przywrócenia do użytkowania. Produkcja plonu energetycznego połączona z jednoczesną fitoremediacją gleb może stanowić obiecującą alternatywę dla zagospodarowania takich obszarów. W celu określenia optymalnych gatunków roślin energetycznych, zarówno pod kątem produkcji biomasy jak i potencjału fitoremediacyjnego, prowadzony jest czteroletni eksperyment polowy zlokalizowany na obszarach zanieczyszczonych metalami ciężkimi: glebie rolniczej (Bytom, Polska) oraz byłym składowisku komunalnych osadów ściekowych (Lipsk, Niemcy). W ramach eksperymentu testowane są cztery gatunki roślin energetycznych: miskant olbrzymi (Miscanthus x giganteus), ślazowiec pensylwański (Sida hermaphrodita), spartina preriowa (Spartina pectinata) oraz proso rózgowe (Panicum virgatum). Na koniec pierwszego sezonu wegetacyjnego pobrane zostały próbki materiału roślinnego w celu określenia miedzy innymi pobierania metali ciężkich przez rośliny oraz określenia różnic w tym procesie pomiędzy miejscami badawczymi w Polsce i Niemczech. Poniższy artykuł przedstawia wyniki badań po pierwszym sezonie wegetacyjnym, wraz z określeniem potencjału remediacyjnego badanych gatunków roślin. Przedstawione badania prowadzone są w projekcie „Phyto2Energy", realizowanym w ramach

Contamination of soil with heavy metals is a problem occurring in Europe but also
ɔrldwide. The affected sites could be either sites of a former industrial activity or arable
nd located in their vicinity. The presence of heavy metals in excessive quanti-ties makes
ese sites either left idle or underused due to contamination and lack of efficient ways
restore them. Phytoremediation driven energy crops production may be a promising
ternative for the management of these sites. A four-year field experi-ment has been on-
ɔing on heavy metal contaminated sites located in Bytom, Upper Silesian Industrial Re-
on, Southern Poland (arable land) and in Leipzig, Germany (post-industrial site) to find
e optimum energy crop species with respect to both: energy crop yield and phytoremedi-
ion potential. It involves testing of 4 preselected plant species: miscanthus (Miscanthus
giganteus), virginia mallow (Sida hermaphro-dita), cordgrass (Spartina pectinata), and
vitchgrass (Panicum virgatum). At the end of the first growing season plant samples
ere collected to determine, among others, heavy metal uptake for the tested species and
ifferences in this process between the investigated sites. The data collected after the
rst year of the experiment are presented together with the remediation potential of the
sted plant species. The PHYTO2ENERGY project has received funding from the Seventh
ramework Pro-gramme for Research, Technological Development and Demonstration of
ie European Union under the Grant Agreement No. 610797.

. INTRODUCTION

Remediation of contaminated soils has become a long-term challenge as it addresses
oth scientific and technical aspects as well as social (rehabilitation of former industrial
ites in ecodistricts, restoration of ecosystem services, etc) and economic issues (markets
f soil rehabilitation; production of plant biomass for feedstock on contaminated soils
ntegrated in the biobased-knowledge for bioeconomy) [1]. In spite of the importance of
nanagement options for sustainable and safe use of heavy metal contaminated (HMC)
oils, little has been investigated on combining the production of energy crops on the con-
aminated areas with phytoremediation of these sites. Whereas HMC soils are unsuitable
or food production, energy crops can allow the commercial exploitation of these soils by
stablishing biofuel feedstock production systems. In addition, the cultiva-tion of plants
ffers opportunities for site stabilization and phytoremediation of con-taminated soils [2].
There is a number of typical energy crop species available on the market which have also
een tested with success for the phytoremediation effect on HMC arable land. They, how-
ever, need further tests for different heavy metals to prove their robustness for large scale
applications.

Until now species used in Poland as well as in other UE countries as energy crops are
different clones of willow and poplar [3], miscanthus [4,5], switchgrass [4-6] and virginia
mallow [7]. All these species are normally grown on non-contaminated agricultural land.
Among the above listed plant species only willow [8,9], switchgrass [10] and miscanthus
[2,11] were also used for phytoremediation of heavy metal contaminated sites.

A well known energy crop Miscanthus x giganteus was indicated as a plant which could be successfully cultivated on heavy metal contaminated soil as a safe energy crop as it does not accumulate heavy metals [12,13]. However, a ten-year studies conducted at the Institute for Ecology of Industrial Areas (IETU) both on clean and polluted soils delivered results contrary to the mentioned data, revealing that the uptake of metals strongly depended on the level of bioavailable forms. Miscanthus x giganteus growing on clean soil may accumulate about 2 mg Pb kg^{-1}, 0.3 mg Cd kg^{-1} and 25 mg Zn kg^{-1} while on contaminated soils - up to 200 mg Pb kg^{-1}, 5 mg Cd kg^{-1} and 700 mg Zn kg^{-1}. The amount of metals observed in crops suggests that miscanthus has a promising potential for Pb and Zn phytoremediation [14,15] and thus shows also phytoextraction properties. These proven features of Miscanthus x giganteus open a new potential for the use of this species as both energy crop and for phytoremediation purposes. At the same time, there is a number of other plant species (*e.g. Sida hermaphrodita, Spartina pectinata, Panicum virgatum, Silphium perfoliatum*) used as energy crops, but only few authors tested them for heavy metal phytoremediation purposes [16-18].

A four-year field experiment has been initiated on heavy metal contaminated sites located in Poland (arable land) and in Germany (post-industrial site). It involves testing of 4 preselected plant species: miscanthus (*Miscanthus x giganteus*), virginia mallow (*Sida hermaphrodita*), cordgrass (*Spartina pectinata*), and switchgrass (*Panicum virgatum*) to find the optimum one with respect to both energy crop yield and phytoremediation capacity. Differences between the test sites as well as the metal uptake by plants after the first year of the experiments are presented below.

2. Materials and methods

2.1 Site description

The Polish test site is located in the Upper Silesian Industrial Region on the outskirts of Bytom - an industrial city about 15 km from Katowice, in the proximity of a shut down large lead/zinc/cadmium works consisting of the ore mining, enriching and smelting facilities. This metallurgical complex was in operation for more than 100 years and contributed significantly to the contamination of the local soils. During the last 30 years the area was used for agricultural purposes. Recently the land has been used for grain crops farming, especially for wheat production. Soil contamination with lead, cadmium and zinc in this area exceeds permissible limits for agricultural soil in Poland.

The German site (so called Schladitz) is a former sewage sludge dewatering plant located in the north of Leipzig. The creation and operation history of this plant is directly related to the main sewage plant of the city. Although both plants are about 9 kilometers away from each other, they operated as one unit from 1952 to 1990. During this time the sewage sludge resulting from municipal and industrial wastewater treatment was pumped to the dewatering plant. In 1990 the operation of the dewatering plant was abandoned and about 800,000 tons of sewage sludge remained in several basins.

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The German site (so called Schladitz) is a former sewage sludge dewatering plant located in the north of Leipzig. The creation and operation history of this plant is directly related to the main sewage plant of the city. Although both plants are about 9 kilometers away from each other, they operated as one unit from 1952 to 1990. During this time the sewage sludge resulting from municipal and industrial wastewater treatment was pumped to the dewatering plant. In 1990 the operation of the dewatering plant was abandoned and about 800,000 tons of sewage sludge remained in several basins.

2.2 Experiment design

Based on the previous IETU experience with energy crop species, four plant were selected for field trials: miscanthus (*Miscanthus x giganteus*), virginia mallow (Sida hermaphrodita), cordgrass (*Spartina pectinata*), and switchgrass (*Panicum virgatum*). Experimental plots ($16 m^2$ each) were established in spring 2014 on each test site. Between the plots a 4 m buffer zone was left to avoid interconnection between experimental options.

The subplots for each species include the following options:

- control (no additives),
- NPK standard fertilization addition - calculation based on specific plant requirements, applied once before plant establishment,
- inoculum addition - commercial microbial inoculum (Em Farma Plus, ProBiotics Polska, Poland) applied on rhizomes before planting and on the leaves as aerosol in the middle of each month of the growing season (from May to September 2014).

2.3 Chemical analyses of soil and plant samples

For site characterization three composite soil samples per plot (from the depth of 0-20 cm) were collected and analyzed. Physical and chemical soil properties such as: soil texture, pH, electric conductivity (EC), content of organic matter, total metal concentration (aqua regia extraction) and bioavailable fractions of metal concentration ($CaCl_2$ extraction) were analyzed.

Soil pH was measured in H2O (1:2.5 m/v) with a combination glass/calomel elec-trode (OSH 10-10, METRON, Poland) and a pH-meter (CPC-551, Elmetron, Poland) at 20°C. The conductivity was determined by an ESP 2ZM electrode (EUROSENSOR, Poland) according to the Polish standard [19]. Soil texture was evaluated using a hydrometric method, according to the Polish standard - PNR-04032:1998. Soil dry mass and water content were measured according to Wilke (2005). The content of bioavailable forms of metals was obtained using extraction with 0.01 M $CaCl_2$. Extraction was conducted with 3 g of airdried soil and 30 ml 0.01 M $CaCl_2$ for 2 hours.

The data for further analyses were collected from five randomly selected plants on each subplot which was not exposed to edge effect. Plant samples were dried at 70 °C and digested using concentrated nitric acid in a microwave system (MDS 2000, CEM, USA). Concentrations of metals both in soil and plants were measured with flame atomic absorption spectrophotometry (Varian Spectra AA300) or by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Varian, USA).

Data reported in this paper were processed using the computer software Microsoft Excel and Statistica 10. Probability of 0.05 or less was considered to be statistically significant. Presented values are means ± standard deviation.

3. Results and Discussion

3.1 Site description

For the Polish site lead and cadmium contamination levels in soil ranged from 357.6 to 646.3 and 13.42 to 26.41 mg/kg d.w., respectively. For zinc the range was from 1273 to 2505 mg/kg d.w. Heavy metal concentrations in soil exceeded Polish limits for arable soil: the total lead and cadmium concentrations exceed these limits 4 to 6-fold, whereas the total zinc concentration - from 4 to 7-fold [20]. The pH-value was almost neutral, followed by moderate content of organic matter and low EC. The level of bioavailable forms of cadmium and zinc were high (about 5% and 2.5% respectively), whereas bioavailability of lead was low (below the detection limit).

For the German site lead and cadmium levels in soil ranged from 462.5 to 696.8 and 25.29 to 39.34 mg/kg d.w., respectively. In the case of zinc, the range was from 2864 to 4488 mg/kg. The pH-value was neutral, followed by high (33%) level of organic matter and high EC. The bioavailability of metals contained in soil was very low, mainly due to high level of organic matter (Pb below detection limit, Cd of 0.25 mg/kg d.w. and Zn of 16 mg/kg d.w.).

Table 1. Formy występowania zanieczyszczeń ropopochodnych w gruncie [16]

Tablica 1. Forms of oil hydrocarbons in soil [16]

Parameter	Polish site	German site
pH (1 : 2.5 soil/KCl ratio)	6.79 ± 0.01	6.374 ± 0.010
Electrical conductivity (μS/cm)	127 ± 0.002	797.45 ± 0.040
Organic matter content (%)	4.0 ± 0.03	32.95 ± 13.04
Sand (1 – 0.05 mm), %	28	58
Silt (0.05 – 0.002 mm), %	56	19
Clay (< 0.002 mm), %	16	23
Total heavy metal concentration (extraction with *aqua regia*)		
Pb (mg kg^{-1})	547.0 ± 27.92	574.8 ± 24.68
Cd (mg kg^{-1})	20.84 ± 1.17	31.20 ± 1.98
Zn (mg kg^{-1})	2174.5 ± 103	3592.0 ± 146
$CaCl_2$ extractable metal fraction^a		
Pb (mg kg^{-1})	0.39 ± 0.03 (0.07)^b	BDL
Cd (mg kg^{-1})	1.20 ± 0.03 (5.76)^b	0.280 ± 0.05(0.89)^b
Zn (mg kg^{-1})	46.52 ± 1.51 (2.13)^b	16.24 ± 1.01(0.45)^b

Values represent mean of three replicate samples ± SE

^{a} – extraction with 0.01 M CaCl2;

^{b} – in parentheses percentages of total metal concentrations are presented

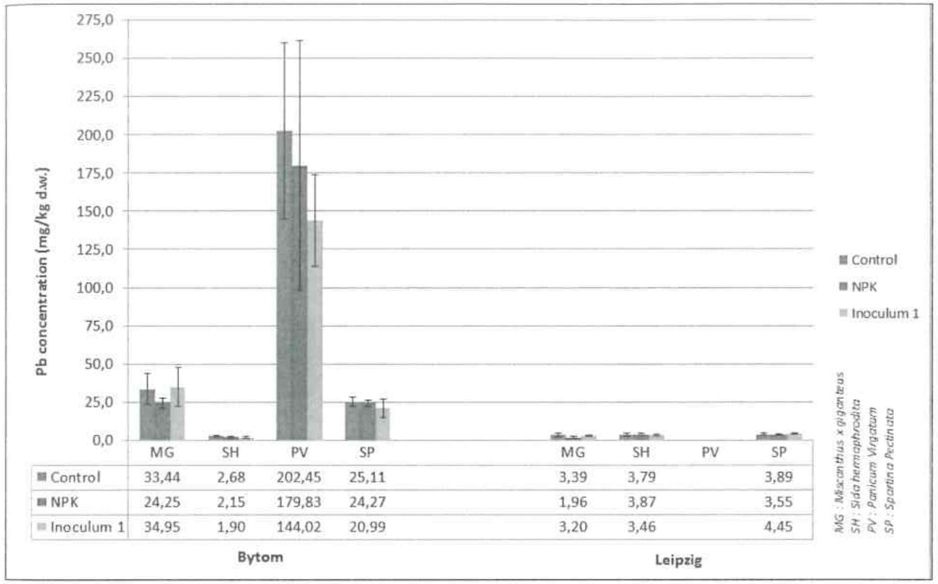
3.2 Heavy metals in biomass after the first growing season

Concentrations of lead in biomass after the first growing season on the Polish and German site are illustrated in Figure 1. In general, higher lead uptake was found in biomass collected on the Polish site. On the one hand, this could be caused by its increased bioavailability observed on the Polish site. On the other hand, this can be attributed to a number of other reasons, for example higher average temperature and rainfall rate on the Polish site and consequently the higher plant size. This favors the transpiration and increases the volume of absorbed water whereby more heavy metals can be transported out of the soil. Differences between heavy metals plant uptake depending on the age and size of the plants were also reported by Korzeniowska and Stanislawska-Glubiak [17].

The lowest concentration of lead (2 mg/kg d.w.) was observed for S. hermaphrodita on the Polish site, irrespectively of the experimental option. The same effect was observed in the plant growth on the German site where lead in soil was not bioavailable. It means that Sida hermaphrodita has a natural ability not to uptake this element and can be used in a phytostabilization process. Low lead uptake ability of Sida plants was also reported by Kocoń and Matyka [18]. For Miscanthus x giganteus and Spartina pectinata the lead uptake was between 20.99 and 34.95 mg/kg d.w. Kocoń and Matyka [18] reported that the

The highest concentration of lead (144 – 202 mg/kg d.w.) was assessed in Panicum virgatum from the Polish site, irrespectively of the experimental option.

On the German site, the total amount of the plant material was limited due to poor plant growth, therefore, no analyses were performed. It was found out that Panicum virgatum could be used in phytoextraction of lead contaminated soils. Johnson [21] confirmed that switchgrass could be recommended for lead contaminated soils as a model plant for phytoextraction because this plant is tolerant of lead contamination, produces high amounts of biomass even under conditions of metal contamination, and is able to accumulate lead both in shoots and roots.



	MG	SH	PV	SP	MG	SH	PV	SP
▨ Control	33,44	2,68	202,45	25,11	3,39	3,79		3,89
▨ NPK	24,25	2,15	179,83	24,27	1,96	3,87		3,55
▨ Inoculum 1	34,95	1,90	144,02	20,99	3,20	3,46		4,45

Fig 1. Concentration of Pb in plant biomass after the first growing season (2014) on Polish and German sites: Values are means ± SD (n=5).

Rys. 1. Zawartość Pb w biomasie roślin po pierwszym roku wzrostu (2014) na poletkach w Polsce i Niemczech: wartości średnie ± SD (n=5).

Cadmium concentrations in biomass after the first growing season on the Polish and German sites are presented in Figure 2. In general, the higher cadmium uptake was found in biomass collected on the Polish site. For M. x giganteus and P. virgatum the cadmium uptake was at the level of about 2 mg/kg d.w., irrespectively of the experimental option. The highest cadmium uptake was determined for S. hermaphrodita for control and NPK fertilized plots (6 mg/kg d.w.), whereas in the case of the plots with inoculum it was 2-fold lower. It was also proven by Wierzbowska et al. [19] that S.hermaphrodita demonstrates high cadmium uptake ability. It was shown that the accumulation in the aerial parts of S.hermaphrodita depended on the heavy metal, and it was concluded that the heavy metals could be ordered as follows: Cd < Cu < Cr < Ni< Zn < Mn. The lowest cadmium uptake was observed for S. pectinata. The obtained results suggest that this species is not a cumulative one. It was also proven by

It means that this species has high suitability for phytostabilization. In the process of hytostabilization, the roots of plants mechanically bind soil particles, control erosion, educe seepage of water, and stabilize contamination using root exudates [22].

Cadmium uptake by plants on the German site was much lower, and correlated with ow bioavailability of this element in soil. For M. x giganteus and S. hermaphrodita o differences were observed in cadmium uptake (about 1.5 mg/kg d.w.). In the case f S. pectinata the uptake was on the level of 0.4 mg/kg d.w., and no statistically significnt difference was observed when compared to the results obtained from the Polish site.

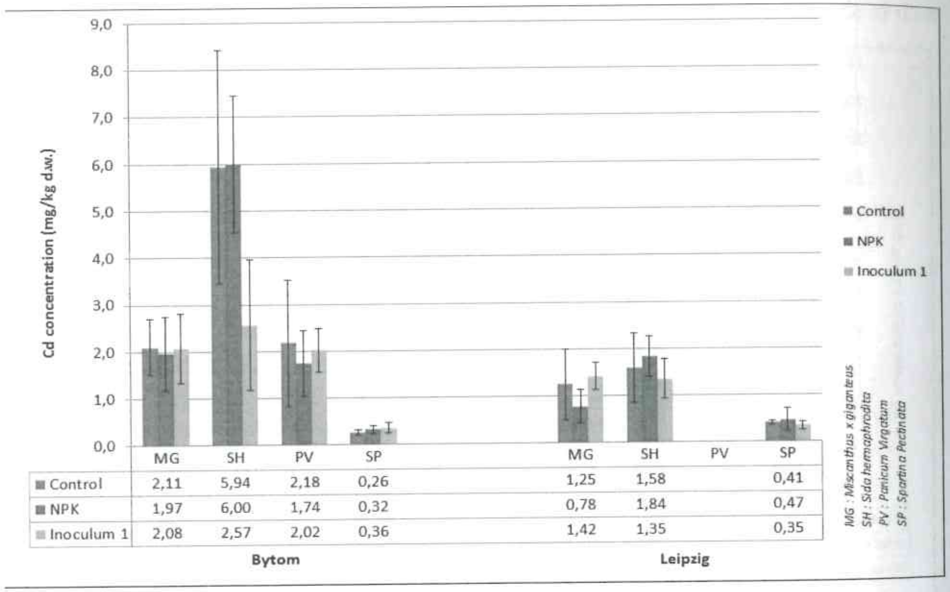


Fig. 2 *Concentrations of Cd in plant biomass after the first growing season (2014) on Polish and German sites: Values are means ± SD (n=5).*

Rys. 2. *Zawartość Cd w biomasie roślin po pierwszym roku wzrostu (2014) na poletkach w Polsce i Niemczech: wartości średnie ± SD (n=5).*

Concentrations of zinc in biomass after the first growing season on the Polish and German sites are illustrated in Figure 3. In general, the higher cadmium uptake was found in biomass collected from the Polish site due to higher bioavailability of this element in arable soil. For M. x giganteus and P. virgatum zinc uptake was on the comparable levels (about 450 mg/kg d.w.), irrespectively of the experimental option. The highest zinc uptake was determined for Sida hermaphrodita for control and NPK fertilized plots (1162-1577 mg/kg d.w.), whereas in the case of plots with inoculum it was more than 2-fold lower. It means that Sida hermaphrodita can be used for phytoextraction of zinc from contaminated soil, which was also confirmed by Kocoń and Matyka [18]. The lowest zinc uptake was found for S. pectinata irrespectively of the experimental options and sites. It suggests that this plant species has a natural ability not to uptake zinc even if high levels of bioavailable fractions occur in the soil. It was proven by Korzeniowska and Stanisławska-Głubiak

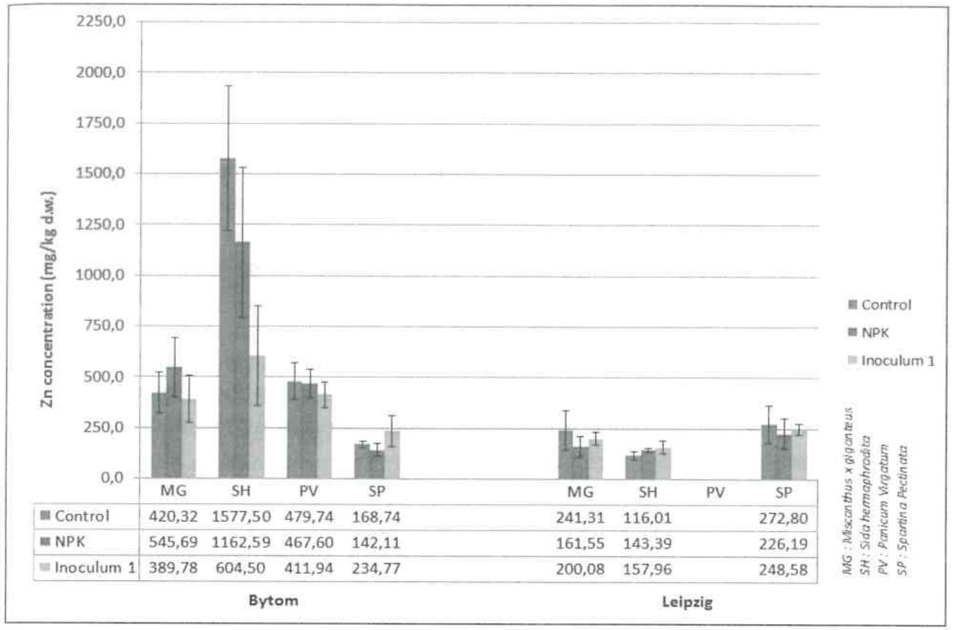


Fig. 3 *Concentration of Zn in plant biomass after the first growing season (2014) on Polish and German sites: Values are means ± SD (n=5).*

Rys. 3. *Zawartość Zn w biomasie roślin po pierwszym roku wzrostu (2014) na poletkach w Polsce i Niemczech: wartości średnie ± SD (n=5).*

After the first growing season almost every result for plants HM uptake at the Polish site was significantly higher than the uptake rates on the German one. The main factor potentially responsible for different uptakes of HM was the level of their bioavailability in the soil. The soil pH has also a substantial influence on the mobility of heavy metals but the pH values for both sites show no significant difference. It means that in this case only soil bioavailability of heavy metals has an impact on the HM uptake to the aboveground parts of the plants. The obtained results suggest that although the metal content in soil was higher for the German site the accumulation of metals in plant tissues was lower than on the Polish site.

Based on the results obtained so far the most suitable species for lead phytoremediation are *Miscanthus* x *gigantheus* and *Panicum virgatum*, whereas for cadmium - Sida *hermaphrodita*. On the other hand, Spartina pectinata seems to be the best candidate for safe biomass production at contaminated areas.

4. Conclusions

The data collected after the first year of the experiment demonstrate that HM uptake by selected species on the Polish site is significantly higher than the uptake on the German site. This situation might be attributed to the level of bioavailable content of metals in the soil. Although the soil pH value is important as it has an effect on the mobility of heavy metals, in this case it was not the main influencing factor. It means that the levels of bioavailability of heavy metals in the soil were responsible for their uptake to the aboveground parts of the plants. The obtained results show that although the content of metals in soil was much higher on the German site, the accumulation of metals in plant tissues was lower than in plant tissues from the Polish site.

After the first year of the experiment on two heavy metal contaminated sites in Poland (arable land) and Germany (postindustrial site) to find the optimum energy crop species with respect to both: the energy crop yield and phytoremediation potential the following conclusions can be drawn:

- the main factor determining the metal uptake by plants is the level of bioavailability of heavy metals in soil (soil solution),
- high bioavailability of metals (especially Cd and Zn) has an influence on higher uptake of heavy metals by plants in the case of all tested species on the Polish site compared to the German one,
- the highest lead uptake was found for Panicum virgatum, whereas the highest cadmium and zinc contents were observed for Sida hermaphrodita grown at the Polish arable soils,
- the lowest concentrations of tested heavy metals was found for Spartina pectinata regardless of the level of their bioavailability in soil; it means that this plant can be used for phytostabilization and treated as a „safe biomass" produced on HM contaminated soils,
- inoculum application diminished the cadmium and zinc uptake by Sida hermaphrodita, when compared to the control plot. For other plant species/metals no statistically significant influence has been observed so far.

Acknowledgements

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