

## IS IT FEASIBLE TO PRODUCE ENERGY CROPS IN HEAVY METALS CONTAMINATED SOILS?

L. Gomes<sup>1</sup>, J. Costa<sup>1,2</sup>, B. Barbosa<sup>1</sup>, F. Santos<sup>3</sup>, A.L. Fernando<sup>1</sup>

<sup>1</sup>MEtRICs/ Departamento de Ciências e Tecnologia da Biomassa, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal e-mail: [ala@fct.unl.pt](mailto:ala@fct.unl.pt)

<sup>2</sup>Instituto Superior de Educação e Ciências, Lisboa, Portugal

<sup>3</sup>Universidade Estadual do Rio Grande do Sul, Porto Alegre, Brazil

**ABSTRACT:** The production of energy crops has been presented as a promising alternative to partially replace fossil fuels and products of fossil origin. Among the various species which can be grown to generate energy, perennial crops are promising because of their high productivity and energy content. Oil crops, as sources for medium-chain fatty acids and medium-chain polymer building blocks, can be used for the production of plastics, surfactants, detergents, lubricants, plasticizers and other products, replacing fossil feedstocks. Yet, the increasing demand for biomass for the production of bioenergy, biomaterials and bioproducts is generating land-use conflicts which might be avoided through the establishment of marginal land for the production of dedicated energy crops, e.g. heavy-metal contaminated land. In this context, perennial and oil crop production under heavy metals contaminated soils was reviewed, with the aim to identify the concentration thresholds for the production of those crops with minor toxic effects. A preliminary evaluation of the data indicates that both perennial grasses and oil crops are potentially useful for phytoremediation of heavy metal contaminated soils. Most of the crops exhibited considerable tolerance to most of the metals and productivity was hardly affected by the potentially toxic concentrations of metals. Concentrations that affected most significantly the productivity of the plants are those that surpass 4 times the concentration limits accepted in soils (according to EU regulations) and when the bioavailable fraction to plants is high (exceeding 50% of the total). Most of the metals are preferentially accumulated in the belowground structures or in the leaves. Cadmium and zinc are the most mobilized elements, presenting higher translocation to the aboveground structures. Biomass obtained in contaminated soils presented higher ash content which can be a constraint for its processing and use. Nevertheless, these crops show potential to simultaneously deliver high yields, restore soil properties and promote groundwater protection by preventing heavy metals leaching. Their production in contaminated soils can also provide social and economic opportunities.

**Keywords:** Energy crops; contaminated soils; heavy metals; phytoremediation; polluted soil; land use.

### 1 INTRODUCTION

Exponential development of technology along with the increase of world population [1] enhances energy demand and other products that currently rely on fossil fuels. Although fossil resources will not be able to indefinitely ensure the security of this demand it also generates by-products that can produce harmful effects to the environment. Biomass from energy crops is a renewable source capable to entirely replace fossil resources without significantly change the conversion processes or products [2], maintaining economic viability and reduce the harmful effects to the environment [3].

Energy crops are among the most promising and subsidized forms of renewable energy [4] because they are highly productive and contribute less to the greenhouse effect [5]. On the other hand, the conversion of forest areas into arable land for energy crops production can lead to imbalance CO<sub>2</sub> cycle, since it releases to the atmosphere high amounts of CO<sub>2</sub> due to the forest removal by fire and microbial root decomposition [6].

The use of plants for energy production, mainly by first generation processes, competes directly with the food products supply both by soil usage and grains diversion for biofuels production. Thus, policies that secure the food production have been implemented, either through incentives for energy production by second generation processes [7] or limiting energy crops production to marginal soils [8].

Marginal soils usually have poor cultivation conditions for plant growth, caused by water stress, nutrient deficiency or contamination [9]. Therefore,

energy crops production in marginal soils, especially contaminated with heavy metals, can reduce food crop competition for agricultural soils [10], [8], promote soil decontamination and be a source of raw material for energy or bioproducts production. In this work a revision from literature was made on perennial grasses and the effects of the heavy metal contamination on the yields were evaluated.

### 2 METHODOLOGY

In order to review the current knowledge of energy crops cultivated in soils contaminated with heavy metals, a set of papers were selected. The objective was to compare different types of crops and different scenarios to understand the effects in the crops subjected to heavy metal contamination, assessing productivity variation, phytoremediation potential and soil phytostabilization.

Perennial grasses (*Miscanthus*, Giant reed, and Switchgrass) were found to be the most representative crops. Although oleaginous crops are still little studied, they are beginning to raise interest due to the possibility of using the produced oil for biofuels manufacture.

In order to evaluate the losses in biomass productivity Tolerance Index (TI) was analyzed. The term TI is determined by the ratio between the plant productivity obtained in the control and in the contaminated trials, being divided into four intervals, according to Table 1. For crop yields presenting values above 75%, it is considered that the metal has little or no influence on plant productivity, classifying the TI as high. Between 75% and 50%, the presence of the contaminant in the soil

moderately affects plant productivity. For yields between 50% and 25%, the presence of the contaminant in the soil has a high effect on plant productivity, classifying the TI as low. Below 25%, the TI is classified as critical, since virtually the entire culture has been lost. A revision of the literature was made and several energy crops were classified according to the TI obtained in Zn and Cd contaminated soils.

Table 1. Tolerance Index levels

Yields <sub>contaminated</sub> /Yields <sub>control</sub>	TI
> 75	High
75-50	Moderate
50-25	Low
< 25	Critical

### 3 RESULTS AND DISCUSSION

It is possible to observe that cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu) are the elements with the highest number of publications related with energy crops. These elements have been identified as the most common in urban soils [11], with the main routes of soil contamination through fertilizers and sludge spreading and wastewater irrigation [12], [13], which justifies the number of publications studying these heavy metals. Cd and Zn are the most mobilized elements, being considered separately.

Cd has no known functions in plant metabolism [12], [14] and the routes of contamination are the use of fertilizers, the dissemination of industrial effluents [15] and the disposal of waste batteries and accumulators [16]. Due to its toxicity and being the seventh most toxic element on the list of substances posing a risk to human health [17], EU regulation imposes restrictive limits on its presence on the soil.

In spite of being a micronutrient with functions of synthesis and enzymatic activity [18], [19] Zn presence at high concentrations presents toxicity to plants [19]. The Zn contamination routes are the use of fertilizers, pesticides and the deposition of industrial effluents, namely from the electroplating, battery, pigment, rubber and plastics industries [20].

Pb negatively affects the metabolism of plants, with respect to photosynthesis and water absorption affecting cellular components and biomolecules [13], [21]. Although some sources of Pb contamination have been combated, such as paints and gasoline, contamination can still occur through various sources such as mining and hunting and fishing materials [22], [23], [24], [25], [26].

Cr is a common heavy metal found in soils entering whether by natural rock weathering [27] or by anthropogenic sources. Cr industrial application includes wood preservation, leather tanning, chrome plating and metallurgy [28], [29] entering the soil by wastewater irrigation and illegal discharges or sludge disposal [30]. In natural environment the dominant oxidation state is Cr(III) being relatively immobile in soils but it can also be present as Cr(VI), which is much more mobile, highly water-soluble and toxic [31], [29], [27], [30] to animals and plants.

#### 3.1 Cadmium

When compared to the control, variations in both aboveground and belowground productivity due to the increase of Cd concentration for each crop are presented

in Figure 1 and Figure 2 respectively. The aboveground productivity of Miscanthus is not significantly affected for concentrations below 50 mg/kg in the soil. For concentrations above 100 mg/kg the plant has a productivity reduction of more than 50%. Similar behavior is observed for the belowground biomass, classifying the plant as tolerant, since it has the capacity to adapt to concentrations ten times higher than the limit defined by regulations.

Cardoon aboveground productivity is not significantly affected for concentrations around 75 mg/kg, nearly twenty times the regulated limit, making it an interesting alternative of cadmium phytoremediation. The aboveground productivity of castor bean is also not significantly affected up to concentrations close to 50 mg/kg.

Both aboveground and belowground productivity of switchgrass are not significantly affected for concentrations up to twice the limit set by regulations, but it has a trend that suggests a significant productivity reduction at concentrations above this value. Similarly, safflower is also significantly affected at concentrations twice the regulated limit, decreasing its productivity to a critical level at concentrations around 90 mg/kg.

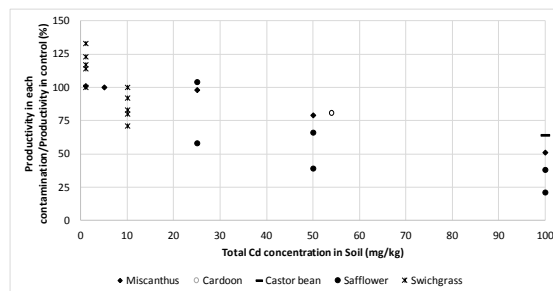


Figure 1. Aboveground productivity compared with control in each Cd concentration.

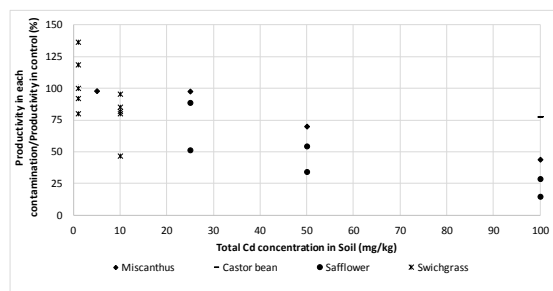


Figure 2. Belowground productivity compared with control in each Cd concentration.

Most of the crops show high TI at concentrations up to 29 mg/kg. For concentrations between 29 and 87 mg/kg, most of the crops present moderate TI. Between 87 and 185 mg/kg of cadmium in the soil, the TI is low and at concentrations above 185 mg/kg the TI is critical. Concerning belowground productivity, crops presented an exponential decrease with the increase of Cd concentration in the soil, obtaining high TI for concentrations up to 21 mg/kg. For concentrations between 21 mg/kg and 55 mg/kg, most crops showed a moderate TI. Between 55 mg/kg and 112 mg/kg, TI is low and above 112 mg/kg, TI is critical.

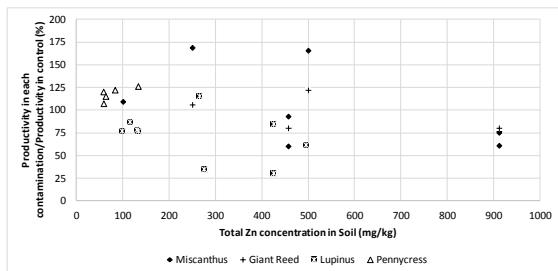
#### 3.2 Zinc

In general, Zn concentration in soils ranges between

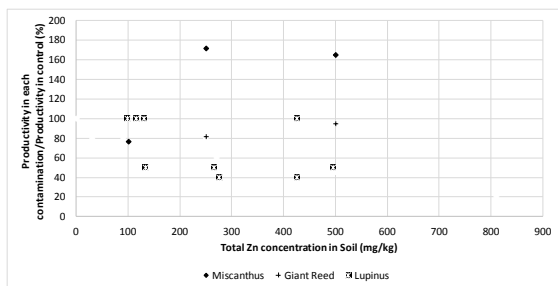
60 and 89 mg/kg [13]. Although these values are below the maximum allowed by the EU regulation (300 mg/kg) the distribution of this metal in some regions of the planet are well above the maximum limit [32], [33], [34].

When compared to the control, variations in both aboveground and belowground productivity due to the increase of Zn concentration for each crop are presented in Figure 3 and Figure 4 respectively.

For the different crops, Zn becomes toxic at a wide range of concentrations. These results are very different from those obtained for Cd, with random results distribution, so a generic TI was not possible to establish.



**Figure 3.** Aboveground productivity compared with control in each Zn concentration.



**Figure 4.** Belowground productivity compared with control in each Zn concentration.

#### 4 CONCLUSIONS

Some energy crops were reviewed in order to study their behavior when exposed to different levels of contamination with heavy metals. In this context, the use of field trials, pots or hydroponics allows the setting of a wide range of scenarios. Cd, Zn, Pb and Cu stand out as the most studied heavy metals, not only because of their toxicity to the plants but also because of the frequency and concentration in which they appear in the contaminated soils. Most of the metals are preferentially accumulated in the belowground structures or in the leaves but Cd and Zn are the most mobilized elements, presenting higher translocation to the aboveground structures of the plants. Although most of the selected papers present enough data to allow the calculation of the phytoremediation indicators, the majority lacks this information impairing the analysis of the biomass potential for phytoremediation. The concept of aided phytoremediation has been gaining interest with some works studying how an amendment of agricultural conditions can potentiate not only the productivity but also the removal of the constituents responsible for soil contamination.

#### 5 ACKNOWLEDGEMENTS

This work received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727698 (Project MAGIC - Marginal lands for Growing Industrial Crops: Turning a burden into an opportunity). This work was also supported by the METRICs unit which is financed by Portuguese national funds from FCT/MCTES (UID/EMS/04077/2019).

#### 6 REFERENCES

- [1] United Nations, 2017. World Population Prospects: The 2017 Revision, Online Demographic Profiles.
- [2] Schröder, P., Beckers, B., Daniels, S., Gnädinger, F., Maestri, E., Marmioli, N., Mench, M., Millan, R., Obermeier, M.M., Oustriere, N., Persson, T., Poschenrieder, C., Rineau, F., Rutkowska, B., Schmid, T., Szulc, W., Witters, N., Sæbø, A., 2018. Science of the Total Environment Intensify production , transform biomass to energy and novel goods and protect soils in Europe — A vision how to mobilize marginal lands. *Sci. Total Environ.* 616–617, 1101–1123. <https://doi.org/10.1016/j.scitotenv.2017.10.209>
- [3] Zhuang, D., Jiang, D., Liu, L., Huang, Y., 2011. Assessment of bioenergy potential on marginal land in China. *Renew. Sustain. Energy Rev.* 15, 1050–1056. <https://doi.org/10.1016/j.rser.2010.11.041>
- [4] Field, C.B., Campbell, J.E., Lobell, D.B., 2007. Biomass energy : the scale of the potential resource 65–72. <https://doi.org/10.1016/j.tree.2007.12.001>
- [5] Chandra, V., Bajpai, O., Singh, N., 2016. Energy crops in sustainable phytoremediation. *Renew. Sustain. Energy Rev.* 54, 58–73. <https://doi.org/10.1016/j.rser.2015.09.078>
- [6] Fargione, J., 2009. No Title 1235. <https://doi.org/10.1126/science.1152747>
- [7] Jiang, W., Zipp, K.Y., Jacobson, M., 2018. Biomass and Bioenergy Economic assessment of landowners' willingness to supply energy crops on marginal lands in the northeastern of the United States. *Biomass and Bioenergy* 113, 22–30. <https://doi.org/10.1016/j.biombioe.2018.03.005>
- [8] Fernando, A.L., Costa, J., Barbosa, B., Monti, A., Rettenmaier, N., 2018. Environmental impact assessment of perennial crops cultivation on marginal soils in the Mediterranean Region. *Biomass and Bioenergy* 111, 174–186. <https://doi.org/10.1016/j.biombioe.2017.04.005>
- [9] Tang, Y., Xie, J., Geng, S., 2010. Marginal Land-based Biomass Energy Production in China 52, 112–121. <https://doi.org/10.1111/j.1744-7909.2010.00903.x>
- [10] Dale, V.H., Kline, K.L., Wiens, J., Fargione, J., 2016. Biofuels: Implications for Land Use and Biodiversity.
- [11] Efremova, V.A., Dabakh, E. V, Kondakova, L. V, 2013. A Chemical and Biological Assessment of the State of Urban Soils 6, 561–568. <https://doi.org/10.1134/S1995425513050028>
- [12] Amjad, M., Khan, S., Khan, A., Alam, M., 2017a. Science of the Total Environment Soil contamination with cadmium , consequences and

- remediation using organic amendments. *Sci. Total Environ.* 601–602, 1591–1605. <https://doi.org/10.1016/j.scitotenv.2017.06.030>
- [13] Kabata-Pendias, A., 2011. Trace elements in soils and plants, *Trace Elements in Soils and Plants*, Fourth Edition. <https://doi.org/10.1201/b10158-25>
- [14] Amjad, M., Khan, S., Khan, A., Alam, M., 2017b. Soil contamination with cadmium , consequences and remediation using organic amendments *Science of the Total Environment Soil contamination with cadmium , consequences and remediation using organic amendments. Sci. Total Environ.* 601–602, 1591–1605.
- [15] Chiao, W., Syu, C., Chen, B., Juang, K., 2019. Cadmium in rice grains from a field trial in relation to model parameters of Cd-toxicity and -absorption in rice seedlings. *Ecotoxicol. Environ. Saf.* 169, 837–847. <https://doi.org/10.1016/j.ecoenv.2018.11.061>
- [16] Moreira, T.F.M., Santana, I.L., Moura, M.N., Ferreira, S.A.D., Lelis, M.F.F., Freitas, M.B.J.G., 2017. Recycling of negative electrodes from spent Ni-Cd batteries as CdO with nanoparticle sizes and its application in remediation of azo dye. *Mater. Chem. Phys.* 195, 19–27. <https://doi.org/10.1016/j.matchemphys.2017.04.009>
- [17] ATSDR - Substance Priority List, 2017.
- [18] Hansch, R., Mendel, R., 2009. Physiological functions of mineral micronutrients (Cu, Zn, Mn, Fe, Ni, Mo, B, Cl). *Curr. Opin. Plant Biol.* 12, 259–266.
- [19] Sturikova, H., Krystofova, O., Huska, D., Adam, V., 2018. Zinc , zinc nanoparticles and plants. *J. Hazard. Mater.* 349, 101–110. <https://doi.org/10.1016/j.jhazmat.2018.01.040>
- [20] Araújo, D.F., Boaventura, G.R., Machado, W., Viers, J., Weiss, D., Patchineelam, S.R., Ruiz, I., Paula, A., Rodrigues, C., Babinski, M., Dantas, E., 2017. Tracing of anthropogenic zinc sources in coastal environments using stable isotope composition. *Chem. Geol.* 449, 226–235. <https://doi.org/10.1016/j.chemgeo.2016.12.004>
- [21] Kumar, A., Narasimha, M., Prasad, V., 2018. Ecotoxicology and Environmental Safety Plant-lead interactions : Transport , toxicity , tolerance , and detoxi fi cation mechanisms 166, 401–418. <https://doi.org/10.1016/j.ecoenv.2018.09.113>
- [22] Ain, D.E.J.P., Isher, I.A.N.J.F., Homas, V.E.G.T., 1997. A GLOBAL UPDATE OF LEAD POISONING IN TERRESTRIAL BIRDS FROM AMMUNITION SOURCES 99–118. <https://doi.org/10.4080/ilsa.2009.0108>
- [23] Gremse, C., 2015. Oxford Lead Symposium Lead Ammunition : understanding and minimising the risks to human. <https://doi.org/10.13140/RG.2.1.3995.2720>
- [24] Plaza, P.I., Uhart, M., Caselli, A., Wiemeyer, G., Lambertucci, S.A., 2018. A review of lead contamination in South American birds : The need for more research and policy changes. *Perspect. Ecol. Conserv.* 16, 201–207. <https://doi.org/10.1016/j.pecon.2018.08.001>
- [25] Plaza, P.I., Lambertucci, S.A., 2019. Science of the Total Environment What do we know about lead contamination in wild vultures and condors ? A review of decades of research. *Sci. Total Environ.* 654, 409–417. <https://doi.org/10.1016/j.scitotenv.2018.11.099>
- [26] Sriram, A., Roe, W., Booth, M., Gartrell, B., 2018. Science of the Total Environment Lead exposure in an urban , free-ranging parrot : Investigating prevalence , effect and source attribution using stable isotope analysis. *Sci. Total Environ.* 634, 109–115. <https://doi.org/10.1016/j.scitotenv.2018.03.267>
- [27] Lilli, M.A., Nikolaidis, N.P., Karatzas, G.P., Kalogerakis, N., 2019. Identifying the controlling mechanism of geogenic origin chromium release in soils. *J. Hazard. Mater.* 366, 169–176. <https://doi.org/10.1016/j.jhazmat.2018.11.090>
- [28] Eyvazi, B., Jamshidi-zanjani, A., Khodadadi, A., 2019. Immobilization of hexavalent chromium in contaminated soil using nano- magnetic MnFe 2 O 4. *J. Hazard. Mater.* 365, 813–819. <https://doi.org/10.1016/j.jhazmat.2018.11.041>
- [29] Li, Y., Wang, W., Zhou, L., Liu, Y., Mirza, Z.A., Lin, X., 2017. Chemosphere Remediation of hexavalent chromium spiked soil by using synthesized iron sul fi de particles. *Chemosphere* 169, 131–138. <https://doi.org/10.1016/j.chemosphere.2016.11.060>
- [30] Wang, T., Liu, Y., Wang, J., Wang, X., Liu, B., Wang, Y., 2019. In-situ remediation of hexavalent chromium contaminated groundwater and saturated soil using stabilized iron sul fi de nanoparticles. *J. Environ. Manage.* 231, 679–686. <https://doi.org/10.1016/j.jenvman.2018.10.085>
- [31] Hu, J., Meng, D., Liu, X., Liang, Y., Yin, H., Liu, H., 2018. Response of soil fungal community to long-term chromium contamination. *Trans. Nonferrous Met. Soc. China* 28, 1838–1846. [https://doi.org/10.1016/S1003-6326\(18\)64828-9](https://doi.org/10.1016/S1003-6326(18)64828-9)
- [32] Křibek, B., Nyambe, I., Majer, V., Kněsl, I., Mihaljevič, M., 2019. Soil contamination near the Kabwe Pb-Zn smelter in Zambia : Environmental impacts and remediation measures proposal. *J. Geochemical Explor.* 197, 159–173. <https://doi.org/10.1016/j.gexplo.2018.11.018>
- [33] Li, Z., Ma, Z., Jan, T., Kuijp, V. Der, Yuan, Z., Huang, L., 2014. Science of the Total Environment A review of soil heavy metal pollution from mines in China : Pollution and health risk assessment. *Sci. Total Environ.* 468–469, 843–853. <https://doi.org/10.1016/j.scitotenv.2013.08.090>
- [34] Pavlovi, P., Markovi, M., Kostić, O., Sakan, S., Dragana, Đ., Perović, V., Pavlovi, D., Pavlovi, M., Dragan, Č., Paunović, M., Mitrovi, M., 2019. Catena Evaluation of potentially toxic element contamination in the riparian zone of the River Sava 174, 399–412. <https://doi.org/10.1016/j.catena.2018.11.034>