Phytoremediation of soils contaminated with Lead by *Arundo donax* L.

S. Sidella & S. L. Cosentino

Dipartimento di Agricoltura, Alimentazione e Ambiente – Di3A, Università degli Studi di Catania, Catania, Italy

A. L. Fernando & J. Costa

Departamento de Ciências e Tecnologia da Biomassa/MEtRiCS, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, Caparica, Portugal

B. Barbosa

Universidade Federal do Oeste da Bahia, Barreiras, Brasil

ABSTRACT: *Arundo donax* L. is a high yielded perennial energy crop. Its cultivation for bioenergy may generate land-use conflicts which might be avoided through the establishment of energy crops on marginal land. In this context, this work aims to study the potentiality of *Arundo donax* in Pb contaminated soils (450 and 900 mg Pb kg^{-1}, dry matter) under a low irrigation regime (475 mm). Results showed that biomass productivity of giant reed was negatively affected by the contamination. Increased higher lead content in the biomass was obtained with increased lead contamination of the soil. Highest accumulation of lead was observed in the roots and rhizomes. Although the lead removal percentages by giant reed accumulation represent 3.2‰ maximum, after two consecutive years, towards the Pb soil bioavailable fraction, the establishment of a vegetative cover represent an approach to attenuate and stabilize contaminated sites with additional revenue to owners.

1 INTRODUCTION

Soil contaminated by heavy metals is a major problem causing vast areas of agricultural land to become derelict and non-arable and hazardous for both wildlife and human populations (Alloway, 1995). The area of soils contaminated with anthropogenic lead (Pb) is high, given its widespread deposition over the course of the last two centuries due to industrial waste, leaded paint, and automobile exhaust (McClintock, 2015). In the late 1970s, the anthropogenic deposition of Pb began to decline due to the gradual phase-out of leaded fuels and paints. Yet, lead historic deposition and Pb soil levels in certain spots (McClintock, 2015) still represent a source of pollution.

Giant reed (*Arundo donax* L.) is a C3 herbaceous perennial non-food crop characterized by relatively high yields (El Bassam, 2010). The plant belongs to the *Poaceae* family and to the *Arundineae* tribe, being the most common of the species of its genus (Mariani et al., 2010), growing spontaneously throughout the Mediterranean basin (Angelini et al., 2005; Cosentino et al., 2014). This perennial grass has been recognized as low-cost and low-maintenance crop and the high yielded biomass can be used for the production of energy (for both solid and second generation biofuels), paper pulp and biomaterials (Alexopoulou et al., 2011 and 2012).

Recent approaches utilize this crop in the phytoremediation of soils contaminated with heavy metals (e.g., Barbosa et al., 2015, Liu et al., 2017, Nsanganwimana et al., 2015, Sidella et al., 2016). Its robustness and physiological characteristics and its deep, dense and extensive root system, allows this grass to easily adapt to different types of soils and ecological conditions (Fernando et al. 2010), offering the possibility to associate soil decontamination and restoration with the production of biomass for bioenergy and biomaterials with additional revenue (Fernando et al., 2016). Additionally, when giant reed is cultivated in marginal/contaminated soils, land use conflicts with food crops are reduced (Dauber et al. 2012, Lewandowski, 2015), minimizing direct and indirect negative effects due to Land Use Change (LUC) (Fritsche et al. 2010). In this context, this research work aims to study the potentiality of giant reed production in Pb contaminated soils. Furthermore, considering the scarcity of water resources in the Mediterranean region, the study was conducted under a low irrigation regime, in order to reduce the impacts associated with irrigation.

2 MATERIALS AND METHODS

The aim of this work was to study the potential of giant reed in the phytoremediation of soils contaminated with lead under a low irrigation regime. The two-year pot experiment was conducted inside the *Campus* area of the Faculty of Sciences and Technology of the Universidade NOVA de Lisboa, from where the soil and rhizomes of *Arundo donax* L. were collected. The trial, established in April 2012, was run in pots containing 12 kg of soil (loam soil previously analyzed) artificially contaminated with a lead rich sludge (waste product derived from a battery manufacturing company, "Sociedade Portuguesa do Acumulador Tudor", located in Castanheira do Ribatejo, near Lisbon), containing 14% Pb (dry weight basis). Two concentrations of lead in contaminated soils were tested (450 and 900 mg $Pb.kg^{-1}$ dry matter, corresponding to maximum allowable and to twice as maximum, respectively, Pb_{450} and Pb_{900}) (Decreto-Lei nº 276/09, 2009). In each pot, two rhizomes were established (10 cm deep) (a pot for each level of contamination with replicates). After the establishment of the rhizomes, pots were fertilized: 3 g N/m^2 (urea, 46% N); 3 g N/m^2 (nitrolusal, mixture of NH_4NO_3+$CaCO_3$, 27% N); 17 g K_2O/m^2 (potassium sulphate, 51% K_2O); 23 g P_2O_5/m^2 (superphosphate, 18% P_2O_5). Simultaneously, a low irrigating regime was applied: 475 mm. The urea was applied when plants reached approximately 40-50 cm height. The same NK fertilization was applied in the 2nd year, when plants reached approximately 40-50 cm height, but not P once P fertilizer applied in the first year is enough for the growth of these perennial grasses for at least 10 years (El Bassam, 2010). Pots without plants were also prepared to investigate the influence of the soil-biomass system versus soil system in the remediation of the contamination.

At the end of each growing season (December-January), during two consecutive years (2012-2013), the plants were harvested and the aerial productivity and lead accumulation was monitored. Total below-ground dry weight and its lead accumulation were also determined in the second year. Lead content was determined by atomic absorption following calcination of biomass at 550ºC for two hours, in a muffler furnace and nitric acid digestion of the ash material. Lead released by percolated waters was also evaluated along the two growing seasons. Bioavailable Pb in the soils at the beginning of the experiment was also evaluated by EDTA extraction (Iqbal et al. 2013).

The statistical interpretation of the results was performed using analysis of variance (one-way ANOVA) by means of CoStat software (version 6.0) and the means were separated according to the test of Student-Newman-Keuls (SNK) when ANOVA revealed significant differences ($p \leq 0.05$).

3 RESULTS AND DISCUSSION

3.1 *Biomass productivity*

Figure 1 presents the aerial biomass productivity obtained in the trials, corresponding to stems leaves and litter produced during two consecutive years. According to the results obtained, there was an increase of productivity from the 1^{st} to the 2^{nd} year: this behavior was observed in all of the studied pots (contaminated and not contaminated). This reflects the energy spent by the plant, on the first years, to develop the extensive under-ground rhizome system (El Bassam, 2010). Leaves fraction represent the highest share in giant reed, ca. 53-58% of the total aerial biomass. Stems represent ca. 28-37% of the total aerial biomass. Litter represents ca. 5-19% of the total aerial biomass. Belowground biomass represents the highest share in the total biomass, ca. 89-92%. This is consistent with the common behavior of perennial crops, that spend more energy on the development and establishment of the belowground organs on the first years of cultivation (Fernando, 2005).

Lead contamination negatively affected biomass, both aerial biomass (Figure 1) and rhizomatous biomass. Roots and rhizome yields in Pb_{450} pots decreased by 37%, and roots and rhizome yields in Pb_{900} pots decreased by 60%, when compared with control (non-contaminated pots, with 3900 mg m^{-2}, dry matter). Yet, the reduction in yields observed in the pots contaminated with lead was not statistically significant ($p > 0.05$). Guo and Miao (2010) also reported phytotoxic effects on giant reed, but only when Pb concentration in soil was higher than 1000 mg kg^{-1}.

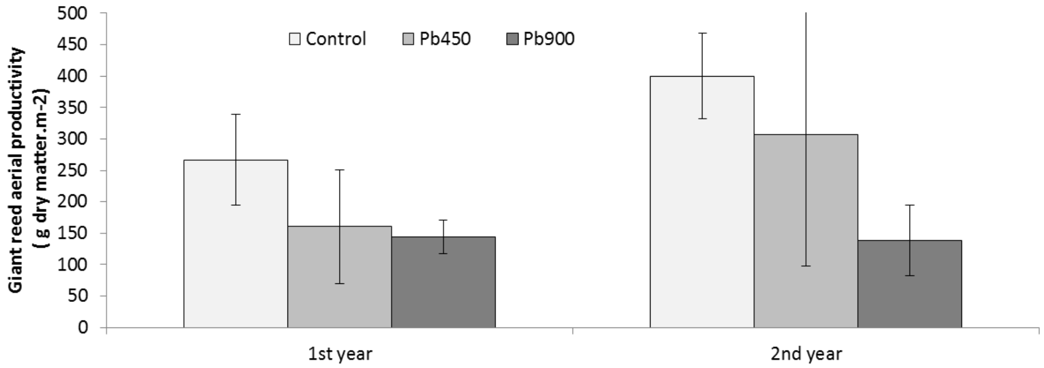

Figure 1. Giant reed aerial productivity ($g.m^{-2}$ dry matter) during two growing cycles.

3.2 *Accumulation of Pb in the biomass*

Figure 2 present the Pb accumulated by the aerial biomass of giant reed in two growing seasons, and in the belowground biomass in the 2nd year.

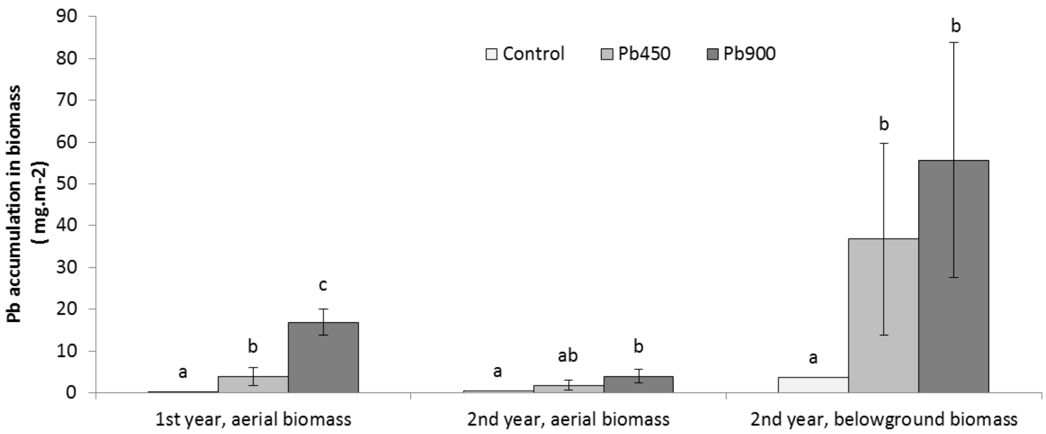

Figure 2. Lead accumulation in giant reed aerial biomass in two consecutive years and in belowground biomass, on the 2nd year (mg $Pb.m^{-2}$). Different lower-case letters indicate statistical significance ($p<0.05$, SNK test) between Pb treatments, for each type of biomass (aerial or belowground) and for each season (1st year or 2nd year).

Results show that biomass (aerial and belowground) obtained in Pb contaminated soils presented significantly higher lead accumulation then biomass from non-contaminated soils, thus showing phytoextraction capacity. The higher accumulation of Pb in the aerial fraction of the plant, from soils contaminated with Pb, shows the capacity of the plant to serve as a phytoextractor, once the metal will be uptaken and collected from the fields (Mirza et al., 2010). Yet, Pb transfer to the aerial fraction is limited and highest Pb remained accumulated in the belowground organs of the plant, which is consistent with other studies reported by Nsanganwimana et al. (2014). According to Kabata-Pendias (2001) the translocation of Pb from belowground organs to the aerial fraction is limited because Pb pyrophosphate bind to cell walls. This indicates that giant reed phytoremediation action is mostly due to its Pb immobilizing and stabilizing capacity in the roots and rhizomes.

3.3 *Pb remediation*

Figure 3 shows the Pb removal (%) by the aerial and belowground biomass of giant reed towards the bioavailable Pb content in the soil (Control, 7.5 mg kg^{-1}; Pb_{450}, 192 mg kg^{-1}; Pb_{900}, 515 mg kg^{-1}), after two consecutive years.

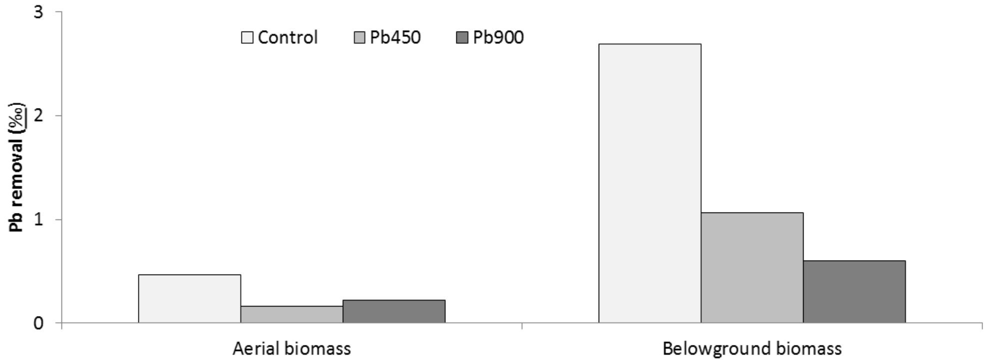

Figure 3. Giant reed biomass Pb removal (‰) from bioavailable lead in the soil, after two consecutive years.

As it is observed by Figure 3, the removal percentage of bioavailable Pb in soil by the aerial biomass is very limited: 0.5‰ maximum and 0.3‰ average. Pb mostly accumulates in the belowground biomass: 2.7‰ maximum and 1.5‰ average. This means that if we consider the phytoextraction process, the results are not optimal, because to remove all the lead in the soil, several years would be needed. But, considering that the aerial biomass does not contain Pb in high amounts, than the aerial biomass can be economically valorized. Moreover, the plant showed tolerance to the contamination, and a vegetative crop can be established in this type of contaminated soil, with the environmental benefits associated with.

3.4 *Pb in percolated waters*

During the two years of trials, percolated waters were monitored. Results were always below 0.10 mg Pb.dm^{-3}, lower than the limit values for irrigation water (Pb, 5.0 mg.dm^{-3}, according to the Portuguese legislation, Decreto Lei n° 236/98, 1998). This means that the amount of Pb in the percolated waters do not represent a risk to ground/surface waters.

4 CONCLUSIONS

Giant reed showed lead phytoextraction and accumulation capacity. The higher the Pb contamination in the soil, the higher the accumulation of Pb in aerial and below ground biomass. The contamination with lead also affected negatively the production of giant reed, but not significantly. Results showed that giant reed have potential to simultaneously deliver high yields and restore soil properties. Due to the extensive radicular system, giant reed is associated with control of soil erosion, carbon sequestration and minimization of nutrient leaching as well as with the restoration of soil properties (fertility, structure, organic matter). The biomass being produced may contribute to a positive energy balance and to greenhouse gases emissions reduction. Yet, the removal of lead from the soil by giant reed is a slow process. Yet, it represents an opportunity to produce sustainable biomass in a resource constrained World.

Further studies are needed to assess the biomass quality obtained from those contaminated fields. The prospect of the valorization of the giant reed aerial biomass, for bioenergy or biomaterials, could lessen the financial costs of soil remediation, compared to the traditional physical – chemical processes with the associated revenue of environmental benefits. However, little is known about the fiber content, or the calorific value of giant reed produced in Pb contaminated soils, and if the contamination affects the contents, compromising the biomass valorization.

ACKNOWLEDGEMENTS

This work was supported by the European Union (Project Optimization of perennial grasses for biomass production (OPTIMA), Grant Agreement No: 289642, Collaborative project, FP7-KBBE-2011.3.1-02).

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