Improving sustainability in the remediation of contaminated soils by the use of compost and energy valorization by *Paulownia fortunei*

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Abstract

The plantation of fast growing trees in contaminated sites, in combination with the use of organic wastes, could partially solve a dual environmental problem: the disposal of these wastes and the improvement of soil quality in these degraded soils. This study evaluated the effects of two composts amendments on the quantity and quality of *Paulownia fortunei* biomass and on syngas production by biomass gasification, produced by plants growing on trace elements contaminated soils. Compost increased biomass production to values similar to those produced in non-contaminated soils, due to the improvement in plant nutritional status. Moreover, biomass quality for gasification was increased by compost addition. Trace element accumulation in the biomass was relatively low and not related to biomass production or the gas quality obtained through gasification. Thus, *P. fortunei* plantations could pose an opportunity to improve the economic balance of the revegetation of contaminated soils, given that other commercial uses such as food or fodder crop production is not recommended in these soils.

Keywords

Biomass, combustion, gasification, heavy metals, fast-growing plants

1. Introduction

The establishment of plantations in degraded sites, such as trace element contaminated areas, in combination with the forestry use of proper organic wastes as soil amendments, might serve as a sink to deposit certain common wastes in the region. Organic materials are among the most commonly used amendments for remediating trace element-contaminated soils, given that the addition of organic matter (OM) can decrease trace element concentration in the soil solution, reducing their availability to plants and the risk of leaching (Pérez de Mora et al., 2007). This practice could partially solve a dual environmental problem, which is the need to find locations for the disposal of this type of waste and the need to improve soil quality in degraded soils, usually poor in organic matter and in semi-arid areas (Bastida et al., 2007). Plantations of fast-growing plant species might provide added interest, as their biomass constitutes a major source of ligno-cellulosic material for the production of biofuels (Lu et al., 2009). As metal-contaminated soils are unsuitable for the cultivation of food or fodder crops, the plantation of these species for biofuel production would not compete with food production in these marginal degraded lands (Schröder et al., 2008).

Some fast-growing tree species, such as *Paulownia spp.*, are particularly promising for the afforestation of trace element-contaminated soils for bioenergy purposes. Recent studies have shown that some *Paulownia* species show a relatively high tolerance to the presence of high concentrations of trace elements in the soil (Jiang et al., 2012; Madejón et al., 2014). Species in the *Paulownia* genus are highly adaptive to a wide range of climate and soil conditions (Yadav et al., 2013), and their use has been proposed for the afforestation of semi-arid areas, given their relatively good performance even under low water irrigation regimens (García-Morote et al., 2014). As

Paulownia biomass is characterized by a high cellulose content and a relatively high gross heating value, its use as an energy crop in Europe and North America has been promoted in the last decade (López et al., 2012). However, because certain amounts of trace elements may be translocated from the soil into the aboveground biomass, it is important to analyze the patterns of trace element accumulation in this species, and to assess whether the accumulation of these elements can affect the quality of the biomass for biofuel production or the processes of thermochemical or biochemical conversion of the lignocellulosic raw materials.

Among the existing conversion technologies, gasification is usually referred to as the most effective treatment for lignocellulosic material valorization (Martínez-Merino et al., 2013). At temperatures of 600 to 1000°C, solid biomass undergoes thermal decomposition to form gaseous products (syngas), typically including carbon monoxide, hydrogen, methane, carbon dioxide, and water. The resulting syngas, once cleaned, can be used for different purposes such as gas turbines, fuel cells, synthesis of liquid fuels like methanol, or chemicals (Yang et al., 2006). Unlike the syngas from the gasification of coal (rich in hydrogen), that produced from raw biomass is rich in carbon oxides. Therefore, to suit the conditions of traditional methanol synthesis, it must undergo a series of processes to improve the H_2/CO_2 proportion, usually the water gas reaction, reforming of methane, or CO_2 elimination (Jun et al., 2004). To date, there is little information regarding how the potential accumulation of trace elements into the biomass of plants grown in contaminated lands could affect the efficiency of gasification processes.

The aim of this work was to evaluate the potential use of *P. fortunei* plants, grown in degraded and contaminated soils for two consecutive years, for syngas production by the gasification of lingo-cellulosic biomass. We tested the effects of two composts on the quantity and quality of *P. fortunei* biomass, to assess whether the combination of plant and amendment addition could be a feasible strategy for the management of degraded and contaminated soils. We hypothesized that the use of these amendments (biosolid and alperujo compost) would increase soil productivity and plant yield, and would improve the quality of biomass for syngas, as indicated by the H_2/CO ratio of the gases obtained after the gasification process.

2. Materials and methods

2.1. Experimental design

The experiment was carried out under semi-field conditions, using two moderately contaminated soils and a non-contaminated control soil from SW Spain (Table 1). Trace-element contaminated soils, Aznalcázar (AZ) and Vicario (V), were collected in an area affected by a mine spill in 1998, the Aznalcóllar mine accident (Grimalt et al., 1999). Non-contaminated soil (NC) was collected in the experimental farm “La Hampa” (IRNAS-CSIC) in Coria del Río (Seville). The experiment was conducted in 27 containers that were placed outdoors. The containers had a capacity of 90 L of volume, a circular base of 45 cm of diameter and 1 m of height. Containers were filled with 110 kg of these soils and arranged according to a complete randomized block design with three treatments (two organic amendments and a control without amendment addition) and three replicates per treatment. The organic amendments were: AC, “alperujo” compost (a semisolid by-product obtained from the two-phase centrifugation system for olive oil extraction), and BC, biosolid compost (see Table 2 for a characterization of amendments). Biosolid compost was collected from the composting plant “EMASESA” (Seville, Spain) and was produced from sewage and pruning from parks and gardens from Seville city. The “alperujo compost” was prepared by the cooperative "Coto Bajo" Guadalcázar (Córdoba, Spain) by mixing alperujo with legume residues and manure from organic farming.

Amendments were added in November 2011 at a dose of 30000 kg ha^{-1}. High acidity, low OM content and moderately high values of total trace elements of soil V (Table 1), advised a second addition of 25000 kg ha^{-1} of each amendment in March 2012. In each container, a *Paulownia fortunei* sapling previously grown in a nursery was planted one week after the amendment addition (sapling height around 10-15 cm).

Containers were irrigated daily during the main growing period (May to October), using a drip irrigation hose with two emitters. The mean water dose during this time was 333 ml per container and day. This value was calculated taken the evapotranspiration demand into account to keep the soil moisture close to its water holding capacity.

2.2. Plant material and analysis

Two harvests were performed, in March 2013 and February 2014 respectively. In the first harvest the biomass of the entire plant (except the root system) was collected and weighed fresh and dry. In the second harvest the entire plant (including the root) was collected and weighed fresh and dry. After determination of total biomass, samples of trunks (wood and bark) were prepared for chemical analysis and for gasification and combustion tests. Plant material was washed with a 0.1N HCl solution for 15 s, and then washed with distilled water for 10 s. Washed samples were oven dried at 70 ºC, and then ground and passed through a 500-µm stainless-steel sieve.

Dried material was digested by wet oxidation with concentrated HNO_3 (65%, trace analysis grade) under pressure in a microwave oven. Determination of trace elements and nutrients in the extracts was performed by ICP-OES (inductively coupled plasma optical emission spectrometry). The accuracy of the analytical methods was assessed through BCR analysis (Community Bureau of Reference) of a plant sample (INCT-TL-1, Tea leaves).

2.3 Gasification and combustion

A laboratory-scale reactor was used for the gasification and combustion experiments (Fig. 1). The experimental system consists of a quartz tube, 10 mm wide, where the sample (approximately 1 g, < 500 µm particle size) is uniformly introduced inside a tube of 35 cm length. A horizontal actuator introduces the tube with the biomass into a furnace maintained at 750 ºC at constant velocity. To determine the optimum stoichiometric ratio, the equivalence ratio (k) was varied from 0.2 to 0.4 (Zainal et al., 2002). An adequate stoichiometric air/fuel ratio in the range of 0.3-0.4 is needed to assure complete gasification of the solid fuel and to obtain the optimal heating value of the gas product. In our case, the stoichiometric ratio (k = 0.30) was fixed by controlling the biomass speed across the furnace and the flow of air in the pipe (0.15 L/min for O_2 and 2.0 L/min for N_2). The raw gas obtained from biomass gasification was analyzed by GC-TCD (Shimadzu GC-14A Gas Chromatograph) and GC-FID (Shimadzu GC-17A).

The gross calorific values were determined at a constant volume according to “CEN/TS 14918:2005 (E) Solid biofuels—Method for the determination of calorific value” and UNE 164001 EX standards by using a Parr 6300 Automatic Isoperibol Calorimeter. The airflow was ranged from 5 L/min, determining the fuel-rich conditions (stoichiometric ratio, $k > 1$). Combustion analyses were performed in a composite sample of three replicates per treatment; therefore, our data can be considered as indicative only, since a more detailed statistical analysis was not possible.

2.4. Statistical analyses

Data were analyzed for normality and homogeneity of variances among treatments. Biomass, plant macronutrient concentrations and gasification data met normality after logarithmic transformation. For some of these variables (H_2, CO and H_2/CO ratio) homogeneity of variances across groups was not met. However, there was not a significant relationship between the mean value of these variables in each group and the corresponding standard deviation values; therefore parametric tests could be applied. Factorial ANOVAs and Tukey´s tests were applied to each harvest separately, to test for the effects of the soil type and the added amendments, as well as to test for possible differences in the effect of the amendments among soil types (soil × amendment interactions). For trace element concentrations, data did not met normality after transformation, and therefore Kruskal-Wallis tests were applied. Significance level was $p<0.05$. Bivariate relationship between plant chemical composition and biomass were explored using Pearson correlational analysis. All these analyses were conducted using STATISTICA 10 (StatSoft Inc., Tulsa, OK, USA)

An assessment of the gas composition from the gasification experiments (data from both harvests pooled) was conducted by applying principal component analysis (PCA) to the log-transformed data, with the amendment type as the categorical grouping variable, using Canoco 5.0 (Ter Braak and Šmilauer, 2012).

3. Results and discussion

3.1 Biomass production

Biomass production was relatively low, not exceeding 300 g per container in any soil or treatment (Fig. 2), indicating the low density (or light wood) of the biomass of this tree species (Akyildiz et al., 2010). In forest science the yield (in terms of dry biomass) is usually related to the density of the wood tissues. For a given stem volume, the wood density determines the biomass of the raw material. Juvenile *Paulownia* trees have usually a light wood, due to the low fraction of cell walls within the wood. At the juvenile stage the wood density of this species is much lower than that of other short-rotation species such as *Populus* or *Eucaliptu*s spp. (Senelwa and Sims, 1999). The maximum biomass produced in the containers would be equivalent to 3.3 t ha^{-1}, which is within the range of 2.14 to 4.50 obtained for one-year old *Paulownia* plants under different water regimes in non-contaminated Mediterranean soils (García-Morote et al., 2014).

In general, in the first harvest biomass was lower than in the second harvest. After the first harvest, sprouts were spontaneously produced in the following spring. This ability to regrow, i.e. biomass production being favored after cutting, is typical of some short rotation coppice tree species (García et al., 2008) and explained the greater production obtained in the second harvest. The established root system and the nutrients stored in roots and stumps allowed for a faster re-growth of the shoots in comparison to the first year after planting.

The addition of soil amendments had a positive significant effect on biomass production in the second harvest, but not in the first one (Table 3, Fig. 2). In the first harvest, biomass production significantly differed among soil types, with plants grown in acidic soil (V) producing less biomass than in neutral soils (NC and AZ), especially in the non-amended treatment (Fig. 2; Table 3). In the second harvest, the positive effects of the amendments on biomass production became more evident, particularly in the trace element-polluted soils (Fig. 2; Table 3). The soil type, with all the amendment treatments pooled together, did not influence the biomass production in this harvest, suggesting that compost addition could have promoted the processes of natural attenuation of trace element toxicity, reducing the differences in plant productivity among soil types.

The addition of the alperujo compost (AC) resulted, on average, in an 8.3% increase in biomass production in the non-contaminated soil (NC) and a 16% increase in the contaminated AZ soil, in comparison to their corresponding non-amended soils. For the biosolid compost treatment (BC), the increases in biomass production (13.8% in the NC soil and 50% in the AZ soil, on average) tended to be greater than for the AC compost, although differences between the two amendments were only marginally significant.

In the acidic soil, the application of the AC and BC amendments resulted in increases of 34% and 53% in biomass production, respectively (Fig. 2). By adding amendments to this contaminated and acidic soil, biomass reached similar values to that produced in non-contaminated soil (Fig. 2), illustrating the benefits of amendment application in this degraded soil by the enhancement of the processes of natural attenuation of metal toxicity. The amendment provoked a clear improvement in soil quality in the studied soils, as indicated by increases in available nutrients and in biochemical indexes of microbial activity (Madejón et al., 2014). Other authors have observed similar results in different experiments with amendment application (Park et al., 2011), pointing out the benefits of quality material addition for plant productivity.

3.2. Plant chemical composition

The addition of amendments did not result, in general, in changes to the chemical composition of the trunks (Table 4). The soil type, rather than the applied amendment, determined the chemical composition of the obtained biomass, particularly the trace element content (Table 4 and Fig. 3). In the acidic soil (V), plants accumulated more As, Cu, Mn, Na and Ni than in the other two studied soils. In the V and AZ soils, plants showed greater Cd, Fe and Zn concentrations than in non-contaminated soil. Macronutrient concentrations (Ca, K, Mg, P, and S) were not influenced by either the type of soil or the amendment. However, in V soil without compost, concentrations of Ca, K and P were lower than in the rest of the treatments, especially in the first harvest, illustrating the beneficial effect of compost addition on the nutritional status of the plants grown in this type of acidic soil. Although trace element accumulation was greater in plants from contaminated soils, the observed values were in general low. Wood concentrations of As were always <0.8 mg kg^{-1}, <0.4 mg kg^{-1} for Cd, <25 mg kg^{-1} for Mn, <25 mg kg^{-1} for Pb and <120 mg kg^{-1} for Zn. These values were within the normal ranges for higher plants, and well below the phytotoxic ranges (Fig. 3; Chaney, 1989). Copper, Pb and Zn accumulation in this species is usually greater in the leaves than in the trunks (Tzvetkova et al., 2015), which could explain the low trace element contents found in the trunks of the studied plants. The exception was Cu, which reached concentrations above the normal value of 20 mg kg^{-1}, even in the non-contaminated soil (maximum value of 120 mg kg^{-1} in V soil). The ability of this species to accumulate Cu has been previously reported by other authors (Jiang et al., 2012).

Biomass production was not related to trace element accumulation. In contrast, it was positively related to the concentrations of macronutrients in the trunks, particularly of K and P (Fig. 4). Fast-growing species are often characterized by a resource-acquisition strategy, which demands considerable amounts of nutrients, in comparison to slow-growing species (Ruíz-Robleto and Villar, 2005). Thus, it is likely that the main chemical constrain for *P. fortunei* to grow is a high availability of nutrients in the soil. Studies on the nutritional requirements of some *Paulownia* species have shown that these species have higher K and P requirements than other short rotation coppice tree species, such as *Populus* spp., and that *Paulownia* growth is positively related to the N content in the leaves (Hui-Jun and Ingestad, 1984). A high trace element concentration in the soil does not seem to impair biomass production in this species, at least at the levels tested in this work. The improvement in the nutritional status of the plants after adding organic amendments to the most degraded soil and the observed increase in biomass yield in both types of contaminated soil after compost addition suggest that the application of certain organic waste could be used to increase *P. fortunei* biomass even in highly degraded soils, in agreement with previous studies describing *Paulownia* species as being highly responsive to fertilization (Joshee, 2012). By planting *P. fortunei* for energy production, the afforestation of contaminated soils could have added economic value, in addition to the environmental benefits derived from the revegetation of contaminated soils. Moreover, the forestry use of composts from organic waste would represent an alternative for the management of these organic materials, as well as waste valorization.

3.3. Gasification and combustion

The gasification results (Table S1) indicated a significant reduction in the quantities of H_2 obtained from the *P. fortunei* biomass compared to similar raw materials (Asadullah, 2014; Parthasarathy and Sheeba, 2015). Carbon monoxide values (8.5% on average) were also slightly lower than the values obtained in other studies (Parthasarathy and Sheeba, 2015). In the same line, the results obtained for CO_2 and CH_4 were also lower than those reported in different works studying the gasification of other lingo-cellulosic raw materials (Skoulou et al., 2008; Weerachanchai et al., 2009). Comparison with other studies must be, however, taken with caution, as the composition of the gas product is highly dependent on operational parameters, which may be very variable among studies.

The addition of amendments had a clear effect on the quality of the gas produced from the gasification of biomass. In general, the quality of the gas for energy purposes (indicated by the H_2 concentration and the H_2/CO ratio) increased in the amended soils for both harvests (Fig. 5 and Table 3). In the first harvest, the H_2 concentration and the H_2/CO ratio increased in the amended soils, without significant differences between the AC and the BC composts when the data for the three soil types were pooled together (Fig. 5). This positive effect on the H_2 concentration was particularly important in the acidic soil (V), for which increases in H_2/CO were greater than 100% in comparison to the corresponding unamended soil. The soil type also influenced the gas composition in the first sampling. Moreover, there was a significant soil × amendment interaction with biosolid compost treatment, with a greater positive effect on the neutral contaminated soil (AZ) than the other two soils (Fig. 5; Table 3). In the second harvest, the positive effect of amendments on gas quality was clearer. Again, there was a significant soil × amendment interaction. The biosolid compost produced a greater increase in the H_2/CO ratio than the alperujo compost in the NC and the AZ soils, while in the V soil, the effect of both amendments was similar (Fig. 5; Table 3).

The multivariate analysis of gas composition confirmed that plants grown in soils amended with the biosolid compost tended to be of higher quality for energy production purposes (Fig. 6). The first component (X-axis) was defined by the H_2 concentration in the gas product, negatively associated to N_2, CO and CH_4 concentrations. The second component (Y-axis) was defined by the H_2O and CO_2 content in the gas product. When gas samples were sorted according to these two components, most of the gas samples from the biomass obtained in the BC treatment got high scores in the component 1, indicating a trend towards greater H_2 and lower CO, CH_4 and N_2 in the gas obtained from gasification of this biomass, in comparison to the other two treatments. Alperujo compost did not have a clear effect on gas composition, as indicated by the broad range of scores that samples from this treatment spanned over the ordination plane. Trace element accumulation in the biomass was not related to the concentration of any of the analyzed gases (Pearson's bivariate correlational analyses were non-significant; data not shown). Composition of the gas product is highly dependent on the relative abundance of the three main components of the cell walls on the woody biomass (cellulose, hemicellulose and lignin of the biomass), as well as on its mineral composition (Hoyosa et al., 2007). It is likely that compost addition produced healthier trees with a higher content of lignin in the wood. Several works have shown that H_2 production in the gasification process is highly related to the lignin content of the material used (Yang et al., 2007; García-Barneto et al., 2009).

Our results clearly show that, in agreement with our original hypothesis, the addition of amendment to soils resulted in an important increase in H_2 produced by the gasification process. This further supports the use of organic amendment in the plantation of *P. fortunei* plants for energy production. Besides the increase in biomass production, the quality of the obtained biomass for gasification purposes was also increased by adding organic waste to the soil.

In agreement with the gasification results, the energetic values of the biomass obtained in our study (ranging 16.7 to 18.4 MJ kg^{-1}) were slightly lower than those found in other studies with *Paulownia* plants grown in different plantations across Spain (18.3-20.3 MJ kg^{-1}; López et al., 2012; Villanueva et al., 2011), but improved when organic materials were applied to the soils (Table 5). Although woody biomass has a higher lignin and cellulose content than herbaceous biomass, leading to higher calorific value, the gross calorific values of the biomass obtained in this study were similar to those found in food plant residues and straw (16.7-17.8 MJ kg^{-1}, Naik et al., 2010; Wang et al., 2011), and lower than the typical calorific values reported for softwood and hardwood (20 MJ kg^{-1} and 18 MJ kg^{-1}, respectively; López et al., 2011; Telmo et al., 2010). This is likely due to the relatively lower lignin content in the one to two-year-old plants used in this study, in comparison with other studies using older plants, given that the accumulation of lignin, with a higher calorific value than cellulose, increases with age (Villanueva et al., 2011).

As found for gasification, the biomass from amended soils tended to have a higher energetic value than the biomass from non-amended soils (Table 5). Thus, the application of amendment to the soil might enhance the potential to produce energy from the biomass, not only through gasification, but also through combustion.

3.4. Potential of Paulownia fortunei *for the afforestation of polluted Mediterranean areas*

To properly assess the economical balance of *Paulownia fortune* plantations in contaminated soils, the costs of production, transportation and application of the organic amendments must be also taken into account. As the materials used as amendment in this study were organic wastes produced by local industries, and thus not specifically produced for fertilization purposes, the cost of acquiring these materials for agroforestry use is usually very low.

The water requirements need also to be considered in the economical balance of *P. fortunei* plantations in degraded lands. In our experiments, plants were irrigated to keep the moisture content close to field capacity. Under natural field conditions, biomass production is likely to be lower, due to water limitations during the summer season. However, different studies have shown that this species shows a relatively high tolerance to water stress, and that a relatively high yield can be obtained even under a low irrigation regime (García-Morote et al., 2014). Thus, the costs of the water inputs in *P. fortunei* plantations would be likely lower than those in other energy crops with greater water requirements, such as sugar beet or switchgrass.

Finally, other environmental factors have to be considered when proposing *P. fortunei* as a target plant to afforest degraded lands. Species in the *Paulownia* genus are not native to the Mediterranean region. Although their expansion as invasive non-indigenous species has not been documented in the Mediterranean region, the invasion of some *Paulownia* species in disturbed areas of North America and central Europe is currently receiving increasing attention (Essl, 2007; Todorović et al., 2010). The potential of these species to invade non-disturbed natural areas is likely to be low, given their requirements for high light conditions for seed germination and the susceptibility of seeds to soil pathogens (Todorović et al., 2010; Yadav et al., 2013). However, in order to avoid the potential expansion of these species beyond the limits of energy crop plantations, it would be advisable to harvest biomass before the plants reach the reproductive stage, which under suitable environmental conditions ranges from 4 to 8 years (Kuppinger et al., 2008).

4. Conclusions

The results of this study show that the combined use of *P. fortunei* and compost addition to soil might be a strategy to promote the economic valorization of the remediation of polluted Mediterranean areas. Compost addition increased biomass production to values similar to those in non-polluted soils. The quality of the biomass for gasification increased after the addition of the compost. Thus, *P. fortunei* could pose an opportunity to improve the economic balance of the revegetation of polluted soils, given that other commercial uses such as food or fodder crop production is not recommended in these soils.

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Figure captions

Fig.1. Schematic diagram of the reactor used for the gasification and combustion tests.

Fig. 2. Fig. 2. Box plot of the plant biomass obtained in each treatment and soil type (SD = standard deviation). Amendment treatment codes: NA = non-amended; AC = alperujo compost; BC = biosolid compost; Soil type codes: NC = non-contaminated; AZ = Aznalcázar (neutral contaminated soil); V = Vicario (acidic contaminated soil). See Table 3 for results of the factorial ANOVA applied to biomass production

Fig.3. Trace elements concentrations in *P. fortunei* wood for each soil and treatment at the two harvests. NA = non-amended; AC = alperujo compost; BC = biosolid compost; Soil type codes: NC = non-contaminated; AZ = Aznalcázar (neutral contaminated soil); V = Vicario (acidic contaminated soil).

Fig. 4. Relationship between the nutrient concentrations in plant material (all treatments and soil types pooled) and the obtained biomass. Correlation parameters are indicated.

Fig. 5. H2/CO ratio in the syngas produced by the gasification of the biomass obtained in each treatment and soil type (SD = standard deviation). Amendment treatment codes: NA = non-amended; AC = alperujo compost; BC = biosolid compost; Soil type codes: NC = non-contaminated; AZ = Aznalcázar (neutral contaminated soil); V = Vicario (acidic contaminated soil). See Table 3 for results of the factorial ANOVA applied to gasification results

Fig.6. Results of a PCA applied to the composition of the gas obtained from the gasification of the biomass in the soils treated with the different amendments Amendment treatment codes: NONE = non-amended; ALP = alperujo compost; BIOS = biosolid compost.

Table 1. Soil properties and total trace element content in the studied soils (NC; no-contaminated, AZ; Aznalcázar site, V; Vicario site). Mean values ± the standard deviation (SD) of three replicates.

	NC	AZ	V
pH	7.50 ± 0.07	6.93 ± 0.08	3.68 ± 0.04
TOC* (g kg^{-1})	5.10 ± 0.15	14.7 ± 3.99	4.54 ± 1.63
As (mg kg^{-1})	8.40 ± 1.90	112 ± 53.0	250 ± 51.0
Cd (mg kg^{-1})	0.59 ± 0.05	3.82 ± 1.23	1.30 ± 0.23
Cu (mg kg^{-1})	19.4 ± 2.00	166 ± 43.0	180 ± 18.0
Mn (mg kg^{-1})	132 ± 30.0	560 ± 98	590 ± 130
Pb (mg kg^{-1})	15.7 ± 0.40	236 ± 14.0	600 ± 140
Zn (mg kg^{-1})	52.2 ± 3.30	307 ± 35.0	370 ± 42.0

*Total Organic Carbon

Table 2: Main physic-chemical properties of the two compost used as amendments (mean values ± the standard deviation of three replicates).

Parameters	AC	BC
Moisture (%)	14.9 ± 0.79	15.6 ± 0.81
pH	8.10 ± 0.21	7.09 ± 0.28
Organic matter (%)	29.1 ± 1.63	22.6 ± 0.39
P (%P_2O_5)	2.54 ± 0.10	3.43 ± 0.11
K (% K_2O)	2.30 ± 0.05	0.82 ± 0.04
Ca (% CaO)	13.8 ± 0.15	12.5 ± 0.37
Mg (% MgO)	1.48 ± 0.02	1.23 ± 0.04
S (% SO_3)	0.90 ± 0.01	2.24 ± 0.06
Na (mg kg^{-1})	0.17 ± 0.00	0.10 ± 0.01
Ni (mg kg^{-1})	15.01 ± 1.15	29.25 ± 0.49
Fe (mg kg^{-1})	11554 ± 103	20786 ± 748
Cu (mg kg^{-1})	94.2 ± 1.12	188 ± 10.9
As (mg kg^{-1})	2.45 ± 0.22	13.5 ± 0.60
Co (mg kg^{-1})	4.11 ± 0.07	7.09 ± 0.10
Cd (mg kg^{-1})	0.25 ± 0.00	1.94 ± 0.09
Pb (mg kg^{-1})	9.77 ± 0.06	61.38 ± 3.73
Mn (mg kg^{-1})	360 ± 5.34	573 ± 36.3
Zn (mg kg^{-1})	185 ± 11.1	601 ± 32.0

Table 3. Results of the factorial ANOVA (F-parameter) applied to biomass production and gas composition obtained by the gasification of plant biomass. Significance values (p-values) are also indicated. The significance level was $p \leq 0.05$.

	Amendment		Soil type		Amendment x soil type	
Variable	F	p	F	p	F	p
First harvest						
Biomass	1.3	0.287	13.7	< 0.001	1.7	0.194
H_2	71.2	< 0.001	35.7	< 0.001	2.9	0.056
CO	22.0	< 0.001	11.0	< 0.001	3.9	0.020
CO_2	32.2	< 0.001	20.8	< 0.001	1.1	0.370
H_20	1.4	0.262	9.2	< 0.001	4.0	0.018
CH_4	63.7	< 0.001	19.1	< 0.001	15.2	0.000
N_2	1.8	0.192	2.5	0.114	1.0	0.417
H_2/CO	65.0	< 0.001	32.1	< 0.001	4.2	0.015
Second Harvest						
Biomass	24.5	< 0.001	8.02	0.003	2.38	0.090
H_2	130.5	< 0.001	78.1	< 0.001	15.07	< 0.001
CO	48.7	< 0.001	21.1	< 0.001	15.47	< 0.001
CO_2	3.8	0.042	12.8	< 0.001	27.33	< 0.001
H_20	17.2	0.000	23.5	< 0.001	35.53	< 0.001
CH_4	13.2	< 0.001	15.5	< 0.001	19.26	< 0.001
N_2	9.3	0.002	17.5	< 0.001	22.45	< 0.001
H_2/CO	109.5	< 0.001	69.7	< 0.001	17.40	< 0.001

Table 4. Results of the Kruskal-Wallis (H parameter) tests applied to plant chemical composition. Effects of the amendment and soil type are analyzed separately. Significance values (p-values) are also indicated. The significance level was $p \leq 0.05$.

	Amendment		Soil type	
Element	H	p	H	p
First harvest				
As	0.63	0.520	9.5	0.009
Ca	1.63	0.440	0.5	0.771
Cu	1.31	0.518	17.5	0.002
Cd	0.49	0.781	17.1	0.002
Fe	0.38	0.824	10.2	0.006
K	2.66	0.203	9.5	0.009
Mg	0.11	0.946	12.9	0.002
Mn	0.01	0.999	21.9	< 0.001
Na	2.19	0.330	12.0	0.003
Ni	0.28	0.866	12.7	0.002
P	4.16	0.124	7.7	0.021
Pb	0.05	0.975	2.8	0.244
S	6.37	0.040	5.8	0.055
Zn	0.31	0.855	17.5	0.002
Second harvest				
As	0.55	0.756	12.3	0.004
Ca	0.44	0.799	0.0	0.984
Cu	0.22	0.895	2.4	0.297
Cd	1.95	0.377	4.8	0.092
Fe	1.42	0.491	165.0	0.004
K	0.52	0.770	4.5	0.107
Mg	0.73	0.692	5.4	0.067
Mn	0.15	0.927	20.5	< 0.001
Na	0.01	0.995	8.0	0.018
Ni	1.86	0.039	15.1	< 0.001
P	7.41	0.024	0.1	0.952
Pb	0.15	0.925	0.7	0.707
S	2.38	0.304	0.3	0.862
Zn	0.96	0.617	18.4	< 0.001

Table 5. Gross heating value (MJ kg^{-1}) of the biomass obtained in each treatment and at each harvest. Amendment treatment codes: NA = non-amended; AC = alperujo compost; BC = biosolid compost; Soil type codes: NC = non-contaminated; AZ = Aznalcázar (neutral contaminated soil); V = Vicario (acidic contaminated soil).

	Soil NC			Soil AZ			Soil V		
	NA	AC	BC	NA	AC	BC	NA	AC	BC
Harvest 1	17.6	17.6	17.8	17.1	17.6	17.9	16.7	18.3	18.1
Harvest 2	16.9	17.4	17.9	16.9	17.8	18.1	16.5	18.4	18.2

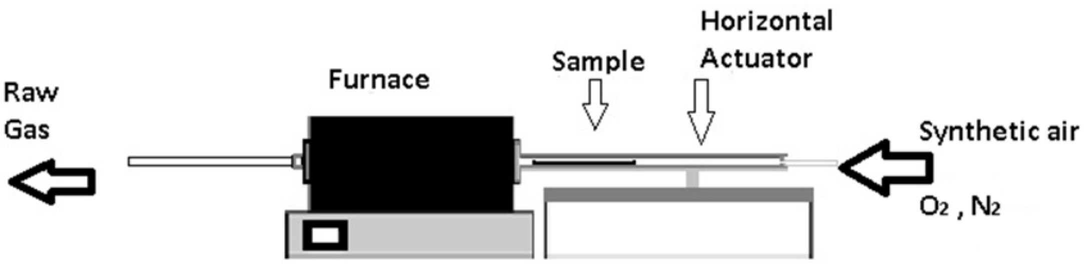
Raw
Gas
Furnace
Sample
Horizontal
Actuator
Synthetic air
O2 , N2

Fig.1.

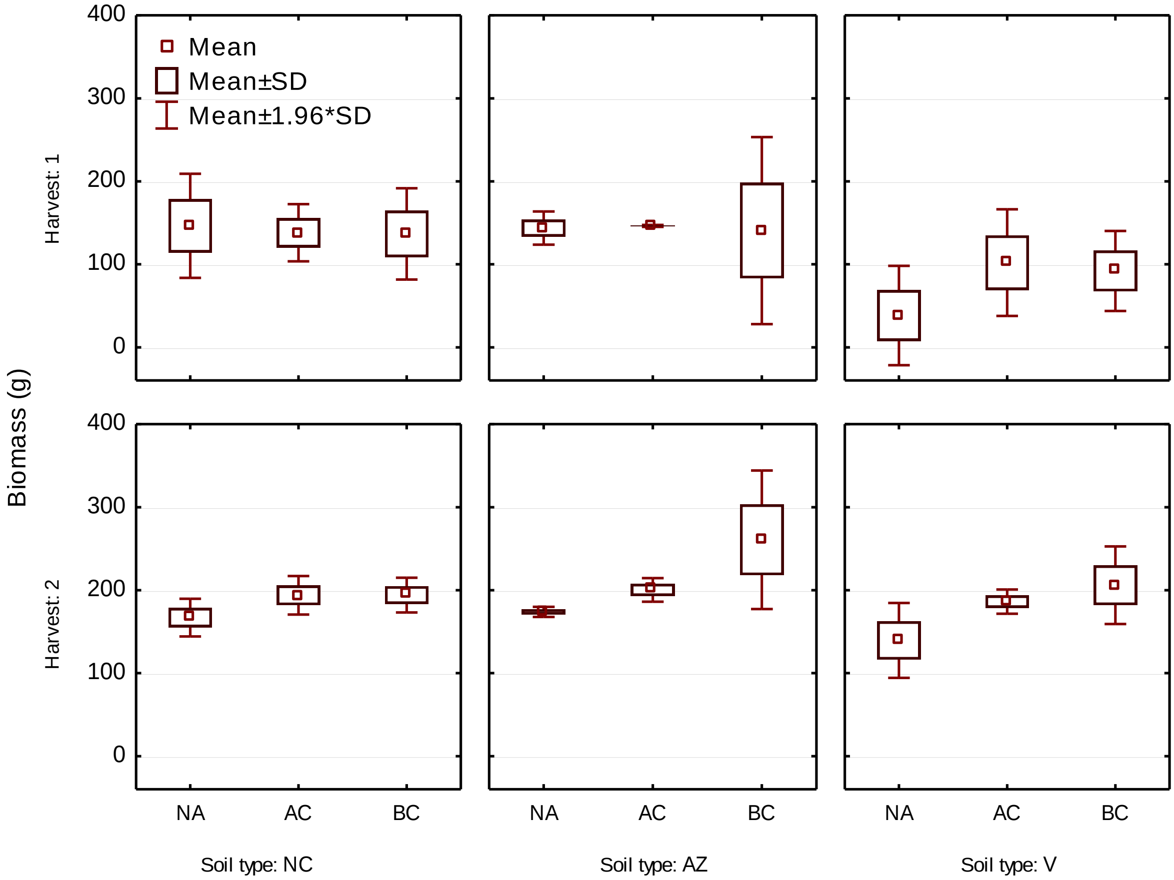
400
300
200
100
0
Mean
Mean±SD
Mean±1.96*SD
Harvest: 1
Harvest: 2
Biomass (g)
NA
AC
BC
Soil type: NC
Soil type: AZ
Soil type: V

Fig. 2.

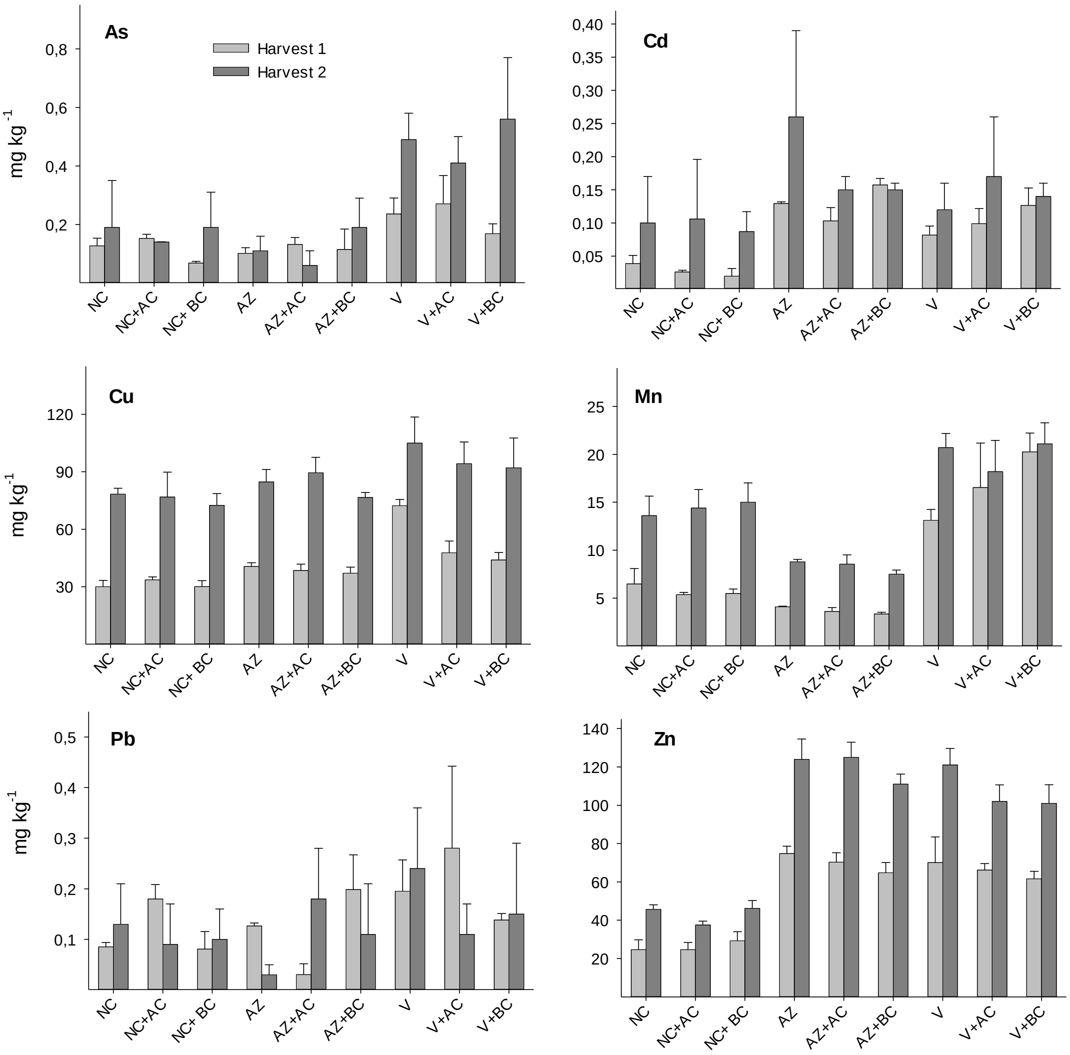
As
Harvest 1
Harvest 2
mg kg^{-1}
0,2
0,4
0,6
0,8
Cd
0,05
0,10
0,15
0,20
0,25
0,30
0,35
0,40
Cu
30
60
90
120
Mn
5
10
15
20
25
Pb
0,1
0,2
0,3
0,4
0,5
Zn
20
40
60
80
100
120
140
NC
NC+AC
NC+ BC
AZ
AZ+AC
AZ+BC
V
V+AC
V+BC

Fig.3.

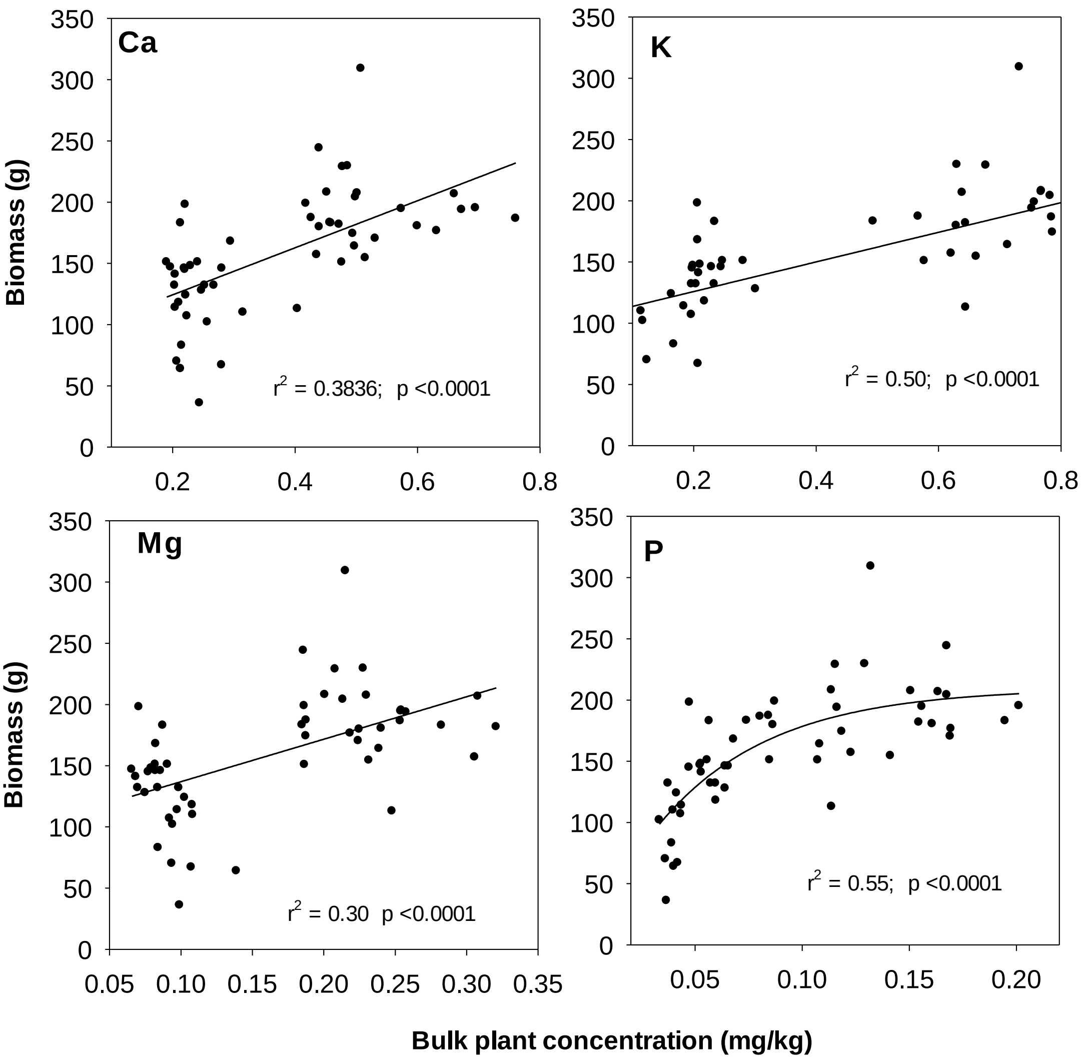
Ca
K
Mg
P
Biomass (g)
Biomass (g)
0
50
100
150
200
250
300
350
0.2
0.4
0.6
0.8
0.05
0.10
0.15
0.20
0.25
0.30
0.35
r² = 0.3836; p <0.0001
r² = 0.50; p <0.0001
r² = 0.30 p <0.0001
r² = 0.55; p <0.0001
Bulk plant concentration (mg/kg)

Fig. 4.

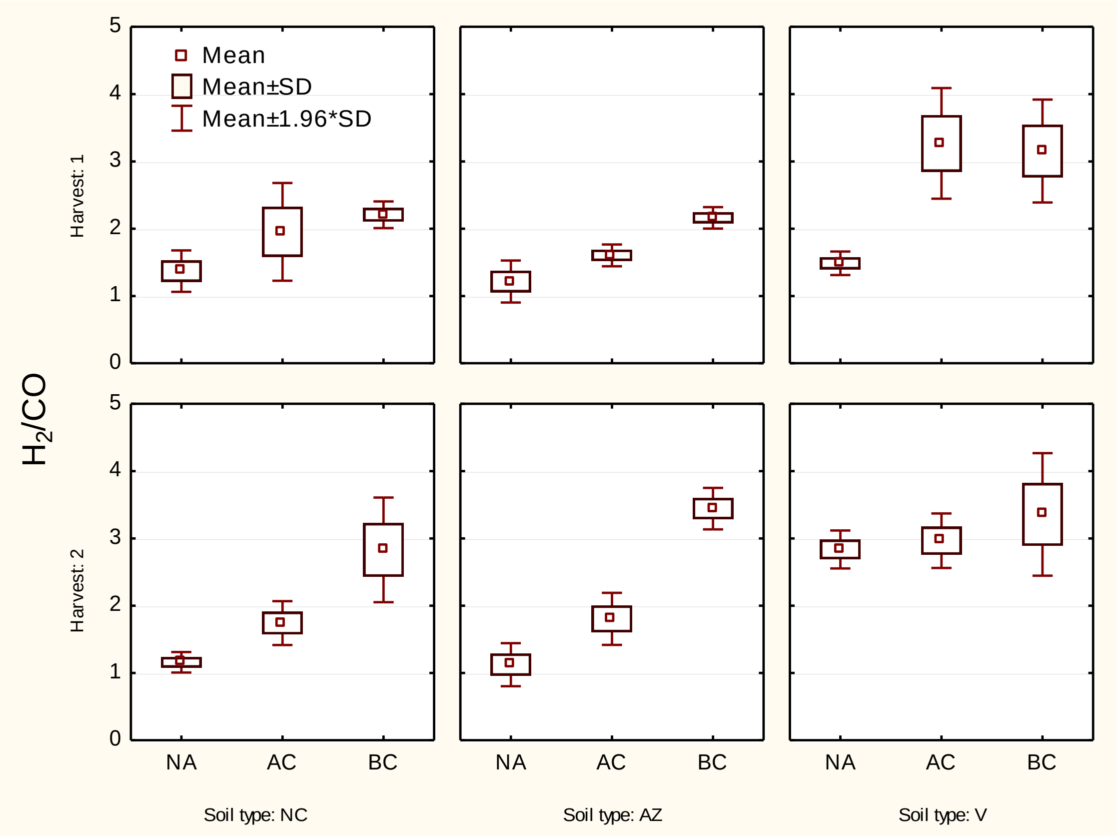
H$_2$/CO
Harvest: 1
Harvest: 2
Mean
Mean±SD
Mean±1.96*SD
0
1
2
3
4
5
NA
AC
BC
Soil type: NC
Soil type: AZ
Soil type: V

Fig. 5

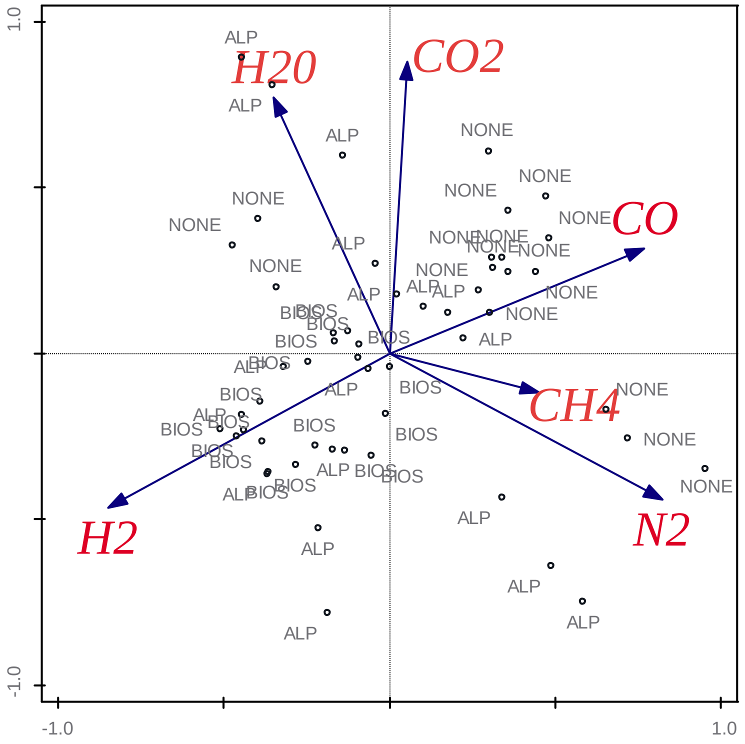

Fig.6.