


Article

Modeling the Ecosystem Services Related to Phytoextraction: Carbon Sequestration Potential Using Willow and Poplar

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Abstract: Poplar and willow demonstrate great potential for the phytoextraction of trace elements (TEs) from soils. In most cases, these species are managed as short-rotation coppice, producing high woody biomass yields, which could provide a valuable contribution toward reducing greenhouse gas emissions in the atmosphere. In the current study, we compared the TE extraction and CO₂ sequestration rates in a four-year field trial in Southern Italy of two arboreal species (willow and poplar). The results show that, once established in the study area, willow extracted more Cd and Cu and less Pb than poplar. The two species demonstrated the same average Ni and Zn extraction rates. Greater biomass yields in poplar suggest that this species was able to fix greater amounts of CO₂ (28.7 Mg ha⁻¹ yr⁻¹) than willow (24.9 Mg ha⁻¹ yr⁻¹). We argue that the choice of the species to be used in phytoextraction should first be made considering the TE-specific affinity and phytoextraction rates. For TEs whose extraction rates were the same (i.e., Ni and Zn), poplar is to be preferred because of its ability to fix greater amounts of CO₂ than willow.

Keywords: Salicaceae; phytomanagement; carbon dioxide sequestration; trace elements; heavy metals

1. Introduction

Soil pollution is a major global concern that occurs after industrial activities on a site have ceased and a variety of heterogeneously distributed pollutants remain. Commonly found contaminants include complex organic compounds such as polycyclic aromatic hydrocarbons and petroleum hydrocarbons, as well as trace elements (TEs). There are 650,000 registered sites where polluting activities took/are taking place in the EU, most of them in need of remediation [1]. TEs are frequently occurring soil contaminants (35%) [2], and most commonly among them Pb, Cr, As, Zn, Cd, Cu, and Hg [3]. The fact that TEs are not degraded overtime means that they persist in the soil, thereby threatening the quality of the environment with potentially detrimental effects on the health of humans and other organisms [4]. Most current decontamination methods for TE pollution have particular technical limitations and often a prohibitive cost that ranges from several hundred euros for deposition in a secure landfill to approximately EUR 1000 per ton for incineration. A promising alternative is phytoextraction, a technique which is applied in situ and can address multiple contaminants simultaneously at costs that are competitive with conventional methods [5]. With phytoextraction, two main strategies can be adopted: using either hyper-accumulators or moderate accumulators, the latter of which

may remove a considerable amount of contaminants from the soil due to their high growth rate and biomass production despite their lower uptake rates [6]. Hyperaccumulator plants have the potential to accumulate very high amounts of one or more TEs in their biomass. They show TE concentrations in their dry biomass that may be 100 times higher than non-hyperaccumulators growing on the same site. Most hyperaccumulator plants are able to concentrate TE over a threshold of 100 mg g^{-1} (0.01% dry weight) for Cd, As, 1000 mg g^{-1} (0.1% dry weight) for Co, Cu, Cr, Ni, and Pb and $10,000 \text{ mg g}^{-1}$ (1% dry weight) Mn and Ni [7]. The most common plant species reported in the literature in phytoextraction are *Pteris vittata* (As), *Alyssum bertolonii* (Ni), *Brassica juncea* (Cd), *Thlaspi caerulescens*, *Arabidopsis halleri*, *Sedum alfredii* (Zn) *Elsholtzia splendens*, and *Commelina communis* (Cu) [8]. Unfortunately, hyperaccumulators do not show very high biomass rates and are very difficult to manage at the field scale (e.g., harvesting the biomass). The second group of plant species commonly used for phytoextraction do not accumulate TE in excessive amounts relative to their weight, but their phytoextraction capacity is compensated by their high biomass yield, making them very attractive for this purpose [9]. Fast-growing species commonly used in phytoextraction, like poplar and willow, are often a valuable choice to address mixed (inorganic and organic) environmental pollution [10]. On a field scale, these species, which are managed as short-rotation coppice stands, have been proposed for the phytoextraction of TEs and other pollutants from different media, including soil [11], municipal sewage sludge [12], landfill leachate [13], and municipal wastewater [14].

Despite the large number of benefits associated with this technique including cost effectiveness [15], high social acceptability [16] and ecological restoration [17], one of the main drawbacks when addressing soil pollution is represented by the long time frame required to reduce pollution below safety thresholds. While the time frame depends on the targeted contaminant(s), the adopted strategy and plant(s) used, studies report that a reasonable estimate for the effectiveness of TE phytoextraction from soil ranges between a few years to more than one century [5]. The undoubtedly long and unpredictable process often discourages stakeholders and policymakers from adopting this approach. Thus, researchers are actively working to enhance the efficiency of this technique by inducing standard plant species to accumulate high TE concentrations by selective breeding [18,19], innovative management techniques [20], gene manipulation [21], and soil conditioners [22] such as biological inocula or TE-mobilising agents [23]. Despite recent advances, there is still no empirical evidence that these strategies will significantly reduce the time needed to address the problem of soil pollution.

One of the main advantages in using plants to address pollution is that they may provide a valuable contribution toward reducing greenhouse gas emissions to the atmosphere. Whilst it is well established that conventional cleanup techniques for polluted soil are associated with the emission of greenhouse gases through the use of heavy duty construction equipment powered by fossil fuels [24,25], information on the actual potential of the plants used in phytoremediation to avoid emissions is widely available. For instance, a recent study conducted in Belgium and the Netherlands comparing the CO₂ abatement potential of willow (*Salix* spp.), silage maize (*Zea mays* L.), and rapeseed (*Brassica napus* L.) grown on contaminated land by means of a life-cycle assessment approach showed the highest net CO₂ abatement for the most productive willow clone compared to the other two crops [26].

The emergence of associated ecosystem services following the application of this technology is a further benefit that should also be considered. Ecosystem services are functions provided by any activity related to the natural environment and ecosystems that could generate externalities. In the field of economics, externalities are defined as costs or benefits that affect a third party who did not choose to incur those costs or benefits (Buchanan and Stubblebine 1962). The concept of ecosystem services and related externalities has been frequently associated to forest systems because they perform a very complex set of functions for the benefit of society, including the production of raw materials and non-wood products, carbon storage, hydrogeological protection, aesthetic/recreational functions, and biodiversity conservation [27–34]. Forests belong to the category ‘mixed goods’ which have no market value, or the market is not capable of correctly defining their value. Quantifying the economic

value of forest resources is difficult because it requires the assignment of a monetary value to the goods and services without a market value which are additionally provided by forest stands. It should also be noted that the objective to be maximized varies with the bodies considered; private entities focus on profit maximization, while public entities focus on the maximizing social welfare [35]. This implies the existence of different mechanisms for assigning values to the same assets.

When estimating ecosystem services of the fast-growing woody species used for phytoextraction, many of the above-mentioned functions cannot actually be considered. TE-contaminated biomass does not represent marketable forest product (e.g., timber production) and its use as energy biofuel is still under evaluation. In addition, most of these stands, compared to actual forest stands, do not perform particular hydrogeological protection activities, they are not optimal for the conservation of biodiversity, and because they are located in contaminated areas, tourism or recreational activities are not allowed. Therefore, the only function that can be considered for these stands is represented by the carbon sequestered by the epigeal biomass that is removed annually and stored in landfills.

The aim of the current study was to highlight how, in addition to the benefits derived from phytoextraction, the use of short-rotation coppice plantations creates the opportunity to restore at least one ecosystem service in the form of carbon dioxide storage. We hypothesized that specific ecophysiological differences between plant species, namely differences in biomass yield, may affect CO₂ fixation capacity over time. This aspect makes short-rotation woody crops for phytoextraction more sustainable, not only from an economic point of view, but socially and environmentally as well.

2. Materials and Methods

2.1. Description of the Experimental Site

The experimental field was set up in Taranto, Italy (40°25'05"N; 17°14'27"E, 2.5 m a.s.l) on a site belonging to the Italian Naval Base. The region has a Mediterranean climate, with mean maximum temperature of 20.9 °C, average minimum temperature of 13.9 °C and average annual rainfall of 480 mm mainly distributed in spring and autumn. Further details about the site and the experimental layout in study published previously [11]. Briefly, the site, which was used for many years for the disposal of different materials (i.e., scrap metal, exhausted batteries and electrical wires), was characterized as having a moderate mixed-contamination where TEs (i.e., Cd, Cu, Ni, Pb, and Zn) were the main pollutants, and Pb and Zn specifically exceeded the safety threshold according to Italian legislation regarding recreational use [36]. The main characteristics of the soil are shown in Table 1. Four different plant species (i.e., willow, poplar, alfalfa, and hemp) were assessed for their phytoextraction potential for two consecutive years. Whilst herbaceous species were abandoned after the second year, willow and poplar were monitored for an additional two years (i.e., 2017 and 2018). Alfalfa and hemp did not perform as well as poplar and willow under the particular site conditions, and it was determined that the limited resources available would be better invested in long-term monitoring of the more promising species in terms of phytoremediation potential.

Table 1. Physical and chemical properties of the soil of the experimental site at the beginning of the trial.

Parameter	Unit	Value	Parameter	Unit	Value
pH		8.5	Cd	Total	1.3
O.M.	%	7.0		DTPA	0.2
Sand	%	83.9	Cu	Total	81.5
Silt	%	6.9		DTPA	11.7
Clay	%	9.2	Ni	Total	28.9
Total N	g kg ⁻¹	0.10		DTPA	0.4
Total P	% ss	0.07	Pb	Total	117.9
Total K	g kg ⁻¹	3.5		DTPA	30.2
C.E.C.	meq 100 g ⁻¹	20.7	Zn	Total	389.3
E.C.	µS cm ⁻¹	145.9		DTPA	75.3

Organic matter concentration was determined following the Walkley and Black method [37]. Soil pH was determined using the method proposed by Conyers and Davey [38]. Soil texture was determined following a standard methodology [39]. Total N was evaluated using Kjeldahl's method [40]. Total trace element (TE) as well as P and K concentrations were determined using the Aqua Regia extraction method whereas extractable (i.e., potentially phytoavailable) TE fraction was determined by the diethylenetriaminepentaacetic acid (DTPA) extraction method. Threshold values for recreational and industrial use according to Italian legislation (Decreto Legislativo n 152, 2006) are 2–10 mg kg⁻¹ (Cd), 120–600 mg kg⁻¹ (Cu), 120–500 mg kg⁻¹ (Ni), 100–1000 mg kg⁻¹ (Pb), 150–1500 mg kg⁻¹ (Zn).

2.2. Determination of the Actual Phytoextraction Rate

Every year (2015 to 2018), the amount of each element extracted by willow and poplar plants was determined following a standard protocol. Firstly, at the end of each growing season, we assessed the total fresh weights of stem and leaves on five randomly selected plants per plot. Subsamples of each plant were oven dried (to constant weight) at 80 °C and the dry biomass used to determine the water content. The yield was adjusted considering the initial and actual planting density. The biomass yield was expressed as (oven dried) Mg ha⁻¹ year⁻¹. Five 0.5 g samples of oven-dried ground biomass per plot were mineralized in a Teflon beaker with 10 mL of HNO₃ and 3 mL of H₂O₂ in a Mars6 Xpress microwave system (CEM[®] Matthews, NC, USA) using the following settings: power level of 1600 W applied at 100%; ramp of 15:00 min to reach 200 °C; held at 200 °C for 15:00 min. The final solution volume of 25 mL was obtained by adding ultrapure demineralized water (resistivity ≤ 18 MΩ cm⁻¹), and the diluted extracts were analyzed for TE (i.e., Cd, Cu, Ni, Pb, Zn) concentrations by means of inductively coupled plasma-optical emission spectrometry (ICP-OES) (Thermo Scientific[™] iCAP[™] 7400). We used a certified reference material (CRM) of ryegrass (ERM[®]—CD281 RYE GRASS, European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Belgium) for method validation and assurance purposes. The phytoextraction rates for each metal were calculated as follows:

$$TE_x \text{ phytoextraction (g ha}^{-1} \text{ yr}^{-1}) = [TE_x] \text{ (mg kg}^{-1}) \cdot \text{Biomass yield (Mg ha}^{-1} \text{ yr}^{-1}) \quad (1)$$

where [TE_x] is the concentration of the element (x) in the plant biomass and Biomass yield is the oven-dried annual aboveground plant biomass.

2.3. Trace Element Assessment in Soil and Evaluation of Phytoextraction

The soil at the experimental site was monitored at the beginning of the trial (prior to planting) and every two years (i.e., 2016 and 2018) using the methodology described elsewhere [11]. Total and DTPA-extractable element concentrations were assessed for Cd, Cu, Ni, Pb, and Zn. The results were expressed as reduction percentages using the following equation:

$$\Delta(\%) = [TE_0] - [TE_f]/[TE_0] \cdot 100 \quad (2)$$

where TE_0 and TE_f are the initial (2015) and final (2018) TE concentration in the soil, respectively. The results were evaluated according to standards set by Italian legislation [36] and phytoextraction process was considered accomplished when the concentration of each specific TE was below the threshold value for recreational use.

2.4. Estimation of Ecosystem Services Provided by Forest

Within a theoretical framework, economic goods can be classified according to two general principles: rivalry and excludability in use [27]. If the use of a good is characterized as having no rivalry, it can be used by several consumers at the same time, without diminishing the satisfaction perceived by each of them. On the other hand, a classification of absolute rivalry indicates that the use of the same unit of goods by several persons is not possible and the total quantity of the goods is therefore proportional to the number of consumers [27,31,41].

Considering both exclusion and rivalry in consumption, goods can be divided into four categories: pure private goods, club goods, common goods, and pure public goods. Pure public goods are characterized by rivalry and no excludability, while pure private goods, on the contrary, by absolute rivalry and absolute excludability. Club and common goods are considered mixed goods and are characterized, respectively, by no rivalry-total excludability and absolute rivalry-no excludability.

The forest is configured as a mixed good, presenting characteristics of public and private good simultaneously. While the private component (i.e., timber production) belongs to the owner, the public component instead represents all the positive externalities that a forest stand generates and from which the community benefits.

Different authors use different methodologies to estimate ecosystem services provided by forests such as Contingent Evaluation, Travel Cost Methods, Subrogation Costs, net income evaluation, etc. [29,35,42–48]. As mentioned above, the only function that the area under study is able to provide is carbon fixation, and that will be calculated using the method described in the section that follows.

2.5. Economic Evaluation of Carbon Dioxide Sequestration

Reducing atmospheric CO_2 concentrations through carbon sequestration has come under intense focus since the end of the last century due to the direct relationship between elevated atmospheric CO_2 concentrations and climate change [29,43,49–51]. Trees directly contribute to a reduction in CO_2 released into the atmosphere; as mentioned by Trexler [52], trees fix carbon in their biomass by absorbing CO_2 . This process represents quantifiable savings when the market price of carbon (based on the Emissions Trading System of the European Union) is considered. This price is defined and regulated in a market of credits related to the implementation of the flexible mechanisms (i.e., the Clean Development Mechanism) outlined in the Kyoto Protocol. The price is further regulated through a series of compensatory measures by local authorities, businesses and private individuals. Considering that carbon sequestration refers to the annual amount of CO_2 accumulated in the epigeal and hypogeal parts of the plant, this amount depends on the species of trees, their age and structure, and the health of the forest. The carbon sequestration function of forests has been previously estimated using different methods [33,53–56] and is primarily focused on calculating the biomass useful for carbon storage. The biomass is then multiplied by the per unit price of carbon dioxide. In this study, the biomass available for carbon storage has already been evaluated (annual dried biomass). These values were then used to calculate the annual value of carbon dioxide sequestration (CS_i) by multiplying the carbon content (expressed as CO_2) in the dried biomass (B) per price of carbon dioxide (P_c).

$$CS_i = B_i \cdot P_c \quad (3)$$

where

CS_i = carbon dioxide sequestration value of i -th trees species (EUR ha^{-1});

B_i = carbon content (expressed as CO_2) in the dried biomass of i -th trees species (Mg ha^{-1});

P_c = pricing carbon dioxide (EUR Mg⁻¹).

2.6. Statistical Analysis

Data concerning the biomass yield and phytoextraction rate were previously tested for normal distribution by the Shapiro–Wilk test. Data that were not normally distributed were log-transformed before further processing. Analysis of variance (ANOVA) was performed using a univariate model and differences were discriminated using Tukey’s HSD test with a threshold of 0.05. A paired sample t-test with a 95% confidence interval was used to compare extractable and total metal concentration in soil at the beginning and the end of the trial. All statistical analyses were performed using the software SPSS version 24 (IBM® Armonk, NY, USA).

3. Results

3.1. Biomass Yield of Willow and Poplar

The biomass production of the two species varied significantly only during the first year and tended to be equal thereafter (Figure 1). In particular, the woody biomass yield (Figure 1A) was significantly higher in poplar (18.2 Mg ha⁻¹) than in willow (8.4 Mg ha⁻¹) in the establishment year and decreased in both species to the same extent, averaging 12.5 Mg ha⁻¹ by the end of the fourth year. The average woody biomass over four years was higher in poplar (15.7 Mg ha⁻¹yr⁻¹) than in willow (13.6 Mg ha⁻¹yr⁻¹). A similar pattern was observed for leaf biomass yield where poplar (6.6 Mg ha⁻¹) showed significantly higher values than willow (2.2 Mg ha⁻¹) in the establishment year and stabilized on average values of 2.9 Mg ha⁻¹ by the end of the fourth year (Figure 1B).

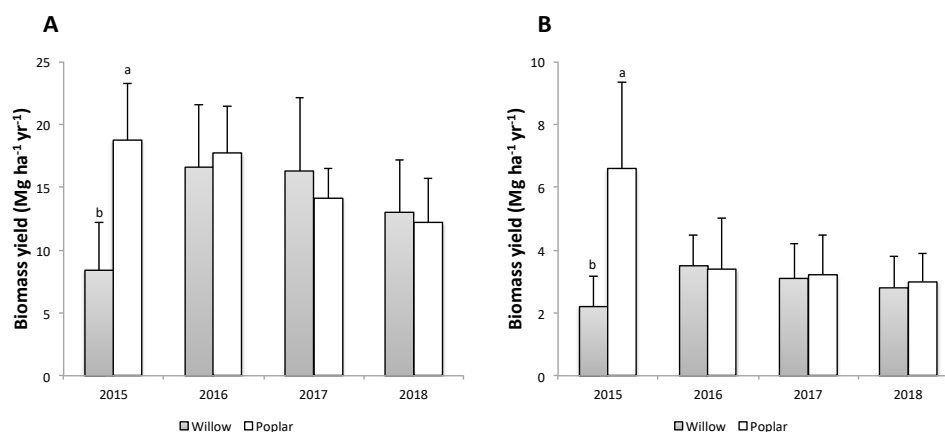


Figure 1. Willow and poplar woody (A) and leaf (B) biomass yields for the four years of the trial. Values are mean \pm SD ($n = 20$) for each species. A 5% significance level was adopted for identifying significant treatment effects according to Tukey’s HSD test. Different letters on bars denote a significant difference among species.

3.2. Phytoextraction and Soil Quality

The recovery rates for trace elements in the standard reference material were between 90.3 and 95% (Table 2), thus validating the generalized high accuracy and precision of laboratory procedures.

Table 2. Recovery rates for the standard material used in the current study.

Elements	Standard Material (mg kg ⁻¹)		Observed in the Current Study (mg kg ⁻¹)		Recovery (%)
	Mean	SD	Mean	SD	
Cd	0.12 ±	0.01	0.11 ±	0.02	91.7
Cu	10.2 ±	0.5	9.2 ±	0.6	90.3
Ni	15.2 ±	0.6	13.9 ±	0.5	91.2
Pb	1.67 ±	0.11	1.53 ±	0.13	91.6
Zn	30.5 ±	1.1	29.1 ±	0.9	95.5

Recovery of elements from analysis of certified reference material (CRM) of ryegrass ERM[®]—CD281 RYE GRASS, European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Belgium (n = 2 ± standard deviation SD).

The observation of the phytoextraction rates overtime highlighted species-specific differences for specific trace elements (Figure 2). Cadmium annual extraction rate was not detectable in the establishment year for both species, averaged around 8 g ha⁻¹ in the second year (2016) and was significantly higher in willow (15 g ha⁻¹) than in poplar (11 g ha⁻¹) in the following two years. The annual rate of copper phytoextraction changed over time. Whilst poplar showed significantly higher phytoextraction in the first year as compared to willow (i.e., 265 vs. 97 g ha⁻¹), the difference tended to reverse over the course of time so that, by the end of 2018, willow showed significantly higher extraction rates compared to poplar for this element (i.e., 146 vs. 96 g ha⁻¹). Nickel was not detected in the biomass of either species in the establishment year and although its extraction rates increased over time, both species showed similar values (average 17 g ha⁻¹ yr⁻¹). Highly significant differences were observed for lead in the establishment year where poplar again was the better performing species as compared to willow. Such differences were also observed in 2016 and 2017, whereas in the last year, no differences were found between the species in terms of Pb phytoextraction. With regard to zinc, except for the first year where poplar extracted more element than willow (i.e., 6500 vs. 2600 g ha⁻¹), the extraction rate was very high for both species, averaging 3800 g ha⁻¹ yr⁻¹ for the following three years.

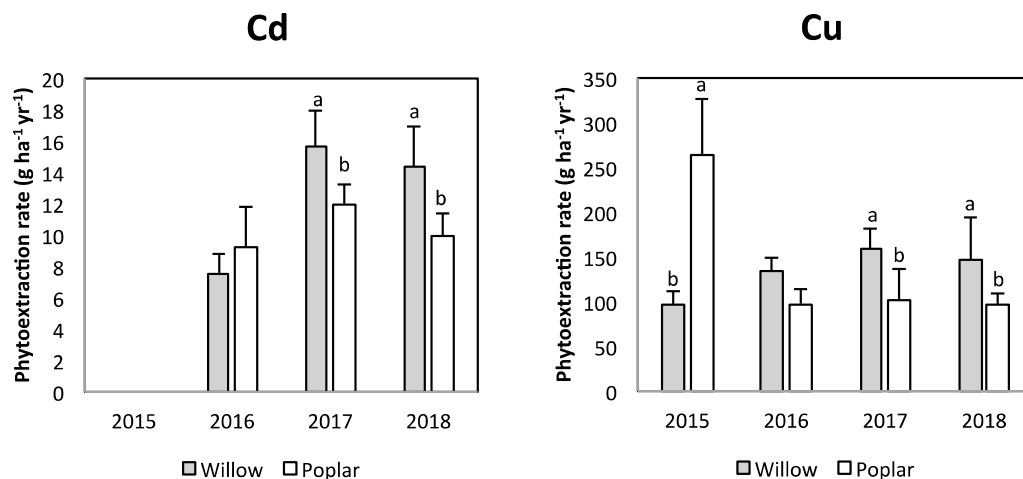


Figure 2. Cont.

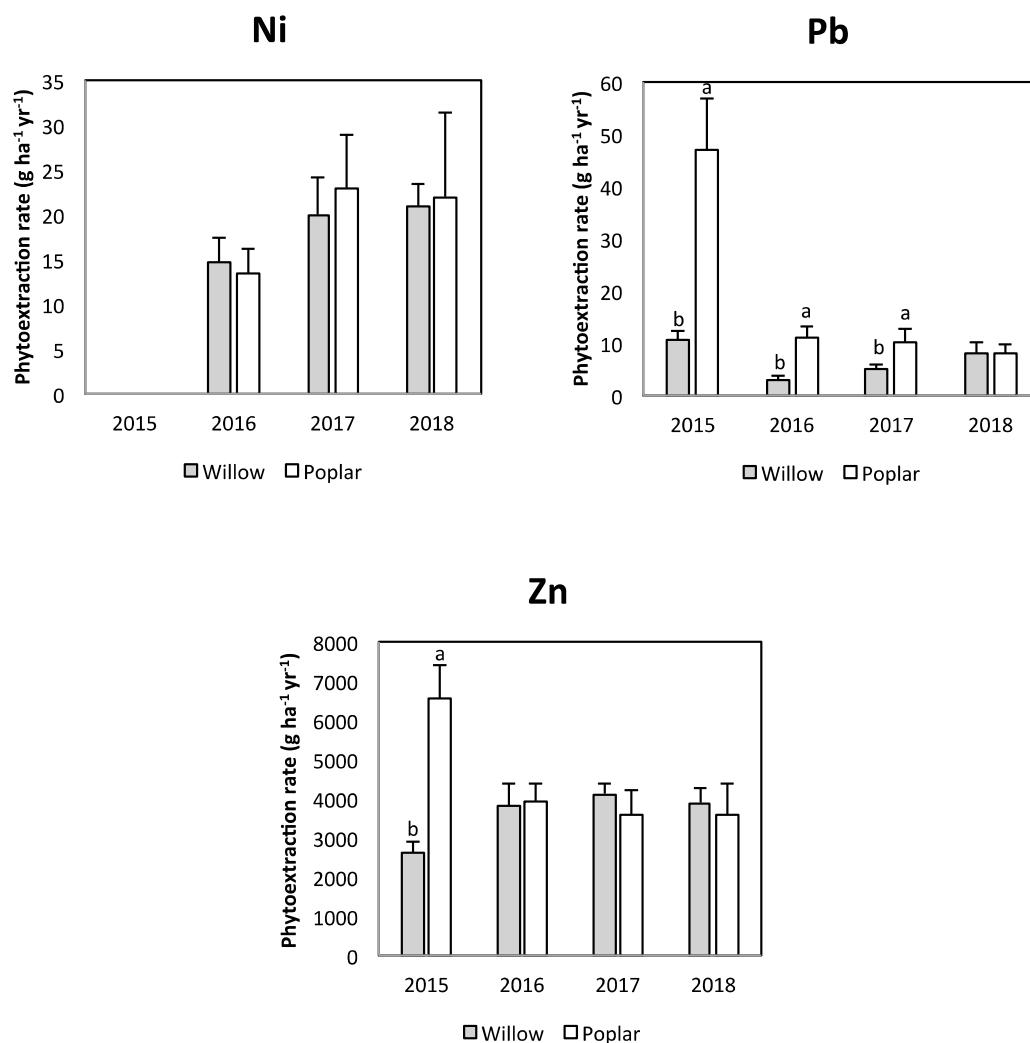


Figure 2. Phytoextraction rates for Cd, Cu, Ni, Pb and Zn of willow and poplar for different years. Data are mean phytoextraction rate values ($\text{g ha}^{-1} \text{ year}^{-1}$) \pm SD ($n = 12$) for each species for each growing season, with the exception of Cd and Ni, which were not detected during the first year. Comparisons were made between species for each year. A 5% significance level was adopted for identifying significant treatment effects according to Tukey's HSD test.

The variation in soil pollution over time is reported in Table 3 and visually in the 2D maps in Figure 3. Although both species proved capable of decreasing the pollution concentration on average to a higher extent (i.e., 38% poplar and 34% willow) than natural attenuation (i.e., 4.5% reduction due to natural attenuation), significant effects were observed only in the DTPA-extractable fraction. Over a period of four years, poplar was able to significantly decrease the initial Cd (62%), Ni (57%), Pb (55%) and Zn (71%) DTPA-extractable fractions and nearly the initial total Cu ($p = 0.055$) and Zn ($p = 0.059$) soil concentrations as well. The plots planted with willow showed a significant reduction in DTPA-extractable Cu (38%) and an almost-significant ($p = 0.06$) decrease in DTPA-extractable Zn (70%). No significant differences were found for unplanted plots, and, for some elements (i.e., DTPA-extractable Pb and Zn), an increase was observed.

Table 3. Comparison between total and extractable trace element (TE) concentrations in soil at the beginning ($T_0 = 2015$) and the end ($T_f = 2018$) of the trial.

Species	Element	Paired Differences (T_0-T_f)		$(\Delta\%)$	95% Confidence Interval of the difference		t	df	Sig. (2-tailed)	
		Mean	SEM		Lower	Upper				
Poplar	Cd	Total	0.05	0.03	19.2	-0.03	0.14	1.94	3	0.147
		DTPA	0.06	0.00	61.8	0.05	0.08	13.71	3	0.001
	Cu	Total	7.28	2.38	26.1	-0.30	14.85	3.06	3	0.055
		DTPA	3.80	2.64	23.9	-4.60	12.20	1.44	3	0.246
	Ni	Total	3.96	1.93	14.0	-2.17	10.08	2.05	3	0.132
		DTPA	0.30	0.07	57.2	0.07	0.52	4.18	3	0.025
	Pb	Total	5.14	10.56	8.1	-28.45	38.73	0.49	3	0.660
		DTPA	15.30	2.33	54.6	7.87	22.73	6.55	3	0.007
	Zn	Total	75.60	25.50	43.9	-5.57	156.77	2.96	3	0.059
		DTPA	38.08	9.64	70.7	7.41	68.74	3.95	3	0.029
Willow	Cd	Total	1.81	2.20	16.6	-5.20	8.82	0.82	3	0.471
		DTPA	0.31	0.24	39.3	-0.47	1.08	1.26	3	0.298
	Cu	Total	42.38	28.94	19.2	-49.74	134.49	1.46	3	0.239
		DTPA	3.73	0.82	38.4	1.11	6.35	4.54	3	0.020
	Ni	Total	8.12	1.31	27.1	3.96	12.28	6.21	3	0.123
		DTPA	0.23	0.17	34.8	-0.31	0.77	1.38	3	0.262
	Pb	Total	44.90	28.39	13.1	-45.45	135.24	1.58	3	0.212
		DTPA	12.08	5.07	38.5	-4.07	28.22	2.38	3	0.098
	Zn	Total	312.23	173.31	41.2	-239.32	863.77	1.80	3	0.169
		DTPA	89.80	31.04	76.1	-8.99	188.59	2.89	3	0.063
Unplanted	Cd	Total	0.03	0.05	2.7	-0.15	0.20	0.48	3	0.663
		DTPA	0.04	0.05	7.7	-0.14	0.21	0.67	3	0.550
	Cu	Total	4.80	1.82	16.0	-1.01	10.61	2.63	3	0.078
		DTPA	1.04	0.65	15.7	-1.03	3.12	1.60	3	0.208
	Ni	Total	2.44	5.27	0.1	-14.35	19.22	0.46	3	0.675
		DTPA	0.08	0.08	14.5	-0.16	0.32	1.04	3	0.374
	Pb	Total	1.33	1.66	2.1	-3.95	6.61	0.80	3	0.480
		DTPA	5.09	6.91	-13.8	-16.91	27.09	0.74	3	0.515
	Zn	Total	27.78	26.05	11.8	-55.14	110.69	1.07	3	0.365
		DTPA	12.10	21.85	-12.0	-57.43	81.63	0.55	3	0.618

The effect of different species on soil TE concentration is presented as the difference between the final and the initial value for each parameter. A paired samples *t*-test was used to compare TE concentration in soil at two time points. Values in bold denote a significant ($p \leq 0.05$) effect.

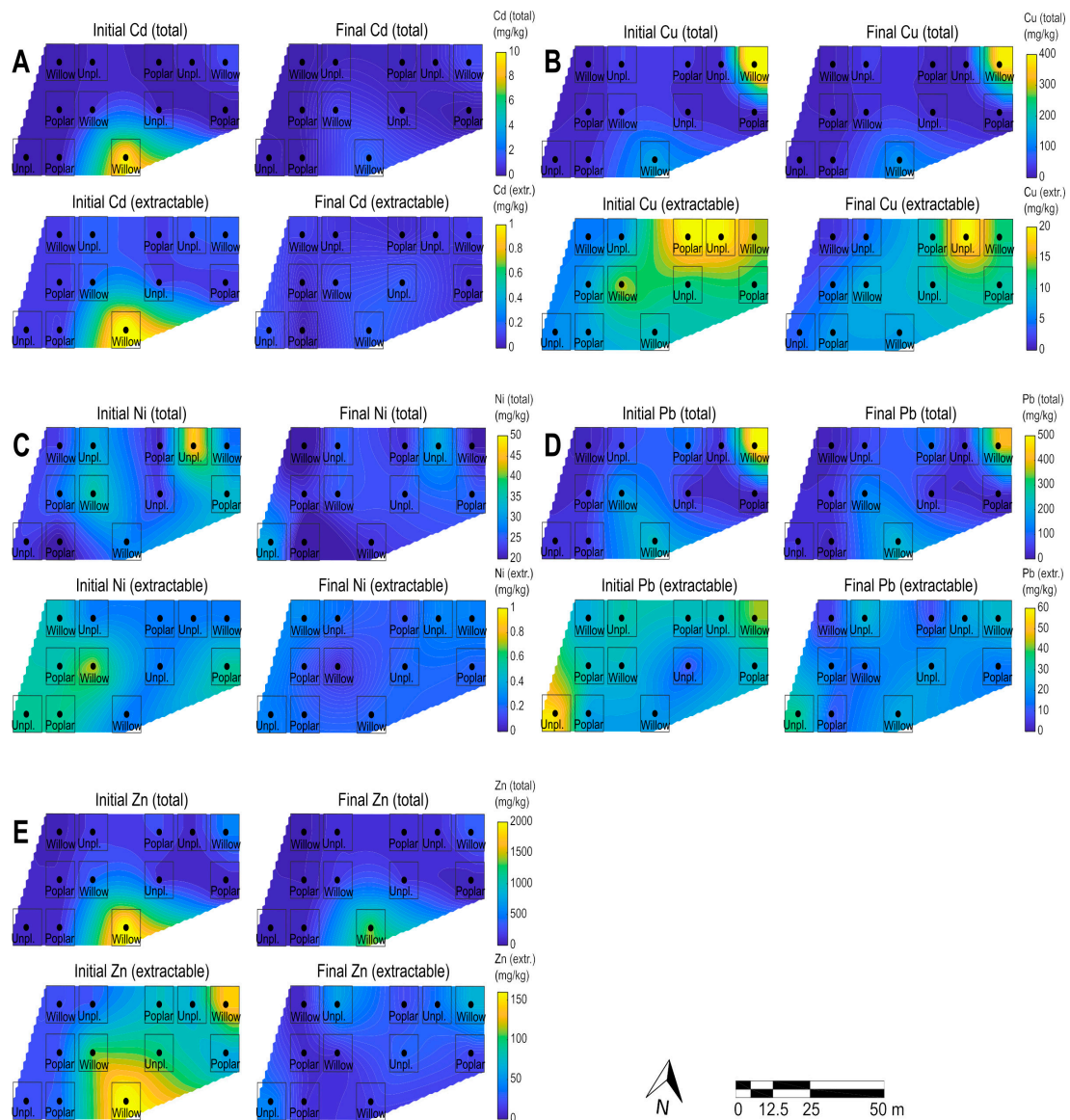


Figure 3. Temporal evolution pattern of total and DTPA-extractable trace element concentrations in the soil at the experimental site for each treatment. Comparisons are made between initial (2015) and final (2018) values for Cd (A), Cu (B), Ni (C), Pb (D) and Zn (E). The 2D maps were obtained by assigning the value observed from each parcel to the midpoint of the respective parcel. The points were spatially interpolated with a natural neighbor method over a 100-by-100 point grid.

3.3. Carbon Dioxide Sequestration Value

Table 4 shows the carbon dioxide sequestration value starting from the annual removed biomass (epigeal) of poplar and willow and the average price of carbon dioxide per year [57]. For the analysis, as argued by Lamlon and Savidge [58], we have considered that carbon stocked is about 50% of the total tree biomass.

Table 4. Carbon dioxide sequestration of willow and poplar.

Carbon Dioxide Stock	Year			
	2015	2016	2017	2018
Willow B (Mg ha ⁻¹)	15.40	30.43	29.88	23.83
Poplar B (Mg ha ⁻¹)	34.28	32.45	25.85	22.37
Carbon dioxide price Cs (EUR Mg ⁻¹)	7.68	5.35	5.83	15.88
Willow Pc (EUR ha ⁻¹)	118.27	162.82	174.22	378.47
Poplar Pc (EUR ha ⁻¹)	263.29	173.60	150.70	355.18

The average carbon price used for the analysis is related to the emission trading system (ETS) that “sets a limit (“cap”) on total direct GHG emissions from specific sectors and sets up a market where the rights to emit (in the form of carbon permits or allowances) are traded. This approach allows polluters to meet emission reduction targets flexibly and at the lowest cost. It provides certainty about emission reductions, but not the price for emitting, which fluctuates with the market” [59]. Considering that the prices used refer to carbon dioxide, we have transformed the biomass carbon stocked into biomass carbon dioxide stocked using a conversion factor equal to 3.67 [60,61].

The analysis considers four annual removed biomasses in four different periods (2015 to 2018). In order to compare (i.e., sum) these values, it is necessary to report them in a single time period, fixed at 2018 (end of our analysis).

For this purpose, a linear model for postponement of capital was applied (Equation (4)), as suggested by Malagoli, Michieli and Michieli, and Gallerani et al. [62–64].

$$C_n = C_0 \cdot q^n \quad (4)$$

where

C_n = value of carbon dioxide sequestration at the end (year n) of our analysis (2018) (EUR ha⁻¹);

C_0 = value of carbon dioxide sequestration at different years (i.e., 2015, 2016, 2017, 2018) (EUR ha⁻¹);

$q = 1 + r$ (r is the market discount rate);

n = length of the period (time between C_0 and C_n).

A problem associated to this type of analysis is the uncertainty related to the choice of discount rate [65–67]. In order to reduce this uncertainty, a sensitivity analysis was conducted [68]. An important assumption is to maintain the permanence of the conditions during the analysis; for this purpose, a sensitivity analysis for one factor at a time was used [69].

In detail, the discount rate was considered variable over time by applying values between 1% and 8% [29,67,70]. Results are shown in Table 5.

Table 5. Sensitivity analysis of carbon dioxide sequestration value CS (EUR ha⁻¹) of poplar and willow. The values of each species are summarized during 2018.

Species	Discount Rate							
	1%	2%	3%	4%	5%	6%	7%	8%
Willow	842.37	851.07	859.88	868.79	877.81	886.94	896.17	905.51
Poplar	955.75	968.92	982.28	995.84	1009.61	1023.57	1037.73	1052.10

The values reflect the biomass obtained annually from the two species; therefore, considerably higher values are obtained for poplar than for willow. This is due to an average biomass collected in the years considered of 15.68 Mg ha⁻¹ (poplar) and 13.58 Mg ha⁻¹ (willow). Considering the different discount rates, the value range (differences between species) is between EUR 110 and 150.

4. Discussion

4.1. Biomass Yield

In the current study, both willow and poplar proved to be more effective in decreasing most trace elements in the soil than natural attenuation. These species belong to the so-called fast-growing woody species that are proposed for phytoextraction because, unlike most hyper-accumulator plants, they are able to produce high amounts of biomass, thus compensating for the reduced trace element uptake rate [71]. Because they also possess other specific properties (e.g., fast and easy establishment, long-lasting, easy to manage, possibility to use the biomass for energy purposes), these species have great potential for use in phytoextraction. Our trial shows that, in the establishment year, poplar is much more productive than willow, whereas after the first cutback, both species showed comparable biomass production values. This response has been observed by other authors, demonstrating that, while poplar does not necessarily need to be harvested during the establishment year [72], it is very useful for willow, as the cutback encourages the formation of vigorous, multi-stemmed stools in the following year [73]. The current study also shows that both species can be managed for a long period of time (4 years), producing a relatively high amount (i.e., 12.5 Mg ha⁻¹) of woody biomass each year. The high biomass yield per hectare was mainly due to a rather low mortality rate of the plants, which is rarely reported in the literature regarding annual rotation cycles. In fact, many studies emphasized the decrease in the aboveground growth of tree species due to increased stump mortality [74,75] following coppicing. For instance, biomass yield decline was observed under a one-year cutting cycle of a poplar short-rotation coppice in Italy following a severe stump mortality [76]. Similar results were also observed on willow when harvested annually [77]. In the present study, the relatively high biomass yield may be attributed to the contribution of irrigation and fertilization, which are very important for plants to be able to take full advantage of the high air temperature and the long growing season of southern latitudes. In the current study, poplar averaged slightly higher woody biomass yield compared to willow, which is in line with other studies carried out under Mediterranean climatic conditions [78].

4.2. Phytoextraction

To date, successful long-term phytoextraction projects are still rare in the literature. A medium-duration field study (18 months) of Cd phytoextraction by *Celosia argentea* showed that this species in combination with soil amendments can greatly improve the quality of Cd-contaminated soils [79]. Other researchers have shown that *Sedum plumbizincicola* was able to reduce Cd and Zn concentration in the soil in long-term studies [80]. In the current study, we observed a species-specific response regarding the phytoextraction potential for some elements. For example, willow showed higher extraction rates for Cd and Cu than poplar over time. Hydroponic screening studies comparing the two species revealed that willow was able to translocate and concentrate Cd in the aboveground organs in association with a greater metal tolerance when compared to poplar [81]. This was particularly true for *S. matsudana*, which ranked among the most efficient willow species for Cd uptake and translocation to aboveground biomass [82]. This would support our findings at the field scale. Although Cu phytoextraction was higher in poplar than in willow in the first year, the tendency reversed in the following year showing better performances for willow than poplar, a result which is in line with data reported by other scientists [83]. Both species performed poorly with regard to Ni and Pb phytoextraction. However it should be noted that Pb, and to a lesser extent Cu and Ni in Salicaceae, are generally accumulated at the root level and this makes them more suitable for phytostabilization rather than phytoextraction [83]. High phytoextraction rates were observed for zinc with both species averaging annual extraction rates of 4000 g ha⁻¹. These figures are in accordance with those observed for poplar and willow in previous studies [84–86]. Finally, paired t-test comparisons of DTPA-extractable TE concentrations in soil after 4 years (Table 3) showed a statistically significant decline in soil concentrations of extractable trace elements compared to natural attenuation (unplanted)

plots. In particular, we observed a significant ($p < 0.05$) Cd (62%), Ni (57%), Pb (55%) and Zn (71%) decrease under poplar and a decrease in Cu (38%) under willow culture. Although a generalized decrease in Total TE concentration in the soil was observed for both species compared with unplanted plots (Figure 3), these differences were not statistically supported and should be regarded only as a qualitative reference. Examples of effective reductions of the TE total pool are very rare. For instance, in one studied carried out in the UK, it was observed that TEs from dredged sediments (mostly present as insoluble sulphides) could decrease due to oxidation following dredging that increased the metal mobility in the soil [87]. In the current study, we did not evaluate the recharge rate of the extractable TEs from the total TE pool. Therefore, it is difficult to predict the actual success of these species in reducing the total TEs in the long-term. There is still uncertainty around the question of whether or not a decrease in available TE soil pool will result in a prompt decrease in total TE concentration and to what extent this process may affect phytoextraction [88]. Therefore, a more in-depth investigation is still needed in regard to this particular aspect of phytoremediation.

4.3. Carbon Dioxide Sequestration

The estimated values of carbon dioxide sequestration are subject to uncertainty related to the economic evaluation of carbon dioxide sequestration [89]. In order to overcome this limitation, a sensitivity analysis was carried out to evaluate the influence of different market conditions on carbon dioxide sequestration estimates. The results obtained may be compared to other studies available in the literature. Sandhu et al. [90] estimated the carbon sequestration value for arable land at USD 210 per hectare per year, while Kumar Lal [91] obtained an annual economic worth of carbon stored in above ground biomass of Indian forests of USD 527 per hectare by using a discount rate equal to 10%. Ibarra et al. [92] obtained an annual value between USD 217.32 and 362.20 per year with a discount rate of 3.5%, and Bottalico et al. [29] obtained a value between 35 and 1300 EUR per hectare per year depending on the different forest management employed (high forest and coppice) and discount rates between 1% and 8%. Riccioli et al. [51] obtained values around 321 EUR ha⁻¹ per year for a Holm Oak forest in a natural reserve. The carbon price used for the analysis is related to the emission trading system and could be a valuable topic for future analysis when thought of in terms of Carbon tax: shifting taxes from people to the environment could reduce CO₂ emissions. Essentially, for every ton of CO₂ emitted, a tax would have to be paid and the revenue of which would benefit the workers who would then see their individual payroll taxes reduced. As argued in The International Monetary Fund [93], there are 57 CO₂ pricing schemes in the world today that are equally divided between regional and state taxes and emission markets, involving 74 countries or regions. However, these schemes cover only 20% of global emissions, and less than 5% impose an appropriate price to keep the average global temperature increase well below 2 °C and aim to limit the increase to 1.5 °C. The International Monetary Fund in the 2019 Fiscal Monitor [94] estimates an appropriate carbon tax of USD 75 per ton of CO₂ to be phased in by 2030.

5. Conclusions

The present work highlights the advantage of using a green approach by considering and evaluating non-market forest functions such as the carbon dioxide sequestration capacity. Unlike a pristine forest landscape (e.g., protected forest land) carbon dioxide sequestration is the only function available due to the presence of heavy metals as in the present case study. Despite this, after the period of phytoremediation (equal to 8 years), the area will be reclaimed, and other species could be planted that would then perform the other function characteristic of an average forest landscape. In conclusion, these considerations could lead stakeholders towards optimizing their planning and decision-making processes by taking into account ecological, environmental and economic issues.

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