Cynara carduncululus as a sustainable solution for phytoremediation of antimony contaminated areas.

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Abstract. *Cynara carduncululus* (cardoon) is a promising bioenergy crop, well-adapted to the Mediterranean climate. Recent studies suggest its potential for phytoremediation of soils contaminated with heavy metals such as Cd, Ni, and As. This study explores the potential of cardoon for remediating soils contaminated with antimony. The following aspects were investigated: (i) effect of Sb contamination on phytomass production, (ii) effect of *Cynara* cultivation on the stabilization of Sb in soils and (iii) assessment of Fe(II) addition in enhancing soil remediation and plants growth. Experiments were conducted in 1.5-liter pots containing 1.3 kg of soil. Four-week-old cardoon seedlings were exposed to Sb at concentrations of 10, 20, and 40 mg/kg. Parallel treatments included Fe(II) addition at a fixed Fe/Sb molar ratio 1.5. The results showed that increased levels of Sb in soil had a negative impact on phytomass production, but simultaneous addition of Fe(II) prevailed over the toxicity of Sb and promoted plant growth. On the other hand, the water-soluble amount of Sb was reduced in the soils where cardoon was grown. Furthermore, Fe(II) addition enhanced Sb immobilization and plant growth. The findings highlighted the dual benefits of *C. carduncululus* in sustainable land management and renewable energy production on contaminated sites. **Keywords:** Phytoremediation, Cynara, antimony, stabilization.

1. Introduction

Antimony (Sb) is a toxic metalloid increasingly recognized as an emerging environmental contaminant due to its extensive industrial use and its release into the environment. Elevated Sb concentrations in soils pose serious ecological and human health risks, primarily through the contamination of groundwater and the food chain. Unlike more extensively studied heavy metals such as lead (Pb) or cadmium (Cd), the behavior, mobility, and bioavailability of Sb in soils remain less understood, complicating remediation efforts. Phytoremediation is a promising, cost-effective, and environmentally friendly strategy for Sb-contaminated sites. Successful phytoremediation requires plant species that can tolerate high Sb levels, produce substantial biomass, and either accumulate or stabilize the metalloid effectively, via phytoaccumulation or phytostabilization mechanisms.

Cynara carduncululus (cardoon) is a plant native to the Mediterranean region, known for its adaptability to harsh environmental conditions (Llugany et al. 2012). Recent studies have demonstrated that cardoon can tolerate and accumulate various heavy metals, such as Cd, Ni and As (Papazoglou 2011, Llugany et al. 2012, Leonardi et al. 2021). Beyond its metal tolerance, cardoon offers additional advantages: its vigorous growth on marginal lands reduces competition with food crops, and its harvested biomass can be valorized for bioenergy production, thereby coupling environmental cleanup with renewable energy generation. In this study the potential utilization of cardoon for the remediation of Sb contaminated soils was explored. The effect of simultaneous Fe(II) addition in alleviating Sb toxic effects was also investigated.

2. Materials and methods

The soil used for the experiments originated from the region of Attica and was provided by a company operating in the field of earthmoving works. Antimony content was equal to 12.8 mg/kg, the pH was 7.2 and the organic carbon content was equal to 2.94 %. Plantlets of *Cynara carduncululus* were procured from a nursery. Transplanting to the final pots and exposure to Sb contamination took place when the plantlets were 74-days old from sowing. Each plantlet was transplanted into a 1.5-liter plastic pot containing 1 kg of Attica soil and 0.3 kg of the humus-rich nursery potting substrate. Treatments included the application of Sb at concentrations of 10, 20, and 40 mg/kg, with or without Fe addition (Fe/Sb molar ratio of 1.5). Antimony and iron solutions were prepared from potassium Sb(III)-tartrate and Fe(II) sulfate salts. Each treatment was conducted in triplicate and the placement of pots followed a randomized design to minimize positional bias. The plants were harvested 30 days after the addition of antimony and were separated into root systems and above-ground plant parts. After washing and drying, the dry biomass of both parts was determined by weighing. The EN 12457.02 test was applied to determine the water-soluble amount of Sb in the soils. The test included leaching of the soil with deionized water at a liquid to solid ratio, L/S = 10 L/kg, for 24 hours and analysis of Sb concentration in the aqueous phase.

3. Results and Discussion

In Figure 1, the effect of increasing antimony (Sb) additions in soil on the production of biomass in the above-ground parts of the plant is presented. In the experiments which were carried out without simultaneous addition of Fe(II), increasing the levels of Sb in soil had a slight negative effect on the aerial parts of the plant. At the lowest level of Sb addition (~10 mg/kg), the biomass of stem and leaves after 30 days was equal to ~3.2 g dry weight (dw). As Sb addition increased to 15 mg/kg and beyond, the produced phytomass decreased to values 1.8-2.1 g. This reduction suggests that Sb has a toxic effect on shoot development, likely due to disruption of nutrient uptake, oxidative stress, or interference with metabolic processes (Vidya et al., 2022). The simultaneous addition of Fe(II), at a molar ratio Fe(II)/Sb=1.5 mol/mol, was found to outweighed the toxicity of Sb on plant growth. This positive effect was particularly clear at the highest level of Sb and Fe(II) additions. The phytomass of the aerial parts increased from 2.5 to 7.4 grams (almost tripled), when Sb and Fe(II) additions increased from 10 and 6.9 mg/kg to 40 and 27.5 mg/kg, respectively. This is due to the fact that iron is an essential micronutrient for plants and is involved in the synthesis of chlorophyll (Routs and Sahoo, 2015). On the other hand, as shown in the following paragraph, iron reduces the water-soluble and bioavailable fraction of Sb in soils, alleviating thus the phytotoxic effects of the contaminant.

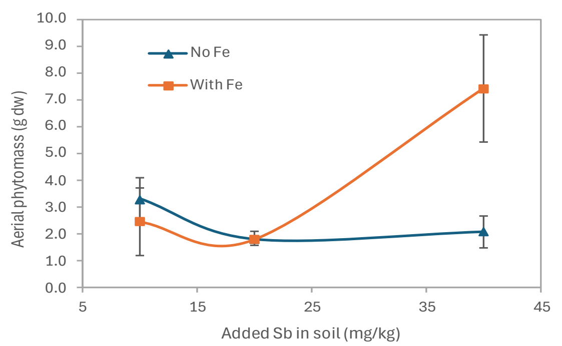

Figure 1. Phytomass of the above-ground parts of *C. cardunculus* as a function of the Sb levels added in soil. Effect of the combined addition of Fe(II).

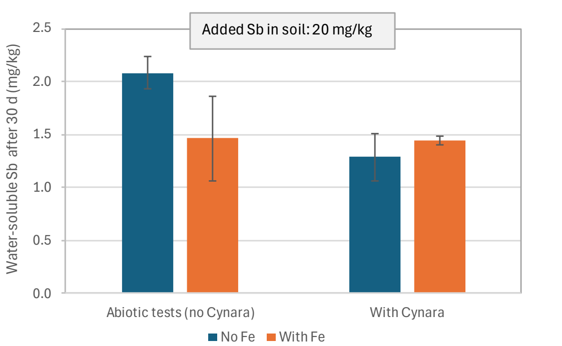

Figure 2. Effect of *C. cardunculus* cultivation on the stabilization of Sb in comparison with the stabilization effect of Fe(II).

Figure 2. presents the water-soluble antimony in soils 30 days after the application of the artificial contamination of soils, involving the addition of Sb at a dose of 20 mg/kg, with and without the simultaneous addition of Fe. Two types of tests are compared, abiotic control tests (without cultivation of plants) and similar tests where the soils are the substrate for the cultivation of *Cynara*. It is seen that the soil has a natural stabilization capacity. Under the abiotic conditions and without addition of Fe, approximately 90% of added Sb was transformed into immobile non-aqueous species. The water-soluble Sb dropped from the initial 20 mg/kg to about 2.1 mg/kg. The possible stabilization mechanisms are adsorption on the Fe- and Al-phases of soil, precipitation, retention on organic matter etc. (Vidya et al. 2022). Addition of Fe(II) in the abiotic tests decreased further the water-soluble fraction of Sb from 2.1 to 1.5 mg/kg. As shown in many published works, iron salts are very efficient compounds in removing Sb oxyanions from the aqueous phase by adsorption or precipitation mechanisms (Leverette et al., 2012, Mitrakas et al. 2018). In the absence of Fe, the cultivation of *Cynara* on the soil had also a prominent stabilization effect and the immobilization of Sb was even more pronounced compared to the simple chemical treatment with Fe. Namely, the water-soluble Sb decreased from 2.1 to 1.3 mg/kg in the presence of *Cynara*, and from 2.1 to 1.5 mg/kg with the simple abiotic addition of Fe. Combined addition of Fe and cultivation of *Cynara* didn't improve the Sb immobilization processes. This highlights the potential of cardoon for phytostabilization of Sb-contaminated soils, even in the absence of chemical amendments. However, addition of Fe promotes phytomass production and increases the expected benefits from the utilization of *C. cardunculus* for renewable energy production on contaminated lands.

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