

# Functionalized biochar for reducing lead bioaccessibility

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## ABSTRACT

- By estimating the fraction of lead available for human uptake in soils, we can more accurately predict associated risks. This study investigates the effects of biochar functionalized through aerobic heating on bioaccessible lead in contaminated soils.
- Soils treated with either heated or unheated biochar showed a significant reduction in bioaccessible lead after 8 weeks.
- Although not statistically significant, heated biochar tended to result in slightly lower lead bioaccessibility compared to unheated biochar.

## INTRODUCTION

A major hurdle to popularizing urban agriculture in the Northeastern US is potential soil contamination by heavy metals, especially legacy contaminants like lead (Pb).

Measurements of total Pb can be misleading since the true health risks depend on the human intake rate and the fraction of Pb that is bioavailable. We estimate this fraction by measuring *in-vitro* bioaccessible Pb - the amount of Pb released into solution when soil is subjected to conditions similar to the human digestive tract.

Amendments for remediating contaminated soil, such as biochar, are well-known for their metal-sorbing properties, but should be tested for their effectiveness in reducing Pb bioaccessibility. Biochar attracts metal ions through physical and chemical interactions. Several methods, primarily involving chemical treatments, can activate biochar to increase these interactions.

We propose using heat instead of chemical reagents to treat biochar. Preliminary results indicate that post-processing heating of biochar in air can create an increased number of surface functional groups. We hypothesize that these functional groups will enhance metal sorption capacity of biochar, thus reducing Pb bioaccessibility in amended soil.

## METHODS

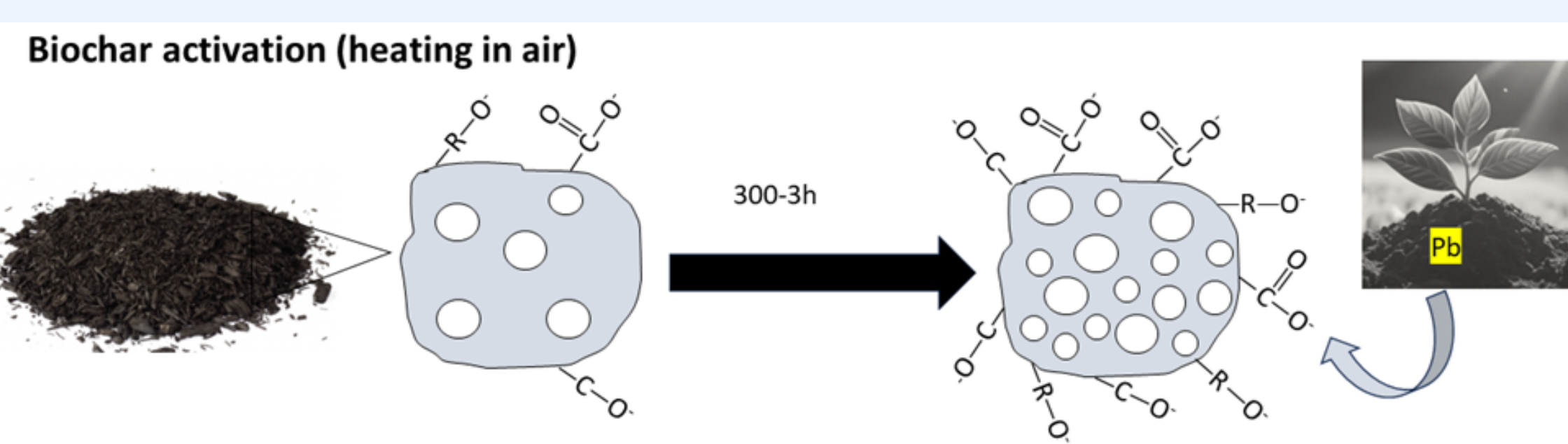


Figure 1. Biochar activation by heating in air should increase both porosity and surface reactivity of biochar, leading to better Pb sorption.

Wood chip biochar was sourced from Metzler Biochar (Reedsville, PA), with the company providing product characterization. Functionalized biochar was prepared by heating crucibles of biochar in air to 300°C in a muffle furnace. The pH of both heated and unheated biochar was measured as well as surface area and pore volume (1:20 biochar:water w/w for pH and BET for surface area).

Soil was collected from a community garden site in Philadelphia, PA, dried, and sieved to 2 mm. The soil was a sandy loam texture with a pH of 7.44 and 6.5% organic matter. The total lead concentration was measured as 576 ppm using XRF on pressed pellet samples. 32 g of soil was placed into each of 36 plastic beakers. The beakers were divided into three treatments: control soil, soil with 5% w/w unheated biochar, and soil with 5% w/w heated biochar. The total lead in the unheated and heated biochar mixtures was remeasured (549 and 550 ppm, respectively). Each beaker was covered in perforated parafilm and maintained at 40% moisture by mass.

## METHODS cont.

At approximately 0, 2, 8, and 13 weeks, three beakers were removed for bioaccessibility and pH tests. The EPA Method 1340: *In-Vitro* Bioaccessibility (IVBA) Assay for Lead in Soil procedure was used (with modification: soil was sieved to 250 µm). The resulting extracts were tested with ICP-OES (MDL = 0.005 and LOQ = 0.025). IVBA calculations were carried out as follows: (Extracted Pb\*100)/(Total Pb \* Mass of Sample).

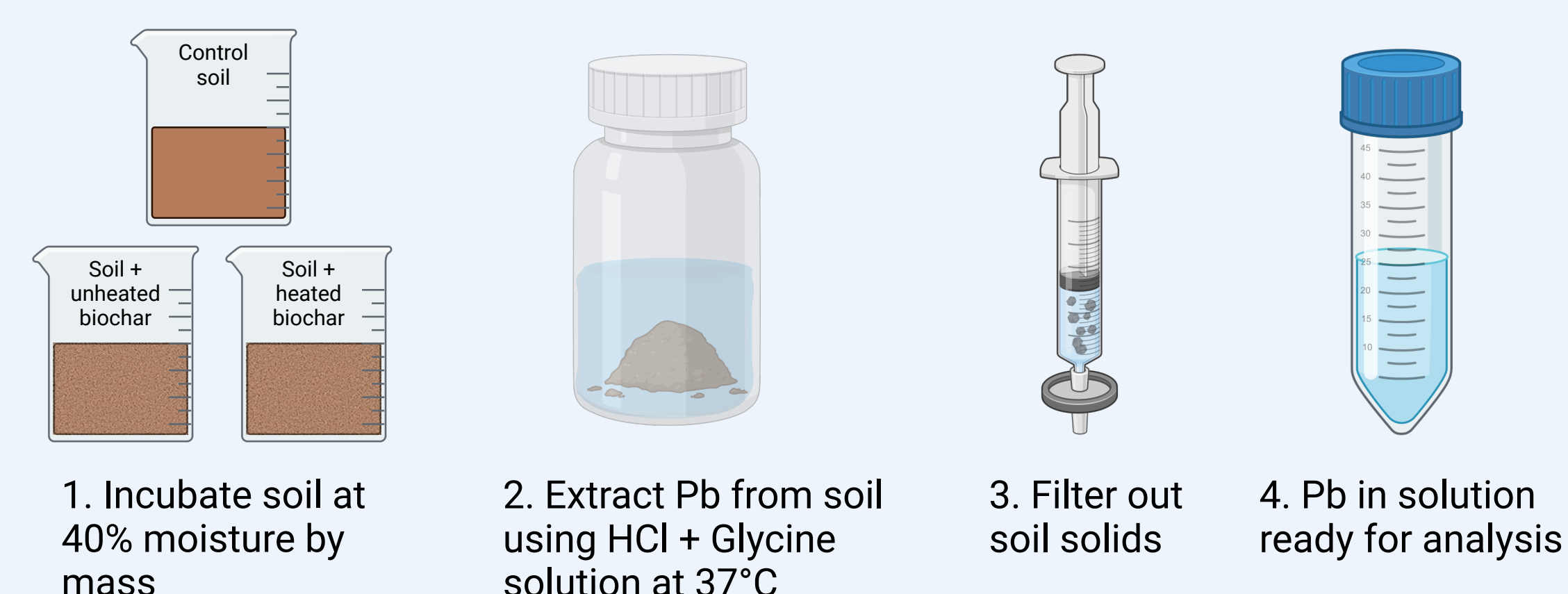


Figure 2. The EPA Method 1340 procedure calls for extracting Pb from sieved soil using 100mL of a 0.4 M glycine solution at pH 1.5 and 37°C for one hour. The solution is then filtered to remove soil particles and stored at 4°C until elemental analysis.

## RESULTS

### Biochar Functionalization

Biochar pH decreased from 10.26 to 8.79 following 3 hours of heating. This pH shift supports the conclusion that heating in oxygenic conditions increases acidic surface groups on biochar surfaces. The surface area also increased from 502.76 m<sup>2</sup>/g to 659.24 m<sup>2</sup>/g (31.1% change), while pore volume increased from 0.227 cm<sup>3</sup>/g to 0.336 cm<sup>3</sup>/g (48.0% change).

Table 1. Changes in chemical and physical properties of biochar after treatment.

Property	Unheated biochar	Heated biochar
pH	10.26	8.79
Surface area (m <sup>2</sup> /g)	502.76	659.24
Pore volume (cm <sup>3</sup> /g)	0.227	0.336

### Pb *in-vitro* Bioaccessibility

As shown in Figure 2, lower bioaccessibility was observed within the first week of the experiment: 77.58% (control), 75.59% (unheated biochar), and 75.62% (heated biochar). After 2 weeks bioaccessibility increased to 89.91% (control), 88.06% (unheated biochar), and 88.51% (heated biochar). As pH was not significantly lowered across time and treatment, this increase in bioaccessible Pb is not likely due to pH-dependent changes in solubility. Instead, the increase may be due to factors such as localized anaerobic conditions releasing Pb from iron oxides, or an initial increase in microbial activity breaking down insoluble organometallic complexes.

The data from 8 and 13 weeks show all samples remaining between about 83% and 86% bioaccessibility. Within these timepoints, both the unheated and heated biochar treatments had significantly lower IVBA measurements than the control soil ( $p < 0.000$ ; Figure 4). And while not statistically significant, there was a small decrease in bioaccessible Pb in the heated biochar treatment compared to the unheated biochar treatment.

Although these differences have been identified between treatments, they may or may not be of practical significance.

## RESULTS cont.

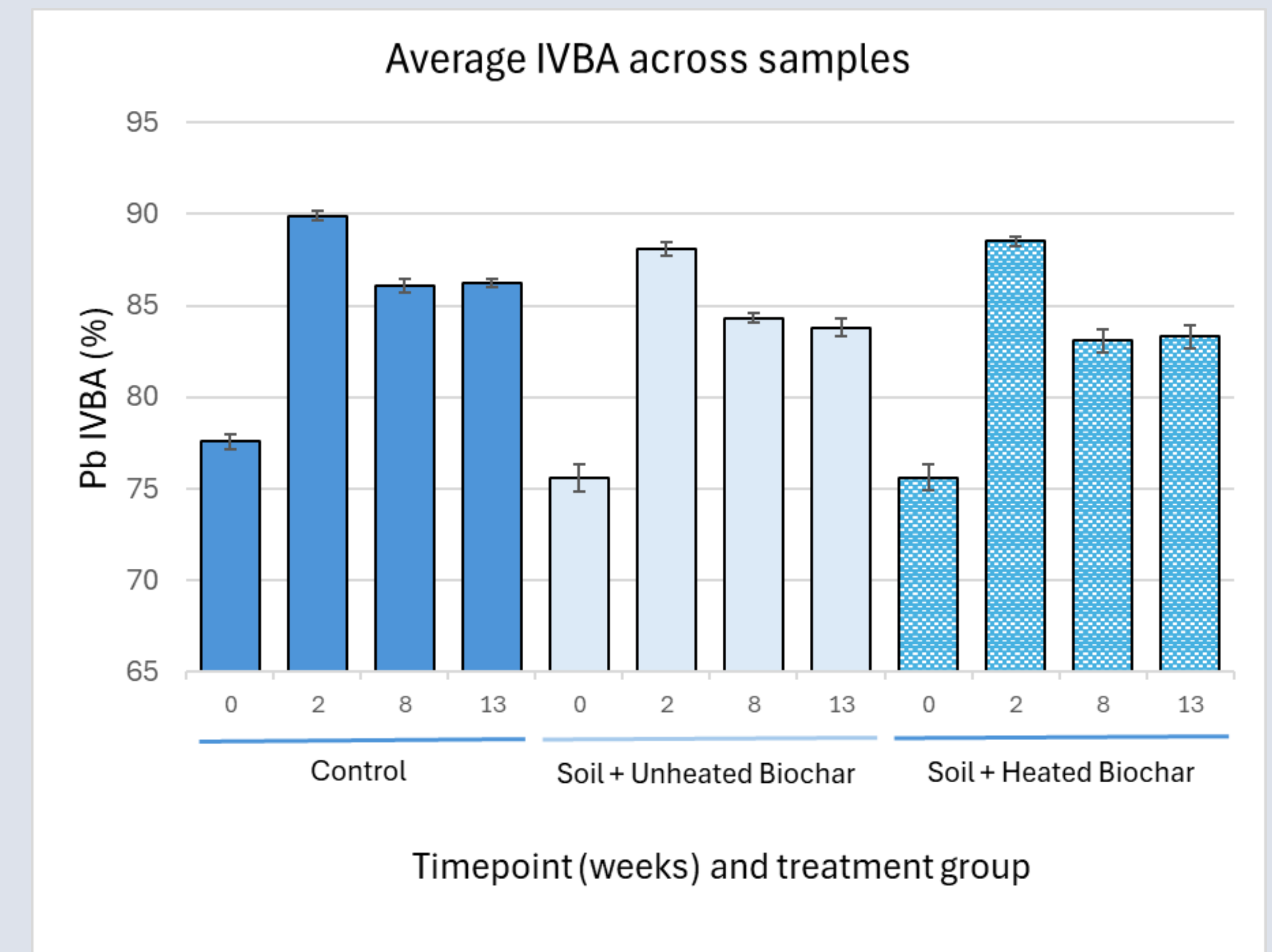


Figure 3. Bar chart showing the average Pb *in-vitro* bioaccessibility (IVBA) for control soil, soil treated with unheated biochar, and soil treated with heated biochar over 13 weeks.

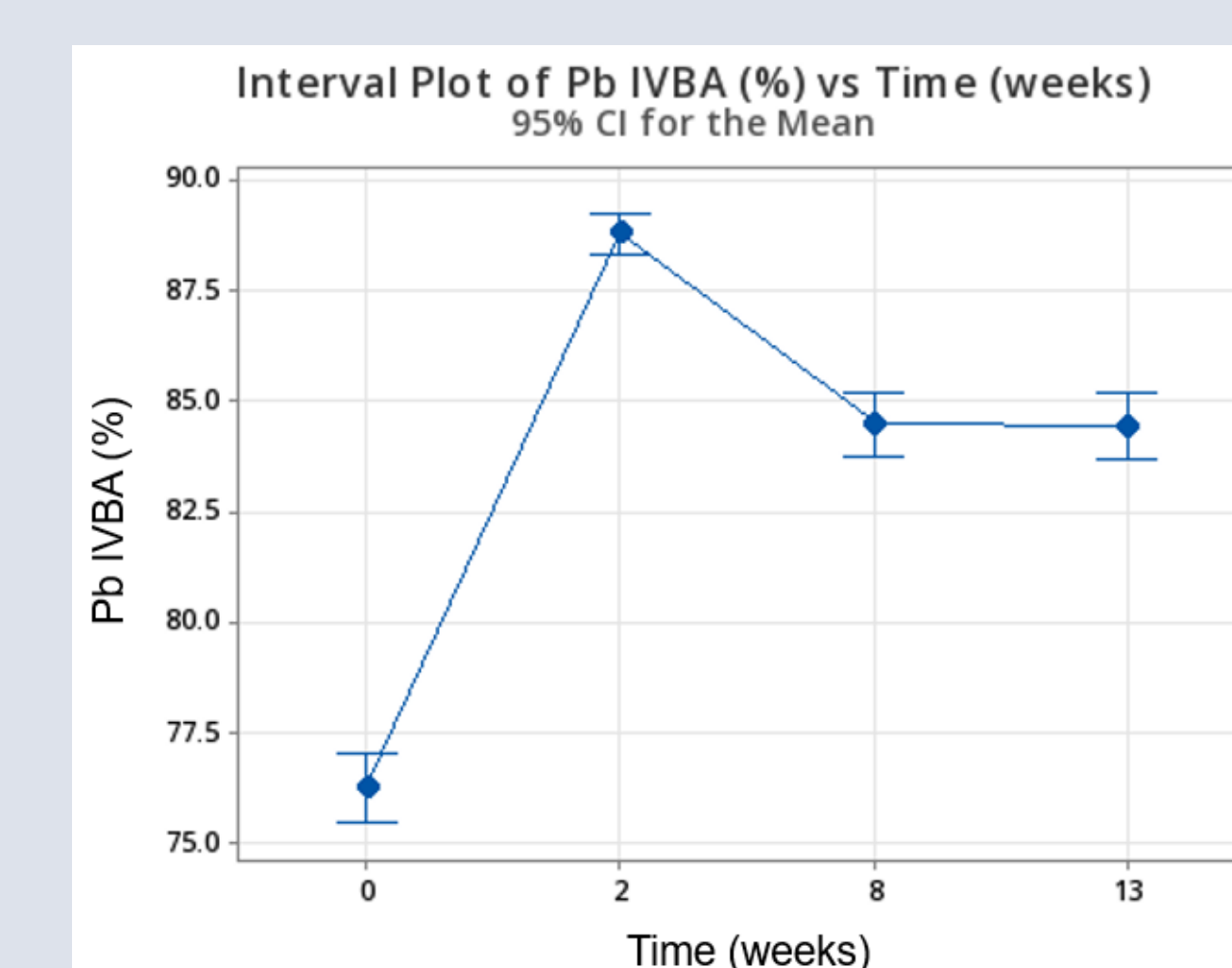


Figure 4. An ANOVA interval plot showing the changes in Pb *in-vitro* bioaccessibility (IVBA) across time.

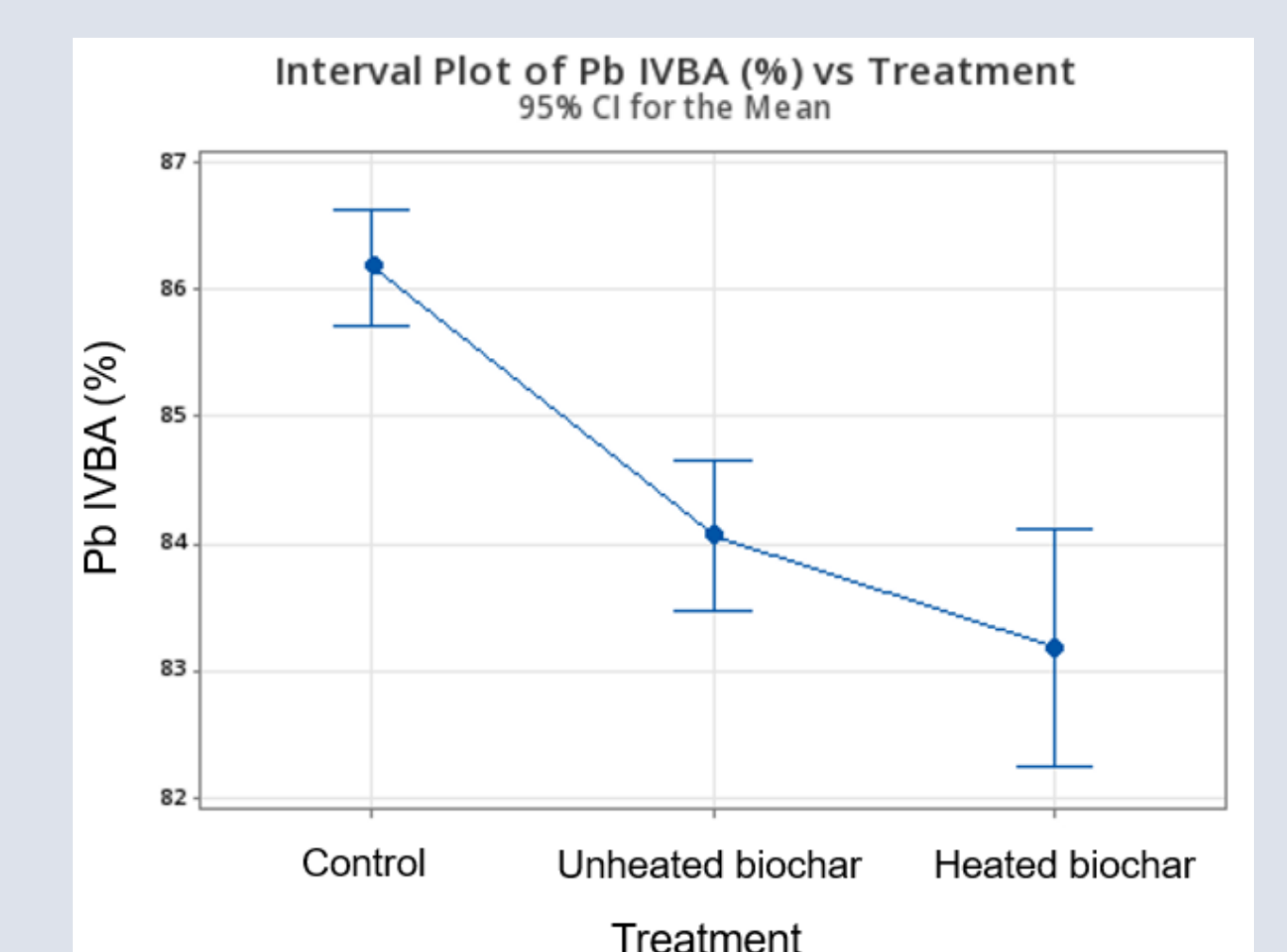


Figure 5. An ANOVA interval plot showing the changes in Pb *in-vitro* bioaccessibility (IVBA) across treatments for the 8 and 13 week timepoints only.

## SUMMARY & FUTURE WORK

- Heat treatment in air decreased pH and increased the surface area and pore volume of biochar, suggesting potentially higher reactivity of the treated material.
- Both unheated and heated biochar treatments significantly reduced Pb bioaccessibility after 8 weeks.
- Heated biochar did not show a statistically significant improvement over unheated biochar in lowering Pb bioaccessibility.
- Future experiments by our lab will include evaluation of different biochar types and loads, varying heat treatments, a larger-scale soil study with increased replicates and different moisture conditions, and Pb sorption experiments with treated biochar in aqueous solutions.

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Works Cited