# Can N-Doped Biochar Achieve Safe Vegetable Production in Soil Heavily Contaminated by Heavy Metals?

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**Text S1 The detailed analysis procedure for soil parameters**

1. pH

10 g of soil (1-mm) was added to a 50 mL beaker containing 25 mL $CO_2$ removed water, then mixing thoroughly with a glass rod for 1 min, and stand for 30 min before measuring with a calibrated pH mater.

2. Cation exchange capacity (CEC)

6.0 g of soil (1-mm) was added to a 100 mL centrifuge tube containing 33 mL $CH_3COONa$ solution (1.0 mol/L, pH = 8.2), shake at 250 rpm on a rotary shaker for 5 minutes, then centrifuged for 5 min at 4000 rpm to remove the supernatant. The soil was re-suspended with 33 mL $CH_3COONa$ solution (1.0 mol/L, pH = 8.2), then shaken at 250 rpm on a rotary shaker for 5 minutes, then centrifuged for 5 min at 4000 rpm to remove the supernatant. Repeat this step 4 times.

The soil was re-suspended with 33 mL absolute alcohol, shaking at 250 rpm for 5 min and centrifuging at 4000 rpm for 5 min to remove the supernatant. Repeat this step for 3 times.

After that, the soil was re-suspended with 33mL of $CH_3COONH_4$ (1 mol/L, pH = 7.0), shaking at 250 rpm for 5 min and centrifuging at 4000 rpm for 5 min, the supernatant was transferred into a 100 mL volumetric flask. Repeat this step 3 times. Then dilute the solution to 100 mL with $CH_3COONH_4$ solution. The content of $Na^+$ in the filtrate was determined by flame photometry after filtering through filter paper.

3. Organic matter content (SOM)

0.25 g of soil (0.15-mm) was added to thermostability test tube (30*200 mm), then 5 mL of $K_2Cr_2O_7$ solution (0.133 mol/L) and 5 mL $H_2SO_4$ ($\rho$ = 1.84) were added. Then place the test tube

into a preheated oil bath (185 $^{\circ}$C), and control the temperature of the oil bath between 170 to 180 $^{\circ}$C for 5 min (start timing from bubbles appear inside the test tube). After that, take out the test tube and cool it to room temperature. Transfer the solution from the test tube into a 150 mL Erlenmeyer flask by rinsing with distilled water. 4 drops of phenanthroline indicator were added and shaken to evenly. Finally, the solution was titrated with calibrated $FeSO_4 \cdot 7H_2O$ (0.2 mol/L) solution until the color changes to red at the endpoint.

4. Available potassium (AK)

5 g of soil (1-mm) was added to a 150 mL Erlenmeyer flask containing 50 mL $NH_4OAc$ solution (1 mol/L, pH = 7.0). The suspension was shaken evenly on a rotary shaker at 175 rpm for 30 min at 25 $^{\circ}$C, then filtered through filter paper. The content of K in the filtrate was determined using flame photometry.

5. Available phosphorus (AP)

2.5 g of soil (1-mm) was added to a 150 mL Erlenmeyer flask containing 50 mL $NaHCO_3$ solution (0.5 mol/L, pH = 8.5). The suspension was shaken evenly on a rotary shaker at 175 rpm for 30 min at 25 $^{\circ}$C, then filtered through phosphorus-free filter paper. 10 mL of the filtrate was transferred into a 50 mL colorimetric tube, and 10~20 mL (depended on the concentration of AP) distilled water was added, then 5 mL of molybdate was added by slowly dropping. Diluted with distilled water to 50 mL and mixed thorough. Then, the content of P was analyzed using ultraviolet and visible spectrophotometer at a wavelength of 700 nm after standing for 30 min.

6. Available nitrogen (AN)

2.0 g of soil (1-mm) was added to outer chamber of a diffusion boat, then 0.2 g of $FeSO_4 \cdot 7H_2O$ was added and mixed thoroughly. The diffusion boat was rotated to ensure even

distribution of the sample. Then, 2 mL of borate indicator solution (20 g/L, pH = 4.5) was added to the inner chamber of the diffusion boat. The alkaline gel was smeared on the exterior edge of the diffusion boat, a glass cover was placed on top and ensuring a complete seal between the diffusion boat and the glass. Open a crack between the glass cover and the diffusion boat, 10 mL of NaOH solution (1.0 mol/L) was added to the outer chamber through the crack and the diffusion boat was promptly sealed immediately, then incubated at 40 °C for 24 h in a constant-temperature incubator. After that, the resulting solution (borate indicator solution) was titrated using a standard $H_2SO_4$ solution (0.005 mol/L).

7. DTPA- extractable HMs

5 g of soil (1-mm) was added to a 100 mL Erlenmeyer flask containing 25 mL DTPA solution (0.005 mol/L DTPA, 0.01 mol/L $CaCl_2$, 0.1 mol/L TEA, and pH=7.3). The suspension was shaken evenly on a rotary shaker at 175 rpm for 2 hours at 25 °C, then filtered through filter paper. The content of HMs in the filtrate was detected by inductively coupled plasma-mass spectrometry (ICP–MS, ICAP 6200, USA Thermo Fisher).

## Table S1 Physiochemical properties of BC and HNC

|  | BC | HNC |
|---|---|---|
| $pH_{pzc}$ | 4.77 | 2.69 |
| carboxyl group (mmol/g) | 1.251 | 2.320 |
| lactonic group (mmol/g) | 1.206 | 1.336 |
| hydroxyl group (mmol/g) | 1.975 | 1.670 |
| C [%] | 76.29 | 57.55 |
| H [%] | 3.88 | 6.26 |
| O [%] | 18.38 | 27.52 |
| N [%] | 0.51 | 4.44 |
| H/C | 0.05 | 0.11 |
| O/C | 0.24 | 0.48 |
| (O+N)/C | 0.25 | 0.56 |
| BET surface area ($m^2$/g) | 3.1764 | 2.7033 |
| BJH pore volume ($cm^3$/g) | 0.012958 | 0.010247 |
| Average diameter of pores (nm) | 10.198 | 13.464 |
| Micropore volume ($cm^3$/g) | 0.0007243 | 0.0004308 |
| Available K (g/kg) | 6.19 | 0.61 |

## Table S2 The selection of the detailed values of these parameters

| Parameters |  | Value |
|---|---|---|
| $IR$ (kg·day$^{-1}$) | Adult | 0.244 |
|  | Children | 0.186 |
| $ED$ (a) | Adult | 70 |

|  |  |  |
|---|---|---|
|  | Children | 12 |
| *EF* (d·a⁻¹) |  | 365 |
| *BW* (kg) | Adult | 63.5 |
|  | Children | 15 |
| *AT* (a) |  | 365×ED |
| R*f*D (mg·kg⁻¹·day⁻¹) | Pb | 0.0035 |
|  | Cd | 0.001 |
|  | Cu | 0.04 |
|  | Zn | 0.3 |
|  | Ni | 0.02 |

Note: These values were referenced from the report of Ruan et al. (2023) [1] and Liu et al. (2021) [2].

**Table S3** The immobilization amount between HNC and other biochar materials.

| Materials | Immobilization amount (mg/g) | | | | | Reference |
|---|---|---|---|---|---|---|
| | Pb | Cd | Cu | Zn | Ni | |
| Phosphorus-loaded biochar | 0.56 | 0.25 | 0.50 | 1.17 | / | [3] |
| Multiple-modified biochar | / | 0.07 | 0.19 | / | / | [4] |
| Mn-modified bamboo biochar | 0.49 | 0.03 | 0.14 | increased | / | [5] |
| Silica–magnesium coupling in lignin–based biochar | 0.24 | 0.23 | 0.03 | 2.54 | / | [6] |
| MgCl$_2$-modified lignin biochar | increased | 0.07 | 0.03 | 4.11 | / | [7] |
| corn stalk biochar | 1.01 | 0.02 | 0.21 | 0.75 | / | [8] |
| Ca-modified cypress biochar | / | 0.30 | 0.02 | 0.08 | / | [9] |
| HNC | 1.53 | 0.05 | 0.13 | 0.18 | 0.01 | This work |

**Table S4** The level of HQ, HI, and CR

| HQ | | HI | | CR | |
|---|---|---|---|---|---|
| HQ≤1 | No obvious noncarcinogenic risks | HI≤1 | No obvious health risks | CR＜$10^{-6}$ | No carcinogenic risk |
| HQ>1 | Having adverse effects on human health | 1<HI≤10 | posed noncarcinogenic risk | $10^{-6}$≤CR≤$10^{-4}$ | Acceptable carcinogenic risk |
| | | HI>10 | Heavily chronic toxicity | CR>$10^{-4}$ | Unacceptable carcinogenic risk |

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