
Supporting Information for

**Impacts of Modified Fly Ash on Soil Available Lead and Copper and Their
Accumulation by Ryegrass**

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18 **Text. S1 Characterization analysis**

19 The brunauere emmete teller specific surface area and porosity of the FA and MFA were
20 determined by recording N₂ adsorption desorption isotherm at 77 K using an Auto-sorb-iQA3200-4
21 instrument (Quantatech Corporation, USA). The particle structure and surface morphology of the FA
22 and MFA were determined using field emission scanning electron microscopy (SEM; Quanta 400 FEG,
23 FEI, USA). Fourier transform infrared (FTIR) spectroscopy was conducted using a Nicolet Nexus 670
24 FTIR infrared spectrometer in the range of 600-4000 cm⁻¹ with a resolution of 2 cm⁻¹. The crystalline
25 components of the FA and MFA were determined by X-ray diffraction (XRD). The diffractometer
26 (Rigaku, Ultima IV, Japan) was equipped with a graphite monochromator in the diffraction beam (at
27 40 kV and 40 mA). XRD scans were conducted in the 2θ range of 10°-60° with a step size of 0.02°.
28 The solid phases were identified using Jade 6 (Material Data, Inc. CA, USA). The compositions of
29 functional groups on the surface of the FA and MFA were determined using X-ray photoelectron
30 spectroscopy (XPS; ESCALAB250 XI, Thermo Scientific Co., USA) with Al Ka radiation (12 kV and
31 6 mA) at a pressure of 5.0 × 10⁻¹² Pa in the analytical chamber. The XPS spectra were split and fitted
32 using the XPSPEAK 4.1 program.
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Text. S2 Soil lead (Pb) and copper (Cu) sequential extraction procedure

A sequential extraction procedure modified from the method of [Tessier, A.; Campbell, P.G.C.; Bisson, M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **1979**, *51*, 844–851] was described as follows:

(1) Exchangeable speciation (EXC): 16 mL magnesium chloride ($1 \text{ mol L}^{-1} \text{ MgCl}_2$, $\text{pH} = 7$) was added in a 100-mL polypropylene centrifuge tube containing $2 \pm 0.0001 \text{ g}$ of soil sieved through a 0.15-mm mesh. The tube was shaken for 2 h at $25 \pm 1 \text{ }^\circ\text{C}$ on an end-over mechanical shaker operating at 120 rpm. After equilibration, the suspension was centrifuged at 4000 rpm for 10 min. The supernatant was decanted and filtered through a 0.45- μm filter and transferred into a polyethylene container and stored at $4 \text{ }^\circ\text{C}$ until analysis.

(2) Bound to carbonates (CA): The residue from (1) was shaken with 16 mL 1 mol L^{-1} sodium acetate (CH_3COONa), with pH adjusted to 5.0 with acetic acid (CH_3COOH). The tube was shaken for 3 h at $25 \pm 1 \text{ }^\circ\text{C}$, and the extraction procedure was the same as in (1).

(3) Bound to Fe-Mn oxides (Fe-Mn): The residue from (2) was shaken with 40 mL hydroxylamine hydrochloride (0.04 mol L^{-1} , $\text{NH}_2\text{OH}\cdot\text{HCl}$) in 25 % (v/v) CH_3COOH . The tube was heated to $96 \pm 3 \text{ }^\circ\text{C}$ in a water bath for 6 h, and the extraction procedure was the same as in (1).

(4) Bound to organic matter (OM): 6 mL nitric acid (0.02 mol L^{-1} , HNO_3) and 10 mL hydrogen peroxide (30 % H_2O_2 , acidified to pH 2 with HNO_3) were added into the residue from (3), and the mixture was heated to $85 \pm 2 \text{ }^\circ\text{C}$ for 2 h in a water bath. Then, 6 mL H_2O_2 (30 %, acidified to $\text{pH} = 2$ with HNO_3) was added, and the sample was heated again to $85 \pm 2 \text{ }^\circ\text{C}$ for 3 h. After cooling, 10 mL ammonium acetate (3.2 mol L^{-1} , $\text{CH}_3\text{COONH}_4$) in 20 % (v/v) HNO_3 was added at $25 \pm 1 \text{ }^\circ\text{C}$ for 30 min. The extraction procedure was the same as in (1).

(5) Residual (RES): The residual fraction of the certified reference material was analyzed by digestion with HNO_3 -HF- HClO_4 (5:10:5 mL). The sum of concentrations of lead (Pb) and copper (Cu) in different speciation was compared with the concentrations obtained by total digestion. Therefore, the difference between the total and non-residual speciation was called the residual speciation.

61 Attachment Chart

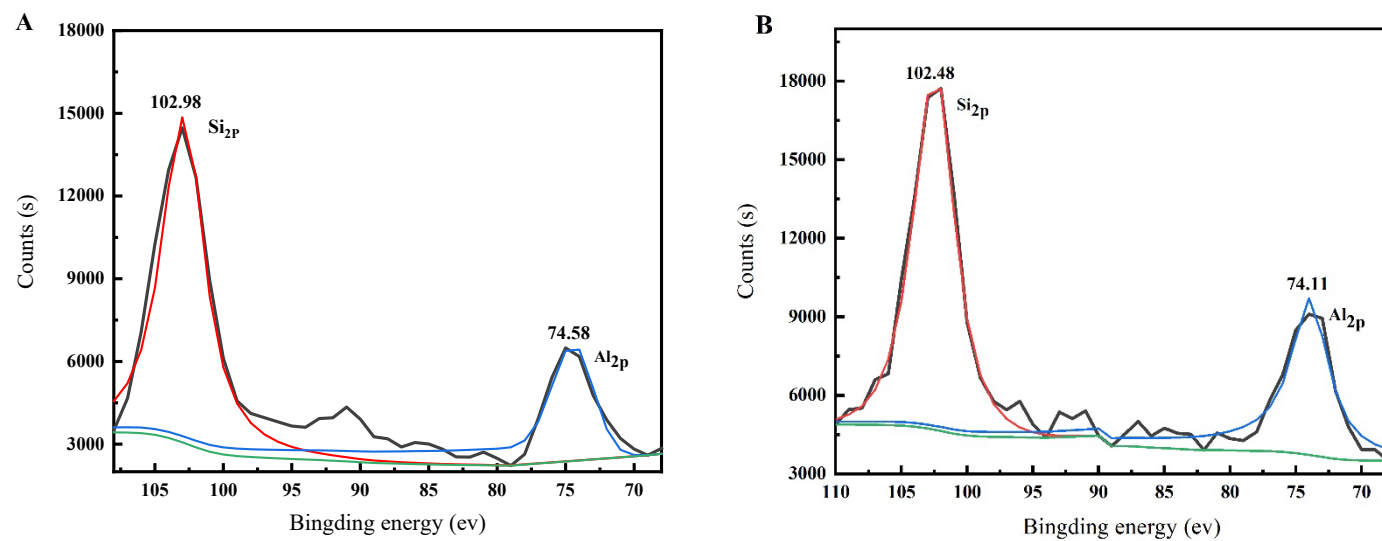
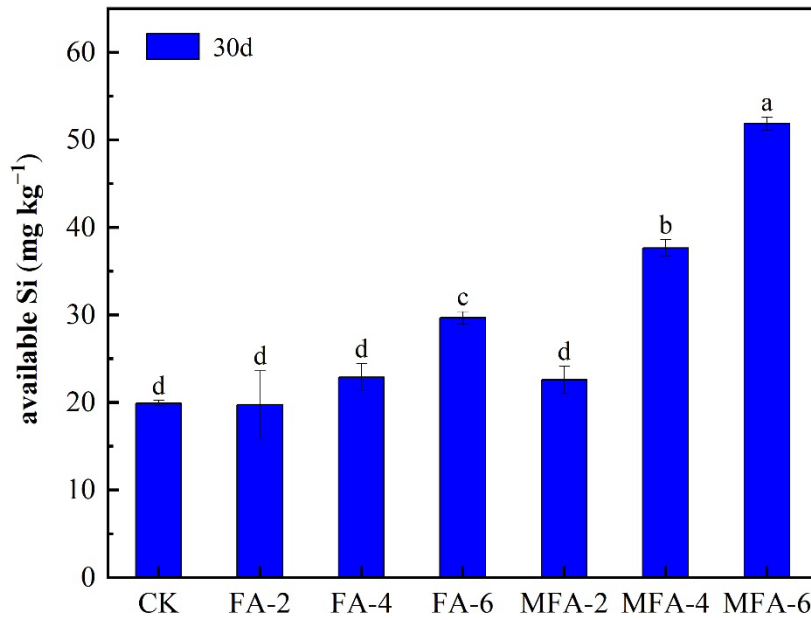


Figure S1. Si_{2p} and Al_{2p} spectrum of FA (A) and MFA (B). Note: FA: fly ash; MFA: modified fly ash.

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70 **Figure S2.** Changes in available silicon (Si) in contaminated soil amended with FA or MFA. Note: CK, the control
71 soil; FA-2, 0.2% FA treated soil; FA-4, 0.4% FA treated soil; FA-6, 0.6% FA treated soil; MFA-2, 0.2% MFA treated
72 soil; MFA-4, 0.4% MFA treated soil; MFA-6, 0.6% MFA treated soil. Different letters above the error bar indicate
73 significant differences between the treatments ($p < 0.05$).

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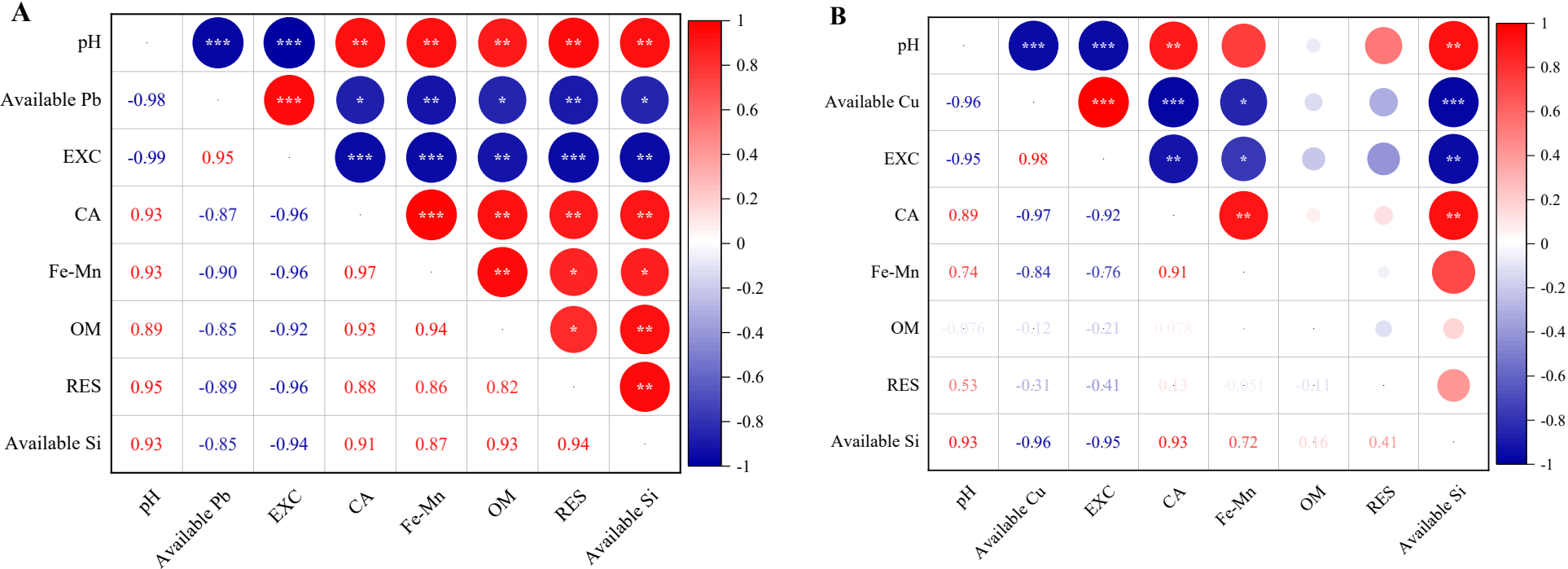
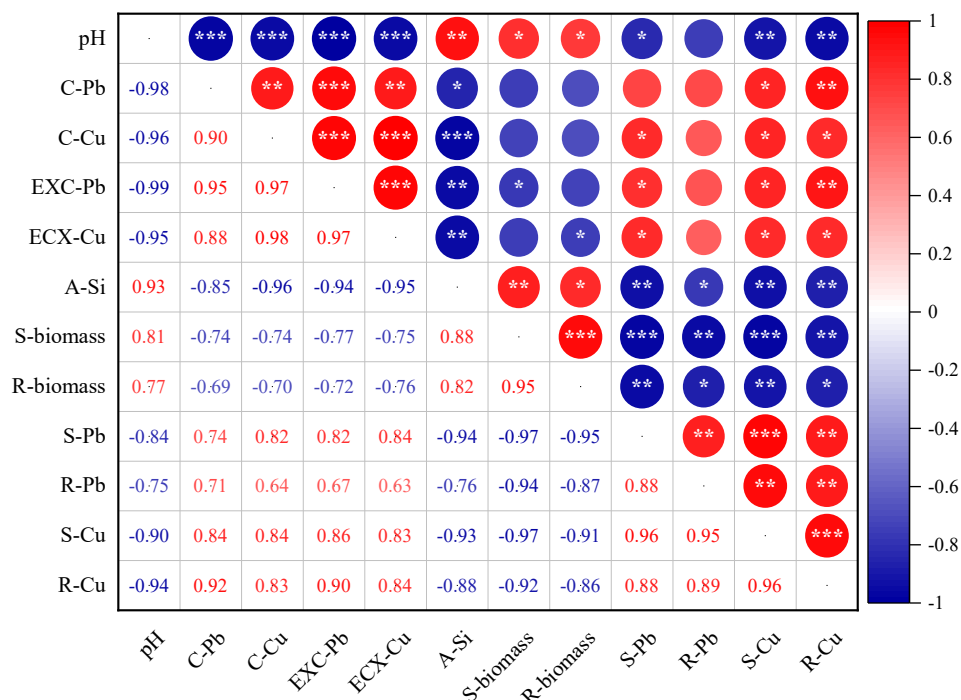


Figure S3. Correlations coefficients among soil pH, available Pb (A) and Cu (B), available Si, and Pb and Cu speciation. available Pb and Cu: CaCl₂-extractable-Pb and Cu, EXC, exchangeable; CA, bound to carbonates; Fe-Mn, bound to iron and manganese oxide oxides; OM, bound to organic matter; RES, residual. Note: ***: Significant correlation at the 0.001 level ($p < 0.001$). **: Significant correlation at the 0.01 level ($p < 0.01$). *: Significant correlation at the 0.05 level ($p < 0.05$).

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Figure S4. Correlation coefficients among soil pH, soil CaCl₂-extractable and exchangeable Pb and Cu, available Si, dry biomass in shoot and root ryegrass, accumulation of Pb and Cu in shoot and root ryegrass. C-Pb, CaCl₂-extractable-Pb; C-Cu, CaCl₂-extractable-Cu; EXC-Pb, exchangeable Pb; ECX-Cu, exchangeable Cu; A-Si, available Si; S-biomass, shoot dry biomass of ryegrass; R-biomass, root dry biomass of ryegrass; S-Pb, shoot Pb in ryegrass; R-Pb, root Pb in ryegrass; S-Cu, shoot Cu in ryegrass; R-Cu, root Pb in ryegrass. Note: ***: Significant correlation at the 0.001 level ($p < 0.001$). **: Significant correlation at the 0.01 level ($p < 0.01$). *: Significant correlation at the 0.05 level ($p < 0.05$).