

# Supplementary Materials: Microscale Heterogeneous Distribution and Speciation of Phosphorus in Soils Amended with Mineral Fertilizer and Cattle Manure Compost.

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(10 pages, 3 tables, 8 figures)

**Table S1.** Composition of cattle manure compost (Dry matter basis)\*.

C	N	P <sub>2</sub> O	K <sub>2</sub> O	CaO
g/kg				
410	18	13	36	21

\*Calculated after Yamamoto et al. (2016).

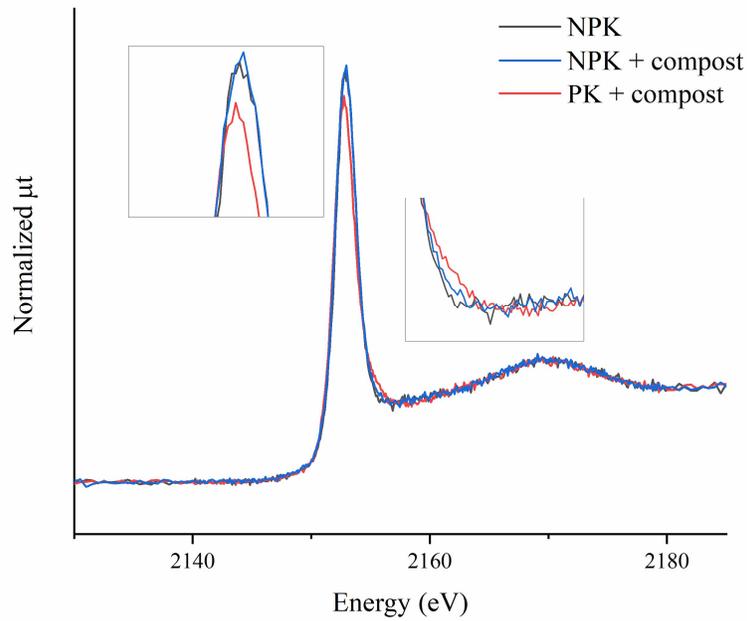
**Table S2.** Peak deconvolution results of solid state <sup>31</sup>P NMR.

		NPK	NPK + Compost	PK +Compost
Peak 1	Center	2.9 ppm	3.0 ppm	2.9 ppm
	FWHM	2.2 ppm	2.4 ppm	4.0 ppm
	Intensity	0.012	0.015	0.27
	Area	0.028	0.038	1.7
Peak 2	Center	-5.6 ppm	-4.4 ppm	-2.8 ppm
	FWHM	19 ppm	19 ppm	17 ppm
	Intensity	0.040	0.044	0.074
	Area	0.82	0.90	1.3

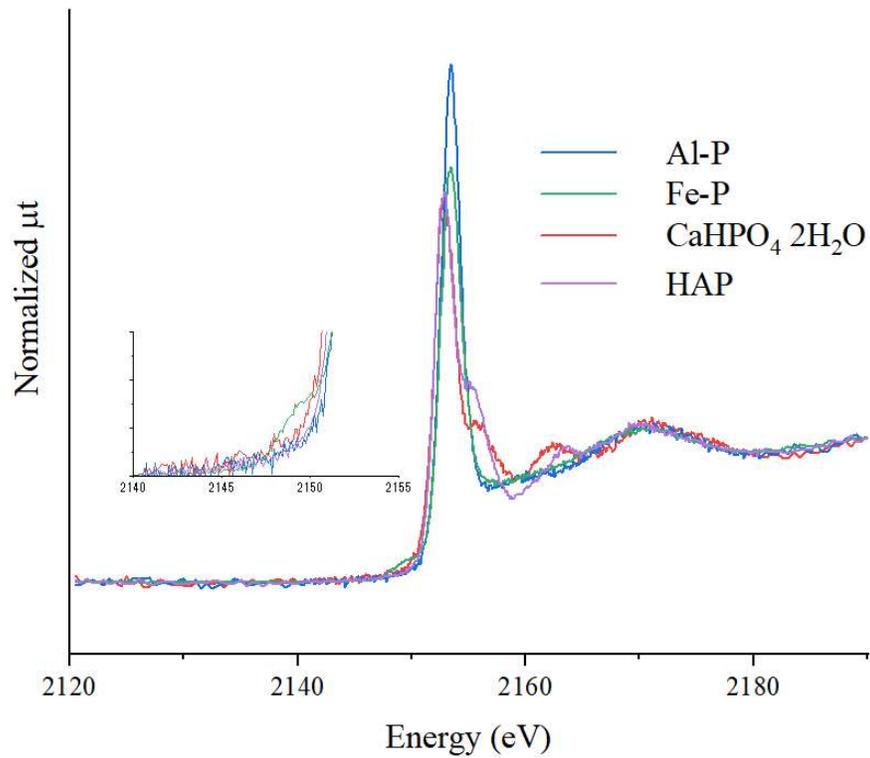
FWHM: Full width at half maximum. Peak 1, which is assigned to hydroxyapatite, was fit by a Lorentzian function and peak 2 was fit by a Gaussian function.

**Table S3.** Average yield and phosphorus uptake of cabbage heads from 16 cycles of cultivation.

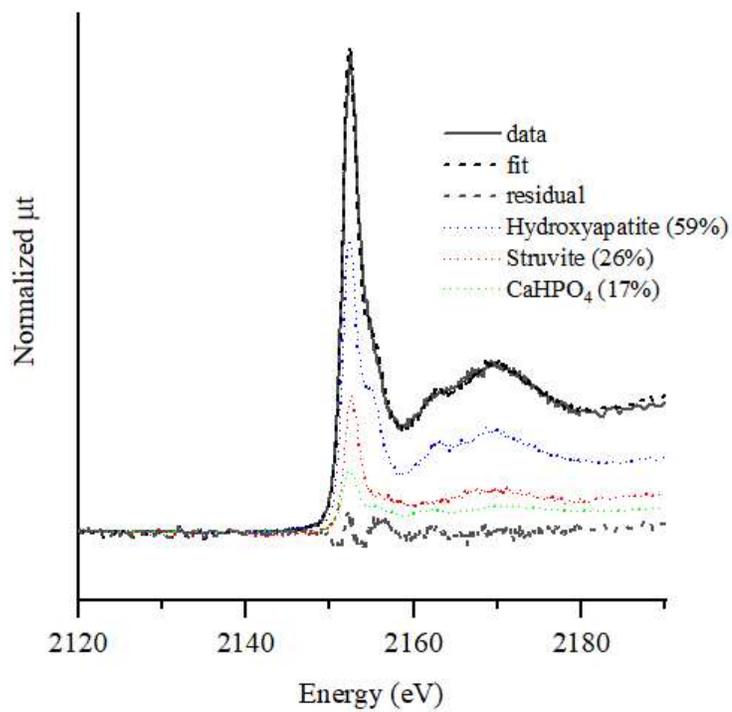
	Head Yield of Cabbage	P uptake by Cabbage Heads
	Mg·ha <sup>-1</sup> , fresh weight	kg·ha <sup>-1</sup>
NPK	57 ± 20	18 ± 6
NPK + compost	55 ± 20	18 ± 6
PK + compost	2 ± 3	1.0 ± 2



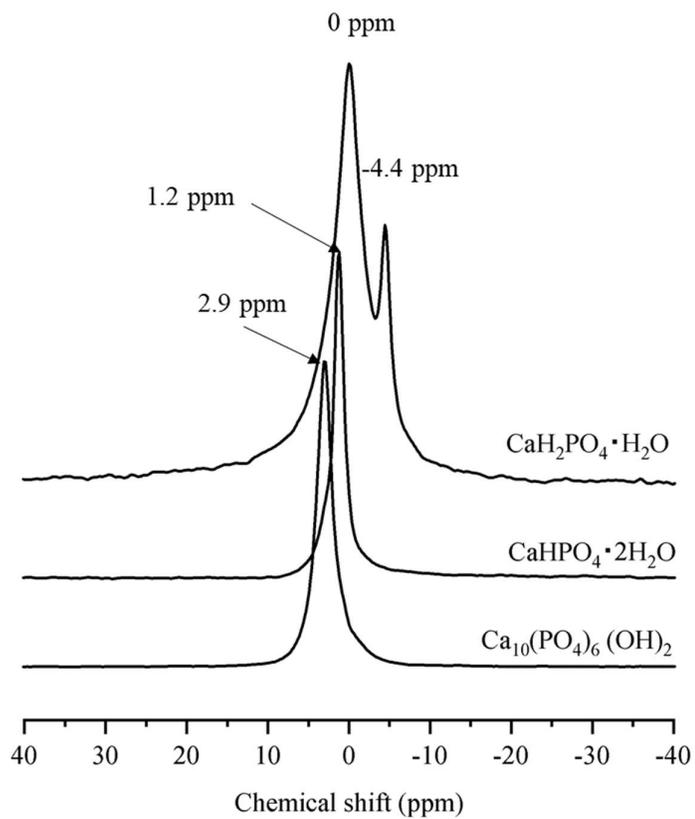
**Figure S1.** Overlaid view of P K-edge XANES spectra of soils amended with mineral fertilizer (NPK), mineral fertilizer and cattle manure compost (NPK + compost), mineral fertilizer without nitrogen fertilizer plus cattle manure compost (PK + compost).



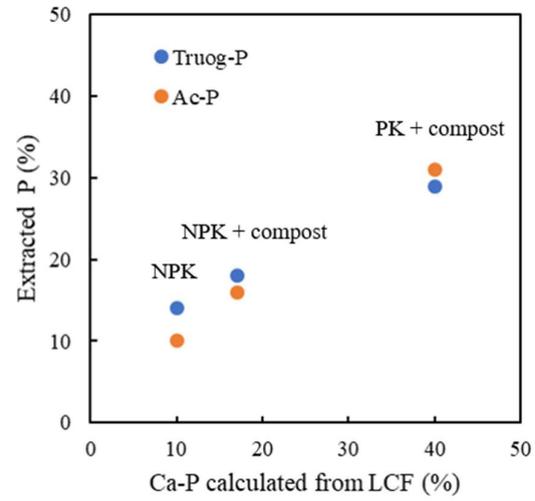
**Figure S2.** Normalized P K-edge XANES spectra of standard materials used for linear combination fitting of bulk XANES spectra. Al-P: phosphate-sorbed gibbsite, Fe-P: phosphate-sorbed ferrihydrite, HAP: hydroxyapatite.



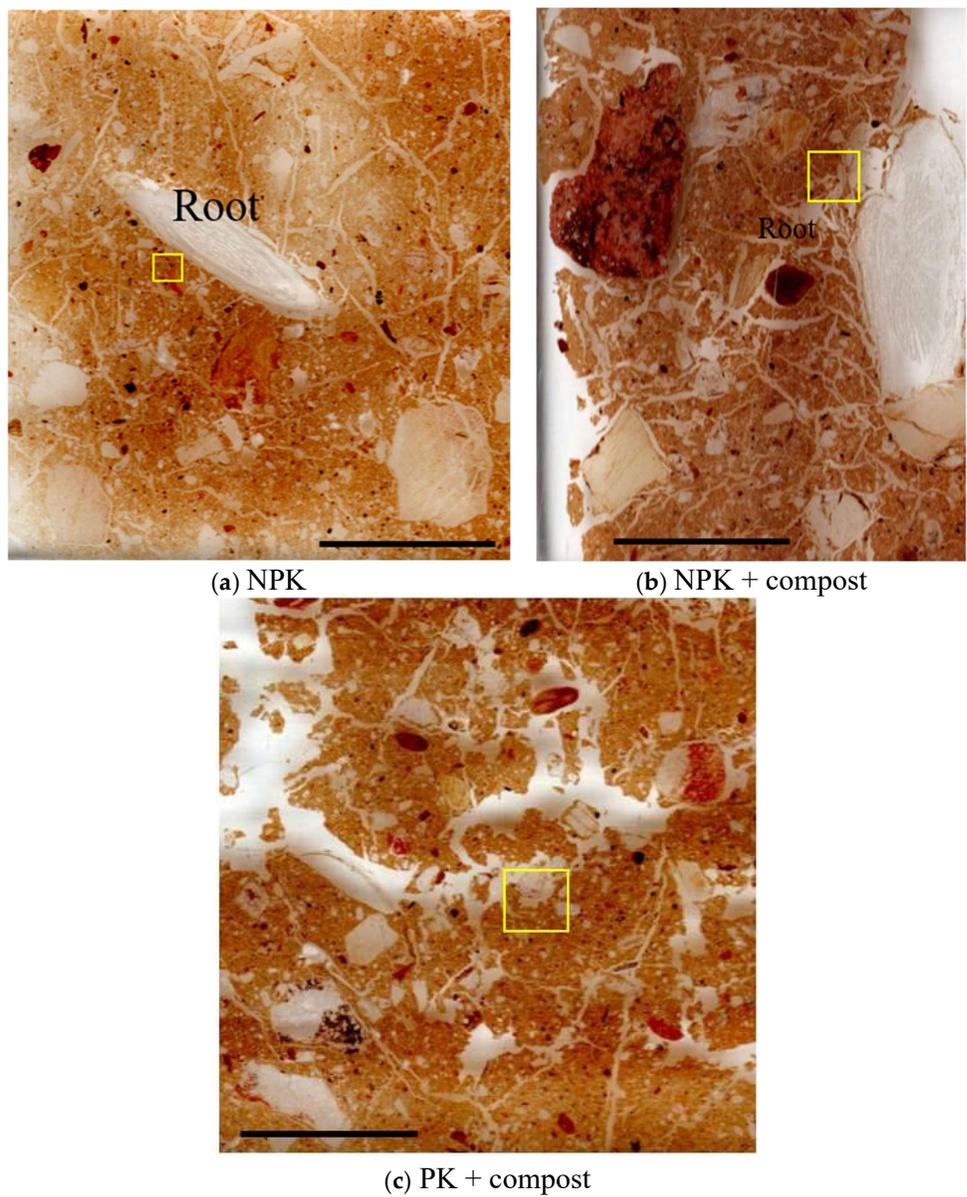
**Figure S3.** Normalized P K-edge XANES spectra of cattle manure compost. Numbers in the parentheses indicate percentage of P species calculated by linear combination fitting. R-factor was 0.003.



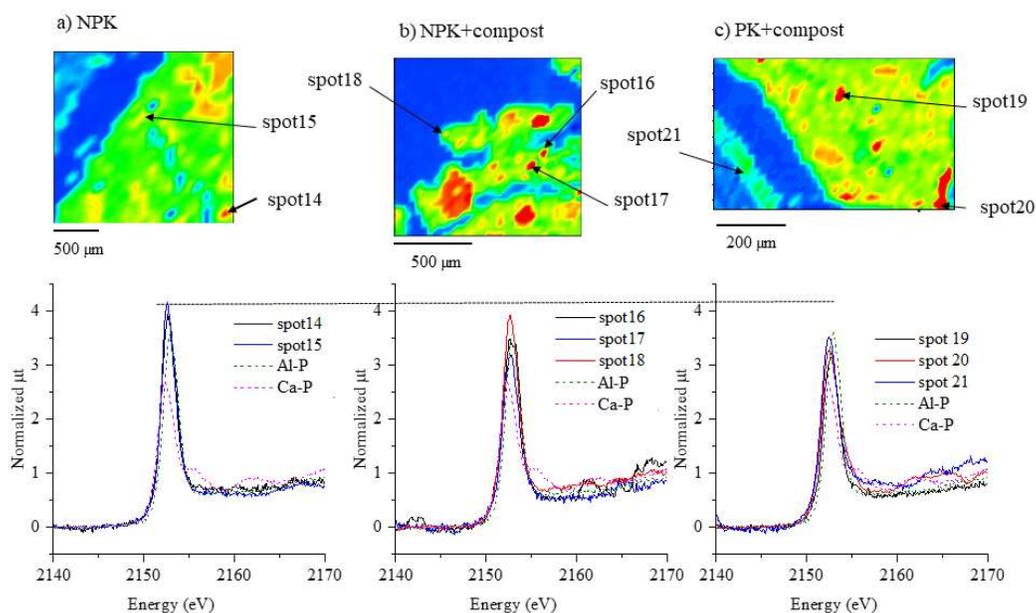
**Figure S4.** Solid-state  $^{31}\text{P}$ -NMR spectra of  $\text{CaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , and hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ).



**Figure S5.** Relationships between percentage of Ca-P determined by linear combination fitting (LCF) of XANES spectra versus that of P extracted by Truog method (Truog-P) and 0.44 mol·L<sup>-1</sup> acetic acid solution (Ac-P).



**Figure S6.** Scanned images for thin sections of soils amended with mineral fertilizer (NPK) (a), mineral fertilizer plus cattle manure compost (NPK + compost) (b), mineral fertilizer without nitrogen fertilizer plus cattle manure compost (PK + compost) (c) at the depth of 0–3 cm. Areas in yellow square roughly indicate the area analyzed by EPMA and SXRF in Figures 4 and 5. Scale bars indicate 5 mm.



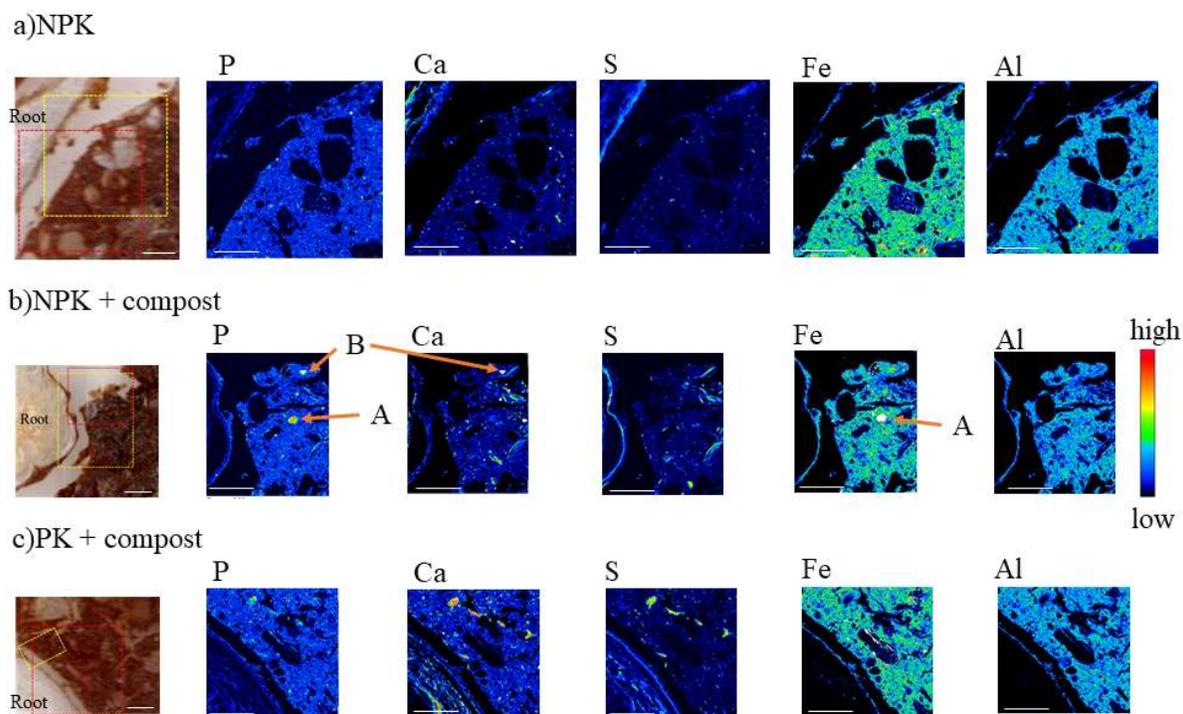
**Figure S7.**  $\mu$ -XRF maps of P (top panels) and normalized P K-edge  $\mu$ -XANES spectra of the selected spots and reference spectra (bottom panels) in soil thin sections from NPK (a), NPK + compost (b) and PK + compost (c) at the depth of 3–6 cm. NPK: mineral fertilizer, NPK + compost: mineral fertilizer with cattle manure compost, PK + compost: mineral fertilizer without nitrogen fertilizer and cattle manure compost. Al-P and Ca-P is spectra of standard materials.

Synchrotron X-ray fluorescence and  $\mu$ -XANES analyses at BL37SU, SPring-8

An incident X-ray beam of 2600 eV was focused to 10- $\mu$ m in diameter on the sample point using KB mirrors. The fluorescent X-rays of P K $\alpha$  was detected using a single-element silicon drift detector (SDD - Amptek SDD, Tsuji). The scan step size and the spectral acquisition time for each spot were 10  $\mu$ m and 2 s, respectively. The fluorescence yield was normalized to the incident photon intensity. Data processing for reproduction of elemental maps were performed using Origin Pro 2020 software (Lightstone, Tokyo). Phosphorus K-edge  $\mu$ XANES analyses of phosphorus hot spots that was selected based on the elemental distribution results from SXRF were obtained by a partial fluorescence yield method with an SDD (Tamenori et al., 2014) using a 10- $\mu$ m X-ray beam and scanning from 2120 to 2200 eV.

## Reference

Tamenori, Y.; Yoshimura, T.; Luan, N. T.; Hasegawa, H.; Suzuki, A.; Kawahata, H.; Iwasaki, N., Identification of the chemical form of sulfur compounds in the Japanese pink coral (*Corallium elatius*) skeleton using mu-XRF/XAS speciation mapping. *J. Struct. Biol.* **2014**, *186*, 214–23.



**Figure S8.** EPMA maps of P, Ca, S, Fe and Al in soil thin sections from NPK (a), NPK + compost (b) and PK + compost (c) at the depth of 3–6 cm. NPK: mineral fertilizer, NPK + compost: mineral fertilizer with cattle manure compost, PK + compost: mineral fertilizer without nitrogen fertilizer plus cattle manure. Scale bars indicate 500 μm. Left panels are scanned images of thin sections and areas in the red and yellow dotted line are those of EPMA and SXRF. The SXRF maps are shown in Figure S7.