Original Paper

Calcium-enriched Biochar: Pyrolysis of Digested Sludge, Phosphorus Recovery, and Fertilizer Properties

Naokatsu KANNARI^{*1†}, Takumi UESUGI^{*1}, Keiichi KUBOTA^{*1}, Daichi MASUDA^{*2},
Kazuyoshi SATO^{*1}, Takayuki TAKARADA^{*1}, and Tomohide WATANABE^{*1}

(Received April 1, 2020)

In this study, we prepared calcium (Ca)-enriched biochar from digested sludge derived from food waste at pyrolysis temperatures in the range of 600 to 900 °C. We evaluated the properties of phosphorus (P) recovery of the biochar and the fertilizer properties of the biochar after the P recovery (P-loaded biochar). The results showed that the amount of P recovery increased with increasing pyrolysis temperature, while the P recovery capacity of biochar was consistently high at all the investigated temperatures. The fertilizer properties of P-loaded Ca-enriched biochar prepared at 600 °C, evaluated by the komatsuna cultivation test were comparable to the chemical fertilizer $\text{Ca}(\text{H}_2\text{PO}_4)_2$. The results suggest that the Ca-enriched biochar could serve as a P recovery material and an environmentally friendly fertilizer.

本研究では、食品廃棄物由来の消化汚泥を異なる温度で熱分解することでカルシウム (Ca) リッチバイオチャーを調製し、そのリン回収特性および肥料特性を評価した。バイオチャーのリン (P) 回収量は熱分解温度の上昇とともに増加した。P 回収後の 600°C 処理バイオチャーの肥料特性を小松菜栽培試験により評価した。その結果、P 回収後のバイオチャーは、化学肥料である $\text{Ca}(\text{H}_2\text{PO}_4)_2$ と同等以上の肥料効果を示すことがわかった。これらの結果より、Ca リッチバイオチャーは、P 回収に対して有用であり、環境負荷の小さい肥料として利用できることを明らかにした。

Key Words

Biochar, Digested sludge, Phosphorus recovery, Calcium, Fertilizer

1. Introduction

One aim of the futuristic sustainable society is the development of methods for effective use of biomass as a carbon-neutral resource. There is an increasing use of biomass for the production of pyrolysis-based biochar, which is identified as a functional material for various applications. Activated carbon is a typical example of functional biochar with a high surface area achieved by the presence of micro- or mesopores in the carbon matrix. Activated carbon is prepared by the pyrolysis of biomass, followed by activation. It is used as a functional material such as adsorbent, in

electrodes, as catalyst support, and similar^{1) 2)}.

Besides the utilization of the biochar pores, biomass ash is another component essential for the biochar to be used as a functional material^{3) 4)}. The type and composition of ash depends on the type of biomass⁵⁾. Its applications can be as a catalyst or as an adsorbent. For example, one study observed that Ni-loaded char derived from chicken droppings showed high catalytic activity for the decomposition of biomass tar at 450 °C⁶⁾. The authors attributed the high activity of the catalysts to the hydroxyapatite phase in the ash of the chicken droppings. As a different example, phosphorus (P) recovery using biochar has been applied for wastewater and agricultural runoff. The recovery function of biochar is related to its suitability as a fertilizer and the biochar after the P recovery was also used as a fertilizer in cultivation. Yao, Y. *et al.* reported that magnesium (Mg)-enriched biochar prepared from tomato leaves was effective for P recovery

^{*1} Division of Environmental Engineering Science, Graduate School of Science and Technology, Gunma University 1-5-1, Tenjin-cho, Kiryu-shi, Gunma 376-8515, Japan

^{*2} Department of Environmental Engineering Science, Undergraduate School of Science and Technology, Gunma University 1-5-1, Tenjin-cho, Kiryu-shi, Gunma 376-8515, Japan

† Corresponding author: nkannari@gunma-u.ac.jp

and that the biochar after the P recovery showed good fertilizer properties for germination and growth of grass^{7,8)}. Similarly, calcium in biochar is also effective for P recovery. For example, Dai, L. *et al.* prepared the calcium (Ca)-rich biochar by the pyrolysis of a crab shell. The biochar showed better P recovery than the common Ca reagents such as CaCO_3 and Ca(OH)_2 ⁹⁾. Here, the biochar properties and morphologies such as Ca content, Ca structure, pore structures would depend on the pyrolysis temperature in biochar preparation, which also would contribute to the properties of the P recovery. However, the relation among the pyrolysis temperature, biochar properties and the properties of the P recovery has not yet been studied. Furthermore, the fertilizer properties of the Ca-enriched biochar after the P recovery also have not been studied.

This study aims to bridge the knowledge gaps related to the mechanisms governing P recovery in Ca-enriched biochar, verify the dependence of these mechanisms on pyrolysis temperature, and confirm if the high P recovery capacity renders Ca-rich biochar a good fertilizer. In this study, we focus on one of the Ca-rich waste biomass, the digested sludge derived from food waste to prepare Ca-enriched biochar. The biochar was prepared at different pyrolysis temperatures ranging from 600 to 900 °C to investigate the influence of the temperature of the sludge on the Ca content in biochar, the P recovery amount, and the morphology of the biochar after the P recovery. The properties of the biochar after the P recovery as fertilizer has also been evaluated by comparing the growth of komatsuna (Japanese mustard spinach) in soil enriched with biochar and with chemical fertilizer.

2. Materials and Methods

2.1 Samples

Ca-rich digested sludge (DS) supplied by a waste treatment facility in Japan was used to prepare biochar. This sludge was a residue of methane fermentation derived from food waste. Before the preparation of biochar, the digested sludge was dried at 170 °C for 24 h and pulverized to particles smaller than 1.0 mm. **Table 1** shows the results of proximate and elemental analyses of the digested sludge. **Table 2** shows the ash composition in DS analyzed by energy dispersive X-ray fluorescence (XRF) spectrometry (Shimadzu, EDX-700). XRF analysis was performed on the DS ash prepared by burning DS at 500 °C for 12 h.

Table 1 Proximate and elemental analyses of DS

Proximate analysis (wt%, d.b.)			Elemental analysis (wt%, d.a.f.)			
V.M.	Ash	F.C. (diff.)	C	H	N	O (diff.)
63.9	26.0	10.1	46.7	4.5	4.5	44.3

Table 2 Composition of the DS ash measured by XRF

Ash composition (wt%)						
Ca	P	Si	Fe	S	K	other
88.9	4.2	2.6	1.9	1.2	1.0	0.1

2.2 Preparation of biochar

Biochar was prepared by the pyrolysis of DS at different pyrolysis temperatures. DS was pyrolyzed at 600, 700, 800, and 900 °C for 1 h at a heating rate of 10 °C min⁻¹ in the N₂ stream. The obtained biochar samples were denoted as DS600, DS700, DS800, and DS900.

The ash and the residual carbon matrix of the corresponding biochar were extracted by burning and acid washing of the biochar, respectively. Biochar ash was prepared by heat treatment of the biochar at 500 °C in air, in order to burn out the residual carbon matrix. In contrast, the residual carbon matrix was prepared by the acid wash of the biochar using 1 M HNO₃ for 1 h to remove the ash component.

2.3 Phosphorus recovery

One gram of biochar was added to 100 mL of P solution (P concentration: 5000 ppm) prepared from KH₂PO₄. The solution containing biochar was stirred for 24 h. The biochar and the residual solution were separated by vacuum filtration. In order to determine the P recovery amount on the biochar, the P concentration in the residual solution was measured by the vanadomolybdate method based on the Testing Method for Fertilizers established by FAMIC (Food and Agricultural Materials Inspection Center, Japan). The biochar after the P recovery (P-loaded biochar) was named P-DS600, P-DS700, P-DS800, and P-DS900, respectively.

2.4 Characterization of DS and biochar

Pyrolysis behavior of DS was evaluated by thermogravimetry (TG) analysis (TGA). The weight loss during the pyrolysis of DS from room temperature to 1000 °C in the N₂ stream was recorded using the TG instrument (ADVANCE RIKO, Inc., TGD-9600).

Proximate analysis of DS and the prepared biochar was conducted using the TG instrument (ADVANCE RIKO, Inc., TGD-9600). The samples were heated in the N₂ stream to 900 °C. After the sample weight became constant, the gas was switched to air to burn out the carbon matrix. During this heating process, the weight change was recorded in order to calculate the contents of volatile matter (VM), ash, and fixed carbon (FC).

The quantities of Ca in the DS and in the prepared biochar were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). DS sample of

1.0 g or the biochar sample of 1.0 g was added to 80 mL of 1.3 M HNO_3 . The solution with the biochar was stirred for 1 h at room temperature to extract Ca in biochar into the solution. The biochar and the solution were separated by vacuum filtration. This extraction procedure was repeated three times in order to dissolve Ca completely from the biochar. The solutions were measured by ICP-AES (Hitachi High-Technologies Corp., SPECTROBLUE FMX26) to determine the Ca amount in the biochar.

The BET (Brunauer-Emmett-Teller) surface area of the prepared samples was evaluated using nitrogen adsorption measurement (Microtrack BEL Corp. BELSORP Max). Prior to the N_2 adsorption, 200 mg of the sample was heated at 200 °C for 2 h under the N_2 stream to remove any adsorbed water. After the heat treatment, the N_2 adsorption isotherm was recorded at the liquid nitrogen temperature. The BET surface area was calculated from the isotherm in $p/p_0 = 0.05$ to 0.5 using the software attached to the equipment.

X-ray diffraction (XRD) measurements were conducted to determine the crystalline structure of the biochar before and after the P recovery using the SmartLab (Rigaku Corp.) operating at 40 kV and 30 mA. The scanning range was from 20° to 80°.

2.5 Biochar as fertilizer

Phosphorus fertilizer property of the P-loaded biochar was evaluated by cultivating komatsuna (Japanese mustard spinach) for four weeks using a method modified from a cultivation test prescribed by FAMIC (Food and Agricultural Materials Inspection Center, Japan). Twenty komatsuna seeds, 500 mL of alluvial soil, and fertilizers of N, P, and K were placed in a pot ($\phi 113 \times 65$ mm). The amounts of fertilizers in each condition were shown in Table 3. In this experiment, three types of testing pots using different phosphorus fertilizer (P-DS600, Control, and No fertilizing) were used, with duplicates. The P-DS600 and Control groups used P-DS600 and calcium superphosphate as the source of P, respectively. These groups used $(\text{NH}_4)_2\text{SO}_4$ and KCl as sources of N and K. The “No fertilizing” group had no fertilizer added to the alluvial soil, which confirms the effects of nutrient salts in the soil on the growth of komatsuna. All pots were cultivated outside, and the

Table 3 P, N, and K amounts in each group in the komatsuna growing test

	P-DS600	Control	No fertilizing
P (mg- P_2O_5 pot ⁻¹)	100	100	0
N (mg-N pot ⁻¹)	100	100	0
K (mg- K_2O pot ⁻¹)	100	100	0

average temperature was 17 ± 5.3 °C during the test. Watering the test pots was carried out once or twice a day, with the amount of water adjusted to approximately 60% of the maximum water holding capacity of the alluvial soil. The rate of seed germination in each group measured the growth of komatsuna two weeks after the start of the cultivation test. The leaf length was measured after four weeks of cultivation.

3. Results and discussion

3.1 Pyrolysis behavior of DS

The increase in pyrolysis temperature decreased the content of volatile matter (VM) and increased the ash content, especially the Ca amount in the obtained biochar. Table 4 shows the result of approximate analysis and Ca content measured by ICP-AES. VM content of DS decreased from 63.9 to 11.2% after pyrolysis at 900 °C, while ash content increased from 26.0 to 75.9%. The Ca content increased from 106 to 392 mg g⁻¹ after pyrolysis at 900 °C. The results indicate that the pyrolysis at a higher temperature enriched Ca content in the obtained biochar.

This decrease in VM content and the increase in the ash and Ca contents by increasing the pyrolysis temperature can be attributed to the elimination of water and organic matter from DS. The result of TGA, as shown in Fig. 1, indicated that there were weight losses from 40 to 200 °C, from 200 to 720 °C and from 720 to 840 °C during

Table 4 Result of approximate analysis and Ca content

Sample	Approximate analysis (wt%)			Ca content (mg g ⁻¹)
	VM	Ash	FC (diff.)	
DS	63.9	26.0	10.1	106
DS600	32.9	51.6	15.5	271
DS700	27.0	61.9	11.1	345
DS800	11.0	73.7	15.3	410
DS900	11.2	75.9	12.9	392

Fig. 1 Thermogravimetric curves of digested sludge

DS pyrolysis. The first weight loss of about 13% corresponds to the desorption of physically adsorbed water molecules in DS. The second broad weight loss from 200 to 720 °C can be attributed to the volatilization of organic matter and its decomposed moieties in DS. The weight loss from 720 to 840 °C originated from the decomposition of CaCO_3 to CaO and CO_2 ^{9) 10)} in the ash of DS. The released CO_2 may have acted as a reagent for developing pores in the carbon matrix of the biochar, which is described in the next section.

3.2 BET surface area

The BET surface area of the biochar increased with the pyrolysis temperature. This effect was caused by the increase in the surface area of the residual carbon matrix. Fig. 2 (a) shows the BET surface area of the biochars prepared at different pyrolysis temperatures. The increase in the pyrolysis temperature increased the BET surface area of the biochars from 20 to 100 $\text{m}^2 \text{g}^{-1}$. The biochars were mainly composed of the ash and the residual carbon matrix. Fig. 2 (b) and (c) show the BET surface areas of the ash and the carbon matrix prepared at different temperatures, respectively (The BET surface area of the

carbon residue derived from the biochar prepared at 600 °C was not measured). The BET surface area of the ash decreased with increasing the pyrolysis temperature. In contrast, the BET surface area of the carbon matrix increased with the increasing the pyrolysis temperature. This increase in surface area of the carbon matrix was caused by the activation of the matrix by CO_2 released from the decomposition of CaCO_3 during heating from 720 to 840 °C, observed in the TG curves shown in Fig. 1. Similar CO_2 activation has been observed in the heat treatment of chicken droppings¹⁰⁾.

3.3 Phosphorus recovery

Fig. 3 shows the P recovery amounts in the biochar prepared at different temperatures. The P recovery amount of the biochar increased with increasing the pyrolysis temperature; the P recovery amounts of DS600, 700, 800, and 900 were 151, 189, 222, and 235 mg g^{-1} .

The types of crystal structures in the biochar before and after the P recovery depended on the pyrolysis temperature. Fig. 4 (a) shows the XRD patterns of the biochar before and after the P recovery. Before the P

Fig. 2 BET surface area of (a) biochar, (b) ash and (c) carbon residue derived from corresponding biochar

recovery, DS600 and DS700 showed the main peaks assigned to CaCO_3 . In contrast, DS800 and 900 showed the main peaks assigned to CaO . The difference of Ca form in the biochar was caused by the decomposition of CaCO_3 to CaO in the temperature interval from 720 to 840 °C, observed by TGA and shown in Fig. 1.

After P recovery, P and Ca combined in the biochars, but the types of Ca and P forms depended on the pyrolysis

Fig. 3 Phosphorus recovery amount of biochar

temperature. The XRD patterns of the biochar after the P recovery in Fig. 4 (b) showed that P was sorbed as CaHPO_4 in P-DS600 and P-DS700. In the case of P-DS800 and P-DS900, P was sorbed as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (hydroxyapatite, HAp) in addition to CaHPO_4 . The difference in the P forms was attributed to the pyrolysis temperature dependence of the pH of the solution with biochar after the P recovery. The pH of the solution with P-DS800 and P-DS900 (7.2 and 7.2) was higher than in P-DS600 and P-DS700 (6.5 and 6.7). The difference in the pH is caused by the alkaline property of CaO observed in DS800 and DS 900 before the P recovery, which results in the different structures of calcium phosphate¹⁴⁾. Fujino *et al.* have reported that the pH of the solution in calcium phosphate synthesis influenced its crystalline form; the pH of the solution near 7 resulted in the formation of highly crystalline HAp while the pH under 6 resulted in the formation of CaHPO_4 and HAp¹⁵⁾. Therefore, different calcium phosphate forms, such as CaHPO_4 and HAp, depended on the calcium form before P recovery. From these results, the P form in the Ca-based biochar after the P recovery could be controlled by adjusting the pyrolysis temperature.

Fig. 5 shows the relation between the Ca amount of the prepared biochar and the P recovery amount. The calculated amounts of the P recovery were also plotted in the figure, which was estimated by using the Ca amount and the corresponding crystal structures (CaHPO_4 and HAp) observed in the XRD profiles (Fig. 4). The P recovery

Fig. 4 X-ray diffraction profiles of the biochar (a) before and (b) after P recovery

Fig. 5 Relation between Ca amount in biochar and P recovery amount

amount increased with increasing the Ca amount, however the P recovery amount did not correspond to the calculated lines. In DS600 and DS700, CaHPO_4 was observed in the XRD profiles (Fig. 4 (b)), while the P recovery amount was below the calculated line of CaHPO_4 (Fig. 5). The difference between the measured and calculated lines might be caused by the existence of Ca components with an amorphous phase which could not be detected by XRD measurement. In contrast, the P recovery amounts of DS800 and DS900 were above the calculated line of HAp, which was observed in the XRD profiles of P-DS800 and P-DS900. The possible reasons for the higher P recovery amounts than the calculated line are described as follows. One is the contribution of the carbon matrix in P-DS800 and P-DS900 for enhancing the P recovery because the BET surface areas of the carbon matrix were highly developed as shown in Fig. 2 (c). The other is the influence of the CaHPO_4 on the P recovery amount because there are not only HAp structure but also CaHPO_4 structure in the XRD profiles

after the P recovery (Fig. 4 (b)).

The P recovery amount of the biochar prepared in this study was much higher than that of the other biochars previously reported^{11) ~ 13)}. For example, Antunes *et al.* prepared the calcium-rich biochars by the microwave pyrolysis of biosolid in the presence of different amounts of $\text{Ca}(\text{OH})_2$ and evaluated their characteristics of the P recovery. The study revealed that the maximum removal capacity of P by the biochar prepared with 20 wt% of $\text{Ca}(\text{OH})_2$ was 147 mg-P g⁻¹. In the present study, the highest P recovery amount in the prepared biochar was obtained in DS900 (235 mg g⁻¹). This remarkable recovery amount was caused by the concentration of Ca during the pyrolysis to form Ca-enriched biochar. From these results, the Ca-enriched biochar could be prepared by simple pyrolysis of Ca-rich DS, which would effectively increase the P recovery.

3.4 Fertilizer properties

From the cultivating test of komatsuna, the fertilizer properties of P-DS600 were comparable to those of the chemical fertilizer. P-DS600 was selected from the prepared biochars for the cultivating test because the main component in P-DS600 was CaHPO_4 (Fig. 4), which was easy to dissolve into solutions compared to HAp observed in the biochar prepared at higher temperatures¹⁶⁾. Table 5 shows the result of the germination rate and leaf length. No differences were observed between groups in the germination rate after two weeks, which suggested that P-DS600 did not influence the germination of the komatsuna. The leaf length in the fertilized groups (P-DS600 and Control) was larger than in the No fertilizing group, and the P-DS600 group had significantly larger leaf length than the Control section ($p < 0.05$). P-DS600 as a phosphorus fertilizer inhibited neither the germination nor

Table 5 Germination rate and leaf length in the komatsuna cultivation test

	P-DS600	Control	No fertilizing
Germination rate (%)	100.0 ± 0.0	97.5 ± 3.5	97.5 ± 3.5
Leaf length (cm)	10.3 ± 0.6	9.6 ± 0.6	4.5 ± 0.6

Fig. 6 Photo of komatsuna after four weeks cultivation in (a) P-DS600, (b) Control, (c) No fertilizing

the growth of komatsuna. Additionally, it is possible that the trace elements in biochar had a positive influence on plant growth. Fig. 6 shows the photos of komatsuna in each section after four weeks. The greenish-yellow leaf color was observed in No fertilizing group due to the shortage of nutrients. This phenomenon was not observed in the P-DS600 and Control groups, and there was no difference between these. These results suggested that the P-loaded biochar has a phosphorus fertilizer performance equivalent to or higher than the chemical fertilizer.

4. Conclusions

We elucidated the P recovery properties of Ca-enriched biochar and their dependence on the pyrolysis temperature during biochar preparation. Ca content in the Ca-enriched biochar increased with the pyrolysis temperature, which was correlated to the P recovery amount. We observed different crystal structures of P-loaded biochars, which we attributed to the Ca form before the P recovery. The fertilizing properties of P-DS600 were comparable to those of the chemical fertilizer. Thus, Ca-enriched biochar is effective for P recovery and that P-loaded biochar could be used as an environment-friendly fertilizer. To clarify the effects of the P recovery amount and form on fertilizer properties, the fertilizer properties of P-loaded Ca-enriched biochar prepared at different pyrolysis temperatures will be investigated in the future. Furthermore, to utilize the biochar in practical applications, the P recovery and fertilizing properties using real wastewater including contaminants such as inorganic ions and organic matters should be also investigated.

Acknowledgement

This study was financially supported by the Strategic International Collaborative Research Program (SICORP) of the Japan Science and Technology Agency (JST).

The ICP-AES measurement was performed at the Center for Instrumental Analysis of Gunma University.

References

- 1) Tan, X.-F.; Liu, S.-B.; Liu, Y.-G.; Gu, Y.-L.; Zeng, G.-M.; Hu, X.-J.; Wang, X.; Liu, S.-H.; Jiang, L.-H., *Bioresour. Technol.*, **227**, 359-372 (2017), <https://doi.org/10.1016/j.biortech.2016.12.083>
- 2) Xiong, X.; Yu, I. K. M.; Cao, L.; Tsang, D. C. W.; Zhang, S.; Ok, Y. S., *Bioresour. Technol.*, **246**, 254-270 (2017), <https://doi.org/10.1016/j.biortech.2017.06.163>
- 3) Buss, W.; Jansson, S.; Mašek, O., *J. Clean. Prod.*, **208**, 960-967 (2019), <https://doi.org/10.1016/j.jclepro.2018.10.189>
- 4) Chen, X.-W.; Timpe, O.; Hamid, S. B. A.; Schlögl, R.; Su, D. S., *Carbon*, **47**, 340-343 (2009), <https://doi.org/10.1016/j.carbon.2008.11.001>
- 5) Liu, W.-J.; Jiang, H.; Yu, H.-Q., *Chem. Rev.*, **115**, 12251-12285 (2015), <https://doi.org/10.1021/acs.chemrev.5b00195>
- 6) Kannari, N.; Oyama, Y.; Takarada, T., *Int. J. Hydrogen Energy*, **42**, 9611-9618 (2017), <https://doi.org/10.1016/j.ijhydene.2017.02.168>
- 7) Yao, Y.; Gao, B.; Chen, J.; Yang, L., *Environ. Sci. Technol.*, **47**, 8700-8708 (2013), <https://doi.org/10.1021/es4012977>
- 8) Yao, Y.; Gao, B.; Chen, J.; Zhang, M.; Inyang, M.; Li, Y.; Alva, A.; Yang, L., *Bioresour. Technol.*, **138**, 8-13 (2013), <https://doi.org/10.1016/j.biortech.2013.03.057>
- 9) Dai, L. C.; Tan, F. R.; Li, H.; Zhu, N. M.; He, M. X.; Zhu, Q. L.; Hu, G. Q.; Wang, L.; Zhao, J., *J. Environ. Manage.*, **198**, 70-74 (2017), <https://doi.org/10.1016/j.jenvman.2017.04.057>
- 10) Sato, K.; Suemune, S.; Nitta, K.; Nakayama, C.; Inokuma, S.; Tonooka, S.; Mamada, Y.; Nakamura, E.; Kaneko, K.; Takarada, T., *J. Anal. Appl. Pyrolysis*, **101**, 86-89 (2013), <https://doi.org/10.1016/j.jaap.2013.02.008>
- 11) Yin Q. Q.; Zhang B. D.; Wang R. K.; Zhao Z. H., *Environ. Sci. Pollut. Res.*, **24**, 26297-26309 (2017), <https://doi.org/10.1007/S11356-017-0338-y>
- 12) Park J. L.; Wang J. J.; Xiao R.; Zhou B. Y.; Delaune R. D.; Seo D. C., *J. Colloid Interface Sci.*, **525**, 143-151(2018)
- 13) Antunes E.; Jacob M. V.; Brodie G.; Schneider P. A., *J. Environ. Chem. Eng.*, 6395-403 (2018), <https://doi.org/10.1016/j.jece.2017.12.011>
- 14) Pham Minh, D.; Lyczko, N.; Sebei, H.; Nzihou, A.; Sharrock, P., *Mater. Sci. Eng. B*, **177**, 1080-1089 (2012), <https://doi.org/10.1016/j.mseb.2012.05.007>
- 15) Fujino, O.; Tamura, H., *Phosphorus Research Bulletin*, **18**, 55-64 (2005), https://doi.org/10.3363/prb1992.18.0_55
- 16) Takahashi, S., *J. Plant Nutr. Soil Sci.*, **176**, 494-496 (2013), <https://doi.org/10.1002/jpln.201200169>