





Kinetics of Phosphorus Release from Vivianite, Hydroxyapatite, and Bone Char Influenced by Organic and Inorganic Compounds

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Abstract: The availability of P is often insufficient and limited by accumulation in soils. This led to the necessity of solutions for the recovery as well as recycling of secondary P resources. Batch experiments were conducted with CaCl₂ and citric acid to characterize P release kinetics from vivianite, hydroxyapatite, and bone char. While the P release during the CaCl₂ treatment was so low that only vivianite and hydroxyapatite showed a slightly higher release with increasing CaCl₂ concentration, the increase of dissolved P was more pronounced for citric acid. The application of citric acid resulted in a 32,190-fold higher P release for bone char. Fourier-transform infrared spectroscopic data suggested higher instability of hydroxyapatite than for bone char. The kinetic data showed that bone char, especially at a lower particle size, had a higher long-term P release than hydroxyapatite or vivianite. The suitability of hydroxyapatite and bone char as a poorly soluble, but sustainable P source is better than that of vivianite. However, the efficiency as a P fertilizer is also dependent on present soil P mobilization processes. The results underline the importance of the accessibility of fertilized or naturally bound P for plant roots to benefit from the excretion of organic acids.

Keywords: bone char; hydroxyapatite; vivianite; phosphorus release; citric acid

1. Introduction

Phosphorus (P) is an essential nutrient for physiological processes during plant growth and fertilization in agriculture is necessary to maintain crop productivity. However, the bioavailability of P is often insufficient and limited by rapid precipitation and adsorption processes in soils [1]. Depending on the soil properties, the P use efficiency is as low as about 20 to 10% [2,3]. As a consequence, many soils worldwide have accumulated substantial amounts of fertilized P because of excessive applications over a longer period of time [4–6]. These soil P reserves, if they cannot be used efficiently, can cause eutrophication to marine and aquatic environments if lost [7]. Therefore, it has become necessary to find sustainable solutions for an efficient use of the existing soil P reserves as well as secondary P sources (e.g., bone char or sewage sludge to substitute conventional fertilizers).

Apatite is a primary source of P in terrestrial ecosystems and occurs as a lithogenic mineral in soils worldwide. The release of P from the lithosphere into the soil is affected by many physical, chemical, and biological processes [8], where weathering and dissolution of apatite will release secondary precipitated P, differing in stability [9]. The use of solid hydroxyapatites (HA) as direct P source is ineffective, because the large size of the particles, in addition to a high soil pH, limits P mobility and hence, bioavailability to plants. For this reason, modified synthetic nano-HA should promote the

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efficiency of P fertilizer [2,10]. The insolubility in water should increase the bioavailability of nano-HA due to limited chemical reactions in soil such as precipitation or adsorption on soil colloids [11]. Vivianite (VI) is one of the most common stable Fe phosphates in anthropogenically influenced soils and sediments. Amongst others, it occurs in the sediments of lakes, rivers canals, or water-saturated soils. In addition, it has been found in sewage sludge as a weathering product in hydrothermal deposits [12]. However, for many P recycling products, the value and fertilizer efficiency are unknown and especially for sewage sludge, heavy metals and contaminants can be discharged back into the environment [13]. Bone char (BC) as an alternative P fertilizer in agriculture contains no heavy metals or organic contaminants, but is rich in P and Ca [14,15]. P in BC is mainly bound in a structure similar to HA, which is of low solubility [16,17] Therefore, untreated HA and BC are expected to have a low P fertilizer efficiency.

One aspect of this study was to evaluate the availability of P resources. On one hand, the unguided and passive P mobilization by inorganic constituents of the soil solution such as CaCl₂ will take place on a large scale. On the other hand, plants that had developed a range of adaptive strategies to enhance the availability of P in case of demand on a smaller scale. This includes symbiotic root-microbe associations, root-mycorrhiza interactions, and the secretion of root exudates [18]. The exudation of low molecular-weight organic acids [19] such as citric acid (CA), which is often detected at a higher concentration in the rhizosphere, has been described as highly effective in mobilizing inorganic P [20,21]. With regard to an efficient use of present P resources in soils, the aim was to characterize P release kinetics from VI, HA, and BC as well as the detection of rapidly and slowly available P over time. Therefore, the amount of inorganic P that can be released by increasing concentrations of CaCl₂ and CA from different P sources has to be determined, and the suitability of low soluble P sources as sustainable P fertilizer with regard to active and passive P mobilization processes will be evaluated.

2. Materials and Methods

The BC used for the P release experiments was produced by Bonechar Carvão Ativado Do Brasil Ltda. (Maringá, Brazil) in 2015. It has been manufactured by pyrolysis of rendered (de-fatted) bovine bones at more than 800 °C. A particle size analysis of BC was carried out, whereby 100 g of BC was divided into three particle size fractions: <200 μ m, 200–2000 μ m, and >2000 μ m. In order to have enough sample material for the P release experiments, coarser material was then ground and sieved. The BC composition was analyzed by determining C, N, and S using a CNS elemental analyzer as well as P, Ca, K, and Mg by pressure digestion with HNO₃ (65%) and measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES).

The P bearing minerals used were the commercially available Ca-phosphate HA (Ca₅[OH(PO₄)₃]) (Acros Organics, Geel, Belgium) and the Fe–phosphate VI (Fe₃²⁺[PO₄]₂·8H₂O). VI was prepared according to [22], where 250 mL of a 0.035 M H₃PO₄-solution was added to solid FeSO₄. The resulting 0.05 M FeSO₄-solution was adjusted to pH 6 with 5 M KOH. The precipitate formed was centrifuged for 5 min at 2090 G and washed with ultrapure water. The prepared VI was dried at 40 °C and ground into powder using mortar and pestle. P, Ca, and Fe were determined using ICP-AES after pressure digestion or aqua regia digestion for VI. The composition of HA and VI was verified using x-ray diffraction (XRD).

Specific surface areas were determined with an Autosorb-1 (Quantachrome, Odelzhausen, Germany) using a multi-point BET-measurement (Brunauer-Emmett-Teller) and N_2 as adsorptive medium. An outgas test was performed to verify the completed outgas procedure for each mineral.

The pH of BC, HA, and VI was measured in both 0.01 M CaCl_2 and deionized H₂O, respectively, with a solid-solution ratio of 1:5. The pH values of BC, HA, and VI were not adjusted prior to the release experiments in order to prevent an undesired P release.

P release experiments were conducted in triplicate by using a batch setup with an initial pH of 6. For this, 2.5 g of HA, VI, and BC in the three particle size fractions of $<200 \ \mu m \ (BC_{200})$, 200–2000 $\mu m \ (BC_{2000})$, and $>2000 \ \mu m \ (BC_{2000})$, respectively, were weighed into polymethylenebottles. Batch

solubilization experiments were performed with CaCl₂ (Merck Millipore) and CA with the formula $C_6H_8O_7$ (99%, Alfa Aesar), adjusted to pH 6 with KOH. These reaction solutions were used in concentrations 0.01 M, 0.05 M, and 0.1 M, respectively. A 50 mL reaction solution was added to the BC samples and 40 mL was added to the HA and VI samples, respectively. The samples were shaken on a horizontal shaker for 24 h at 200 motions min⁻¹, centrifuged for 15 min at 2090 G, and the supernatant was filtrated by using P-poor Whatman 512 1/2 filters. Following that, 50 mL of fresh reaction solution was added to the samples. Samples for P measurement were taken after 2, 6, 24, 48, and 168 h. Additionally, P, Ca, Fe, Mg, and K were determined using ICP-AES as well as Cl using ion chromatography. In the sample solutions using citric acid, only P, Ca, and Mg were measured. K was not determined due to the high KOH additions at the pH adjustment. The pH of the sample solution was calculated for each mineral and reaction solution. Different kinetic models (Table 1) were fitted to the data.

Table 1. Selected kinetic equations	5.
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Kinetic Model	Linearized Equation	Declaration
Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	Q_t - amount of released P in mg P m ⁻² at time t
Exponential	$\ln Q_t = \ln a + b \ln t$	α/a - initial P release constants in mg P m ⁻² min ⁻¹
Parabolic	$Q_t = Q_0 + k_p t^{\frac{1}{2}}$	β/b - P release rate constants in mg P m ⁻² min ⁻¹ k_p - diffusion rate constant in m s ⁻¹ Q_0 - equals 0 at the beginning of P release

Fourier-transform infrared spectroscopy will be used to estimate the stability of the investigated materials and to draw conclusions about the mechanisms of P release. After the P release experiments, the samples were oven-dried at 40 °C and stored in a desiccator. The FT-IR spectroscopic measurements were performed without further treatment of the samples prior to analyses. Absorbance was measured in the FT-IR DRIFT mode (Tensor 27 HTS-XT, Bruker), with a wavenumber range from 4000 to 400 cm⁻¹. The spectrum of each treatment was created by generating the average of the three replicated samples, where each sample included 40 scans. For analyses, the spectra were baseline corrected with regard to the respective reference spectrum (without P release), truncated in the range 4000 to 550 cm⁻¹, and normalized with respect to the highest absorbance.

3. Results

3.1. Characterization of Bone Char (BC), Hydroxyapatite (HA), and Vivianite (VI)

The particle size analysis of BC revealed that 99% of BC particles were in the size range of >2000 μ m and only 0.1% of the particles were smaller than 200 μ m. The BET specific surface area was lowest for VI with 39.49 m²·g⁻¹, followed by HA with 68.39 m²·g⁻¹ (Table 2). The specific surface area of BC increased slightly with decreasing particle size and amounted to 94.78 m²·g⁻¹ for BC₂₀₀.

The initial P concentration of BC was in a similar range as for HA, but higher than for VI. The total content of P, C, N, S, Ca, Fe, Mg, and K are shown in Table 2.

	Vivianite	Hydroxyapatite	BC ₂₀₀	BC ₂₀₀₋₂₀₀₀	BC ₂₀₀₀		
			$m^2 \cdot g^{-1}$				
BET	39.49	68.39	94.78	94.41	92.12		
			mg·g ^{−1}				
Р	96.59 ± 5.71	159.61 ± 2.33		142.8 ± 1.96			
Ca	-	370.32 ± 4.67		308.8 ± 4.63			
Fe	268.47 ± 15.43	-		-			
С	-	-		114.9 ± 0.31			
Ν	-	-	12.4 ± 0.36				
S	-	-		0.23 ± 0.05			
Mg	-	-		5.4 ± 0.12			
ĸ	-	-		2.1 ± 0.26			

Table 2. Brunauer Emmett Teller (BET) specific surface area and elemental composition* of vivianite, hydroxyapatite, and bone char. Given are the mean and standard deviations (SD).

* n = 4.

3.2. P Release Efficiency

The cumulative P release based on 168 h with CaCl₂ was very low for all used materials. While the total P release for BC was close to the detection limit, minor P concentrations were measured for VI and HA, which increased slightly with increasing CaCl₂ concentration. The use of CA enabled significantly more P to be solved, whereby an increase of dissolved P with increasing CA concentration was also measured (Table 3). At a low CA concentration of 0.01 M, the lowest amount of P was released from BC, where most P was released from the smallest particle fraction. In total, most P was released from HA after 168 hours.

Table 3. Efficiency of P release after 168 h reaction time. Given are the mean* and standard deviations (SD).

		CaCl ₂		Citric Acid			
	0.01 M	0.05 M	0.1 M	0.01 M	0.05 M	0.1 M	
			Released P	$[mg \cdot m^{-2}]$			
Vivianite	0.0005 ± 0.00	0.0006 ± 0.00	0.0012 ± 0.00	0.16 ± 0.01	0.28 ± 0.07	0.48 ± 0.07	
Hydroxyapatite	0.0012 ± 0.00	0.0155 ± 0.00	0.0233 ± 0.00	0.26 ± 0.01	0.56 ± 0.01	0.68 ± 0.02	
BC200	0.0000 ± 0.00	0.0000 ± 0.00	0.0000 ± 0.00	0.05 ± 0.00	0.22 ± 0.00	0.39 ± 0.00	
BC ₂₀₀₋₂₀₀₀	0.0001 ± 0.00	0.0002 ± 0.00	0.0001 ± 0.00	0.04 ± 0.00	0.18 ± 0.01	0.32 ± 0.00	
BC2000	0.0001 ± 0.00	0.0001 ± 0.00	0.0001 ± 0.00	0.04 ± 0.00	0.15 ± 0.01	0.29 ± 0.01	
			Release	d P [%]			
Vivianite	0.02 ± 0.00	0.03 ± 0.00	0.05 ± 0.00	6.50 ± 0.30	11.46 ± 2.88	19.58 ± 2.68	
Hydroxyapatite	0.05 ± 0.00	0.66 ± 0.17	1.00 ± 0.19	11.13 ± 0.27	24.10 ± 0.49	29.34 ± 0.91	
BC ₂₀₀	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	3.24 ± 0.07	14.87 ± 0.09	26.12 ± 0.04	
BC ₂₀₀₋₂₀₀₀	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	2.33 ± 0.02	11.59 ± 0.38	21.18 ± 0.20	
BC2000	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	2.47 ± 0.11	9.95 ± 0.76	18.43 ± 0.89	

* n = 3.

3.3. Kinetics of P Release

The percentage of P release shown in the kinetic curves refers to the amount of mobilized P related to the amount of total P of the minerals (= 100%), given in Table 2. The P kinetic curves showed a fast release from 0 to 24 h, and a slow release from 24 to 168 h, respectively. The time-dependent data of the CaCl₂ treatment showed that for VI between 45 and 52% and for HA between 92 and 99% of the

totally mobilized P was solved during the first 24 h. Even at the highest CaCl₂ concentration of 0.1 M, HA and VI showed only a very low P release after 24 h (Figure 1).



Figure 1. P release kinetics of (**a**) hydroxyapatite and vivianite as well as (**b**) bone char using CaCl₂ at pH 6.

In contrast, BC had an ongoing P release after 24 h despite a very low total amount of release P. This was especially observed for $BC_{200-2000}$. The proportion of mobilized P within the first 24 h ranged between 60% and 82% for BC_{200} , 46% and 60% for $BC_{200-2000}$, and 49% and 56% for BC_{2000} , respectively.

During the CA treatment, P was also predominantly released in the first 24 h, but lasted notably longer than during the CaCl₂ treatment (Figure 2). The time-dependent data of the CA treatment showed that for VI between 41% and 57% and for HA between 77% and 82% of the totally mobilized P was solved during the first 24 h. For the BC samples, the values ranged between 52% and 65% for BC₂₀₀, 67% and 72% for BC_{200–2000}, and 69% and 71% for BC₂₀₀₀, respectively.

The coefficients of determination (\mathbb{R}^2) for the applied kinetic models indicated that the kinetics of P release for all treatments and materials fitted best with the Elovich equation (mean $\mathbb{R}^2 = 0.95$), followed by the Exponential (mean $\mathbb{R}^2 = 0.90$) and the Parabolic function (mean $\mathbb{R}^2 = 0.86$) (Table 4). The kinetic parameters obtained from Elovich and Exponential functions showed a lower initial P release (α , a) and a higher P release over time (β , b) (Table 5) for the CaCl₂ treatment. While α increased and β decreased for VI and HA with increasing CaCl₂ concentration, the converse was calculated for the BC samples. For the CA treatment, the kinetic parameters of the Elovich equation showed a higher initial P release and a lower release over time for the investigated materials. The BC samples certainly had a lower initial release than the P release over time for the 0.01 M CA treatment. The kinetic parameters of the Exponential function also had a higher *a* and a lower *b* for the used materials, except for HA. Altogether, the initial P release increased while the continuous release decreased with increasing CA concentration. For the Elovich equation, the initial P release was higher for CA and the release over time was higher for CaCl₂.



Figure 2. P release kinetics of (**a**) hydroxyapatite and vivianite, as well as (**b**) bone char using citric acid (CA) at pH 6.

Table 4. Co	oefficients of	determination ((\mathbb{R}^2) and stan	dard errors	(S.E.) for the	ne kinetic eq	uations used to
describe th	ne kinetic rele	ease of P with Ca	aCl ₂ and citr	ic acid.			

			Elovich		Expon	ential	Parabolic	
			R ²	S.E.	R ²	S.E.	R ²	S.E.
Vivianite	CaCl ₂	0.01 M	0.98 ***	0.001	0.95 ***	0.158	0.94 ***	0.001
		0.05 M	0.95 ***	0.002	0.96 ***	0.164	0.96 ***	0.002
		0.1 M	0.97 ***	0.003	0.97 ***	0.136	0.96 ***	0.003
	CA	0.01 M	0.96^{0}	0.468	0.94 ***	0.260	0.87^{0}	0.858
		0.05 M	0.83^{0}	1.912	0.92 **	0.351	0.80^{0}	2.064
		0.1 M	0.90 *	2.322	0.96 *	0.272	0.94^{0}	1.849
Hydroxyapatite	CaCl ₂	0.01 M	0.87 ***	0.008	0.82 ***	0.173	0.62 ***	0.013
		0.05 M	0.52 ***	0.220	0.59 ***	0.247	0.35 ***	0.257
		0.1 M	0.74 ***	0.336	0.69 ***	0.602	0.48 ***	0.475
	CA	0.01 M	0.94 ***	1.260	0.85^{0}	0.211	0.72 ***	2.762
		0.05 M	0.98 ***	1.585	0.92^{0}	0.135	0.80 ***	4.722
		0.1 M	0.96 ***	2.391	0.89^{0}	0.145	0.78 ***	5.771
BC ₂₀₀	$CaCl_2$	0.01 M	0.96 ***	0.000	0.93 ***	0.100	0.86 ***	0.000
		0.05 M	0.78 ***	0.000	0.72 ***	0.358	0.60 ***	0.000
		0.1 M	0.89 ***	0.000	0.91 ***	0.135	0.78 ***	0.000
	CA	0.01 M	0.98^{0}	0.201	0.96 ***	0.174	0.93 **	0.416
		0.05 M	1.00 ***	0.468	0.92^{0}	0.235	0.88 **	2.442
		0.1 M	0.99 ***	0.878	0.91^{0}	0.215	0.86 ***	4.533
BC ₂₀₀₋₂₀₀₀	$CaCl_2$	0.01 M	0.94 ***	0.001	0.96 ***	0.184	0.91 ***	0.001
		0.05 M	0.80 ***	0.003	0.89 ***	0.406	0.76 ***	0.004
		0.1 M	0.79 ***	0.001	0.72 ***	0.724	0.70 ***	0.001
	CA	0.01 M	0.99^{0}	0.103	0.93 ***	0.185	0.85 **	0.413
		0.05 M	0.98 ***	0.716	0.90^{0}	0.231	0.82 *	2.314
		0.1 M	0.98 ***	1.215	0.90^{0}	0.219	0.82 ***	4.179
BC ₂₀₀₀	CaCl ₂	0.01 M	0.73 ***	0.001	0.84 ***	0.294	0.68 ***	0.001
		0.05 M	0.96 ***	0.001	0.92 ***	0.230	0.91 ***	0.001
		0.1 M	0.90 ***	0.001	0.86 ***	0.311	0.85 ***	0.001
	CA	0.01 M	0.98^{0}	0.164	0.92 ***	0.192	0.83 **	0.475
		0.05 M	0.97 ***	0.816	0.90^{0}	0.209	0.82^{0}	1.952
		0.1 M	0.98 ***	1.224	0.90^{0}	0.213	0.82 ***	3.632

⁰ not significant at p < 0.05, * significant at p < 0.05, ** significant at p < 0.01, *** significant at p < 0.001.

			Elovich		Expon	Exponential		
			α	β	а	b	k _p	
Vivianite	CaCl ₂	0.01 M	$7.9 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	$5.7 \cdot 10^{-5}$	0.43	$3.3 \cdot 10^{-5}$	
		0.05 M	$8.8 \cdot 10^{-5}$	$8.4 \cdot 10^{-3}$	$6.5 \cdot 10^{-5}$	0.46	$4.6 \cdot 10^{-5}$	
		0.1 M	$1.8 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$1.3 \cdot 10^{-4}$	0.45	$8.6 \cdot 10^{-5}$	
	CA	0.01 M	0.02	27.97	0.01	0.60	0.01	
		0.05 M	0.03	15.72	0.01	0.72	0.02	
		0.1 M	0.04	9.50	0.01	0.77	0.04	
Hydroxyapatite	CaCl ₂	0.01 M	$2.1 \cdot 10^{-3}$	$5.8 \cdot 10^{-3}$	$4.6 \cdot 10^{-4}$	0.22	$5.5 \cdot 10^{-5}$	
		0.05 M	0.06	496.91	$7.1 \cdot 10^{-3}$	0.18	$6.2 \cdot 10^{-4}$	
		0.1 M	0.01	200.28	$2.6 \cdot 10^{-3}$	0.53	$1.5 \cdot 10^{-3}$	
	CA	0.01 M	0.14	22.31	0.07	0.31	0.01	
		0.05 M	0.36	10.31	0.16	0.27	0.03	
		0.1 M	0.55	9.42	0.21	0.25	0.04	
BC ₂₀₀	CaCl ₂	0.01 M	$2.6 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$	$7.9 \cdot 10^{-6}$	0.22	$1.1 \cdot 10^{-6}$	
		0.05 M	$9.6 \cdot 10^{-6}$	$3.1 \cdot 10^{-5}$	$4.0 \cdot 10^{-6}$	0.35	$1.1 \cdot 10^{-6}$	
		0.1 M	$7.6 \cdot 10^{-6}$	$5.1 \cdot 10^{-5}$	$3.6 \cdot 10^{-6}$	0.26	$6.9 \cdot 10^{-7}$	
	CA	0.01 M	0.01	99.37	$4.5 \cdot 10^{-3}$	0.51	$3.7 \cdot 10^{-3}$	
		0.05 M	0.04	22.12	0.03	0.47	0.02	
		0.1 M	0.09	13.10	0.06	0.41	0.03	
BC ₂₀₀₋₂₀₀₀	CaCl ₂	0.01 M	$1.3 \cdot 10^{-5}$	$4.2 \cdot 10^{-4}$	$8.2 \cdot 10^{-6}$	0.55	$8.8 \cdot 10^{-6}$	
		0.05 M	$2.0 \cdot 10^{-5}$	$2.3 \cdot 10^{-4}$	$7.8 \cdot 10^{-6}$	0.68	$1.6 \cdot 10^{-5}$	
		0.1 M	$7.7 \cdot 10^{-6}$	$7.2 \cdot 10^{-4}$	$2.5 \cdot 10^{-6}$	0.70	$4.9 \cdot 10^{-6}$	
	CA	0.01 M	0.01	146.37	0.01	0.40	$2.4 \cdot 10^{-3}$	
		0.05 M	0.05	29.33	0.03	0.41	0.01	
		0.1 M	0.09	16.27	0.05	0.39	0.02	
BC ₂₀₀₀	CaCl ₂	0.01 M	$1.4 \cdot 10^{-5}$	$7.2 \cdot 10^{-4}$	$1.0 \cdot 10^{-5}$	0.40	$5.1 \cdot 10^{-6}$	
		0.05 M	$1.3 \cdot 10^{-5}$	$5.9 \cdot 10^{-4}$	$8.5 \cdot 10^{-6}$	0.48	$6.3 \cdot 10^{-6}$	
		0.1 M	$9.8 \cdot 10^{-6}$	$8.7 \cdot 10^{-4}$	$6.6 \cdot 10^{-6}$	0.46	$4.3 \cdot 10^{-6}$	
	CA	0.01 M	0.01	136.08	0.01	0.38	$2.6 \cdot 10^{-3}$	
		0.05 M	0.04	34.43	0.03	0.38	0.01	
		0.1 M	0.08	18.24	0.05	0.39	0.02	

Table 5. Kinetic parameters of the Elovich, Exponential, and Parabolic function equations.

3.4. Elemental Composition during P Release

The elemental composition of the reaction solutions and its change in concentration was measured and correlated to the amount of released P in mg g⁻¹ for each time step. For the CaCl₂ treatment, no correlations between P–Ca (HA), P–Ca, and P–Fe (VI), and P–K, P–Cl as well as P–Ca (BC) were detected. This also included P–Mg (BC) for the CA treatment. However, a strong linear correlation was revealed for P–Ca at the CA treatment for HA and BC as well as P–Fe for VI (Figures 3–5). With increasing P release for both CaCl₂ and CA, an enrichment of Ca (HA, BC), Fe (VI), and Mg (BC) in the reaction solution was measurable. However, the Fe concentration in CA for VI remained constant at the highest concentration of 0.1 M and no correlation was found. For BC, the concentration of dissolved Mg initially increased in the CaCl₂ solution, but decreased during P release (Figure 6).



Figure 3. Correlation between dissolved P and Ca during P release using (**a**) CaCl₂ and (**b**) CA from hydroxyapatite.



Figure 4. Correlation between dissolved P and Fe during P release using (**a**) CaCl₂ and (**b**) CA from vivianite.



Figure 5. Correlation between dissolved P and Ca during P release using (**a**) CaCl₂ and (**b**) CA from bone char.



Figure 6. Correlation between dissolved P and Mg during P release using (**a**) CaCl₂ and (**b**) CA from bone char.

3.5. pH

The pH of the reaction solution was adjusted prior to the release experiments at a value of 6. Then, the pH was measured again after the 2 h step and the 48 to 168 h step. The pH of the minerals itself was lowest for VI with 4.27 and highest for BC with 9.69 (in H_2O), respectively. HA had a pH of 7.28 (Table 6). During P release, the pH of the solutions increased with increasing CaCl₂ and CA concentrations for VI. For the CA treatment, the pH of the solution even exceeded the initial solution pH of 6, despite the lower pH of VI itself.

			Vivianite	Hydroxy Apatite	BC ₂₀₀	BC ₂₀₀₋₂₀₀₀	BC ₂₀₀₀
Initia	al pH	H ₂ O	4.27	7.28		9.69	
		CaCl ₂	4.17	6.45		8.58	
CaCl ₂ *	0.01 M	2 h	4.72 ± 0.03	6.62 ± 0.04	7.48 ± 0.08	7.48 ± 0.23	7.62 ± 0.09
		48–168 h	4.82 ± 0.05	6.46 ± 0.05	6.91 ± 0.05	6.94 ± 0.01	6.97 ± 0.03
	0.05 M	2 h	4.84 ± 0.02	6.28 ± 0.03	6.90 ± 0.04	6.93 ± 0.03	7.09 ± 0.07
		48–168 h	4.85 ± 0.05	6.25 ± 0.02	6.70 ± 0.07	6.74 ± 0.06	6.83 ± 0.13
	0.1 M	2 h	4.88 ± 0.02	6.24 ± 0.06	6.90 ± 0.04	6.98 ± 0.06	7.02 ± 0.21
		48–168 h	4.86 ± 0.04	6.07 ± 0.02	6.66 ± 0.03	6.63 ± 0.04	6.72 ± 0.00
CA*	0.01 M	2 h	5.30 ± 0.08	7.47 ± 0.05	8.67 ± 0.05	7.54 ± 0.15	7.44 ± 0.07
		48–168 h	6.76 ± 0.05	6.71 ± 0.02	7.60 ± 0.03	7.00 ± 0.06	7.10 ± 0.04
	0.05 M	2 h	5.86 ± 0.01	7.06 ± 0.02	7.52 ± 0.04	7.05 ± 0.06	6.61 ± 0.01
		48–168 h	6.43 ± 0.01	6.68 ± 0.01	6.39 ± 0.01	6.21 ± 0.01	6.23 ± 0.03
	0.1 M	2 h	5.93 ± 0.01	7.03 ± 0.05	6.97 ± 0.02	6.69 ± 0.03	6.36 ± 0.01
		48–168 h	6.61 ± 0.10	6.64 ± 0.02	6.20 ± 0.02	6.10 ± 0.01	6.08 ± 0.01
			* n :	= 3.			

Table 6. pH value of the raw material and in the reaction solution after 2 h and 48–168 h reaction time.

For HA and BC, the pH decreased with increasing $CaCl_2$ and CA concentrations. During the $CaCl_2$ treatment, the pH increased with increasing particle size of BC, while for the CA treatment, the pH decreased with increasing particle size. No clear correlations were detected between the changing H⁺ concentration and dissolved P, Fe, Ca, or Mg.

3.6. Fourier-Transform Infrared Spectroscopy

VI showed a broad OH stretching vibration of the Fe–OH groups in the range from 3750 to 2500 cm⁻¹, a H₂O (HOH) bending vibration at 1629 cm⁻¹, and an OH libration mode at 827 cm⁻¹, respectively (Table 7). The four PO₄^{3–} vibrational modes were observed at 1155, 1023, and 993 cm⁻¹ (v3), 954 cm⁻¹ (v1), 621 cm⁻¹ (v4), and very weak at 522 cm⁻¹ (v1), respectively.

Vivianite ¹	Hydroxyapatite ²		BC ³		Assignment
		<200 µm	200–2000 μm	>2000 µm	
	3745-2570	3737-2585		3737-2585	H ₂ O
3750-2500	3571	3571	3571	3571	OH stretching
1629	1640	1633		1633	H ₂ O
	1452	1480	1480	1480	CO3 ²⁻
	1418	1424	1424	1424	U U
1155			1176		$PO_4^{3-}\nu 3$
	1086	1136	1115	1136	1
1023					
993					
954	1014	1003	1077	1003	$PO_4^{3-} \nu 1$
	963	963	963	963	CO_3^{2-}
827	876	877	877	877	OH libration
	647		647		$PO_4^{3-} \nu 4$
621	619	620	620	620	-
	586	586	586	586	
522	552				$PO_4^{3-} \nu 2$

Table 7. Observed wavenumbers [cm⁻¹] of vivianite, hydroxyapatite, and bone char.

After P release using CaCl₂, the intensity of the OH stretching vibration decreased clearly, but increased slightly with increasing CaCl₂ concentration and was similar for 0.005 M and 0.1 M CaCl₂ (Figure 7A). Similar results were observed for the H₂O peak at 1629 cm⁻¹ and the OH libration vibration. In addition, the intensities of the PO₄^{3–} vibrations in the wavenumber ranged from 1350 to 550 cm⁻¹ decreased during P release. After P release using CA, similar developments of the spectra as for CaCl₂ were observed. However, a new band at 1392 cm⁻¹ and a weak shoulder of the degraded H₂O vibration at 1629 cm⁻¹ were formed.



Figure 7. Fourier-transform infrared spectra of (**A**) vivianite and (**B**) hydroxyapatite during P release. (a) reference (b) 0.01 M CaCl₂, (c) 0.05 M CaCl₂, (d) 0.1 M CaCl₂, (e) 0.01 M CA, (f) 0.05 M CA, and (g) 0.1 M CA.

HA showed a broad H₂O absorption band from 3745 to 2570 cm⁻¹ with a characteristic OH stretching vibration at 3571 cm⁻¹ (Table 7). Adsorbed H₂O also showed a peak at 1640 cm⁻¹, and an OH libration vibration can be observed at 876 cm⁻¹. Phosphate (PO₄³⁻) was represented by four infrared active vibrational modes: a v3 band from 1353 to 982 cm⁻¹ with two peaks at 1173 and 1086 cm⁻¹, a v1 vibration at 1014 cm⁻¹, three peaks at 647, 619, and 586 cm⁻¹ of the v4 vibration, and a weak v2 vibration at 552 cm⁻¹. The vibrational modes of v1 and v2 appeared only as shoulders before desorption, and v2 was particularly very weak. Furthermore, carbonate (CO₃²⁻) related vibrations were observed at a broad band with two vibrations at 1452 and 1418 cm⁻¹, and a vibration at 963 cm⁻¹. Vibrations in the range from 1555 to 1360 cm⁻¹ can be attributed to CO₃²⁻ on the surface of the mineral rather than in the lattice [26], where CO₃²⁻ can substitute either OH (A–type substitution) or PO₄³⁻ groups (B-type substitution) of HA [24,33].

After P release using CaCl₂, the intensities of the OH, H_2O , CO_3^{2-} , and PO_4^{3-} vibrations decreased, but increased again with the rise of the CaCl₂ concentration near the initial level (Figure 7B). The initial decline and the increase with increasing concentration of the reaction solution were also observed during P release with CA. However, as already observed in VI, a vibration at 1610 cm⁻¹ and a slight shoulder at 1388 cm⁻¹ appeared. In addition, a very weak peak at 841 cm⁻¹ was formed.

The BC samples showed a weak, but broad adsorbed H_2O band in the range from 3737 to 2585 cm⁻¹ and a weak OH stretching vibration at 3571 cm⁻¹ (Table 7). The FT-IR spectrum of BC₂₀₀₋₂₀₀₀ showed no broad H_2O adsorption band, though only a more pronounced OH stretching vibration at

 3571 cm^{-1} than the other BC samples. A broader band in the range from 1815 to 1380 cm^{-1} with three peaks at 1633, 1480, and 1424 cm⁻¹ can be assigned to adsorbed H₂O and CO₃²⁻. Additionally, in this case, there was only a very weak H₂O peak in BC₂₀₀₋₂₀₀₀. This BC sample showed the characteristic PO₄³⁻ vibrations at 1176 and 1115 cm⁻¹ (v3), 1077 cm⁻¹ (v1) as well as 647, 620, and 586 cm⁻¹ (v4), respectively. BC₂₀₀ and BC₂₀₀₀ showed PO₄³⁻ vibrations at 1136 cm⁻¹ (v3) with a shoulder at 1079 cm⁻¹, at 1003 cm⁻¹ (v1) as well as at 620 and 586 cm⁻¹ (v4), respectively. The weak v2 stretching vibration was not visible for all BC samples. Furthermore, BC₂₀₀ and BC₂₀₀₀ had, in accordance with the HA spectrum, a CO₃²⁻ vibration at 963 cm⁻¹ and an OH libration mode at 877 cm⁻¹. Both were very weak for BC₂₀₀₋₂₀₀₀.

During P release using CaCl₂, the intensities of the OH and H₂O bands between 3737 and 2585 cm⁻¹ fluctuated and increased with increasing particle size at the highest concentration of 0.1 M (Figure 8A–C). The other H₂O, OH, CO_3^{2-} , and PO_4^{3-} bands also showed an irregular behavior with regard to the used solution concentrations during P release. Merely a new H₂O band at 1633 cm⁻¹ was formed in BC_{200–2000}, and the intensity of the P bands increased with increasing particle size and even exceeded the baseline level. When CA was used, a degradation of the H₂O, OH, CO_3^{2-} , and PO_4^{3-} bands occurred. Again, an additional vibration at 1633 cm⁻¹ was formed, which differed from the H₂O band in the broader slope at a higher wavenumber.



Figure 8. FT-IR spectra of bone char divided into (**A**) BC₂₀₀, (**B**) BC_{200–2000}, and (**C**) BC₂₀₀₀ during P release. (a) reference (b) 0.01 M CaCl₂, (c) 0.05 M CaCl₂, (d) 0.1 M CaCl₂, (e) 0.01 M CA, (f) 0.05 M CA, and (g) 0.1 M CA.

4. Discussion

The release of P from primary and secondary P minerals depends on several factors such as mineral stability and solubility properties regarding dissolution by ionic substitution, particle size, or pH [17,34–36]. The mobilization of these P resources can take place by different processes, while the cumulative P release using CA was clearly higher than with CaCl₂. It is well known that the exchange with inorganic ions plays an inferior role compared to organic components [37–39]. Inorganic reaction solutions such as CaCl₂ contribute to the mobilization of P from nonspecific adsorbed P from low-affinity sites, while structural bound or specific adsorbed P from high-affinity sites can hardly be affected due to the strong bonds [2,40,41]. In addition, if P was released from the minerals, PO_4^{3-} had a higher affinity to adsorb again on the mineral surface due to the higher valence and ionic radius compared to Cl⁻ [42]. Hence, it is possible that free P was bound again and therefore not measured as dissolved P in the reaction solution. Another explanation for the very low P mobilization from BC by using CaCl₂ could be the point of zero charge, which was described at around pH 7.7 [43]. Above this pH value, BC has a negative charge of the surface, which led to a lower affinity for anion exchange and hence, a lower capacity for PO_4^{3-} mobilization. In comparison, the pH of the point of zero charge

reported for HA was in the range from 6.7 to 8.6 [44,45]. Thus, there was a more positive surface charge, especially for BC, which can lead to even small differences in P mobilization.

Both the CaCl₂ and the CA treatment showed a higher P release capacity for HA. Although VI had a higher P release than the BC samples at the lowest CA concentration of 0.01 M, the P release capacity of BC increased more strongly with increasing concentration of the reaction solution. The beneficial effect on P release of further organic acids such as oxalic acid, hydrochloric acid, or sulfuric acid and their increasing concentration were also described for rock phosphates, iron phosphates, and soils [46–50]. While the P release during the CaCl₂ treatment was so low that only VI and HA showed a slightly higher release with increasing CaCl₂ concentration, this effect was more pronounced for the CA treatment. Although more P was dissolved with increasing CA concentration, this was different for HA, VI, and BC.

BC mainly consists of the elements Ca, P, and Mg, which is similar to other BC obtained by pyrolysis (350 °C–800 °C) of rendered material [15,16,51–54]. However, the Ca and P concentrations were higher than in other bio and bone chars from nutrient-rich feedstocks such as pig manure or sewage sludge [55–58]. Since HA is the dominant P compound in BC, and a rising pyrolysis temperature increased the proportion of HA, the specific pre-treatment of BC influenced the P solubility characteristics [14-16,52,59]. While higher ion strength of the CA (0.01 M:0.05 M:0.1 M = 1:5:10) increased the P release of HA proportional slightly (1:2.2:2.6), a significantly stronger effect was observed for BC. For $BC_{200-2000}$, P release was most efficient (1:5.0:9.1), followed by BC_{200} (1:4.6:8.1) and BC₂₀₀₀ (1:4.0:7.5). Furthermore, a larger P release was observed with a smaller particle size of BC, which is consistent with the results of Ma and Matsunaka [60], Morshedizad and Leinweber [61] as well as Morshedizad et al. [62] during pot and leaching experiments. This can be explained by the larger specific area, where reactants can dissolve P [60,63]. Although the measured specific surface areas of the different BC fractions differed only slightly at first glance, the surface area increased by more than 2.5 m² g⁻¹ from BC_{2000} to BC_{200} . For VI, the increase in CA concentration was the least efficient (1:1.8:3). The effectiveness of CA is particularly influenced by the strength of the acid [46], which is why P mobilization also rose with increasing concentration. The critical factor leading to different P release efficiencies with increasing CA concentration could be the higher specific surface area of the BC samples compared to HA. Thus, more exchange sites are available for ionic substitution during the initial phase of P release, whereas the stability of the minerals with regard to dissolution only becomes apparent in a later phase of mobilization. Nevertheless, the chosen CA concentrations exceeded the concentrations commonly measured in the soil or litter solution, which were in the range from 0 to 122 µmol. However, due to the small particle size and envelope density, fine BC particles should be mixed with manure, sludge, or compost prior to field application to reduce a loss of up to 25 mass% by dust formation [64] to maintain a long-term improvement effect in soils.

The best fit of the time-dependent release data was observed by applying the logarithmic Elovich equation. This biphasic kinetic behavior revealed a faster release of easier accessible P from the mineral surface and a slower release phase. This slower second phase can be controlled by diffusion kinetics including the mobilization of more heavily bound P, which can be embedded within the mineral particles or resorption processes [65]. This suggests chemisorption reactions, which were corroborated by previous studies with P desorption from soils [66,67]. The calculated kinetic parameters α and β of the Elovich equation (Table 5) clearly indicated a low initial P release from the mineral phase and a distinct ongoing mobilization over time within the CaCl₂ treatment. Regarding the low total P release, it was assumed that a chemical equilibrium between the solid and the liquid phase was desired rather than a significant P release through anion exchange, and hence, the high values of β do not seem realistic.

For the CA treatment, the initial P release increased with increasing CA concentration. The P release rate over time declined with increasing CA concentration, but nevertheless showed a strong ongoing P mobilization process. The presence of a higher concentration of citrate anions can therefore lead to a higher initial P release rate by ligand exchange, followed by dissolution of the mineral particles.

The interpretation of the fit parameters is difficult, since an empirical model like the Elovich equation describes a process in an ideal system. This is therefore not necessarily transferable to a real system such as soils [68]. On one hand, an increase in β or a decrease in α can indicate an increase of the reaction rate [69], while on the other hand, the slope of the equation may also depend more on the conditions of the reaction than to characterize it [70]. Nevertheless, it is possible that the weak curvature of the P release kinetics by using CA can be poorly described by the Elovich equation [68], which is why the release in the range over 48 h can be underestimated, whereas the P release over time can be overestimated for CaCl₂.

The release of inorganic bound P by organic acids includes the processes of dissolution of minerals, the direct ligand exchange, and replacement of P by organic acid anions or the formation of metal–organic complexes and blocking of P adsorption sites [18–21]. It was identified that CA promotes the dissolution of PO_4^{3-} adsorbing minerals [50,71–73], and that the P availability as well as the release of (e.g., Si, Fe, and Al increased with increasing CA concentration) [46,74]. Both the increase of dissolved Fe (VI), Ca (HA, BC), and Mg (BC) with continuing P release showed the dissolution of the minerals by using CA. The same was concluded for VI and the dissolved Fe concentrations. A constant Fe concentration of approximately 15 mg g⁻¹ was measured in the reaction with 0.1 M CA for VI. This could indicate that VI was only soluble to a certain degree which limited P release.

Often P compounds containing Fe are very sensitive to changes in reductive conditions and can be dissolved in anoxic environments. However, Fe-associated P, which is related to VI, remained stable to reductive dissolution in anoxic soils and lake sediments [75]. The extraction of P from VI strongly depends on the crystallinity of the mineral, whereas P was not completely released from highly crystalline VI [12]. HA is also considered to be a poorly soluble mineral, where biological HA is characterized by a smaller crystal size and a higher proportion of PO_4^{3-} substituted by CO_3^{2-} compared to geological HA, which enhances the solubility of biological HA [17]. In particular, thermal treatment led to a decreasing CO_3^{2-} and H_2O content and an increasing crystal size, resulting in a higher stability of HA [76,77]. The addition of CO_3^{2-} through decreased crystallinity enhanced the amenability to dissolution and the potential of the biodegradation of HA [17,78-80]. The stability or solubility of carbonated HA was thus defined by the presence of CO_3^{2-} [17,76,81]. The observed FT-IR spectroscopic data revealed CO₃²⁻ related vibrations for the HA and BC samples, respectively. The higher intensities of the CO_3^{2-} bands for HA at 1452 cm⁻¹, 1418 cm⁻¹, and 963 cm⁻¹ than for the BC samples (Figure 8) suggest a lower stability regarding the dissolution of the former and, hence, a higher P release efficiency. In summary, the kinetic data indicated that BC samples, especially BC₂₀₀, had a lower short-term P release [53], but a higher long-term P release than HA or VI. The fluctuations of Ca, Fe, and Mg concentrations in the CaCl₂ reaction solution may be due to low solution or release from the sample material with respect to an equilibrium in the reaction solution, since no correlation to the dissolved P concentrations was detected.

Gypser and Freese [82] determined the concentration of C_{Total} in CA during desorption experiments with VI and HA. Despite a fluctuation around the initial C_{Total} concentration, no distinctive change or even decrease during P desorption was measured. Thus, the formation of metal–organic complexes in the reaction solution was excluded. In this case, the possible enrichment of metal–organic complexes in the reaction solution was not considered as there was no reddish-brown coloring of the reaction solution. Further possibilities of differentiation between ligand exchange and metal–organic complexes should be taken into account. Possible evidence of the presence or absence of organic ligands at the surface of HA, VI, and BC could be the formation of C-related vibrations in the FT-IR spectra. For CA, a bond is formed by carboxyl groups (–COOH) of the citrate anion (C₆H₆O₇^{2–} at pH 6), which should be visible by characteristic C=O and C–O peaks in the FT-IR spectra. A vibrational analysis of the –COOH groups included vibrations of C=O, C–O, and OH, where the characteristic C=O stretching vibration was usually detected between 1800 cm⁻¹ and 1680 cm⁻¹, and the C–O stretching vibration between 1320 cm⁻¹ and 1210 cm⁻¹ [83,84], depending on the compound. The position of the band can vary accordingly with intermolecular OH⁻⁻⁻ O hydrogen bonding within the material [85]. For the samples VI, HA, BC₂₀₀, and BC₂₀₀₀, a distinctive H₂O vibration ranged in the region of possible C=O peaks. During P release using the CA treatment, the peak of the H₂O related vibration shifted to a lower wavenumber or possibly formed a new vibration at 1610 cm⁻¹ for HA and at 1633 cm⁻¹ for BC₂₀₀ and BC_{2000} . For $BC_{200-2000}$, a new vibration was formed at 1633 cm⁻¹ where the H₂O vibration was missing. The spectrum of VI revealed a shoulder at the degraded H_2O vibration at 1629 cm⁻¹. These features can be related to a newly formed C=O peak. Additionally, for VI, a new band was formed at 1392 cm⁻¹, which occurred as a slight shoulder at 1388 cm⁻¹ for HA. This feature can be related to a possible C–O binding. For the BC samples, the range between 1550 cm^{-1} and 1340 cm^{-1} was dominated by the CO₃²⁻ bands. Johnson and Loeppert [21] described the P release from Fe-hydroxides by both ligand exchange and dissolution, because ligand adsorption onto the surface is important for dissolution mechanisms. The accumulation of Fe, Ca, and Mg in the CA reaction solution suggested that dissolution played a major role in P release, while the C-associated changes of the FT-IR spectra, either dried CA residues in the pore space or on the surface of the investigated materials, or indicating ligand exchange took place, played a minor role. Although metal-organic complexes could also form with these dissolved metals, no reddish-brown color change (ferric citrate), or white precipitation (calcium citrate) were observed in this study. Since calcium citrate in particular is poorly soluble in H_2O (950 mg l^{-1} at 25 °C), and 1700 mg l^{-1} of dissolved Ca was detected in 0.1 M CA after a reaction time of 168 h (in the BC₂₀₀₀ samples), it was suggested that no calcium citrate developed. The development of magnesium citrate could not be excluded due to its high solubility in H₂O. Overall, the possibility of the formation of metal–organic complexes should not be discarded, since especially ferric citrate plays an important role in the nutrient uptake of some plants and microorganisms [86].

One of the main aspects of the changes of the solution pH was the attempt to achieve a chemical equilibrium between the solid mineral phase and the reaction solution due to the different pH values. Particularly for the CaCl₂ treatment, this chemical equilibrium seemed to be the driving force for pH changes due to the low P mobilization as well as missing correlations to other dissolved elements. For the CA treatment, in addition to the influence of the mineral pH itself, the release of P also changed the pH value of the respective reaction solution. This could also be measured between the individual particle sizes of BC, where the smaller particles of BC₂₀₀ delivered a higher amount of P than the larger particles of BC₂₀₀₀, thus slightly lowering the pH more. The rise of the pH value above 6 for VI can be possibly caused by the oxidation of dissolved Fe²⁺ to Fe³⁺ by atmospheric O₂ (Equation (1)).

$$2 \operatorname{Fe}^{2+} + 0.5 \operatorname{O}_2 + 2 \operatorname{H}^+ \leftrightarrow 2 \operatorname{Fe}^{3+} + \operatorname{H}_2 \operatorname{O}$$
(1)

In acidic to near-neutral soils, the availability of P is mainly limited by processes of adsorption, desorption, and precipitation on soil particle surfaces where the strong binding to Fe- and Al-hydroxides plays a major role in P immobilization [21,40]. However, Roberts and Johnston [3] pointed out that the P fixation and thus unavailability for plants was not supported by field experiments. Rather, they emphasized the presence of an immediately available P pool in the soil solution as well as the further readily available P pool, which are mainly used for the supply of the plants. In addition, a less and much less readily available P pool was formed where the availability for plants was determined on their accessibility to plant roots and its extractability by soil test reagents. If the P use efficiency was balanced according to these P pools, the P recovery is often in the range of 50 to 70% [87]. This means that in addition to the readily available P pools, soil reserves can be used in the long-term, hence, reducing agricultural runoff and eutrophication of natural waters. Depending on the crystallization grade and the Fe/Al-ratio, the P mobilization capacity of these hydroxides can be increased up to 49% by using CA [39]. In particular, the comparison of the efficiency and kinetics of P release from VI and BC showed that VI, despite the influence of CA, had less available P in both the short- and long-term, which can cause an increase in the less available P pool. The very low P release using CaCl₂ underlines once again the importance of the accessibility of fertilized or naturally bound P for plant roots to benefit from the excretion of organic acids as a strategy to enhance the P uptake.

5. Conclusions

P release experiments in batch showed a distinctive higher effect of CA on P mobilization than

CaCl₂. While the P release during the CaCl₂ treatment was so low that only VI and HA showed a slightly higher release with increasing CaCl₂ concentration, the increase of dissolved P was more pronounced for the CA treatment. At the same concentration, the use of CA resulted in a 32,190-fold higher P release compared to CaCl₂ (0.1 M for BC₂₀₀). The lowest increase was measured for VI with a 29-fold higher release. The observed FT-IR spectroscopic data suggested lower stability of HA than for BC and despite a higher mobilization of P from HA, the kinetic data indicated that BC samples, especially at lower particle size, had a higher long-term P release than HA or VI. The accumulation of Fe, Ca, and Mg in the Ca reaction solution suggested that dissolution played a major role in P release, while ligand exchange seemed to play a subordinate role. In summary, it can be said that the suitability of HA and BC as a poorly soluble, but sustainable P source is better than that of VI. However, the efficiency as a P fertilizer is also dependent on present soil P mobilization processes, since the sole release of P by the soil solution is not remarkable. Accumulated P, precipitated or adsorbed on hydroxides or soil colloids, represents a high potential secondary P source that requires a detailed characterization of easily and heavily releasable fractions for a sustainable recovery.

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