Improving the prediction of fertilizer phosphorus availability to plants with simple, but non-standardized extraction techniques

(Supplementary Material)

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MATERIALS AND METHODS

List of the fertilizers

Table S1: Description of the fertilizers used in this study (n=79). HTC= Hydrothermal Carbonization

Sample ID	Description	Sourced from / Processed by	P total (*aqua regia*; g P 100g dry matter^{-1})*	Used in pot experiment	Used in Duboc et al. (2017) (ID given if applicable)
BGSL-1	Biogas slurry from food and agricultural wastes. The slurry was freeze-dried before use.	Biogas Bruck/Leitha GmbH & Co KG (Bruck /Leitha, Austria)	1.73	X	BGSL
BGSL-1-BC 400-1	BGSL-1 pyrolyzed at 400 °C in an experimental lab reactor with nitrogen as flush gas	Austrian Institute of Technology (AIT) (Tulln, Austria)	3.37		BGSL-BC
BGSL-1-BC 400-2	Same as above	AIT (Tulln, Austria)	2.79	X	
BGSL-1-BC 500	Same as above, T = 500°C	AIT (Tulln, Austria)	2.85		
BGSL-2	Biogas slurry, same origin as BGSL-1, but material was not freeze-dried before treatment	Biogas Bruck/Leitha GmbH & Co KG (Bruck /Leitha, Austria)	1.37		
BGSL-2-HC	BGSL-2 treated by HTC, 225 min at 200°C	Institute for Chemical and Energy Engineering (IVET), BOKU, Vienna	1.89		
BGSL-3	Same as BGSL-2 (subsample of the same sampling date)	See BGSL-2	2.10		
BGSL-3-HC	BGSL-3 treated by HTC, 225 min at 200°C	See BGSL-2-HC1	2.16		
BGSL-4	Same as BGSL-2 and -3 (subsample of the same sampling date)	See BGSL-2	1.82		
BGSL-4-HC	BGSL-4 treated by HTC, t = 390 min; T = 175°C	See BGSL-2-HC1	1.77		
CatM-1	Cattle Manure	Beckmann & Brehm	0.82		

		GmbH (Beckeln, Germany)			
CatM-1-BC 500	CatM-1 pyrolyzed at 500°C for 20 min in a PYREKA (Pyreg GmbH, Dörth/Germany)	AIT (Tulln, Austria)	2.91	X	
CatM-1-BC 700	CatM-1 pyrolyzed at 700°C as above	AIT (Tulln, Austria)	1.86		
CatM-1-HC	CatM-1 treated by HTC: 60 min ramp + 60 min at 200°C + cooling. Lab reactor model 4740, Parr Instrument GmbH (Frankfurt/Main, Germany). 24 g+ 24mL H_2O	IVET, BOKU, Vienna	0.95		
ChM-1	Chicken manure (ChM)	Egg producing farm	1.97	X	CM
ChM-1-BC 400-1	ChM-1 pyrolyzed at 400 °C (see BGSL-1)	AIT (Tulln, Austria)	4.14		CM-BC
ChM-1-BC 400-2	Same as above	AIT (Tulln, Austria)	3.30		
ChM-1-BC 400-So	Same as above but with addition of Na_2CO_3.	AIT (Tulln, Austria)	4.02		
ChM-1-BC 500	ChM-1 pyrolyzed at 500 °C (see BGSL-1)	AIT (Tulln, Austria)	3.62	X	
ChM-1-BC 500-So	Same as above but with addition of Na_2CO_3.	AIT (Tulln, Austria)	3.62		
ChM-1-HC	ChM-1 treated by HTC, 225 min at 180°C	IVET, BOKU, Vienna	2.52	X	
ChM-2	Chicken manure	Egg producing farm	1.53		
ChM-2-HC-1	ChM-2 treated by HTC, 120 min at 180°C	IVET, BOKU, Vienna	2.03		
ChM-2-HC-2	ChM-2 treated in 2 steps by HTC. Step 1: 120 min at 220°C; Step 2: 120 min at 220°C	IVET, BOKU, Vienna	3.05		
ChM-3	Chicken manure	Egg producing farm	1.25		
ChM-4	Chicken manure	Egg producing farm	1.19		
ChM-5	Chicken manure	Italpollina Deutschland (Aschau im Chiemgau, Germany).	1.41	X	
ChM-5-BC 500	ChM-5 pyrolyzed at 500°C (see CatM-1-BC 500)	AIT (Tulln, Austria)	4.02	X	

ChM-5-BC 700	ChM-5 pyrolyzed at 700°C as above	AIT (Tulln, Austria)	4.29		
ChM-5-HC	ChM-5 treated by HTC (see CatM-1-HC-1)	IVET, BOKU, Vienna	1.72		
MBM-1	Meat and bone meal (MBM)	Steirische Tierkörperverwertungs GmbH & Co KG (Gabersdorf, Austria	4.72	X	MBM
MBM-1-BC 400-1	MBM-1 pyrolyzed at 400°C (see BGSL-1)	AIT (Tulln, Austria)	10.69		MBM-BC
MBM-1-BC 400-2	Same as above	AIT (Tulln, Austria)	10.24		
MBM-1-BC 500	Same as above but at 500°C	AIT (Tulln, Austria)	10.85	X	
MBM-1-HC	MBM-1 treated by HTC, 225 min at 180°C	IVET, BOKU, Vienna	8.84		
MBM-2	Meat and bone meal	Steirische Tierkörperverwertungs GmbH & Co KG (Gabersdorf, Austria	4.84	X	
MBM-2-BC 500	MBM-2 pyrolyzed at 500°C (see CatM-1-BC 500)	AIT (Tulln, Austria)	10.76	X	
MBM-2-BC 700	MBM-2 pyrolyzed at 700°C (see above)	AIT (Tulln, Austria)	12.52		
MSS-1-BC	MSS pyrolyzed at 400°C (see BGSL-1)	AIT (Tulln, Austria)	9.26		MSS-BC-1
MSS-2-BC	Pyrolyzed MSS	WPA beratende Ingenieure (Vienna, Austria)	6.85	X	MSS-BC-2
MSS-3-BC	Pyrolyzed MSS	AIT (Tulln, Austria)	9.14		MSS-BC-3
MSS-4	Municipal sewage sludge	Municipal wastewater treatment plant (Tulln, Austria)	2.13	X	
MSS-4-BC 500	MSS-4 pyrolyzed at 500°C (see CatM-1-BC 500)	AIT (Tulln, Austria)	6.59	X	
MSS-4-BC 700	MSS-4 pyrolyzed at 700°C (see above)	AIT (Tulln, Austria)	5.50	X	
MSS-4-HC	MSS-4 treated by HTC (see CatM-1-HC-1)	IVET, BOKU, Vienna	2.31		
MSS-5	Municipal sewage sludge	Municipal wastewater treatment plant (Traismauer, Austria)	4.01	X	
MSS-5-HC-1	MSS-5 treated by HTC with addition of $MgCl_2$ and adjusted at pH 10.5, T = 240°C	IVET, BOKU, Vienna	4.45	X	

MSS-5-HC-2	MSS-5 treated by HTC with addition of K-citrate and adjusted at pH 3.5, T = 240°C	IVET, BOKU, Vienna	4.83	X	
MSS-6-AshDec-Mg	MSS treated by pyrolysis and gasification with addition of $MgCl_2$	Activil corp. (Moscow, Russia) [a]	7.30		MSS-G-1
MSS-7-AshDec-Mg	MSS treated by pyrolysis and gasification with addition of $MgCl_2$	Activil corp. (Moscow, Russia) [a]	9.77	X	MSS-G-2
MSS-8-AshDec-Mg	MSS treated by AshDec process with addition of $MgCl_2$	Bundesanstalt für Materialforschung (BAM) (Berlin, Germany) [a]	10.18	X	
MSS-AshDec-K/Na-1	MSS treated by AshDec process with addition of K_2SO_4 and Na_2SO_4	BAM (Berlin, Germany) [b]	7.57		
MSS-AshDec-K/Na-2	MSS treated by AshDec process with addition of K_2SO_4 and Na_2SO_4	BAM (Berlin, Germany) [b]	7.65	X	
MSS-AshDec-Na-1	MSS treated by AshDec process with addition of Na_2SO_4	BAM (Berlin, Germany) [b]	7.65		
MSS-AshDec-Na-2	MSS treated by AshDec process with addition of Na_2SO_4	BAM (Berlin, Germany) [b]	7.95	X	
MSS-AshDec-Na Low	MSS treated by AshDec process with addition of Na_2SO_4 at suboptimal Na/P molar ratio	BAM (Berlin, Germany) [b]	7.44	X	
MSSA-1	Municipal sewage sludge ash	Undisclosed origin [c]	7.55	X	
MSSA-1-Slag-1a	MSSA-1 (25 %) fused with Linz-Donawitz steel slag (75 %) for 30 min, quenched.	Undisclosed origin [c]	2.29		
MSSA-1-Slag-1b	As above, but not quenched	Undisclosed origin [c]	2.37	X	
MSSA-1-Slag-2a	MSSA-1 (26 %) fused with Linz-Donawitz steel slag (67 %) and CaO (7 %) for 30 min, quenched.	Undisclosed origin [c]	2.31		
MSSA-1-Slag-2b	As above, but not quenched	Undisclosed origin [c]	2.39	X	

MSSA-1-Slag-3a	MSSA-1 (12.5 %) fused with Linz-Donawitz steel slag (72 %) and CaO (15.5 %) for 30 min, quenched.	Undisclosed origin [c]	1.83		
MSSA-1-Slag-3b	As above, but not quenched	Undisclosed origin [c]	1.87	X	
MSSA-2-Slag	Fused municipal sewage sludge ash with Linz-Donawitz steel slag	FEhS - Building Materials Institute (Duisburg, Germany) [c]	2.38	X	
Prec-P-RoC-1	P-RoC process: Precipitated Ca-phosphate from liquid fraction of centrifuged MSS	Karlsruhe Institute of Technology (KIT) (Karlsruhe, Germany)	3.72	X	
Prec-P-RoC-2	P-RoC process: Precipitated Ca-phosphate from percolation water of a dry fermentation plant	KIT (Karlsruhe, Germany)	1.59	X	
Prec-Struvite-1	"Berliner Pflanze": Struvite from municipal WWTP	Berliner Wasserbetriebe (Berlin, Germany)	12.18	X	Struvite
Prec-Struvite-2	"CrystalGreen" Struvite	Ostara Nutrient Recovery Technologies Inc. (Vancouver, Canada)	12.72	X	
Ref-Di Calcium P	$CaHPO_4$	Sigma Aldrich; CAS: 7757-93-9	22.16	X	
Ref-Mono Calcium P	$Ca(H_2PO_4)_2$	Alfa Aesar; CAS: 301524-28-7	24.37	X	
Ref-Rock P-1	Rock phosphate	Undisclosed origin	13.57	X	RP
Ref-Rock P-2	Rock phosphate	Eppawala, Sri Lanka	14.86	X	
Ref-SSP	Commercial Single Superphosphate ("DC Superphosphate")	Timac Agro Düngemittelproduktions- und HandelsgmbH, (Zwentendorf, Austria)	8.98	X	SSP
Ref-ThermoP	Thermophos: Fused Ca-Mg-Phosphate, by melting phosphate rock and serpentine rock	Nelisfert (New Zealand)	7.96	X	
Ref-ThomasP	Thomas slag	FEhS - Building Materials Institute (Duisburg, Germany)	3.98	X	

				X	
Ref-TSP	Commercial Triple Superphosphate	Raiffeisen-Lagerhaus (Austria)	21.57		

* Dry matter basis after drying at 50°C for 24 h, except the Ref- and Prec- products which were analyzed and used without additional drying.

[a] Thermo-chemical treatment described in Adam et al.(2009)

[b] Process described in Herzel et al. (2021)

[c] process as in Bartsch et al. (2013) and Rex et al. (2014)

RESULTS AND DISCUSSION

Solubility of struvite in 0.5 mol L^{-1} NaHCO$_3$ solution. Comparison of experimental data with calculations from Visual MINTEQ 3.1

Table S2: Input concentrations for calculation of struvite dissolution equilibrium in 0.5 mol L^{-1} NaHCO$_3$ with Visual MINTEQ 3.1 (https://vminteq.lwr.kth.se). Comparison of 1 : 200 and 1 : 1000 fertilizer : solution ratio (w : v).

	Ion	Concentration (mg L^{-1})	
		1 : 200	1 : 1000
Input	Mg^{2+}	495	99.1
	NH$_4^+$	367	73.4
	PO$_4^{3-}$	1936	387.3
	Na$^+$	11500	11500
	CO$_3^{2-}$	30000	30000

Table S3: Output of calculation of struvite dissolution equilibrium in 0.5 mol L^{-1} NaHCO$_3$ with Visual MINTEQ 3.1 (https://vminteq.lwr.kth.se). Comparison of 1 : 200 and 1 : 1000 fertilizer : solution ratio (w : v) with MgCO$_3$ allowed to precipitate (X) or not (-). By default, struvite was allowed to precipitate in both scenarios. Starting concentrations as in Table S2. pH was set to 8.3 since it is buffered by the HCO$_3^-$ ions of the extraction solution.

	% of total P dissolved	
MgCO$_3$	1 : 200	1 : 1000
-	16.4	100
X	100	100

Table S4 Results of an extraction experiment using 1 : 200 and 1 : 1000 fertilizer : solution ratio (w : v; 150 and 30 mg struvite in 30 mL extraction solution respectively) at 0.5, 4 and 21 h. Results expressed as mean ± u where u (coverage factor = 1) encompasses the respective uncertainties of total P and extracted P. pH remained between 8.25 and 8.35 during the extraction.

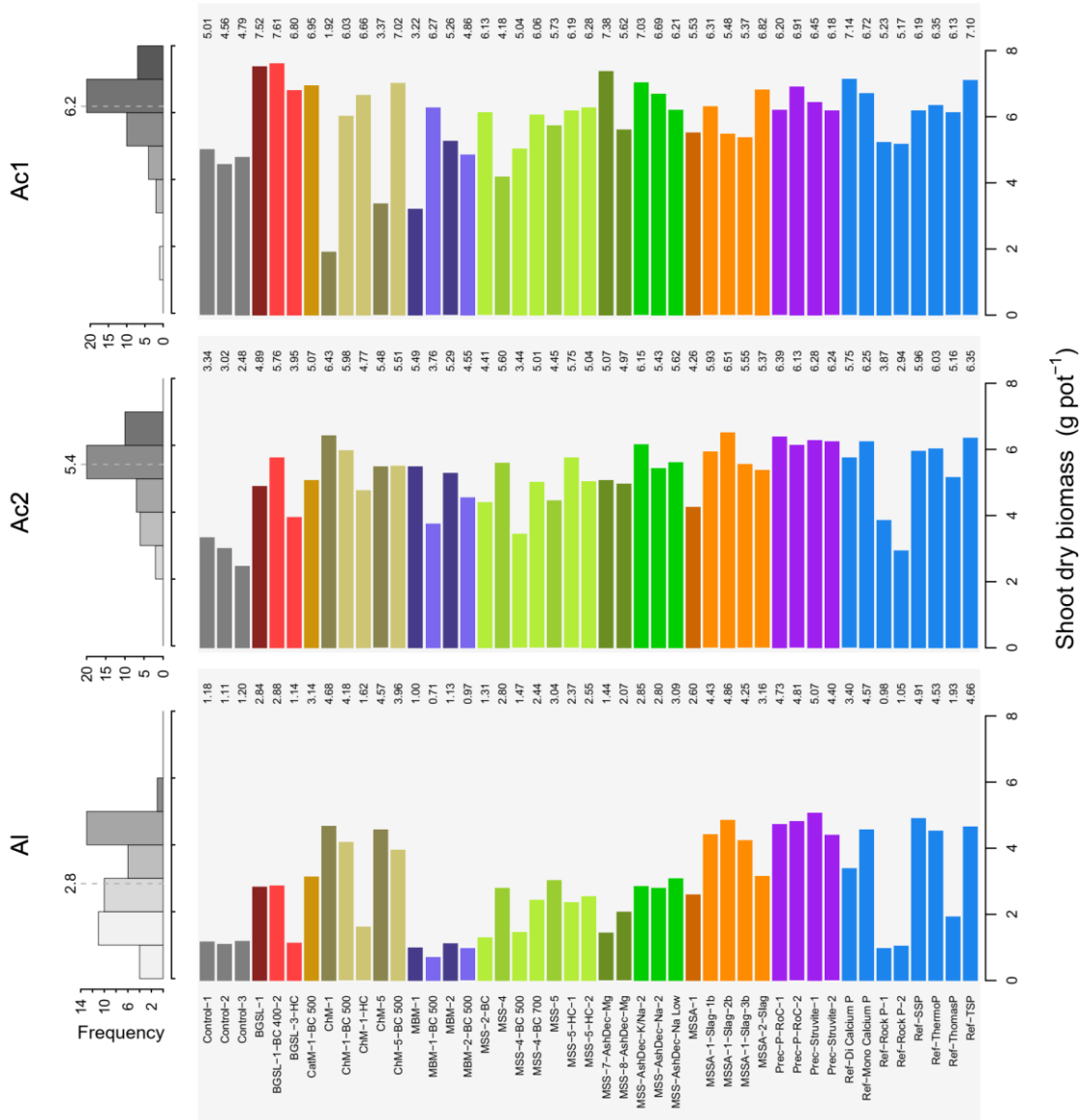|	% of total P dissolved	
Time (h)	1 : 200	1 : 1000
0.5	26.6 ± 2.3	93.8 ± 6.4
4	24.6 ± 1.8	98.9 ± 6.5
21	26.0 ± 2.4	101.4 ± 7.6

Figure S1: Shoot dry biomass harvested from each pot. In the histograms, the dotted line and the value above it is the median.
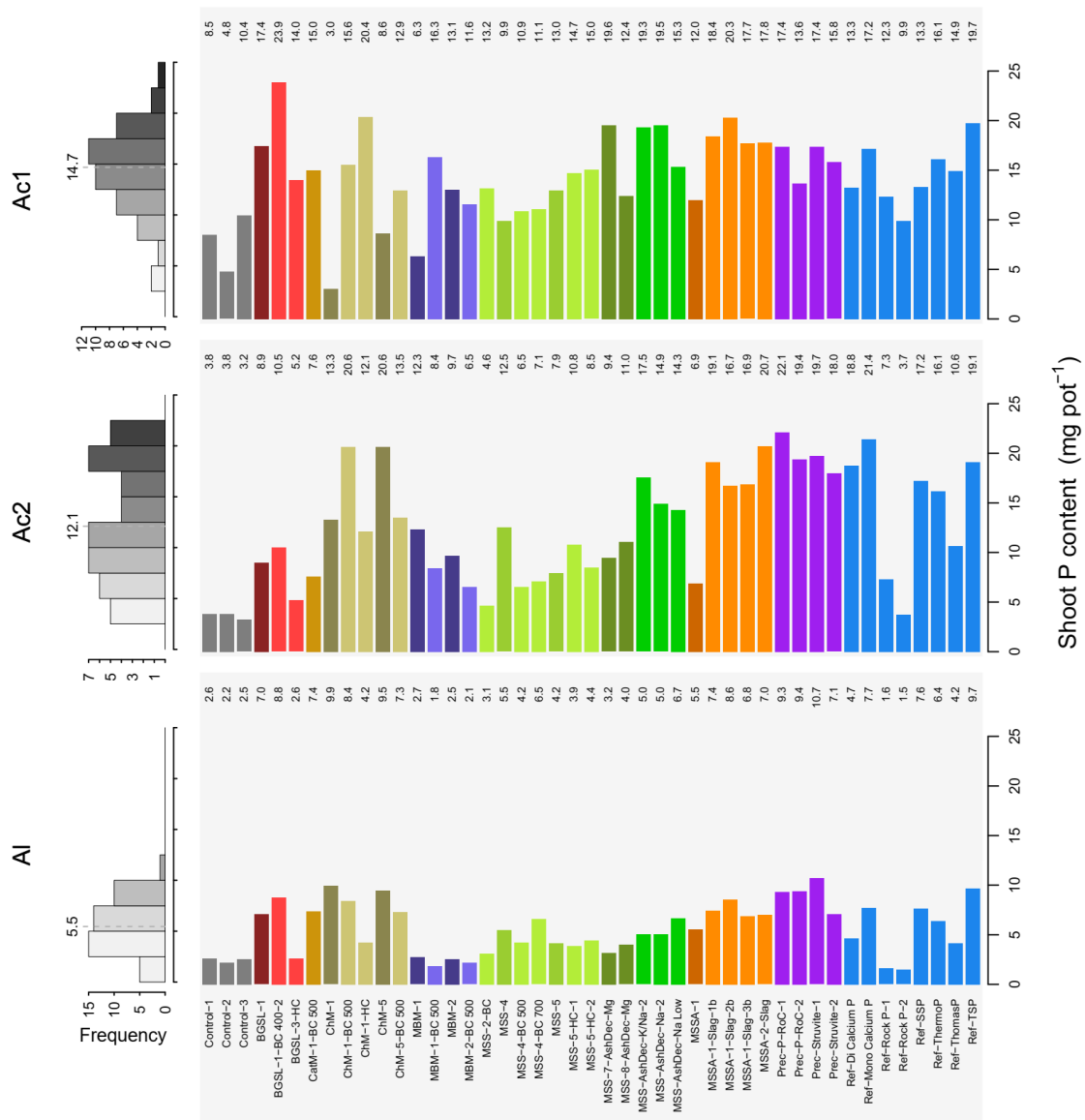
Figure S2: Shoot P content in each pot. In the histograms, the dotted line and the value above it is the median.
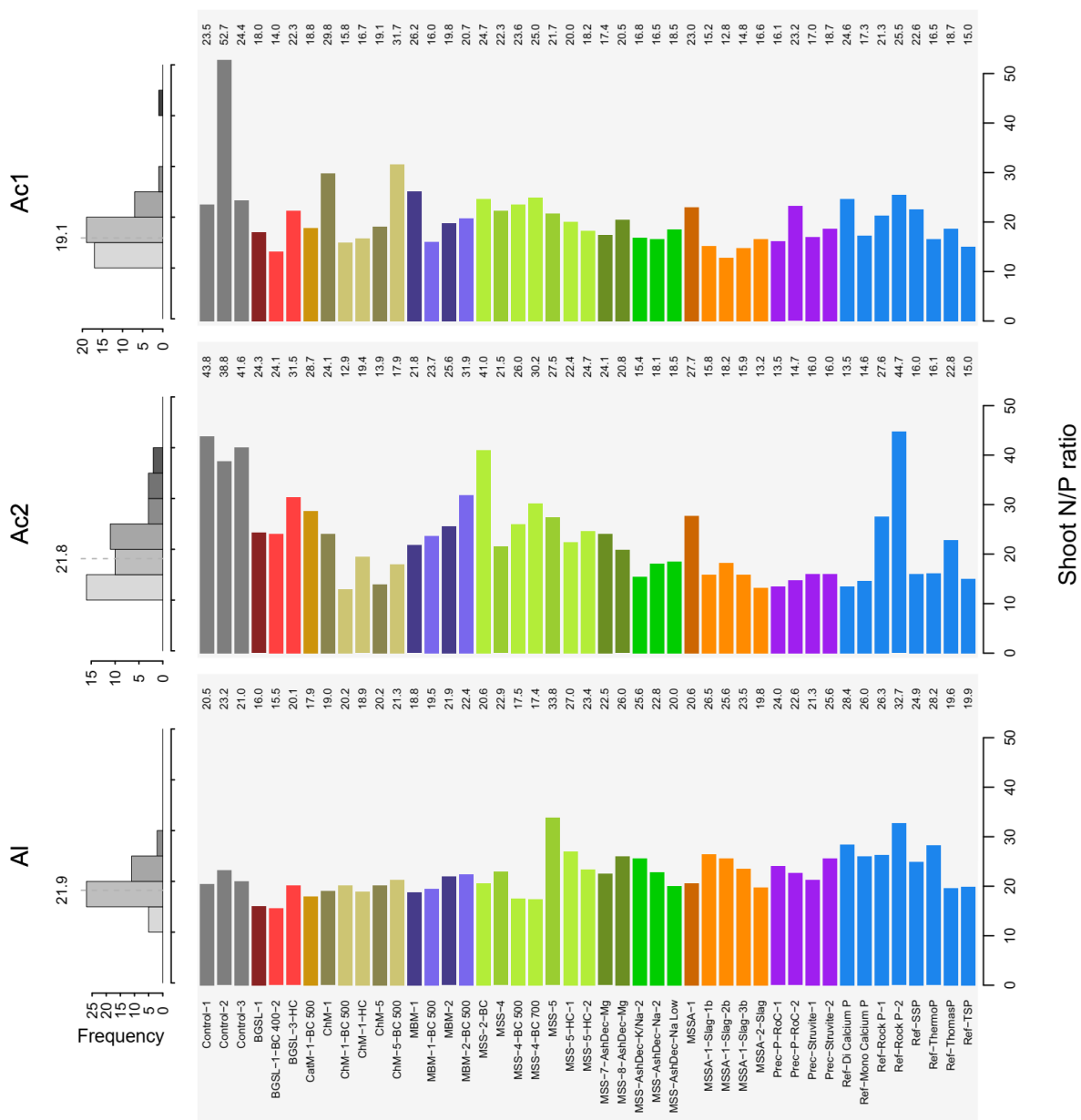
Figure S3: Shoot N/P mass ratio. In the histograms, the dotted line and the value above it is the median.

Responsiveness of the Ac1 soil to P fertilizer

Among the three soils used in this study, the Ac1 soil showed the weakest regressions between fertilizer extraction methods and plant growth or P uptake. To some extent, it appears that the soil was not responsive to P addition. Here we show that despite this appearance, there was in fact a response to P addition.

Although we cannot directly compare fertilizers against each other (n = 1), it is possible to compare different fertilizer groups. In Table S5 we show the difference of shoot biomass between (1) the three unfertilized controls and the three water-soluble references ("Ref-SSP", "Ref-TSP" and "Ref-Mono Calcium P") and (2) the three unfertilized controls and the three pots with the largest biomass. The results confirm that there was a response to P addition in that soil.

Table S5: Difference of shoot biomass (g pot^{-1}) in the Ac1 soil between the three unfertilized controls and selected groups of fertilized treatments: either (1) the three soluble references or (2) the three pots with the largest biomass.

		Mean of the controls	Mean of the alternative	p-value (Welch's t-test)
		g pot^{-1} ± standard deviation of means		
(1)	Unfertilized controls vs H$_2$O-soluble fertilizers "Ref-TSP", "Ref-SSP", "Ref-Mono Calcium P")	4.79 ± 0.13	6.67 ± 0.26	0.00841
(2)	Unfertilized controls vs pots with the largest biomass	4.79 ± 0.13	7.50 ± 0.07	0.00035

Comparison of regressions on the neutral soil between this study and our previous study
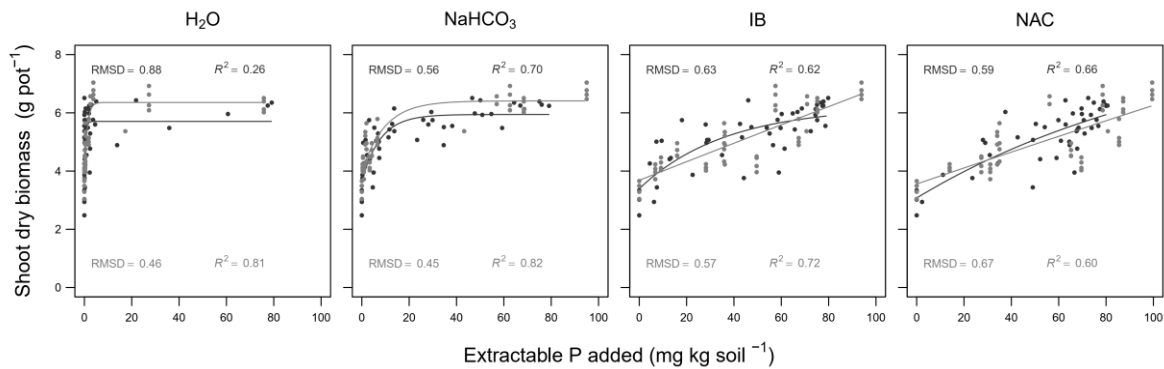

Figure S4: Comparison of the regressions of shoot biomass vs. extractable P in this study (dark color) and our previous study (Duboc et al., 2017) (light color) for the slightly acidic (Ac2) soil. In the previous study, soil was fertilized with 100 mg P kg^{-1} while in this study we used 80 mg P kg^{-1}. To make the results comparable, the independent variable is the amount of extractable P *added to the soil* (mg P kg soil^{-1}), and not the amount of extractable P in % of total P as in the main part of the publication.
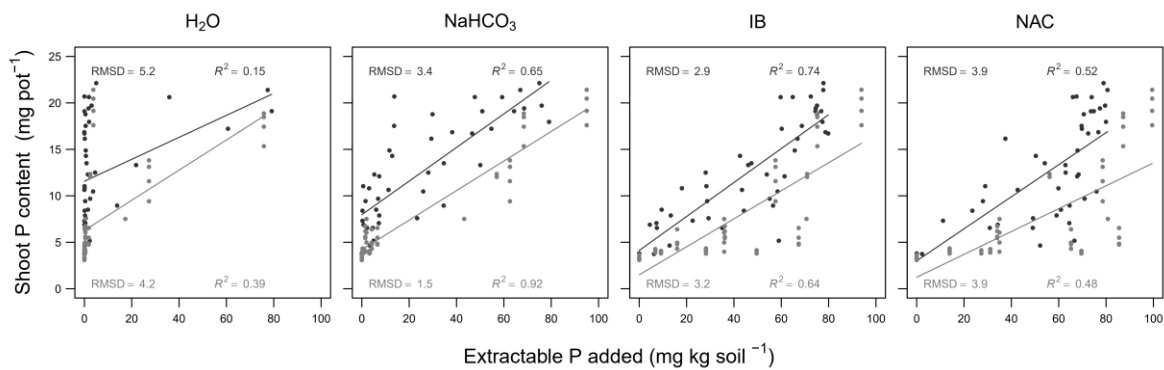

Figure S5: Comparison of the regressions of shoot P content vs. extractable P in this study (dark color) and our previous study(Duboc et al., 2017) (light color) for the slightly acidic (Ac2) soil. In the previous study, soil was fertilized with 100 mg P kg^{-1} while in this study 80 mg P kg^{-1} was used. To make the results comparable, the independent variable is the amount of extractable P added to the soil (mg P kg soil^{-1}), and not the amount of extractable P in % of total P as in the main part of the publication.

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