The chemical interaction of Biochar with Fe and Phosphate might explain the effects of Biochar in alkaline and calcareous Soils

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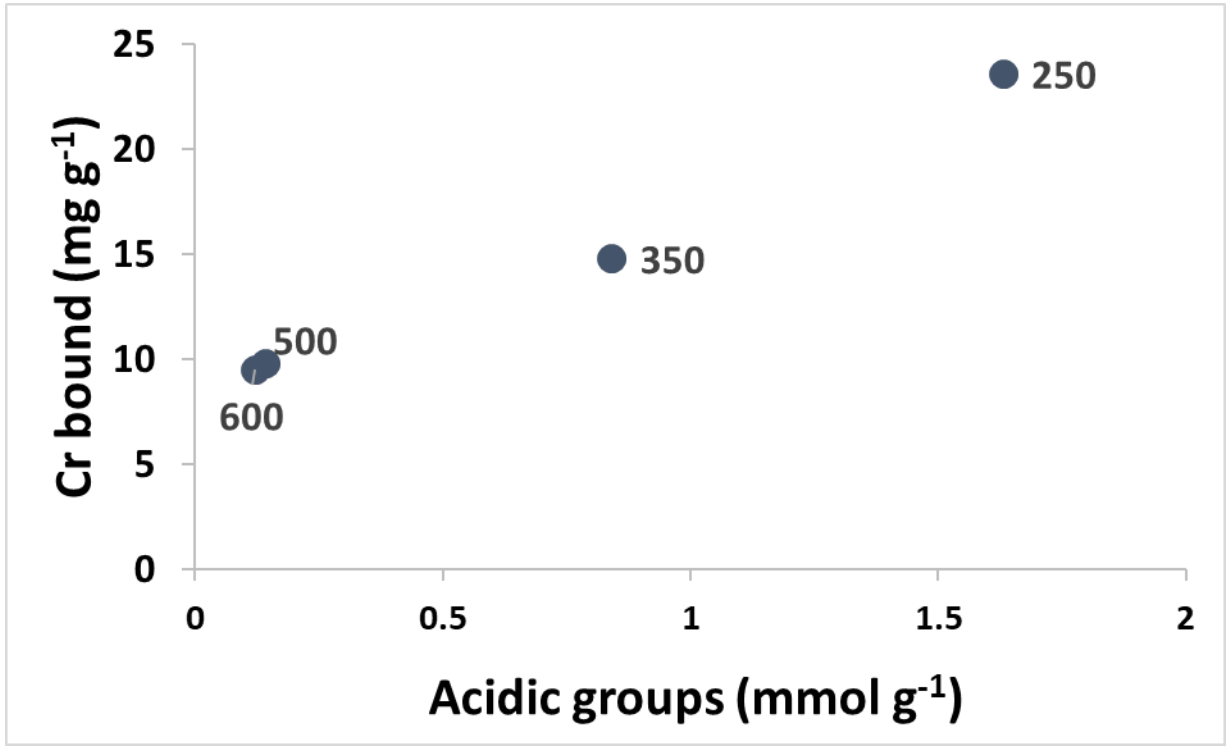
- Biochar applications as soil amendments in acidic soils has positive effects.
- But, biochar applications on alkaline or calcareous soils have not effects or indeed negative effects.

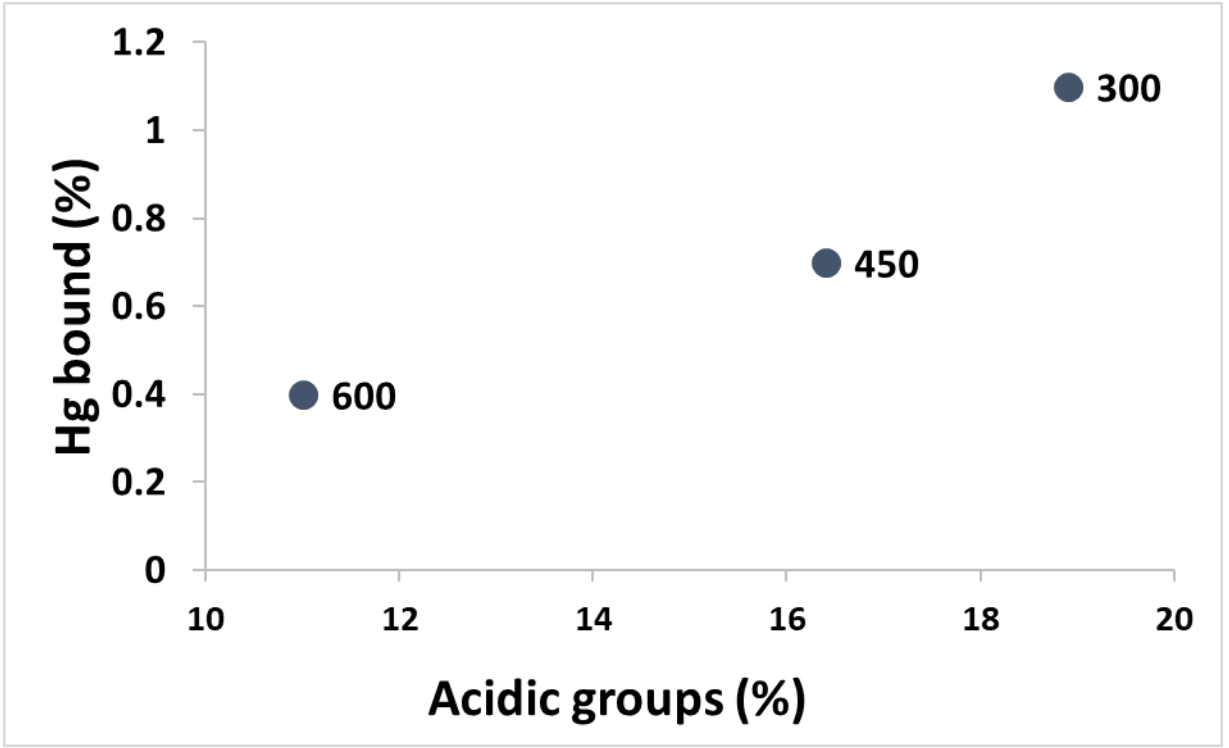
So Biochar as amendment is controversial among scientific community

In this way, we tried to explain why biochar shows this behavior in each different pH soil.

Biochar Election

As Literature shows, the most manufacturing temperature the less reactive (carboxylate) groups. Biochar chosen was manufactured at 400 °C, so a well-balanced biochar.





Shen et al. (2012) Bioresource Technology, 104, 165–172

Dong et al. (2013) Environmental Science and Technology, 47, 12156−12164

Biochar Characterization

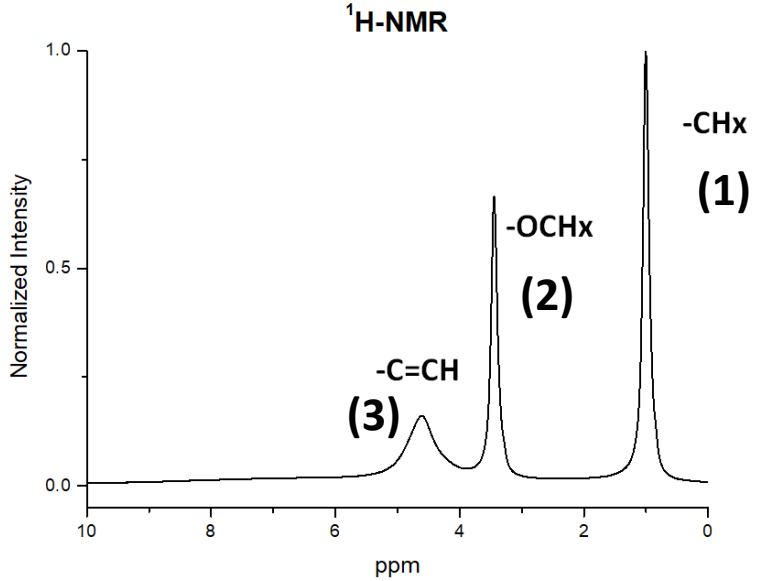
- Nutrients content by ICP.
- Structure by H^1- and C^{13}-NMR as well as FTIR.

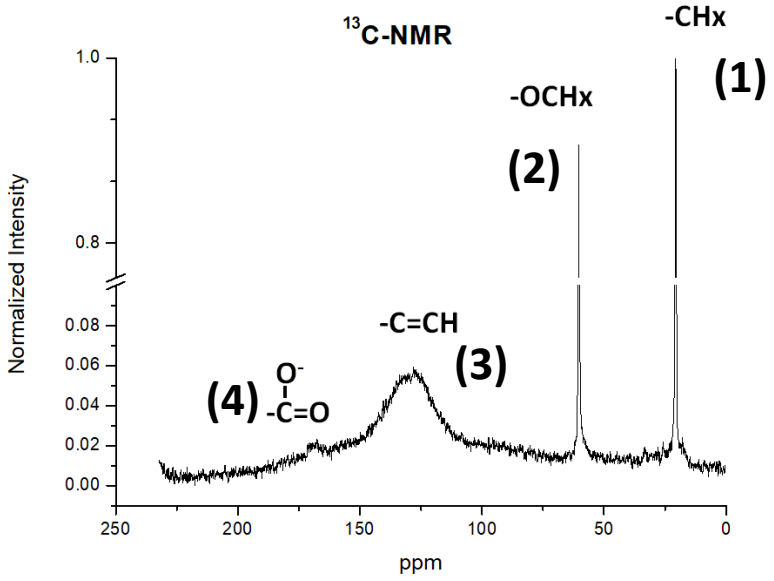
A Calcium carboxylate Biochar with mainly aromatic character completed with aliphatic chains and methoxy groups.

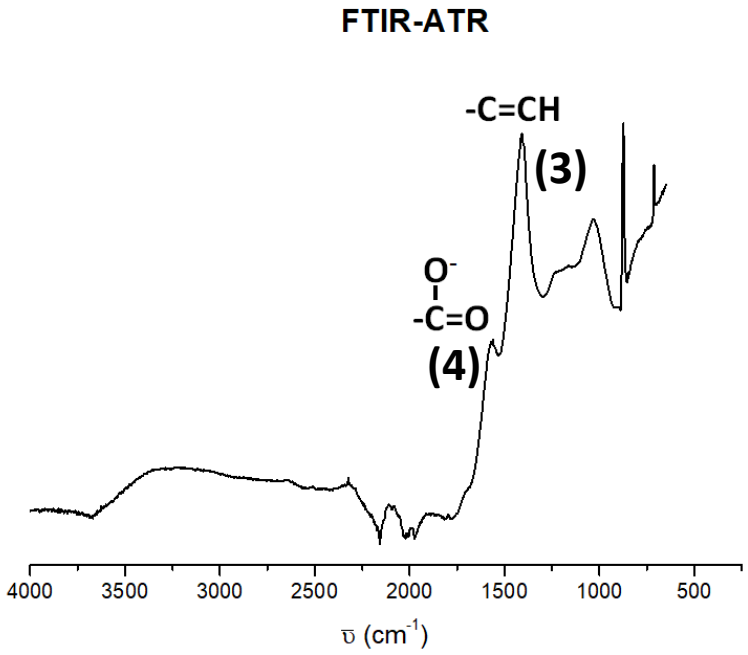
Biochar Characterization

Nutrients content by ICP

mg kg^{-1}	Al	B	Ca	Cu	Fe	K	Mg
Biochar	1092	70.8	58492	26.5	953	6601	6459
	Mn	Mo	Na	P	S	Si	Zn
	678	< 0.1	1005	1981	663	1715	70.8







- Aliphatic chains (1)
- Methoxy groups (2)
- Double C (Aromatic) bounds (3)
- Carboxylate groups (4)

Experimental Scheduled

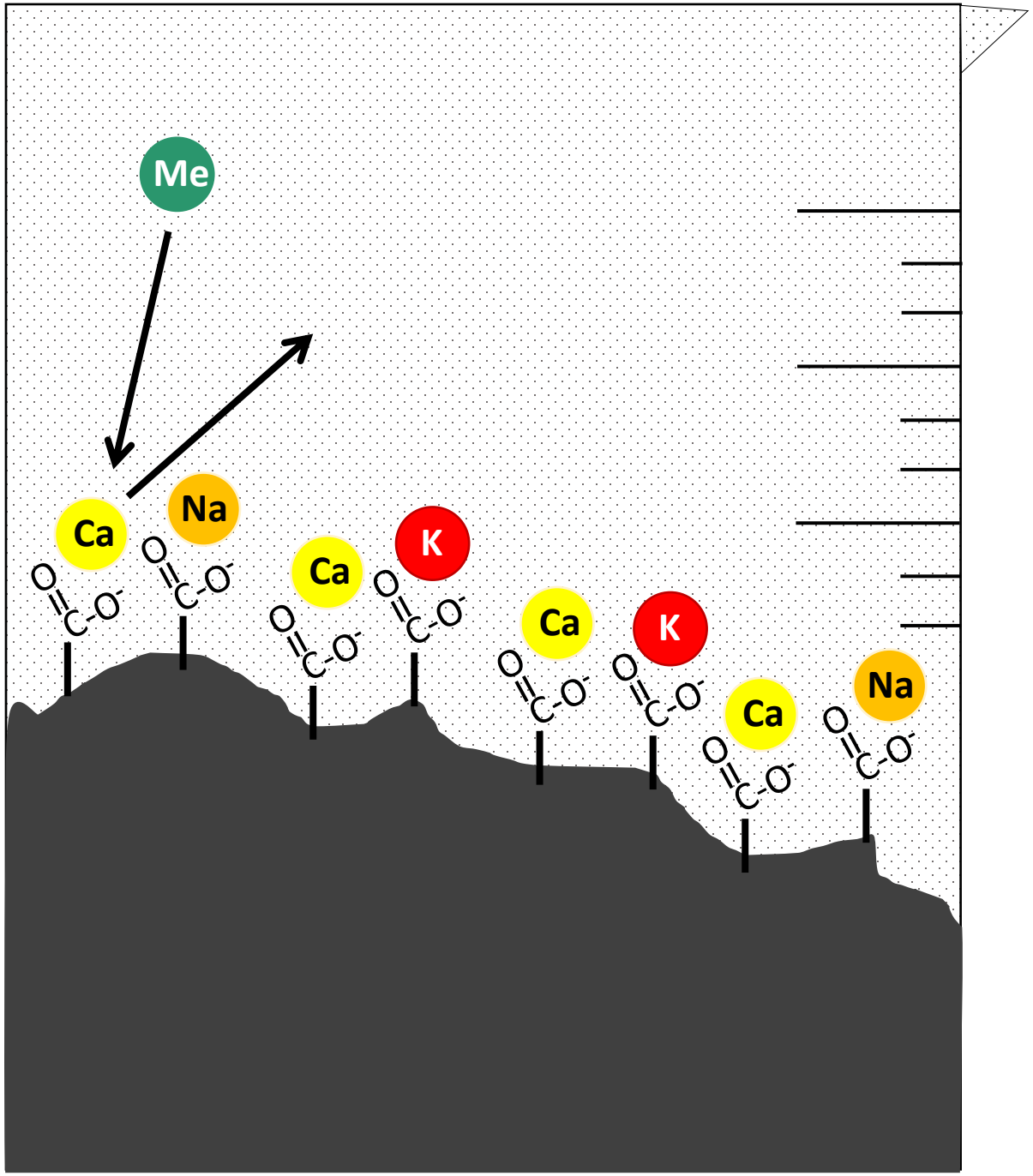
1. Biochar as Amendment:

- Adsorption kinetics.
- Desorption kinetics.
- Soil incubations.
- Greenhouse experiment in acidic and alkaline soil.

2. Biochar into Fertilizer matrix:

- Integration in complex fertilizer.
- Growth chamber experiment.
- Field experiment in alfalfa and vineyard.

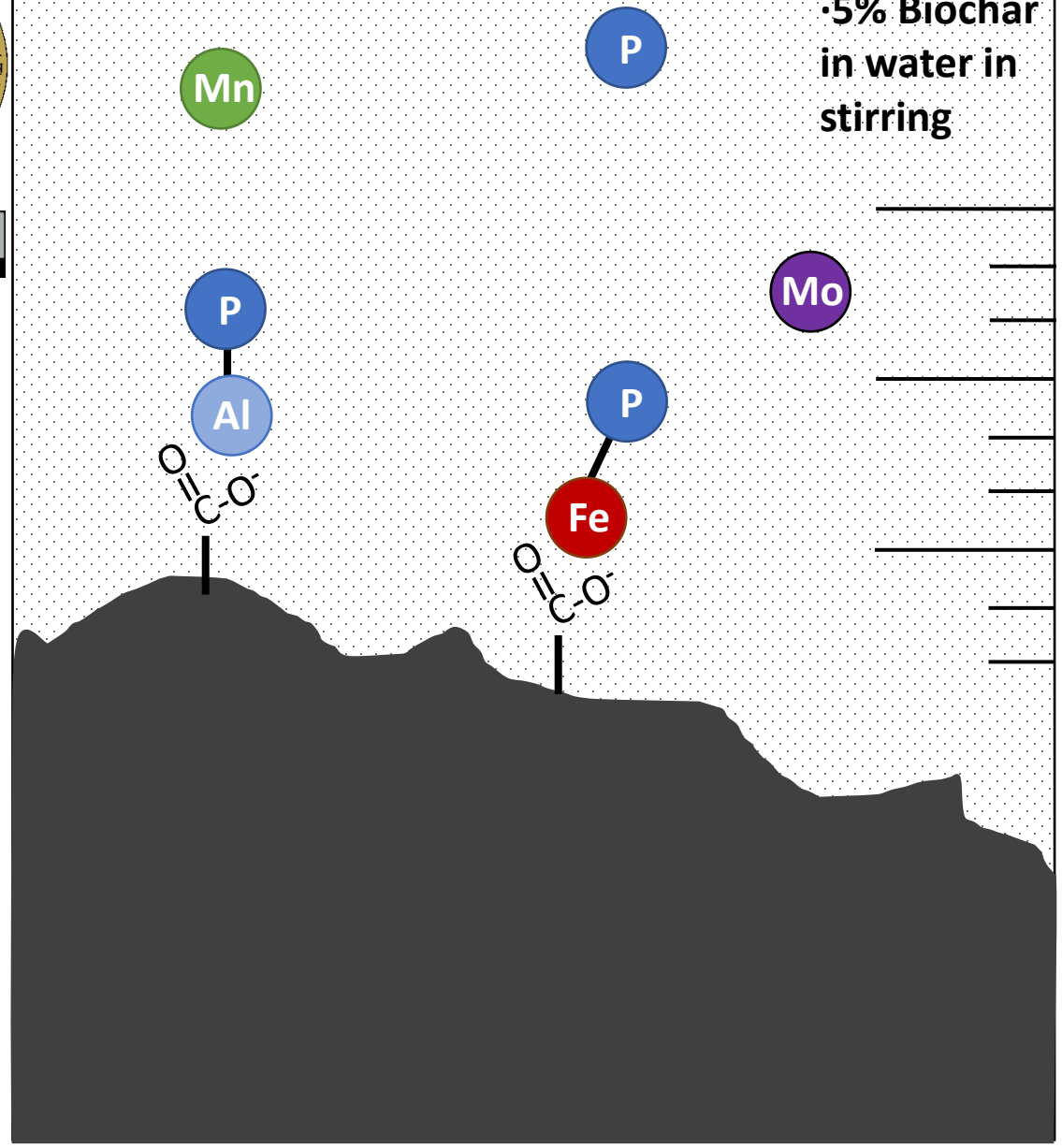
1. Biochar as Amendment

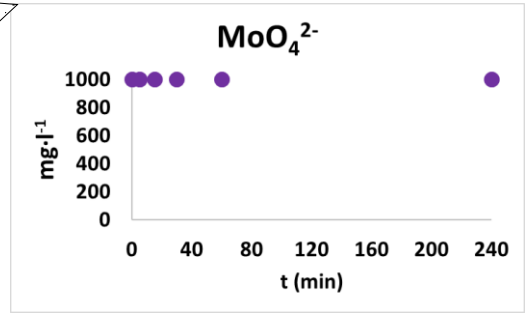


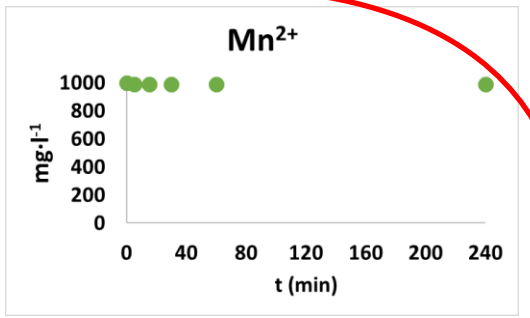
Absorption kinetics by substitution of Ca with micronutrients (metals) and macronutrient (phosphorus)

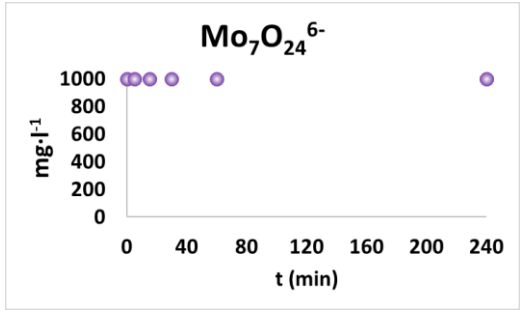
Absorption

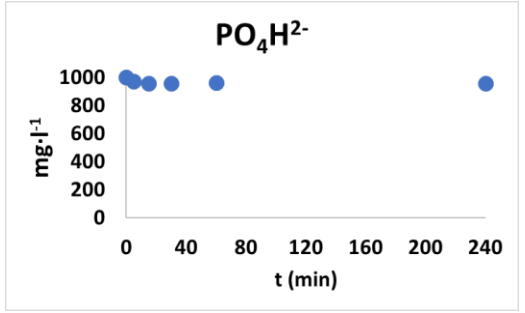
- 1000 ppm
- 240 min
- 5% Biochar in water in stirring

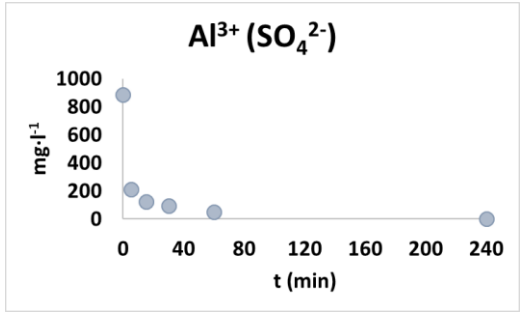


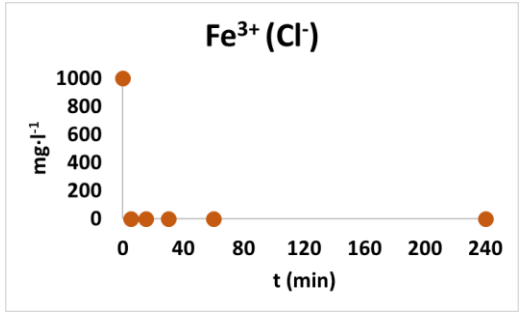


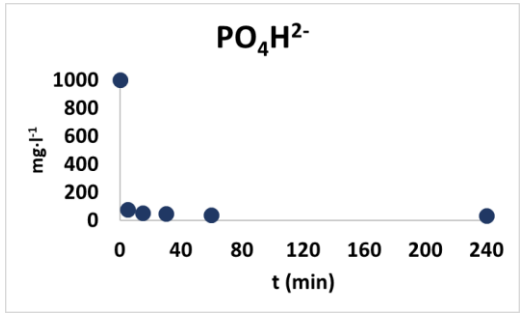


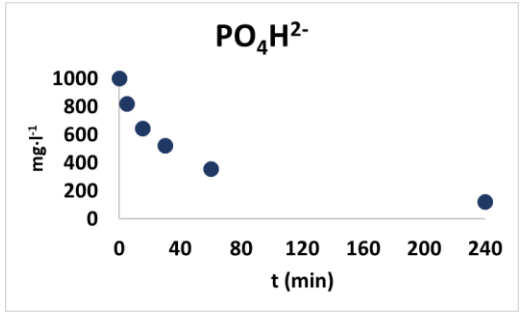




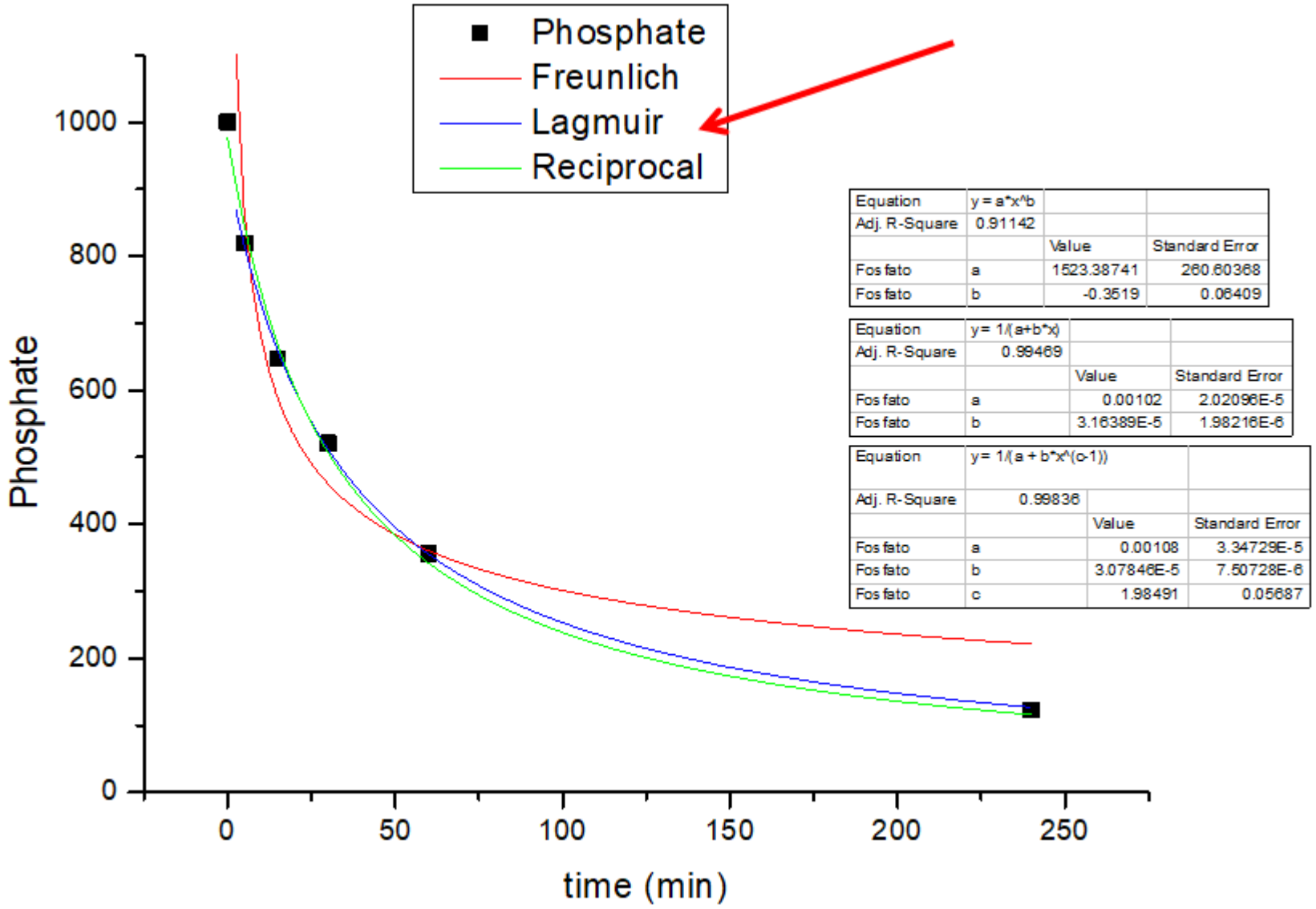








Phosphate adsorption



Equation	y = a*x^b		
Adj. R-Square	0.91142		
		Value	Standard Error
Fosfato	a	1523.38741	260.60368
Fosfato	b	-0.3519	0.06409

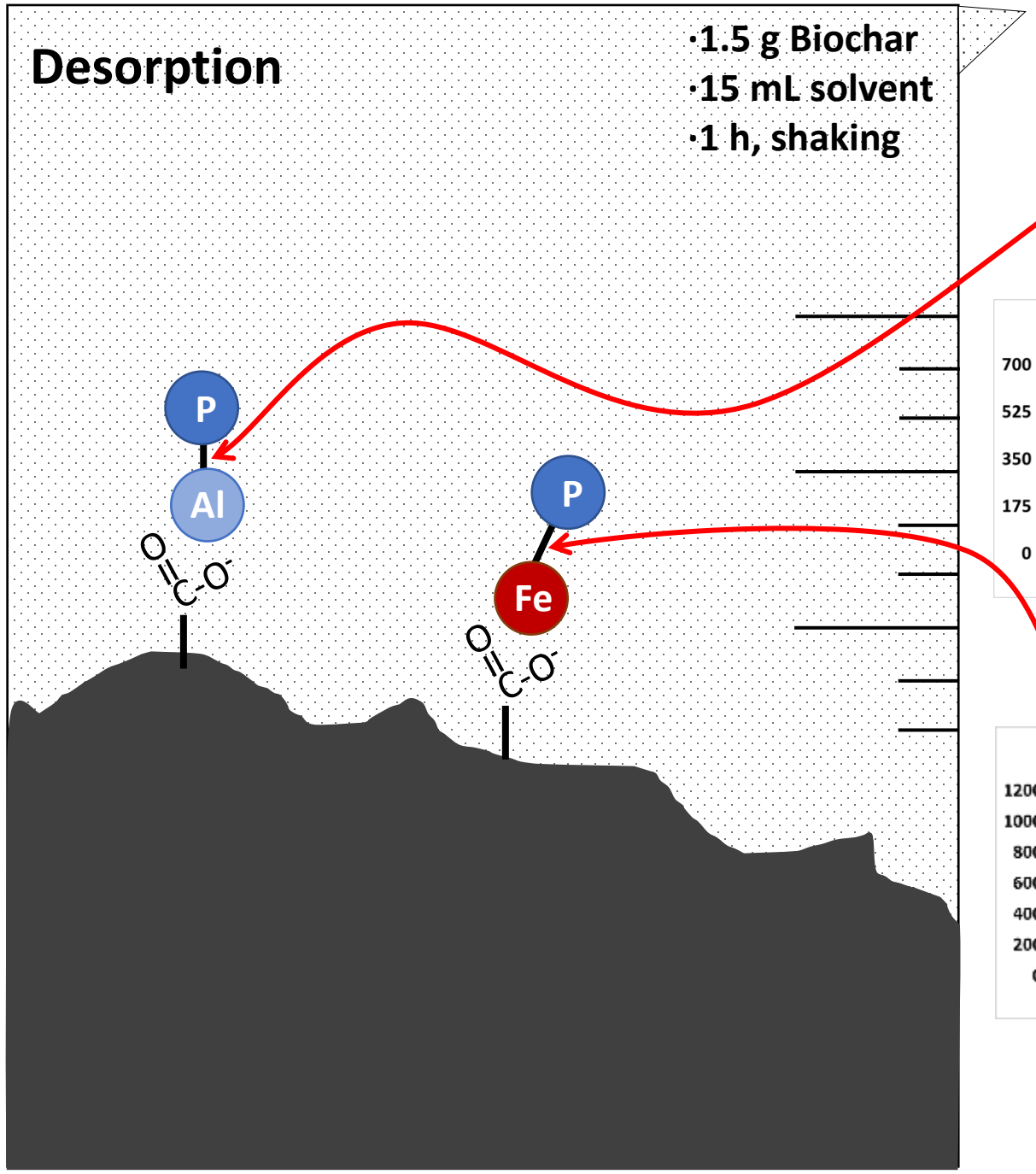
Equation	y= 1/(a+b*x)		
Adj. R-Square	0.99469		
		Value	Standard Error
Fosfato	a	0.00102	2.02096E-5
Fosfato	b	3.16389E-5	1.98216E-6

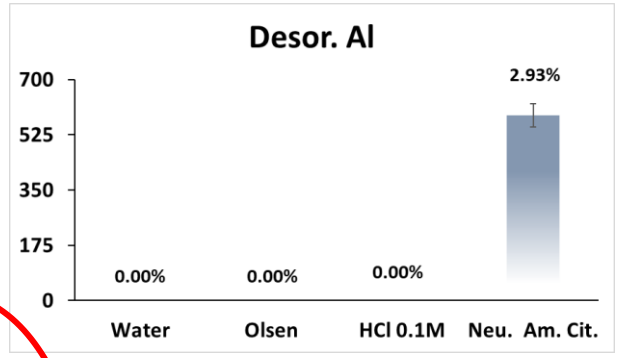
Equation	y= 1/(a + b*x^(c-1))		
Adj. R-Square	0.99836		
		Value	Standard Error
Fosfato	a	0.00108	3.34729E-5
Fosfato	b	3.07846E-5	7.50728E-6
Fosfato	c	1.98491	0.05687

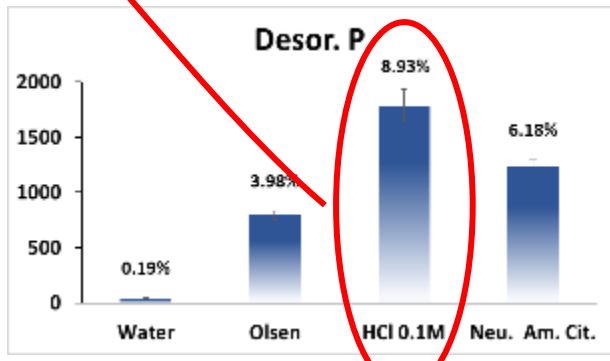
Phosphate adsorption

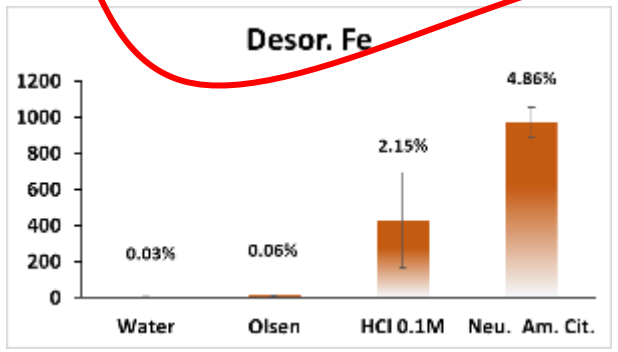
- Mn, Mo or P directly, were not adsorbed.
- Al and Fe yes, were adsorbed.
- P is only adsorbed when previously Al or Fe are before adsorbed onto biochar.

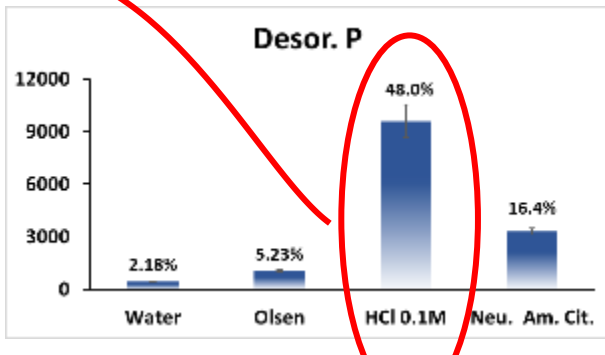
  following a Langmuir or reciprocal mathematical model.


Desorption
·1.5 g Biochar
·15 mL solvent
·1 h, shaking
P
Al
O=C-O-
P
Fe
O=C-O-


Desor. Al
700
525
350
175
0
0.00%
0.00%
0.00%
2.93%
Water
Olsen
HCl 0.1M
Neu.
Am. Cit.

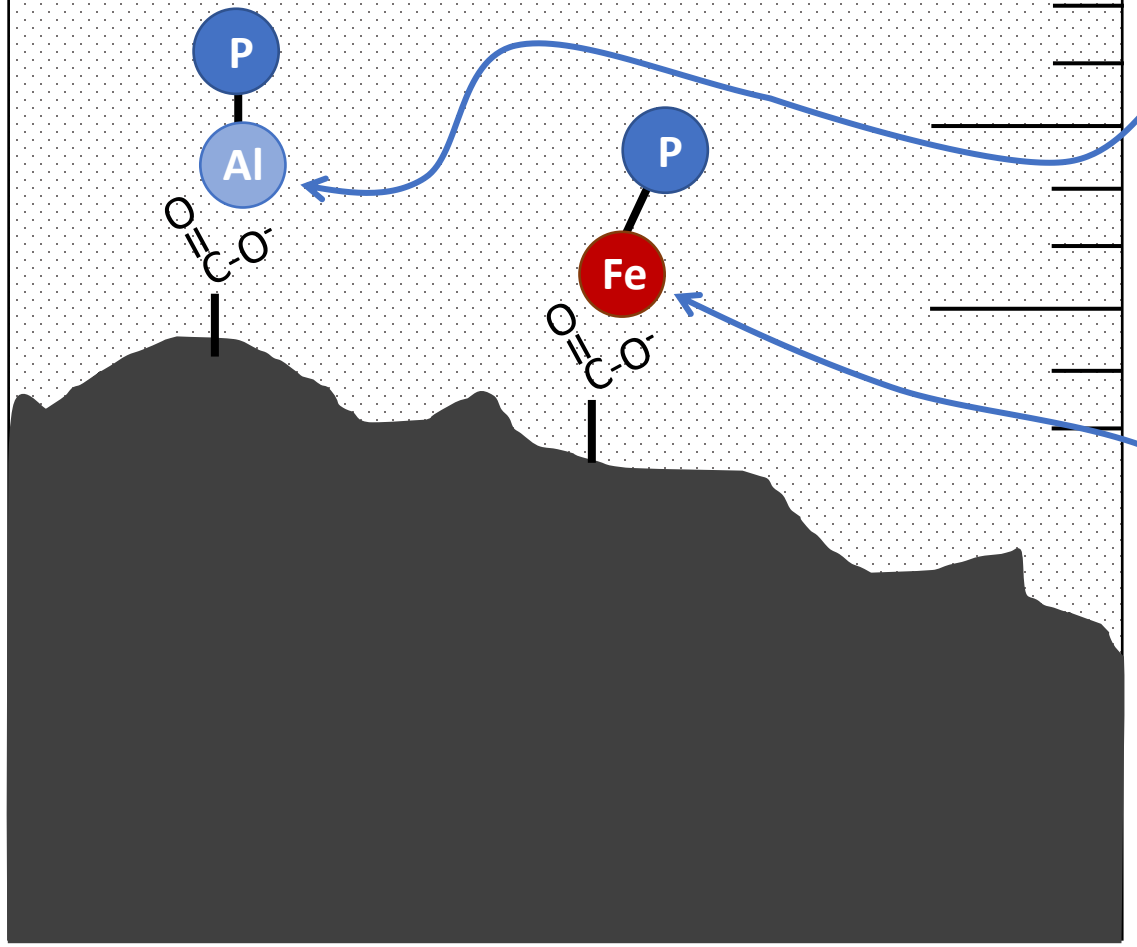

Desor. P
2000
1500
1000
500
0
0.19%
3.98%
8.93%
6.18%
Water
Olsen
HCl 0.1M
Neu.
Am. Cit.

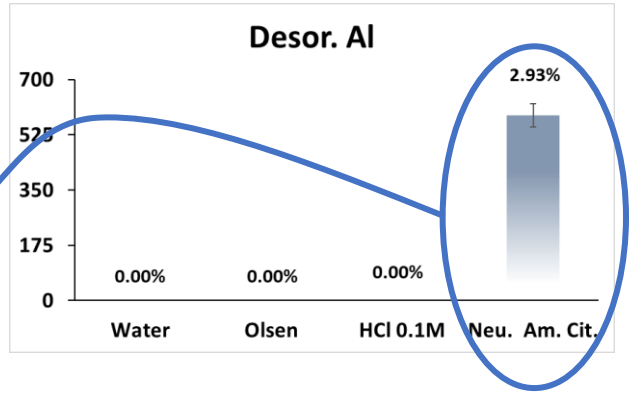

Desor. Fe
1200
1000
800
600
400
200
0
0.03%
0.06%
2.15%
4.86%
Water
Olsen
HCl 0.1M
Neu.
Am. Cit.

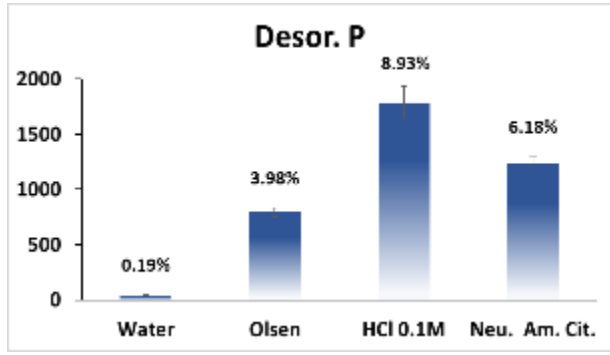

Desor. P
12000
9000
6000
3000
0
2.18%
5.23%
48.0%
16.4%
Water
Olsen
HCl 0.1M
Neu.
Am. Cit.

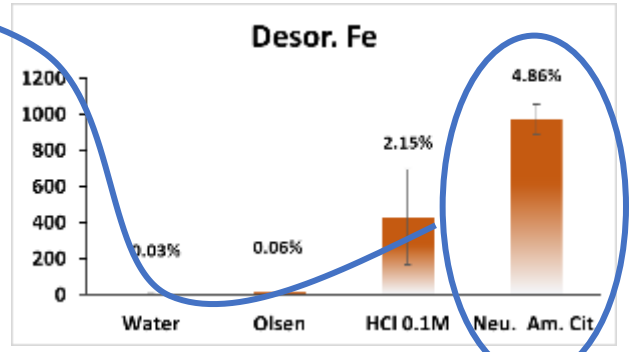
Desorption

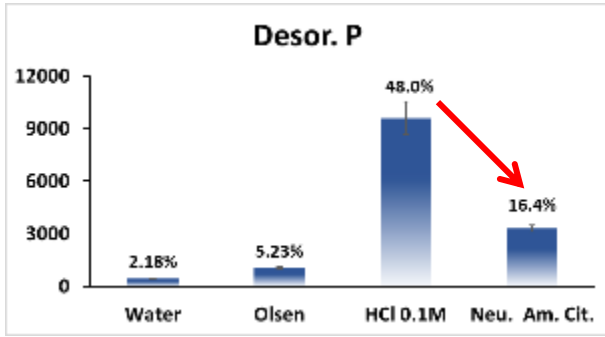
·1.5 g Biochar
·15 mL solvent
·1 h, shaking











Phosphate desorption

- P was desorbed by acidic hydrolysis principally.
- Al and Fe were desorbed by neutral ammonium citrate bound breakdown.
- This implies two different desorption mechanisms.

Soil incubations

EGU European Geosciences Union

Δ%= Difference in relation to soil without biochar

Soil Avaibility

+

-

Acidic Soil

Alkaline Soil

Major

Macros

Micros

7 days

Δ %	Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	P	S	Zn
Eugi												
Girona												
Zizur												
Marcilla												

15 days

Δ %	Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	P	S	Zn
Eugi												
Girona												
Zizur												
Marcilla												

In acidic soils, Al, Cu, Fe, Zn and P were less available after 15 days but Ca and Mg were more.

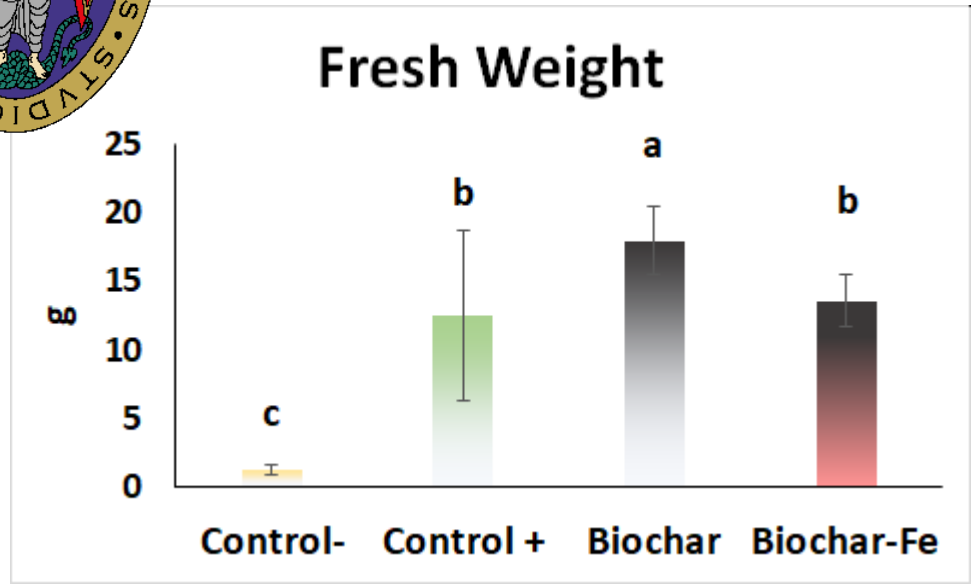
Greenhouse Experiment

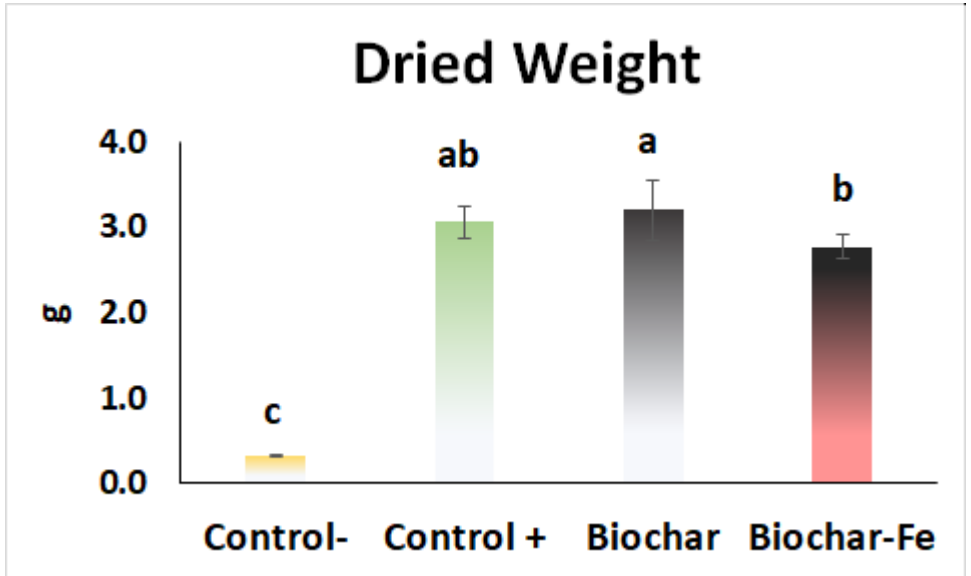
Acidic soil

Alkaline soil

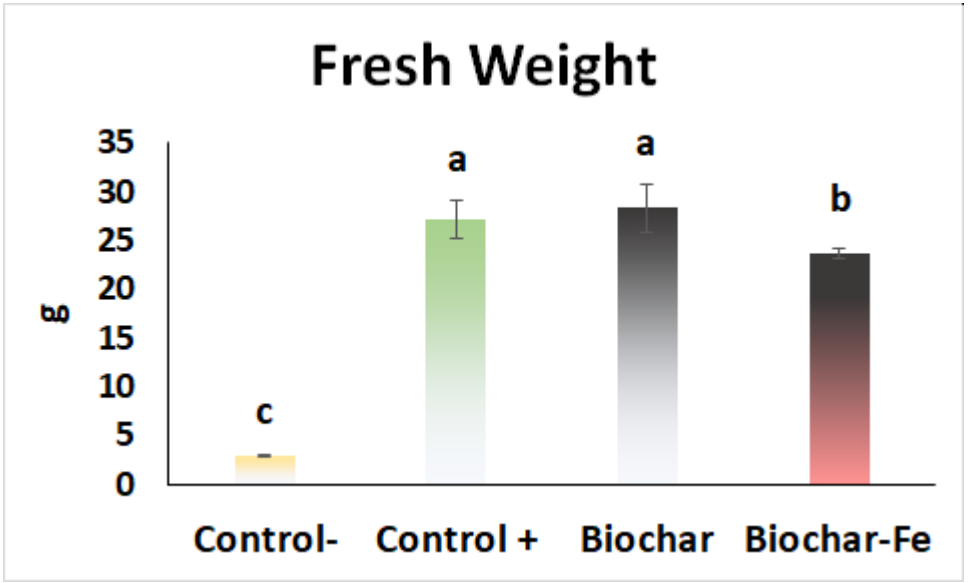
Greenhouse Experiment

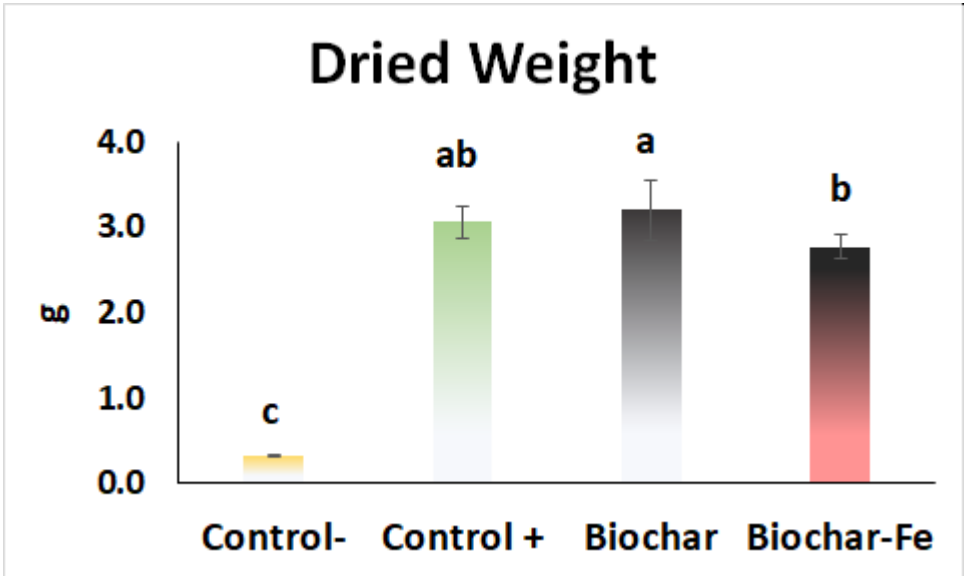
Acidic soil





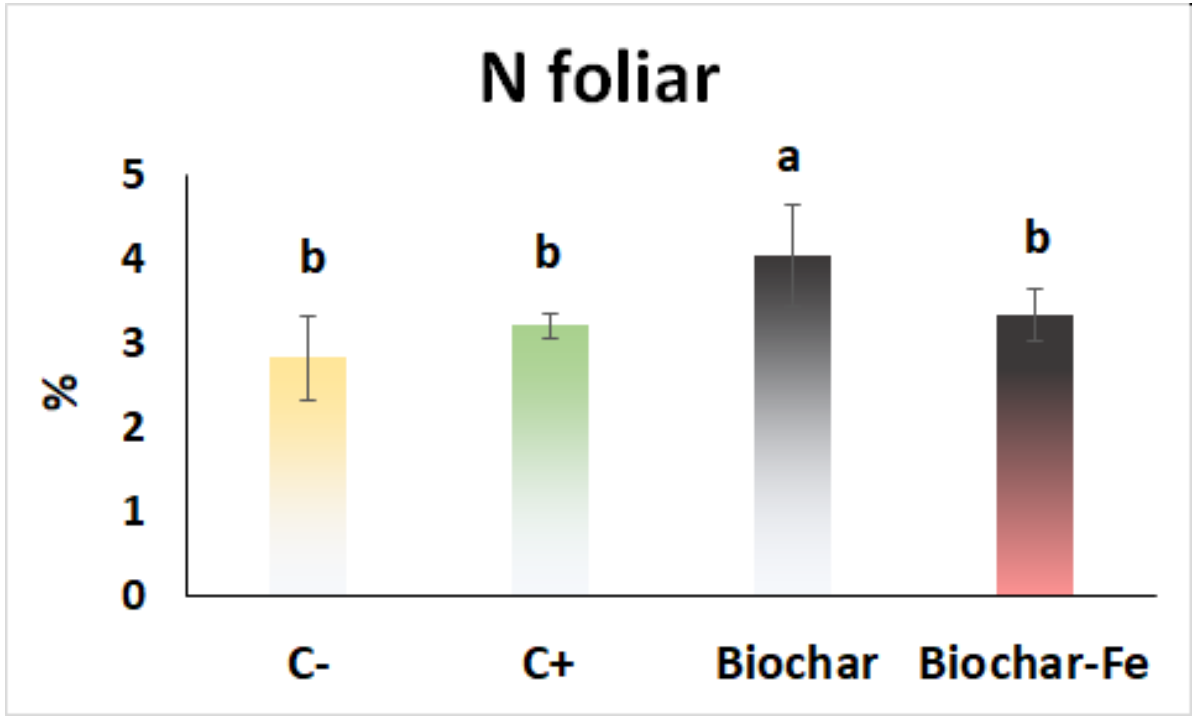
Alkaline soil



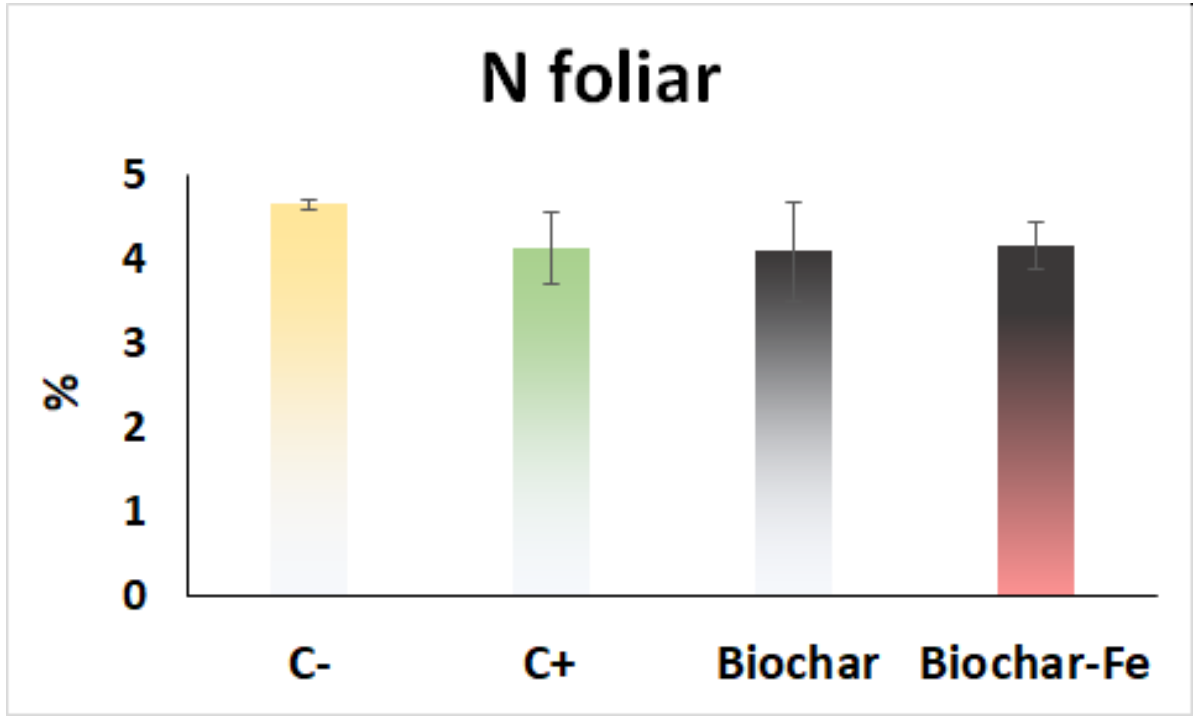


Greenhouse Experiment

Acidic soil



Alkaline soil



Greenhouse Experiment

Acidic soil

	mg k^{-1}	C-	C+	Biochar	Biochar-Fe		C-	C+	Biochar	Biochar-Fe
mean	Al	296	134	97.8	121	Mn	201	381	207	442
S.D.		43.8	57.4	44.6	40.4		45.5	78.6	24.7	89.6
	B	23.6	16.7	34.6	25.4	Mo	0.67	0.25	0.21	0.25
		8.35	1.54	3.55	2.66		0.29	0.00	0.09	0.00
	Ca	21991	20252	30832	22595	Na	596	192	266	370
		44.9	1017	2340	3909		38.1	476.3	71.2	101
	Cu	13.9	19.8	16.1	21.8	P	525	819	834	844
		5.08	1.97	1.34	2.50		107	77.9	45.7	97.7
	Fe	268	165	137	136	S	3462	2250	2701	2253
		40.1	51.6	34.0	27.6		204	179	213	330
	K	26922	27385	26323	28469	Si	124	72.0	139	116
		3764	4408	2911	4552		69.0	27.8	24.8	51.8
	Mg	1539	991	972	1099	Zn	74.8	37.0	34.0	41.7
		502	123	159	200		23.4	8.04	6.90	9.39

Alkaline soil

	mg k^{-1}	C-	C+	Biochar	Biochar-Fe		C-	C+	Biochar	Biochar-Fe
mean	Al	83.2	49.7	60.5	59.7	Mn	112	52.1	57.5	53.8
S.D.		22.6	18.5	17.7	9.52		33.4	8.83	10.0	4.7
	B	27.3	31.2	36.4	34.9	Mo	1.97	2.62	2.80	2.43
		8.46	3.48	3.18	2.82		1.76	0.38	0.21	0.47
	Ca	49453	50746	51925	56174	Na	512	344	368	279
		883	1406	1711	3854		61.7	25.1	12.0	26.3
	Cu	15.6	12.9	11.6	11.7	P	1127	2221	2454	2363
		2.80	1.17	2.19	1.01		182	268	410	342
	Fe	149	165	153	144	S	4119	3097	3859	3849
		0.15	29.0	26.0	8.03		11.5	143	468	256
	K	32160	30398	35320	35534	Si	74.4	87.9	118	125
		5843	3067	3647	1387		13.6	13.1	18.5	42.6
	Mg	4207	3356	3673	3769	Zn	52.5	37.1	37.3	33.5
		424	268	454	371		15.6	8.14	4.92	3.04

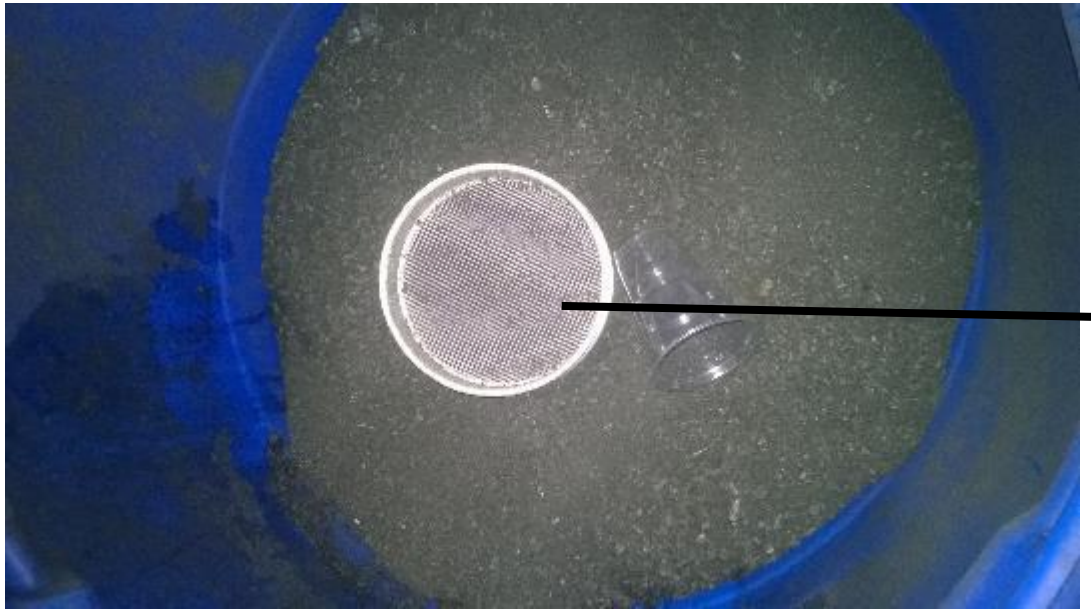
Conclusion

1. Biochar as Amendment

- Phosphate is adsorbed through Fe and Al bridges in adsorption experiments and release by acidic hydrolysis.
- In soil incubation, P and micronutrients are less available in both acidic and alkaline soils. Ca, Mg and S are more available in acidic soil.
- There are and increase in Fresh and Dried weight in acidic soil in Biochar treatment in comparison to Control+. But not in alkaline soil.
- N followed the same behavior.
- In acidic soil Ca, Mg and S, in general, are more limitans than P and micronutrients, this could be the reason of the improvement of biochar.

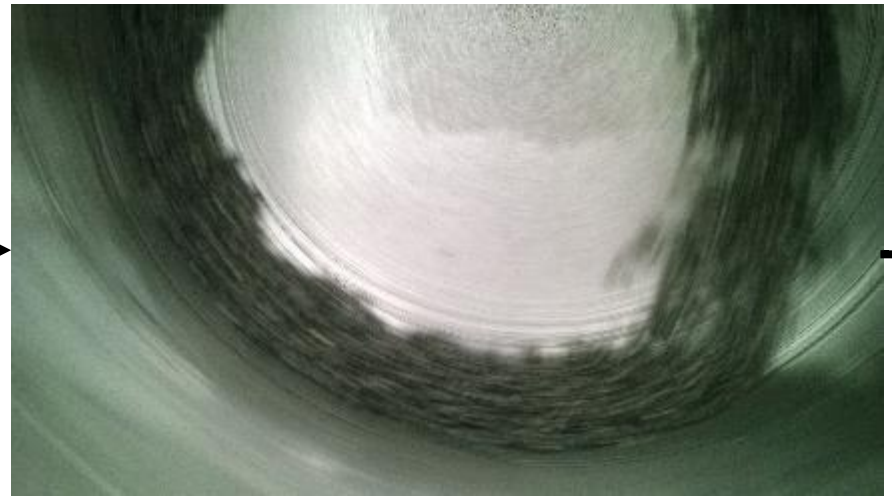
2. Integration in complex fertilizer

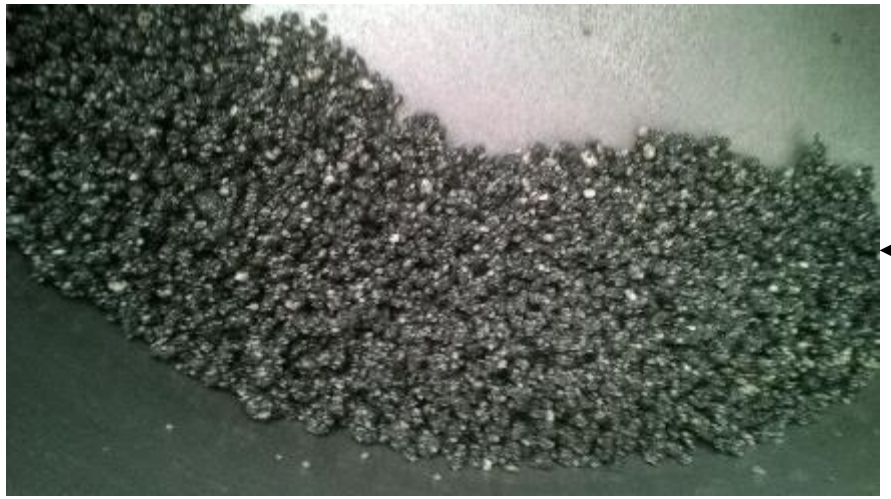
Size no available to make granulated fertilizer



Essential to sieve < 1.6 mm

Biochar-N fertilizer





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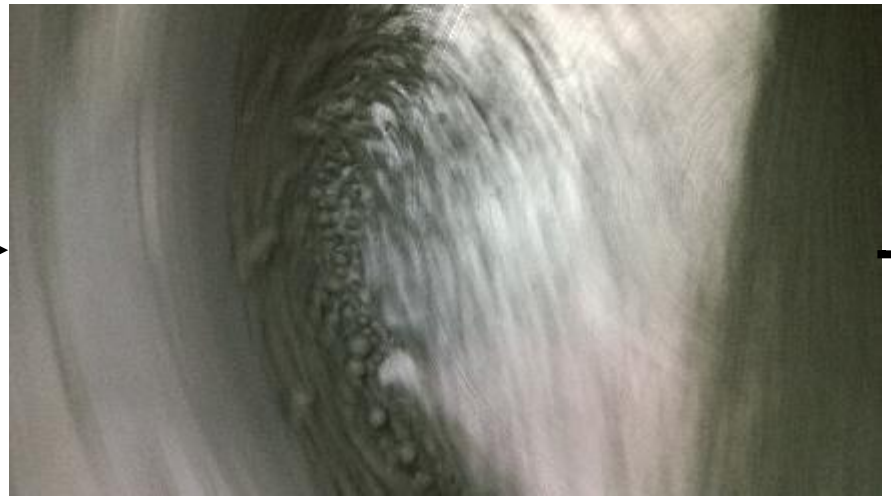
Biochar-P fertilizer



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1% Biochar

5% Biochar

Growth chamber Experiment

Fertilization (kg/ha)

- N23 300 ≡ 30 g/ m^2
- 0-8-12 500 ≡ 50 g/ m^2
- Pot: 81 cm^2 ≡ 0.0081 m^2
- 0.25 g/pot N23
- 0.41 g/pot (0-8-12)

Irrigation

- Field Capacity: 140 g of Water/pot
- 480g of Soil/pot
- 6 Ippon R1 variety wheat plant/pot

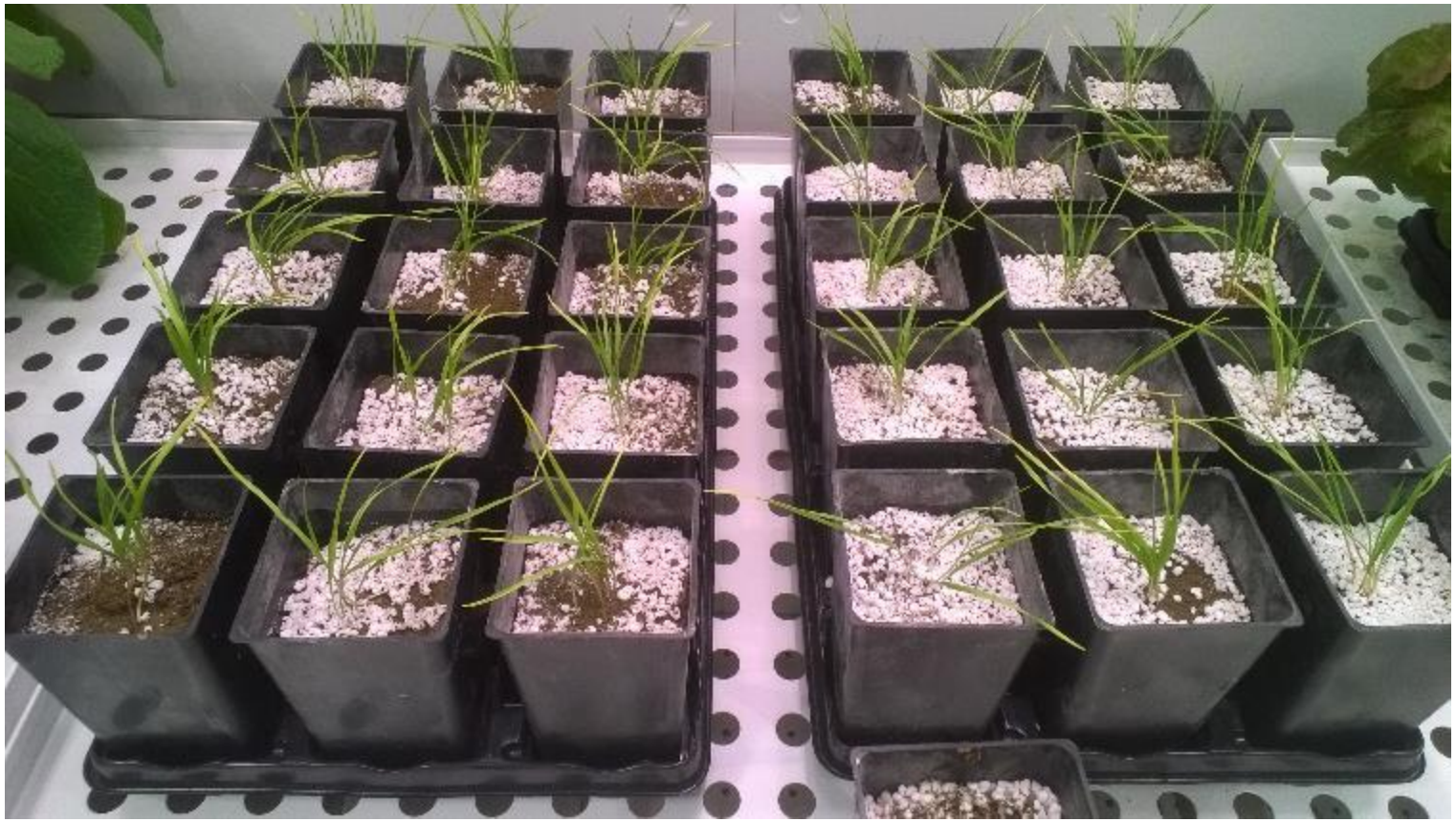
Growth chamber Experiment

Day 1

P Assay

N Assay

N23

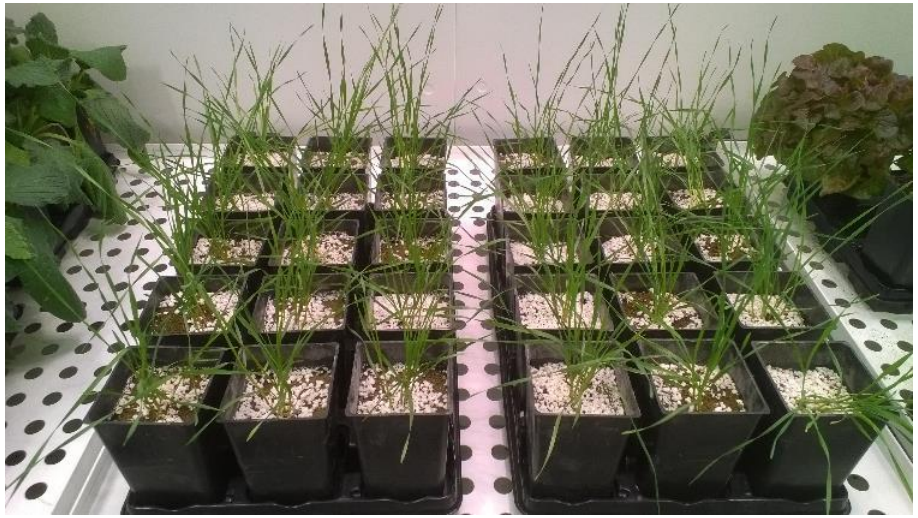


0-8-12

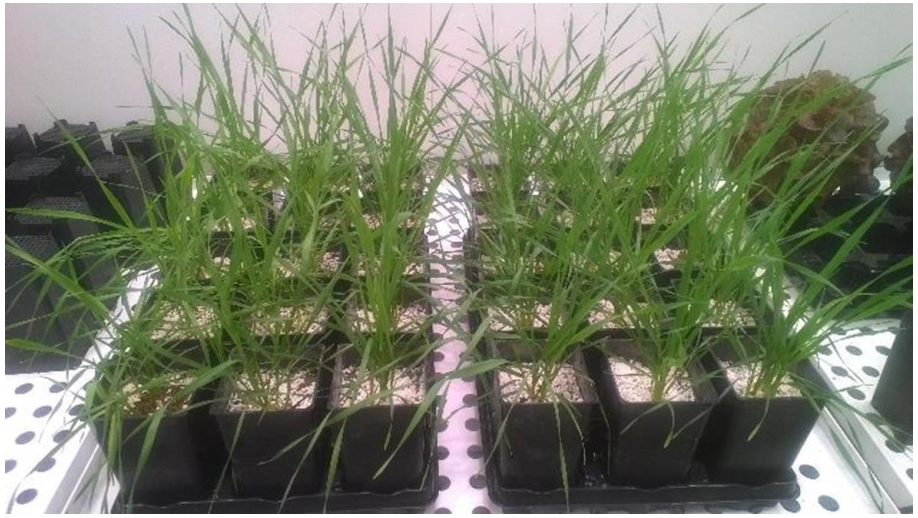
Pchar-5 Pchar-1 0-8-12 N23 Nchar-1 Nchar-5

Growth chamber Experiment

Day 13



Day 25



Day 41

Day 60

Growth chamber Experiment

N Assay

FW (g)	N23	N-CHAR1	N-CHAR5
1	8.81	11.15	11.77
2	12.75	10.72	10.54
3	11.27	11.43	8.63
4	10.47	12.14	9.89
5	10.01	12.32	9.71

DW (g)	N23	N-CHAR1	N-CHAR5
1	1.46	1.75	2.01
2	1.91	1.48	1.68
3	1.73	1.64	1.37
4	1.42	1.72	1.38
5	1.49	1.97	1.32

LSD test; variable PF (g) (Spreadsheet1)
Homogenous Groups, alpha = .05000
Error: Between MS = 1.3137, df = 12.000

Cell No.	Trat	PF (g) Mean	1
3	NChar5	10.10800	****
1	SUL23	10.66200	****
2	NChar1	11.55200	****

LSD test; variable PF (g) (PS NChar)
Homogenous Groups, alpha = .05000
Error: Between MS = .05390, df = 12.000

Cell No.	Trat	PF (g) Mean	1
3	NChar5	1.552000	****
1	SUL23	1.602000	****
2	NChar1	1.712000	****

No differences were observed either in Fresh Weight or in Dried Weight in samples treated with nitrogenated fertilizers with any percentage of Biochar.

Growth chamber Experiment

P Assay

FW (g)	0-8-12	P-CHAR1	P-CHAR5
1	10.42	11.43	8.12
2	10.66	10.72	8.79
3	10.55	9.35	9.88
4	10.69	9.87	9.46
5	10.17	10.17	10.33

DW (g)	0-8-12	P-CHAR1	P-CHAR5
1	1.58	1.70	1.16
2	1.63	1.42	1.14
3	1.57	1.27	1.35
4	1.49	1.41	1.28
5	1.40	1.49	1.42

LSD test; variable PF (g) (PChar)
Homogenous Groups, alpha = .05000
Error: Between MS = .48424, df = 12.000

Cell No.	Trat	PF (g) Mean	1	2
3	PChar5	9.31600		****
2	PChar1	10.30800	****	
1	DCTop11	10.49800	****	

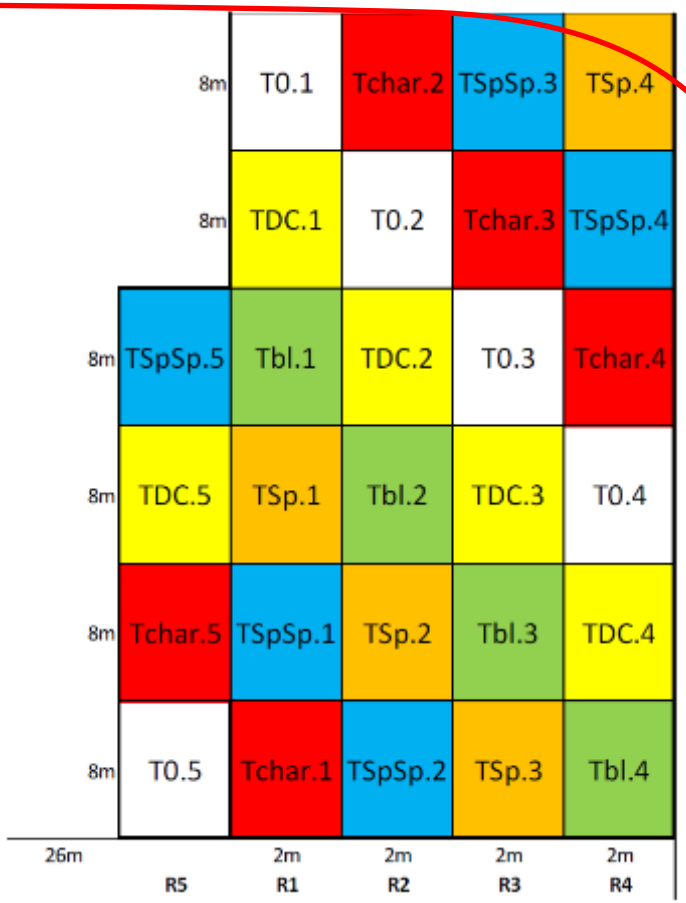
LSD test; variable PF (g) (PS PChar)
Homogenous Groups, alpha = .05000
Error: Between MS = .01577, df = 12.000

Cell No.	Trat	PF (g) Mean	1	2
3	PChar5	1.270000		****
2	PChar1	1.458000	****	
1	DCTop11	1.534000	****	

In this case, statistical differences were observed in both Fresh Weight and Dried Weight in samples treated with Phosphated fertilizer with 5% of Biochar.

Field Assay

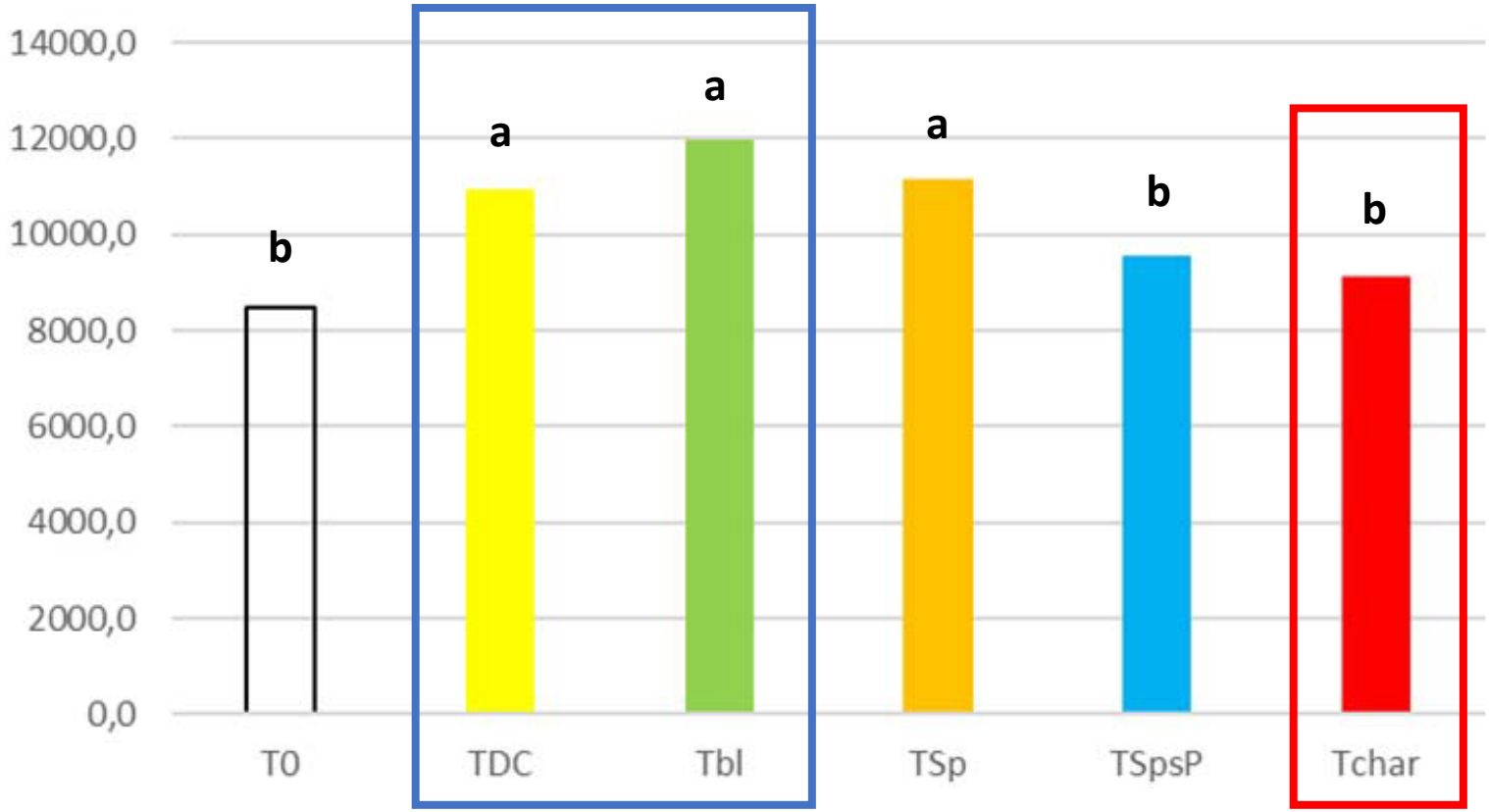
Alfalfa



	Tratamiento	dosis/ha	dosis/microparcela
T0	testigo Sin fertilización	---	---
TDC	D-CODER 11 (0-8-12 (4-2-16)) época fin marzo	500 kg	0,800 kg
Tbl	blending 0-8-12 época fin marzo	500 kg	0,800 kg
TSp	Supractyl Orbe época tras 1er corte	2L	3,2ml
TSpsP	Supractyl Orbe 2 aplicaciones época tras 1er corte y antes de 3º	2L	3,2ml
Tchar	0-8-12 Char **época fin marzo**	500 kg	0,800 kg

Field Assay

Alfalfa



Control treatments

Biochar-fertilizer treatment

Field Assay

Vineyard

Margen
CONTROL (C)
CHAR (CH)
D-CODER (DC)
RHIZOVIT (RZ)

Field Assay

Vineyard

Field Assay

Vineyard

Control treatments

Biochar-fertilizer treatment

TIMAC AGRO 2019		Treatment	Bunch per vine	Kg/ha	100 grapes weight (g)	pH	Probable Volume	Total Acidity	Soluble Solids
Ensayo nº 1	C	Control sin fertilización	15	10096,2 a	184,8	3,44	14,5	6,88	241,4
	DC	D-CODER 5 (7-5-12)	15	9024,4 a	188,2	3,51	13,8	5,71	232,8
	RZ	RHIZOVIT 1 (6-5-8)	14	9792,3 a	167,4	3,63	15,0	5,06	256,3
	CH	CHAR (7-5-12)	16	10509,0 a	181,6	3,62	15,2	5,31	255,7
	Average		15	9855,4	180,5	3,55	14,6	5,74	246,6
	Coefficient of variation (%)		4,1	6,4	5,1	2,6	4,3	14,0	4,7
	P-value		0,942	0,907					
	Signification level		ns	ns					

Total Acidity ↓ , pH ↑ → Quality ↓

Conclusion

2. Biochar into Fertilizer matrix

- Biochar introduction as fertilizer phase is able only up to 5% in mass.
- In growth chamber experiment decrease in Fresh and Dried weight under P-Char treatment was observed in comparison to Control+. But not under N-Char treatment.
- In field trials Biochar treatment showed less yield in alfalfa and less quality of grapes in vineyard, in alkaline/calcareous soils.

Final Remarks

- Biochar in acidic soil could be more an pH (Ca) amendment than a nutritional like-fertilizer.
- Biochar as amendments as well as fertilizer phase gives doubtful results in alkaline soil as growth chamber, greenhouse and field experiment showed.
- In this conditions, P is retained by biochar through metal (Fe and Al) bridges being released at least partially by acidic hydrolysis.
- P foliar content seems not be affected. On the opposite, N foliar content followed the same pattern that weight decrease in biochar treatment.
- This may affect to yield and/or quality on field in alkaline/calcareous soils.

Thank you very much for your attention and your effort!!!