Fe-coated biochar for P removal and recovery of slow release fertilizers

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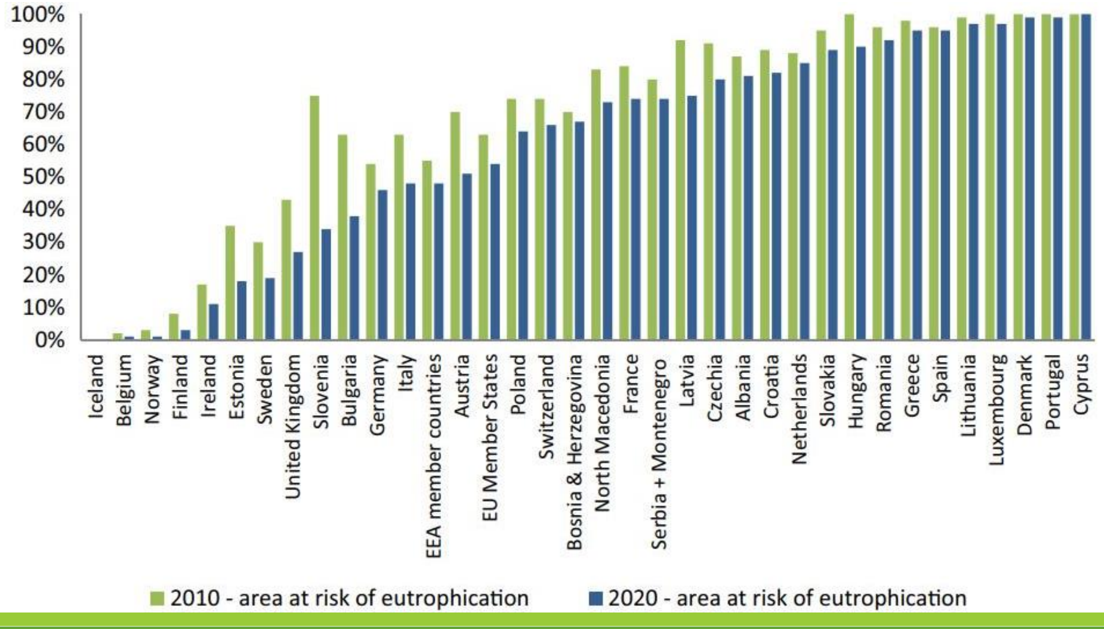
Excess phosphorus causes eutrophication

- External inputs of P: runoff from fertilized fields or point sources
- Eutrophication → algae and microorganisms ↑: affects ecological state of water bodies
- Phosphate concentration in European rivers has halved in the last decade: thanks to protective Directives (e.g., WFD, UWWTD, MSFD, …)
- In most EU countries more than 40% of aquatic ecosystems are at risk
- Global warming → intensified eutrophication by promoting the growth of algae

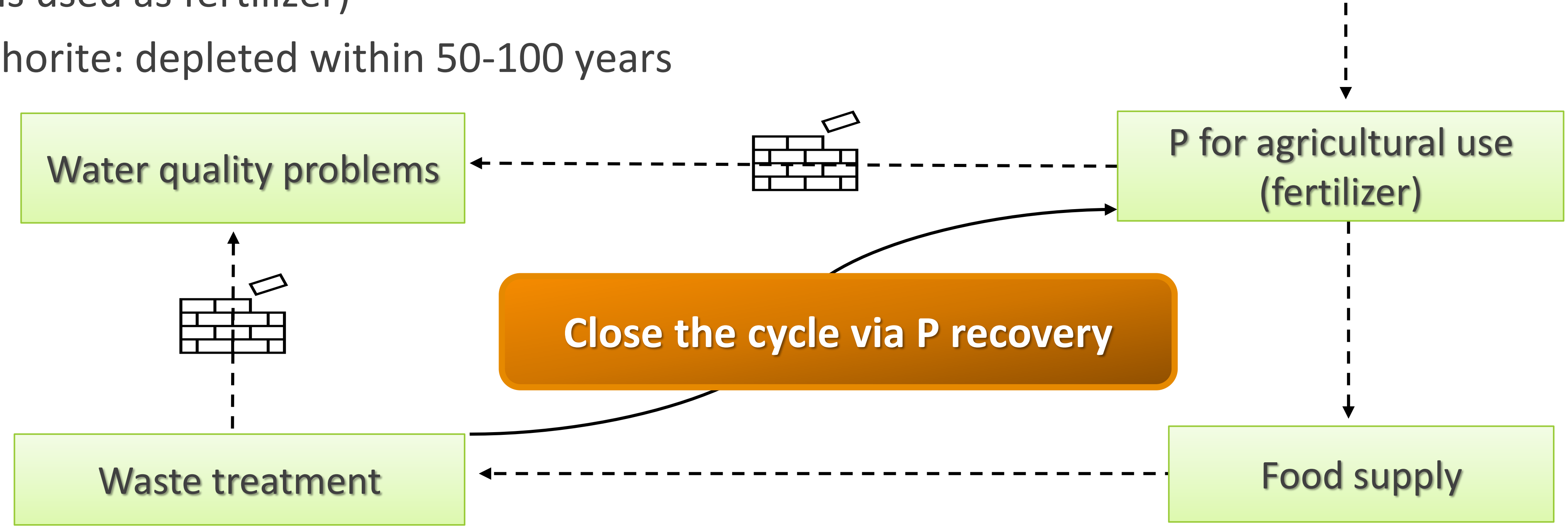
Eutrophicated water



WFD: Water Framework Directive; UWWTD: Urban Wastewater Directive; MSFD: Marine Strategy Framework Directive

P as critical raw material

- Phosphorite (phosphate rock): 81%, P: 100% dependent on third countries for its supply
- Their end-of-life recycling rate is very low
  (Phosphorite: 17%, P: 0%)
- Annual extraction of P is approximately 53 million tons P_2O_5
  (80% is used as fertilizer)
- Phosphorite: depleted within 50-100 years



sensitive to influent flow and pollution load variations

Disadvantages

Biological method

large sludge production, secondary contamination

Chemical method

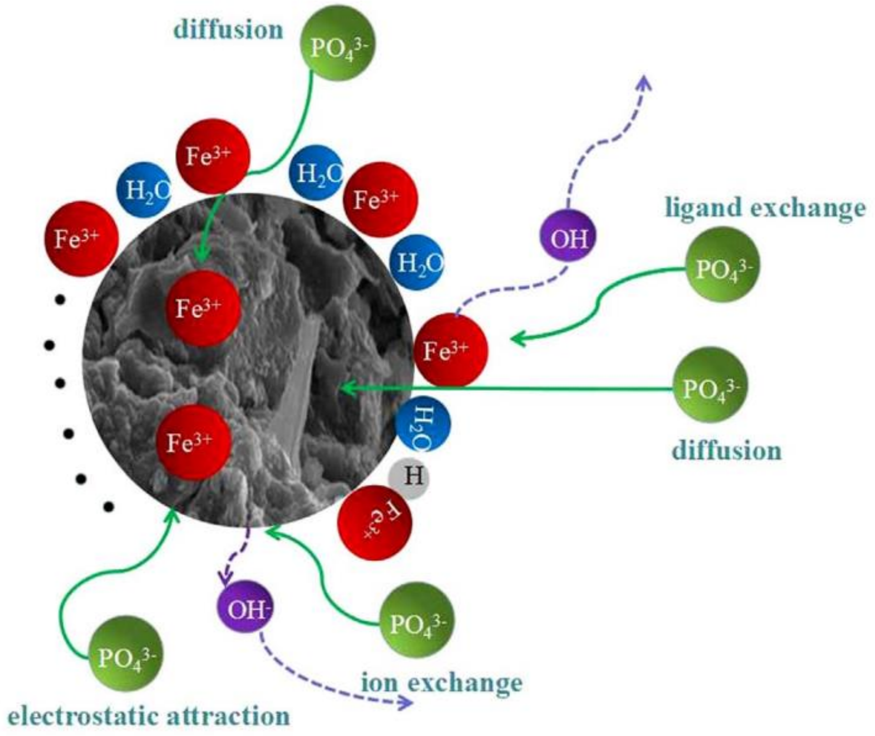
P removal technologies

Adsorption

Cheap and simple operation, high removal efficiency
Both removal and recovery

P recovery

adsorption materials



Phosphate adsorption on Fe-coated biochar (*(Yang et al., 2018)*

Fe-coated Biochar

Carbon-rich material obtained by anaerobic pyrolysis of organic materials coated with FeOOH:

high natural affinity towards phosphates

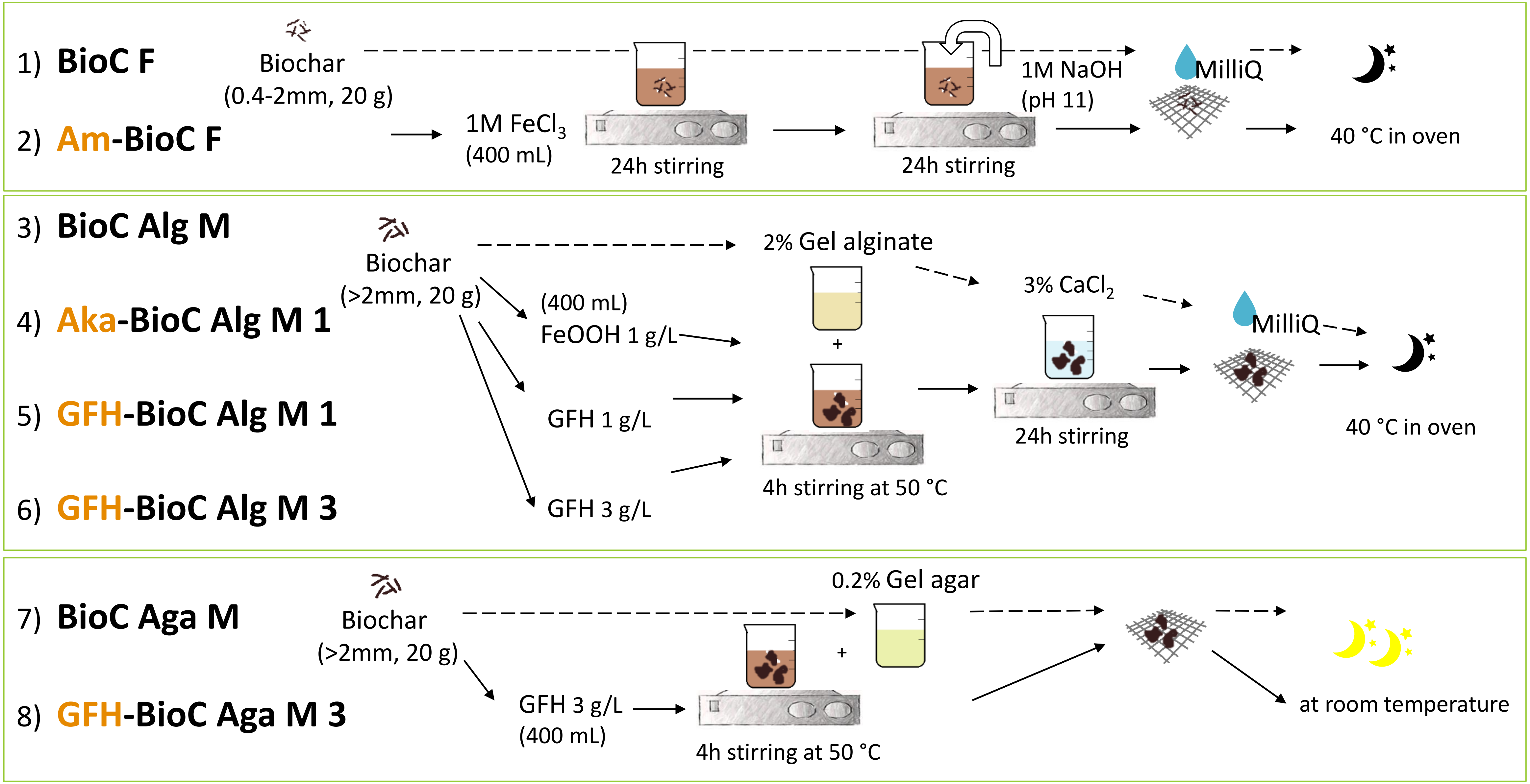
→ enhance the phosphate adsorption capacity

Aims of the study

- Optimization of synthesis process of different Fe-coated biochars (with different FeOOH and gels)
- Study of phosphate adsorption processes (kinetic & thermodynamic) to evaluate the removal efficiency and stability of the selected materials
- Study the microbial colonization on optimized materials in laboratory & field (wastewater)
- Evaluation of the possible reuse of the Fe-P-rich spent material as an amendment

MATERIALS AND METHODS

Preparation of 8 materials



BioC: Biochar; Materials of Iron: Am: Amorphous, Aka: Akaganeite, GFH: Granular Ferrous Hydroxide; F: fine (0.42-2mm), M: medium (>2mm); 1, 3: g FeOOH/L

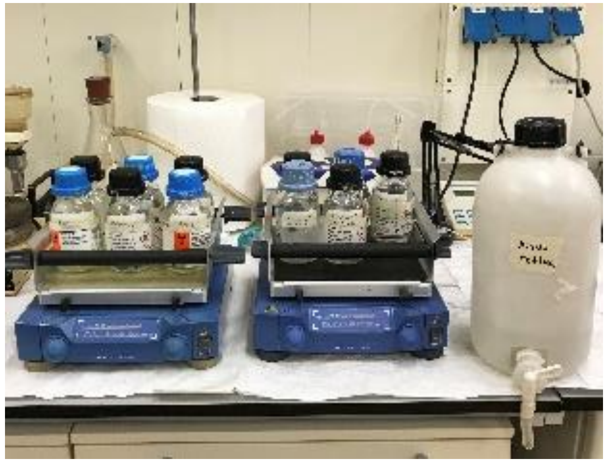
Phosphate adsorption and analytical methods

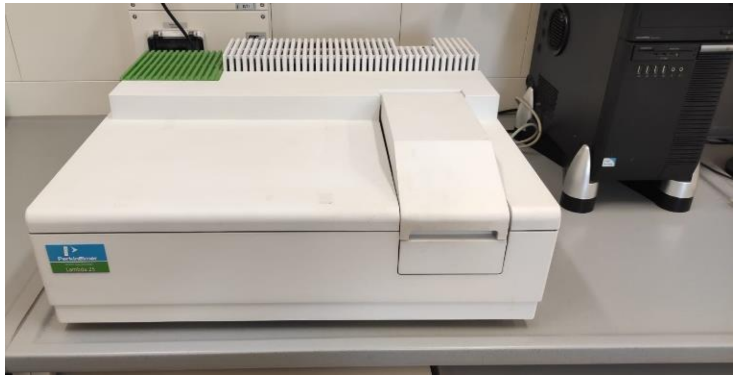
Isotherms and adsorption kinetics

- 0.25 g of 8 materials in 100 mL of PO_4 solution (L_1=1, L_2=5, L_3=10, L_4=20 mg/L)
- 3 mL samples were taken (t_0=0, t_1=1, t_2 =24), C_0 = 5 mg/L PO_4

Adsorption in consecutive cycles in synthetic waters and real matrices

500 mg of 8 materials in 250 mL of MilliQ or treated wastewater (C_0=5 mg/L PO_4) stirred for 24h X 3 consecutive cycles

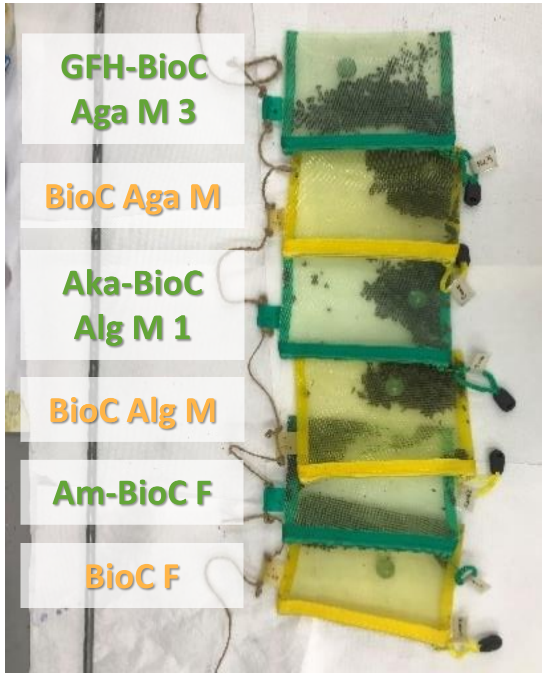




Concentration of PO_4 and total Fe

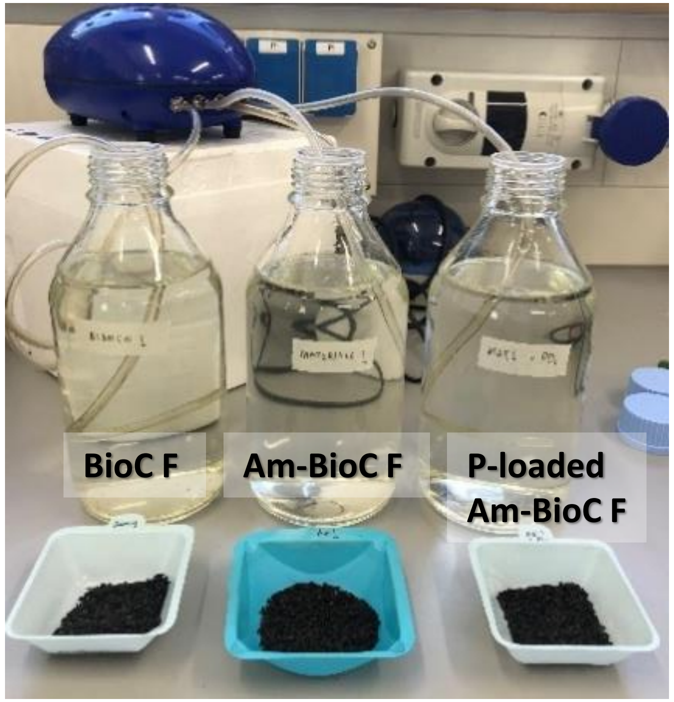
UV-VIS Spectrophotometry

Microbial biomass development



Submerged in the wastewater treatment plant

2 g of selected materials submerged for 14 days

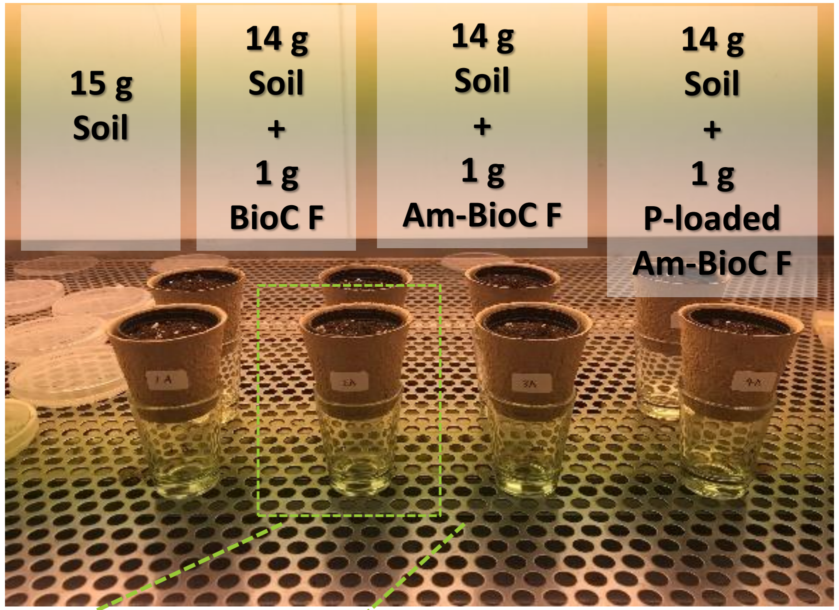


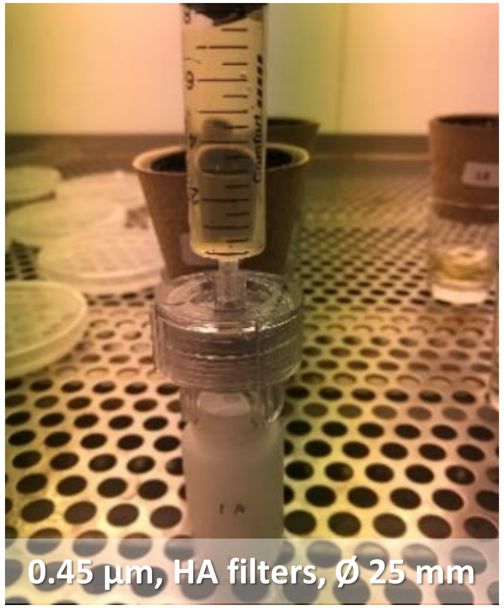
Incubation in laboratory conditions

1.5 g of biochar (BioC F, Am-BioC F, and P-loaded Am-BioC F) : incubated for one month in 1 L aerated reactors filled with wastewater

Bacterial abundance: epifluorescence microscopy

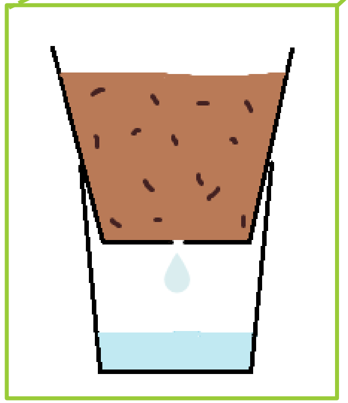
PO_4 release in soil by P-loaded biochar





0.45 µm, HA filters, Ø 25 mm

Climatic chamber

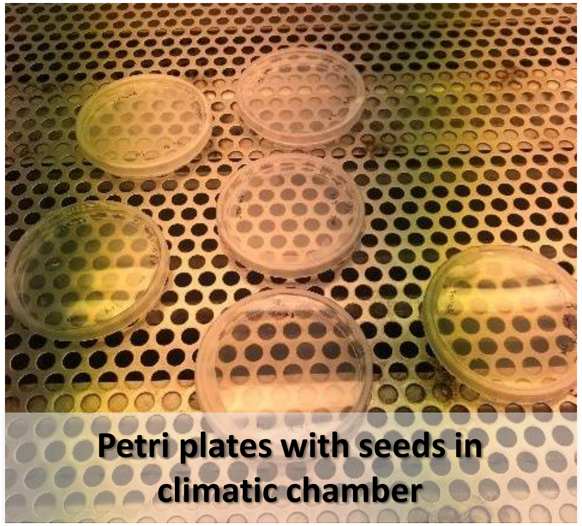


To evaluate the release and retention capacity of PO_4 by materials in the soil (1 g + 14 g of soil, 6.7%)

Each pot was watered with 20 mL of distilled water every two days X 5 cycles

After 1 h, 5 mL of samples were taken and filtered

Plant preparation and morpho-anatomical analyses

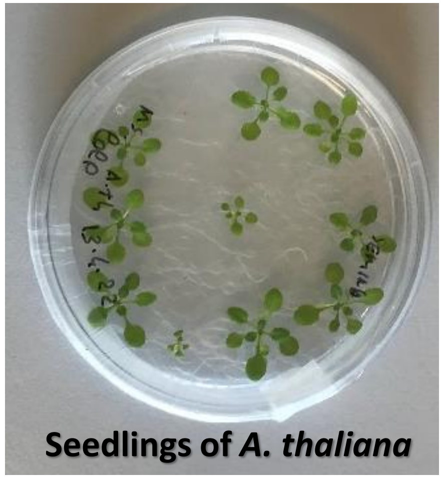


Petri plates with seeds in climatic chamber

Plant material and incubation conditions

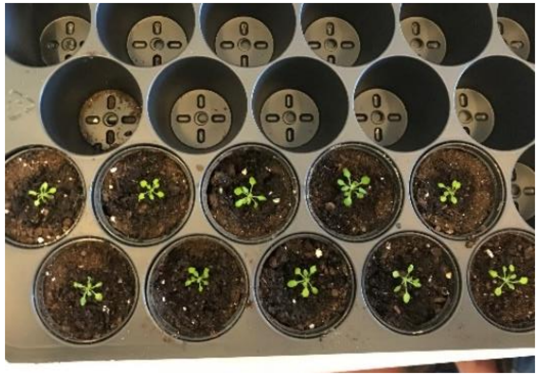
Seeds of *Arabidopsis thaliana* (L.) Heynh were sown on petri plates (Murashige and Skoog) with 0.5% sucrose and 0.8% agar

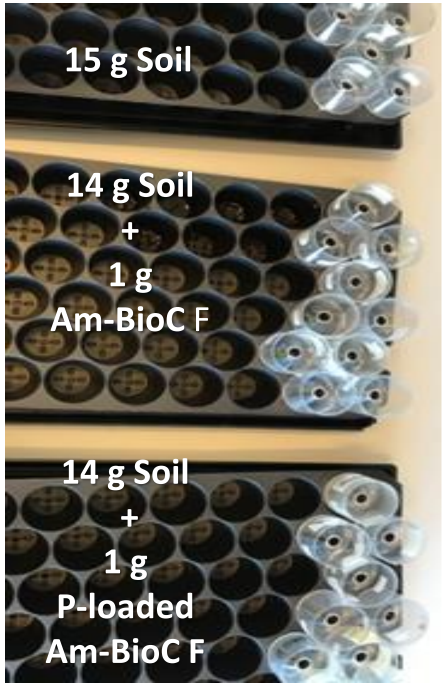
Incubated under long day conditions (16/8h light/dark) at 22 ± 2°C and 70% relative humidity



Seedlings of *A. thaliana*

Plant growth





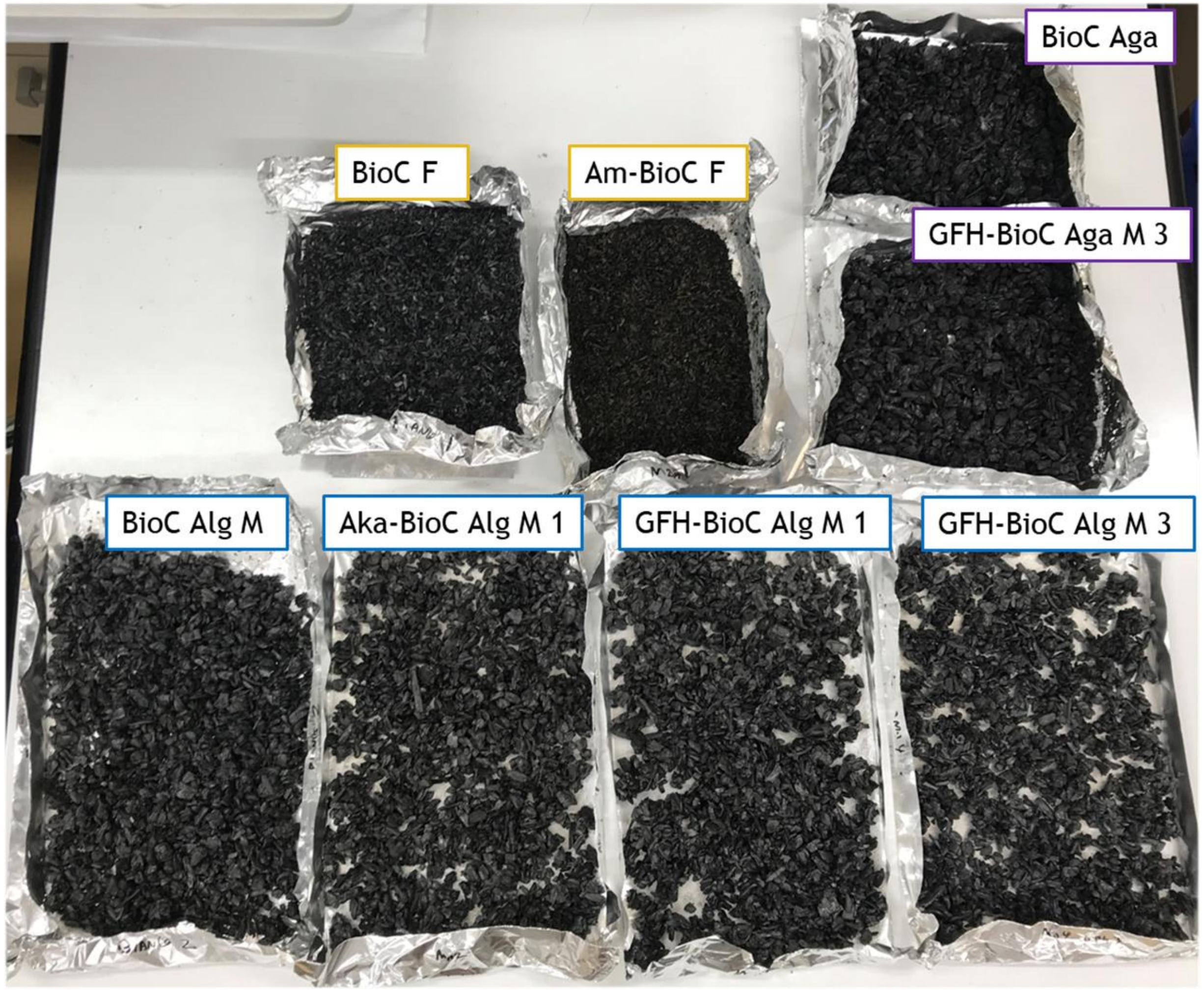
A. thaliana (L.) seedlings: transplanted 3 weeks after sowing
10 seedlings were used per treatment and watered with 200 mL of distilled water every 4-5 days for 8 cycles

Morpho-anatomical analyzes:

- height of the plants
- diameter of the main stem (of 5 plants and cut at 5 cm of height)
- number of siliques, length of the silique (20 siliques per treatment)

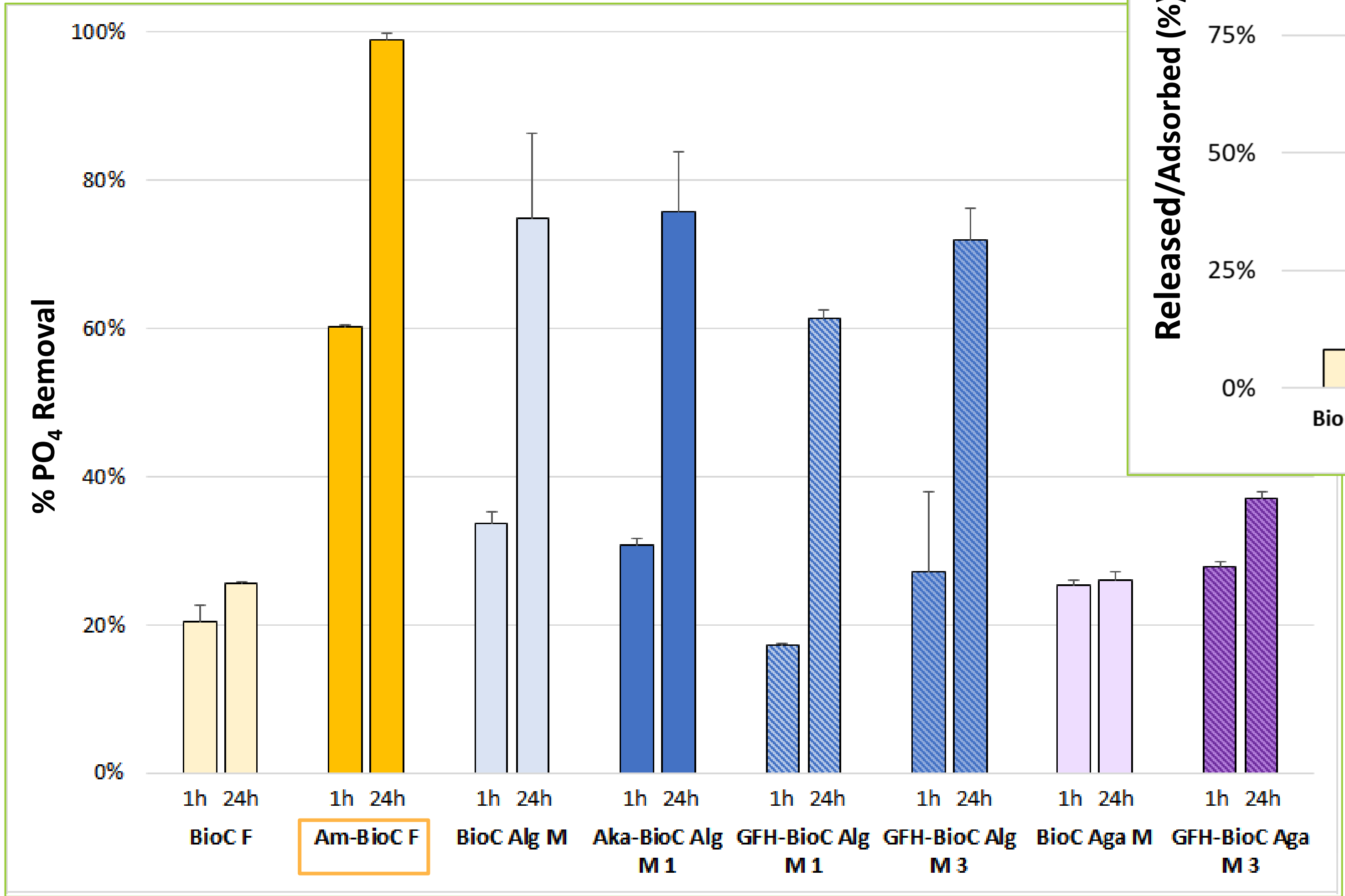
RESULTS

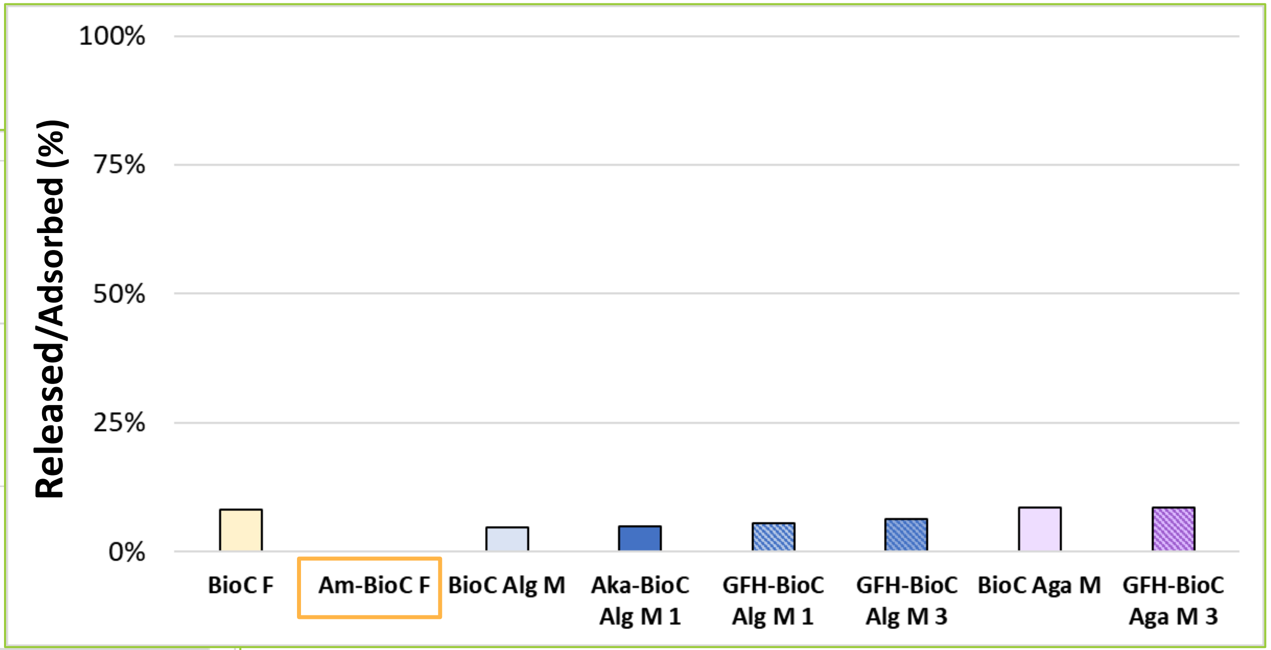
8 optimized materials



Code	Recipe	Fe %
BioC F	Biochar (0.4 -2 mm)	0.0 %
Am-BioC F	Biochar (0.4 -2 mm) + 1M $FeCl_3$ + 1M NaOH	3.8 %
BioC Alg M	Biochar (>2 mm) + 2% Alginate	0.0 %
Aka-BioC Alg M 1	Biochar (>2 mm) + 2% Alginate + FeOOH 1 g/L	0.1 %
GFH-BioC Alg M 1	Biochar (>2 mm) + 2% Alginate + GFH 1 g/L	0.1 %
GFH-BioC Alg M 3	Biochar (>2 mm) + 2% Alginate + GFH 3 g/L	1.1 %
BioC Aga M	Biochar (>2 mm) + 0.2% Agar	0.0 %
GFH-BioC Aga M 3	Biochar (>2 mm) + 0.2% Agar + GFH 3 g/L	0.3 %

Adsorption kinetics



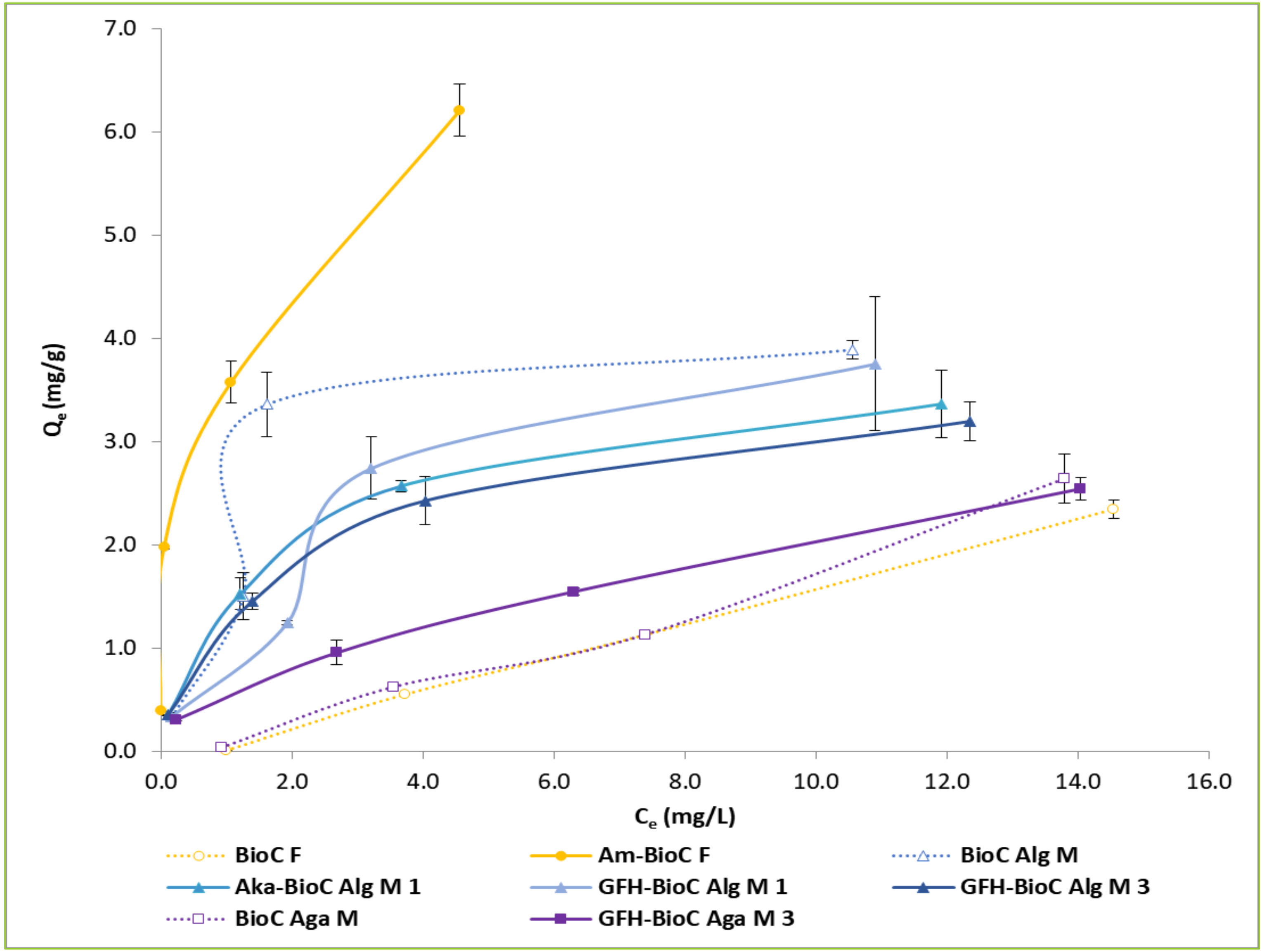


Capacità di adsorbimento a 1h (max: 2 mg PO_4/g abs)							
BioC F	Am-BioC F	BioC Alg M	Aka-BioC Alg M 1	GFH-BioC Alg M 1	GFH-BioC Alg M 3	BioC Aga M	GFH-BioC Aga M 3
0.4	1.2	0.7	0.6	0.3	0.4	0.5	0.6

Am-BioC F

- the best adsorption capacity of PO_4^{3-} (99% removal after 24h in contact with synthetic water, C_0 = 5 mg/L)
- no release of PO_4^{3-} adsorbed in water

Adsorption isotherms



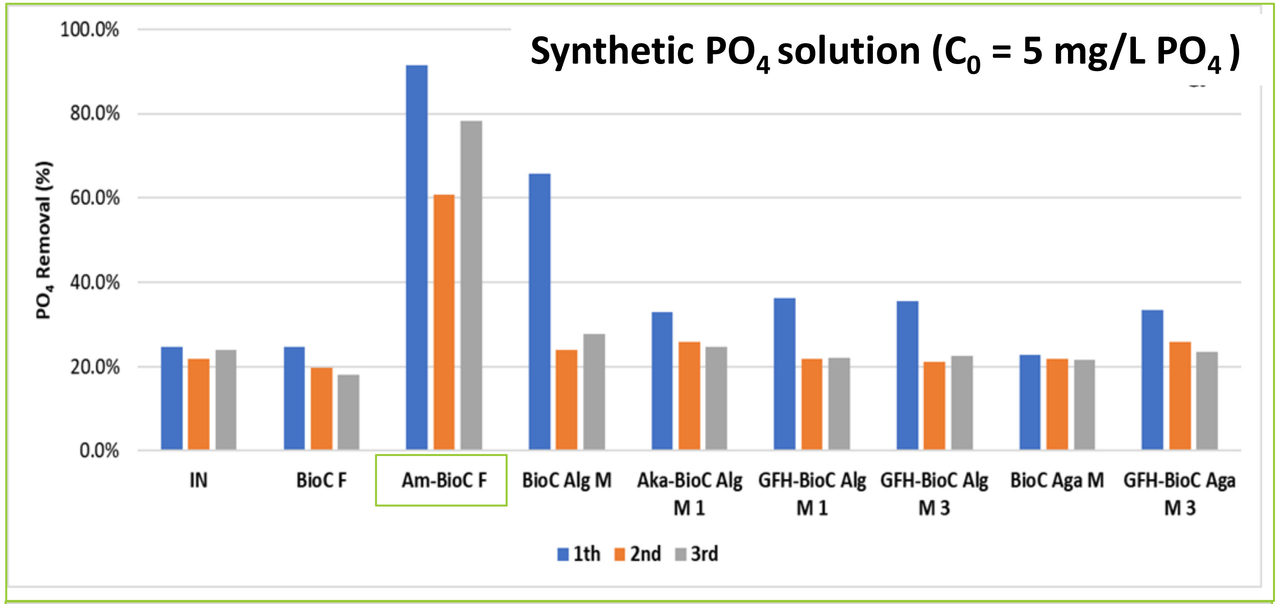
Am-BioC F

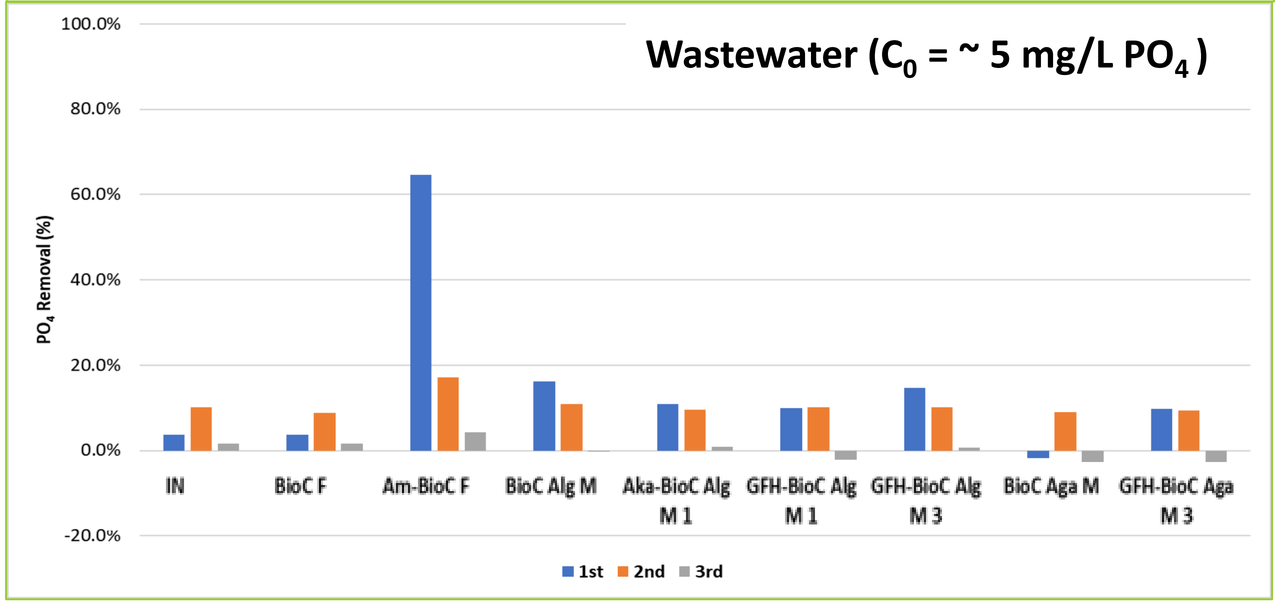
maximum phosphate adsorption capacity (q_{max}) : 7.1 mg/g according to the Langmuir model

Other materials

: 3.7-5.3 mg/g

Adsorption at 3 cycles of batch experiment





Am-BioC F

80% removal rate after the 3rd cycle

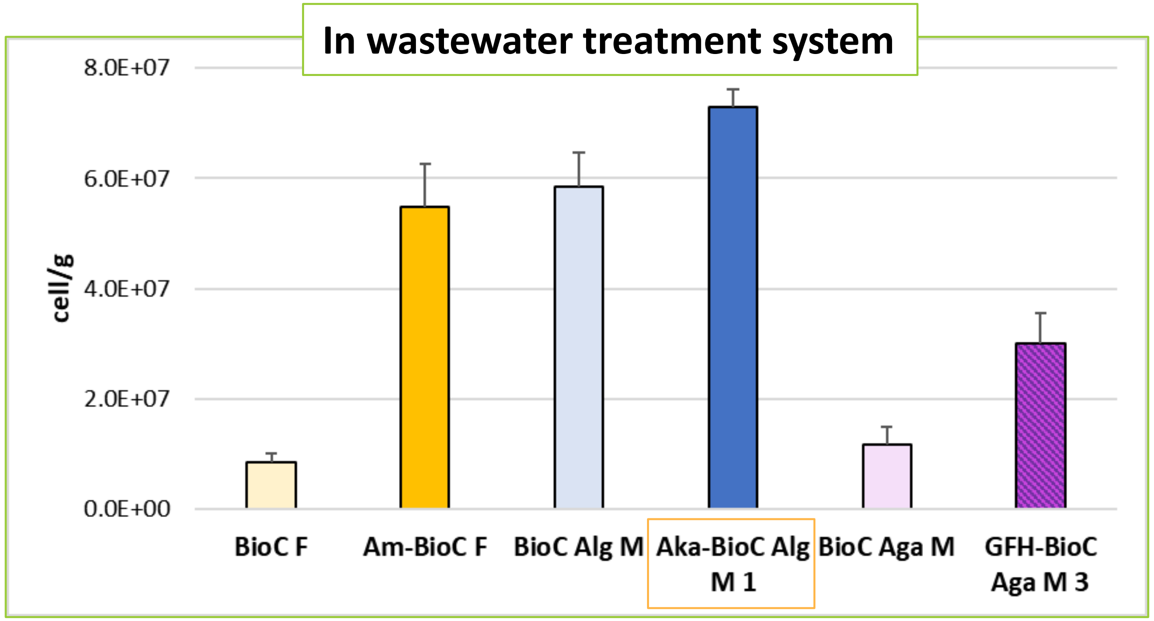
Other materials: 20%

PO_4 saturated surface area disturbed the following adsorption

The removal rate has drastically ↘ for all materials → presence of complexing agents and biomass

Should be carefully considered in the use of modified biochar for long-term exposure

Microbial biomass on materials

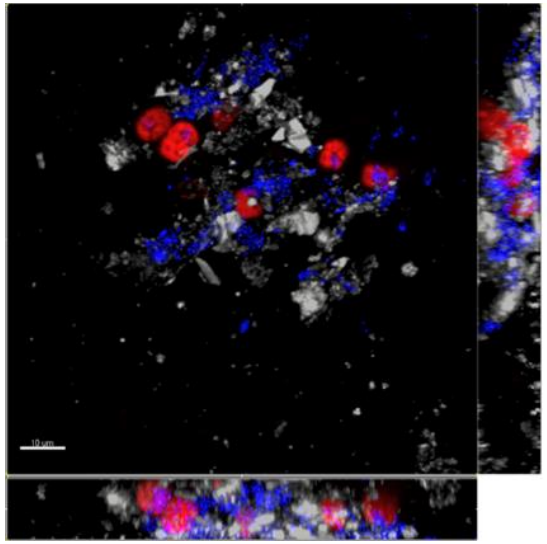


Aka-BioC Alg M1

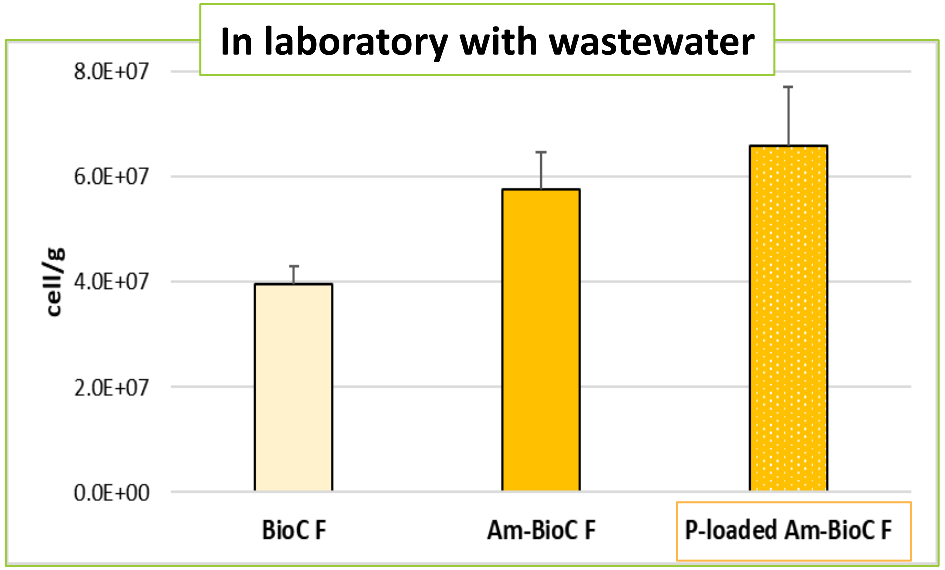
- Materials coated with Fe and alginate : the highest growth of microbial biomass
- Fe or alginate may have created a suitable nutrient source for bacteria

P-loaded Am-BioC F

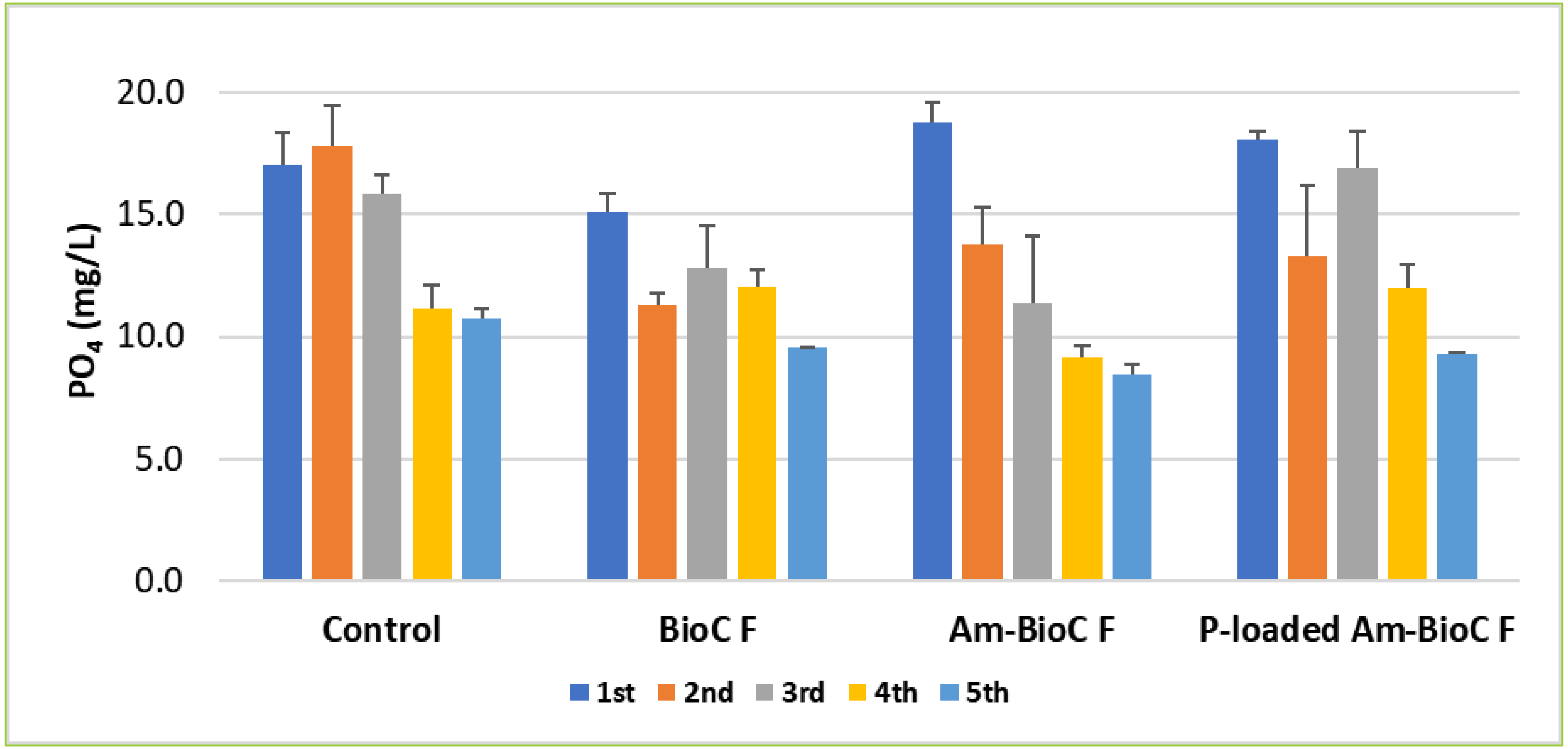
stimulated by the coexistence of phosphate and Fe used as nutrients in biofilm growth



BioC F - Images (spatial distribution) by confocal laser scanning microscopy (CLSM)



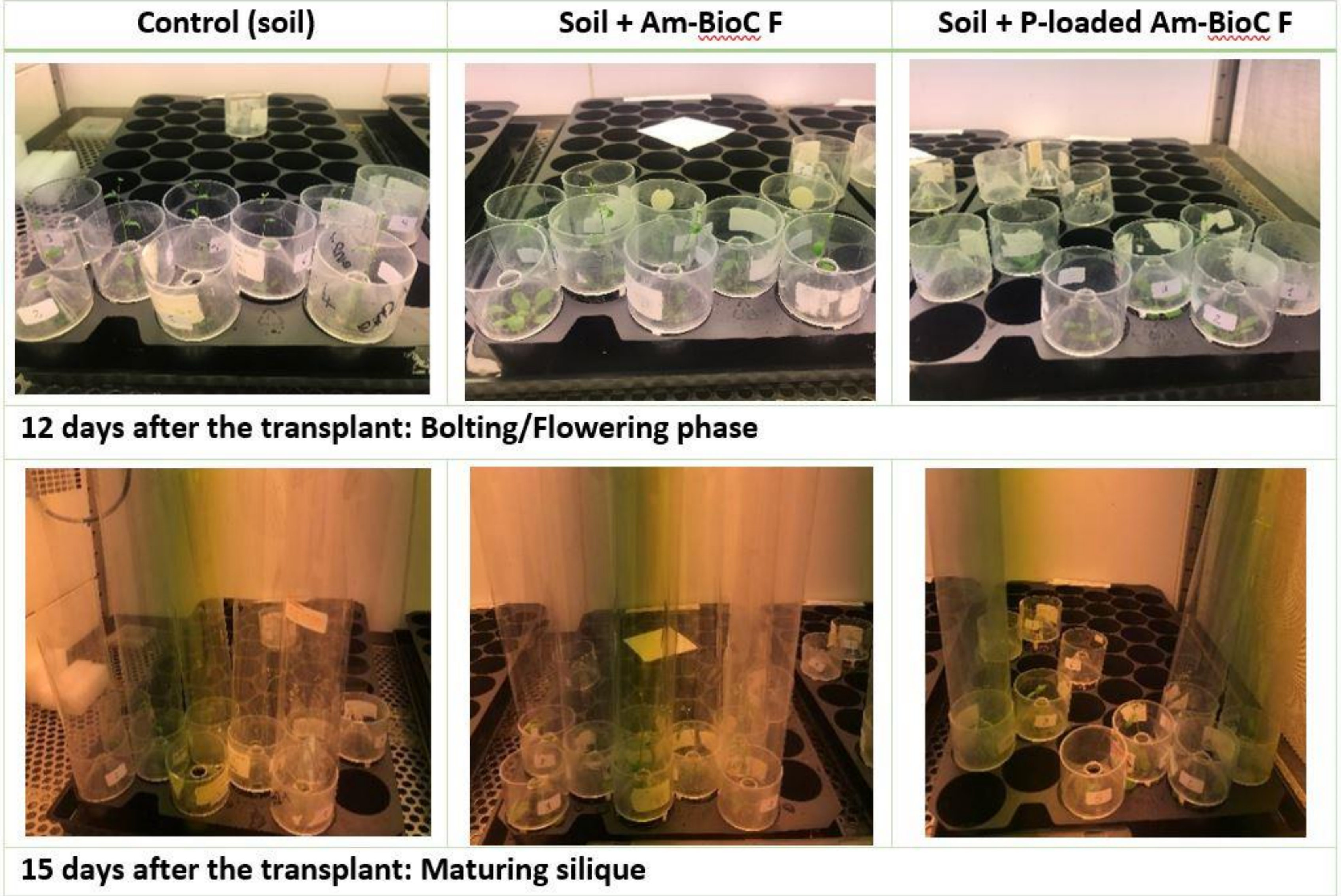
PO_4 release in soil by P-loaded biochar



Total average of leached PO_4 concentration of 5 cycles: **BioC F** - the lowest (12.2 ± 0.6 mg/L)
Control - the highest (14.5 ± 0.5 mg/L)

Nutrient loss prevention was not visible under the examined condition in nutrient-rich soils

Growth of *Arabidopsis thaliana*

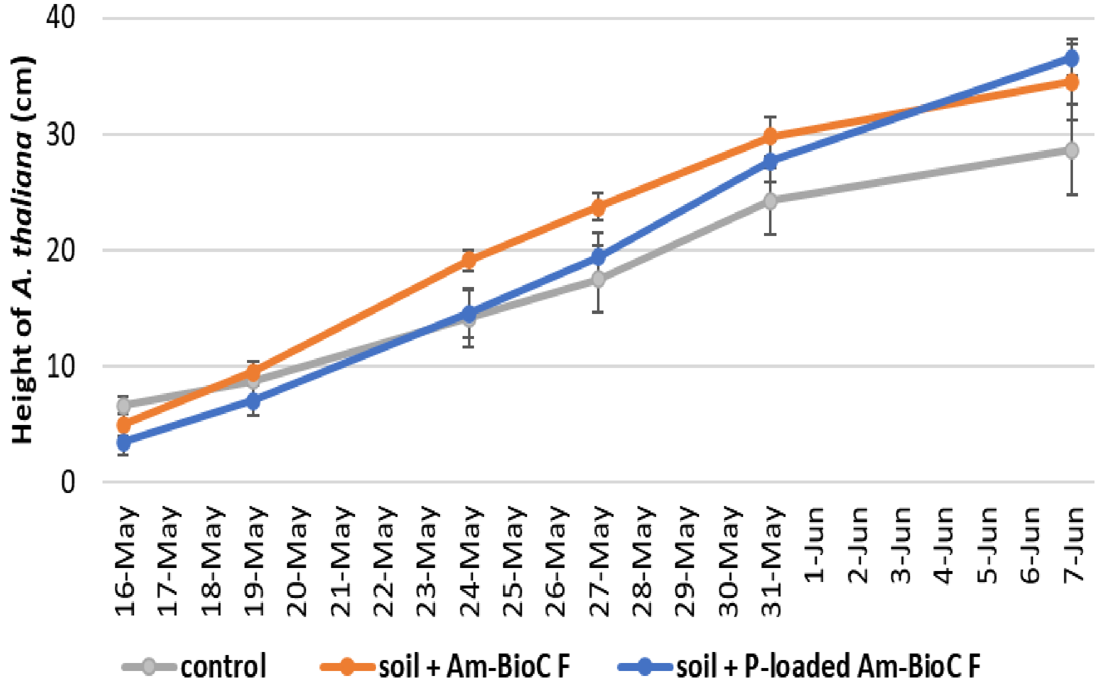


Delayed flowering was observed in plants treated with Fe-coated biochar 4-5 days after Control

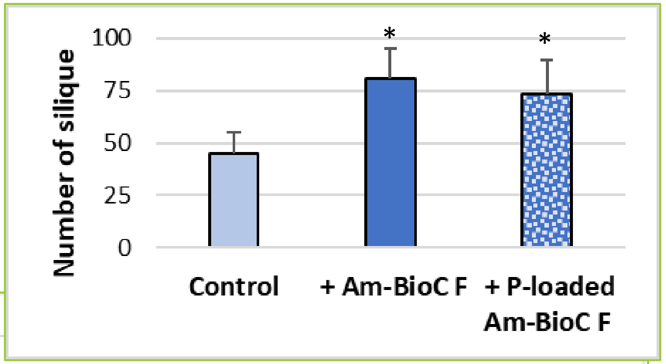
→ prolonged their vegetative stage to ensure the fruiting cycle

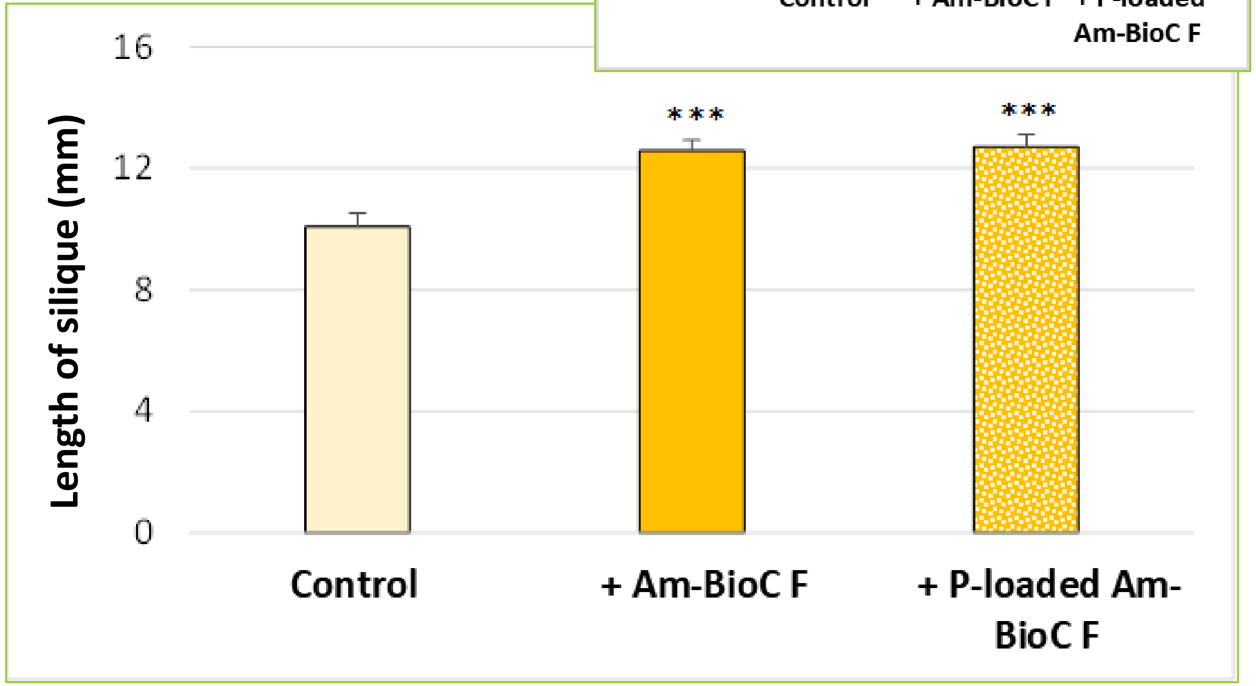
Control (soil)	Soil + Am-BioC F	Soil + P-loaded Am-BioC F
		

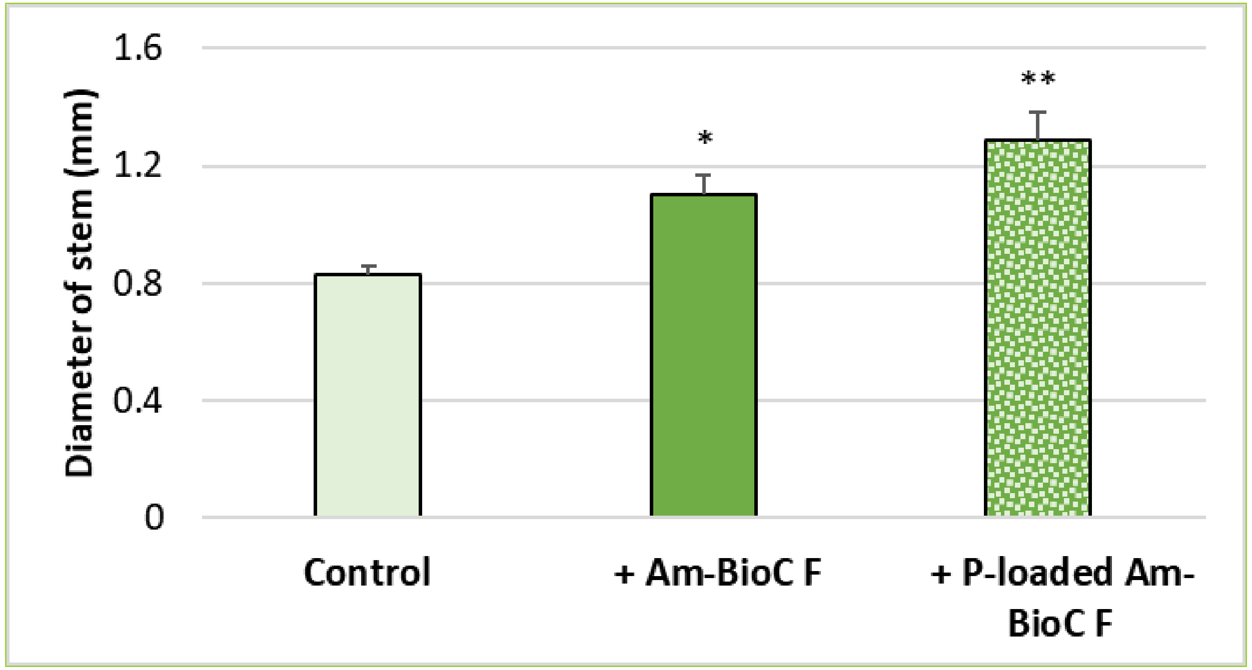
1 month after the transplant: Used for morpho-anatomical analyzes



Length of silique and diameter of stem







Plants grown on soil enriched with Fe-coated biochar (with and without P)

→ a statistically significant difference (P-loaded Am-BioC F: $p<0.01$, Am-BioC F: $p<0.05$) compared to Control

CONCLUSION

Optimization of materials

- Am-BioC F: removal efficiency of 99%, q_{max} equal to 7.1 mg/g
- Gel-coated materials: ↓ adsorption (alginate > agarose)
- During consecutive cycles : a drastic ↘ in P adsorption efficiency (in real matrices)

Microbial biomass on materials

- (wastewater treatment system) Aka-BioC Alg M1: highest microbial biomass growth
- P-loaded Am-BioC F: highest abundance of bacteria compared to the control

Growth of *Arabidopsis thaliana* with materials

- Plants grown on soil treated with Fe-coated biochar (with, without P): statistically significant difference (with P: $p<0.01$, without P: $p<0.05$) compared to Control (lengths & numbers of siliques, stem diameter)

Background

Water bodies contaminated by phosphate

↓

Treatment to avoid eutrophication

Phosphorus (P): critical raw material

↓

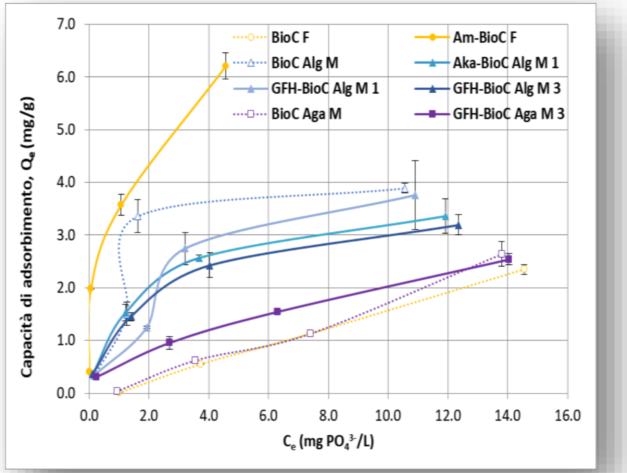
P recovery and recycling

Biochar

Fe-coating

Modified materials

PO_4^{3-} Adsorption



P - loaded materials

Amendment

Arabidopsis thaliana

Fe-coated Biochar

Optimization of materials to enhance the phosphate adsorption capacity → real "traps" for the phosphorus present in water

Laboratory & real water exposure

The study was carried from both lab experiments and field

Collaboration network

Sapienza University – Water Research Institute (IRSA-CNR)

Collaboration with municipalities, local authorities and protected areas managers → will provide a good network to facilitate its application

Interdisciplinary approach

Chemistry, botany, microbiology, environmental science

Tandem-style research

Optimization of a material that adsorbs P present in water

|

Its reuse as an amendment

Circular economy

Green materials like biochar, once enriched with phosphate in eutrophicated environment, can then find direct use as fertilizers

Let's continue the conversation!

Post questions and comments in the IAIA24 app.

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