Interreg North-West Europe Phos4You
European Regional Development Fund

RESOURCE AND MATERIALS EFFICIENCY

We deliver Phosphorus made in Europe

Recommendations towards EU standards to assess quality of recovered P materials based on Phos4You works

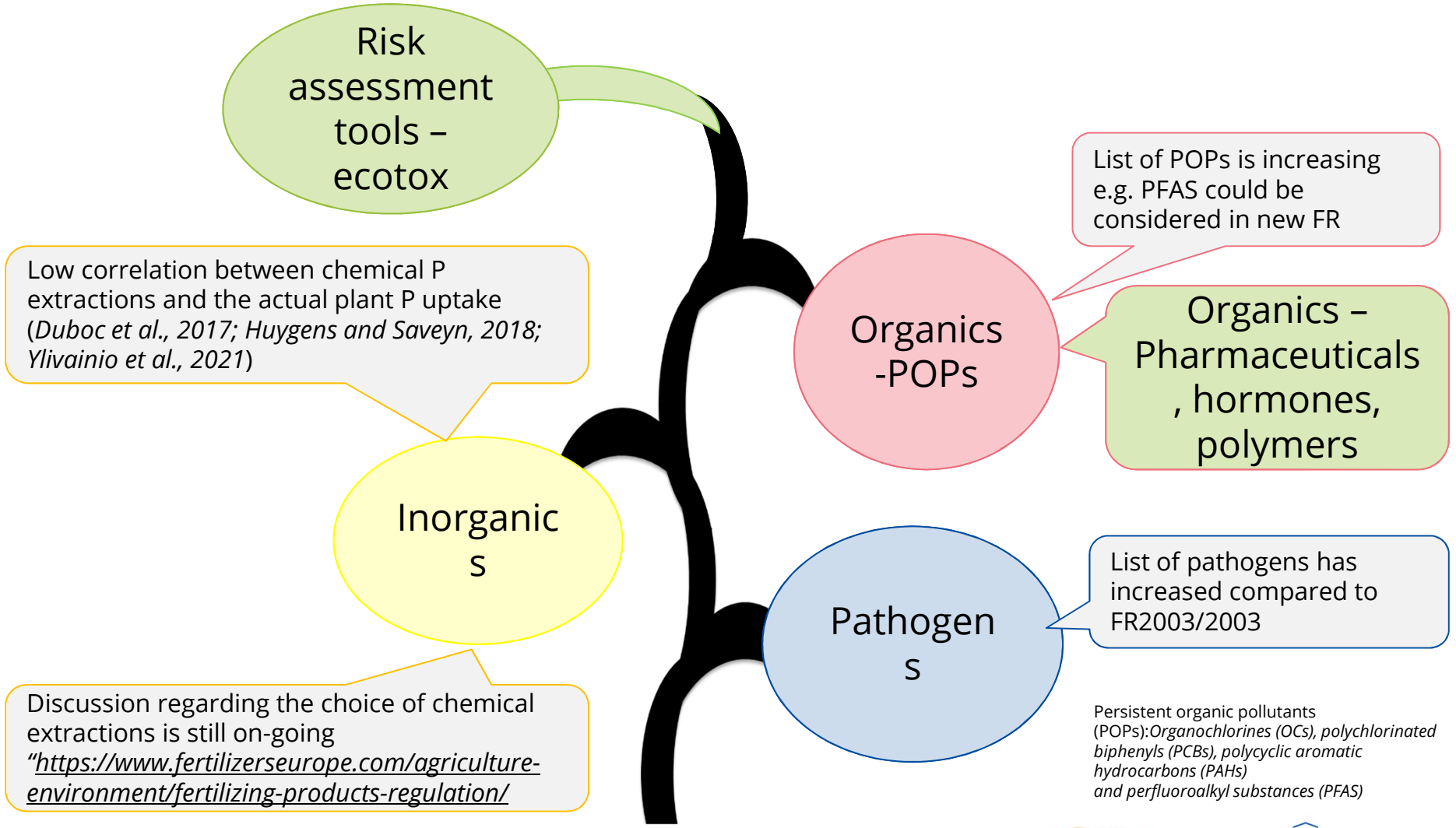
Phos4you final conference - 21-22.09.2021, Essen and on-line

Fertilizer Regulation in EU

REGULATION 2019/1009

- *"…EU fertilising products should be placed on the market only if they are **sufficiently effective and do not present a risk** to human, animal or plant health, to safety or to the environment when properly stored and used for their intended purpose, or under conditions of use which can be reasonably foreseen, that is when such use could result from lawful and readily predictable human behavior…"*

Demand for QA standardization



Phos4You
WPT2 Quality assessment group

- Phos4You has recognized the standardization challenge and created QA to:
  - Increase understanding of fertilizing P materials quality and behavior,
  - Compare the different classic and novel methods,
  - and give recommendation for the best methods to assess the quality of new P fertilizers

Nutrients ***Contaminants***

P availability	Inorganics	Organics	Ecotox	Pathogens
• UGhent • LEB /INRAE • MTU • EuPhoRe	• UGhent • ERI • INRAE	• HVC /UGhent • ERI • GCU • INREA	• GCU • LEB	• ERI

- UGhent: lead partner of WPT2

Secondary P fertilizers samples

QA1 -> 5 commercial secondary P fertilizers were used for setting up the methods

Sludge drying	P precipitation		Thermal treatment	
FeP	P salt SL	P salt LQ	ASH 2	ASH 1

QA2 -> 6 Phos4You products tested with the previously defined methods

P precipitation			Natural P adsorption		Thermal treatment
P salt4_SL	P salt3_CL	P salt5_BL	BioP1_MA	BioP2_CCP	Ash2.2_RK_PI

SL-sludge; LQ-liquor; CL-Chemical leaching; BL- Bio leaching; MA-MicroAlgae; CCP-Crab carapace phosphate; PI- Pyrolysis/Incineration

Sample preparation

Drying



- Fertilizers were dried at room T, 50°C, and 105°C
- **Samples should be dried at low temperatures (<50°C) and kept in a desiccator prior to analysis for preservation of their moisture content**

Grinding

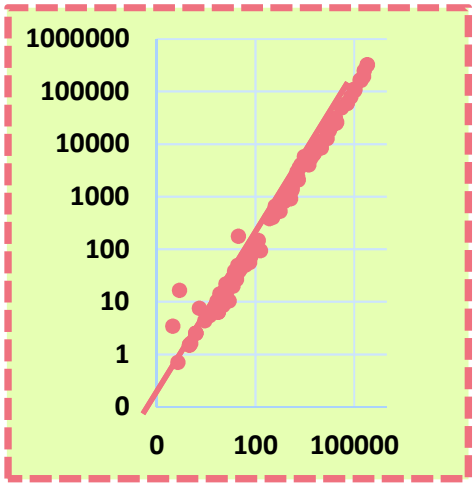

- Chemical composition of TSP after grinding with stainless steel vs agate balls showed that: Cr and Ni in TSP ground with agate and stainless gave the same results
- As occasional wearing out may occur during grinding
  agate should be preferred over stainless steel jars and balls

Inorganics: P extraction methods

Nutrients and contaminants

METHOD	EXTRACT	EXTRACT RATIO, mL	MASS, g
Closed microwave digest with Aqua Regia (UGhent)	HNO_3:HCl	2.5:7.5 (1:3 ratio)	0.15
Closed microwave digest with Aqua Regia (ERI)	HNO_3:HCl	1.2:4.8 (1:4 ratio)	0.25
Closed microwave digest with Nitric acid/hydrogen peroxide (ERI)	HNO_3:H_2O_2	5:1.5	0.25

1 2 3



- **Two AR and HNO3/H_2O_2 "pseudo –total" methods were found comparable for most of the elements tested**
- CNS gave comparable Sulphur concentrations as AR1, AR2, Nitric/Peroxide (with slight deviations in the case of Ashes)
- Automated and simple elemental methods (CHN & Hg) are robust and sensible

Inorganics: analyses of solubility

METHOD	EXTRACT	EXTRACT RATIO, mL	MASS, g
Water (ERI)	H_2O	25	0.5
2% Citric acid (ERI)	$C_6H_8O_7$	25	0.5

HIGH

Product

LOW

	S	Na	K	Mg	Ni	P	Ca	Co	Zn	Mn	Cu	Cd	Al	Cr	Fe	Pb	As
TSP	81.4	71.0	99.4	90.6	68.2	99.7	77.8	44.7	65.9	62.0	12.7	44.0	18.1	11.2	1.9	~	~
BioP1	31.2	76.1	81.2	38.3	33.8	1.6	5.1	16.2	3.9	3.0	20.3	~	~	1.9	1.3	~	~
P-Salt-3	43.0	90.1	77.3	30.0	29.7	1.7	4.9	20.7	~	0.3	15.0	~	~	0.0	~	~	~
Ash3	66.7	23.8	28.0	~	~	~	0.3	~	~	~	~	~	14.8	2.3	~	~	~
P-Salt-4	20.3	36.7	8.3	12.1	~	8.1	0.1	~	~	0.1	4.3	~	~	~	~	~	~
Ash2.2	67.8	3.0	0.7	1.0	~	0.3	0.8	~	~	~	~	~	0.5	~	~	~	~
BioP2	28.9	15.2	14.0	5.5	~	0.1	0.1	~	~	~	~	~	~	~	~	~	~

HIGH — *Element solubility in **water*** — LOW

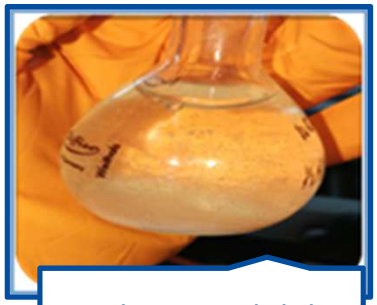
- P, Mg, K, S, and Na are readily soluble components
- toxic elements of concern (i.e., Pb, As, Cd) are rather unavailable

>20% 'water soluble' marked in YELLOW

P availability: method comparison

- Paralleled pot trials were set using the same design and TSP as a reference material
  - Comparable shoot P concentrations were measured in pot trials at UGhent and L
  - Comparable dry matter yield were measured in pot trials at UGhent and MTU

- Plant P parameters were further used to assess quicker P methods
  - Common chemical and alternative P availability methods



Fertilizer P solubility

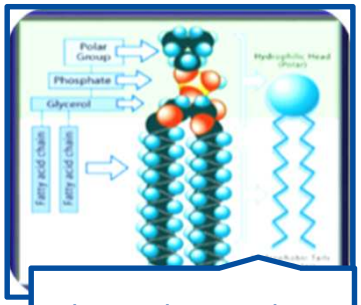
UGhent

Plant DM and P content

MTU, INREA, UGhent, EuPhoRe

Substrate pore water sampling with Rhizon

UGhent



Plant P biomarkers

LEB

P availability: Fertilizer P extraction methods

- Publication in preparation:
  "*Comparison of methods to assess phosphorus availability of secondary phosphorus fertilizers*" Bogdan *et al.*

Example: Correlation (Pearson, *r*) plant P uptake (mg P g fert.$^{-1}$) of fertilizer during seven-month trial with chemically extracted P (mg P g fert.$^{-1}$) using standard fertilizer methods. Values in brackets represent *r* calculated for secondary P fertilizers only, excluding TSP.

Extraction method, mg P kg fert.$^{-1}$	P dose, mg P pot $^{-1}$	plant P uptake per P applied, mg P kg fert.$^{-1}$							
		1st Cut	2nd Cut	3rd Cut	4th Cut	5th Cut	6th Cut	7th Cut	Cumulative
WAT	35	0.835** (0.902**)	0.884** (0.854**)	0.901** (0.864**)	0.825** (0.841**)	0.153 (0.628**)	0.441* (0.894**)	0.039 (0.834**)	0.345 (0.879**)
MA	35	0.882** (0.762**)	0.933** (0.838**)	0.902** (0.828**)	0.916** (0.798**)	0.482* (0.586**)	0.829** (0.912**)	0.589** (0.894**)	0.686** (0.732**)

- MW HN, MW AR, MA, CA, NAC, AL AA) were strongly correlated to plant P uptake over time
- WAT, CACL, BR 2 and MECH 3 extraction provided a good correlation over time
  - if secondary P fertilizers are examined separated from TSP confirming secondary P fertilizers slow-release effect
- The lowest correlation was obtained with the Olsen method

MA-mineral acids, MW AR-microwave digestion aqua regia, MW NA-microwave digestion nitric acid, NAC-neutral ammonium citrate, CA-2% citric acid, AL AA-ammonium lactate acetic acid buffer, MEH 3-Mehlich 3, BR 2-Bray 2, OLS- Olsen's, WAT-water, CACL-0.01% Calcium chloride, Nit/peroxide -microwave digestion nitric acid/peroxide

P availability
Other P measurement methods

Rhizon soil moisture samplers a quick method

- The P in substrate solution: struvites >> than in other fertilizers
- For ashes, the differences between two time points proved the slow P release patter
- Pearson correlation coefficient, r, between the all fertilizer shoot P and substrate pore water P on sand **after 4 cuts was 0.72**

Lipid P biomarker as a pertinent biomarker for assessment of P availability

- Shoot P concentration correlate **positively and significantly** with the shoot PC/DGDG, %C16:1t and Root Lipid P Index
- Root P lipid and leaf PC/DGDG indexes should be considered in ER

	Leaf P concentration	Leaf PC/DGDG	Root P lipid Index	%C16:1t	Leaf fresh biomass
Leaf P concentration	1	0.97***	0.83***	0.92***	0.86***
Leaf PC/DGDG		1	0.84***	0.85***	0.77**
Root P lipid Index			1	0.89***	0.69*
%C16:1t				1	0.91***
Leaf fresh biomass					1

Organics

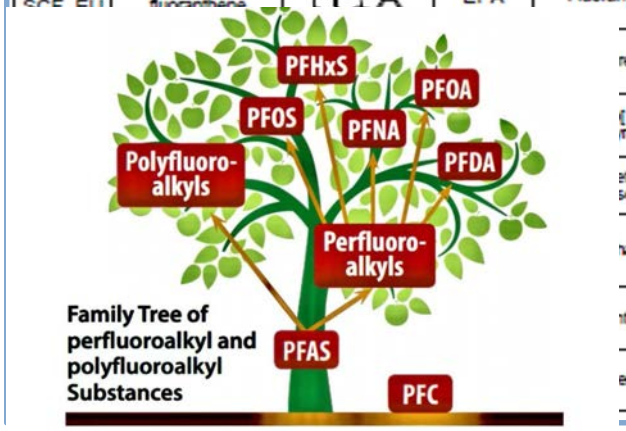
Persistent organic pollutants (POPS)

- methods are standardized
- Some PFAS were detected in recovered P fertilizers

Recommendation

- **not all POPs e.g. PFAS are currently listed in the legislation**
- **PFAS presence is concerning given their propensity to persist and bio-accumulate**

List	Common Name	Structure	List	Common Name	Structure
EPA, SCF, EU	Benzo[a] pyrene		EPA, SCF, EU	Dibenz[a,h] anthracene	
EPA	Acenaphthene		EU+SCF	Dibenzo [a,e]pyrene	
EPA	Acenaphthylene		EU+SCF	Dibenzo [a,h]pyrene	
EPA	Anthracene		EU+SCF	Dibenzo [a,l]pyrene	
EPA, SCF, EU	Benz[a] anthracene		EU+SCF	Dibenzo [a,l]pyrene	
EPA, SCF, EU	Benzo[b] fluoranthene		EPA	Fluoranthene	

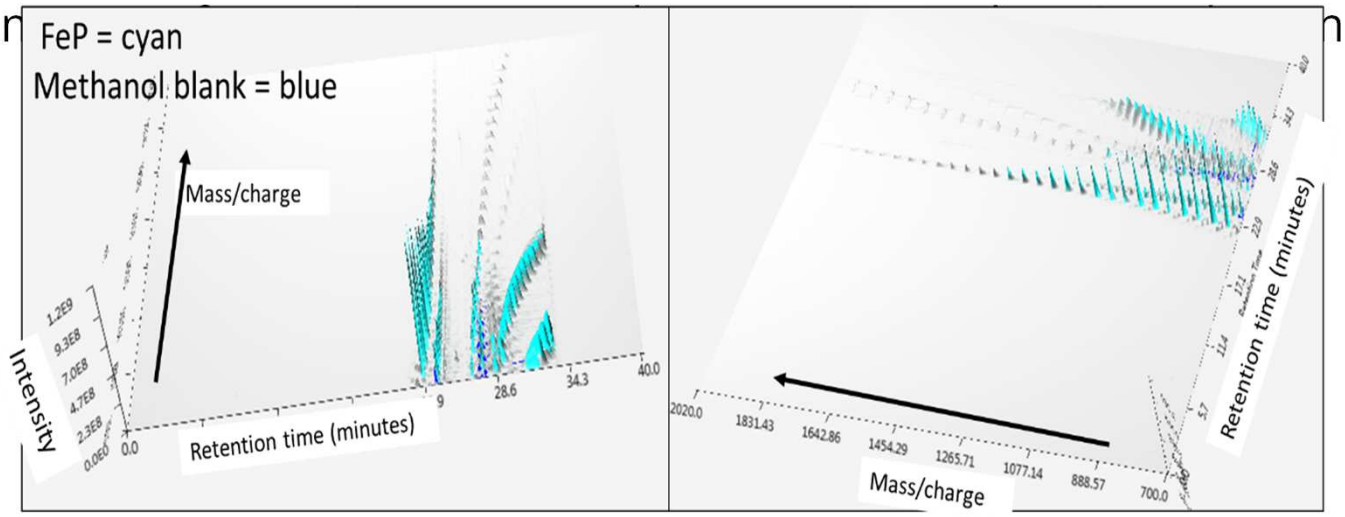


Persistent organic pollutants (POPs):*Organochlorines (OCs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and perfluoroalkyl substances (PFAS)*

Organics

Untargeted approach (HRMS)

- identified a broader range of potential organic compounds compared to targeted
- The ar[illegible]nount in TSP



Recommendation

- **This type of analysis may be a useful tool for the evaluation of**
  - **highly rich organic fertilizing materials**
  - **fertilizing materials produced from various wastewater sources**

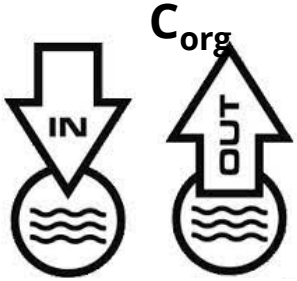
Organics

Pharmaceuticals, pesticides and hormones by coupled UHPLC-MSMS

- two methods
  - 1) the most readily 'water' soluble fraction
  - 2) and a **specific QuEChERS** (quick, easy, cheap, effective, rugged, and safe) **solvent extraction method**
- The highest concentrations were detected in the organic fertilizing materials
- Using the QuEChERS concentrations of 45 compounds were qualified in the dried sewage sludge FeP, but only 20 using water extraction
- Two hormones and two pesticides were detected only in P salt produced from sludge (having the highest organic and total carbon among the P salts)

Recommendation

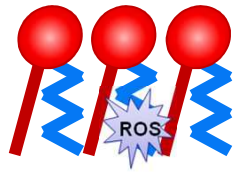
- Organic carbon is a good indicator o ıic pollutants
- **QuEChERS method can be used to tect pharmaceuticals, pesticides and hormones**



Ecotox

Triad approach

- The Tier 1 of Triad approach utilizes five ISO published ecotoxicological test systems
- **Earthworm avoidance test** - the tested fertilizers demonstrated an effect, especially at the higher application rates



Omega - 3 index

- No toxic effect was observed for P salt SL, P salt CL and ASH PI
- For **CCP** the Omega-3 Index decreased but only at 300kg P_2O_5 ha^{-1}

Recommendation

- **The Tier 1 Triad approach outlined in ISO 19204 (ISO, 2017) appears suitable as a primary screen of fertilizers derived from wastewater**
- **Omega - 3 index (NF X31-233, ISO 21479) is recommended to evaluate the overall toxicity of the recovered P-fertilizers**

Pathogens

- Methods used for those analyses are rather standardized

CFU in 1 g		Presence/Absence in 1 g		Presence/Absence in 25 g	Aerobic plate count
E. coli	Enterococcus spp.	E. coli	Enterococcus spp.	Salmonella spp.	

- **Positive growth of Gram variable rod-shaped bacteria (not defined in legislation) was identified in organic rich P salt**

Recommendation

- **several microbial colonies, other than the one defined in the legislation were detected and their inspection may be advisable to ensure the safety of the novel P fertilizing materials**

Phos4You contribution towards EU standard

- Common manuscript with recommended harmonization from Phos4you results

Recommendation/Proposal

Scientific paper
Deliverable

European Commission

EU call / request

Harmonisation

Thank you

Interreg North-West Europe Phos4You
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Investigated parameters:

- Major elemental analyses by CNS analyzer ; total mercury by automated AAS method
- Pharmaceuticals/hormones/pesticides by coupled UHPLC-MSMS: two extraction methods i) the most readily 'water' soluble fraction, ii) a specific QuEChERS (quick, easy, cheap, effective, rugged, and safe) solvent extraction to quantify a large range of contaminants commonly found in wastewaters (56 priority and emerging substances)
- Major (P) and trace elements in plants by ICP-OES and ICP-MS

Highlights of the observations:

- The organic fertilizing products contain the highest concentrations in organic carbon and organic contaminants
- Using solvent extraction (QuEChERS), 3 to 5 pharmaceuticals were quantified per product, generally at low concentrations
- 2 pesticides (diuron and its metabolite DCPMU) were quantified at low concentrations only in P-salt and BioP1
- 2 hormones were quantified only in P-salt produced from sludge (with the highest organic and total carbon content)
- Fewer compounds were quantified using water extraction

Recommendations:

- Automated and simple elemental methods (CHN & Hg) are robust and sensible
- The QuEChERS method is a strong extraction method that can be used to effectively detect and quantify priority and emerging substances potentially present in fertilizers
- Organic carbon is a good indicator of the presence of organic pollutants in the products

Munster Technological University - Highlights

Interreg North-West Europe Phos4You
European Regional Development Fund

Investigated parameters

- Production of an artificial mineral based growing medium.
- Analysis of the growth response of the recovered calcium phosphate (Psalt4_SL) produced at Macroom WWTP using the Struvia pilot plant.

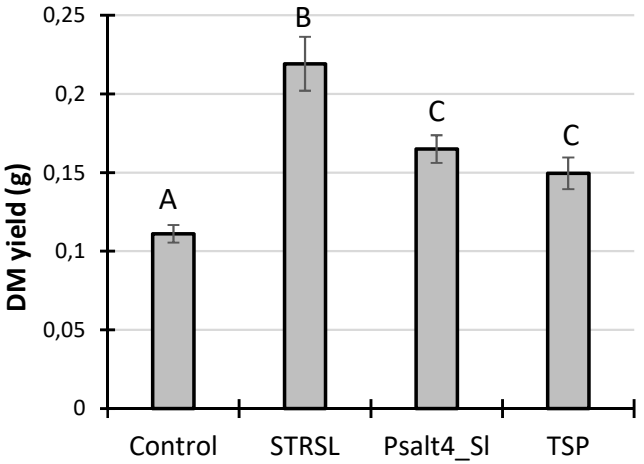
Highlights and observations

- Over five design generations, an artificial growing medium was produced from commercially available mineral products, creating a uniform and repeatable platform to test P fertilisers.
- The 5G growing medium has deficient levels of P which assists the analysis of P availability of applied fertiliser.
- The 5G growing medium presents similar physical and chemical characteristics to a typical Irish soil.
- The recovered phosphate (Psalt4_SL) produced a comparable dry matter yield to TSP over the 17 week trial (Figures 1 & 2).

Recommendations

- Where possible future growth trials should reflect fertiliser end use conditions, this may be achieved by using a growing medium with similar physical and chemical properties to a range of typical agricultural soils.

Figure 1: Test case growth comparison from the left: TSP,Psalt4_SL, STRLQ and Control.



Note: No statistical difference occurs between items sharing the same

Figure 2: Combined grass DM yields comparing fertiliser performance.

MTU Ollscoil Teicneolaíochta na Mumhan Munster Technological University

Quality assurance of recovered P

Investigated parameters in mono-incineration ashes:
ds, org stof, Cd, Cr III, Cu, Ni, Pb, Zn, Mo, Sb, Hg, Al, Ca, Fe, K, Mg, Ma, P, (PO4 en P2O5), S, S als SO4, SO3, Si,Be, Se , Te, Tl, Mn, Sn, V, W, en Cr VI

Highlights of the observations:
- challenges in P-recovery techniques are (partly) related to high Pb, Arsenic, iron and aluminium in ashes.
- Extraction methods in lab: Hf or aqua regia, give slightly difference in results
- No need to analyse for dioxins, organics, as these are < d.l. due to high T in incineration process.

Recommendations when moving towards a more standardized approach:
- Always use same extraction procedure (and preferable same lab)
- Improtant for possible future end of waste needs for recovered P

Investigated parameters :

- P availability : lipid biomarkers (root P lipid and leaf PC/DGDG indexes) based on the remodelling of some lipids under P-deficient conditions
- Ecotoxicity : ecotoxicological test using the Omega-3 Index calculated from the leaf fatty acid composition of *Lactuca sativa* (NF X31-233, ISO 21479)

Highlights of the observations :

- Root P lipid and leaf PC/DGDG indexes : both methods were able to distinguish P availability between the secondary P-fertilizers. Strong correlations were observed between these lipid biomarkers and leaf P concentration.
- Omega-3 Index : Slight effects were observed with some of the secondary P-fertilizers at the highest concentration. However, the secondary P-fertilizers did not lead to strong toxicity.

Recommendations :

- P availability : Root P lipid and leaf PC/DGDG indexes should be strongly considered in a more standardized approach. These methods bring additional insight as they reflects P's level that plants can efficiently metabolize. The leaf PC/DGDG index is more recommended since it does not require sacrifice of plants unlike the root P lipid Index.
- Ecotoxicity : The Omega-3 index (NF X31-233, ISO 21479) is recommended to evaluate the overall toxicity of the secondary P-fertilizers

Interreg North-West Europe
Phos4You

GCU Glasgow Caledonian University

Investigated parameters

- Polymers and surfactants; Perfluorinated alkyl substances (PFAS) & Untargeted analysis by high resolution mass spectrometry (HRMS)
- Ecotoxicity - earthworm avoidance, inhibition of: *Lactuca sativa* germination, dehydrogenase activity of *Arthrobacter globiformis* and microtox bioluminescence.

Polymers and surfactants - Although time consuming, polymers and surfactants (including benzalkonium compounds) detected in the products.

PFAS - Low concentrations (below the limits in drinking water) of these pollutants were detected and quantified in some products.

Untargeted Analysis by HRMS - The untargeted HRMS analysis worked well and identified a broader range of potential organic compounds rather than a few targeted pollutants. No illegal or highly toxic chemicals were determined in any of the products.

Ecotoxicity - Evaluation of the recovered P fertilizers indicates that there was no toxicity caused by these products identified. However, the recovered P fertilizers did have a slight impact in the soil organisms and plants growing in the amended soils.

Recommendations:

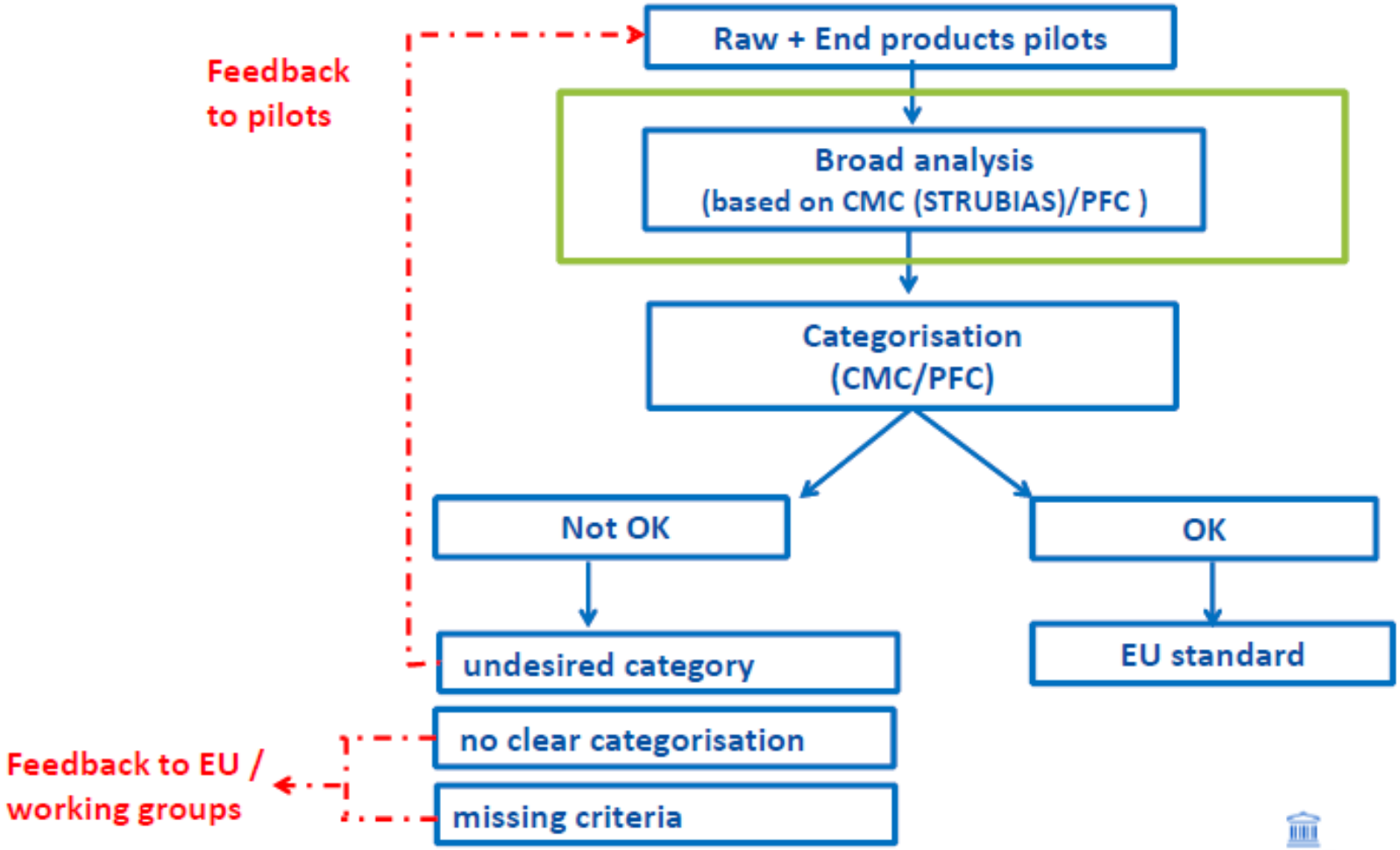
PFAS - Quantitation of PFAS should be included to monitor these new POPs as well as the original POPs (PCBs and PAHs etc).

Untargeted – This state of the art analysis should be developed further as an initial screening and monitoring process to provide consumer confidence.

Ecotoxicity - Soil quality TRIAD approach (Toolbox T-I: Toxicology) (ISO, 2017) is recommended when the overall toxicity of the recovered P products is evaluated.

GHENT UNIVERSITY

Phos4you WPT2 plan towards EU standardization



Phos4you WPT2
Nutrients and safety of new fertilizing materials

P salts

- P salt CL had a fast initial P release same as TSP
- P salt CL was having the highest concentrations of P, but also other contaminants compared to P salt4 SL and P salt5 BL
- P salt5 BL as produced from liquid fraction of sludge was the purest in terms of contaminates

Ashes

- P availability of ASH PI stayed limited by high concentration of Fe
- The presence of other elements and its bound to P in ASH PI is most likely the reason why it was not affected by substrate type and maintained comparable P release at both substrates tested
- Rather no or low organic pollutants were detected in ASH PI but higher concentrations of inorganic contaminants and other trace elements compared to TSP were detected in ash-based materials.

Bio phosphates

- For MA a comparable shoot dry matter as TSP was observed on sand
  - a higher shoot dry matter than TSP from the 3rd cut onwards, suggesting a delay in growth attributed to a delay in mineralization of P as a consequence of high carbon concentration in MA
- MA had significantly higher and comparable shoot P concentrations to TSP on substrate 1 and 2
- MA contained higher concentrations of contaminants than TSP, but within legislative limits, as being produced from wastewater after primary settling step in WWTP
- CCP achieved a lower dry matter compared to the commercial TSP treatment
- CCP treatment was able to increase shoot P concentration compared to the unfertilised treatment (ZeroP) but lower than the commercial TSP treatment
  - It is possible that the presence of calcium carbonate might have lowered the decomposition rate of the fertiliser
- CCP was the purest product (better than TSP) in terms of inorganic contaminants, since produced from the effluent wastewater of a small WWTP
- Several organic pollutants were detected in products that had high carbon concentration, CCP and MA

Problem statement

- Different response criteria and descriptive terms for QA of secondary P fertilizers have been used in the literature of the past decades
- These differences make it difficult to compare results obtained by using different techniques in different laboratories
- In an attempt to improve this situation Phos4You WP2 aim to propose protocols for the QA of secondary P products

Outline

- Key findings concerning methods and assessed criteria
- Summary and conclusions for proposed EU standard to assess quality of novel P containing products regarding fertiliser value and contaminant risks

P availability - Recommendation

- ***Aqua regia* and nitric acid**
  - method can be conducted in various modifications => stricter standard needed
  - MW over hot plate
  - MW protocol should be standardized

- **Mineral acids (MA) protocol**
  - possibility for errors caused by the evaporation and overheating of the novel P fertilizers
  - should be further tested in closed MW

- **2% Citric acid (CA) is defined in FR as only applicable to Basic slag**
  - its easy to use
  - often, as in our study, disputed as suitable for analysis of more than one element
  - it may be suitable for struvites at least

- **Neutral ammonium citrate (NAC) method**
  - deviations have been reported if the method was repeated

MW = microwave

AB28

Sample preparation

Drying

QA1-> Comparison of various drying Temperatures (desicator-50-105°C)



Recommendation

- High drying temperatures (> 50°C) were found unsuitable for the non-thermally treated products
- Drying of thermally treated products at high temperatures (105°C) does not affect their dry matter content and is thus also not required for their sample preparation
- Samples should be dried at low temperatures (<50°C) and kept in a dissector prior to analysis for preservation of their moisture content

QA2-> All P recovery processes had drying integrated in their production line
(Dry matter results confirmed that all products have DM > 90 %)
=> No additional drying was needed

AB28 perhaps sample preparation can be reduced or erased

Aleksandra Bogdan; 06.09.2021

Sample preparation

Grinding

All products were ground into fine powder

QA1-> Grinding using ball mills of stainless steel (and different materials) jars and balls

QA2-> Grinding using one ball mill with agate jars and balls

Chemical composition of TSP after grinding with stainless steel vs agate balls showed that :

- Cr and Ni in TSP ground with agate and stainless gave the same results

Recommendation

- As occasional wearing out may occur during grinding
  agate should be preferred over stainless steel jars and balls

Inorganics: analyses of solubility

- water and citric acid extracts indicate how the solubility of elements varies by product

>20% 'water soluble' marked in YELLOW

HIGH

Product

LOW

	S	Na	K	Mg	Ni	P	Ca	Co	Zn	Mn	Cu	Cd	Al	Cr	Fe	Pb	As
TSP	81.4	71.0	99.4	90.6	68.2	99.7	77.8	44.7	65.9	62.0	12.7	44.0	18.1	11.2	1.9	~	~
BioP1	31.2	76.1	81.2	38.3	33.8	1.6	5.1	16.2	3.9	3.0	20.3	~	~	1.9	1.3	~	~
P-Salt-3	43.0	90.1	77.3	30.0	29.7	1.7	4.9	20.7	~	0.3	15.0	~	~	0.0	~	~	~
Ash3	66.7	23.8	28.0	~	~	~	0.3	~	~	~	~	~	14.8	2.3	~	~	~
P-Salt-4	20.3	36.7	8.3	12.1	~	8.1	0.1	~	~	0.1	4.3	~	~	~	~	~	~
Ash2.2	67.8	3.0	0.7	1.0	~	0.3	0.8	~	~	~	~	~	0.5	~	~	~	~
BioP2	28.9	15.2	14.0	5.5	~	0.1	0.1	~	~	~	~	~	~	~	~	~	~

HIGH — *Element solubility in **water*** — LOW

Inorganics: P extraction methods

Carbon

- **CNS (INRAE): Inorganic, organo-mineral and organic secondary P fertilizer**

	P salt_CL	P salt_SL	P salt_BL	ASH PI	MA	CCP
Corg., %	4.8	6.1	2.4	<0.15	41.7	8.3

Nutrients and contaminants

METHOD	EXTRACT	EXTRACT RATIO, mL	MASS, g	
Closed microwave digest with Aqua Regia (UGhent)	HNO_3:HCl	2.5:7.5 (1:3 ratio)	0.15	1
Closed microwave digest with Aqua Regia (ERI)	HNO_3:HCl	1.2:4.8 (1:4 ratio)	0.25	2
Closed microwave digest with Nitric acid/hydrogen peroxide (ERI)	HNO_3:H_2O_2	5:1.5	0.25	3
Water (ERI)	H_2O	25	0.5	
2% Citric acid (ERI)	$C_6H_8O_7$	25		

3 "Total" digests

2 "Solubility" indicators

Inorganics: AR – nutrients and contaminants

- Two AR and HNO3/H2O2 “pseudo –total” methods were found rather comparable

AR – Nutrients

	P salt_CL	P salt_SL	P salt_BL	ASH PI	MA	CCP
AR -P_2O_5,%	25	4.9	6.5	14	1.9	2.6

- All fertilizers had CaO and MgO > 1.5 %, while MA had even TN of 6.2 %

AR - Contaminants (Pb, Hg…) and other elements (Fe, Al…)

- **ASHes > MA > P salt CL > TSP > CCP**
- Copper (Cu) and zinc (Zn) > legislative limit in ASH PI,
- Copper (Cu) > legislative limit in MA
  - but P: Cu or P: Zn ratio is not higher than plant need, so rather micronutrient
- high total chromium (Cr) was found in Psalt CL
  - originates from a industrial wastewater intrusion where the P recovery technology was situated at the time, and would not be expected in typical MWW composition

P availability: Substrate pore water sampling with Rhizons

QA 1 -> Rhizon soil moisture samplers a quick method that can mimic plant P uptake

- a good correlation between the shoot P uptake in plant and P in substrate solution *r (p < 0.001)*

	18 mg P pot-1		35 mg P pot-1		53 mg P pot-1	
	2nd week	4th week	2nd week	4th week	2nd week	4th week
Secondary P fertilizers and TSP	0.795	0.741	0.806	0.505	0.722	0.664
Secondary P fertilizers	0.743	0.714	0.779	0.651	0.744	0.687

- The P in substrate solution: struvites >> than in other fertilizers
- For ashes, the differences between two time points proved the slow P release patter

QA 2 -> Differences between the fertilizer P release at 2 different substrates were also visible in substrate pore water P after 1 cut

- The highest substrate pore water P concentration had TSP and MA, higher at substrate 1 than at substrate 2
- Significantly higher P concentration in substrate pore water and rather comparable among the substrates had P salt CL
- For Zero P the P concentration in substrate pore water was under or near detection, same as for CCP
- For ASH PI the P concentration in substrate pore water was low and comparable between the substrates

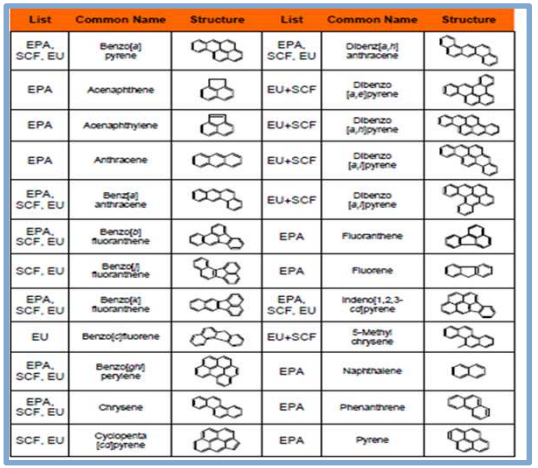
Organics: Persistent organic pollutants (POPs)

Organochlorine (OC) pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH) and perfluoroalkyl substances (PFAS)

QA1 -> some POPs were detected in FeP

QA 2 ->

- Several PAHs, PCBs or OCs were detected in products that had high carbon concentration, CCP and MA
- One PCB (53) was found in P salt CL
- Some PFAS were detected all tested secondary P fertilizers



List	Common Name	Structure	List	Common Name	Structure
EPA, SCF, EU	Benzo[a] pyrene		EPA, SCF, EU	Dibenz[a,h] anthracene	
EPA	Acenaphthene		EU+SCF	Dibenzo [a,e]pyrene	
EPA	Acenaphthylene		EU+SCF	Dibenzo [a,h]pyrene	
EPA	Anthracene		EU+SCF	Dibenzo [a,i]pyrene	
EPA, SCF, EU	Benz[a] anthracene		EU+SCF	Dibenzo [a,l]pyrene	
EPA, SCF, EU	Benzo[b] fluoranthene		EPA	Fluoranthene	
SCF, EU	Benzo[j] fluoranthene		EPA	Fluorene	
EPA, SCF, EU	Benzo[k] fluoranthene		EPA, SCF, EU	Indeno[1,2,3-cd]pyrene	
EU	Benzo[c]fluorene		EU+SCF	5-Methyl chrysene	
EPA, SCF, EU	Benzo[ghi] perylene		EPA	Naphthalene	
EPA, SCF, EU	Chrysene		EPA	Phenanthrene	
SCF, EU	Cyclopenta [cd]pyrene		EPA	Pyrene	

Findings:

Organic carbon is a good indicator of potential POPs presence

Overall, secondary P products were found to have POPs tested below legislative limits for secondary P fertilizers (PAH_{10} << 6 mg kg^{-1} dm; PCB_7 << 0.8 mg kg^{-1} dm; OC << 20 ng kg^{-1} (

Organics: Pharmaceuticals

QA 1 -> Queschers VS water extraction

- FeP product - quantified concentrations of **45 compounds** (few ng/g up to 86 ng/g (for amitriptyline) **via Queschers and 20 via water**
- Only 3 to 8 compounds - detectable in the other products
- **QA 2** -> Queschers extraction
- 16 pharmaceuticals were not detected in all the secondary P fertilizers, but few were

[c] µg/kg	P_salt5_BL	P salt 4_SL	Biop 1	Biop 2	P salt3-CL	LQ (µg/kg)
alprazolam	<LQ	<LQ	<LQ	<LQ	0,9	0,6
carbamazepine	<LQ	1,5	11	<LQ	<LQ	1,2
diazepam	<LQ	<LQ	<LQ	<LQ	0,8	0,6
metformin	<LQ	<LQ	3,3	<LQ	<LQ	0,8
nordiazepam	<LQ	<LQ	<LQ	<LQ	0,8	0,6
oxazepam	1,0	1,4	1,6	<LQ	<LQ	0,6
paracetamol	2,0	21	108	4,3	<LQ	0,8
theophylline	1,4	21	139	1,9	27	0,6

Organics: untargeted compounds

QA 1 -> methanol and acetonitrile extraction and analysis with HRMS

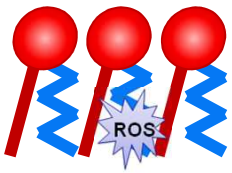
- HRMS determined **numerous organic contaminants**
- However, since no standards were available the amount can only be estimated
- **Quaternary ammonium compounds** consistent with anti-microbials and surfactants were determined in some of the products, particularly **TSP and FeP**
- Polymer type products were also determined in TSP and FeP. It could not be verified if these were part of the fertiliser as polymers can sometimes be used in slow release products.

QA2 ->

- **Suspected polymers in secondary P fertilizers were in higher concentration than in the TSP**
- None of the secondary P fertilizers contained higher levels of the Quaternary ammonium compounds when compared t

Ecotox : omega – 3 - index

"**Omega-3 Index**" = Fatty acid ratio C18:3/(C18:0 + C18:1 + C18:2)



QA 1 -> Pot trials according to the standard **NF EN ISO 21479**

- with the fertilizing products applied at a rate of 60 kg P_2O_5 ha^{-1} showed no phytotoxicity of the P fertilizing products


Lactuca sativa

QA 2-> **The AFNOR standard NF XP31-233** and ISO 21479 test six rates of fertilizer: 0, 30, 60, 90, 180 and 300kg $P_2O_5ha^{-1}$

- **Biomass of lettuce shoots**
  - no toxic impact was observed for P salt CL and ASH PI
  - **P salt SL and CCP** had a linear decrease of the fresh biomass of lettuces with the increase of the fertilizer concentrations
- **Omega - 3 index**
  - No toxic effect was observed for P salt SL, P salt CL and ASH PI
  - For **CCP** the Omega-3 Index decreased but only at 300kg P_2O_5 ha^{-}

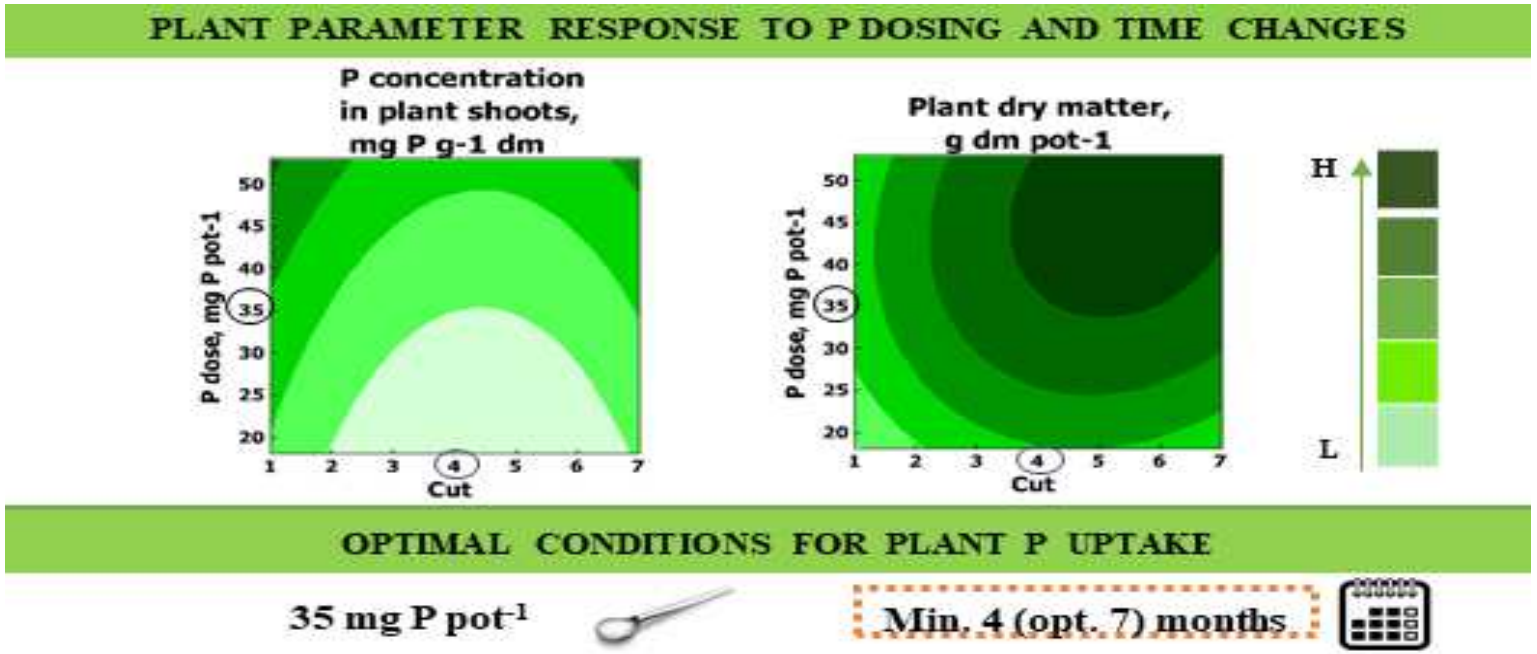

Gas Chromatography (GC-FID)

Findings

Overall, as fertilizers are typically applied at P doses of 60 kg $P_2O_5ha^{-1}$ or lower, the use of novel secondary P fertilizers may be considered safe, but attention should be given at the quantity given in time to avoid possible overdosing negative effects, especially in case of CCP and P salt SL

P availability: Recommended P dose & experimental time

QA1-> Results based on STRSL, STRSL, FeP, ASH1 and ASH2 (*Bogdan et al. 2021*)



QA2-> Results based on MA, CCP, ASH PI and P salt CL

- Confirmed the finding that 4 cuts/months is a minimum time needed to observe the slow release
  effect of secondary P fertilizers
- Longer trial may show full P release capacity of secondary P fertilizers, especially MA and CCP

P availability: Substrate effect River sand vs artificial mineral substrate

QA 1 -> washed P-poor **river sand** was shown as an adequate substrate for the repetitive testing of the P availability in the novel secondary P fertilizers

- it has the **low trace element** composition
- the **ability of zero P treatment to become exhausted** within 3 cuts

QA 2 -> Low P substrates can also be used for testing the P retention and release; however, there are discrepancies for some products with the results on P availability obtained by growing plants in the river sand

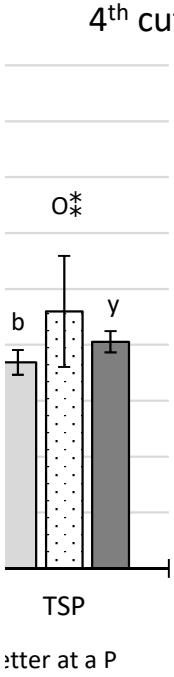
- **P uptake on sand : MA > TSP = P salt CL > CCP > ASHPI > ZeroP**
- **P uptake on artificial mineral substrate: P salt CL > TSP > ASH PI > ASHGC ≥ MA = CCP ≥ Zero P**

Findings

- **Sand allowed all secondary P fertilizers to express their highest P release potential**
- **Physico-chemical characteristics (Presence of clay and all other elements (Fe, Al…),high pH) of artificial mineral substrate reduced the P uptake of all P fertilizers, especially MA and CCP**

P availability: Substrate effect Growing medium development

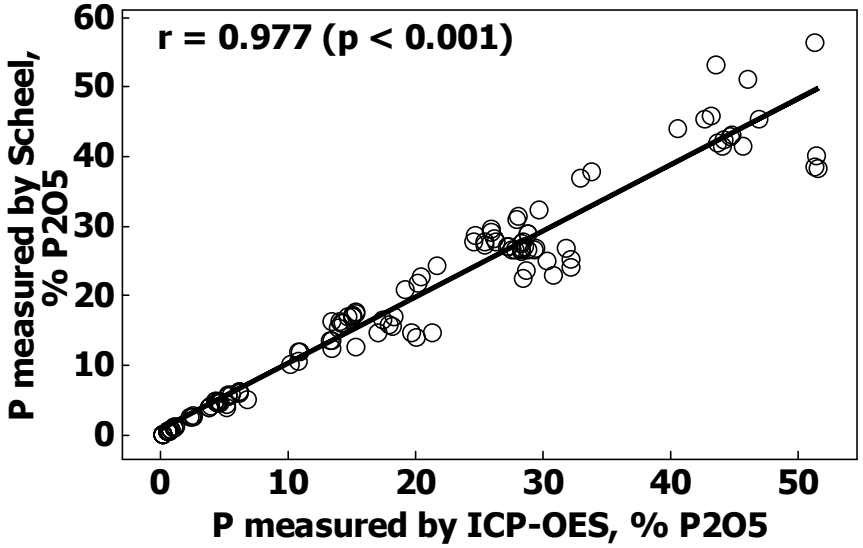
- P salt SL was tested on 3 low P growing mediums (GM) developed within project
- P salt SL proved to have fast P release and comparable shoot dry matter as TSP starting from the 1st cut on all 3 GMs



GM characteristics	GM_1	GM_2	GM_3
Granite Sand %	65	60	55
Vermiculite ,%	5	10	15
pH	6.7 ± 0.48	7.0 ± 0.42	7.3 ± 0.28
Morgan's P	0.49	0.49	0.49
Morgan's K	84.6	119.6	217.8
CEC meq/100g	15.5	13.5	11.25
Electrical conductivity (EC) µS cm^{-1}	21.02	49.9	24.01
Bulk Density (g/cm^3)	1.21	1.13	1.08
Total porosity (%v/v)	31.3	37.1	48.4
Air filled porosity (%v/v)	6.6	11.2	14
Container water capacity (%)	18.84	24.2	27

P availability
P determination methods

- P determination using ICP-OES and spectrophotometric molybdenum-blue, modification by Scheel (Van Ranst, 1999), method after 6 chemical P extractions of secondary P fertilizers were compared and found equally applicable



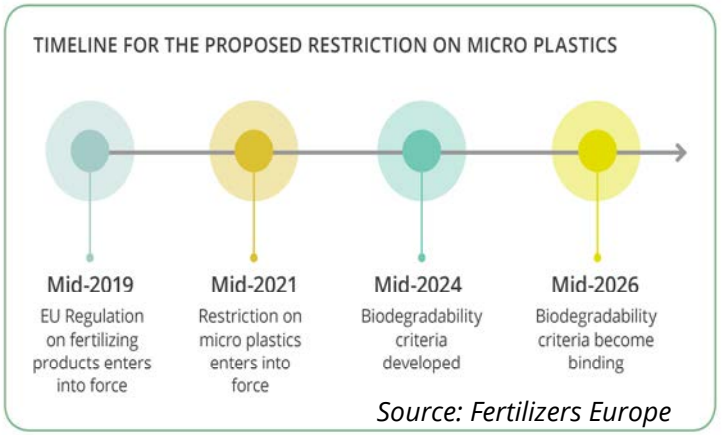
Recommendation

- **More procedures for P determination should be added into legislation if not fully replacing the old ones**
- **Exception: general sensitivity of NAC P extracts to the P determination method used afterwards**

Demand for QA standardization

Other emerging tests

- Hormones, Pharmaceuticals
  - Organic pollutants traceability should be under evaluation of each technology (*ESPP*)
- Ecotoxicity
  - risk assessment tools are welcomed by consumers
- P availability
  - A relevant number of pot trials with P-fertilizers recovered from wastewater treatment has been conducted, but their uneven designs had caused difficulty in interpretation and comparison of the results (*Huygens and Saveyn, 2018; Kratz et al., 2019*).
  - Previous investigations using secondary P fertilizers did not show, in most cases, a good correlation between chemical P extractions and the actual plant P uptake (*Duboc et al., 2017; Huygens and Saveyn, 2018; Ylivainio et al., 2021*).



Source: Fertilizers Europe

"While routine standardised measurement techniques for plastic in soils or biofertilizers do not exist, such techniques can be expected to be developed in the relatively short term." (EIP-AGRI)