Quality assessment of fertilizing P materials recovered from municipal wastewater

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1. Introduction

Demand for alternative and renewable phosphorus (P) sources, such as municipal wastewater, has led to production of novel fertilizing P materials.

Applied P recycling technology	Fertilizing P material
Thermal process	ASH (PI – pyrolysis/incineration)
Sludge leaching	P salt (CL – chemical and BL – biological leaching)
Ash Leaching	DCP/P acid
Microalgae photobioreactor	Microalgae (MA)
P adsorption	Granules (CCP – crab carapace P)
P salt precipitation	P salt (SL - sludge)

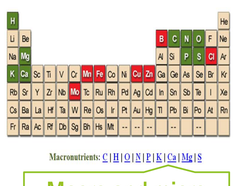
To allow wider application of fertilizing P materials on the market, it is necessary to asses their quality (QA) in terms of:

1. Their **nutrient availability** dependency on time, P dose, and growing medium
2. Their **safety** in terms of their chemical inorganic and organic composition, ecotoxicity as well as pathogens content

2. Quality Assessment methodology

Inorganics


Fertilizer P solubility

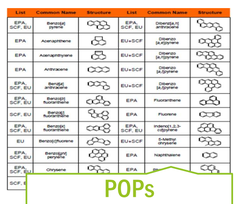

Macro and micro nutrients


Heavy metals

Organics


Pharmaceuticals

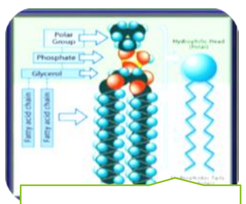

Hormones


POPs (PCBs, PAHs, etc.)

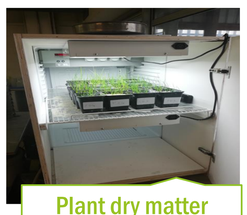
Plant P availability

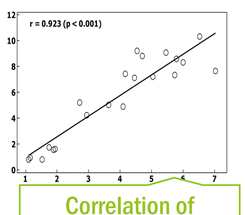

Plant P content (time & dose effect)


Pore water sampling with Rhizon



Plant P lipid index


Plant dry matter (Substrate effect)



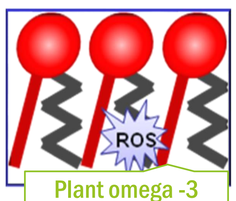
Correlation of chemical P/plant P


Field trials

Ecotoxicity And Pathogens


Salmonella/E-coli/Enterococcaceae


Terrestrial/aquatic tests



Plant omega -3 index

3. Results and Discussion

Carbon and inorganic content of fertilizing P materials

Carbon and nutrients

- Inorganic, organo-mineral and organic fertilizing P materials
- All fertilizing P materials *aqua regia* (AR) **P content > 1.5 % P_2O_5**
- All fertilizing P materials had CaO and MgO > 1.5 %
- MA with TN of 6.2 % is N-P compound fertilizer

	P salt_CL	P salt_SL	P salt_BL	ASH PI	MA	CCP
C_{org}, %	4.8	6.1	2.4	<0.15	41.7	8.3
AR -P_2O_5,%	25	4.9	6.5	14	1.9	2.6

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

- **Copper (Cu) and zinc (Zn)** in **ASH PI** > EU legislative limit (EC, 2019) and Copper (Cu) in **MA** > EU legislative limit (EC, 2019)
  - However P: Cu and P: Zn ratio were not higher than plant need and thus could be considered micronutrients rather than contaminants
- High **total chromium (Cr)** was found in **P salt CL**
  - not expected in municipal wastewater, originates from a industrial wastewater intrusion where the P recovery technology was situated

Organic pollutants in fertilizing P materials

Persistent organic pollutants (POPs):

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

- Several PAHs, PCBs or OCs were detected in fertilizing P materials with high C_{org} concentration, CCP and MA
- One PCB (53) was found in P salt CL
- Some PFAS were detected all tested fertilizing P materials

Overall, fertilizing P materials were found to have POPs tested below legislative limits (EC, 2019) for fertilizing P materials (PAH_{10} << 6 mg kg^{-1} dm; PCB_7 << 0.8 mg kg^{-1} dm; OC << 20 ng kg^{-1} d)

Hormones

- 18 hormones (over 20) < detection in all fertilizing P materials
- **Androstenedione and epitestosterone**, were detected only in P salt SL

Pharmaceuticals

- 16 pharmaceuticals were not detected in all the fertilizing P materials. Few pharmaceuticals were quantified (except for ASHPI), generally at low concentrations:

[c] µg/kg	P salt BL	P salt SL	MA	CCP	P salt 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

Untargeted compounds

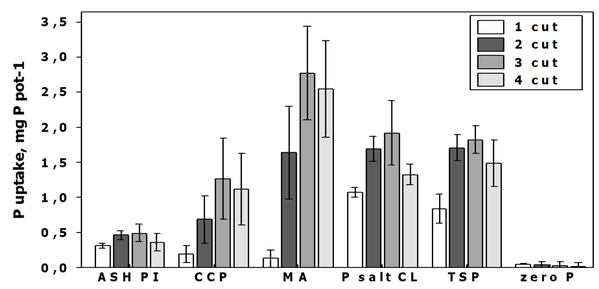
- Higher concentration of several polymers were detected in fertilizing P materials (P salt CL, MA, P salt SL) compared to the TSP
- All fertilizing P materials contained lower levels of the Quaternary ammonium compounds compared to TSP

Plant P availability of fertilizing P materials

Substrate and time effect on plant P uptake and PUE

- This study was used to compare the P release of fertilizing P materials at river sand during four month growth of perennial ryegrass
- Plant P uptake of P salt CL was high from the 1st cut and increased in time
- Plant P uptake of ASH PI was stable and controlled by a high concentration of Fe
- Plant P uptake for MA rich in C_{org}, and CCP rich in Ca and C_{org} increased in time and reached its maximum only after 3rd plant cut
- **Four months proved as a minimum time** needed for observing the P uptake of fertilizing P materials. Longer trials may show their full P release capacity, especially for MA and CCP
- **Overall fertilizing P material effect:**

MA > TSP = P salt CL > CCP > ASHPI > Zero P



Leaf and root P biomarkers

- Leaf P concentration correlated significantly with the leaf PC/DGDG, %C16:1t and Root Lipid P Index for both substrates

	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

Pearson's correlation coefficients between all parameters measured on ryegrass grown under controlled condition for one month calculated from all substrates (sand and artificial mineral substrate) taken together

Low P growing medium development and effect on plant dry matter

- 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

Eco toxicity and Pathogens content in fertilizing P materials

Biomass of lettuce shoots

The AFNOR standard NF XP31-233 and ISO 21479 test was performed on *Lactuca sativa* on six rates of fertilizing P materials : 0, 30, 60, 90, 180 and 300kg $P_2O_5 ha^{-1}$

- Non toxic effect (decrease in the fresh shoot biomass) was observed for P salt CL and ASH PI with increase in the fertilizing P materials dose
- P salt SL and CCP had a linear decrease of the fresh biomass of lettuces with the increasing fertilizing P materials dose

Omega - 3 index

- No decrease (toxic effect) was observed for P salt SL, P salt CL and ASH PI when concentrations of fertilizing P materials were increased
- For CCP the Omega-3 Index decreased at 300kg P_2O_5 ha^{-1}

Overall, as optimal plant P dose is 60 kg $P_2O_5 ha^{-1}$ or lower, the use of novel fertilizing P materials 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

Pathogens

- No sample harboured detectable levels of the target pathogens (Table below)
- Only the P salt SL sample yielded growth—non-lactose fermenting colonies— on the MAC plate from the 25 g enrichment. This growth tested oxidase positive, ruling it out as *Shigella spp.*
- Positive growth of Gram variable rod-shaped bacteria was identified in both sample P salt SL and MA

Fertilizing P materials	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.*	
ASH PI	<1	<1	Absent	Absent	Absent	0
P salt SL	<1	<1	Absent	Absent	Absent	>300
P salt CL	<1	<1	Absent	Absent	Absent	0
MA	<1	<1	Absent	Absent	Absent	>300
CCP	<1	<1	Absent	Absent	Absent	>300

4. Conclusions

P salts

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

Ashes

- P availability of ASH PI was higher than Zero P, but limited by high concentration of Fe
- Higher concentrations of inorganic contaminants and other trace elements compared to TSP were detected in ash-based materials, as this ash was not yet chemically post-treated

Bio phosphates

- For MA a comparable shoot dry matter as TSP was observed
- MA had significantly higher shoot P concentrations compared to TSP
- MA contained higher concentrations of contaminants than TSP
- CCP had lower dry matter compared to TSP but it increased shoot P concentration compared to Zero P
- Presence of $CaCO_3$ in the CCP potentially lowered its decomposition rate
- CCP was the purest product in terms of inorganic contaminants but several organic pollutants were detected, as well as in MA

References:
EC (2019) REGULATION (EU) 2019/1009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003. Official Journal of the European Union, L170/1.
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