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Fertilization efficiency of thirty marketed and experimental recycled phosphorus fertilizers

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ABSTRACT

Recycling phosphorus (P) from waste streams like sewage sludge, animal manures or food industry by-products is required to sustain soil fertility without depleting non-renewable P resources. Several technologies are available for P recovery, leading to fertilizers differing in P solubility and bioavailability. In this study, thirty fertilizers obtained through different technologies were tested to assess if their fertilization efficiency was equivalent to mineral soluble fertilizer applied as triple superphosphate (TSP). The main selection criteria were (1) ensuring a wide chemical diversity, and (2) choosing products already on the market or at a late stage of development, to encompass a representative selection of current and future recycled fertilizers. The products were classified according to their organic carbon content and neutral ammonium citrate (NAC), and the main P species of each fertilizer was determined through K-edge and L_{2,3}-edge X-ray absorption near edge structure spectroscopy (XANES). Three pot experiments with wheat, barley and ryegrass were conducted in three growing substrates with contrasting properties, all within a pH range of 5.8–6.9. Fertilizers containing ammonium magnesium phosphate, monoammonium phosphate, monocalcium phosphate, and dicalcium phosphate type species as dominant P species showed a similar fertilization efficiency to TSP, while fertilizers with hydroxyapatite, tricalcium phosphate, phytic acid or iron phosphates as their main P species had lower fertilization efficiencies. We conclude that while the trend towards high-efficiency, refined inorganic recycled P fertilizers is positive, lower-performing, mostly unrefined fertilizers must be assessed in light of their long-term P supply potential and additional benefits to soil health owing to their content of organic matter and other nutrients.

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1. Introduction

Phosphorus (P) plays a crucial role in agriculture as it is an essential element for plants. Phosphate rock (PR) is the conventional raw source for P fertilizers, with global market fluctuations due to its limited and concentrated reserves. Currently Europe is highly dependent on imported P fertilizers (84% of total PR used, [European Commission, 2020](#)). However, the European reliance on PR has shifted since 2018, when Norge Mining obtained a licence to examine the exploitation potential of PR deposits in Rogaland, Norway ([Ihlen et al., 2014](#)). Although this might alleviate the European (and global) dependency on PR for decades, the European strategy of P recovery and recycling from side- and waste streams needs to be further implemented for meeting European ([Garske et al., 2020](#)) and global ([Brownlie et al., 2022](#); [Richardson et al., 2023](#); [United Nations, 2015](#)) food security and environmental targets. Therefore, it is of strategic importance to transform alternative P-rich side streams into fertilizer. In 2019, the EU published a new Fertilizing Products Regulation (FPR) (EU, 2019/1009) ([European Parliament, 2019](#)) which aims to promote the use and trade of fertilizers derived from nutrient-rich side streams, thus attempting to close the P cycle, reduce the environmental impact of nutrient-rich side streams and diminish the reliance on finite resources.

Due to long-term P sorption in soil ([Frossard et al., 2000](#)) and losses through erosion, runoff and leaching ([Rittmann et al., 2011](#)), only around 16% of the applied P fertilizer is estimated to be consumed by humans. There are inherent and external factors conditioning P bioavailability in a fertilizer. Chemical composition, structure and crystallinity of the active ingredients, and formulation of the product determine its solubility, and hence its nutrient use efficiency ([Kratz et al., 2019](#)). Once in the field, reaction time and environmental conditions such as climate, soil pH, texture, mineralogy and P sorption capacity influence the final bioavailability of the nutrient ([Kratz et al., 2019](#)).

There is a wide array of P-rich streams suitable for fertilizer production, including biogas digestates, rendering by-products, farmyard manures and sewage sludge ([Kratz et al., 2019](#)). Additionally, different technologies are available for P-recycling, namely from targeted processes such as precipitation from liquid waste streams, extraction from solid phase and recovery as pure P compounds, or thermo-chemical P species transformation, to less targeted processes such as pyrolysis, carbonization, composting and fermentation ([Kratz et al., 2019](#)). The P forms in these streams and the processing methods determine the main phosphorus species present in the obtained recycled fertilizers. This leads to a broad array of recycled P fertilizers which range widely in their dominant P species, which results in variable P bioavailability once applied in the field. There is still little insight into the dominant P species in recycled fertilizers, in particular those obtained with the most novel technologies, and how these species determine the efficiency of the recycled P fertilizer.

Fertilization efficiency, which can be defined in terms of the amount of applied P used by crops or the yield per unit of applied P, of recycled P fertilizers has been evaluated in several studies ([Cabeza et al., 2011](#); [Christiansen et al., 2020](#); [Duboc et al., 2017](#); [Vaneckhaute et al., 2016](#)). However, these experiments often test only a small set of fertilizers. Given the current variety of recycled P fertilizers already on the market or under development, it is necessary to assess their fertilization efficiency, and how it is affected by the main P species present in the product. This will expand the knowledge base for rational and sustainable P fertilization based on recycled resources and consequently help to achieve fertilization strategies based on a circular economy approach.

The objective of this study was to assess the fertilization efficiency of a wide, chemically diverse set of marketable recycled P fertilizers to evaluate their potential as alternatives to conventional P fertilizers from finite deposits. To this end, a set of 30 fertilizers from contrasting P-rich streams and processing methods were characterized according to their total organic carbon content (TOC), neutral ammonium citrate (NAC)

solubility and P species as determined by synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy. Subsequently, the fertilizers were tested in three different pot experiments, in which wheat, barley and ryegrass were grown to maturity in two soils with contrasting properties and a sand-peat-clay substrate, all with a pH range of 5.8–6.9 and at experimental stations in Tulln (Austria), Jokioinen (Finland) and Frick (Switzerland), respectively. The crops and soils selected are representative of typical conditions found in these countries. Given that the tested products are already on the market or at a late developmental stage, we hypothesized that most of them have a comparable fertilization efficiency to conventional mineral P fertilizers like triple superphosphate. Overall, the fertilization efficiency was expected to be explained mainly by the P species present in each product, with reportedly less available species like hydroxyapatite or iron phosphates performing worse than fertilizers with more soluble P species like monoammonium or monocalcium phosphate. Additional differences deriving from the growing media used and testing conditions in each of the three experiments were also expected.

2. Material and methods

2.1. Fertilizer selection

Thirty fertilizers from recycling sources were selected considering agronomic and environmental aspects as well as the EU Fertilizing Products Regulation, FPR (2019/1009) ([European Parliament, 2019](#)). First, an online survey was distributed among stakeholders and science networks to identify possible materials with at least 1% P₂O₅ content, taking into account physical properties and water content. Fertilizers had to comply with the FPR requirements, except for products of sewage sludge origin. The final product selection intended to include fertilizers representing different product function categories (PFC) and component material categories (CMC) of the FPR to include a chemically diverse group of fertilizers in the study. Fertilizers in which the feedstock material, processing and homogeneity were not clear were discarded. Most of the selected materials had a technology readiness level (TRL) above 6, with 13 of the selected products being already on the market, either in the entire EU or in individual member states. A summary of the fertilizer characteristics can be found in [Table 1](#).

2.2. Fertilizer analyses

2.2.1. Elemental composition

The elemental composition of the fertilizers was analyzed at the Natural Resources Institute Finland (Luke). Fertilizers were dried at 37 °C and ground to 1 mm prior to their elemental analysis. Total P was analyzed, after an *aqua regia* digestion, with ICP-OES (Perkin Elmer Optima 8300). TOC was determined by dry combustion in a solITOC instrument (Elementar Analysensysteme GmbH).

2.2.2. Fertilizer P extractability analysis

A neutral ammonium citrate (NAC) extraction was carried out at the University of Natural Resources and Life Sciences, Vienna (BOKU), adapting the BS EN 15957:2011 method. The NAC solution was prepared by adding a 28–30% w/v ammonia solution to a 18.5% w/v citrate solution until reaching pH 7. Fertilizers were milled to pass a 0.2 mm sieve, extracted at a solution to solid ratio of 1:10 (50 ml NAC:500 mg fertilizer) by placing vials into a 65 °C shaking water bath for 60 min. The solutions were then cooled and brought to a volume of 250 ml with laboratory grade water type I. The extracts were filtered through Munktell filter paper (grade 1290, Ahlstrom-Munksjö Munktell) and aliquots were acidified to 2% HNO₃ w/w. The phosphorus concentration in the extracts was measured by ICP-OES (Optima 8300, Perkin Elmer).

2.2.3. Fertilizer classification used in this study

Due to the large number of products tested, the fertilizers were

Table 1
Overview of the recycled fertilizers investigated in this study and the reference fertilizer TSP.

Acronym	Fertilizer	PFC ^a	Fertilizer class	Development status ^b	Granulation ^c	Dry matter content (%)	TOC (%)	P (g kg ⁻¹ DM)	P NAC extracted (% of total P)
TSP ^d	Triple superphosphate	Inorganic (mineral)	Reference	M	Granular	93.0	0.5	206	90.3
CGO	Struvite	Inorganic (mineral)	Struvite	M	Granular	54.8	0.3	228	94.0
PCS	Struvite	Inorganic (mineral)	Struvite	M	Granular	54.9	0.3	233	92.7
SSW	Struvite	Inorganic (mineral)	Struvite	M	Granular	59.7	0.2	213	99.0
EPS	Struvite	Inorganic	Struvite	D	Powder	61.0	1.8	203	88.6
STR	Struvite	Inorganic	Struvite	D	Powder	62.2	1.8	196	95.3
EPH	Sunflower husks ash	Inorganic	Inorganic soluble	M	Granular	97.1	1.2	19.5	80.5
ADC	Na-AshDEC	Inorganic (mineral)	Inorganic soluble	D	Powder	100	0.5	80.5	96.0
BZH	TSP from sewage sludge ash	Inorganic (mineral)	Inorganic soluble	D	Granular	95.5	0.1	181	91.4
DCP	Dicalcium phosphate from sewage sludge ash	Inorganic (mineral)	Inorganic soluble	D	Powder	96.6	0.0	222	79.8
MAP	Monoammonium phosphate from mining waste	Inorganic (mineral)	Inorganic soluble	D	Powder	99.9	0.0	249	104.9
PRC	P-RoC	Inorganic	Inorganic soluble	D	Granular	94.1	3.3	38.3	79.5
VVB	Vivianite recovered from sewage sludge	Inorganic	Inorganic soluble	D	Granular	83.9	4.0	122	78.1
PLA	Turkey litter ash	Inorganic	Inorganic insoluble	M	Powder	92.1	0.5	52.3	35.2
BES	BioEcoSIM	Inorganic	Inorganic insoluble	D	Powder	67.4	1.6	180	66.0
KBT	Sewage sludge slag	Inorganic	Inorganic insoluble	D	Powder	99.8	0.0	110	72.0
PKA	Sewage sludge ash	Inorganic	Inorganic insoluble	D	Powder	100	0.0	22.8	11.6
ABP	Animal biochar	Inorganic	Pyrolyzed product	D	Granular	72.8	10.7	150	40.7
BAG	Sewage sludge char	Inorganic	Pyrolyzed product	D	Granular	99.4	13.6	52.3	53.6
CRA	Hydrochar from fruit juice sludge	Organic	Pyrolyzed product	D	Granular	28.9	48.6	9.1	73.5
MBC	Poultry litter biochar	Organic	Pyrolyzed product	D	Granular	98.3	31.5	30.6	70.4
PPS	Pyrolyzed pig slurry digestate	Organic	Pyrolyzed product	D	Granular	98.9	47.6	43.6	69.7
BA1	Wheat and maize fermented and distilled	Organic	Organic fertilizer	M	Granular	90.4	44.2	13.6	78.3
MB1	Meat and bone meal	Organic	Organic fertilizer	M	Powder	97.6	34.3	63.4	80.8
MO10	Vegetable and animal biomass waste	Organic	Organic fertilizer	M	Granular	91.3	32.2	50.9	40.4
MO14	Vegetable biomass waste	Organic	Organic fertilizer	M	Powder	91.7	24.1	67.4	16.5
OG1	Meat and bone meal	Organic	Organic fertilizer	M	Granular	94.9	40.9	34.9	85.9
OPU	Chicken manure and grape residue pellets	Organic	Organic fertilizer	M	Granular	84.9	32.5	19.6	81.5
PRV	Biogas slurry from biowaste and sewage sludge	Organic	Organic fertilizer	M	Granular	25.1	22.3	28.5	88.7
RAN	Biowaste and sewage sludge	Organic	Organic fertilizer	M	Granular	84.6	27.2	35.2	86.5
NNP	Dried municipal and industrial sludge	Organic	Organic fertilizer	D	Granular	91.3	34.8	25.4	78.8

^a Product function category according to EU 2019/1009.

^b Developmental status: M: in the market. D: in development.

^c Granulation of the original product, in some pot trials these products were milled before application.

^d Fertilizer used as reference material.

classified into categories with comparable characteristics and number of products in order to facilitate meaningful data interpretation. Using the PFCs and CMCs proposed by the EU regulation 2019/1009 was impractical, as the PFC classification was too unspecific regarding contained P forms and overall material properties, and the number of products per CMCs was uneven. Fertilizers were thus qualitatively classified into five categories named "Fertilizer class" (Table 1):

struvites, inorganic NAC soluble fertilizers, inorganic NAC insoluble fertilizers, pyrolyzed products and organic fertilizers. This grouping expanded the initial PFC classification and adapted it to the fertilizers included in this study (Table 1). To define a threshold to distinguish between organic and inorganic products, we followed the FPR, which states that solid organic fertilizers are required to have a minimum of 15% TOC (European Parliament, 2019). Within this organic group, there

were enough pyrolyzed products to group them into a separate category. Additionally, two products with $7.5\% < \text{TOC} < 15\%$ were included in the pyrolyzed products category. The division between inorganic insoluble and inorganic soluble products was also based on the FPR, according to which at least 75% of total P shall be NAC-extractable for the commercialization of an inorganic fertilizer as “mineral fertilizer”. The number of struvites tested (five) was high enough to group them separately from the NAC soluble inorganic group (seven).

2.3. Synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy

The tested fertilizers were analyzed using P K-edge and $L_{2,3}$ -edge XANES to identify the major P species present. The analysis took place at the Canadian Light Source (CLS, Saskatchewan, Canada). A collection of 21 reference materials were included for K-edge XANES and 18 for L-edge analysis. A detailed list of all analyzed materials can be found in [Tables S1 and S2](#). Where available, the reference materials were bought from reliable lab chemical suppliers. Some minerals (vivianite, variscite, strengite) were purchased through online retail platforms. Amorphous iron phosphate, K-taranakite and NH_4 -taranakite were synthesized according to [Abd El-Lateef et al. \(2018\)](#) and [Taylor and Gurney \(1961\)](#), respectively. P adsorbed on ferrihydrite (1% m/m) was prepared according to the protocol included in the supplementary material. No additional analyses were conducted to assess the purity of the reference materials. All products were milled to < 0.2 mm.

2.3.1. K-edge XANES

Phosphorus K-edge XANES measurements were collected at the Soft X-ray Microcharacterization Beamline (SXRMB) of CLS. Samples were mounted onto double-sided, conductive carbon tape and loaded into the vacuum chamber with a 10^{-7} torr vacuum with an in-vacuum 7-element Silicon Drift Detector (SDD) (RaySpec Ltd.) at room temperature. The spectra were recorded over the energy range of 2140–2210 eV in fluorescence yield (FLY) and the total electron yield (TEY) modes. For each sample, two measurements were collected and merged using the Demeter program package ([Ravel and Newville, 2005](#)). The different spectra were then normalized to allow comparison. Fertilizers and reference materials were compared to find common features and identify P species present in each fertilizer.

2.3.2. $L_{2,3}$ -edge XANES

Phosphorus $L_{2,3}$ -edge XANES were recorded at the Variable Line Spacing Plane Grating Monochromator (VLS-PGM) beamline [Ref VLSPGM] using the high-energy grating monochromator over the energy range of 130–155 eV. The data acquisition occurred every 0.1 eV and the dwelling time was 1s. The angle between the incident beam and the sample surface was kept constant at 45° . The powder samples were spread as a thin layer on the sample holder, and loaded in the absorption chamber/end station (base pressure low 10^{-8} torr). The beamline slits were set at $50 \mu\text{m} \times 50 \mu\text{m}$. Spectra were recorded at room temperature in total fluorescence yield mode (FLY) using an in-vacuum micro-channel-plate detector [Ref FY detector]. All spectra were normalized to the intensity of the incident beam, which was simultaneously measured as drain current emitted from a nickel mesh located just upstream the sample. There were four scans per sample and the spectra of each material results from the merging of the four scans. A spectral scaling was carried out to compare the different materials, but no normalization was performed. Spectra of fertilizers and reference materials were compared to find common features and allow the identification of P species.

2.3.3. Spectra data processing

Both P K-edge and $L_{2,3}$ -edge XANES spectra were processed using Athena [XAS data processing] of the Demeter package, version 0.29.6., available at <http://bruceravel.github.io/demeter/> ([Ravel and Newville, 2005](#)). Since the basis of the P species identification was performed

based on the visual comparison of spectral features indicative of relevant standards, the possibility of misinterpretation cannot be ruled out entirely.

2.4. Pot experiments

Three pot experiments were conducted at experimental stations in Tulln (Austria), Jokioinen (Finland) and Frick (Switzerland) to evaluate the fertilization efficiency of the selected fertilizers. Spring wheat, spring barley and ryegrass were used as test crops, respectively. Fertilizers were added at a rate of 50 mg P kg^{-1} growing media and mixed thoroughly within the substrate. Each treatment had four replicates. Triple superphosphate was chosen as the reference fertilizer and applied at $12.5, 25, 50$ and 100 mg kg^{-1} soil (Tulln) or growth substrate (Frick) and $10, 25, 50, 100$ and 200 mg kg^{-1} soil (Jokioinen). These P rates were chosen to reach the plateau of the yield response curve in all sites. Control treatments did not receive any P. A basal fertilization was applied to all pots to avoid other nutrient deficiencies and subsequent yield and P uptake differences. In spring wheat (Tulln) and spring barley (Jokioinen), the basal fertilization was applied before sowing and supplied the following: 230 mg kg^{-1} N (143 mg kg^{-1} as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 87 mg kg^{-1} as NH_4NO_3), 310 mg kg^{-1} K (KCl), 45 mg kg^{-1} Mg ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), 3 mg kg^{-1} Fe ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 3 mg kg^{-1} Zn ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), 3 mg kg^{-1} Mn ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), 1.5 mg kg^{-1} Cu ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 65 mg kg^{-1} S ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and H_2SO_4), 0.3 mg kg^{-1} B (H_3BO_3) and 0.3 mg kg^{-1} Mo ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$). In addition, N fertilization consisting of 150 mg kg^{-1} N (93 mg kg^{-1} as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 57 mg kg^{-1} as NH_4NO_3) was applied at the stem elongation stage. Basal fertilization in the Frick experiment was performed after germination of ryegrass by applying a dilute nutrient solution containing $4.24 \text{ mM Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $1.02 \text{ mM MgSO}_4 \cdot 6\text{H}_2\text{O}$ and 4.95 mM KNO_3 to the saucers, reaching a final nutrient input per kg substrate of 453 mg kg^{-1} N, 59 mg kg^{-1} Mg, 407 mg kg^{-1} Ca and 78 mg kg^{-1} S. A summary of the pot experiment setup at each location is shown in [Table 2](#).

2.4.1. Jokioinen

Spring barley (*Hordeum vulgare* var. Einari) was grown in an open wall glass roof greenhouse in 6 kg pots filled with a sandy, low-P content topsoil (5–25 cm depth) already used in [Kahiluoto et al. \(2015\)](#) and [Ylivainio et al. \(2021\)](#). The soil was air-dried and sieved to pass 14 mm and had an initial $\text{pH}_{\text{H}_2\text{O}}$ of 5.8. Fertilizers in this experiment were not milled and were divided into two batches, which were tested in subsequent years and included each a control and TSP reference treatments. In the first batch, additional treatments with some of the granular fertilisers milled to < 1 mm (TSP, CGO, OG1 and NNP) were included to account for a possible difference with the same products in their granular format. The plants were harvested when maturity was reached, which was after 103 and 94 days in the first and second year, respectively. Fresh biomass was dried at 65°C , then grain and straw were separated and milled. Phosphorus concentration was analyzed by ICP-OES (Perkin Elmer Optima 8300) after digestion with concentrated HNO_3 .

2.4.2. Tulln

A local low P content clayey top-soil (5–30 cm depth) with $\text{pH}_{\text{H}_2\text{O}}$ 6.9 was selected for the experiment. The soil was air-dried and sieved to pass 10 mm. Spring wheat (*Triticum aestivum* var. Quintus, Wiersum Plant-breeding BV) was grown in 2 kg pots in a greenhouse under controlled conditions for 131 days until it reached maturity. Plants were harvested at maturity and dried at 65°C for one week. Straw and grain were separated and milled. 150 mg of straw and grain were digested separately in a microwave (MARS 6, CEM) with 3 ml HNO_3 65% and 0.76 ml H_2O_2 30%. The P concentration in the digests was analyzed by ICP-OES (Optima 8300, Perkin Elmer). P was measured at 213.617 nm, and the spectra were normalized using yttrium as the internal standard.

Table 2
Experimental setup of each pot trial at the different experimental locations.

Location	Growth facility	Crop	Fertilizer granulation	Amount of soil/substrate per pot (kg)	Soil classification ^a	Soil texture ^a	Soil pH _{H2O}	Number of batches ^b	Experimental periods (per batch)
Jokioinen	Outdoor below roof	Spring barley (Hordeum vulgare var. Einari)	Used as provided by producer	6	Gleyic podzol	Sand	5.8	2	20.05.2020–31.08.2020 28.05.2021–30.08.2021
Tulln	Greenhouse	Spring wheat (Triticum aestivum L. var. Quintus)	Milled to ≤0.2 mm	2	Chernozem	Clay	6.9	1	18.12.2020–28.04.2021
Frick	Climate chamber	Ryegrass (<i>Lolium multiflorum</i> var. Gemini)	Milled to ≤1 mm	1.2	Artificial substrate	Substrate of 90% peat 10% clay - sand mixture (1:1 v:v)	6.7	3	15.05.2020–21.08.2020 15.09.2020–21.12.2020 17.08.2021–23.11.2021

^a According to IUSS Working Group WRB 2014.

^b Number of batches needed to test all the fertilizers.

2.4.3. Frick

This experiment was performed in three batches and each batch included a control and TSP reference treatments. A mixture of 303 g sand with 94 g commercial standard substrate EEO (Unitersdewerke Werkverband e.V.), composed of >90% peat, and <10% clay, containing 340 mg L⁻¹ N, 113 mg L⁻¹ P and 183 mg L⁻¹ K was prepared to reach a sand to commercial substrate ratio of 1:1 v:v. This substrate had an initial pH_{H2O} of 6.9. Ryegrass (*Lolium multiflorum* var. Gemini, UFA Samen, Wintherthur) was grown in 400 g pots in a climatic chamber, with three pots per replicate, and four replicates, i.e. 12 pots per treatment. The ryegrass was cut 3 times, i.e. after 42, 70 and 98 days. Biomass was dried at 55 °C for 48 h, and milled in an ultra-centrifugal mill (Retsch, Typ ZM 300 Retsch GmbH, Germany). Shoot P concentrations were analyzed using the molybdate blue method (Murphy and Riley, 1962) on a Segmented Flow Analyzer (Skalar Analytical B.V., San++ Automated Wet Chemistry Analyzer, Breda) following incineration of the plant powder and subsequent acid extraction.

2.5. Data evaluation and statistical analysis

Mineral replacement value (MRV) was used as the main parameter for data evaluation, calculated according to the following formula:

$$MRV (\%) = \frac{P_{up} - P_c}{P_{ref} - P_c} \times 100$$

Being:

- o P_{up} : total P uptake of the fertilized treatment in mg pot⁻¹ P.
- o P_c : total P uptake of the control (P zero) treatment in mg pot⁻¹ P.
- o P_{ref} : total P uptake of the reference (50 mg kg⁻¹ TSP-P) treatment in mg pot⁻¹ P.

Additionally, we calculated the agronomic mineral replacement value (aMRV) to include a commercial biomass related parameter:

$$aMRV (\%) = \frac{B_f - B_c}{B_{ref} - B_c} \times 100$$

Being:

- o B_f : total commercial biomass of each treatment, in g pot⁻¹.
- o B_c : total commercial biomass of the control treatment (P zero), in g pot⁻¹.
- o B_{ref} : total commercial biomass of the reference (50 mg kg⁻¹ TSP-P) treatment at the same P dose than the fertilizers, in g pot⁻¹.

Commercial biomass is the grain biomass in the Tulln and Jokioinen

pot experiments (wheat and barley respectively) and the aboveground biomass in the Frick pot experiment (ryegrass).

MRV and aMRV were used as data evaluation parameters, because these parameters are normalized to the control and reference fertilizer treatments, thereby ensuring comparability between the three locations and between individual batches within the locations (Meisinger et al., 1992). We use the term “fertilization efficiency” to describe this comparative analysis of P uptake and yield. Data analyses were performed in R version 4.2.1 (R Core Team, 2022). The normality and variance homogeneity of the residuals were confirmed graphically with Q-Q plots and “residuals vs. fitted value” plots, respectively. One-way analysis of variance (ANOVA) of the MRV and aMRV were conducted, one with location as factor to compare experimental conditions among each location, and then one for each location separately with the individual fertilizers as factor, to determine the fertilization efficiency of individual products. Then, two two-way ANOVAs were conducted: one with location and fertilizer class as factors, and another one with location and P species. The location factor was included to correct its influence when evaluating the effect of the P species and fertilizer class in their overall MRV and aMRV. Mean comparisons were done by performing Tukey’s HSD post-hoc tests using the emmeans package (Lenth et al., 2023). R packages ggplot2 (Wickham et al., 2023a), dplyr (Wickham et al., 2023b), ggpubr (Kassambara, 2023) and viridis (Garnier et al., 2023) were used to visualize the data. In all analyses, differences were considered significant at $p < 0.05$.

3. Results

3.1. Identification of P species in recycled fertilizers using XANES

Self-absorption of fluorescent radiation during XANES analyses occurred in many samples due to the high P concentrations, which attenuated spectral features (Gräfe et al., 2014). As a result, we identified major P species for every fertilizer based on clear spectral features but could not use K-edge spectra to assess relative quantification of P species using linear combination fitting. However, the combination of both K- and L-edge XANES allowed conformation of major species in almost all materials tested.

As expected, in all struvites the main P species was ammonium magnesium phosphate. The inorganic soluble fertilizers group had a greater diversity of P species that included monoammonium phosphate, monocalcium phosphate, dicalcium phosphate type species, hydroxyapatite/tricalcium phosphate and vivianite (Table 3). Inorganic insoluble fertilizers, pyrolyzed products and organic fertilizers included dicalcium phosphate, hydroxyapatite/tricalcium phosphate, iron (III) phosphate dihydrate and amorphous iron (III) phosphate as their main P

Table 3
Matrix relating the fertilizer class and the tested fertilizers with the P species found.

	Reference	Struvite	Inorganic soluble	Inorganic insoluble	Pyrolyzed product	Organic fertilizer
Ammonium magnesium phosphate (n = 5)		SSW, STR, CGO, PCS, EPS				
Monoammonium phosphate (n = 1)			MAP			
Monocalcium phosphate (n = 2)	TSP		BZH			
Dicalcium phosphate type species (n = 6)			DCP, ADC	BES	CRA, PPS	OPU
Phytic acid (n = 1)						BA1
Hydroxyapatite/tricalcium phosphate (n = 9)			EPH, PRC	PLA	MBC, ABP	OG1, MB1, MO10, MO14
Iron phosphate (n = 5)			VVB	PKA		PRV, RAN, NNP
Unidentified (n = 2)				KBT	BAG	

species. Additionally, there was one inorganic insoluble fertilizer (KBT) and one pyrolyzed product (BGA) whose main P species could not be identified. Details on the K-edge and L-edge spectral features and main P species identification can be found in [Tables S1 and S2](#), and [Fig. 1 and S1](#). [Table 3](#) shows the relation of each fertilizer class with the corresponding main P species found for each fertilizer.

3.2. Crop responsiveness to P fertilization

All crops in all pot experiments exhibited a positive response to the reference material (TSP), compared to the control (no added P) ([Fig. S2](#)). The biomass and P uptake in pots fertilized with TSP increased with increasing fertilization rate. In Jokioinen and Frick, the TSP reference points did not coincide between the different experimental batches.

3.3. Fertilization efficiency of recycled P fertilizers

The P availability from the individual fertilizers to the crops, and thus crop yield, varied strongly between individual fertilizers and experimental conditions, thus MRV ranged from -13% to 149% and aMRV ranged from -7% to 139% ([Table S3](#)). Negative values in MRV and aMRV occur when P uptake or yield of a given fertilized treatment was lower than that of the non-fertilized control.

3.3.1. Differences between experimental locations

The data evaluation (one-factorial ANOVA with location as factor) found no significant difference between Jokioinen and Tulln in MRVs, but showed MRVs to be significantly lower in Frick. In contrast, aMRV was not significantly different between Tulln and Frick but was significantly higher than Jokioinen ([Fig. 2](#)).

3.3.2. Fertilization efficiency according to P species and experimental location

In Jokioinen, there were clear differences in replacement values between fertilizers ([Figs. 3 and 4](#)) where MRV ranged from -13% to 149% and aMRV from -7% to 140%. Results obtained with fertilizers containing monoammonium phosphate, monocalcium phosphate, dicalcium phosphate type species as well as ammonium magnesium phosphate were not significantly different from those with TSP reference with respect to MRV and aMRV. Monoammonium phosphate and monocalcium phosphate were only contained in one product each. The MRV of ammonium magnesium phosphates ranged from 99% to 149% and the corresponding aMRV from 87% to 140%. For dicalcium phosphate type species, the MRV ranged from 67% to 147%, and the aMRV from 57% to 106%. The phytic acid fertilizer (BA1) had a high standard deviation and only aMRV was significantly lower when compared with other products. Hydroxyapatite/tricalcium phosphate products varied in their fertilization efficiency. Their MRV ranged from 3% to 135%, and their aMRV from 5% to 99%. Three out of nine products (ABP, MO14 and OG1) had significantly lower MRVs and aMRVs than TSP and were not significantly different from the control. The MRV of the remaining

hydroxyapatite/tricalcium phosphate were not significantly different from TSP. Besides ABP, MO14 and OG1, EPH and PLA had a significantly lower aMRV than TSP. The MRV of the iron phosphates ranged from 23% to 56%, with all MRVs except that of NNP being significantly lower than that of TSP. aMRV ranged from 8% to 45%, with all values being significantly lower than TSP, and only NNP was significantly higher than that of the control. One of the products with an unidentified P species (BAG) had the overall lowest MRV and aMRV. The other product with an unidentified P species (KBT) had a significantly lower aMRV than TSP. Results of the additional treatments of milled fertilizers are shown in the supplementary material ([Fig. S6](#)). The milled hydroxyapatite product (OG1) performed significantly better than its granular counterpart. For the remaining three fertilizers (TSP, CGO and NNP) no significant differences were found between a granular and a milled application.

In Tulln, the MRV ranged from 22% to 132% and the aMRV ranged from 21% to 129% ([Figs. 3 and 4](#)). The MRV of ammonium magnesium phosphates ranged from 104% to 132%, and aMRV from 99% to 114%. The MRV of dicalcium phosphate type species ranged from 75% to 108%, and aMRV from 67% to 105%. The MRV of hydroxyapatite/tricalcium phosphate ranged from 55% to 102%, and aMRV from 38% to 110%. The MRV of iron phosphate ranged from 22% to 95%, and aMRV from 21% to 82%. Only one iron phosphate fertilizer (PKA) showed a significantly lower MRV than TSP. This product, together with one of the unidentified P species products (BAG), two hydroxyapatite/tricalcium phosphate fertilizers (ABP and MO14) and a dicalcium phosphate type species fertilizer (CRA) had significantly lower aMRVs than TSP, with PKA being the only one not significantly different from the non-fertilized control.

In Frick, the MRV ranged from 8% to 106%, and aMRV from 9% to 107% ([Figs. 3 and 4](#)). All the ammonium magnesium phosphate, monoammonium phosphate and monocalcium phosphate products were not significantly different from TSP in their MRVs and aMRVs. The MRV of ammonium magnesium phosphate ranged from 92% to 99%, and aMRV from 89% to 105%. The MRV of dicalcium phosphate type species ranged from 37% to 106%, and aMRV from 64% to 103%. One dicalcium phosphate type species product (CRA) had significantly lower MRV and aMRV than TSP, and another dicalcium phosphate type species product (PPS) a significantly lower MRV than TSP. The phytic acid fertilizer (BA1) had a significantly lower MRV than TSP. The MRV of hydroxyapatite/tricalcium phosphate ranged from 9% to 94%, and aMRV from 9% to 98%. All the hydroxyapatite/tricalcium phosphate products had a significantly lower MRV than TSP. In addition, ABP, MBC, MO10, MO14, PLA and PRC had also a significantly lower aMRV than TSP. ABP was not significantly different from the control for MRV and aMRV. The MRV of iron phosphate ranged from 16% to 62%, and aMRV from 27% to 87%. All the iron phosphate fertilizers had a significantly lower MRV than TSP, and only two (PRV and RAN) did not have a significantly lower aMRV. PKA was not significantly different from the non-fertilized control for MRV. One of the products with an unidentified P species (BAG) was not significantly different from the non-fertilized control for MRV.

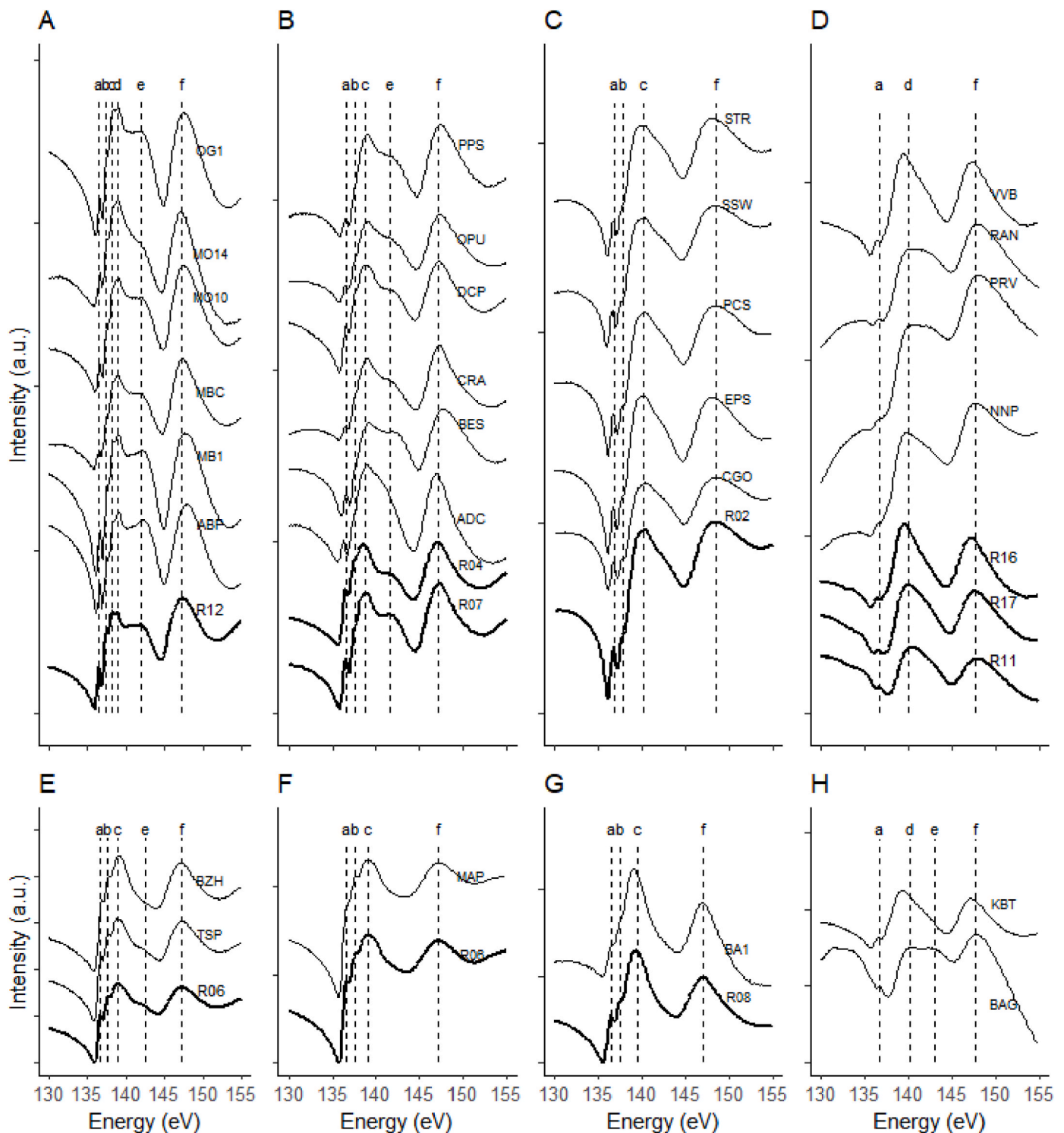


Fig. 1. $L_{2,3}$ spectra of tested products: A = hydroxyapatite, B = dicalcium phosphate type species, C = ammonium magnesium phosphate, D = iron phosphates, E = monocalcium phosphate, F = phytic acid, G = monoammonium phosphate, H = unidentified. Dashed lines with letters correspond to the features of the reference spectra. The reference spectra are signalled in bold.

Across all locations, ammonium magnesium phosphate (struvite), monoammonium phosphate and monocalcium phosphate fertilizers were not significantly different from TSP (Figs. 3 and 4). In the dicalcium phosphate type species group, ADC, BES, DCP, and OPU were not significantly different from TSP. However, CRA had a significantly lower MRV at Frick, and a significantly lower aMRV at Tulln and Frick. The MRV of PPS was also significantly lower than that of TSP at Frick. The phytic acid product (BA1) had a significantly lower MRV than that of

TSP at Frick, and a significantly lower aMRV than that of TSP at Jokioinen. Hydroxyapatite/tricalcium phosphate products often had significantly lower MRV and aMRV than TSP, but these differences varied partly with experimental location and individual fertilizer. All the hydroxyapatite/tricalcium phosphate fertilizers were significantly lower at least in one location for either MRV or aMRV. All iron phosphates had significantly lower MRV than TSP in Jokioinen and Frick, but only one (PKA) was significantly lower in Tulln. Regarding the aMRV, all

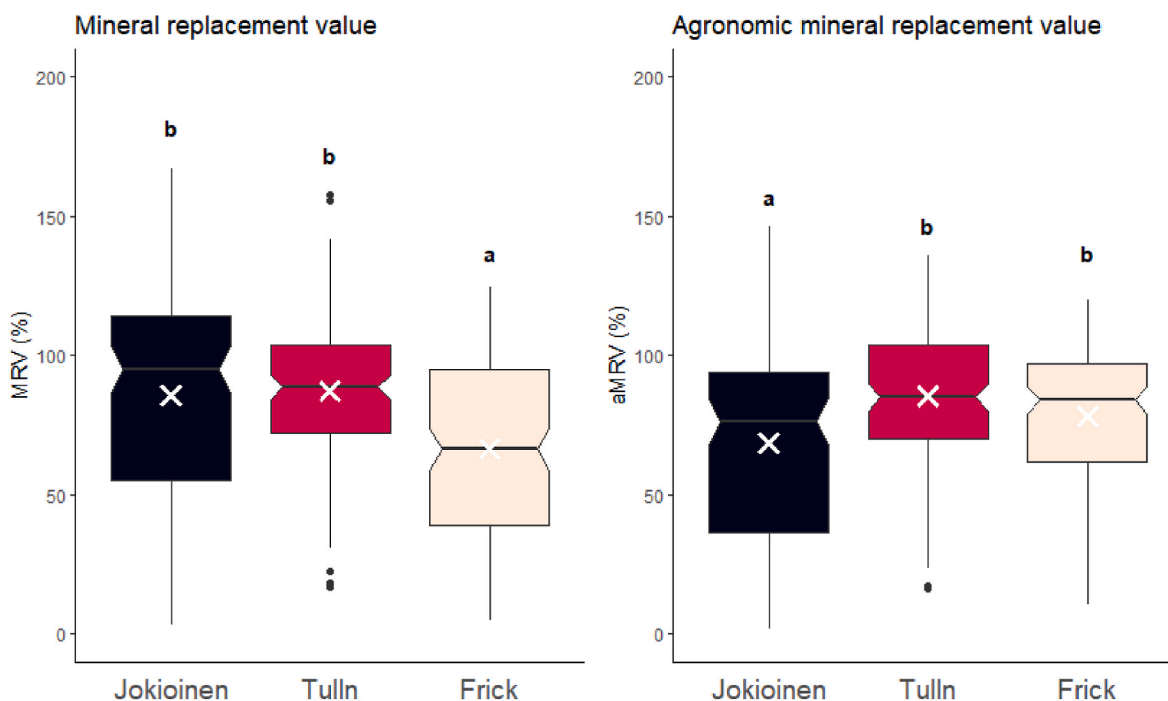


Fig. 2. Mineral replacement value (MRV) and agronomic mineral replacement value (aMRV) of all tested products at each location. For each location, boxplots with the same letter are not significantly different, based on Tukey's HSD test with $\alpha \leq 0.05$.

iron phosphate products had a significantly lower value than that of TSP in Jokioinen. All but PKA were not significantly different from TSP in Tulln, and all but two (PRV and RAN) were significantly lower in Frick. One of the unidentified P species fertilizers (BAG) had significantly lower MRV and aMRV in all locations except Tulln for the MRV, which was not significantly different from TSP. The other product for which the P species could not be identified (KBT) had a significantly lower aMRV than that of TSP in Jokioinen.

3.3.3. Average fertilization efficiency

The two-factorial ANOVA with location and P species as factors showed significant differences in MRV and aMRV between fertilizers with different dominant P species (Fig. 5, left). Here, ammonium magnesium phosphate, monoammonium phosphate, monocalcium phosphate and dicalcium phosphate type-containing fertilizers were not significantly different from TSP. It is worth keeping in mind the number of fertilizers that contained each P species: the five struvites were identified as ammonium magnesium phosphates, four products contained dicalcium phosphate type species as their main P species, but only one product each had monoammonium phosphate (MAP) or monocalcium phosphate (BZH) as their main P species. The phytic acid product, hydroxyapatite/tricalcium phosphate and iron phosphate products had significantly lower MRV and aMRV than TSP. The two unidentified P species products (BAG and KBT) differed in their MRV and aMRV: BAG had significantly lower MRV and aMRV than TSP, while KBT was only significantly lower for aMRV at Jokioinen. Additionally, a significant interaction between locations and P species was found in the case of MRV, due to the contrasting MRVs of hydroxyapatites and iron phosphates between locations (Fig. S3).

A similar analysis was conducted for the fertilizer classes as defined in Table 1 (two-factorial ANOVA with location and fertilizer class as factors) and showed significantly different MRV and aMRV (Fig. 5, right), without significant interaction between the two factors. Only struvites and inorganic soluble products were not significantly different from TSP. Inorganic insoluble fertilizers, pyrolyzed products and organic fertilizers had similar MRV and aMRV averages, which were significantly lower than the MRV and aMRV of the reference. Graphical

information on the MRV and aMRV of the individual fertilizers as by fertilizer class is available in Figs. S4 and S5.

4. Discussion

4.1. Fertilization efficiency of recycled fertilizers in relation to P species and fertilizer class

As expected, the investigated recycled fertilizers exhibited contrasting fertilizer effects, which were ascribed to the main P species present in the products (Fig. 5, left) as well as to the fertilizer class (Fig. 5, right). The investigated fertilizers will be discussed here according to their performance, which broadly results in two groups contrasting in their fertilizer efficiency: (1) a high-efficiency group with mostly refined inorganic recycled fertilizers found mainly in the inorganic soluble and struvite groups of the fertilizer class (Fig. 5, right) and (2) a more diverse, low-efficiency group composed of largely unrefined products that could be found in all PFC categories (i.e., inorganic, organo-mineral, organic). It is important to note that the results are valid for the soil conditions tested in this study, i.e., European soils with neutral to slightly acidic pH, in which P solubility is high for many P species. In soils with different properties, for instance higher pH values, P solubility could be lower. For instance, in a soil-fertilizer incubation experiment with seven soil types, Meyer et al. (2020) found that P availability of monocalcium phosphate, monoammonium phosphate and diammonium phosphate was low for the calcareous soil, probably due to the precipitation of the fertilizers as Ca-P. Conversely, for the six non-calcareous soils, decreasing pH values decreased availability, probably due to the precipitation of Fe-P and Al-P minerals (Meyer et al., 2020).

4.1.1. High-efficiency products: the refined P fertilizers

The fertilization efficiencies of the fertilizer classes struvites and inorganic soluble fertilizers were not significantly different from that of TSP (Fig. 5, right). Inorganic soluble fertilizers are a heterogeneous group containing many different P species (Table 3), with some products performing differently across the experiments, which partially explains

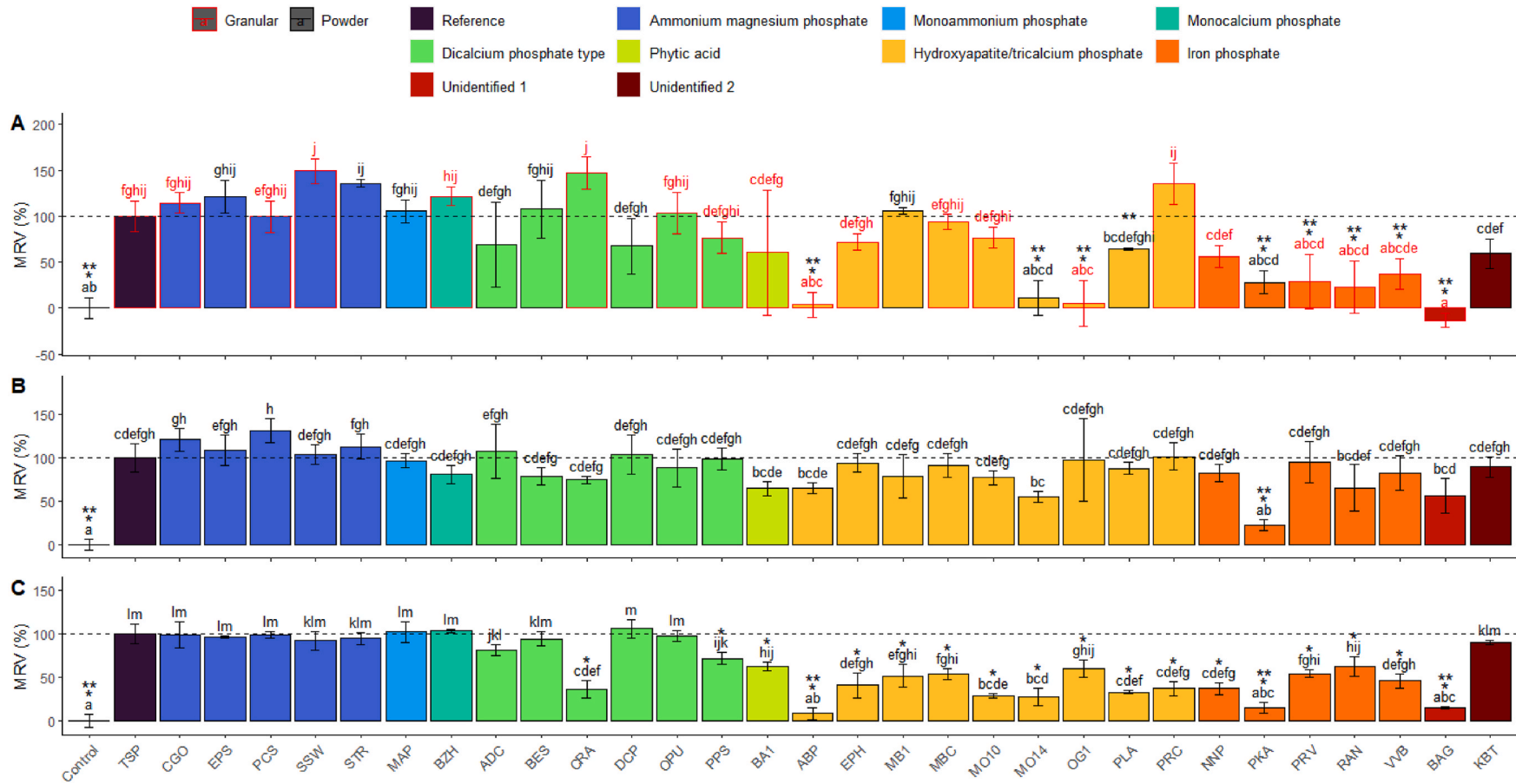


Fig. 3. Mineral replacement values (MRVs) of all fertilizers coloured by P species, for (A) spring barley at Jokioinen, (B) spring wheat at Tulln and (C) ryegrass at Frick. Data shown as mean \pm standard deviation ($n = 4$). For each location, bars with the same letter are not significantly different, based on Tukey's HSD test with $\alpha \leq 0.05$. Products marked with an asterisk "*" were statistically different from the TSP reference. "***" indicate products that were not significantly different from the control treatment. A red bar outline indicates that the fertilizer was applied as granules. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

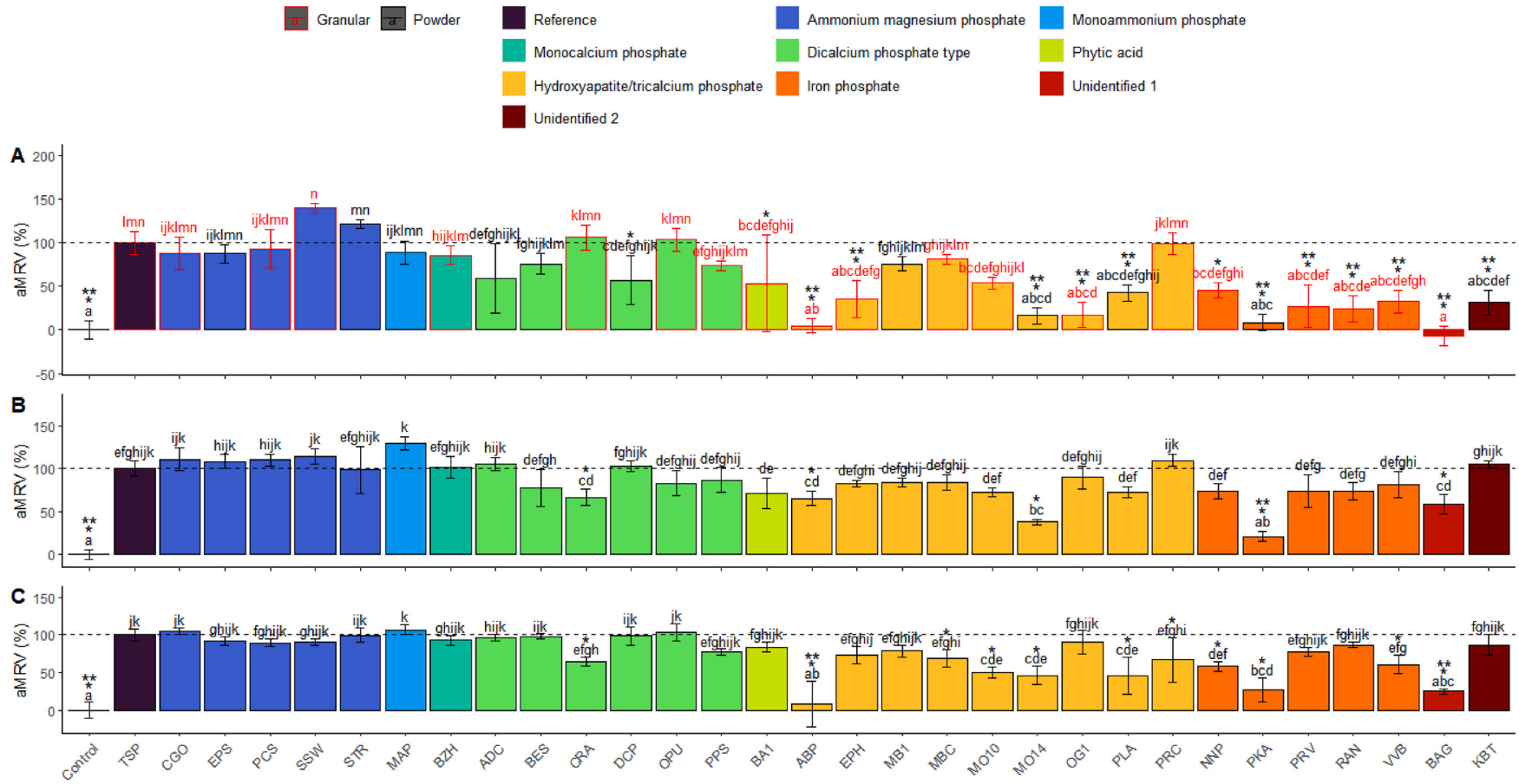


Fig. 4. Agronomic mineral replacement values (aMRVs) of all fertilizers coloured by P species, for (A) spring barley at Jokioinen, (B) spring wheat at Tulln and (C) ryegrass at Frick. Data shown as mean \pm standard deviation ($n = 4$). For each location, bars with the same letter are not significantly different, based on Tukey's HSD test with $\alpha \leq 0.05$. Products marked with an asterisk "*" were statistically different from the TSP reference. "***" indicate products that were not significantly different from the control treatment. A red bar outline indicates that the fertilizer was applied as granules. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

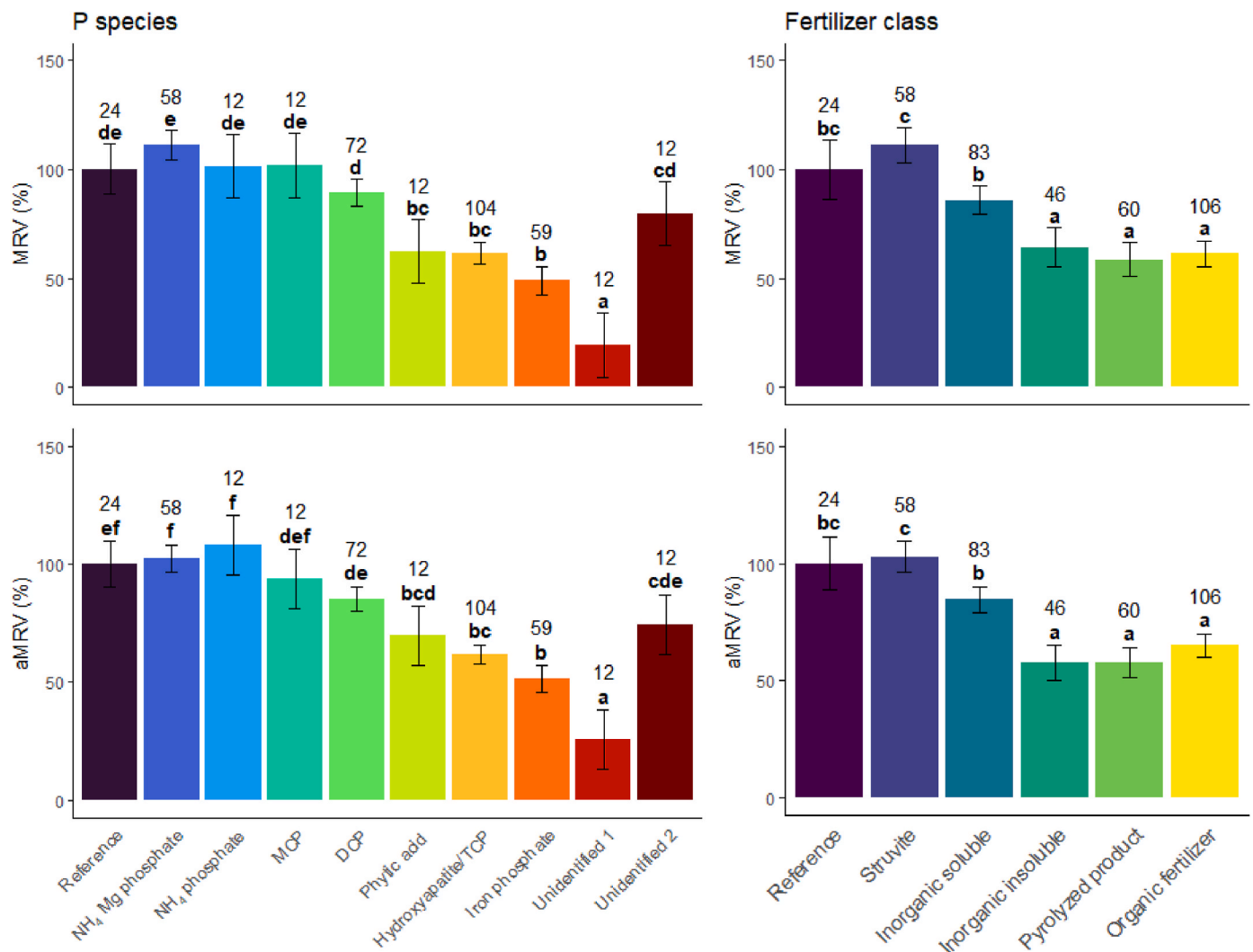


Fig. 5. Average mineral replacement value (MRV) and agronomic mineral replacement value (aMRV) for each P species and fertilizer class. Two-way ANOVA. Data shown as mean averaged over the location factor $\pm 95\%$ confidence intervals. Bars with the same letter are not significantly different, based on Tukey's HSD test with $\alpha \leq 0.05$. Numbers above bars indicate the number of replicates per fertilizer group/P species that was the basis for this statistical evaluation. NH₄ Mg phosphate: ammonium magnesium phosphate. NH₄ phosphate: monoammonium phosphate. MCP: monocalcium phosphate. DCP: dicalcium phosphate type species. TCP: tricalcium phosphate.

the slightly (non-significantly) lower overall performance of this group relative to struvites (Fig. 5, right). The high-efficiency group contains products consisting of monoammonium phosphate, monocalcium phosphate, ammonium magnesium phosphate (*i.e.* struvite) and dicalcium phosphate type species.

In the case of monoammonium phosphate and monocalcium phosphate, these are water-soluble P species used as conventional P fertilizers, and accordingly, the products containing these as main species (MAP and BZH) exhibited an equivalent MRV to the reference (Figs. 3 and 4). Likewise, the high fertilization efficiency of ammonium magnesium phosphate (struvite) products has often been described, as reviewed by (Kratz et al., 2019), Huygens and Saveyn (2018), and Hertzberger et al. (2020). In their meta-analysis, Huygens and Saveyn (2018) concluded that precipitated phosphate salts like struvite have a consistently high agronomic efficiency independently of soil pH and texture, feedstock, application form, crop species, or assessment time. However, Hertzberger et al. (2020) found a trend for struvite agronomic efficiency to decrease with increasing pH, but the proportion of data originating from alkaline soils was low and the regressions' R^2 values were < 0.1 . Although struvite granules dissolved very slowly in an alkaline soil ($\text{pH}_{\text{H}_2\text{O}}$ 8.5 $\text{pH}_{\text{CaCl}_2}$ 7.6), struvite powder was found to give

similar results as MAP powder in the same soil (Degryse et al., 2017). Thus, our results and previous literature validate struvites as a highly valuable substitute for conventional, PR-based P fertilizers in non-acidic and non-calcareous soils, while the literature points to a decreasing trend in efficiency in alkaline soils, most evident when applied as granule.

Similar to struvite, dicalcium phosphate is only sparingly soluble in H₂O, but it is highly soluble under an ion sink (adsorption) effect and in NAC (Duboc et al., 2022). It is considered to be as plant-available in non-calcareous and in calcareous soils as monocalcium phosphate (superphosphate). Only two (CRA and PPS) out of the six products with dicalcium phosphate type species had a significantly lower MRV in Frick. CRA had also a significantly lower aMRV in Tulln. CRA, PPS, ADC and BES showed XANES L-edge features that indicate the presence of additional P species. Not much is known about the P forms present in char derived from pig slurry (PPS) (Christel et al., 2014), but in manure char, apatite and octacalcium phosphate have been found (Bruun et al., 2017; Huang et al., 2018; Kratz et al., 2019), as well as amorphous calcium phosphate and nano-sized P-containing crystals (Christel et al., 2014; Uchimiya and Hiradate, 2014). According to the literature, the P species in ADC is buchwaldite (CaNaPO_4), (Stemann et al., 2015; Herzel

et al., 2016; Kratz et al., 2019), which was not a standard material included in this XANES analysis. Buchwaldite is $85 \pm 2\%$ NAC soluble (Kratz et al., 2019) and has been previously reported as plant available (Stemann et al., 2015). Positive Na-AshDEC fertilization results have been reported by other authors (Hauck et al., 2021), matching ADC results in Tulln and Frick.

PRC (P-RoC) is a particular precipitation product categorized in the inorganic soluble fertilizer class. According to our analysis it contains hydroxyapatite/tricalciumphosphate (Table 3) although it has been previously identified as a mixture of poorly crystallized Ca-deficient hydroxyapatite with struvite (Duboc et al., 2022; Kratz et al., 2019). This product performed very well except in Frick, and is known for its high solubility with different extraction methods, except H₂O (Duboc et al., 2022).

BES performed well in our three experiments, in spite of being among the inorganic insoluble products. Ehmann et al. (2017) characterized BES as a mixture of struvite, magnesium phosphate and calcium phosphate, and observed higher dry matter yield and P uptake on sandy soil, compared to clay soil. In contrast, we could not identify any clear differences between our experiments.

4.1.2. Low-efficiency products: the unrefined fertilizers

This group consists mostly of fertilizers categorized as inorganic insoluble, pyrolyzed products and organic fertilizers (Fig. 5, right). The main P species identified in these groups were hydroxyapatite, tricalcium phosphate, iron phosphate and phytic acid. Species belonging to dicalcium phosphate type species were also identified, and there were also two products with unidentified species (Fig. 5, left, Table 3).

In their review, Kratz et al. (2019) reported tricalcium phosphate and apatite to be less bioavailable than other inorganic phosphates, and that amorphous iron and aluminium phosphates are more available than their crystalline equivalents. Organic P forms like phytates, nucleic acids and phospholipids have to undergo enzymatic hydrolysis to become plant available and are therefore often found to exhibit low fertilization efficiency on short-term supply trials as in the present study. Besides, the different organic P sorption capacity of soils influences the enzymatic hydrolysis rate, and thus affects the fertilization efficiency of organic P fertilizers.

Overall, hydroxyapatite- and iron phosphate-based fertilizers can be expected to perform poorly, especially under certain field conditions. Phosphorus in PR and other apatite-based fertilizers will solubilize in acidic soils but remain non-available in calcareous soils (Brod et al., 2015b; Christiansen et al., 2020), while the opposite is true for iron phosphate fertilizers (Kratz et al., 2016; McLaughlin et al., 2011). Ylivainio et al. (2021) showed that the (Fe + Al)/P molar ratio can be used to accurately predict the relative agronomic efficiency of digested and composted sewage sludge and cattle and pig manures, while for calcium phosphates, lime stabilized sewage sludge and fox manure, P availability is mostly influenced by soil pH.

Hydroxyapatite and tricalcium phosphate-containing products generally had a significantly lower fertilization efficiency than TSP, although in Tulln none of the apatite products had a significantly lower MRV than TSP, and only two out of the nine apatite products (ABP and MO14) had a significantly lower aMRV compared to TSP (Figs. 3–5). Milling of the products for the experiment in Tulln may have increased P availability from these products, as suggested by the comparison of non-milled vs. milled products done in Jokioinen (Fig. S6). Besides OPU and PPS, which have dicalcium phosphate type species as their main P species, all other animal-derived organic fertilizers and pyrolyzed products (ABP, MB1, MBC, MO10, OG1) were found to contain hydroxyapatite (Table 3). This coincides with the findings of other authors, who have found different apatite forms to be present in raw meat and bone meal (Brod et al., 2015a; Kratz et al., 2019; Zwetsloot et al., 2015), chicken manure ash (Kratz et al., 2019; Yusiharni et al., 2007), meat and bone meal ash (Alotaibi et al., 2018; Kratz et al., 2019) and bone meal biochar (Kratz et al., 2019; Morshedizad et al., 2018; Rajendran et al.,

2013; Zwetsloot et al., 2015).

All products with iron phosphate as the main P species were derived from sewage sludge and exhibited a low fertilization efficiency in the pot experiments at Jokioinen and Frick, while in Tulln only PKA had a significantly lower MRV and aMRV than TSP (Figs. 3–5). Besides VBB, whose spectrum coincided accurately with the vivianite reference, the other iron phosphate products contain presumably other P species besides Fe (III) phosphate dihydrate and amorphous iron phosphate. Raw municipal sewage sludge has been found to contain different P species, including iron phosphates like strengite, vivianite, lipscombite, and P absorbed to amorphous iron phosphates (Kratz et al., 2019). Other authors have also found low fertilization efficiencies for iron-precipitated P fertilizers from sewage sludge ((Jarosch et al., 2018; Vaneekhaute et al., 2016; Ylivainio et al., 2021), although they do not agree on whether iron phosphates become plant available with time.

VVB (vivianite) was not significantly different in its fertilization efficiency compared to TSP in Tulln but significantly lower in Frick and Jokioinen (Figs. 3 and 4). This higher P availability in Tulln in comparison to Jokioinen was not expected, as the soil pH in Tulln is neutral but the pH at Jokioinen is slightly acidic, and would have therefore been able to solubilize iron phosphates better. Vivianites are known to be mostly insoluble under aerobic conditions as commonly found in soils but can solubilize and therefore release P under reducing conditions, such as in a flooded soil with labile organic matter (Saracanalao et al., 2023). Thus, in accordance with our results in Frick and Jokioinen, other authors have documented the low fertilization efficiency of different vivianites (Ayeyemi et al., 2023; Saracanalao et al., 2023). The NAC extraction, which is based on the strong ligand effect of citrate, obviously does not reflect the most relevant processes and conditions prevalent in the soils used in our experiments.

BA1 was the only fertilizer with an organic compound (phytic acid) as its main P species, and its fertilization efficiency varied across locations. In Jokioinen, its aMRV was significantly lower than that of TSP, and in Frick, a significantly lower MRV was found. In contrast, in Tulln there was no significant difference between BA1 and TSP. Phytic acid is a P storage molecule of plant seeds and fruits, which commonly accumulates in soils. Phytate is generally not plant-available and requires enzymatic hydrolysis by phytases for its P to get solubilized (Liu et al., 2022). Some plants and soil microorganisms can release phytase as root exudate to mobilize phytate-P in soils (Li et al., 1997; Liu et al., 2022; Richardson and Hadobas, 1997). Results may have been affected by different enzyme activities in the soils used in the different locations.

4.2. Effect of feedstock composition and processing

The high-efficiency fertilizers mostly consisted of inorganic refined products obtained from (1) specific P recovery processes from e.g. municipal sewage sludge ash through thermo-chemical treatment (ADC) or solubilisation and precipitation processes (DCP, MAP, BZH, BES), and (2) precipitation from diverse P-rich liquid streams (struvites and PRC). Among the low-performance unrefined products there were differences related to the feedstock composition and the type of processing.

Regarding processing, OPU, MBC and PLA, which are made from a similar raw material (poultry litter), exhibited a decreasing trend of fertilization efficiency from OPU > MBC > PLA following increasing treatment temperature from raw feedstock to pyrolysis and combustion (Bruun et al., 2017). Similarly, the performance of OG1 and MB1 (meat and bone meal) tended to be higher than that of ABP (animal biochar).

Regarding a possible influence of the feedstock, bone char and sewage sludge char (ABP and BAG) had a low fertilization efficiency compared to pyrolyzed fruit residue, poultry litter ash and pig slurry (CRA, MBC and PPS, respectively). The fertilization efficiency of the ashes was in the order EPH ~ PLA > PKA. EPH (sunflower husk ash) was classified as inorganic soluble with hydroxyapatite/tricalcium phosphate as the main species and performed relatively well, while PLA (hydroxyapatite/tricalcium phosphate) and PKA (iron phosphate) had

low replacement values.

In Huygens and Saveyn (2018), the agronomic efficiencies of thermal oxidation products were found to be dependent on the feedstock, with products originating from crop residues, poultry litter and pig manure exhibiting comparable performances to conventional fertilizers. Conversely, sludge-derived products showed significantly lower agronomic efficiency. Schiemenz and Eichler-Löbermann (2010) found fertilization results comparable to TSP using rape meal ash, straw ash and cereal ash, which is in line with our results obtained for the sunflower husk ash, EPH. Ylivainio et al. (2021) reported a decreasing fertilizing effect of manures > sewage sludges > thermochemically treated sewage sludges. Low fertilization efficiency of sewage sludge biochar was already reported by other authors (Christiansen et al., 2020; Duboc et al., 2017). Zhu et al. (2022) found that the P bioavailability of pyrolyzed sewage sludge depends on the raw material used and the pyrolysis temperature. During pyrolysis, the presence of Ca, Mg, Fe and Al in raw sludges promotes the formation of minerals and, increasing the pyrolysis temperature converts organic P into inorganic species, transforming non-apatite P species into less soluble apatites. For meat and bone meal, it is also known that P solubility in water decreases after pyrolysis (Duboc et al., 2022; Zwetsloot et al., 2015). Duboc et al. (2022) also measured a decrease in NAC solubility in meat and bone meal and cattle manure after pyrolysis, suggesting decreased P availability. This is in contrast with the high formic acid solubility of different meat and bone meal chars in Zwetsloot et al. (2015).

Overall, these findings indicate that pyrolysis and combustion are not optimal processes for meat and bone meal and manure in terms of P availability, but that the effect also depends on the composition of the raw material and combustion/pyrolysis temperatures (Zwetsloot et al., 2015; Bruun et al., 2017; Piash et al., 2023). Depending on the original composition of the feedstock and the pH of the soil, biochar and ash can be relatively efficient as P fertilizers. But to consistently improve P efficiency, further processing (i.e., upgrade to refined high-performance products) is required.

4.3. Inconsistent fertilization efficiency results of specific recycled fertilizer products

There were exceptions and inconsistent fertilization efficiency results between products of the same P species and/or fertilizer class, reflecting a gradient of solubility, dependent on experimental conditions, P species composition, and their interaction.

First, we expect the main P species identified in some fertilizers to be accompanied by additional P species that also can affect the overall bioavailability of the product. This is not surprising as minor species (e.g. representing less than 10% of total P) are not easily identified by XANES unless they exhibit strong spectral features (e.g. Gräfe et al., 2014). If a fertilizer contains two or more P species of different solubilities, the resulting bioavailability of that fertilizer will be controlled by the most soluble species during initial dissolution, even when they represent only a small percent of the P contained in the product. At equilibrium, the P concentration is controlled by the least soluble stable species, however, during reaching equilibrium (i.e. during the process of precipitation), part of the solubilized P may be taken up by close-by plant roots. In soils where indigenous bioavailable soil reserves are close to meet the crop requirements, even a small addition of bioavailable P may suffice to produce maximal yield. However, in our study, both soil P status and total P application rates were low to ensure the reliable determination of bioavailable P contained in the fertilizers, and maximum yield was not observed. Furthermore, the presence of poorly soluble species like hydroxyapatite, tricalcium phosphate and iron phosphate as additional P species could be the reason for the varying

performance of a particular fertilizer under different testing conditions, because the interaction of these P species with the local experimental conditions was found to be significant (Fig. S3). This, combined with the fact that non-specific processes like pyrolysis or combustion further change the P speciation of raw materials helps to explain inconsistent fertilization efficiencies within groups. For instance, among the inorganic insoluble fertilizers, KBT and BES were in most cases not significantly different from TSP, but PLA and even more so PKA had comparatively lower fertilization efficiencies. Four products (BES, CRA, PPS, OPU) which were identified to contain dicalcium phosphate type species performed relatively well but were among the fertilizer classes of inorganic insoluble, pyrolyzed products and organic fertilizers (Table 3), i.e., the groups with the lowest replacement values. Conversely, several products with hydroxyapatite/tricalcium phosphate as main species were NAC-soluble; EPH and PRC as inorganic soluble, and the organic fertilizers OG1 and MB1 (Table 3).

Besides, the main P species could not be identified in two products (BAG and KBT). For BAG (sewage sludge char), literature shows that this type of product might contain a mixture of whitlockite and tricalcium phosphate (Kratz et al., 2019). Regardless of its P species, it had a poor fertilization efficiency across the three experiments. For KBT (sewage sludge slag), no information was found in the literature indicating its P species, and given the specific processing for this product (furnace thermo-chemical process at 1300 °C with Fe-oxide and Ca(OH)₂ additives) no further assessment appears possible without further solid state speciation analysis.

The granulation of the products also had an impact in the fertilization efficiency. The fertilizers were not milled in Jokioinen but applied with the granulation received by the producer. Fertilizers were milled in Tulln and Frick, but the final particle size differed slightly (Table 2). Consequently, the specific surface areas of the fertilizers were much lower in Jokioinen than in Tulln and Frick. In the pot experiment at Jokioinen, the inclusion of the four additional fertilizers in milled format showed a significant increase of MRV and aMRV for the hydroxyapatite product (OG1) and a trend for lower MRVs for the iron phosphate (NNP) (Fig. S6 in the supplementary information). While there may be punctual variations in the fertilization efficiency of specific fertilizers (especially low-solubility fertilizers) caused by the different granulation used in each pot experiment, there was no overall difference in MRVs and aMRV between the three pot experiments (Fig. 2).

Degryse et al. (2017) reported a higher P uptake for milled than for granular struvite, both in acidic and in alkaline soil. They attributed this increase to the higher specific surface area of the ground struvite and the subsequent improvement of P solubility. They also found a higher P uptake of granular monoammonium phosphate, compared to milled counterpart in the alkaline soil, which they attributed to an early enhanced root P uptake, if some granules were located close to the seeds. Moreover, the influence of particle size on P dissolution rates of dicalcium and tricalcium phosphates in the soil has been reported previously (Kirk and Nye, 1986). The less soluble hydroxyapatite/tricalcium phosphate products applied in a granular format in Jokioinen (ABP, EPH, MO10, OG1 and PRC) could have reached higher MRVs if they had been milled and mixed with the soil. Indeed, an earlier study had shown that MRVs of meat and bone meal, similar to OG1, increased in slightly acidic soils as growing season advanced, indicating that the full potential of milled fertilizers was reached faster as compared to granular form (Ylivainio et al., 2008).

Lastly, the conditions of the three pot experiments were also different from one another. In Jokioinen and Tulln, real soils were used (Table 2), with a higher pH buffering capacity than in the artificial substrate used in Frick. Other soil properties differed between the three experiments. These properties, especially pH, will impact P availability, especially for

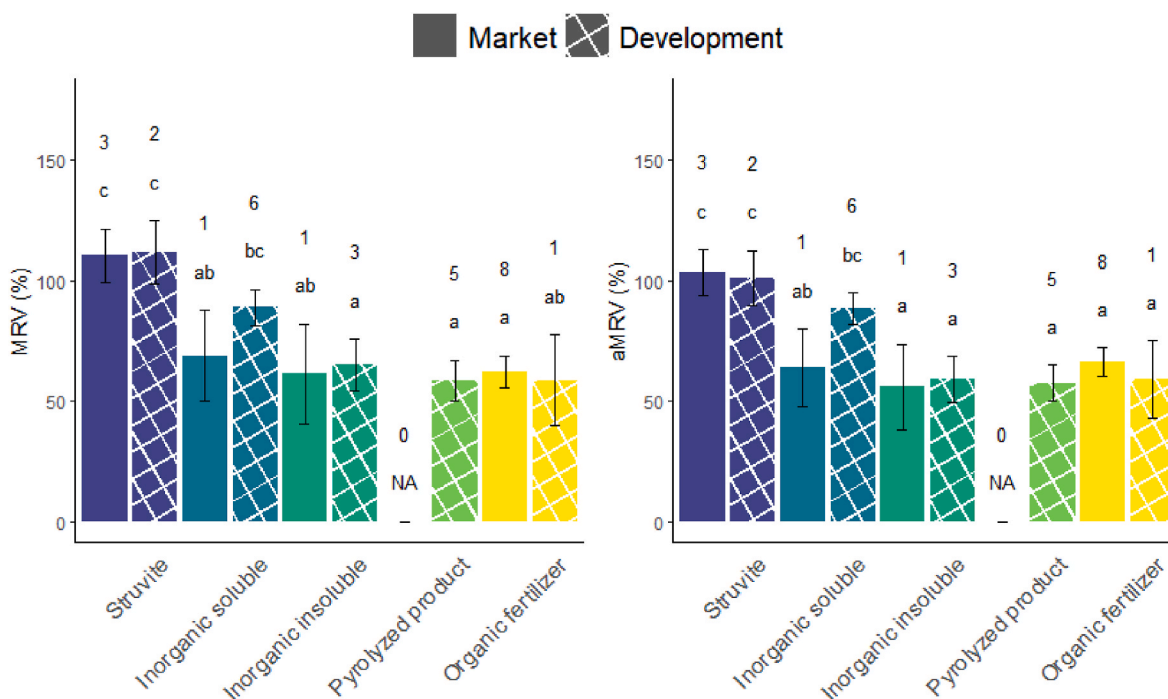


Fig. 6. Mineral replacement value and agronomic mineral replacement value of fertilizer class groups according to their market status at the time of study. Data shown as mean \pm confidence intervals. Bars with the same letter are not significantly different, based on Tukey's HSD test with $\alpha \leq 0.05$. Number above bars indicate the number of fertilizers. None of the pyrolyzed products tested were on the market at the time of this study.

less available P species. Non-soluble calcium phosphates and iron phosphates will increase their availability under acidic conditions. Moreover, the outdoor conditions at Jokioinen, particularly the lower temperatures, could have hindered P dissolution from the fertilizers, compared to Tulln and Frick, where the environmental conditions were more controlled.

4.4. Fertilization efficiency vs. market status of fertilizers

At the time of the study, 13 out of the 30 tested fertilizers were on the market. Fig. 6 compares marketed products and those in development within the fertilizer class groups. Because the sample size was often very small (only one marketed inorganic soluble fertilizer and one marketed insoluble fertilizer respectively, and only one non-marketed organic fertilizer) the differences could not be statistically confirmed. Nevertheless, in the inorganic soluble group, the products in development tended to perform better than the ones already on the market, while there were no apparent differences within the other fertilizer class groups.

In contrast to the previous fertilizer regulation (EU, 2003/2003), the new FPR (EU, 2019/1009) does not set solubility thresholds for compliance, except for the labelling of an inorganic fertilizer as "mineral fertilizer", where a minimum of 75% of total P in NAC (or 40% in H₂O) is required. The absence of a solubility threshold is notable since a significant difference was found for MRV ($p = 0.014$) and aMRV ($p < 0.001$), depending on their NAC value being above or below 75%. From the 13 tested fertilizers already available on the market, only three had P-NAC <75%: two organic fertilizers (MO10, MO14) and one inorganic fertilizer (PLA). This means that most of the marketed organic fertilizers (OPU, OG1, BA1, MB, RAN, PRV) had >75% P-NAC solubility. The remaining marketed products exceeding this threshold were mostly struvites. Conversely, for all five pyrolyzed products – none of which are currently on the market – had P-NAC <75% (Table 1).

Although NAC was previously found to overestimate P availability in soil (Duboc et al., 2017, 2022), these results point to its potential as a discriminant for P efficiency in this diverse set of fertilizers. Therefore,

the P-NAC threshold currently set for mineral fertilizers in the regulation might be useful to ensure a minimum efficiency of inorganic and organic P fertilizers alike. At the least, labelling of P-NAC content (as % of total P) for organic fertilizers could be a useful information.

5. Conclusion and outlook. Quo vadis recycled P fertilizers?

Our results indicate that there is potential for recycled fertilizers to partially replace conventional inorganic fertilizers and thus reduce the import of mined phosphate rock into the EU while recovering P from wastes and thus promoting the circular economy. The current limited use of recycled P fertilizers must stem from challenges in their implementation rather than from the lack of adequate feedstocks and technologies for P recycling.

We observed a trend toward specific recycled inorganic P fertilizers, often produced from municipal sewage sludge, which have properties and compositions that are equivalent to conventional P fertilizers. This trend is beneficial to P recycling overall: it facilitates the integration of recovered P into existing industrial fertilizer value chains, and in most instances a contaminated raw material with poor P availability is upgraded through these processes into an efficient and safe fertilizer.

Nevertheless, the products classified here as low-performance fertilizers require nuanced and broadened scrutiny. Being unrefined and often only slightly processed, products in this group contain organic matter, along with several macro- and micronutrients. This is particularly important in light of a recently proposed new definition of a plant nutrient (Brown et al., 2022) that moves away from the strict criteria of essentiality towards a broader, more ecologically-oriented definition encompassing beneficial elements, by recognizing a) their importance under certain growth conditions (growth under stress) b) the specific requirements of different species and, c) other factors that may indirectly benefit the crop.

Thus, in the absence of hazardous substances these unrefined products are expected to benefit soil health by providing a variety of nutrients in addition to their less plant-available P. To make them more efficient as P fertilizers, further processing would be required, ideally

without compromising their other beneficial properties. The benefit of processing P-rich organic residues by thermal treatment (pyrolysis, combustion) might be questioned since while providing safety (pathogens, persistent organic pollutants), these treatments often tend to decrease P availability. Finally, considering the slow release and pH dependency of less available P species, long-term experiments are required to evaluate their potential. Taking all these factors into account, the need for solubility requirements for organic and organo-mineral fertilizers should be carefully evaluated.

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CRediT authorship contribution statement

A. Hernandez-Mora: Writing – original draft, Visualization, Investigation, Formal analysis, Conceptualization. **O. Duboc:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **E. Lombi:** Writing – review & editing, Validation, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **E.K. Bünemann:** Writing – review & editing, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **J. Ylivainio:** Writing – review & editing, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **S. Symanczik:** Writing – review & editing, Investigation. **A. Delgado:** Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **N. Abu Zahra:** Investigation, Formal analysis. **J. Nikama:** Investigation. **L. Zuin:** Writing – review & editing, Investigation. **C.L. Doolette:** Writing – review & editing, Methodology, Formal analysis. **H. Eigner:** Resources, Conceptualization. **J. Santner:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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