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# Evaluation of six phosphorus extraction methods for compliance testing of recycled P fertilizers

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## ABSTRACT

Phosphorus (P) recycling for fertilizer production addresses the dependency on phosphate rock and mitigates P losses to the environment. However, predicting plant-available P in recycled fertilizers is challenging due to their diverse chemical composition. This study aimed at identifying the most suitable P extraction method for fertilizer compliance testing, considering their correlation with actual fertilization efficiency, as well as their simplicity, throughput, recognition and cost. Studies on fertilizer P compliance testing often lack recommendations on minimum P extractability threshold values. Here, thresholds are calculated based on actual fertilization efficiency of a large, chemically diverse set of recycled P fertilizers, many of which are already marketed. Thirty recycled P fertilizers were extracted with $H_2O$, neutral ammonium citrate (NAC), electro-ultrafiltration (EUF), ferrihydrite-filled membranes (iron bag; IB), sodium bicarbonate ($NaHCO_3$) and diffusive gradients in thin films (DGT). The mineral replacement value (MRV) of the fertilizer set was previously evaluated in three pot experiments at a fertilization rate of 50 mg kg$^{-1}$ soil. MRV correlations with the extractions methods showed similar results for all besides $H_2O$, which cannot be a reliable indicator for P availability. Fertilizers were classified as efficient or inefficient based on their MRV exceeding or falling below 60 % of the triple superphosphate reference value. The minimum P extractability threshold value (MPETV) for each method was based on the efficiency classification and it minimized the number of misclassified

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fertilizers. NAC, with a 60 % extractable minimum P threshold value, was the most adequate method for compliance testing, despite its overestimation of iron phosphate availability.

## 1. Introduction

The depletion of phosphorus (P) in agricultural soils generates the need to resupply P through application of fertilizers. (Cordell et al., 2009). Conventionally, P fertilizers are produced from phosphate rock, a non-renewable commodity that is unevenly distributed around the world (U.S. Geological Survey, 2023). Presently, recycled P fertilizers are obtained from various P-rich side streams through different processing methods, and could reduce the dependency on phosphate rock-derived fertilizers (Huygens and Saveyn, 2018). Since pot and field experiments for testing fertilizers are expensive and lack standardized protocols, laboratory extraction methods remain the most practical option to evaluate the potential efficiency of P fertilizers (Kratz et al., 2019).

Aside from external conditions such as the climate and soil properties, the agronomic efficiency of P fertilizers is determined by their physico-chemical characteristics, with the P species playing a crucial role of their plant P availability. Compliance testing methods for P fertilizers are extraction methods utilized on a (supra-)national level to test quality aspects such as nutrient extractability. In many cases, these extraction methods were developed by the fertilizer industry to guarantee the quality and homogeneity of their products and to evaluate P extractability in fertilizers.

Facilitating the commercialization of fertilizers made from nutrient-rich recycled materials was one of the main aims of the EU's fertiliser products regulation (FPR) (European Parliament, 2019). With regard to P extractability, the new FPR was simplified compared to the previous regulation (EC 2003/2003 (European Parliament, 2003)) by reducing the compliance testing methods to only $H_2O$ and neutral ammonium citrate (NAC) extractions for most fertilizer materials, with only rock phosphate still being tested with formic acid.

Beyond compliance testing for product homogeneity, a minimum P extractability threshold is necessary to guarantee the fertilizers' agronomic efficiency. This aspect, often disregarded in the literature on relations between P extractability and fertilization efficiency, is currently not implemented in the FPR (European Parliament, 2019): the only requirement is a *declaration* set for organo-mineral and inorganic P fertilizers about P extractability in $H_2O$ and NAC. The only exception is a requirement of P solubilities of at least either 40 % in a $H_2O$ or 75 % in a NAC extract for inorganic fertilizers to be labelled as mineral fertilizer. There is, however, scientific literature questioning the suitability of these extraction methods to predict plant availability of P (Duboc et al., 2022, 2017; Kratz et al., 2019; Meyer et al., 2018). Alternative extraction methods, such as sodium bicarbonate extractions (Christiansen et al., 2020; Duboc et al., 2022), anion and cation exchange membranes (Nanzer et al., 2019) or diffusive gradients in thin films (DGT) (Duboc et al., 2017; Kiani and Ylivainio, 2024) have led to better results in predicting plant P availability when compared to $H_2O$ and NAC extractions. These alternative extractions follow different approaches from the current compliance testing methods in some cases, aiming at e.g. mimicking the sink effect that takes place in the fertilizer-soil-plant environment. The inclusion of recycled P fertilizers in the FPR has increased the complexity of compliance testing, because now the chemical diversity of the marketable P fertilizers is wider and finding a unique solvent capable of reflecting the actual P availability under field conditions in all cases is challenging.

The interests of stakeholders in the use and outcomes of compliance testing methods for P fertilizers reflecting P bioavailability are diverse. Farmers and fertilizer producers need to know the agronomic efficiency of a product and adapt the fertilization strategy accordingly. Governmental institutions and environmental organisations aim at increasing the resource use efficiency and reinforcing circular economy while avoiding possible pollution problems derived from excessive P application. Researchers aim at improving the fertilization efficiency of different P-rich streams by optimizing processing methods. In addition to providing such information, compliance tests should be easy, fast and cost-effective to make their implementation feasible in routine laboratories.

The aim of the present work was to provide a basis for compliance testing recommendations for P fertilizers that respond to factual P bioavailability and align with practical considerations as well. To that end we measured the P extractability of thirty different recycled fertilizers using the FPR compliance testing methods ($H_2O$ and NAC) (European Parliament, 2019), as well as four alternatives: sodium bicarbonate extraction ($NaHCO_3$), a ferrihydrite-filled dialysis membrane (Iron Bag; IB), electro-ultrafiltration (EUF) and diffusive gradients in thin films (DGT). IB, EUF and DGT were chosen as these methods are kinetic, sink-based P extraction procedures, aiming at mimicking fertilizer P availability in soil as affected by sorption to soil particles and P uptake activity of plant roots, whereas the other methods are conventional, equilibrium-based extraction techniques. $NaHCO_3$ and DGT were assessed in this study because they have been previously reported as good predictors of P availability in fertilizers (Brod et al., 2015; Christiansen et al., 2020; Duboc et al., 2022). To assess the suitability of the different extraction methods for P fertilizer compliance testing, we tested the thirty recycled fertilizers in pot experiments with wheat, barley and ryegrass in Tulln (Austria), Jokioinen (Finland) and Frick (Switzerland), respectively. We then correlated the fertilizer P extractability measured with the different extraction methods with the pot experiments results. Subsequently, we set a minimum fertilization efficiency to discriminate effective and not effective fertilizers, and proposed a minimum P extractability threshold value (MPETV) for each of the extraction methods, taking into account the correlation results. Based on the results of previous studies (Brod et al., 2015; Christiansen et al., 2020; Duboc et al., 2022, 2017), we hypothesized that:

- The correlation of the $H_2O$ extraction of recycled P fertilizers with the pot experiments shows that the $H_2O$ extraction underestimates plant available P.
- The correlation of the NAC extraction with the pot experiments shows that the NAC extraction overestimates plant available P.
- The $NaHCO_3$ extraction and infinite-sink methods correlate better with plant P availability than $H_2O$ and NAC extractions.

## 2. Materials and methods

### 2.1. Fertilizer selection

Thirty recycled fertilizers were selected according to the following requirements: (1) The products should cover a wide range of product function categories (PFCs) and component material categories (CMCs), both of which are defining fertilizer characteristics according to the EU's FPR (European Parliament, 2019), (2) the minimum total P ($P_t$) content is 1 % $P_2O_5$, (3) the fertilizers had a high technology readiness level. The fertilizers selected are listed on Table 1.

CRA was the sole exception to the required $P_t$ of 1 % $P_2O_5$. This material had a $P_t$ of 0.91 % $P_2O_5$, but was included in the fertilizer set because it was the only hydrochar obtained from fruit juice sludge.

### 2.2. Fertilizer analysis

To characterize the fertilizers, their elemental composition and organic carbon content were analysed, and six conventional and potential fertilizer P compliance test methods were evaluated: $H_2O$, NAC, $NaHCO_3$, IB, EUF and DGT. Results were expressed as relative extractability (% of $P_t$ extracted), except for DGT (see 3.2.6). Before the analyses, fertilizers were dried at 37°C overnight and milled to $< 0.2$ mm. Struvites were not dried because they contain water of crystallization, and drying could have altered their molecular structure, and thus P extractability.

#### 2.2.1. Fertilizer composition

The $P_t$ content of each fertilizer was determined after an *aqua regia* digestion, using inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Jarrell Ash Iris Advantage), at the Natural Resources Institute Finland (Luke). Total organic carbon (TOC) was analyzed in a soliTOC instrument (Elementar Analysensysteme GmbH) by dry combustion at the University of Natural Resources and Life Sciences, Vienna (BOKU) (for more details see Hernandez-Mora et al. 2024).

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

P K-edge and $L_{2,3}$-edge XANES spectroscopy were conducted at the Canadian Light Source (Saskatchewan, Canada) to determine the main P species present in each product. 21 reference materials were included for the K-edge XANES and 18 for the L-edge analysis. The spectral data was processed with the Athena [XAS data processing] software of the Demeter package, version 0.29.6., available at

**Table 1**
Fertilizers selected for the study.

| Acronym | Description | Fertilizer class | Main P species | Market status* |
|---|---|---|---|---|
| **TSP** | Triple superphosphate | Reference | Monocalcium phosphate | M |
| **CGO** | Struvite | Struvite | Ammonium magnesium phosphate | M |
| **PCS** | Struvite | Struvite | Ammonium magnesium phosphate | M |
| **SSW** | Struvite | Struvite | Ammonium magnesium phosphate | M |
| **EPS** | Struvite | Struvite | Ammonium magnesium phosphate | D |
| **STR** | Struvite | Struvite | Ammonium magnesium phosphate | D |
| **EPH** | Sunflower husks ash | Inorganic NAC soluble | Hydroxyapatite/tricalcium phosphate | M |
| **ADC** | Na-AshDEC | Inorganic NAC soluble | Dicalcium phosphate | D |
| **BZH** | TSP from sewage sludge ash | Inorganic NAC soluble | Monocalcium phosphate | D |
| **DCP** | Dicalcium phosphate from sewage sludge ash | Inorganic NAC soluble | Dicalcium phosphate | D |
| **MAP** | Monoammonium phosphate from mining waste | Inorganic NAC soluble | Monoammonium phosphate | D |
| **PRC** | P-RoC | Inorganic NAC soluble | Hydroxyapatite/tricalcium phosphate | D |
| **VVB** | Vivianite recovered from sewage sludge | Inorganic NAC soluble | Iron phosphate | D |
| **PLA** | Turkey litter ash | Inorganic NAC insoluble | Hydroxyapatite/tricalcium phosphate | M |
| **BES** | BioEcoSIM | Inorganic NAC insoluble | Dicalcium phosphate | D |
| **KBT** | Sewage sludge slag | Inorganic NAC insoluble | Unidentified | D |
| **PKA** | Sewage sludge ash | Inorganic NAC insoluble | Iron phosphate | D |
| **ABP** | Animal biochar | Pyrolyzed product | Hydroxyapatite/tricalcium phosphate | D |
| **BAG** | Sewage sludge char | Pyrolyzed product | Unidentified | D |
| **CRA** | Hydrochar from fruit juice sludge | Pyrolyzed product | Dicalcium phosphate | D |
| **MBC** | Poultry litter biochar | Pyrolyzed product | Hydroxyapatite/tricalcium phosphate | D |
| **PPS** | Pyrolyzed pig slurry digestate | Pyrolyzed product | Dicalcium phosphate | D |
| **BA1** | Wheat and maize fermented and distilled | Organic fertilizer | Phytic acid | M |
| **MB1** | Meat and bone meal | Organic fertilizer | Hydroxyapatite/tricalcium phosphate | M |
| **MO10** | Vegetable and animal biomass waste | Organic fertilizer | Hydroxyapatite/tricalcium phosphate | M |
| **MO14** | Vegetable biomass waste | Organic fertilizer | Hydroxyapatite/tricalcium phosphate | M |
| **OG1** | Meat and bone meal | Organic fertilizer | Hydroxyapatite/tricalcium phosphate | M |
| **OPU** | Chicken manure and grape residue pellets | Organic fertilizer | Dicalcium phosphate | M |
| **PRV** | Biogas slurry from biowaste and sewage sludge | Organic fertilizer | Iron phosphate | M |
| **RAN** | Biowaste and sewage sludge | Organic fertilizer | Iron phosphate | M |
| **NNP** | Dried municipal and industrial sludge | Organic fertilizer | Iron phosphate | D |

* Market status: M… available in the market. D… in an advanced development stage.

http://bruceravel.github.io/demeter/ (Ravel and Newville, 2005). The P species identification was based on a visual comparison of spectral features of the fertilizers and the reference materials. The main P species of each product is shown in Table 1. A more detailed description on these analyses is reported by Hernandez-Mora et al. (2024).

### 2.2.3. $H_2O$ extraction

$H_2O$ extraction was conducted following the DIN EN 15958:2012–02 protocol. 300 mg of fertilizer were added to 30 mL $H_2O$ (1:100 w/v ratio). The vials were placed on a plate shaker at 80 rpm for 30 minutes. Then the samples were filtered using 0.45 µm syringe filters. An aliquot was added in a 15 mL vial and acidified to reach 2 % (v/v) $HNO_3$. The samples were analyzed for P by ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA).

### 2.2.4. NAC extraction

The NAC extraction was conducted adapting BS EN 15957:2011. 28–30 % w/v ammonia solution was added to an 18.5 % w/v citrate solution until reaching pH 7 to obtain the NAC extraction solution. Vials containing 500 mg of fertilizer and 50 mL NAC solution were placed into a 65°C shaking water bath for 60 minutes. Right afterwards the vials were cooled down and their content was brought to 250 mL with laboratory grade water type I. The extracts were filtered using Munktell filter paper (grade 1290, Ahlstrom-Munksjö Munktell) and acidified to 2 % $HNO_3$ v/v. P concentrations were measured by ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA).

### 2.2.5. IB extraction

Iron oxide slurry was prepared by dissolving 100 g $L^{-1}$ $Fe(NO_3)_3 \times 9\,H_2O$ in water. Precipitation took place when 1 mol $L^{-1}$ NaOH was added to adjust the solution pH to 6.5–6.8. Vials were centrifuged twice for 3 min at 70 × g. After each centrifugation, the supernatant was removed, replaced with water and the ferrihydrite re-suspended. 30 mmol $L^{-1}$ 3-(N-morpholino) propanesulfonic acid (MOPS) solution was prepared and its pH was adjusted to 6.8 by adding NaOH. Micropur (Katadyn Micropur Classic MC 1000 F) was added to suppress microbial activity. 30 mg of fertilizer were added to 150 mL of MOPS solution. Dialysis membranes (Visking dialysis tubing, size 3, 20/32, 12.000–14.000 MWCO) were cut and boiled twice in laboratory grade water type I to soften. Each membrane was filled with 20 mL iron oxide slurry and closed with clips (Medi-Clip for 6.3–28.6 mm, Medicell Membranes Ltd., London, UK). One filled membrane was added to each vial with MOPS solution. Samples were shaken for seven days in a head-over-head shaker. Then, the membranes were removed, the ferrihydrite suspension was recovered and acidified with 1 mL of 96–98 % concentrated $H_2SO_4$. Afterwards the acidified suspension was diluted to 0.25 mol $L^{-1}$ $H_2SO_4$. P concentrations were measured by ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA).

### 2.2.6. EUF extraction

The EUF extraction method is a soil multi-nutrient status assessment method used for fertilizer recommendations in sugar beet production and also for further crops (Horn and Fürstenfeld, 2001; Németh, 1982; Teklić et al., 2002). It utilizes a specific apparatus to apply an electrical field and a vacuum to a soil suspension (or, in this study, fertilizer suspension) located in an extraction chamber. The solution used for the fertilizer suspension is deionized water. Due to the action of the electrical field, nutrient ions accumulate adjacent to their respective electrode. Because these electrodes are located adjacent to an ultrafilter membrane, behind which the vacuum is applied and through which dialysate is collected, an anion- and cation- enriched solution is collected in this apparatus. The extraction chamber is continuously refilled with solution to maintain sufficient volume while dialysates are collected during the entire extraction process. After the sampling process, these solutions are combined and analysed for their total elemental content. Keupp et al. (2015) showed that EUF can describe P availability for recycled fertilizers from sewage sludge.

In this study, we applied the standard extraction parameters for soil samples, but extracted only 200 mg of fertilizer instead of the usual 5 g of soil in the extraction chamber, because P fertilizers are much more concentrated than soils. The first, easily available P fraction was collected after a 30 min extraction at 20°C and 200 V. The second, less available fraction was collected afterwards, after 5 min extraction at 80°C and 400 V. A third, least available fraction was obtained, by adding 5 mL 0.02 mol $L^{-1}$ diethylentriaminepentaacetic acid (DTPA) to the suspension and extracting for 5 min at 80°C and 400 V. The P concentrations in the dialysates were analyzed by ICP-OES (ICP Spectro Flame -Modula SOP-).

### 2.2.7. $NaHCO_3$ extraction

The $NaHCO_3$ extraction was conducted according to Duboc et al. (2022). 30 mg of fertilizer were put into vials with 30 mL $NaHCO_3$ 0.5 mol $L^{-1}$ solution and shaken for 4 h on a plate shaker. Samples were filtered afterwards using a 0.45 µm syringe filter. 16 mL aliquots were taken, acidified with 1 mL $HNO_3$ 65 % and brought to 20 mL with $H_2O$. P concentrations were determined by ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA).

### 2.2.8. DGT

0.8 mm and 0.4 mm thick polyacrylamide hydrogels were prepared according to Zhang and Davison, (1995). The 0.4 mm gels were used as P-binding medium after precipitation with $ZrOCl_2$* 8 $H_2O$ following the method by Guan et al. (2015). 0.8 mm gels were used as diffusive medium. Gels were cut to 25 mm diameter discs. DGT samplers with an exposure window of 3.14 $cm^2$ (DGT Research Ltd. Lancaster, UK) were used for the extraction. A P-binding gel, a diffusive gel, and finally a polyethersulfone membrane (Supor®, 0.14 mm thickness, 45 µm pore size) were placed on the sampler piston, the assembly was then closed by carefully pushing the sampler ring onto the piston. The membrane serves for protecting the gels from particle contamination.

DGT analyses were conducted with fertilizer-amended soil to avoid gel saturation, which would result from direct fertilizer application on the DGT sampler. The same soil that was used for the pot experiment at Tulln was chosen for the DGT analysis. This soil was fertilized with the different products at a rate of 50 mg P $kg^{-1}$ soil. Unfertilized controls were included in the experiment. Vials with fertilized soil were watered to reach 60 % water holding capacity (WHC) and were incubated for 96 h at 20°C. More water was then added to reach 90 % WHC and the vials were incubated again for 24 h. Approximately 10 g of fertilized soil were placed on top of each DGT sampler for a deployment time of 24 h. Afterwards, the binding gels were retrieved from the samplers and eluted in 5 mL 0.75 mol $L^{-1}$ NaOH while on a plate shaker. Eluate P concentration was measured using blue molybdate method at 881 nm. Results are expressed as $C_{DGT}$:

$$C_{DGT} = \frac{M\Delta g}{DAt} \tag{1}$$

Being:

- $C_{DGT}$:time-averaged solute concentration at the sampler-soil interface (μg $cm^{-3}$).
- $M$:mass of P collected on the sampler after 24 h (μg).
- $\Delta g$:thickness of the diffusive gel (cm).
- $D$:phosphate diffusion coefficient of the diffusive gel ($cm^2$ $s^{-1}$) (Zhang et al., 1998, available at https://www.dgtresearch.com/diffusion-coefficients/).
- $A$:sampling area ($cm^2$).
- $t$:deployment time (s).

## 2.3. Fertilizer classification

Two different classifications were developed to group the fertilizers and allow for linking fertilizer extractability (*i.e.* extraction results) to fertilization efficiency (Table 1). The first classification was based on the XANES results. Fertilizers were classified according to their main P species: (1) Ammonium magnesium phosphate, (2) hydroxyapatite/tricalcium phosphate, (3) dicalcium phosphate type, (4) monocalcium phosphate, (5) phytic acid, (6) monoammonium phosphate and (7) iron phosphate.

The second classification is an expansion of the PFC established in the FPR (European Parliament, 2019), which classifies fertilizers into organic, organo-mineral and inorganic depending on their TOC content (>15 % TOC for organic fertilizers, 7.5–15 % TOC for organo-mineral fertilizers and <7.5 % TOC for inorganic fertilizers), and the NAC extractability of the products, which in the FPR is specific only to label inorganic fertilizers as “mineral” given that the $P_t$ extractability is higher than 75 %. This classification consisted of the following groups: (1) struvites, (2) inorganic NAC-insoluble fertilizers, (3) inorganic NAC-soluble fertilizers, (4) organic fertilizers and (5) pyrolyzed products. The number of struvites included in the study was high enough to justify separating them from the rest of the inorganic NAC-soluble products. Similarly, the pyrolyzed products group was separated from the organic fertilizers group. Details on these classifications are available in Hernandez-Mora et al. (2024).

## 2.4. Pot experiments

Three pot experiments were conducted using spring wheat (*Triticum aestivum* L. var. Quintus), spring barley (*Hordeum vulgare* var. Einari) and ryegrass (*Lolium multiflorum* var. Gemini) as test crops at experimental stations in Tulln (Austria), Jokioinen (Finland) and Frick (Switzerland), respectively, to evaluate the fertilization efficiency of the selected fertilizers. These gramineous crops chosen represent the most important crops in each respective region, and were grown up to maturity (barley and wheat) or underwent three subsequent cuts (ryegrass). 50 mg P $kg^{-1}$ soil of each fertilizer were added to soil/growing medium and were mixed in thoroughly. Each treatment had four replicates. Triple superphosphate served as reference fertilizer and was applied at 12.5, 25, 50 and 100 mg $kg^{-1}$ soil (Tulln) or growing medium (Frick) and 10, 25, 50, 100 and 200 mg $kg^{-1}$ soil (Jokioinen) on a basis of $P_t$. Control treatments did not receive any P. The characteristics of the soils and growing medium used are available on the supplementary information (Table S1). Further details on the pot experiments are available in Hernandez-Mora et al. (2024).

## 2.5. Data evaluation

Data analysis was conducted mainly in Microsoft Excel version 2018 and R version 4.2.1 (R Core Team, 2022). Figures were created using either base R or ggplot2 (Wickham et al., 2023a), with the colour palettes from the viridis package (Garnier et al., 2023). Additionally, the dplyr package (Wickham et al., 2023b) was used for data processing.

### 2.5.1. Pot experiments

To allow the comparison between the different pot experiments, the mineral replacement value (MRV) was used as data evaluation parameter instead of P uptake. MRV was calculated according to the following formula:

$$MRV(\%) = \frac{P_{up} - P_c}{P_{ref} - P_c} \quad x \quad 100 \tag{2}$$

Being:

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

### 2.5.2. *Correlation analysis*

Correlation analyses were conducted to assess the relationship between the percentage of $P_t$ extracted with each method and the MRV. Linear regression analysis was discarded due to the non-normality of most of the extraction results, as calculated with a Shapiro-Wilk test in R. The goodness of fit for the correlation analysis was measured with Kendall's τ coefficient was calculated using base R, with the cor.test() function.

### 2.5.3. *Threshold selection*

Fertilizer ordinances mandate specific, numeric MPETVs to determine whether candidate materials can be marketed as a fertilizer. For being able to calculate MPETVs it was necessary to define a minimum acceptable MRV based on the results of the pot experiments in order to categorize fertilizers as effective or ineffective. A fertilizer was considered effective when its average MRV was higher than 60 %. Exceptions were made for CRA, PLA and OG1s. OG1 gave a much lower MRV in Jokioinen than in the other two pot experiments, likely because it was applied as pellets there, and based on the other two locations it was decided to consider it as effective. CRA gave an exceptionally high MRV in Jokioinen, but it performed poorly in the other two experiments. This inconsistent performance could be due to the lower P concentration in CRA and the presence of additional nutrients that might have favoured its performance in the Jokioinen pot experiment. Therefore it was decided to classify CRA as an ineffective fertilizer. PLA gave a much higher MRV in Tulln than in the other two locations, and given that in Tulln fertilizers generally performed better, it was decided to classify PLA as ineffective fertilizer. This classification is shown in Table S3.

Once the fertilizers were categorized, a MPETV could be established for each extraction method, aiming at minimizing the number of misclassified fertilizers (e.g. a fertilizer that meets the MPETV but has a low average MRV would be wrongly categorized as effective). The methodology to establish the MPETV is a simplification of the Receiver Operating Characteristics (ROC) methodology. To calculate MPETV (in % of $P_t$) for the different extraction methods, the number of false positives (*ineffective* fertilizers exceeding the MPETV) and false negatives (*effective* fertilizers falling below the MPETV) was counted for all potential MPETVs between 0 % and 100 % in steps of 1 %. The respective threshold chosen was the value with the lowest sum of false positives and false negatives. In most cases, there was a range of extractability with the same sum of false positives and false negatives. The threshold chosen was the nearest multiple of 5 situated as close as possible to the middle of that range. The threshold range width, that is, the range of P extractability values around the MPETV in which the number of misclassified fertilizers was constant, was considered when evaluating the goodness of MPETVs. A wide threshold width is positive, because it implies that minimal variations of the extraction parameters (temperature,

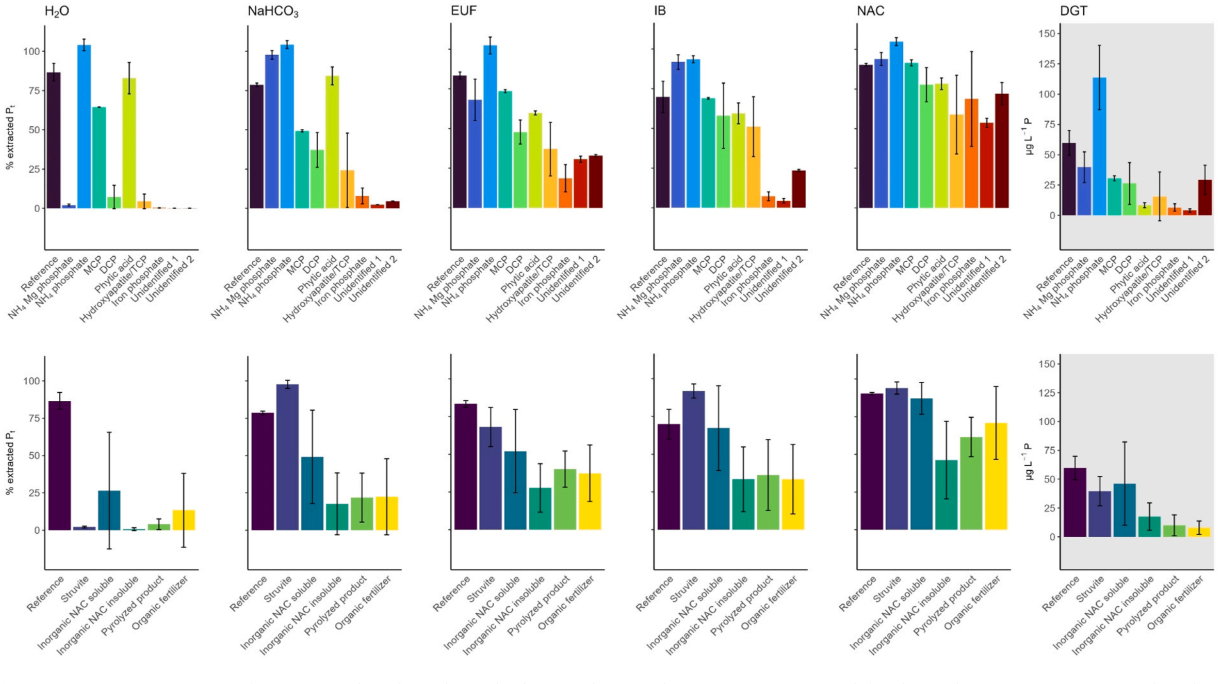

**Fig. 1.** Average percentage of $P_t$ extracted with each method, according to the main P species and fertilizer class groups. $NH_4$ Mg phosphate: ammonium magnesium phosphate (n=5), $NH_4$ phosphate: monoammonium phosphate (n=1), MCP: monocalcium phosphate (n=1). DCP: dicalcium phosphate type (n=6). Phytic acid (n=1), TCP: tricalcium phosphate (n=9). Struvite (n=5), inorganic soluble (n=7), inorganic insoluble (n=4), pyrolyzed product (n=5), organic fertilizer (n=9).

pH, etc) will not result in a slightly different percentage of P extracted that causes a fertilizer to be classified differently.

### 2.5.4. *Selection of the most convenient compliance testing method*

The extraction methods were compared to one another considering their τ correlation coefficient, the number of fertilizers misclassified at the optimized MPETV, the threshold range width and the following practical considerations, according to the experience of the researchers: 1) simplicity of the method, 2) sample throughput, 3) recognition of the method and 4) cost and financial investment required.

## 3. Results

### 3.1. *Agronomic efficiency of recycled P fertilizers (pot experiments)*

The agronomic P efficiency of the recycled fertilizers is described in detail in our previous publication (Hernandez-Mora et al., 2024). Fertilizers with monoammonium phosphate, ammonium magnesium phosphate, monocalcium phosphate and dicalcium phosphate did not have MRVs significantly different from the reference fertilizer TSP (a monocalcium phosphate). Fertilizers with phytic acid, hydroxyapatite/tricalcium phosphate and iron phosphate as their main species had significantly lower MRVs compared to those of TSP. Struvites and inorganic NAC-soluble fertilizers yielded MRVs similar to the MRV of TSP, while inorganic NAC-insoluble, organic fertilizers and pyrolyzed products had significantly lower MRV than those of TSP (Table S3).

### 3.2. *Extractable P using different methods*

Results of the percentage of extractable P for each extraction method according to the two fertilizer classifications (see 2.3) are shown in Fig. 1. P extractability for individual fertilizers is shown in Table S2 and Fig. 2. The median percentage of extractable P increased in the following order: $H_2O < NaHCO_3 <$ EUF < IB < NAC (Fig. 2). The DGT result is expressed in μg P $L^{-1}$, which cannot, for methodological reasons (see 3.2.6) be transformed into a percentage of $P_t$. Therefore, it cannot be compared to the other extraction methods in terms of proportion of P extracted. Besides the EUF extraction, the result data of the extractions were not normally distributed (as calculated with a Shapiro-Wilk test and shown in the histograms in the top part of Fig. 2).

### 3.2.1. *$H_2O$ extraction*

Most fertilizers tested were hardly extractable in $H_2O$, with a median $P_t$ extracted of 2 % (Fig. 2). The extractability of ammonium magnesium phosphates, iron phosphates, all dicalcium phosphate type fertilizers besides OPU and hydroxyapatites/tricalcium phosphates except OG1 was below 10 % $P_t$. Only MAP, BZH and BA1 reached extractabilities above 40 %, which is the MPETV defined by the FPR (European Parliament, 2019) for inorganic fertilizers to be classified as “mineral”.

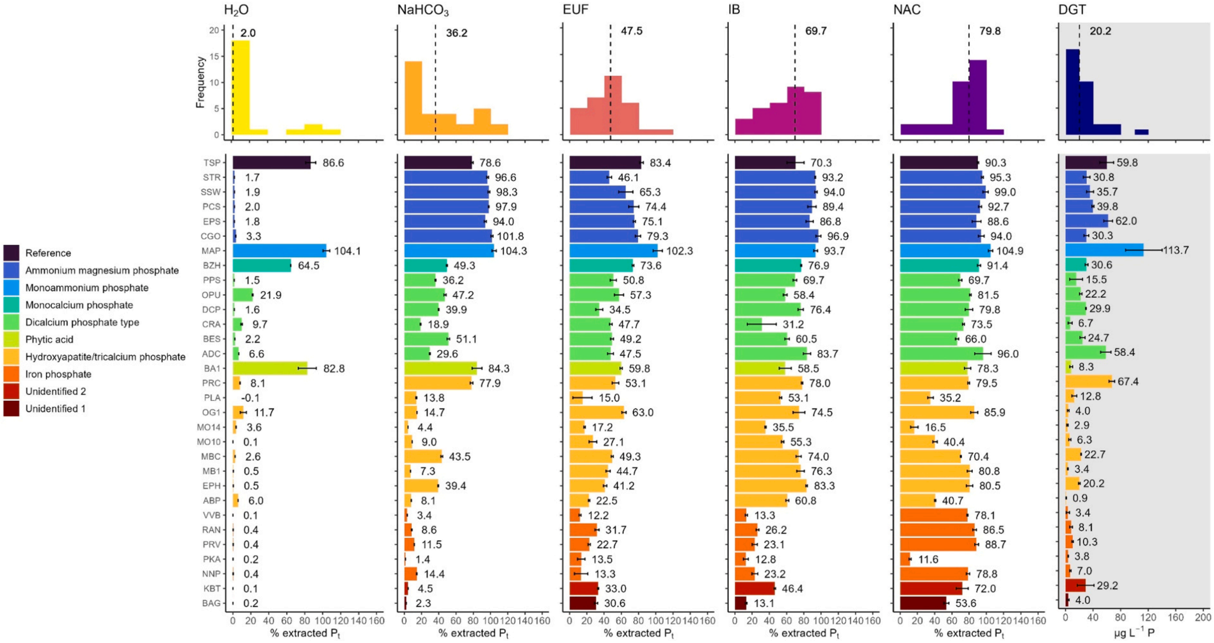

**Fig. 2.** Histograms of the six extraction methods (top), and individual fertilizer extraction results. Dashed line in the histograms corresponds to the median. Error bars correspond to standard deviations (n = 3). Colours of the individual extraction results correspond to the main P species detected in the fertilizer.

### 3.2.2. $NaHCO_3$ extraction

$NaHCO_3$ extractabilities varied considerably depending on the main P species of the fertilizer. The median $P_{NaHCO3}$ extractability was 36.2 % of $P_t$ (Fig. 2). P contained in ammonium magnesium phosphates was on average (97.7 %) $NaHCO_3$-extractable. The extractability of dicalcium phosphate type species varied from 18.9 % $P_t$ (CRA) to 51.1 % $P_t$ (BES). Monoammonium phosphate (MAP) and phytic acid (BA1) were highly $NaHCO_3$ extractable (104 % and 84.3 % respectively). Besides one fertilizer (PRC), hydroxyapatites/tricalcium phosphates showed $NaHCO_3$ extractabilities below 50 %. Iron phosphates were barely $NaHCO_3$ extractable (7.9 % $P_t$ on average).

### 3.2.3. Electro-ultrafiltration

The median $P_{EUF}$ was 47.5 % (Fig. 2). Besides the only monoammonium phosphate product (MAP) and monocalcium phosphate product (BZH), ammonium magnesium phosphates were the most EUF-extractable group, with an average $P_{EUF}$ of 68.1 %, followed by dicalcium phosphate type fertilizers ($P_{EUF}$ 47.8 %), hydroxyapatite/tricalcium phosphates ($P_{EUF}$ 37 %) and iron phosphates ($P_{EUF}$ 18.7 %).

### 3.2.4. Ferrihydrite-filled membrane bag extraction

IB exhibited the second highest median value of extracted P (69.9 %, Fig. 2). Ammonium magnesium phosphates were on average 92 % IB extractable. MAP was also highly IB extractable (94 %). BZH extractability in IB was medium-high (69 %). The extractability of dicalcium phosphate type species was highly variable, from 22 % $P_t$ (CRA) to 81.3 % $P_t$ (ADC). The IB extractability was also irregular for the hydroxyapatite/tricalcium phosphates (from 14 % $P_t$ for MO14 to 77 % for PRC). Iron phosphates were barely IB-extractable (average 7 % $P_t$).

### 3.2.5. Neutral ammonium citrate extraction

The NAC extractant was the strongest among the tested methods and showed less variation in P extraction among the materials tested. The median extractability was 79.8 % (Fig. 2). Ammonium magnesium phosphates, MAP and BZH- NAC extractabilities were > 85 % of $P_t$. The average $P_{NAC}$ for dicalcium phosphate type species was 78 %. The extractability of hydroxyapatite/tricalcium phosphate species varied from 17 % $P_t$ for MO14 to 86 % $P_t$ for OG1. Except for the low $P_{NAC}$ registered for PKA, the iron phosphates were highly NAC extractable (69 % $P_t$ on average).

### 3.2.6. Diffusive gradients in thin films

The DGT method is substrate-dependent and this prevents the interpretation of DGT results as percentage of total fertilizer P (Davison, 2016). Therefore, results have to be shown as time-averaged P concentrations at the soil-sampler interface in µg $L^{-1}$. The median $P_{DGT}$ value was 20.2 µg $L^{-1}$ (Fig. 2). The highest $P_{DGT}$ was obtained for MAP (114 µg $L^{-1}$). $P_{DGT}$ for ammonium magnesium

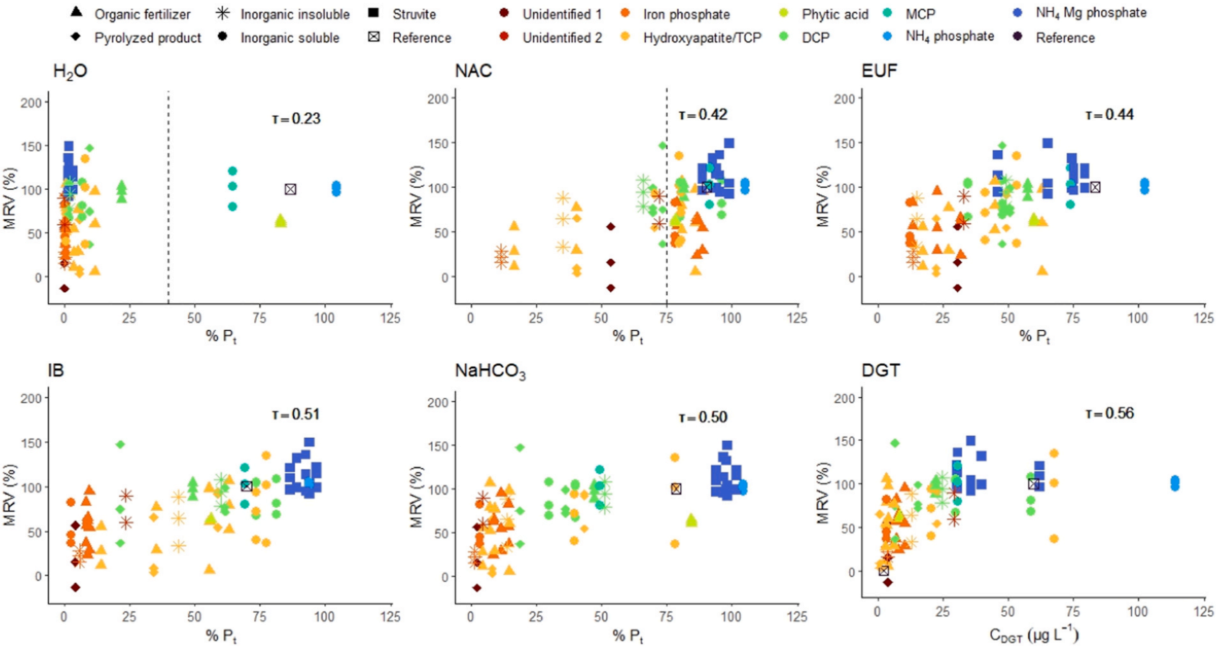

**Fig. 3.** Correlation plots of the phosphorus extractability for each method, with the average mineral replacement value obtained for each fertilizer in each of the three pot experiments. Colours correspond to the main P species detected in each fertilizer. Point shapes correspond to the fertilizer class. The dashed vertical line corresponds to the current MPETVs of the FPR for inorganic fertilizers to be labelled as *mineral*. Kendall's τ coefficient assesses the goodness of fit for the correlations, with p values ≤ 0.05 in for all cases.

phosphates was 40 μg $L^{-1}$ on average, with EPS being much more extractable (62 μg $L^{-1}$) than the rest of the group. The monocalcium phosphate product (BZH) had an average $P_{DGT}$ of 31 μg $L^{-1}$. $P_{DGT}$ varied in the dicalcium phosphate type group between 7 μg $L^{-1}$ for CRA and 58 μg $L^{-1}$ for ADC. Hydroxyapatite/tricalcium phosphates were less DGT extractable (15.6 μg $L^{-1}$), except for PRC (67 μg $L^{-1}$). Iron phosphates gave very low DGT values (7 μg $L^{-1}$ on average).

### 3.3. Relationship between P extracted and fertilization efficiency

Correlation results between P extractability for each extraction method and MRV are shown in Fig. 3. All correlations between the extraction methods and MRV were significant ($p \leq 0.05$). The τ values varied between 0.23 and 0.56. Individual results of the correlation analysis per pot experiment and per batch within each pot experiment are available in the supplementary information document (description and Figs S1, S2 and S3).

Scatterplots of P extracted with different methods vs. MRV are shown in Fig. 3. For EUF and IB the points are evenly scattered. The iron phosphates are clustered around 20 % and 10 % $P_t$, respectively, and the ammonium phosphate products appear clustered at 80 % and 90 % $P_t$, respectively, with hydroxyapatite/tricalcium phosphates and dicalcium phosphate type fertilizers scattered, displaying variable extractabilities. Most fertilizers were highly extractable in NAC and thus there is a distinct cluster from ca. 70–100 % $P_t$. $NaHCO_3$ has three-point clusters: one formed by iron phosphates and hydroxyapatites around 10 % $P_t$, another one with dicalcium phosphate type products at 40 % $P_t$ and a third one of ammonium magnesium phosphate fertilizers at 100 % $P_t$. A similar pattern is observed for the DGT data, but the clusters are intertwined to one another and there are four products with $P_{DGT}$ values above 50 μg $L^{-1}$, which are considerable more extractable than the rest of the fertilizer set.

### 3.4. .MPETV for the extraction methods

The number of fertilizer misclassifications (false positives and false negatives) as a function of the chosen MPETV is shown in Fig. 4. MPETVs were selected to keep the total number of misclassifications at minimum. Potential MPETVs for each extraction method and their correspondent misclassifications are shown in Table 2 and Fig. 5. Proposed MPETVs vary between 1 % ($H_2O$) and 60 % (NAC). For $H_2O$ we did not round up to the nearest multiple of 5 due to the strong concentration of points around 1 % P extractability. The number of misclassifications ranged from two to seven (6.4–23 % of all fertilizers). No MPETV was considered for DGT because this extraction is conducted on fertilized soil.

## 4. Discussion

### 4.1. Need of a unique P extractability threshold for all fertilizers

Table 1 shows that the PFC-based fertilizer class and main P species do not have a clear correspondence (e.g. MBC (manure biochar)

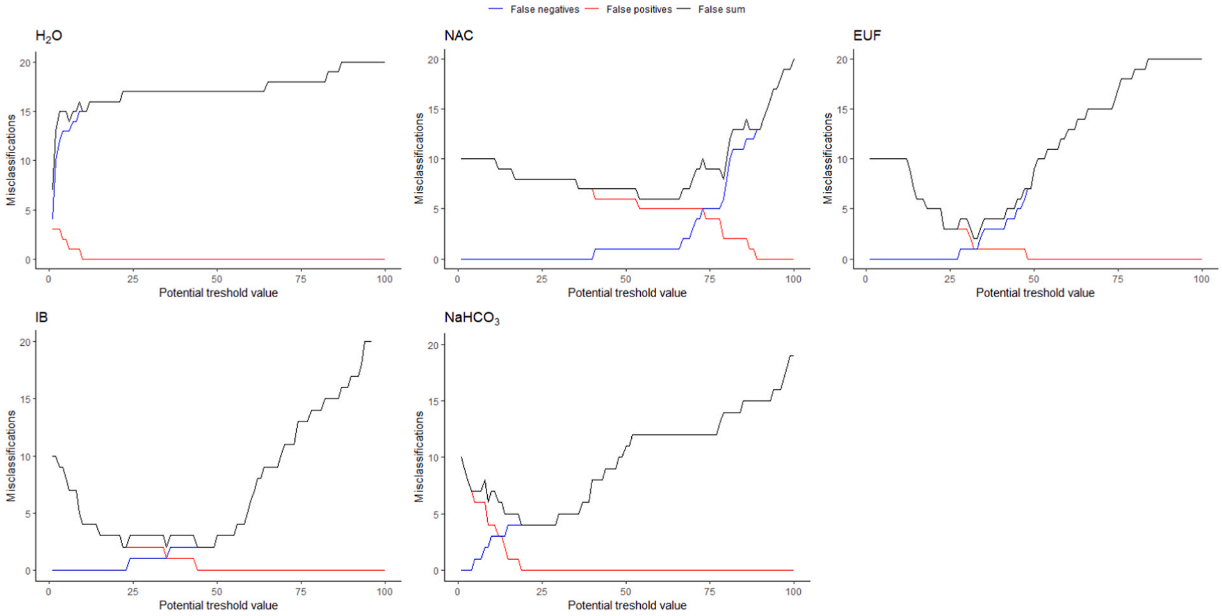

**Fig. 4.** Number of misclassifications of fertilizers as effective or ineffective for each extraction method as a function of the potential MPETV. The point where the false negatives line and the false positives line cross each other corresponds to the MPETV calculated, which was then rounded up to the closest multiple of 5.

**Table 2**
Potential MPETV for the extraction methods and associated number of true and false positive and negative classifications.

| Method | Threshold range | Threshold range width (extractability points, %) | MPETV suggested (% of $P_t$) | True positives | False positives | True negatives | False negatives | Total number of misclassifications |
|---|---|---|---|---|---|---|---|---|
| **$H_2O$** | 0–1 | 1 | 1 | 17 | MO14, ABP, CRA | 7 | MO10, KBT, MB1, EPH | 7 |
| **NAC** | 54–66 | 12 | 60 | 20 | CRA, VVB, NNP, RAN, PRV | 5 | MO10 | 6 |
| **EUF** | 23–27 | 4 | 25 | 21 | BAG, RAN, CRA | 7 | - | 3 |
| **IB** | 44–49 | 5 | 45 | 19 | - | 10 | KBT, MO10 | 2 |
| **$NaHCO_3$** | 19–29 | 10 | 25 | 17 | - | 10 | KBT, MO10, MB1, EPH | 4 |

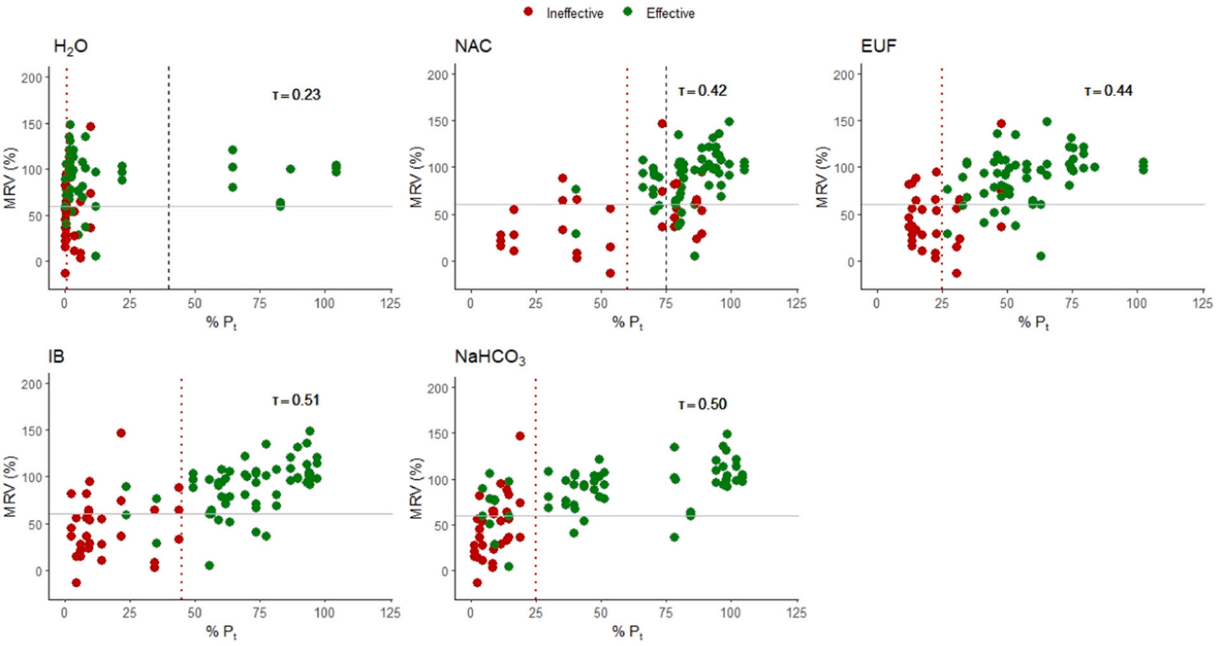

**Fig. 5.** Correlation analysis for each extraction method. The black dashed line corresponds to the current FPR MPETVs for inorganic fertilizers to be labelled "mineral". The red dotted line corresponds to the optimized threshold for each method. The horizontal grey line represents 60 % MRV, which was used for the fertilizer classification as effective or ineffective. Kendall's τ coefficient assesses the goodness of fit for the correlations, with p values $\leq$ 0.05 in for all cases.

and PLA (poultry litter ash) are an organic and inorganic fertilizer respectively, but in both the main P species is hydroxyapatite). Therefore, it makes sense to enforce a general MPETV for fertilizers regardless of their PFC-based fertilizer class. MPETVs should be low enough not to hinder the commercialization of P effective fertilizers, but high enough to ensure a fertilization effect in soils with low P content. Currently, there are no compulsory MPETVs for P fertilizers in the FPR (European Parliament, 2019). Only inorganic fertilizers aiming at being classified as *mineral* fertilizers require either at least 40 % of $P_t$ extractable in $H_2O$ or 75 % $P_t$ extractable in NAC, but inorganic fertilizers that do not reach these MPETV can still be marketed as inorganic CE fertilizer. However, a MPETV as a quality parameter for all P fertilizers would be beneficial. A MPETV related to plant availability ensures farmers that the products have a positive fertilization effect and encourages producers to develop better products. Authorities benefit from MPETV because it helps to optimize the P resource. Omitting MPETV jeopardizes P circular economy by promoting the use of products with less plant available P species, which would result in a large proportion accumulating in the soil or getting lost through erosion. MPETV are often missing in studies on fertilizer P extractability and corresponding fertilization efficiencies, limiting the practical applicability of their findings.

## 4.2. Selecting an extraction method and respective threshold

### 4.2.1. Performance evaluation of the extraction methods

The correlation analysis results indicate that for MRV, DGT was the extraction method with the highest τ (Fig. 3). This is in agreement with results in previous studies (Duboc et al., 2017). However, the DGT results are soil-specific (see 3.2.6) and the measurement was only performed with the soil used in the pot experiment at Tulln. Besides, no threshold could be proposed for DGT due to this substrate dependency. A suitable range of standard substrates representative of the typical soils found in the EU would have to be adopted for DGT to be a feasible compliance testing method.

The compliance methods currently in use, $H_2O$ and NAC, offer contrasting results (Fig. 3). $H_2O$ underestimated the P availability for plants of many of the fertilizers, and this resulted in the lowest τ of the methods tested. This strong underestimation of P availability was already identified in previous studies (Duboc et al., 2022, 2017; Meyer et al., 2018). A sharp MPETV of 1 % extractability was found to give 3 false positives and 4 false negatives (Table 2). There is no threshold range width for $H_2O$, and that implies that small variations in the extraction procedure can easily result in misclassifications. These are clear arguments against using $H_2O$ for compliance testing of recycled P fertilizers.

Conversely, NAC performed moderately well compared to the alternative extraction methods proposed, since its τ is only 0.14 points lower than the most accurate method (DGT, see Fig. 3). The extraction results are left-skewed and a large residual variance is apparent among the most NAC-extractable products. Part of that variance was caused by five false positive samples, (PRV, RAN, NNP, VVB and CRA), i.e. recycled fertilizers that were relatively highly NAC-extractable but deemed ineffective for the market due to poor MRV (Fig. 5). Four out of these five false positives had iron phosphate as their main P species, and all were derived from sewage sludge (NAC extractability in fertilizers with iron phosphate as the main species is discussed in 4.3). There was only one false negative (MO10). This MPETV has a range width of 12 percent points, so minor variations in the extraction results would mostly not result in misclassifications. Duboc et al., (2022) concluded that NAC generally overestimates P availability, but the effect was more pronounced than in the present study, possibly because of the shorter plant growth in that study, together with a larger proportion of products in an earlier developmental stage tested, which implies that the efficiency of those products could had been improved in late development stages. Other authors found that NAC is not a good predictor of the fertilization efficiency of sewage sludge-derived fertilizers (Delin, 2016; Ylivainio et al., 2021). However, Kratz et al., (2010) recommend NAC as compliance testing method not only for its good correlation results with P uptake, but also on the ground of practical reasons.

IB was the extraction method with the second highest τ (Fig. 3), matching results by Duboc et al. (2022), (2017). Besides, a MPETV of 45 % P extractability for this method results in only two false negatives (KBT, MO10) (Table 2), the smallest number of misclassifications of all the tested methods (excluding DGT, where no MPETV could be calculated for the reasons stated in 3.2.6). The IB method displays a medium threshold range width (5 percent points).

$NaHCO_3$ has the third highest τ (Fig. 3). Good correlation results for this method have been reported previously by other authors (Duboc et al., 2022). Its proposed MPETV of 25 % $P_t$ extractability results in four false negatives (KBT, MB1, OG1, MO10) (Table 2), two of them being meat and bone meal products (OG1 and MB1), and three (MB1, OG1 and MO10) having hydroxyapatite/tricalcium phosphate as the main P species. $NaHCO_3$ is an alkaline extraction (pH 8.5) that is not able to dissolve basic calcium phosphates. The threshold range width was of 10 percent points, the second highest after NACs.

EUF had a similar τ as NAC. A 25 % P extractability MPETV resulted in three false positives (CRA, BAG, RAN) and no false negatives (Table 2), and the threshold range width was 4 percent points. In another study with recycled P fertilizers, Hauck et al. (2018) found no relation between P uptake and the sum of P extracted with 10 successive 5 min EUF fractions with mild (1–5) and harsh (6–10) extraction conditions. However a major difference between that and the present study is, that the authors extracted 100 mg fertilizer using EUF, while Hauck et al. (2018) extracted 500 mg. This higher amount may exceed the water solubility especially of highly soluble fertilizers. The 100 mg we utilized were chosen after preliminary experiments on the EUF system that were performed to ensure that solubility is not limiting the EUF-P-extractability in this study (data not shown).

#### 4.2.2. *The importance of misclassifications when selecting MPETVs for P compliance testing*

Both false positives and false negatives hinder the optimal use of fertilizer-P resources. False positives imply that a fertilizing product will not function as well as predicted by its extractability in the lab. It is likely not going to solubilize and will add to the insoluble soil P pool. To obtain the potential yield, higher P doses would need to be applied. Beyond the inefficient use of the P resource, building up a pool of insoluble P in the soil can have negative environmental implications: In case of soil erosion and after subsequent sedimentation in aqueous systems, the particles are likely to experience very different environmental conditions (e.g. low redox, high salinity, etc.) which may induce the release of phosphate into solution and contributing to eutrophication of water bodies.

False negatives primarily have market-related implications at the disadvantage of the fertilizer producers, who are not able to sell their agronomically efficient product if the MPETV becomes a barrier to market entry. In that case the resource may be used inefficiently by farmers (resulting in over-fertilization) or may undergo additional and unnecessary processing to meet the extractability standards.

Some specific fertilizers (CRA, OG1, KBT and MO10) were consistently classified incorrectly when the proposed MPETVs were applied (Table 2). This was partially a result of the non-homogeneous efficiency of these fertilizers across the experiments, which complicated their classification into the effective and ineffective categories (see 2.5.4).

#### 4.2.3. *Practical considerations for selecting a compliance testing method and final recommendation*

Although the most important requirement for a compliance testing method is its accuracy, the method should also be feasible for routine analyses. Practical aspects like low analysis cost, high sample throughput, low technical requirement and high reproducibility were taken into account according to the laboratory experience of the authors.

**Simplicity.** Simple methods are more appropriate for compliance testing, because they often require less human and technical inputs. $H_2O$, NAC and $NaHCO_3$ extractions follow roughly a similar, simple protocol, differing mostly in the reactants used, and thus comply with this simplicity requirement. However, EUF requires a specific apparatus, which is nevertheless easy to operate. IB and DGT require a higher level of operator expertise.

**Sample throughput.** Fast methods are ideal for compliance testing. Multiple $H_2O$, NAC and $NaHCO_3$ extractions can be conducted per day. The EUF apparatus is able to perform one extraction in 40 minutes, and several devices are required to increase sample throughput, although many elements can be measured simultaneously in one extraction. Several samples can be analysed at once with IB and DGT, but each experiment lasts seven and six days, respectively.

**Recognition.** A compliance testing method is established more easily if the extraction protocol is already widely known. $H_2O$ and NAC extraction methods have been implemented for decades both at national and EU levels. $NaHCO_3$ is similar to an Olsen extraction used to assess the P content of soils. EUF is used to evaluate the availability of the main plant nutrients in soils in Germany, Austria, Poland, Hungary, Croatia and Moldova, but it is almost unknown for P fertilizer compliance testing. IB and DGT are more novel methods that are currently mostly used in research.

**Cost.** Compliance testing methods should be affordable, which depends on the consumables and equipment needed and on the personnel cost. $H_2O$, NAC and $NaHCO_3$ are fast and simple methods. Therefore, their personnel and consumable costs are going to be low. EUF is a fast method but requires an initial investment for the EUF device. When processing many samples and analysing other nutrients simultaneously, low costs per sample can be expected. DGT costs increase due to the time required for the extraction which implies higher personnel costs. For IB, operator time for setting up and terminating the experiment is needed but samples can otherwise essentially be left unsupervised during the actual extraction.

### 4.3. *The case of iron phosphate fertilizers*

In this study, NAC was found to be the most suitable compliance testing method for recycled P fertilizers. However, NAC overestimates the P availability of iron phosphates due to the stable citrate-Fe complexes, while Fe-$PO_4$ bonds impair P solubility in fertilizers under real conditions. Previous studies have already reported low P fertilization efficiencies with Fe-rich sewage sludge-derived materials (Øgaard and Brod, 2016; Römer and Samie, 2002; Saracanlao et al., 2023; Ylivainio et al., 2021). In agreement with our results, Steckenmesser et al., (2017), reports that NAC can only predict P availability of calcium phosphate-based fertilizers. Given that the testing conditions in this study are limited to acidic and neutral soils, more research on the efficiency of iron phosphate fertilizers under different soil conditions is recommended, particularly reductive conditions or calcareous soils.

### 4.4. *Representativity of current results*

The current study is limited to relating the extractability of the recycled P fertilizers to their agronomic efficiency as evaluated in pot experiments. It should be noted again here that the soils used in the pot trials covered a limited range of soil conditions and therefore more testing with more problematic soils in terms of P management should be considered (e.g. tropical weathered soils and calcareous soils). Nevertheless, we also investigated the fertilization efficiency of some of these recycled fertilizers under field conditions in four different locations during two crop cycles (Frick et al., in preparation). One ammonium magnesium phosphate product (CGO), the phytic acid product (BA1), two dicalcium phosphate-type products (OPU and ADC) and three hydroxyapatite/tricalcium phosphate products (MB1, MO14 and PLA) were included in these field experiments. The reported trends in fertilization efficiencies in the pot and field experiments were similar. In the field, the ammonium magnesium phosphate and dicalcium phosphate-type fertilizers had high fertilization efficiencies. The phytate-based fertilizer BA1 had better results in the field experiment than in the pot trials, probably because the longer duration of the field experiments allowed the enzymatic hydrolysis of phytate for P to become plant available. Hydroxyapatite/tricalcium phosphate fertilizers had low fertilization efficiencies both in pot and field trials.

### 4.5. *Limitations and possible improvements of extraction methods in the future*

DGT was the method with the highest $\tau$ correlation coefficient. However, the P extractability of a fertilizer through DGT described here is mediated by the specific substrate used in the analysis. Hence, it is complicated to extrapolate this extractability to actual fertilization efficiency in different soils. A possible solution could be finding a suitable range of standard substrates representative of the typical soils found in the EU, and then conducting a similar study to confirm the correlation between DGT extracted P and fertilization efficiency. Although pre-assembled P-DGT devices are commercially available, the operational intensity and time required for this analysis would need a drastic reduction, for instance, through shorter incubation times. Contrary to that, other authors have found DGT conducted with longer incubation times to correlate better with actual plant P availability (Duboc et al., 2017; Vogel et al., 2017).

The $H_2O$ method has been used at a 1:100 (*w:v*) solid:liquid ratio, which is not well suited for fertilizers that do not dissolve at that ratio but would dissolve in the soil under the sink effect of soil particles (as exemplified in the IB method). A possible improvement would be to increase the liquid:solid ratio.

A modification of the current NAC method should be carefully considered, e.g. changing the molarity of citrate to avoid dissolving iron phosphates. However, previous studies have shown that variations in organic ligands resulted in poor predicting performance (Duboc et al., 2017; Kratz et al., 2019, and references therein), and therefore the prospects for major improvements seem small.

IB could be further improved by reducing manipulation time, but the room for improvement is small. The method is time-consuming due to core steps like the precipitation of ferrihydrite, its retrieval and subsequent dissolution in acid, and to the manipulation of the dialysis membranes. The pH buffer solution could be excluded from the method if it is proven that the ferrihydrite might act as a pH buffer itself.

The $NaHCO_3$ underestimated P solubility in acid to neutral soils. Its MPETV (25 % $P_t$) would prevent meat and bone meal products (OG1 and MB1) from entering the EU market. This could be sorted out by recommending a formic extraction for basic calcium phosphate products. Alternatively, the scope of use for $NaHCO_3$ could be limited to estimating fertilizers P availability in alkaline soils (Duboc et al., 2022).

The main disadvantage of the EUF is the high cost of its device. This cost would probably decrease if this method was more recognised internationally to estimate the nutrient content of fertilizers and soils. Moreover, the EUF device easily allows for a modification of the extraction parameters tested, e.g. changing the time, temperature or voltage of the extractions, to calibrate the method and get better correlation results. Possible P extractability limitations due to the high P concentrations in some fertilizers disrupting the electric field of the EUF device, or the EUF cell volume not harbouring enough water for the full P extraction need to be investigated to evaluate the feasibility of the current EUF apparatus design for fertilizer compliance testing. In preliminary tests with 50, 100 and 200 mg of fertilizer we found the EUF procedure used in this study to be free of such artefacts (data not shown).

Beside the extraction methods tested in this study, the anion/cation exchange membranes are worth considering, particularly because Nanzer et al., (2019) found good correspondence between the P extracted from products derived from sewage sludge ashes and the P uptake of a ryegrass pot experiment.

## 5. Conclusions

In this study, we correlate the P extractability of a large set of chemically diverse recycled P fertilizers, which are already on the market or at a high developmental stage, with their actual fertilization efficiency as tested in three pot experiments. Simplicity, throughput, recognition and cost are considered to recommend a P fertilizer compliance testing method. We complete this analysis by proposing a MPETV for each method, based on the fertilization efficiency of the products.

DGT was the most accurate method correlating to the fertilization efficiency, but it would require deep modifications to improve its practicability. Other alternative extraction methods did not display a high enough accuracy that justifies them overrunning the already well-established NAC method for compliance testing of P fertilizers. Given its low $\tau$ with the MRV, $H_2O$ does not correspond to real P solubility conditions. IB was the second most accurate method, but it is disfavoured by its impracticability. $NaHCO_3$ is a feasible method, but it underestimates the availability of basic calcium phosphate products. EUF is a promising method, but it requires a costly initial investment. We recommend maintaining the NAC method as the current most feasible extraction to implement in a routine laboratory, until further development of an alternative is available for estimating the extractability of iron phosphate more accurately. We propose a 60 % $P_t$ extractability threshold for inorganic, organo-mineral and organic fertilizers aiming at getting the CE marking, while keeping the optional 75 % $P_t$ NAC threshold for inorganic fertilizers aiming to obtain the *mineral* fertilizer label.

## Abbreviations

CMC: component material category. DGT: Diffusive gradients in thin films. EUF: Electro-ultrafiltration. FPR: fertilizer product regulation. IB: Iron bag (ferrihydrite-filled dialysis membrane). MPETV: minimum P extractability threshold value. MRV: mineral replacement value. NAC: neutral ammonium citrate. $NaHCO_3$: sodium bicarbonate extraction. PFC: Product function category. $P_t$: total phosphorus. TOC: total organic carbon.

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## 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

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.eti.2024.103913.

## Data Availability

Data will be made available on request.

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