Improving the prediction of fertilizer phosphorus availability to plants with simple, but non-standardized extraction techniques

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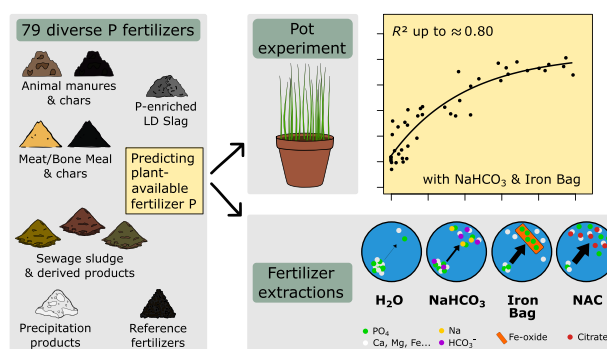[b] University of Natural Resources and Life Sciences, Institute of Agronomy, Konrad-Lorenz-Strasse 24, 3430 Tulln, Austria
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HIGHLIGHTS

- 79 P-fertilizers were characterized with 4 contrasting extraction methods.
- Plant P availability in neutral and alkaline soil was predicted with R^2 up to 0.80.
- $NaHCO_3$ and infinite sink extraction were the best predictors.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

In the framework of the circular economy, new P fertilizers produced from diverse secondary raw materials are being developed using various technologies. Standard extraction methods (neutral ammonium citrate (NAC) and H_2O) provide limited information about the agronomic efficiency of these often heterogenous new products. Here, we compared these extractions with two alternative methods: 0.5 mol L^{-1} $NaHCO_3$ and a sink extraction driven by phosphate adsorption onto ferrihydrite ("Iron Bag") on 79 recycled and mineral reference fertilizers. We compared their capacity to predict shoot biomass and P content of rye (*S. cereale* L.) grown in a greenhouse on three soils of contrasting pH with a subset of 42 fertilizers.
The median extracted P (% of total P) was H_2O (1%) < $NaHCO_3$ (25%) < Iron Bag (67%) < NAC (85%). The $NaHCO_3$ extraction stood out as a cost-effective and reliable method to predict plant shoot biomass and P content (R^2 ranging between 0.65 and 0.86 in the slightly acidic and alkaline soil). Notwithstanding, the other methods provide complementary information for a more detailed characterization of how P solubility may be impacted by e.g. soil pH, granulation, or time. The implications of this work are therefore significant for fertilizer production, regulation, and use.

1. Introduction

Phosphorus is an essential mineral nutrient for all life forms. Although the demand for P fertilizer is still mainly covered by the mining of non-renewable fossil reserves, interest in P recycling has grown considerably in the recent decades, triggered by the need to cope with the

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geopolitical supply risk and to secure long-term supply without depleting fossil reserves. In this context, the European Union (EU) lists phosphate rock as a critical raw material and initiated a circular economy action plan in 2015 (European Commission, 2019, 2015). This resulted in the revision of the EU fertilizer regulation (EU 2019/1009) (European Union, 2019), allowing secondary raw materials such as municipal sewage sludge, meat and bone meal and animal manures as renewable sources to produce EU fertilizing products that can be traded and used within the union market.

Recovered P fertilizers are very diverse, owing to the diversity of input materials and of recovery technologies. They can be chemically equivalent to standard mineral fertilizers (e.g. mono ammonium phosphate (MAP), dicalcium phosphate (DCP)), but many products have less standardized compositions, often exhibiting heterogenous mineral phases of varying solubility (Kratz et al., 2019). With many technologies still being at an early stage of development, reliable testing methods are essential to evaluate P availability from such heterogenous materials.

Despite the significant advances in the field of P recycling, prediction of nutrient availability from recycled P fertilizers remains challenging (Kratz et al., 2019). In the new EU fertilizing products regulation (EU 2019/1090), solubility of (organo)mineral P fertilizers should be measured with neutral ammonium citrate (NAC) and H_2O extractions. Although a routine-proofed, standard measure of P solubility for regulatory purposes is necessary, these extraction methods (and similar ones such as 2% formic acid or 2% citric acid) have been developed for relatively uniform phosphate rock-based fertilizers and are considered unreliable to measure P availability from very diverse fertilizers (Kratz et al., 2019). Alternative methods based on sink extraction of fertilizer in pH-adjusted solutions were shown to better predict P availability (Duboc et al., 2017; Nanzer et al., 2019), but they are less suitable for routine analysis. Moreover, in the regulation no method is prescribed for organic fertilizers, showing the lack of standardization for the characterization of some categories of novel recycled fertilizers.

Extraction of fertilized soil with $NaHCO_3$ or diffusive gradients in thinfilms (DGT) was also found to give excellent results, often better than fertilizer extractions (Christiansen et al., 2020; Duboc et al., 2017). However, the purpose of a fertilizer assay is not only to predict plant availability on a given soil, but to provide a standardized measure of the plant-available P fraction contained in the fertilizer, without the effect of a specific soil sample on fertilizer solubility. This approach is also time-consuming and costly compared to the extraction of fertilizer products directly.

Fertilizer extraction with $NaHCO_3$ has also been identified as a promising approach (Brod et al., 2015b; Christiansen et al., 2020). Meyer et al. (2018) concluded that the sum of resin- and $NaHCO_3$-extractable P (the first two steps of their sequential extraction procedure) gave the best estimate of the plant available P fraction in an alkaline soil. In all available studies a 0.5 mol L^{-1} $NaHCO_3$ solution was used but the fertilizer:solution ratio varied from 1:20 (Brod et al., 2015b) to 1:200 (Christiansen et al., 2020; Meyer et al., 2018) and 1:600 (Meyer et al., 2018). Considering the results of those studies, there remains room for improvement of the $NaHCO_3$ extraction, given that (1) in Christiansen et al. (2020) the struvite did not solubilize completely although struvite is known to have similar plant availability as water-soluble reference fertilizers (Kratz et al., 2019), and (2) in Meyer et al. (2018) the $NaHCO_3$ was part of a sequential extraction procedure. Therefore, a single-step $NaHCO_3$ extraction at a wide fertilizer:solution ratio might be a good predictor of fertilizer P availability (including struvite) while being more suitable for routine analysis (compared to a sequential extraction).

A further limitation of previous studies is, that to date most of them have been performed by comparing ca. 8 to 15 fertilizers. Increasing the number and the variety of the tested fertilizers would be required to better assess the suitability of different extractants across chemically diverse fertilizers. Besides, in Duboc et al. (2017) we found that a sink extraction with ferrihydrite (the "Iron Bag") gave superior results

compared to conventional extraction methods, but in that study only one soil was used (pH $CaCl_2$ = 6.2). Since fertilizer dissolution in soil is strongly affected by soil properties (primarily pH) it is necessary to test this method in different soil types.

Therefore, the objectives of this study were

(1) to assess whether the Iron Bag can predict fertilizer P availability to plants in a strongly acidic, a slightly acidic and an alkaline soil,
(2) to determine whether a modified 0.5 mol L^{-1} $NaHCO_3$ extraction (regarding fertilizer:solution ratio and time of extraction) is a good predictor of P availability while simplifying the extraction procedure (compared to the Iron Bag) for routine analysis, and
(3) to perform the analyses on a large set of contrasting recycled and conventional/reference fertilizers.

2. Materials and methods

2.1. Fertilizers

Seventy-nine P-rich biowastes and fertilizers (subsequently referred to as fertilizers) were selected to represent a broad range of potential P sources as well as P species. A summary of the most likely P species for each category is shown in Table 1. A complete list of the fertilizers with a description of origin, processing and total P content is given in Table S1.

We focused on products originating from sources that were either rich in P and/or accounting for a major P flow in society. Therefore, most products originated from animal manures (cattle manure (CatM), chicken manure (ChM)), the slaughter industry (meat and bone meal (MBM)), and municipal sewage sludge (MSS) or its ash (MSSA). Biogas slurry (BGSL) from food and agricultural wastes was also included.

Moreover, the selection encompassed not only the raw, unprocessed materials, but also products processed through various technologies which aim at hygenizing or decontaminating the product, at extracting or concentrating P, and/or at recovering energy from the raw material before its final use as a fertilizer. This includes various thermochemical treatments like pyrolysis, gasification, hydrothermal carbonization or smelting, with or without additives. Precipitation processes (Prec) are also represented (struvites, Ca-phosphates) because they are expected to play an important role in P recycling.

Several reference materials (Ref) were also included to provide a basis for comparison with conventional mineral fertilizers and to further increase the chemical diversity of the fertilizers in our study. They consisted of two rock phosphates, single and triple superphosphate, a thermophosphate, a Thomas phosphate (Thomas slag, a former fertilizer commercially available until the early 1990s), as well as pure monocalcium phosphate and di-calcium phosphate.

2.2. Sample preparation and total P analysis

Prior to all analyses and pot experiment, the fertilizers were dried (50 °C, 24 h, except Ref- and Prec-products) and milled to <200 μm in a vibratory ball mill using stainless steel grinding equipment. They were then stored in screw-cap vials at room temperature (inorganic products) or at 4 °C (organic products).

Total P (P_t) was measured for all fertilizers after digestion with *aqua regia* (100 mg sample with 4.5 mL 37% HCl + 1.5 mL 65% HNO_3). Although *aqua regia* does not always extract 100% of P in complex matrices, this method is considered suitable for a broad range of different fertilizers including organic and MSS-derived products (Duboc et al., 2017; Herzel et al., 2016). Digestions were performed in a Multiwave 3000 microwave system (Anton Paar GmbH, Graz, Austria) using Teflon liners and the following conditions: 1400 W (for 16 tubes), 10 min ramp time, 40 min hold time and 10 min cooling time. Temperature and pressure were regulated with threshold values of 210 °C and 40 bar,

Table 1

Phosphate species that are likely to be found in the different categories of fertilizers used in this study. In each category, the listing order follows the expected proportion (or likelihood) of each species, from high to low. If applicable, information within each category is separated in sub-categories highlighted in italic between the raw (untreated) material and the products that resulted from a particular treatment (e.g. pyrolysis) of that raw material.

Fertilizer category	Sub-category	P species	Reference
Biogas slurry (BGSL)	*Raw*	Dicalcium phosphate ($CaHPO_4$), struvite ($MgNH_4PO_4 \cdot 6H_2O$)	(Kratz et al., 2019)
	Pyrolysis	Hydroxy apatite ($Ca_5(PO_4)_3OH$)	
	Hydrothermal	No data	
Cattle manure (CatM) and chicken manure (ChM)	*Raw*	Phytic acid, amorphous Ca-Mg phosphate, $AlPO_4$, dicalcium phosphate, struvite, hydroxy apatite, octacalcium phosphate ($Ca_8H_2(PO_4)6 \cdot 5H_2O$)	(Huang et al., 2018; Kratz et al., 2019)
	Pyrolysis	Hydroxy apatite, $AlPO_4$, amorphous Ca phosphate	
	Hydrothermal	Hydroxy apatite, $AlPO_4$	
Meat/bone meal (MBM)	*Raw*	Octacalcium phosphate, biological apatite (with low degree of crystallinity), hydroxy apatite, chloro apatite ($Ca_5(PO_4)_3Cl$), fluoro apatite ($Ca_5(PO_4)_3F$), phytate	(Kratz et al., 2019; Zwetsloot et al., 2015)
	Pyrolysis	Biological apatite (with high degree of crystallinity), octacalcium phosphate, dicalcium phosphate	
	Hydrothermal	No data	
Municipal sewage sludge (MSS)	*Raw*	Octacalcium phosphate, hyrdroxy apatite, tricalcium phosphate ($Ca_{3x}(PO_4)_2$), dicalcium phosphate, variscite, strengite (($Al,Fe)PO_4 \cdot 2H_2O$), wavellite ($Al_3(PO_4)_2 \cdot 5H_2O$), vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), lipscombite ($Fe_3(PO_4)_2(OH)_2$), P adsorbed to (amorphous) Al/Fe-(hydr)oxides	(Kratz et al., 2019)
	Pyrolysis	Tricalcium phosphate/whitlockite ($Ca_{3x}(Mg,Fe^{2+})_x(PO_4)_2$),	
	Hydrothermal	No data	
MSS-AshDec-Mg		Chloro apatite ($Ca_5(PO_4)_3Cl$), stanfieldite ($Ca_4Mg_5(PO_4)_6$), farringtonite ($Mg_3(PO_4)_2$)	(Kratz et al., 2019)
MSS-AshDec-Na and -K/Na		$CaNaPO_4$, $Ca(Na,K)PO_4$, $Ca_{13}Mg_5Na_{18}(PO_4)_{18}$	(Kratz et al., 2019; Herzel et al., 2021)
MSS ash + steel slag (MSSA-Slag)	*Raw MSS ash*	Tricalcium phosphate/whitlockite. Dicalcium phosphate/brushite ($CaHPO_4$)	(Kratz et al., 2019; Rex et al., 2014)
	Processed (melting)	Calcium phosphate silicates ($Ca_5(PO_4)_2(SiO_4)_6$; $Ca_7(PO_4)_2(SiO_4)_2$; $Ca_{15}(PO_4)_2(SiO_4)_6$)	
Precipitation products (Prec)	Struvites	$MgNH_4PO_4 \cdot 6H_2O$	(Kratz et al., 2019)
	P-RoC	Poorly crystalline Ca-deficient (carbonate-) hydroxyapatite, mixed with struvite	
Reference fertilizers (Ref)	Ref-Di Calcium P	Dicalcium phosphate	(Pitawala et al., 2003; Sinaj et al., 1994)
	Ref-Mono Calcium P, Ref-SSP, Ref-TSP	Monocalcium phosphate ($Ca(H_2PO4)_2$)	
	Ref-Rock P-1	Apatite	
	Ref-Rock P-2	Chlorofluoroapatite	
	Ref-Thermo P	Calcium magnesium phosphate silicate	
	Ref-Thomas P	Calcium silicate phosphate (Nagelschmidite ($2(Ca_2SiO_4)Ca_3(PO_4)_2$))	

respectively, above which heating was suspended. Phosphorus in the digested samples was measured colorimetrically with a molybdate blue assay.

2.3. Fertilizer P solubility characterization

H_2O extraction was performed according to EN 15958:2011. Most of the samples were extracted as follows: 100 mg fertilizer in 10 mL H_2O shaken on overhead shaker at 20 rpm for 30 min, filtered through Ahlstrom-Munktell, grade 14/N filter papers. An aliquote was acidified to 0.25 mol L^{-1} H_2SO_4 and analyzed colorimetrically with a molybdate blue protocol. A smaller subset of fertilizers was extracted as follows: 150 mg fertilizer in 15 mL H_2O for 30 min, filtered with a 0.45 μm syringe filter. An aliquote was acidified to 2% HNO_3 and measured on ICP-OES. This is because these fertilizers were characterized later after we changed our laboratory workflow, and because ICP-OES simplifies the requirements for sample dilution compared to the molybdate blue method. It concerns the following fertilizers: MSS-8, MSS-8-HC1, MSS-8-HC2, MSSA-1-Slag-1b, MSSA-1-Slag-2b, MSSA-1-Slag-3b, P-Roc-1, P-Roc-2, Ref-Rock P-2, Ref-Struvite-2, Ref-ThomasP, Ref-Mono Calcium P, Ref-TSP.

Neutral ammonium citrate (NAC) extraction was performed according to EN 15957:2011 with 100 mg fertilizer and 10 mL NAC solution (4.8% w/v ammonium + 18.5% w/v citrate solution at pH 7) in a shaking hot water bath at 65 °C for 1 h. After the extraction, the samples were cooled in a water bath. The sample was then diluted with 40 mL H_2O (final volume: 50 mL) and filtered with 0.45 μm syringe filters. An aliquote of the filtrate was diluted (dilution factor = 5) with HNO_3 to reach a HNO_3 concentration of 2% w:w. The samples were measured on ICP-OES (see details further below).

The Iron Bag (IB) extraction is a measure of the total water-soluble P, using dialysis membrane tubes filled with a ferrihydrite slurry that act as an infinite sink. The method was developed for soil extraction by Freese et al. (1995) and adapted for fertilizer analysis by Duboc et al.

(2017). In brief, 30 mg fertilizer (20 mg for very soluble and concentrated products like Ref-TSP, Ref-Mono Calcium P and Ref-Di Calcium P) were extracted in 250 mL sample vials filled with 150 mL of a 30 mmol L^{-1} 3-(N-morpholino)propanesulfonic acid (MOPS) buffer adjusted to pH 7. A ferrihydrite-filled membrane was added to each vial. Afterwards, the vials were placed on an overhead shaker at 5 rpm. The membrane was sampled and replaced once or twice during the experiment: after 7-10 days (optional) and/or 21 days. The final sampling was done after 42 days. After each sampling, the ferrihydrite was dissolved with 1 mL of 96-98% H_2SO_4 and the solution was diluted to 0.25 mol L^{-1} H_2SO_4. For more details, please refer to our previous publication (Duboc et al., 2017).

The $NaHCO_3$ extraction was performed with 30 mg fertilizer in 30 mL 0.5 mol L^{-1} $NaHCO_3$ (fertilizer to solution ratio 1:1000; no pH adjustment) for 4 h on an overhead shaker at 15 rpm. The extracts were filtered through 0.45 μm syringe filters. 3 mL H_2O and 1 mL 65% HNO_3 were added to a 16-mL sample aliquot, to remove HCO_3 and acidify the sample to 2% HNO_3. Samples were analyzed by ICP-OES. If necessary, samples were diluted with acidified extraction solution prepared in the same way as the samples.

For all analyses on ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA) we measured at 213.617 nm. Matrix-matched calibration standards were used, as well as an internal standard (Y) to normalize the signal. Measurement stability was monitored with regular measurements of quality control standard solutions approximately after every 15-20 samples. Colorimetric measurements (H_2O and IB) were performed with a molybdate blue assay as described in Duboc et al. (2017).

2.4. Pot experiment

A pot experiment with rye (*Secale cereale* L.) was conducted in the greenhouse with three soils of contrasting pH. Soil characteristics and the respective analysis methods are shown in Table 2. There was a

Table 2
Characteristics of the three soils used in the pot experiment.

Soil	Soil abbreviation	pH[a]	CAL-P[b]	Olsen-P[c]	Organic C[d]	Carbonates[d]	Sand	Silt	Clay
			mg P kg^{-1}	mg P kg^{-1}	g C 100 g^{-1}		g 100 g^{-1}		
Strongly acidic	Ac1	5.5	11.4	14	2.37	0.45	53.2	36.8	10.1
Slightly acidic	Ac2	6.2	13.4	10.7	1.32	0.17	14.4	56.2	29.4
Alkaline	Al	7.4	9.5	7.4	4.04	37.6	5.3	43.9	50.8

[a] measured in 10 mmol L^{-1} CaCl$_2$ at 2.5:1 v:w solution:soil ratio.
[b] Calcium-acetate-lactate (ÖNORM L1087, 2006).
[c] Olsen et al. (1954).
[d] Organic and inorganic C measured in a soliTOC (Elementar Analysensysteme GmbH, Langenselbold, Germany) by dry combustion at 600 and 900 °C, respectively.

strongly acidic soil (pH 5.5, referred to as "Ac1"), a slightly acidic soil (pH 6.2, referred to as "Ac2"), and a carbonate-rich alkaline soil (pH 7.4, abbreviated "Al"). The Ac2 soil used in this study was the same as in Duboc et al. (2017). The soils had P-CAL values between 9.5 and 13.4 mg P kg^{-1} and P-Olsen values between 7.4 and 14 mg P kg^{-1}, which both correspond to low plant-available P: for P-CAL the optimum is between 47 and 111 mg P kg^{-1} (BMLFUW, 2017), while for P-Olsen the mean critical value (at 95% of maximum yield) was 19 mg P kg^{-1} in European soils (Nawara et al., 2017). Because of their heavy texture, the Ac2 and Al soils were mixed with quartz sand (2 / 3 soil + 1 / 3 sand), to facilitate drainage during irrigation.

Given that the main aim of the study was to compare extraction methods for prediction of P availability, we selected a large number of fertilizers but set up only one pot (without replication) per fertilizer-soil combination. We selected 42 fertilizers from the 79 products that were characterized by the extraction procedures (see Fig. 1 and Table S1). For each soil, 3 unfertilized control pots were set up. This resulted in 45 pots per soil, and 135 pots in total. The 42 fertilizers were selected according to the following criteria: (1) all fertilizer categories had to be represented, (2) products of contrasting solubility were selected where available within each category, and (3) the product had to be available in sufficient amount. Criteria 3 led to the exclusion of some products from which not enough material was available.

One kg soil was added to each pot and the finely ground fertilizer was thoroughly mixed at a rate of 80 mg P$_t$ kg^{-1} soil. Water was added to reach 65% WHC. Before seeding, the moist pots were left to rest in the greenhouse for one week, covered by a plastic sheet to avoid drying. Seeds were pre-germinated on tissue paper and 21 seeds were laid on the soil surface, covered with dry soil and moistened. After emergence, the pots were thinned to 17 seedlings. Phosphorus contained in the 17 seeds amounted to 1.32 mg P (17 seeds weighed 0.424 g and their P concentration was 3.12 mg P g^{-1}).

The controlled growth conditions in the greenhouse included day/night temperatures of 25/15 °C and day/night cycle of 16/8 h with artificial lighting to complement daylight. Photosynthetically active radiation (PAR) was on average ~600 μmol m^{-2} s^{-1}. All nutrients except P were supplied by weekly donations of 50 mL of a nutrient solution, at 7, 14, 21, 28 and 35 days after planting (DAP): The solution was modified from Middleton and Toxopeus (1973) and contained 4 g L^{-1} NH$_4$NO$_3$, 1.47 g L^{-1} K$_2$SO$_4$ anhydr., 444 mg L^{-1} MgSO$_4$ 7H$_2$O, 360 mg L^{-1} CaCO$_3$, anhydr., 7.2 mL L^{-1} 1 M HCl (to solubilize CaCO$_3$), 600 μg L^{-1} H$_3$BO$_3$, 158 μg L^{-1} CuCl$_2$, 5.5 mg L^{-1} MnCl$_2$ 4H$_2$O, 80 μg L^{-1} (NH$_4$)Mo$_7$O$_{24}$ 4H$_2$O, 300 μg L^{-1} ZnCl$_2$ and 2.5 mg L^{-1} Fe EDDHA. This resulted in a total addition of 350 mg N, 165 mg K, 82 mg S, 11 mg Mg, 36 mg Ca, 26 μg B, 19 μg Cu, 382 μg Mn, 12 μg Mo, 36 μg Zn and 36 μg Fe over the course of the experiment.

Plant shoots were harvested at 42 DAP by cutting with scissors at the level of the pot's edge (ca. 1.5 cm above soil surface level), and dried for 48 h at 65 °C. Shoot dry matter was weighed, and then milled in a Retsch GM 200 at 8500 RPM for 30 s. The ground sample was digested in a microwave (150 mg sample with 3 mL 65% HNO$_3$ + 0.76 mL 30% H$_2$O$_2$ in a MARS 6 microwave system (CEM corporation, Matthews, USA)). After the digestion, 40 mL H$_2$O was added so that the final HNO$_3$ concentration was 6% (w:w). The P concentration was measured by

ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA) at 213.617 nm, and the spectra were normalized with Y as internal standard. Shoot N concentration was analyzed by dry combustion in an elemental analyzer.

2.5. Data evaluation

Data evaluation and figures were done with the software 'R', version 3.6.1 (R Core Team, 2019).

Results of the fertilizer solubility tests (extractions) are given as % of total P measured in the *aqua regia* digests. They are expressed as mean + u (k = 1), where u is the combined uncertainty of the measurement of total P and of extractable P.

Linear regression models for plant P uptake and non-linear regression models for plant biomass were fitted with the functions lm() from the "stats" package (R Core Team, 2019) and nlsLM() from the "minpack.lm" package (Elzhov et al., 2016), respectively. The controls receiving no P were considered as treatments with a fertilizer having 0% soluble P.

For plant biomass, a Mitscherlich model as in Eq. (1) was fitted:

$$y = y_0 + a \left(1 - e^{-bx} \right) \tag{1}$$

where y is the fitted plant biomass, x is the P extracted by the respective extraction method in % of total P, y_0 is the fitted (minimum) yield at zero P application, and $y_0 + a$ is the predicted maximum yield (a is a fitted parameter, it is the difference between maximum yield and y_0).

For all regressions, goodness of fit was given as in Eq. (2):

$$R^2 = 1 - \frac{RSS}{SS} \tag{2}$$

where RSS is the residual sum of squares of the fitted model and SS is the total sum of squares.

In addition, root mean squared deviation (RMSD) was calculated as in Eq. (3):

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n} (y - y)2}{n}} \tag{3}$$

where y and ŷ are the observed and fitted values, respectively.

3. Results and discussion

3.1. Fertilizer P solubility (extractions)

Total P concentrations of the fertilizers ranged from 8.23 to 244 mg P g^{-1} (Table S1 of the Supplementary material). The amount of P extracted by the four methods (median value in % of total P) increased in the order H$_2$O (1%) < NaHCO$_3$ (25%) < IB (67%) < NAC (85%) (Fig. 1). These highly contrasting results are due to their different mechanisms of extraction (Table 3).
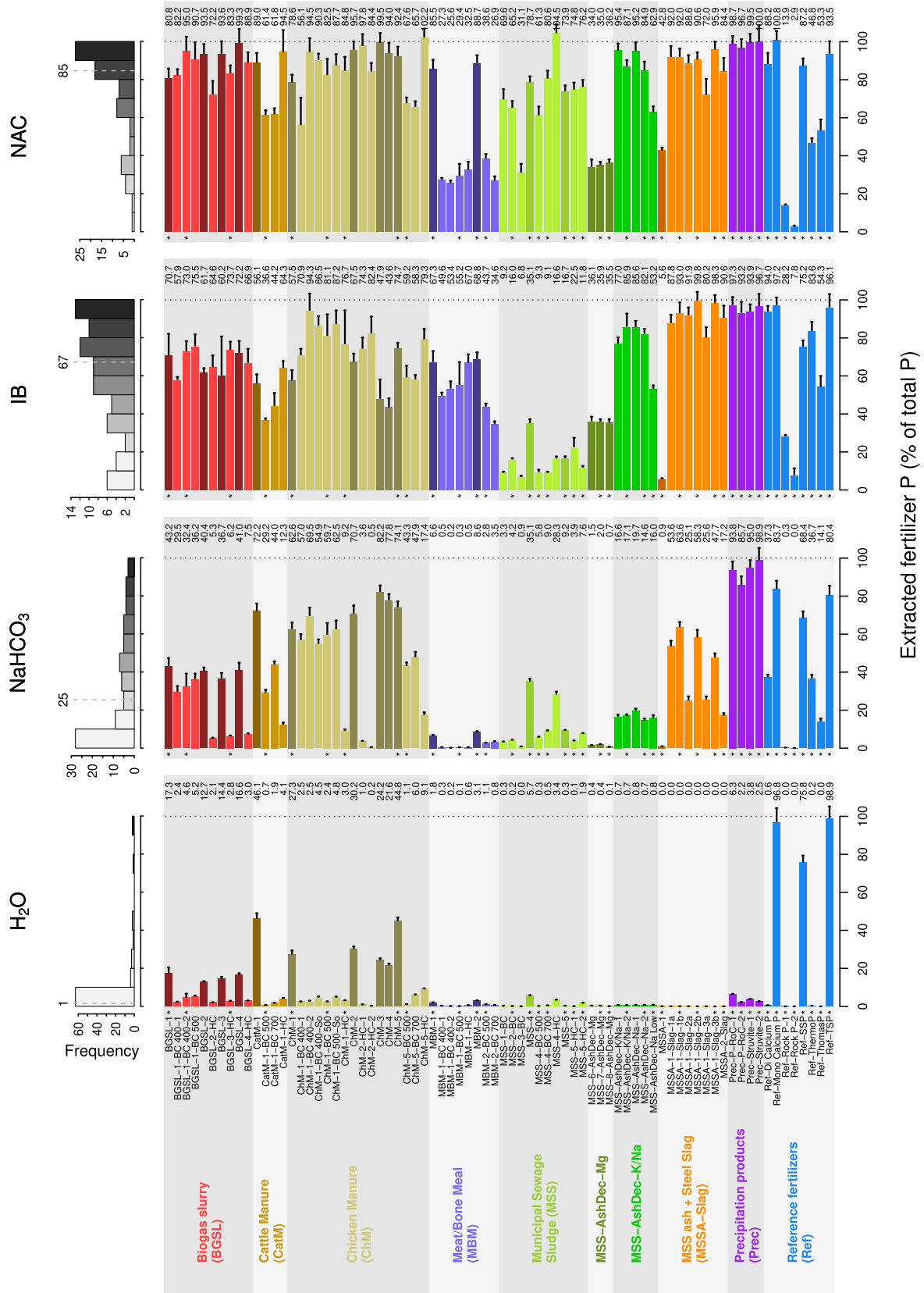
Fig. 1. Amount of P extracted by the four extraction methods and its distribution. Data shown in the barplot as mean + u (k = 1). Bars marked with an asterisk denote fertilizers that were used in the pot experiment. In the histograms (frequency), the dotted line and the value above it is the median of total P extracted. The fertilizer categories are highlighted with their own color, visible on the web version of this article.

Table 3

Overview of the main extraction mechanisms and of the most relevant extraction conditions in the four fertilizer extractions methods used in this study.

Extraction method	Main mechanisms of extraction/relevant extraction conditions
H_2O	Near-equilibrium dissolution in water. High fertilizer:solution ratio (1:100).
Neutral ammonium citrate (NAC)	Strong cation complexation (mainly Ca and Fe) inducing P co-dissolution. pH 7.
Iron Bag	Strong P adsorption (infinite sink) on ferrihydrite, which enhances fertilizer P dissolution through concentration gradient. pH 7 buffered extraction solution, i.e. in the optimal range for agricultural soil. This reproduces the buffering effect of soil around fertilizer particles and prevents fast dissolution of apatite-P (Duboc et al., 2017).
$NaHCO_3$	Solution buffered by HCO_3 (pH 8.3; no adjustment to 8.5 as in Olsen (Olsen et al., 1954) method). High pH (OH^-) and HCO_3 ions enhance desorption of inorganic P from Al- and Fe- oxides and of weakly adsorbed organic P. High pH hinders dissolution of apatites. High ionic strength reduces ion activity which enhances dissolution. Effect of $CaCO_3$ complexation on reduction of Ca^{2+} and Mg^{2+} activity likely less relevant in comparison to Olsen solution adjusted to pH 8.5 (Olsen et al., 1954). Low fertilizer:solution ratio (1:1000) enhances dissolution compared to previous studies with fertilizers.

Apart from the conventional superphosphates (Ref-SSP, Ref-TSP) and pure monocalcium phosphate (Ref-Mono Calcium P), most of the tested fertilizers were not soluble in H_2O (median = 1% of total P). By contrast, IB extracted a median value of 67% of total P. This shows that the disruption of equilibrium by the sink dramatically increases fertilizer dissolution, without further addition of ligand or other chemicals to enhance solubilization. In a soil, this sink can be provided by adsorption sites on mineral particles (mainly Fe and Al-oxides), as well as by plant roots. The most extreme contrasts between H_2O and IB were found for the precipitation products, the MSSA-Slag products, the MSS-AshDec-K/Na and several biochars (Fig. 1).

The precipitation products (struvites and P-RoC) were dissolved to nearly 100% in the $NaHCO_3$ extract. The result for the struvites (≥95% extracted P in $NaHCO_3$) is in contrast to Christiansen et al. (2020) (24.7% of total P extracted). Given that the low P extraction resulted in struvite being an outlier in the regression of that previous study, and that struvite fertilizers are relatively pure (single species fertilizer), it is worth taking it as an example and examine the reason for the better extractability in our study using speciation modeling. According to a chemical speciation calculation using Visual MINTEQ 3.1 (Tables S2 and S3 of the Supplementary material), 16.4% and 100% of struvite P dissolve in this extractant at fertilizer:solution ratios of 1:200 and 1:1000, if $MgCO_3$ is not allowed to precipitate. This confirms a strong increase of struvite solubility with the decreased fertilizer:solution ratio in our study. However, in a scenario where $MgCO_3$ can precipitate, struvite solubilizes completely also in the 1:200 extraction (Table S3 of the Supplementary material). To verify whether this scenario is relevant but requires a longer extraction period to reach equilibrium, we reproduced both extractions (i.e. at 1:200 and 1:1000) for 0.5, 4, and 21 h. The results showed that there was no further increase of P solubility beyond ~25% in the 1:200 extraction, whereas in the 1:1000 extraction extracted P was already >90% of total P after 0.5 h (Table S4). This suggests that (1) the increased P extraction in our method is mainly due to the modified fertilizer:solution ratio rather than the extraction time, since both extractions reached (near-)equilibrium already after 0.5 h and (2) that precipitation of $MgCO_3$ does not occur, or is very slow.

At the other end of the spectrum, the MBM products were insoluble in $NaHCO_3$. This can be explained by the alkalinity of the HCO_3 solution (pH 8.3), which prevents the dissolution of the different types of Ca-phosphates (octacalcium phosphate, hydroxyapatite, chlorfluorapatite), which are the main P compounds in those products (Brod et al., 2015a; Zwetsloot et al., 2015) (Table 1). In previous studies

using $NaHCO_3$ as a fertilizer extractant, only Brod et al. (2015b) adjusted the pH to 8.5, as is usually done in the Olsen-P extraction of soils. This pH adjustment could enhance dissolution of Ca-phosphates by slightly increasing the CO_3^{2-}:HCO_3 molar ratio of the solution, which reduces Ca^{2+} activity through $CaCO_3$ complexation (Olsen et al., 1954).

The MSS–AshDec—K/Na group, the MSSA—Slag group, Ref-Di Calcium P and Ref–ThermoP and the Prec- products exhibited a low solubility in H_2O and a high solubility in Iron Bag. Contrastingly, in $NaHCO_3$ only the Prec- products were highly soluble. The other ones only exhibited a low to medium solubility.

Phosphorus solubility from biochars and hydrochars was often lower than from the respective raw material with the H_2O and $NaHCO_3$ extraction methods. This may be explained by the transformation of P forms to less soluble apatites during pyrolysis (Huang et al., 2018; Robinson et al., 2018), and possibly also by hydrophobicity of the chars. This effect was not seen with IB, which suggests that most of these newly formed compounds can be easily dissolved and that hydrophobicity is only an initial effect. Consequently, these P species should also become plant-available within a relatively short time.

Significant increases in P solubility from MSS or MSSA is achieved by treatments with AshDec-Na or -Na/K (a thermo-chemical treatment at 900-1000 °C (Herzel et al., 2016; Herzel et al., 2021)) and fusion with steel slag. This is the case with all extractions except with H_2O.

3.2. Fertilizer extractions as predictors for shoot dry matter and P content

The results of the pot experiment (shoot biomass and P content) are presented in Figs. S1 and S2 (Supplementary material). This data is for reference only and cannot be used to compare fertilizers among each other because only one pot was grown with each fertilizer (i.e., no replication; see aims of study and materials and methods for justification). The N/P mass ratio is shown in Fig. S3, to indicate that plant growth was limited by P and not by N. For optimal growth, an N/P mass ratio of 8 to 10 is required (Kirkby, 2012; Knecht and Göransson, 2004). In this experiment, the median was around 20 in the three soils and the overall minimum was 12.8 (Fig. S3), which strongly suggests that plants were adequately supplied with N.

The regressions of plant shoot biomass vs. extractable fertilizer P (Fig. 2) and P content vs. extractable fertilizer P (Fig. 3) revealed that the best predicting capacity was obtained by $NaHCO_3$ in the Al soil, as well as - to a lesser degree - in the Ac2 soil. Furthermore, the difference of slope of the fertilizer response between the Ac2 and Al soil shows that more P is required in the Al soil to obtain the same effect as in Ac2 (mind the different y-axis scaling in Fig. 3). This is likely due to P precipitation as Ca-phosphate in addition to the relative unsolubility of many fertilizers in the Al soil.

The excellent fits of $NaHCO_3$ in the Al soil particularly stand out with $R^2 = 0.86$ for shoot biomass and $R^2 = 0.74$ for shoot P content (Figs. 2 and 3, respectively). This confirms the suitability of an $NaHCO_3$ extraction which was already identified in previous studies (Brod et al., 2015b; Christiansen et al., 2020; Meyer et al., 2018). Given that pH is a major factor for fertilizer P dissolution, this can be at least partly explained by the similarity of pH between the extraction solution and the experimental soil. In addition, the modifications adopted here (wide fertilizer:solution ratio of 1:1000, and possibly the longer extraction of 4 h) seem to critically improve the quality of the method in terms of prediction of plant P availability compared to previous studies. As discussed above, in Christiansen et al. (2020) struvite did not solubilize completely and the authors removed it from the regression analysis. Indeed, to be in line with its high plant availability (Kratz et al., 2019) in particular when applied to soil as a powder (Degryse et al., 2017), the proportion of P extracted from struvite by a given extraction method should be close to 100%.

The promising results obtained previously with the IB extraction (Duboc et al., 2017) were confirmed here for the Ac2 soil, which is the same soil as in the previous study, albeit in a 1/3 sand +2/3 soil mixture.
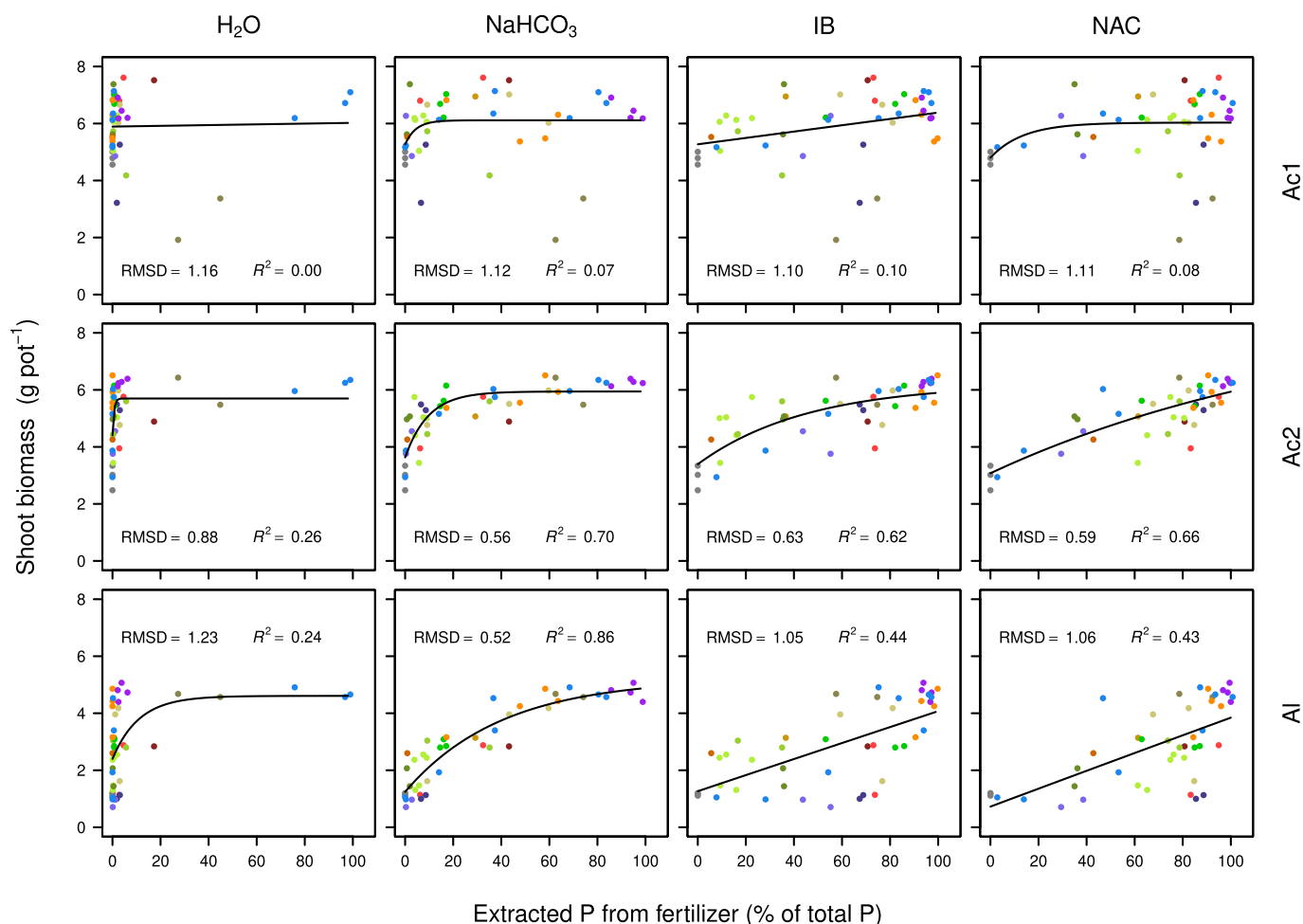
Fig. 2. Regression of shoot biomass vs. extracted P from fertilizer for the four extraction methods (H_2O, $NaHCO_3$, IB and NAC) in the three soils (strongly acidic (Ac1), slightly acidic (Ac2) and alkaline (Al)). Dot color indicates fertilizer category as in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A more detailed comparison of the results of both studies is shown in Figs. S4 and S5 (Supplementary material). It shows that the IB extraction remained a reliable predictor of P availability in this soil (consistently high R^2) while in the present study the fertilizer selection was greatly extended and diversified. In the Al soil, in contrast, the IB extraction was not better suited than NAC, as both had similar R^2 and *RMSD* (Figs. 2, 3).

H_2O was the least accurate extraction method, regardless of the soil type. This is due to the distribution of the extracted P which is very low with an extractability median of 1% (Fig. 1), resulting in a cluster of values to the left in Figs. 2 and 3 that spread along the y-axis preventing differentiation between fertilizers. This is in line with the low coefficients of determination already found in numerous previous studies (Table S2 in Kratz et al. (2019)).

No extraction method was suitable to assess fertilizer plant P availability in the Ac1 soil ($R^2 \leq 0.30$). Although not indicated by the soil P extractions (Table 2) this soil may exhibit a higher P availability compared to the two other soils, resulting in a weaker responsiveness of plant biomass production to P fertilization. However, we show in the Supplementary material that the Ac1 soil was responsive to P addition (section "Responsiveness of the Ac1 soil to P fertilizer" and Table S5). Moreover, differences in P efficiency between fertilizers is less likely to be visible in an acidic soil, because most P species contained in those diverse fertilizers are more soluble in this type of soil: The increase of solubility at low soil pH is well known for various Ca-phosphates, which are expected to be major P compounds in recycled P fertilizers like BGSL, CatM, ChM, MBM and their conversion products. A similar

increase of solubility at low pH was also shown for AshDec-Mg products (Nanzer et al., 2019) in which P is mainly present as chloroapatite and stanfieldite (Kratz et al., 2019; Nanzer et al., 2019) (Table 1). As a result, the Ac1 soil showed the highest median shoot P content (14.7 mg pot⁻¹; Fig. S2 of the Supplement) and shoot biomass (6.2 g pot⁻¹; Fig. S1 of the Supplement). In addition, three fertilizers had markedly lower shoot biomass than in the control pots (ChM-1, ChM-5 and MBM-1), which were not observed on the Ac2 and Al soil and further weaken the regressions (Figs. 2, 3).

3.3. Implications for the development, testing and use of P fertilizers

3.3.1. Testing and prediction of P availability

For quality assurance and marketing purposes, fertilizers must be evaluated with practicable methods, which optimally provide meaningful information on fertilizer performance. The currently used extraction procedures (e.g. NAC) and threshold values do not necessarily relate to the fertilizer's agronomic performance in the field, especially regarding the large variability in chemical composition of the emerging recycled fertilizers. Thus, a main question in this study was whether alternative extraction methods can provide better estimates of agronomic efficiency in different soils.

The $NaHCO_3$ method is a good candidate to estimate the short-term P availability in slightly acidic to alkaline pH and would be suitable for routine fertilizer testing.

The IB extraction is among the best predictors of P availability, and although the regressions were generally not as good as with $NaHCO_3$,
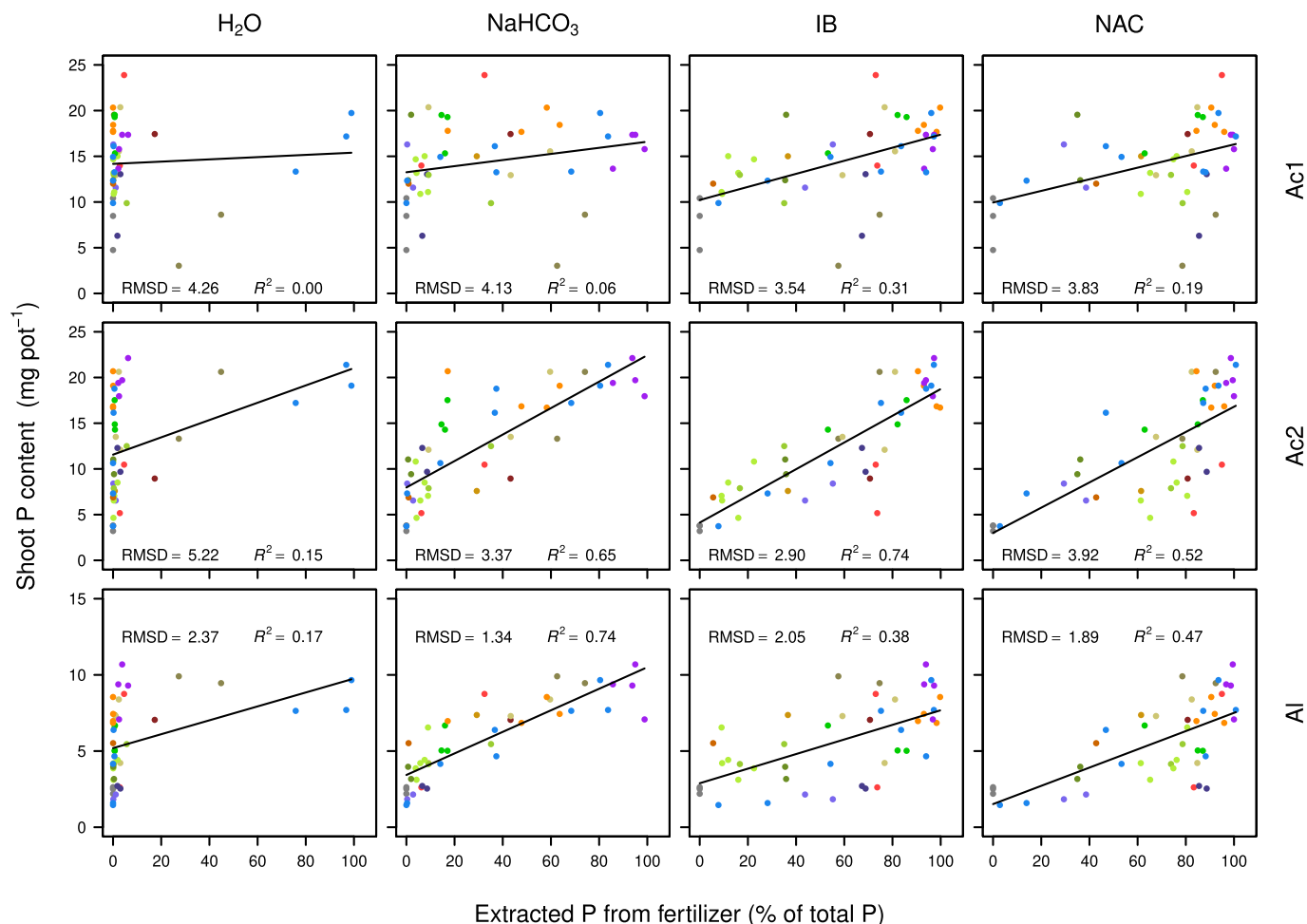
Fig. 3. Regression of shoot P content vs. extracted P from fertilizer for the four extraction methods (H$_2$O, NaHCO$_3$, IB and NAC) in the three soils (strongly acidic (Ac1), slightly acidic (Ac2) and alkaline (Al)). Dot color indicates fertilizer category as in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the method has the benefit to provide an estimate of the maximum amount of P that is soluble in water, at a given pH value, under the action of an infinite sink. The IB is overall a "gentle" extraction, i.e. not based on the addition of chelants or other chemicals that increase the extraction efficiency in a way that may not reflect the conditions in the soil and the rhizosphere. It may be assumed that for less soluble fertilizers with a high IB:NaHCO$_3$ extractable P ratio, the fraction not extracted by NaHCO$_3$ solubilizes over time under the action of soil particles (P adsorption, precipitation, etc.) and plant roots (P absorption) which both deplete pore water P. Additional rhizosphere and microbial processes based on chelation and pH shifts would also enhance dissolution, but are not mimicked by this extraction method. In its present form, however, the IB extraction is not suitable for routine analysis due the tedious laboratory procedure (high labor cost) and the time of extraction required (days to weeks). The data also suggests that this extraction method is less suitable for alkaline soils. Here it was partly due to the relatively high fraction of fertilizer P extracted from MBM, which conversely showed a low plant P availability in this soil.

The NAC extraction method extracts too much P from several fertilizers which only exhibit a moderate to low P efficiency (mainly in the MSS and MBM groups) and is not the best estimate of P availability, at least in the short-term of the present pot experiment (6 weeks growth experiment). It is unclear under which conditions (number of cropping seasons, types of crops and/or soils) this method would give a realistic estimate of the P availability in the chemically diverse P fertilizers.

While the H$_2$O extraction is not suitable as a predictor of P availability, it may remain an interesting method to characterize P fertilizer

solubility. Knowing that a low H$_2$O-solubility does not incur low plant-availability, even on the short-term, the result of a H$_2$O extraction can be used with the result of other extraction methods to describe the potential fertilizer behavior immediately after its application to the soil. For instance, a high H$_2$O-solubility could indicate increased risk of losses by runoff or leaching. Privileging low H$_2$O-solubility as in most recycled fertilizers could become part of environmental measures. In this pot experiment, we used milled fertilizers (<200 μm) to compare them based on their chemistry, leveling off effects that are influenced by fertilizer conditioning. In particular, fertilizer particle and granule size have a major impact on the interaction with the soil solution, soil particles and plant roots: the finer a fertilizer particle or granule is, the larger the specific surface area will be, which increases the contact with the soil environment and in turn accelerates the dissolution of non-H$_2$O-soluble fertilizers. The importance of an intense interaction between fertilizer and the soil environment has been shown by Degryse et al. (2017) for the dissolution of struvite, which was limited by soil solution Mg and high pH at the fertilizer-soil interface in the spot-applied treatment, and was much faster when the struvite powder was mixed with the soil. Although this interaction between fertilizer chemistry and the degree of contact with the soil (through specific surface area influenced by spot-application or granulation vs. powder mixed in the soil) was not studied here, we assume that the wider the P extractability ratio between IB and H$_2$O, the larger the effect of granule or particle size on plant P availability would be. Such a strong effect would be expected not only for struvite, but also for MSS–AshDec−Na and −K/Na, MSS-Slag as well as Prec-P RoC

products. They exhibit a high solubility in IB, but are not H_2O-soluble (Fig. 1), meaning that their dissolution is enhanced by the sink created by the soil (P precipitation and adsorption) and the roots (P uptake) Knowing that a sparingly H_2O soluble fertilizer is nearly 100% effective as a powder relative to a water-soluble P source would allow tailoring products that dissolve more or less quickly, depending on their specific surface area.

Low H_2O solubility is also a selection criterion for fertilizer use in organic crop production. This means that evaluating P fertilizers with a plant-availability index ($NaHCO_3$, IB or to some extent NAC) along with its H_2O-solubility could become relevant, given the intended increased share to 25% of the EU agricultural area managed organically by 2030 (European Commission, 2020).

A decade ago, Kratz et al. (2010) argued that the number of P fertilizer extraction methods listed in the national and the EU fertilizer regulations could be greatly reduced because they all produced relatively similar, not very satisfying predictions of P availability. For instance, the previous EU fertilizer regulation (2003/2003) listed citric and formic acid extractants, which were relatively similar to NAC but with a very acidic pH that is unrelated to soil conditions, and the new EU regulation (2019/1090) has simplified the set of methods, leaving mainly H_2O and NAC. The present work shows that alternative extraction methods can help to improve prediction of P availability from contrasting P fertilizers, which is important in the context of the circular economy. However, ultimately there may not be a single extraction method that stands out as a universal, one-method-to-fit-all-conditions approach. Instead, making use of contrasting extraction mechanisms, as in the four methods used here, could be an advantage to obtain a more informed, differentiated characterization of the fertilizers and of their potential behavior in different soil types on the short- and long-term, to predict the effect of granule size, etc. With that in mind, it could be judicious to examine the introduction of such new, complementary extraction methods in fertilizer testing regulations. The $NaHCO_3$ procedure, which is a simple batch extraction, would be a good candidate suitable for routine analysis. A sink extraction like the Iron Bag could be interesting as well, although a drastic simplification of the procedure would be required before routine implementation.

3.3.2. Use of recycled P fertilizers according to P speciation & solubility, and soil pH

The present study provides an overview of a wide diversity of potential P fertilizers which have been characterized with chemical extractions and in a short-term (6-week) pot experiment. It may be argued that the development of fertilizer tests based on short crop growth periods (weeks to months) could create a bias toward a short-term view on nutrient dynamics in agricultural production. However, a contemporary view on fertilizer P cycling considers that solubilization should occur within roughly a season, after which fertilizer P cycles in the soil as part of the soil P pools (Schnug and Haneklaus, 2016). According to this view, fertilizers that are not (nearly) completely soluble in a citrate extract should be avoided, as P would likely remain undissolved in the soil and would not contribute to the soil labile P pool within an acceptable timescale (Schnug and Haneklaus, 2016). Moreover, when investing in a fertilizer, farmers most likely expect a fast, visible effect. We believe that the short growth period in our (and similar) studies is not a disadvantage. For example, a study on broiler manure has revealed a strong reduction of solubility after manure pyrolysis, and a 30-40% lower P uptake by ryegrass over 4 months compared to the untreated manure (Sarvi et al., 2021). In that study, although the effect was more drastic during earlier growth (1 and 2 months) the trend remained the same after 4 months.

The variable, but often dominant proportion of apatites of different compositions and crystallinity in recycled fertilizers (Table 1) suggests that at least the soil pH should be considered to select an appropriate P fertilizer. Indeed, acidic soils may be the only appropriate soils for fertilizers in which P is mainly present as apatite. The benefit of pyrolyzing

animal manures and (meat &) bone meal should be carefully considered to reach a compromise between P solubility, intended use (soil pH) and other requirements such as hygiene, reduction of mass and/or volume for storage and transport, stability for storage, conditioning, etc. Moreover, because the most common soil pH values in temperate regions are close to pH 7, efforts have been deployed to produce fertilizers that are soluble in neutral and alkaline soils. The development of the AshDec process, from AshDec-Mg to AshDec-Na (and -K/Na) is a good example of this endeavour (see Kratz et al. (2019) (p. 6-7) and Vogel et al. (2018)). Chemically pure P fertilizers such as monoammonium phosphate or dicalcium phosphate that are also suitable for a wide range of soil pH values are also being produced from municipal sewage sludge.

4. Conclusions

Given the past and ongoing progress in the sector of nutrient recycling, a stage has now been reached where many technologies and products are developed enough for full scale implementation. Major progress has also been made in Europe at the policy level, and business cases are also multiplying. This work is an important contribution to this trend, given that product characterization/testing has not yet fully matured to be able to reflect the variety of products and their potential uses. Here we showed that the $NaHCO_3$ extraction method could improve prediction of P availability in routine analysis, while a more labor-intensive sink extraction like the Iron Bag can help gain further information about P solubility in particular during product development.

Credit author statement

Herewith we declare that no excerpts from other copyrighted works are included in this manuscript.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.150486.

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