



Predicting phosphorus availability from chemically diverse conventional and recycling fertilizers

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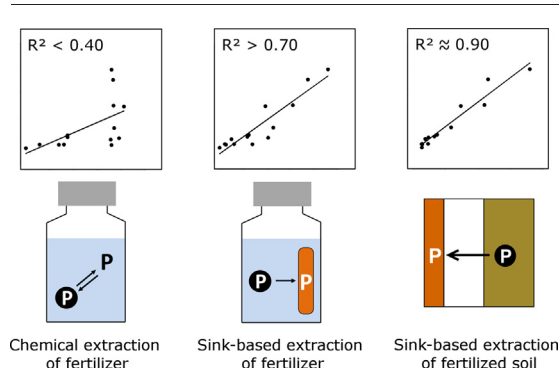
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HIGHLIGHTS

- Sink extraction was used to quantify available P in chemically diverse fertilizers.
- A second sink method was used for measuring P in fertilized soil samples.
- Both quantities closely correlated with plant P, outperforming classical methods.
- These novel approaches may assist fertilizer development from waste streams.

GRAPHICAL ABSTRACT



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ABSTRACT

Fertilizers produced from heterogeneous, phosphorus-rich biowastes are becoming increasingly relevant. Treatment and processing (combustion, pyrolysis, anaerobic digestion, etc.) increase the diversity of their physico-chemical composition even further.

We investigated several approaches to characterize P availability from a set of 13 contrasting fertilizers. We tested them directly using standard fertilizer extractions, as well as a continuous, sink-based P extraction (iron bag) method. We also performed Olsen, CAL and diffusive gradients in thin films (DGT) tests on fertilized soil.

Standard extractions correlated only weakly, whereas the iron bag method correlated highly ($0.73 < R^2 < 0.85$) with plant P uptake. Among the tests conducted on fertilized soils, DGT was equivalent or slightly better than Olsen, showing R^2 's of about 0.90 for P uptake and plant growth.

Our results suggest that the validity of standard P fertilizer tests needs to be reassessed in the context of increasingly diverse recycling fertilizers.

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1. Introduction

Phosphorus is an essential plant nutrient which often limits plant growth. Awareness about the limited global rock phosphate reserves

and their strong concentration in few main producer countries has raised public concern and interest in recovering and recycling P from diverse waste flows (Schoumans et al., 2015). The major residual P flows to be tapped are slaughterhouse waste, waste water and municipal sewage sludge, from which P is currently often lost (van Dijk et al., 2016). Moreover, efficient use of animal manures is often complicated due to strong regional concentrations of animal farms, which are often located

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close to urban centers (Gerber et al., 2010), requiring proper management and/or treatment in view of nutrient recycling to agriculture.

Phosphorus-rich residues may either be applied directly as fertilizer, or can be processed by anaerobic digestion, pyrolysis, hydrothermal carbonization (HTC), combustion, acidulation, etc., to ensure product hygienization and stabilization, facilitate storage, recover energy, mobilize and/or extract nutrients in pure form, etc. (Schoumans et al., 2015). Moreover, the direct use of some biowastes – in particular municipal sewage sludge (MSS) – is increasingly restricted due to potential contamination with trace metals, organic pollutants and pathogens. Many processes have been developed to recover P while discarding pollutants from municipal wastewater, MSS and MSS ash (Sartorius et al., 2012; Schoumans et al., 2015). Struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), is one of the most common products from P recovery technologies, which exhibits low P solubility in H_2O along with excellent plant availability (e.g. Cabeza et al., 2011). Future P inputs to agriculture will therefore consist of an increasing variety of fertilizers originating from diverse waste materials, which will be treated through different processes. This will require methods capable of accurately determining the P availability from such heterogeneous materials and their conversion products.

A number of standard batch extractions exist to characterize P solubility in fertilizers. According to the European regulation on fertilizers (European Commission, 2003) declaration of P concentration must generally include a fraction extractable by mineral acid. Depending on the type of fertilizer, it requires also information on P solubility either in 2% citric acid (Thomas phosphate and Thomas slag), H_2O (partially acidulated rock phosphate), 2% formic acid (soft ground rock phosphate), or neutral ammonium citrate and H_2O (superphosphates). Although the water and diluted organic acid extractions are commonly used as a measure of P availability, their limitations have been recognized (Kratz and Schnug, 2009). It should be stressed that they are primarily empirical methods which do “*not attempt to accurately reproduce the properties of the soil solution in the immediate vicinity of the plant roots, but to provide a standard measure of phosphate extraction roughly comparable to that available to the plant, which can be related to the observable plant growth*” (Faithfull, 2002). The lack of mechanistic background and the empirical nature of these methods leave room for improvement. In fact, when these solubility tests were assessed on various recycling fertilizers they have generally shown weak correlations with plant P content or biomass, with R^2 values rarely above 0.5 (Brod et al., 2015; Cabeza et al., 2011; Delin, 2016; Kratz et al., 2010; Steckenmesser et al., 2017), while they gave good results only exceptionally, mainly in cases where a limited range of fertilizer types was investigated (Falk Øgaard and Brod, 2016; Steckenmesser et al., 2017; Wang et al., 2012).

Accounting for soil properties improves the accuracy of the prediction of P availability to the plant (Cabeza et al., 2011). The most common soil P availability tests include calcium acetate lactate (CAL), Mehlich 3, Olsen or Colwell (Moody et al., 2013; Wuenschel et al., 2015). Acetate lactate (AL) which is similar to CAL (Schick et al., 2013) has failed to predict P availability from recycling fertilizers (Bøen and Haraldsen, 2013; Delin, 2016). In a field experiment with biosolids and meat and bone meal based P fertilizers, Olsen-P correlated better than AL-P with plant P content (Bøen and Haraldsen, 2013).

As plant assays of P availability are time-consuming, expensive and sensu stricto limited to the experimental plant, we still need to improve the prediction of P availability from diverse recycling fertilizers without relying only on plant bioassays. Depletion-based extraction procedures are an alternative to the standard equilibrium- or ligand-based extractions. They may involve a short- or long-term extraction of a given amount of soil or fertilizer with e.g. iron oxide or ion exchange resin (Freese et al., 1995; Nanzer, 2012; Santner et al., 2015). Santner et al. (2015) found that P uptake by maize grown in small pots was quantitatively predicted by the total labile soil P using ferrihydrite as an infinite (or zero) sink, that is, a technique capable of taking up ions from the surrounding solution with an ion capacity exceeding the amount of ion

resupplied by the sampled material, and which is able to maintain the ion concentration in its vicinity very low during the course of the experiment. Nanzer (2012) used combinations of cation and anion exchange resins in their H^+ , Na^+ and HCO_3^- forms, respectively, in 3-day extractions to test the P availability from two recycling fertilizers, evaluating the effect of solution pH and of the depletion of P and/or cations from the solution on fertilizer P dissolution. It is the combination of these factors which determines P dissolution in soils, and Nanzer (2012) inferred the main controlling factors in the different soil \times fertilizer treatments of the bioassay from the processes prevalent in the combination of ion sinks that exhibited the best correlation with plant growth. Compared to ion exchange resins, ferrihydrite has the advantage to bind phosphates specifically; it is not influenced by the ionic content of the solution and does not affect the solution pH – which can be buffered at a target value relevant for the intended soil properties. Due to the comparatively large P binding capacity, using a dialysis membrane filled with ferrihydrite slurry (Freese et al., 1995) appears to be a good option for depletion-induced quantification of available P from fertilizers.

The diffusive gradient in thin films (DGT) technique is a particular implementation of the infinite ion sink approach which mimics plant roots by simulating the diffusive solute flux towards the root, also allowing to measure the ion concentration in soil solution under constant uptake (as opposed to under equilibrium) (Davison, 2016; Degryse et al., 2009; Zhang and Davison, 2015). This technique has been shown to be superior in predicting plant yield in field experiments compared to conventional soil tests for wheat (Mason et al., 2010) and it has recently been shown by isotope dilution studies that the DGT method samples the same soil P pool as accessed by plants (Mason et al., 2013; Six et al., 2013).

The objective of this study was to test several approaches for their ability to determine the P plant availability from fertilizers/amendments varying in P solubility and composition, including standard batch fertilizer extractions, a sink method for fertilizer P extraction, standard P availability extractions of fertilized soil, and a sink-based P extraction from fertilized soil. Therefore, we selected 13 P-rich samples consisting of conventional fertilizers, manures, biowastes, as well as biochars and ashes from different sources. A six-week greenhouse pot experiment was conducted to determine which method(s) could deliver the best correlation of fertilizer P test value and P availability to plants. We hypothesized that infinite sink methods simulating plant uptake in terms of depletion of P in solution would perform better than equilibrium-based approaches in predicting yield and P uptake in the crop.

2. Materials and methods

2.1. Characteristics of fertilizers and soil

2.1.1. Sample description

Thirteen P-rich biowastes and fertilizers (subsequently referred to as fertilizers) were selected to represent a broad range of potential P sources (Table 1). As some of the materials originate from fertilizer development projects, we are not able to fully disclose the origin of all materials used in the following.

Meat and bone meal (MBM) was collected from Steirische Tierkörperverwertungsgesellschaft m.b.H. & Co KG, Gabersdorf, Austria. Chicken manure (CM) was from an egg producing farm (Leithaprodersdorf, Austria), and the biogas slurry (BGS) originated from a biogas production plant in Bruck a.d. Leitha, Lower Austria. The feed materials for biogas production were food and agricultural wastes, the slurry had a dry mass of about 5 wt% and a pH of 8 and was freeze-dried prior to further treatment. Biochars of MBM, CM, and BGS were produced by pyrolyzation at 400 °C in an experimental lab reactor with nitrogen as flush gas at the Austrian Institute of Technology (AIT, Tulln, Austria).

Municipal sewage sludge was collected from the municipal wastewater treatment plant of Tulln a.d. Donau, Austria and pyrolyzed

Table 1Total carbon, nitrogen and phosphorus concentrations of the studied fertilizers. Mean \pm SD.

Fertilizer	Sample code	C total (mg g ⁻¹)	N total (mg g ⁻¹)	P total (<i>aqua regia</i>) (mg g ⁻¹)
Biogas slurry (solid fraction)	BGSL	441	23.6	19.1 \pm 0.1
Chicken manure	CM	371	32.5	22.4 \pm 0.3
Chicken manure biochar	CM-BC	371	24.0	43.7 \pm 0.6
Meat & bone meal	MBM	409	79.4	54.7 \pm 1.8
Meat & bone meal biochar	MBM-BC	276	37.7	114 \pm 1
Gasified municipal sewage sludge 1	MSS-G-1	43.9	1.2	79.5 \pm 1.9
Gasified municipal sewage sludge 2	MSS-G-2	89.0	2.6	104 \pm 4
Municipal sewage sludge biochar 1	MSS-BC-1	314	44.1	90.6 \pm 0.8
Municipal sewage sludge biochar 2	MSS-BC-2	237	24.6	68.8 \pm 0.9
Municipal sewage sludge biochar 3	MSS-BC-3	225	14.9	92.1 \pm 0.6
Rock phosphate	RP	N/A	N/A	143 \pm 3 ^a
Single superphosphate	SSP	N/A	N/A	83.7 \pm 5.3 ^a
Struvite	Struvite	N/A	N/A	124 \pm 2 ^a

^a Air-dry weight equivalent; all other P concentrations are reported on oven-dry weight equivalent basis (60 °C, 24 h).

under the same conditions to produce the municipal sewage sludge biochar 1 (MSS-BC-1). The municipal sewage sludge biochars 2 and 3 (MSS-BC-2 and MSS-BC-3 respectively) originated from pilot sewage sludge treatment plants, therefore we cannot disclose their origin. Two thermo-chemically treated municipal sewage sludge samples (MSS-G-1 and MSS-G-2, respectively) were produced by gasification of MSS biochars themselves produced from MSS collected in Moscow, Russia. During gasification, MgCl₂ was added to remove contaminant metals by volatilization as chloride complexes. The MSS-derived samples were collected/produced independently from each other. Only MSS-G-1 and MSS-G-2 originated from the same treatment plant. The Struvite sample is a commercial product (Berliner Pflanze; Berliner Wasserbetriebe, Berlin, Germany) produced by precipitation in a wastewater treatment plant. Finally, a commercial single superphosphate (SSP) (DC Superphosphate; Timac Agro Düngemittelproduktions- und HandelsgmbH, Zwentendorf, Austria) was used as reference fertilizer. (Table 1).

A carbonate-free arable soil with low available P concentration (pH_{CaCl2} = 6.2; pH_{H2O} = 7.0, CAL P = 13.4 mg kg⁻¹) was used as test soil for the pot experiment and for the DGT, Olsen and CAL extraction experiments (see below). The soil water holding capacity (WHC) was determined as 465 g (kg dry soil)⁻¹.

2.1.2. Sample preparation

All fertilizers were milled to <200 μ m in a vibratory ball mill (Retsch ® MM 200) at 80 Hz using stainless steel grinding equipment. Individual milling steps were limited to a maximum duration of 3 min. After each milling step the sample was sieved and the fraction retained in the sieve was milled again. In order not to discard any fraction, this process was repeated until all material passed through the 200- μ m sieve.

2.1.3. Total P, C and N concentrations

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% HNO₃). For comparison, ten selected samples were also digested with HNO₃/H₂O₂ (100 mg sample with 5 mL 65% HNO₃ + 1 mL 30% H₂O₂). 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, respectively, above which heating was suspended. Phosphorus in the digests was measured by ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA) at 213.617 nm with matrix-matched standards. Total carbon (C_t) and nitrogen (N_t) concentrations were analyzed by dry combustion in a NA 1500 Series 2 elemental analyzer (Carlo-Erba).

Total P concentrations of the fertilizers ranged from 19 to 143 mg g⁻¹ (*aqua regia*), and the C and N concentrations of the recycling materials varied widely from 43.9 to 441 mg g⁻¹ and 1.2 to 79.4 mg g⁻¹, respectively (Table 1).

2.2. Pot experiment

A pot experiment with rye (*Secale cereale* L., var. “Amilo”) was conducted in the greenhouse with four replicates in each treatment, except for BGSL ($n = 1$), and CM-BC ($n = 2$) due to limited sample amount. One kg soil was added to each pot and the finely ground fertilizer was thoroughly mixed at a rate of 100 mg P_t kg⁻¹ soil. This rate was 85% of the dose required for maximum shoot dry matter production during 6 weeks (7.05 g pot⁻¹), as was determined in a preliminary P dose-response trial using only SSP as fertilizer with P fertilization rates from 0 to 210 mg P_t kg⁻¹, applied in 15 mg P_t kg⁻¹ increments.

Water was added to the soil to reach 65% WHC, the moist pots were left to incubate in the greenhouse for one week. Afterwards, 40 seeds per pot were planted and thinned to 25 plants seven days after planting (DAP). All nutrients except P were supplied by weekly donations of 50 mL of a nutrient solution (modified from Middleton and Toxopeus (1973)) containing: 3.4 g L⁻¹ NH₄NO₃, 1.47 g L⁻¹ K₂SO₄ anhydr., 444 mg L⁻¹ MgSO₄ 7H₂O, 360 mg L⁻¹ CaCO₃, anhydr., 7.2 mL L⁻¹ 1 M HCl (to solubilize CaCO₃), 600 μ g L⁻¹ H₃BO₃, 158 μ g L⁻¹ CuCl₂, 5.5 mg L⁻¹ MnCl₂ 4H₂O, 80 μ g L⁻¹ (NH₄)₂MoO₇ 24 H₂O, 300 μ g L⁻¹ ZnCl₂ and 2.4 mg L⁻¹ Fe EDDHA. This resulted in a total addition of 298 mg N, 165 mg K, 82 mg S, 11 mg Mg, 36 mg Ca, 26 μ g B, 19 μ g Cu, 382 μ g Mn, 12 μ g Mo, 36 μ g Zn and 34 μ g Fe over the course of the experiment. Controlled growth conditions included humidity of 60%, day/night cycle of 16/8 h, with day/night temperature of 25/15 °C and artificial lighting to complement daylight. Photosynthetically active radiation (PAR) was on average ~600 μ mol m⁻² s⁻¹. The rye shoots were harvested at 42 DAP by cutting evenly with scissors at the level of the pot's edge (ca. 1.5 cm above soil surface level), washed with deionized water and dried for 48 h at 65 °C. Shoot dry matter was determined by weighing the dried biomass. A sample aliquot was milled in a Retsch GM 200 at 8500 RPM, and digested in a microwave (200 mg sample with 8 mL HNO₃ + 2 mL H₂O₂ in a MARS 6 microwave system, CEM corporation, NC, USA), and the P concentration was measured by ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA) at 213.617 nm.

2.3. P solubility in the fertilizer materials

2.3.1. Standard fertilizer P extractions

Phosphorus fertilizer batch extractions were performed according to EN 15920:2011-08 (2% w/v citric acid soluble P), EN 15919:2011-08 (2% w/v formic acid soluble P), EN 15957:2011 (4.8% w/v ammonium

+ 18.5% w/v citrate solution at pH 7; 'neutral ammonium citrate') and EN 15958:2011 (H₂O soluble P). The different extractions will be referred to as CA, FA, NAC and H₂O, respectively, throughout the manuscript.

For CA, FA and H₂O, 100 mg fertilizer were shaken overhead for 30 min at 20 rpm in 10 mL of the respective solution in 15 mL vials. For NAC, 90 mg fertilizer were extracted in 9 mL NAC solution at 65 °C in a shaking water bath for 1 h. Subsequently, the NAC extracts were immediately cooled and diluted 1:5 with H₂O.

After extraction, the samples were filtered through filter papers (Ahlstrom-Munktell, grade 14/N). The H₂O extract was acidified to 0.25 mol L⁻¹ H₂SO₄ and the other extracts to 2% HNO₃. The H₂O extract was analyzed via spectrophotometry with a molybdenum blue protocol. The CA, FA and NAC extracts were analyzed by ICP-OES (Optima 8300, Perkin Elmer, Waltham/MA, USA) at 213.617 nm. For each extraction, matrix-matched calibration standards were used. Results are given as % of total P measured in the *aqua regia* digests.

2.3.2. Depletion-induced P solubilisation from fertilizers (iron bag method)

To measure total water-soluble fertilizer P, we used an infinite sink method that employs iron oxide slurry-filled dialysis tubes as P sink (Freese et al., 1995). Ferrihydrite was precipitated by adding 1 mol L⁻¹ NaOH to a 100 g L⁻¹ Fe(NO₃)₃ × 9H₂O solution, which was stirred using a magnetic stirrer, until pH 6.5–6.8 was reached. The ferrihydrite slurry was centrifuged for 3 min at 70×g and the supernatant was discarded to wash off excess reactants. The centrifugate was re-suspended in H₂O and the procedure was repeated. Finally, the slurry was re-suspended in water and topped up to twice the initial volume.

Dialysis membrane tubing (Visking dialysis tubing, size 3, 20/32, 12,000–14,000 MWCO. Medicell Membranes Ltd., London, UK) was cut to 30 cm long strips and placed in H₂O. The strips were then boiled twice for 5 min in H₂O and transferred to H₂O at ambient temperature inbetween. The strips were closed at one end with a clip (Medi-Clip for 6.3–28.6 mm, Medicell Membranes Ltd., London, UK), filled with 20 mL slurry and closed at the other end as well. It was found useful to fold the membrane 2–3 times before sealing with the clip to avoid leakages. The membrane bags were then washed in deionized H₂O.

Preliminary capacity tests had shown that one membrane bag could take up at least 3 mg P while keeping the solution P concentration below the limit of quantification of the molybdenum blue method (10 µg P L⁻¹). Below this P loading the iron bags were thus considered an infinite sink. To ensure to not exceed the iron bag P capacity, 30 mg fertilizer were weighed in 250 mL shaking bottles (three replicates) together with 150 mL of a 30 mmol L⁻¹ 3-(N-morpholino)propanesulfonic acid (MOPS) buffer adjusted to the pH of a saturated paste of our test soil (pH = 6.8). A ferrihydrite membrane bag was added, and the bottle was placed on an overhead shaker at 5 rpm.

After 10 and 20 days, respectively, the membrane bag was removed and replaced. The third and last sampling was performed after a total of 37 days of extraction. Particles adhering to the surface of the membrane were washed back into the bottle with deionized H₂O. For analysis of extracted P, the iron bags were opened and the ferrihydrite slurry was transferred to vials. One mL of 96% H₂SO₄ was added for dissolving the ferrihydrite, afterwards the solution was diluted to 0.25 mol L⁻¹ H₂SO₄.

The extracted P was measured at 881 nm with a molybdenum blue method based on Murphy and Riley (1962) by adding successively (1) 1 mL of sample with up to 0.5 mg P L⁻¹ (diluted if required with 0.25 mol L⁻¹ H₂SO₄), (2) 0.06 mL of 88 g L⁻¹ ascorbic acid, and (3) 0.14 mL of a solution containing 6 g L⁻¹ ammonium heptamolybdate tetrahydrate and 0.14 g L⁻¹ potassium antimony tartrate hydrate. The high concentration of Fe(III) in the samples required to increase the amount of ascorbic acid - which is used as reductant in the molybdenum blue assay. 88 g L⁻¹ is the 5-fold concentration of ascorbic acid reactant used for the other analyses. In each measurement series, ferrihydrite slurry from a non P-loaded membrane bag was used

as a reagent blank, i.e. for correcting for the background absorbance of iron.

2.4. P availability in fertilized soil

Thirty grams of air-dry soil were weighed into 100 mL PE vessels. Fertilizer was added at the same rate as for the pot experiment (i.e., 100 mg P kg⁻¹) and mixed homogeneously with the soil. Water was added so as to reach 60% WHC and homogenized with a spatula. Then, the vessels were covered with parafilm and placed at 20 °C in an incubator. The atmosphere in the incubator was kept humid with a wet tissue paper. With these measures, soil water content remained constant over time - as controlled by total vessel weight. Measurements of fertilizer P availability in the experimental soil (soil extractions, DGT) were performed after 5 days incubation (all tests), and additionally after 20 days (for DGT only). All experiments were performed in triplicate.

2.4.1. Soil extractions

Olsen-P (Olsen et al. (1954) as described in Schoenau and O'Halloran (2008)), and calcium acetate lactate (CAL (ÖNORM L1087:2006-01, 2017)) extractions were performed. 2.25 g soil (dry weight equivalent) were extracted in 45 mL extractant on an overhead shaker at 20 rpm for 30 min (Olsen) and 120 min (CAL). The P concentration in the extracts was measured at 881 nm using the molybdenum blue method after removing the carbonate by adding 1.05 mL of 0.25 mol L⁻¹ H₂SO₄ to 1 mL Olsen extract (sample dilution factor = 2.05). 0.2 mL of a staining solution containing 1.25 mol L⁻¹ H₂SO₄, 6 g L⁻¹ ammonium heptamolybdate tetrahydrate, 0.14 g L⁻¹ potassium antimony tartrate hydrate and 5.28 g L⁻¹ ascorbic acid were added to 1 mL of the carbonate-free sample. The P concentration in soil was expressed in mg P kg⁻¹.

2.4.2. Diffusive gradients in thin films

Polyacrylamide hydrogels (0.8 mm and 0.4 mm thick) were prepared according to Zhang and Davison (1995). The 0.8-mm gels were used as diffusive layer and the 0.4-mm gels were used as P-binding layer after impregnation with ferrihydrite by precipitation (Santner et al., 2010). DGT sampler housings with an exposure window of 3.14 cm² (DGT Research Ltd. Lancaster, UK) were filled with gel and membrane discs (25 mm diameter) as follows: (1) ferrihydrite binding gel, (2) polycarbonate membrane (Nucleopore, 0.01 mm thickness, 0.2 µm pore size) for separating the gel layers, (3) diffusive gel, and (4) polyethersulfone membrane (Sartorius® Type 154, 0.15 mm thickness, 45 µm pore size) as protective layer.

The DGT measurements were performed on soil fertilized with 100 mg P kg⁻¹ (see details about fertilization rate in Section 2.2). The fertilized soil was incubated as described above for 5 days and 20 days, respectively, before measurement. Approximately 24 h before DGT deployment, water was added to the soil to obtain a paste at 90% WHC. After 24 h of deployment at 20 °C, the soil paste was removed and the DGT device was cleaned to avoid contamination by soil particles. The binding layer was retrieved and eluted in 5 mL 0.25 mol L⁻¹ H₂SO₄. The eluates were measured photometrically with molybdenum blue colorimetry as described for the iron bag method, but with the ascorbic acid reactant at 17.6 g L⁻¹. The results are expressed as c_{DGT} which is calculated according to:

$$c_{DGT} = \frac{M\Delta g}{DA t} \quad (1)$$

where c_{DGT} (µg cm⁻³) is the time-averaged soil solution concentration at the sampler-soil interface, M is the mass of P accumulated over 24 h on the sampler (µg), Δg is the diffusion layer thickness (cm), D is the phosphate diffusion coefficient in the diffusion layer (cm² s⁻¹; (Zhang et al., 1998)), A is the sampling area (cm²) and t is the deployment time (s). In the results section, c_{DGT} is given in µg L⁻¹.

2.5. Data evaluation

Data evaluation and figures were done with the software 'R', version 3.3.1 (R Core Team, 2016). The Welch *t*-test (two tailed) was used for two-sample comparisons. It is the default in the *t.test()* function of R and is recommended over other comparison methods (Rasch et al., 2011). When comparing multiple groups, analysis of variance and Tukey HSD post-hoc test at $\alpha = 0.05$ were performed (*HSD.test()* from the R package "agricolae" (de Mendiburu, 2016)). Linear (plant P uptake) and non-linear models (plant biomass) were fitted with the functions *lm()* (R base package) and *nlsLM()* (R package "minpack.lm" (Elzhov et al., 2015)), respectively. The control receiving no P was considered as a sample in all correlations. For correlations with the fertilizer tests, the control treatment was considered equivalent to applying a fertilizer without soluble P. For non-linear models, goodness of fit was given as

$$R^2 = 1 - \text{RSS}/\text{SS} \quad (2)$$

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

The Mitscherlich equation

$$y = y_0 + a \left(1 - e^{-bx}\right) \quad (3)$$

was fitted to plots of plant biomass vs. P test result (respective units as described above) where y_0 is the calculated (minimum) yield at the origin, $y_0 + a$ is the calculated maximum yield, and x is the result from the respective P availability/solubility test. The parameters y_0 , a , and b were fitted. The value of $y_0 + a$ was considered to assess how the maximum yield from the fitted equations would compare with the experimental maximum yield (y_{max}), which was measured during a growth response experiment under the same experimental conditions.

3. Results and discussion

3.1. Total P concentrations

Phosphorus concentrations in samples originating from municipal sewage sludge (MSS) were significantly larger in *aqua regia* digests than in $\text{HNO}_3/\text{H}_2\text{O}_2$ digests (Fig. 1). In contrast, the two digestion methods were very similar for the other tested fertilizers. For this reason, P measured in *aqua regia* was used as the measure of total P in this study.

The highly variable composition of recycling fertilizers makes it difficult to choose the proper digestion method, and the lack of a consistent procedure in the literature is not surprising. Nitric acid, or more commonly $\text{HNO}_3/\text{H}_2\text{O}_2$ has been mainly used for digesting materials rich in organic matter such as plant tissues or wood, and it appears to be most often used for manures, biochars, MSS-derived samples, etc. (Agrafioti et al., 2013; Christel et al., 2014; Delin, 2016; Hossain et al., 2011). Various combinations of HClO_4 , H_2SO_4 , HNO_3 and/or HF have been also used for recycling fertilizers (Cabeza et al., 2011; Herzel et al., 2016; Hossain et al., 2011; Komiya et al., 2014; Lu et al., 2013; Weber et al., 2014). Despite its efficacy, the use of HClO_4 is decreasing due to hazardous handling (Enders and Lehmann, 2012) and HF is toxic. Sulfuric acid could have some limitations due to the low solubility of some sulfate salts (Jones (2001), as cited in Enders and Lehmann (2012)). *Aqua regia* has been mainly used for samples with a predominant mineral fraction, such as soil, and it is not commonly used in the context of recycling fertilizers, possibly due to its limited oxidative capacity for organic matter. Nevertheless, Krüger and Adam (2017) recently showed that *aqua regia* was suitable for P analysis in various MSS and MSS-derived recycling fertilizers. They also introduced "inverse *aqua regia*" digestion (4 mL $\text{HNO}_3 + 1$ mL HCl) as an alternative for this type of samples.

In spite of the yellow to brownish coloration of some of the *aqua regia* digests which suggested that some dissolved organic matter was still present, the P concentrations measured by *aqua regia* were the same as those measured by $\text{HNO}_3/\text{H}_2\text{O}_2$ except for the four MSS-based materials. The addition of Fe salts to wastewater is a standard procedure to remove P from the liquid phase. In fact, the iron concentration in these samples measured after $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion was only one fourth or less than that measured with *aqua regia*, which strongly suggests that a large portion of Fe-P was not dissolved by the former. The higher capacity of *aqua regia* to dissolve Fe-P is likely due to the complexation of Fe and other cations by Cl^- in the HCl/HNO_3 mixture, resulting in more complete dissolution of mineral phases. Herzel et al. (2016) measured on average 16% more P in HClO_4/HF digests than in *aqua regia* digests of municipal sewage sludge ashes. Considering the hazardous handling of HClO_4/HF , our results further suggest that microwave assisted *aqua regia* digestion can be used as a safe method to measure near-total P concentration in diverse recycling fertilizers including those with predominantly organic matrix. As was also shown by Krüger and Adam (2017), it should clearly be preferred over $\text{HNO}_3/\text{H}_2\text{O}_2$ when measuring MSS-derived samples. The "inverse *aqua regia*" which was proposed by these authors may be even better than *aqua regia* for fertilizers with organic matrix due to the increased proportion of the

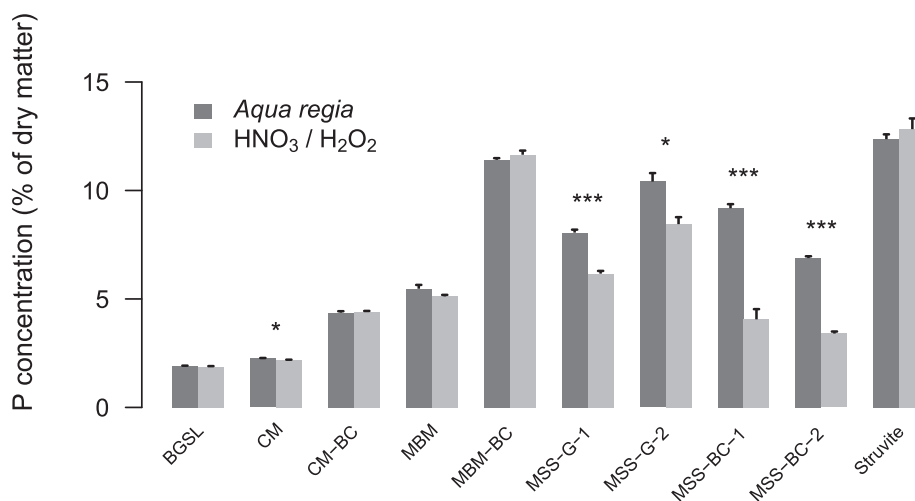


Fig. 1. Total P concentrations measured in the tested fertilizer materials after *aqua regia* and $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion. Mean + SD ($n = 3$, except for *aqua regia* of MSS-G-2 ($n = 2$)). *, **, and *** for $\alpha < 0.05$, < 0.01 and < 0.001 , respectively (2-tailed Welch's *t*-test). Refer to Table 1 for sample names.

oxidative HNO_3 . Its potential as a more universal digestion method for recycling fertilizers should be investigated in more detail.

3.2. Phosphorus solubility in the fertilizer materials

3.2.1. Phosphorus in fertilizer extracts

On average, extractable P (as % of P_t) increased in the order $\text{H}_2\text{O} < \text{IB} < \text{NAC} < \text{FA} < \text{CA}$. In the H_2O extract only three samples (CM, BGSL and Struvite) showed $>5\%$ of total P (Fig. 2). In contrast, the other extracts showed a more even spread of P solubility ranging between 12% and 83%, 12% and 106%, and between 35% and 97% for NAC, FA and CA, respectively. The IB method extracted between 6% and 92% of P_t after 37 days (Fig. 2A). There was no clear trend in solubility between samples: although CA and FA generally extracted more than NAC, the samples MSS-BC-1 and MSS-BC-2 were in strong contrast with this trend.

3.2.2. Phosphorus in fertilized soils (soil tests)

Overall, the CAL method extracted larger P quantities from the fertilized soils as compared to the Olsen method (Fig. 2B), with values

ranging from 13 to 67 mg P kg^{-1} and 9 to 83 g P kg^{-1} , respectively. An outlier was removed for CAL (BGSL: 131 mg P kg^{-1}) because P extracted was $>$ fertilizer P + P in control soil. The C_{DGT} values ranged from 14 to 180 $\mu\text{g P L}^{-1}$. Thus, the amount of P in the ferrihydrite binding layer was always $<3 \mu\text{g P}$, which is far below their capacity of ca. 35 $\mu\text{g P}$ (Santner et al., 2010).

3.2.3. Shoot dry matter production

Shoot dry matter production in the plant experiment ranged from 4 g (MSS-BC-3) to 6.7 g (Struvite) (Fig. 3). Overall, the MSS- and MBM-derived samples were in the low productivity groups together with the RP sample (mainly group “c” in Fig. 3), while the high productivity group consisted of the CM-derived samples together with SSP and Struvite (group “a” in Fig. 3).

3.2.4. Correlation of phosphorus tests with shoot dry matter production and P content

None of the four standard fertilizer extracts correlated strongly with plant P content ($R^2 < 0.40$; Fig. 4). Hence, among the fertilizer

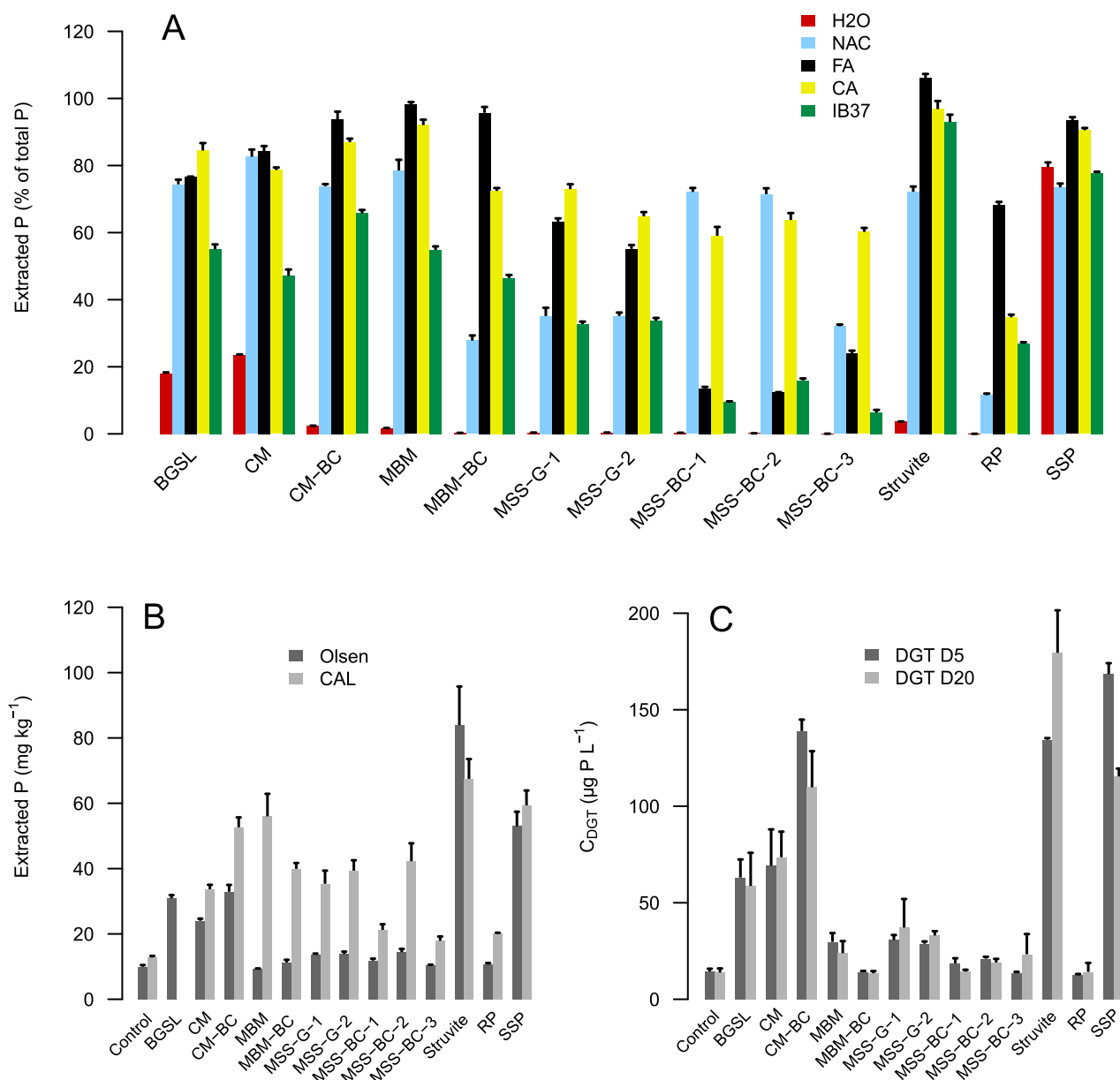


Fig. 2. Results of P tests: Fertilizer extractions (A), soil extractions (B), and DGT after 5 and 20 days (C). Mean + SD ($n = 3$). Refer to Table 1 for sample names. Refer to the electronic version for colours in panel A.

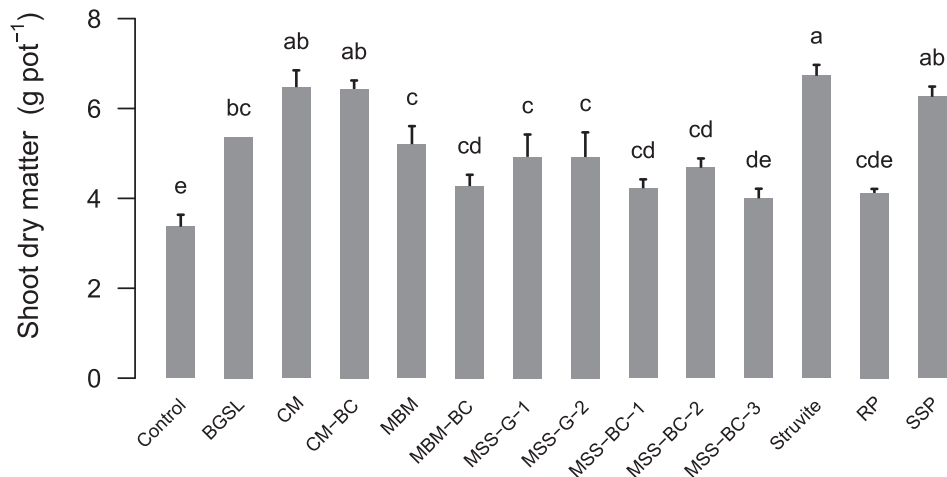


Fig. 3. Shoot dry matter production of rye upon termination of the pot experiment. Mean \pm SD ($n = 4$, except BGSL ($n = 1$) and CM-BC ($n = 2$)). Means with the same letter are not significantly different (Tukey HSD, $\alpha = 0.05$). Refer to Table 1 for sample names.

extractions, only the iron bag method correlated well with plant P content, whereby the shorter extraction (10 days) correlated more strongly than the longer extraction period of 37 days ($R^2 = 0.85$ vs. 0.73 ; Fig. 4). The fertilizer extracts were generally not suitable for predicting **shoot dry matter** with the Mitscherlich equation (Fig. 5, white panels). The iron bag method after 10 d of extraction ($R^2 = 0.84$, $y_0 + a = 7.8$ g) followed by H_2O extraction ($R^2 = 0.83$, $y_0 + a = 6.19$ g) were the best among all soil-independent fertilizer tests, while the other methods showed unsatisfactory R^2 and/or prediction of $y_0 + a$ as compared to the experimentally determined maximum dry matter production ($y_{max} = 7.05$ g). In the case of H_2O , R^2 was high (0.83) but the steep slope of the response curve does not allow for a reliable prediction of plant biomass, in particular when compared to the 10-day IB extraction. The datapoints of CA, NAC, FA and IB (37 d) were hardly distinguishable from a linear relationship and exhibited $y_0 + a$ values far off the measured y_{max} .

Among the *soil-based P* fertilizer tests performed after incubation of soil with fertilizer, Olsen and DGT were the best indicators of plant **P content** with R^2 ranging from 0.88 (Olsen and DGT after 5 days of incubation) to 0.94 (C_{DGT} after 20 days of incubation) (Fig. 4, grey panels). For CAL the coefficient of determination ($R^2 = 0.57$) was clearly lower than for the other methods. Similarly, DGT was the best predictor of **shoot dry matter**, both after 5 and 20 days incubation ($R^2 = 0.91$ and 0.88 , respectively), followed by Olsen ($R^2 = 0.77$), (Fig. 5, grey panels). The model with DGT after 20 days of incubation predicted a maximum yield of $y_0 + a = 6.78$ g per pot, which among all predictive models was the closest to the measured y_{max} . With $y_0 + a = 6.52$ g Olsen and DGT (5-day incubation) were the second best predictors of y_{max} , while CAL clearly performed worst ($y_0 + a = 15$ g).

To our knowledge, apart from the work of Nanzer (2012) with ion exchange resins, it is the first time that an infinite sink method such as IB was tested in the context of recycling fertilizers. Overall, the better predictive power of this method over other fertilizer extractions is evident for P uptake (Fig. 4, white panels) and to a lesser extent for shoot dry matter (Fig. 5, white panels). The iron bag was the only method which could predict the gradient in P availability, whereas other methods either had a bimodal distribution (NAC, FA), or the data were limited to a narrow range of extracted P (CA in the high range, H_2O in the low range). At a first glance FA and NA appeared to be superior to CA at assessing the low P availability of some samples (Fig. 4, Fig. 5). But a closer look at the results (Fig. 2) reveals that the samples with low solubility were different between the two extracts. The stronger extraction by CA might be due to the higher stability constants of its Ca and Fe(III) complexes compared to FA (Martell and Smith, 1977).

Regarding the standard fertilizer solubility tests (H_2O , FA, CA, NAC), the weak correlation with plant P content confirms earlier findings (Brod et al., 2015; Cabeza et al., 2011; Delin, 2016; Kratz et al., 2010). Contrastingly, Wang et al. (2012) obtained good results with FA, but not with CA and NAC. Falk Øgaard and Brod (2016) also found a good prediction of P availability from MSS by CA ($R^2 = 0.69$ after 6-week growth) and also by oxalate-extractable Fe and Al concentrations. In both cases, the results might be due to the narrower range of materials tested in comparison to our study: Wang et al. (2012) studied biochars from anaerobically digested biosolids and cattle manure + two reference samples, and Falk Øgaard and Brod (2016) limited their investigations to different types of MSS.

Olsen P, one of the most common soil P tests, gave satisfactory results for residual P availability from two recycling fertilizers (MBM and MSS) in a field experiment, with $R^2 = 0.73$ and 0.96 in a silt loam and a loam soil, respectively (Bøen and Haraldsen, 2013). The weak correlations with the CAL method in our study ($R^2 \leq 0.5$) corroborate results obtained by Delin (2016) and Bøen and Haraldsen (2013) with the similar AL extraction. The DGT technique is known for its superior prediction of plant P content in annual crops grown on soils with large variation of their characteristics (e.g. pH, carbonate content) as compared to other methods such as Colwell P or Resin P (Mason et al., 2010). Being an infinite-sink method, DGT can be considered a mechanistic surrogate of P uptake by plant roots (Degryse et al., 2009), and with ferrihydrite as binding agent it performs well under a wide range of soil chemical properties (Mason et al., 2008, 2013).

Strictly speaking, our interpretations are limited to our experimental crop and soil, but it can be expected that for cereals and other annual crops the DGT method will perform better than other tests (Mason et al., 2010; Six et al., 2013).

3.3. Implications for the development of recycling fertilizers

Plant P availability from (recycling) fertilizers samples is typically assessed by chemical extractions. Our data confirmed existing evidence that standard fertilizer extracts (FA, CA, NAC, H_2O) are poor predictors of plant availability from highly contrasting recycling fertilizers. They may describe P availability well for certain types of samples such as FA for some biochars from manure and anaerobic residue (Wang et al., 2012), but the accuracy of the method must be verified beforehand for the specific set of fertilizers.

Although plant experiments may have to be performed at final stages of product development, their costs and time requirements limit their applicability during the early phases of fertilizer development, during which multiple process parameters need to be varied for

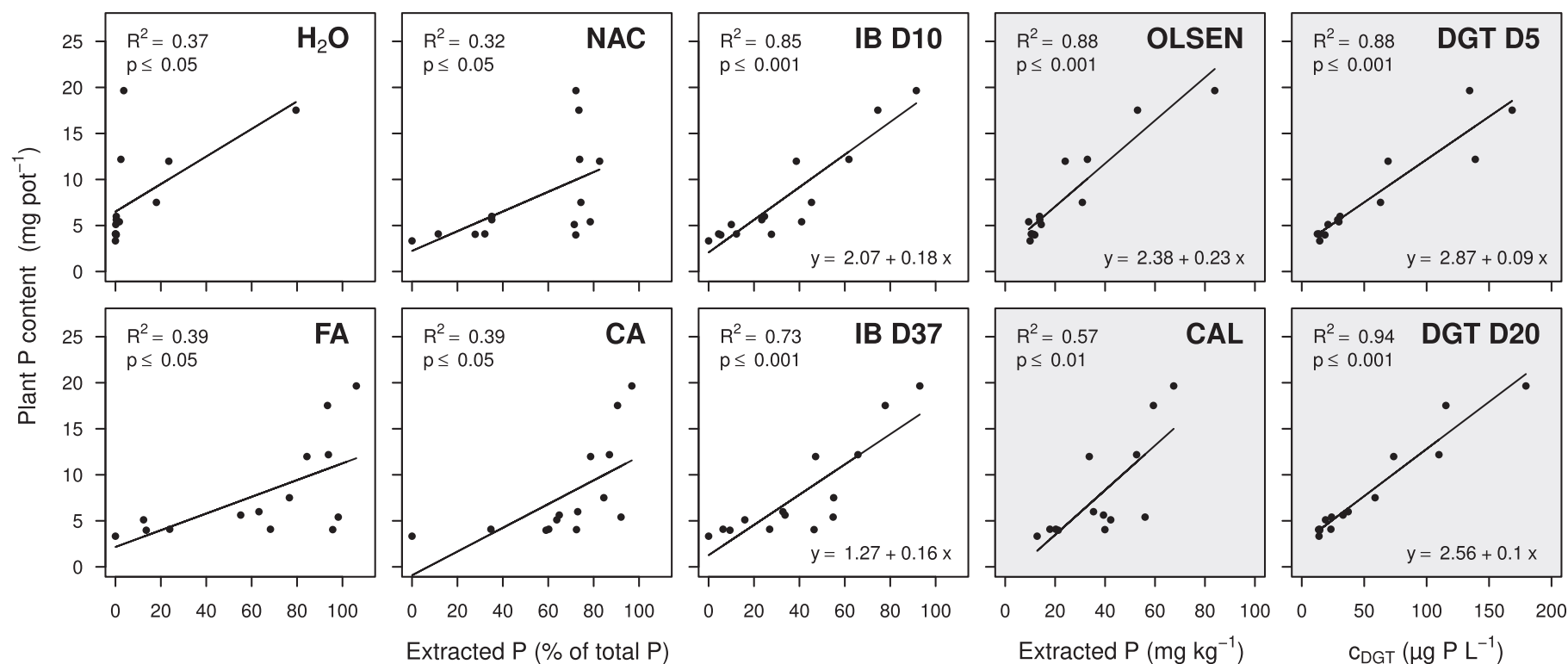


Fig. 4. Linear fitting of plant P content in shoot dry matter vs. P tests. Fertilizer tests (white background): Water (H₂O), neutral ammonium citrate (NAC), 2% formic acid (FA), 2% citric acid (CA), and iron bag (IB) after 10 and 37 days of extraction (IB D10 and IB D37 respectively). Soil P tests performed on fertilized soils (grey background): Olsen P, calcium acetate lactate (CAL), diffusive gradient in thinfilms after 5 and 20 days of incubation (DGT D5 and DGT D20, respectively). Each point is the mean of 3 (x-axis) and 4 replicates (y-axis), except y-axis for biogas slurry ($n = 1$) and chicken manure biochar ($n = 2$). Linear equations are given only for the best fits ($R^2 > 0.7$).

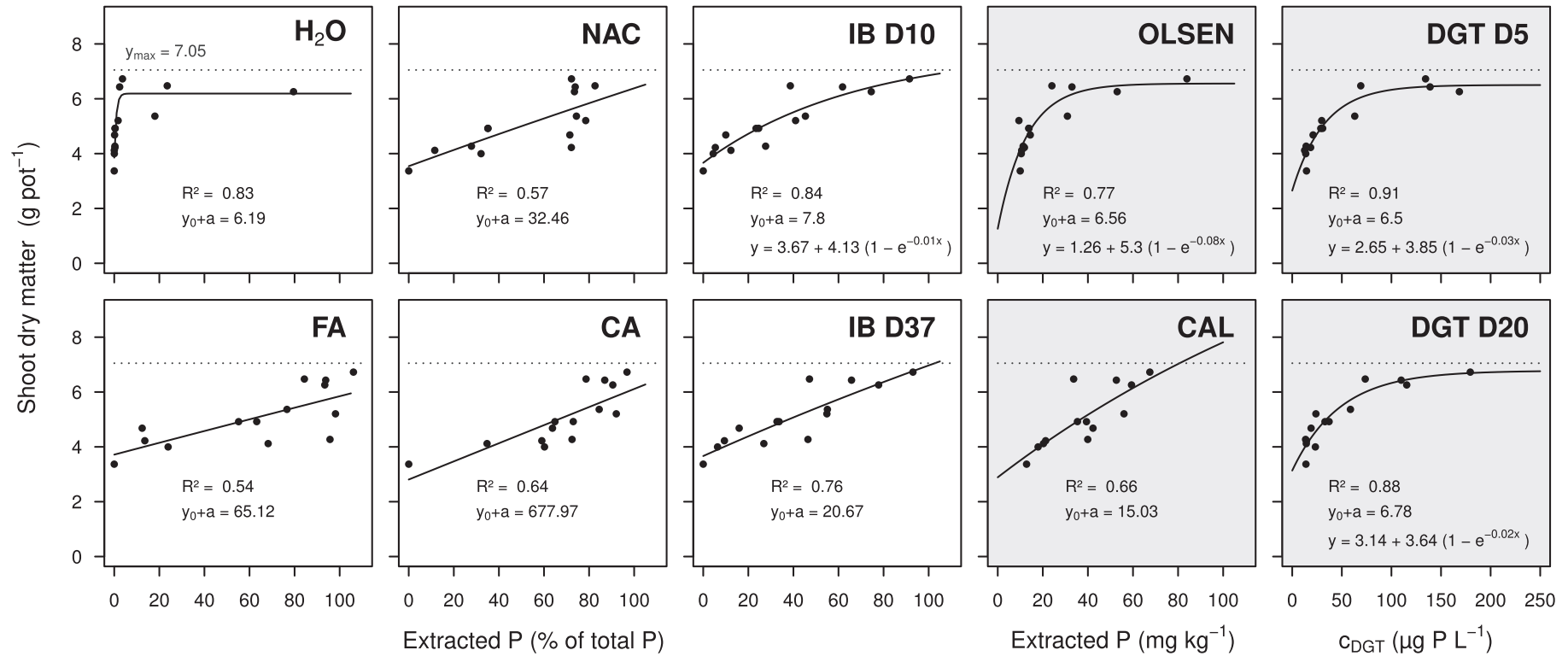


Fig. 5. Fitting of rye shoot dry matter production at termination of the pot experiment (6 weeks after planting) against fertilizer extracts with Mitscherlich function. Fertilizer tests (white background): Water (H₂O), neutral ammonium citrate (NAC), 2% formic acid (FA), 2% citric acid (CA), and iron bag (IB) after 10 and 37 days of extraction (IB D10 and IB D37, respectively). Soil P tests performed on fertilized soils (grey background): Olsen P, calcium acetate calcium lactate (CAL), diffusive gradient in thinfilms after 5 and 20 days of incubation (DGT D5 and DGT D20, respectively). y₀ + a represents the fitted maximum yield. Dotted horizontal line: Measured maximum yield (y_{max}) under the same experimental conditions in a preliminary experiment. Each point is the mean of 3 (x-axis) and 4 replicates (y-axis), except y-axis for biogas slurry (n = 1) and chicken manure biochar (n = 2). Equations of the fitted Mitscherlich curve are given only for the best fits (R² > 0.7 and y₀ + a = y_{max} ± 15%).

screening and product optimization in terms of nutrient solubility and release kinetics. Moreover, results of plant experiments strongly depend on the particular experimental system (soil-crop combination) chosen. As we could show, infinite-sink methods are superior to classical extractions and can be considered surrogates of plant uptake while being independent of plant factors such as root exudation and root growth, which vary largely with plant species, cultivar, soil and environmental growth conditions.

To account for fertilizer properties as such, as well as the fate of the nutrient in contact with soil we propose a combined approach, using the soil-independent IB method along with assessment of nutrient availability by DGT in standardized test soils of contrasting diffusibility and desorption controls for nutrients. This could include a set of soils with different texture, organic matter content, pH and carbonate content. Our approach holds also promise for routine testing of conventional as well as recycling fertilizers.

4. Conclusions

Our results provide further evidence that the validity of standard P fertilizer tests as a measure of plant available P has to be reconsidered in the context of recycling fertilizers, in particular when very contrasting samples are investigated. The need to use a mechanistic approach to soil P testing and to account for soil chemistry does not yet allow for an inexpensive and universal test to replace them. However, the main application of the more time consuming methods presented here is the screening of new fertilizers to refine process parameters prior to more expensive experiments. Confirmation of our results with other soils and crops are still required.

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