



Predicting relative agronomic efficiency of phosphorus-rich organic residues



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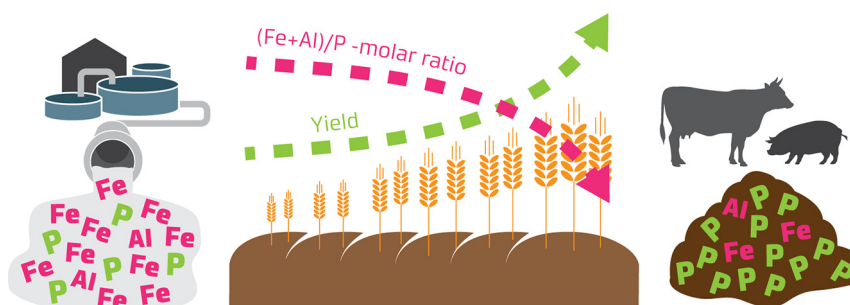
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HIGHLIGHTS

- The RAE of organic P sources must be known to optimize their use as fertilizers.
- RAE was determined by growing barley to maturity in three consecutive years.
- Molar ratio of (Fe+Al)/P in residues with low Ca content predicted RAE best.
- Pyrolyzation and HTC treatment depressed RAE of sewage sludge down to a few percent.

GRAPHICAL ABSTRACT



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ABSTRACT

Relative agronomic efficiency (RAE) of phosphorus (P) in nutrient-rich residues with different chemical characteristics must be known in order to optimize their use as fertilizers, to avoid underfertilization of crops or eutrophication of surface waters due to overfertilization. In this study, we determined the chemical characteristics and RAE of manures (cattle, pig, fox) and sewage sludges subjected to different treatments (anaerobic digestion, composting, lime stabilization, thermal hydrolyzation, pyrolyzation, hydrothermal carbonization (HTC)) by growing barley (*Hordeum vulgare*, var. Elmeri) to maturity in three independent growth trials. All manures had high RAE (up to 189% in pig slurry), while RAE was only 6–17% for digested and composted sewage sludges when precipitation with Fe used for P removal from wastewater. Pyrolyzation and HTC further depressed RAE to 1–6%. Alternative wastewater treatment processes are therefore needed to increase P recycling potential. For cattle and pig manures and anaerobically digested or composted sewage sludges, molar ratio of (Fe + Al)/P, varying from 0.08 to 2.69, was the best predictor of RAE ($R^2 = 0.99$), with negative correlations with grain yield. Sources in which calcium was more influential for P solubility (fox manure and lime-stabilized sewage sludge) and pyrolyzed and HTC-treated residues did not follow this trend. Conventional extraction methods (2% formic acid, 2% citric acid, neutral ammonium citrate, water and 0.5 M NaHCO_3) either underestimated or overestimated RAE of P-rich organic residues, depending on their chemical characteristics.

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1. Introduction

Efficient recycling of nutrient-rich residues is needed to decrease the current dependency on mineral phosphorus (P) fertilizers based on finite P resources (Cordell et al., 2009). To fully close P cycles, it is

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essential to optimize use of nutrient-rich residues in crop production and to assess their relative agronomic efficiency (RAE) against that of mineral P fertilizers. Manures and sewage sludges, the major contributors to these residues, have different chemical characteristics and P solubility rates, which complicates interpretation of their P fertilization value. Moreover, processing of residues is needed to reduce transportation costs and to allow distribution of nutrients to wider areas, thus avoiding nutrient accumulation in hot-spot regions, but it also modifies the properties of the residues and concentrates the non-volatile nutrients present. Thermochemical treatments, such as slow pyrolysis and hydrothermal carbonization (HTC), can be applied to reduce the volume of residues. The end-product, biochar, is suggested to allow carbon sequestration and improve soil fertility (Bolan et al., 2012; Lehmann et al., 2006).

The fertilizer value of nutrient-rich residue-based products depends on their chemical composition. For manures, it is greatly affected by the diet of the animals, while for sewage sludge the P removal technology used in wastewater treatment plants is critical for the RAE. In wastewater treatment plants P is often removed from the incoming effluent by precipitation chemicals containing iron (Fe) and aluminum (Al), but these can drastically lower P solubility in the resulting sewage sludge (Elliott et al., 2005; Kahiluoto et al., 2015; Maguire et al., 2001; Miller and O'Connor, 2009; Vogel et al., 2015; Øgaard and Brod, 2016). The RAE values reported for sewage sludges show great variation, ranging from 0 to over 100% (Delin, 2016; Elliott et al., 2005; Kahiluoto et al., 2015; Krogstad et al., 2005; Miller and O'Connor, 2009; Oladeji et al., 2008; Wang et al., 2012; Vogel et al., 2015; Øgaard and Brod, 2016). For different types of manures, reported RAE values vary from 30% to over 100% (Delin, 2016; Kahiluoto et al., 2015; Oladeji et al., 2008; Ylivainio et al., 2008). For biochars RAE is dependent on the feedstock and the processing conditions, but very little research has been conducted, especially with sewage sludge-based biochars (Huygens and Saveyn, 2018).

Relative agronomic efficiency is commonly determined in growth (pot) trials that are often terminated at the vegetative growth stage, before maturation of the crop. Therefore P uptake rather than crop yield is generally used to determine the fertilizer value (Delin, 2016; Elliott et al., 2005; Huang et al., 2012; Miller and O'Connor, 2009; Oladeji et al., 2008; Vogel et al., 2015). In some studies, high soil test P has been found to mask crop yield response to P fertilization (Vogel et al., 2015). In other studies, P application has been found to increase the P content in crop biomass, but not the final yield (O'Connor et al., 2004). Therefore P uptake during vegetative growth, rather than actual yield, is suggested to be the better metric when yield responses are difficult to detect (Vaneckhaute et al., 2016). However, considering only P uptake or shoot concentration in early growth stages may lead to

overestimation of the P need, due to luxury uptake with no effect on yield (Ylivainio et al., 2018). Temporal changes in crop P requirement between the biomass and grain yield formation phases (Sutton et al., 1983) further complicate yield prediction based on P uptake.

Since pot experiments are expensive, RAE is also commonly estimated for fertilizers by chemical extraction with e.g., neutral ammonium citrate, 2% citric acid, 2% formic acid, or water. These methods are included in the EU fertilizer regulations (EU 2003/2003, EU 2019/1009) for evaluating P solubility in mineral fertilizers, whereas in the new EU Fertilising Products Regulation (EU 2019/1009) only total P is considered for organic P fertilizers. However, the RAE values obtained following extraction are often poorly correlated with crop growth (Brod et al., 2015; Elliott et al., 2005; Wang et al., 2012; Vogel et al., 2015; Øgaard and Brod, 2016). Against this background, in this study we: 1) estimated RAE for different types of P-rich organic residues by growing barley to maturity in pot experiments; and 2) used the grain yields obtained as reference to evaluate simple laboratory tests for their ability to estimate the RAE of the different P-rich organic residues tested in the pot experiments.

2. Materials and methods

2.1. P-rich organic residues

A total of 19 P-rich organic residues with differing chemical composition, some represented by more than one independent sample, were used in three independent pot experiments (I-III) (Table 1). Cattle slurry (CS) and pig slurry (PS) were obtained from the Natural Resources Institute Finland (Luke) research stations at Maaninka and Hyvinkää, respectively. These represented slurries from farm animals fed typical production diets. Composted (over 12 months) cattle manure (CMC), containing both peat and straw bedding material, fox manure (FoxM), from under the cages on a fur production farm, were collected from private farms in the Jokioinen region of Finland. Anaerobic digestate containing a mixture of pig slurry and side-streams from enzyme production and the food industry (PS-EF) was obtained from a commercial biogas plant operated by Biovacka (now Gasum) in Vehmaa, Finland.

Sewage sludge samples were obtained from three facilities, two in Finland (from Helsinki Region Environmental Services Authority, HSY (SS-H) and Biovacka Turku (SS-T)) and one in Sweden (Gothenburg) (SS-G). Sewage sludge treatment in Helsinki comprises mesophilic, anaerobic digestion, while in Turku it comprises thermal hydrolyzation (150 °C, 20 bar, 20 min). The Helsinki facility uses Fe-salts for chemical P precipitation, while SS-T originates mainly from surrounding

Table 1
Chemical composition (g kg⁻¹, air-dry weight basis) of the different P-rich organic residues used in three independent (I, II, III) pot experiments with barley.

Material	Material processing	P	N	Fe	Al	Ca	C	(Fe + Al)/P-molar ratio
Cattle slurry (CS): I	Untreated	6.3	24.7	2.0	0.3	10.6	400	0.24
Cattle manure (CMC): I	Composting	3.0	18.7	1.0	0.5	3.8	440	0.37
Pig slurry (PS): I, II	Untreated	10.9	20.2	1.2	0.2	13.0	408	0.08
Fox manure (FoxM): I	Untreated	33.1	37.9	1.4	0.2	47.1	342	0.03
Pig slurry and side-streams from enzyme and food industry (PS-EF): III	Digesting	19.9	19.8	21.0	8.1	12.3	147	1.06
Sewage sludge (SS-H): I-III	Digesting	28.4–34.0	28.9–34.8	88–121	4.0–7.7	19.4–29.9	248–268	2.00–2.18
Sewage sludge (SS-T): I, II	Thermal hydrolyzation	28.3, 34.2	26.9, 30.0	93, 111	14.7, 9.2	19.6, 24.9	261, 275	2.42, 2.11
Sewage sludge (SS-G): III	Digesting	27.4	51.9	29.0	7.0	15.6	376	0.88
SSc: I, II	Composting	17.8, 26.8	19.6, 25.3	75, 91	5.3, 5.2	17.0, 19.1	269, 282	2.69, 2.11
Sewage sludge (SSIs): I, II	Lime stabilization	21.0	15.4	83	5.3	117	185	2.33
Digested pig slurry and side-streams from enzyme and food industry (PS-EF-HTC): III	HTC	21.5	14.3	24	9.2	13.8	129	1.12
Sewage sludge (SS-H-Pyr): II	Pyrolysis	48.6	30.0	169	9.5	43.0	193	2.16
Sewage sludge (SS-H-HTC): II, III	HTC	45.1, 43.4	24.3, 23.3	148, 159	6.2, 6.1	43.2, 38.5	263, 275	1.97, 2.18
Sewage sludge (SS-G-HTC): III	HTC	37.8	40.3	42	10.3	22.9	415	0.94

wastewater treatment plants also using Fe-salts for P precipitation. Sewage sludge treatment and P removal in Gothenburg involves a combination of biological and chemical treatments. All three products are dewatered by centrifuging after processing.

SS-H was further composted (SSc) or stabilized with lime (SSIs) by HSY. Composting was done by mixing SS-H with peat at a ratio of 1:1 (v/v) and composting for: i) about 6 months, with mixing twice during the composting period (used in experiment I); or ii) for about 10 months, with mixing three times during the composting period (used in experiment II). Stabilization with lime was performed by mixing SS-H with CaO at a rate of 95 kg t⁻¹. Samples for the experiments were taken from the pile 6 months after lime addition.

SS-H was also pyrolyzed (SS-H-Pyr) in the laboratory. First, the sludge sample was dried at 105 °C, crushed, and fractionated by sieving. Pyrolysis was performed on the 1–4 mm size fraction, which was transferred to a laboratory oven constantly flushed with nitrogen gas and heated to 300 °C, kept at the target temperature for 60 min, and cooled in a desiccator.

Samples of SS-H, SS-G, and PS-EF were also hydrothermally carbonized (SS-H-HTC, SS-G-HTC, PS-EF-HTC, respectively) in the laboratory for pot experiment III. For pot experiment II, the same batch of SS-H was both pyrolyzed and HTC-treated. Hydrothermal carbonization was carried out using a rotating air bath autoclave reactor with four parallel 300 g Stainless Steel 316 l tube reactors. The reactors were first heated to 230 °C for 60 min and, after 20 min residence time, the reactors were cooled for 20 min to 180 °C, where the residence time was 60 min.

All manure- and sewage sludge-based P sources were air-dried at room temperature and milled to pass through a 1-mm sieve prior to the laboratory analyses, or passed through a 6-mm sieve prior to the pot experiments (I–III). The reference for P-rich organic residues used was superphosphate, which was only milled for the laboratory analyses.

2.2. Laboratory analyses

The materials were analyzed according to a modified Hedley fractionation scheme (Sharpley and Moyer, 2000) for distributing P to different solubility fractions. Fractionation consists of sequential extraction with water (twice), 0.5 M NaHCO₃, 0.1 M NaOH, and 1 M HCl, with extraction ratio 1:60 (w/v). Residual P content was not analyzed. Extraction was conducted in an end-over-end shaker (27 rpm) and extraction time was 16 h except for the first water extraction, for which it was 4 h. Following extraction, the samples were centrifuged at 3000g for 15 min. Inorganic P (Pi) was determined after the supernatants were filtered through a 0.2 µm nucleopore membrane (Whatman, Maidstone, UK). Total P was determined on unfiltered supernatant after autoclave digestion at 120 °C with sulfuric acid and peroxodisulfate. All P concentrations were analyzed using the molybdate colorimetry method (Murphy and Riley, 1962). Organic P (Po) was taken as the difference between total P and Pi.

Extraction of P-rich organic residues with 2% formic acid and 2% citric acid followed the method of Rajan et al. (1992). Extraction was conducted in 1:100 (w/v) solid to solution ratio on an end-over-end shaker (27 rpm) at room temperature for 30 min. Centrifuged (3000g, 15 min) and filtered (0.2 µm membrane) supernatants were analyzed as above (Murphy and Riley, 1962). Neutral ammonium citrate was prepared according to AOAC Official Method (2005) using these same settings with the exception that the extraction time was 24 h.

Total P, Fe, Al and Ca concentrations in the P sources were analyzed by ICP-OES (Thermo Jarrell Ash Iris Advantage) after aqua regia digestion. The carbon (C) and nitrogen (N) concentrations were analyzed using the Dumas method (LECO TruMacCN). All laboratory analyses were conducted in duplicate.

2.3. Pot experiment

The soil used in the pot experiments was a P-deficient sandy topsoil (5–25 cm layer) (Table 2). Due to a previous cropping history of unfertilized grass, the 0–5 cm surface layer was excluded. The soil was taken from the same field as used by Kahiluoto et al. (2015). The soil was air-dried, passed through a 14-mm sieve, and used in the three independent pot experiments (I–III) during three consecutive years (2012–2014). Soil texture was analyzed by the pipette method (Elonen, 1971). Extractable P content was analyzed using the following soil test P methods: Mehlich-3 (Mehlich, 1984), Olsen (Kuo, 1996), acid ammonium acetate, pH 4.65 (Vuorinen and Mäkitie, 1955) and Hedley fractionation as described in Section 2.2. Soil pH was measured in water suspension (1,2.5 v/v).

Barley (*Hordeum vulgare* var. Einari) was grown in the pots under a glass roof at ambient summer air temperature. Soil (6.5 kg) was weighed into Mitscherlich type pots. For experiment I, the soil (pH 5.8) was not limed. For experiment II, the soil (pH 5.5) was limed (9 days prior to planting) to raise the pH to the same value as in experiment I, by adding 5.6 g of Ca(OH)₂. For experiment III, 20.8 g of Ca(OH)₂ were added (14 days prior to planting) to raise the soil pH to 6.5. Before mixing nutrients into the soil, 0.5 l of soil was removed and sieved (4 mm), after which the following amounts of nutrients (mg kg⁻¹) were mixed into the soil volume to avoid deficiency: 308/231 N (as Ca(NO₃)₂ and NH₄NO₃), 308 potassium (K, as KCl), 46 magnesium (Mg, as MgSO₄), 220 calcium (Ca, as [Ca(NO₃)₂]), 3 Fe (as FeSO₄), 3 zinc (Zn, as ZnSO₄), 3 manganese (Mn, as MnSO₄), 1.5 copper (Cu, as CuSO₄), 0.3 boron (B, as H₃BO₃), and 0.3 molybdenum (Mo, as Na₂MoO₄). Sulfur (S) was added in a total amount of 66 mg kg⁻¹ as sulfates. Of the applied N, 25% was given as NH₄-N and 75% as NO₃-N, to reduce the pH effect on soil caused by the uptake of NH₄-N and NO₃-N by barley. In experiments I and II, an N dose of 308 mg kg⁻¹ was applied when establishing the experiment, whereas 231 mg kg⁻¹ N was applied in experiment III. Sources of P-rich organic residues (40–150 mg P kg⁻¹) and increasing superphosphate P rates (Experiment I: 0, 10, 50, and 100 mg kg⁻¹, Experiment II: 0, 10, 25, 50, 100, and 150 mg kg⁻¹ and Experiment III: 0, 10, 50, and 150 mg kg⁻¹) were mixed with the soil at the same time as the other nutrients, based on the total P content. Based on our earlier experience of the yield responses, different amounts of P-rich organic residues were applied to obtain grain yields on the increasing part of the yield response curve produced by superphosphate. The actual P sources used in each of the three independent pot experiments

Table 2
Properties of the soil used in the pot experiments.

<i>Particle size distribution, %</i>	
<0.002 mm	4
0.002–0.02 mm	4
0.02–0.2 mm	58
0.2–2 mm	34
<i>Soluble nutrients</i>	
Olsen-P, mg kg ⁻¹	12.6
Mehlich 3-P, mg l ⁻¹	12.6
<i>AAAc^a</i>	
P, mg l ⁻¹	1.9
Ca, mg l ⁻¹	911
Mg, mg l ⁻¹	115
K, mg l ⁻¹	74
<i>Hedley fractionation, mg kg⁻¹</i>	
Water	9.1 (17% as Pi)
0.5 M NaHCO ₃	65.2 (47% as Pi)
0.1 M NaOH	224 (62% as Pi)
1 M HCl	115
pH (1:2.5), water extraction	5.8
Total C	2.82
Total N	0.17

^a Acid ammonium acetate, pH 4.65.

are indicated in Table 1 and the application rates in Table 3. In the case of SSIs and PS, the same air-dried material was used in experiments I and II, whereas the other P-rich organic residues used in experiments I-III were collected prior to the experiments. All treatments had four replicate pots.

A total of 25 seeds per pot were sown and covered with soil (sieved 0.5 l). After emergence, the plants were thinned to 20 per pot. Throughout the experiments, the plants were irrigated with deionized water based on evapotranspiration. At the stem elongation stage, an additional N dose of 154 mg kg⁻¹ (25% as NH₄-N, 75% as NO₃-N) was applied to all treatments.

Matured barley plants were cut about 3 cm above the soil surface and the biomass was dried at 65 °C and weighed. The grains were then separated out and the thousand grain weight was recorded. Whole grain yields were milled in a hammer mill and the P concentration was analyzed by ICP-OES (Thermo Jarrell Ash Iris Advantage/Perkin Elmer Optima 8300) after digestion with concentrated HNO₃. Concentration of N in grains was analyzed with the Kjeldahl method.

To estimate RAE of P in the P-rich organic residues tested, barley grain yields were evaluated against the yield response curve for superphosphate-P, fitted with equation: $y = A + B * (1 - e^{-Cx})$, where A is the minimum grain yield (y-axis intercept), B is the maximum yield, C is a fitting coefficient, and x is the amount of P applied (mg kg⁻¹). For calculating RAE, this equation was used to calculate the amount of superphosphate-P required to produce the corresponding yield to a given P-rich organic residue, and this amount was then made proportional to the amount of total P applied in the P-rich organic residues.

For the soil used in experiment I, each pot was cored at five spots after harvest and the cores were pooled to give a sample of about 200 g. These were air-dried (35 °C), milled (2 mm) and analyzed for P solubility according to the Hedley fractionation scheme (Sharpley and Moyer, 2000) and for soil pH.

2.4. Statistical analyses

Logarithmic (soil pH in experiment II), square root (barley grain yield in experiment III and N content in barley grain in experiment III) or reciprocal (thousand grain weight in experiment II and P concentration of

Table 3

Barley grain yield (g pot⁻¹) and relative agronomic efficiency (RAE, %) of phosphorus (P) in three pot experiments in consecutive growing seasons. For treatment abbreviations, see Table 1.

Treatment	P application rate, mg kg ⁻¹ soil	Experiment I Year 2012		Experiment II Year 2013		Experiment III Year 2014	
		Yield	RAE	Yield	RAE	Yield	RAE
Control	0	7.0 ^a		11.3 ^a		3.1 ^a	
CS	40	53.7 ^{ef}	137				
CMc	40	47.1 ^{de}	106				
PS	40	61.3 ^{ef}	189	55.6 ^{de}	137		
FoxM	100	59.9 ^{ef}	71				
PS-EF	150					49.2 ^e	35
SS-H	150	35.3 ^{cd}	17	30.2 ^{bc}	11	21.1 ^d	10
SS-T	150	24.1 ^{bc}	10	21.7 ^{abc}	6		
SS-G	150					65.5 ^f	68
SSc	150	17.4 ^{ab}	6	28.0 ^{bc}	10		
SSIs	150	57.8 ^{ef}	43	51.1 ^d	31		
PS-EF-HTC	150					7.6 ^b	2
SS-H-Pyr	150			16.5 ^{ab}	3		
SS-H-HTC	150			12.5 ^a	1	4.9 ^{ab}	1
SS-G-HTC	150					14.5 ^c	6
SP	10	14.3 ^{ab}		21.6 ^{abc}		14.4 ^c	
SP	25			35.2 ^c			
SP	50	54.1 ^{ef}		56.1 ^{de}		48.8 ^e	
SP	100	65.5 ^f		67.7 ^{ef}			
SP	150			76.0 ^f		71.4 ^f	

Values within columns followed by different letters are significantly different ($p < 0.05$, Tukey's test). Experiments tested separately.

barley grain in experiment III) transformation was applied for data normalization and homogenization of variance (Levene's test). After transformation, one-way ANOVA with a Tukey's post-hoc test or, in the case of unequal variances (Hedley fractionation for experimental soil in experiment I) Games-Howell post-hoc test, were used to evaluate the statistical significance of differences ($p < 0.05$) in barley yield, thousand grain weight, P and N concentration in grains, total N and P content in grain yield, and soil parameters (Hedley fractionation, soil pH) between treatments, using SPSS software (IBM SPSS Statistics 26).

3. Results and discussion

3.1. Phosphorus content and solubility in P-rich organic residues

Total P content in the 19 P-rich organic residues sources tested varied between 3.4 and 48.6 g kg⁻¹, with the lowest value obtained for CMc and the highest for SS-H-Pyr (Table 1). Most of the P in the CS, PS and CMc was water-extractable, whereas that contained in FoxM was mostly acid-soluble P, confirming findings in our earlier study (Ylivainio et al., 2008). In sewage sludges, P was mainly extracted by 0.1 M NaOH (Fig. 1), representing P bound to precipitation chemicals of Fe and Al, i.e., with limited solubility (Elliott et al., 2005; Kahiluoto et al., 2015; Maguire et al., 2001; Miller and O'Connor, 2009; Vogel et al., 2015; Øgaard and Brod, 2016). The sewage sludge-based materials used in this study had a high (Fe + Al)/P molar ratio (Table 1) and Fe concentration was much higher than the Al concentration (Table 1), and thus P solubility was likely controlled more by Fe. Among the sewage sludges, the water-soluble P fraction was highest (16.8%) for the Swedish product (SS-G), which had the lowest (Fe + Al)/P molar ratio (0.88). Similarly, Qian and Jiang (2014) found that the share of water-extractable P in sewage sludge was as high as 20.7% despite high (Fe + Al)/P molar ratio (1.56), but low Fe/P molar ratio (only 0.19). In the sewage sludges of Finnish origin, the water-soluble P fraction was at most 0.2% and (Fe + Al)/P molar ratio was 2.0–2.7 (Table 1). Composting SS-H had no effect on its P solubility, whereas lime stabilization reduced the proportion of Fe-bound P and increased the proportion of acid-soluble (1 M HCl) P (Fig. 1). Similar transformation has been observed in other studies (Huang et al., 2008; Kahiluoto et al., 2015). It has been attributed to increased solubility of Fe-associated P as a result of competition from OH⁻ anions and simultaneous precipitation of solubilized P as Ca-phosphates (Brown, 1981; Hingston et al., 1967; Hsu, 1964), and was probably the reason for the increased 0.5 M NaHCO₃-extractable P content (Fig. 1).

Both pyrolysis and HTC treatment reduced the proportions of water-extractable and 0.5 M NaHCO₃-extractable P forms, HTC more than pyrolysis, as reported by Fei et al. (2019). The proportion of acid-soluble P forms increased, as also shown by others (Fei et al., 2019; Keskinen et al., 2019; Mackay et al., 2017; Qian and Jiang, 2014), probably originating from the originally Fe-bound (0.1 M NaOH) P fraction (Fig. 1). Increases in acid-soluble P forms may also indicate formation of hydroxyapatite (Robinson et al., 2018) after changes in the chemical and physical states of P (Huang and Tang, 2015). The share of organic P was highest in CS (18.2%), followed by SSc (8.4%) and PS (7.7%). The majority of the organic P was extracted with 0.1 M NaOH (Fig. 1). The share of organic P found is comparable to that reported by Sharpley and Moyer (2000).

The P extraction efficiency of formic acid, citric acid, and neutral ammonium citrate was similar for all manures tested, with a minimum extraction efficiency of 75% of total P. In contrast, there was great variation in extraction efficiency for the sewage sludge-based materials, with formic acid extracting least total P (Fig. 2). The extraction efficiency of formic acid correlated well with the molar ratio of (Fe + Al)/P ($R^2 = 82\%$) and Fe/P ($R^2 = 87\%$), whereas the correlation was weaker for citric acid and neutral ammonium citrate (Fig. A.1). In this study, neutral ammonium citrate extracted the majority of total P when the molar ratio of Fe/P was low, as observed previously by Elliott et al. (2005) for biosolids

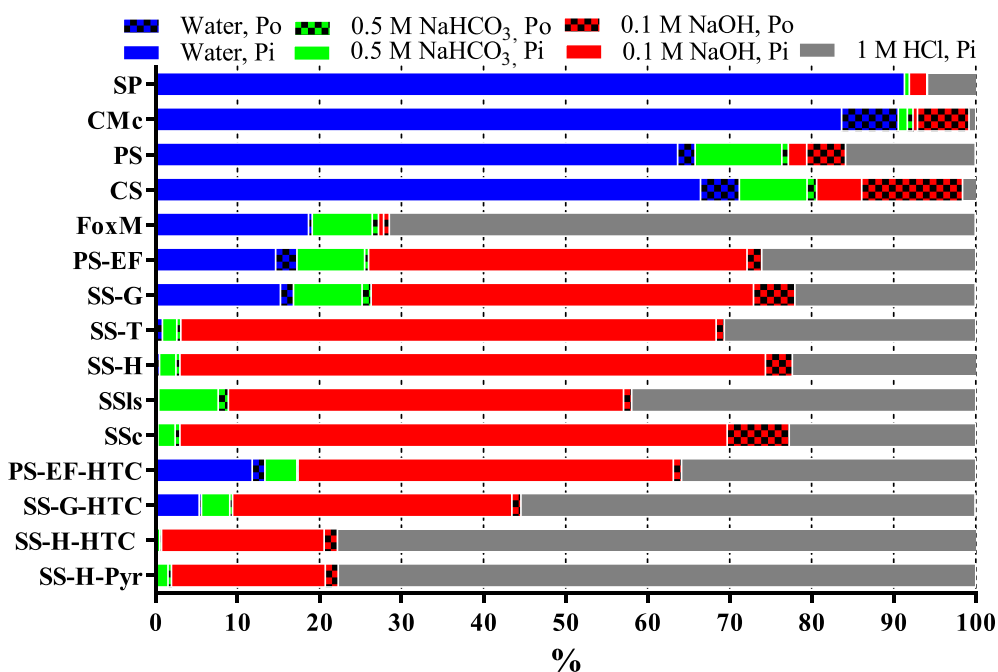


Fig. 1. Share of inorganic phosphorus (Pi) and organic phosphorus (Po) fractions in the different P sources studied, according to the Hedley fractionation scheme (without residual P). On average, sum of P fractions was 1% less than total P (Table 1). For treatment abbreviations, see Table 1.

and by Wang et al. (2012) for pyrolyzed sewage sludge. The HTC treatment reduced P solubility most for sewage sludges with a high (Fe + Al)/P molar ratio (Fig. 2). In contrast, HTC increased the P solubility of PS-EF estimated with all three extraction methods (Fig. 2). These results indicate that the Fe content of the material may be decisive for P solubility following treatment with HTC, so this treatment would be better suited to sewage sludges originating from wastewater treatment plants with biological P removal. The Fe in the liquid phase during the HTC process (Huang and Tang, 2015) would probably lower the P solubility in biochar.

3.2. RAE of P-rich organic residues in the pot experiments

In the pot experiments with P-deficient soil, barley grain yield was increased by up to 22-fold by P fertilization (Table 3). This high yield

response was due to extremely low soluble P content in the experimental soil, which belonged to the lowest P fertility class in Finland. The yield responses after superphosphate application were comparable in experiments I-III (Fig. A.2), indicating similar growing conditions. Furthermore, variations in soil pH between the experiments (Table A.1) did not affect superphosphate-P bioavailability. This is in line with Barrow (2017) and with studies on RAE of precipitated phosphate salts (Huygens and Saveyn, 2018). The fertilizing effect of P-rich organic residues decreased in the order: manures > sewage sludges > thermochemically treated sewage sludges (Table 3). The suggestion by Delin (2016) that the RAE of various residues depends more on their pH-altering effect on soil than on their chemical composition was not supported by our results. In our study, PS had the highest RAE (189%, soil pH 5.8), followed by CS (137%, soil pH 6.0), SS-G (68%, soil pH 6.4), SSIs (43%, soil pH 6.3), PS-EF (35%, soil pH 6.4), and SS-H

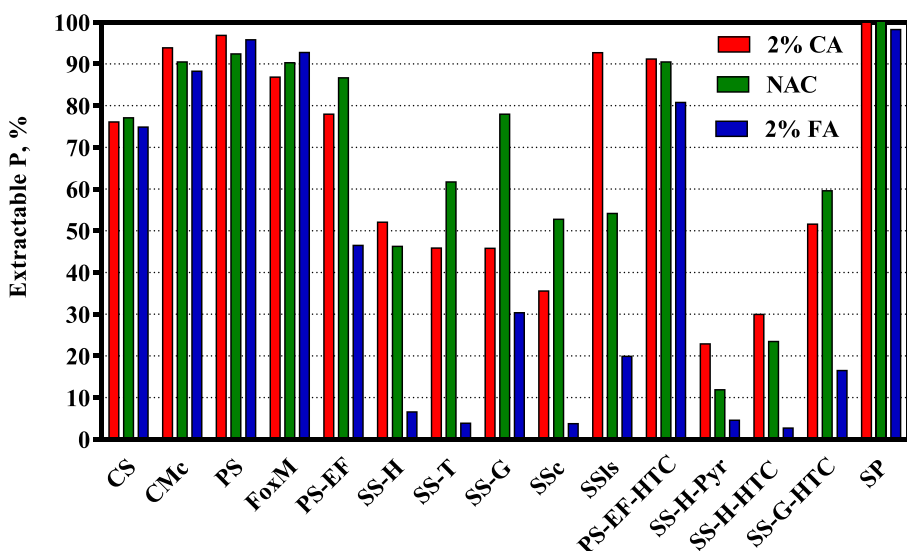


Fig. 2. Phosphorus extracted (% of total P) with 2% citric acid (CA), neutral ammonium citrate (NAC), and 2% formic acid (FA). For treatment abbreviations, see Table 1.

(10%, soil pH 6.2). The SS-H material was tested in all independent growing seasons and RAE was found to be at the same level in all three years, while soil pH at the end of the experiment varied from 5.4 to 6.2 (Table A.1). This suggests that other characteristics of the P-rich organic residues, rather than their pH effect, were more important in determining their RAE in the present study. Although total N application rate in P-rich organic residues was higher than in superphosphate treatments, N concentration and content in barley yields were not higher than in the best grown superphosphate-P treatment (Table A.3), suggesting no confounding effect of N on barley yields.

In our study, all P sources were mixed with the whole soil volume just before planting, to ensure better comparability between the materials. In the study by Delin (2016), P-rich organic residues were added to soil two months prior to planting and mineral P was applied upon planting. This may have affected P solubility, which is known to decline with time when in contact with soil (Sillanpää, 1961). Moreover, we tested P-rich organic residues in soil with extremely low soil test P value (Table 2), which is in line with the principle of fertilizing with P only in cases where P application produces clear yield increases (Valkama et al., 2011). With this same P-deficient soil, PS and CS increased water-soluble P content to a higher level than the corresponding amount of superphosphate-P after a two-week incubation period (unpublished data). It is argued that the high phytic acid content in pig manure (He and Honeycutt, 2001) and high organic matter content in cattle slurry (Siddique and Robinson, 2003) decrease the P sorption capacity of the soil.

Yield responses to P fertilization in field conditions are far lower than observed in this study, where P availability was the only growth-limiting factor. However, RAE has been found to be similar for the same P-rich organic residues in pot trials (Ylivainio et al., 2008) with ryegrass as test plant and field trials (Ylivainio et al., 2018) with barley as the test plant. This supports the view that pot trials can be used for determining RAE for various P sources, but that application rates of P sources need to be adjusted to soil P status in order to avoid over-fertilization, which will lead to maximum yield, so RAE cannot be determined.

When interpreting Hedley fractionation results for soil P, acid-soluble P is considered to be unavailable for plants and to represent apatite-type P (Hedley et al., 1982). However, acid-soluble P in manures in this study was evidently available to plants and, especially in FoxM, represented a significant share of available P in slightly acidic soils (Ylivainio et al., 2018; Ylivainio et al., 2008). The same may also apply to SSIs. This is supported by the finding that the acid-soluble P fraction in the soil was at the same level in the control, FoxM, and SSIs treatments after the growth trial (Table A.2). These results indicate that although 71 and 42% of the P in FoxM and SSIs, respectively, was in the acid-soluble form (Fig. 1), this fraction comprised mainly secondary calcium phosphate minerals and not apatite-type P as originally suggested by Hedley et al. (1982), and their solubility is mainly governed by soil pH (Ylivainio et al., 2008).

Phosphorus originating from digested or composted sewage sludges was poorly utilized by barley. This contradicts earlier findings by Kahiluoto et al. (2015) that sewage sludge-based P can be considered a comparable P source to mineral P fertilizer. In their study, “potentially plant available P” was interpreted as the sum of ryegrass P uptake and Hedley fractions of water-, 0.5 M NaHCO₃- and 0.1 M NaOH-extractable P in soil after the experiment. However, our data do not support the view that 0.1 M NaOH-extractable P of sewage sludge origin is plant-available, at least during one growing season, as also concluded by McCoy et al. (1986). After the pot experiment, 80% of the P originating from chemically precipitated sewage sludge was in 0.1 M NaOH-extractable form (Table A.2), and probably still bound to the P precipitation chemicals (mainly excess Fe). Superphosphate also increased 0.1 M NaOH-extractable P content in soil, most probably due to inherent soil Fe being able to bind the applied P (Ylivainio and Peltovuori, 2012). Thus, depending on the quality of the P source applied to soil, the

resulting changes in the NaOH-extractable P fraction in soil may have drastically different interpretations in terms of P availability to plants.

Pyrolyzation and HTC both reduced the RAE of P to a few percent (Table 3). This contradicts Wang et al. (2012), who found that the fertilizer value of manure- and biosolid-based biochars was comparable to that of mineral P fertilizers, and lower only when the pyrolysis temperature was above 450 °C. However, in their study only around 40 mg P kg⁻¹ soil (soil mass 250 g) were required to achieve maximum yield of ryegrass at the first three cuts, whereas in our study much more (100–115 mg P kg⁻¹ soil; soil mass 6.5 kg) was needed to achieve 90% of the maximum barley grain yield. Soil volume in pot experiments may affect RAE, in addition to soil characteristics and crop type. Smaller soil volume may lead to better utilization of P, as roots occupy a larger relative volume when soil volume decreases and may be able to utilize P sources with lower solubility to a higher degree, increasing apparent RAE. In our study, RAE of pyrolyzed and HTC-treated sewage sludge matched the sum of water- and 0.5 M NaHCO₃-soluble P fractions, which was very low in both materials (3% and 1%, respectively).

Thousand grain weight of barley was correlated with grain yield (Fig. A.3). The number of grain heads in barley is determined in early growth stages and is affected by P availability (Brenchley, 1929) and winter wheat grain yield or grain weight has been shown to increase with P availability up to maturity (Sutton et al., 1983; Talboys et al., 2016). In our study, barley yield was similar in the PS-EF and superphosphate-P (50 mg P kg⁻¹) treatments (Table 3), but PS-EF increased thousand grain weight more (Fig. A.3), compensating for lower grain numbers. This indicates improved P availability from PS-EF for barley during the growing season, so it acts as a slow-release P fertilizer.

Phosphorus concentration in barley grain was a poor indicator of P deficiency (Table A.3). The highest concentrations, mainly above the critical concentration of 2.0–2.7 mg g⁻¹ (Hoppo et al., 1999), were in treatments with the lowest yields and extreme P deficiency, indicating that P concentration in barley grain is genetically controlled (Wang et al., 2016).

3.3. Predicting RAE of P-rich organic residues

Molar ratio of (Fe + Al)/P in manures and digested and composted sewage sludge varied from 0.03 to 2.7 (Table 1). As the molar ratio decreased, RAE improved exponentially (Fig. 3). The relationship between RAE and (Fe + Al)/P molar ratio followed the same pattern as in earlier studies on biosolids with lower (Miller and O'Connor, 2009) or higher (Fe + Al)/P molar ratio (Oladeji et al., 2008), as indicated in Fig. 3. In both those studies, P uptake was used as the criterion for P availability to a bahiagrass crop. In one, four bahiagrass stands were harvested during a four-month period (Miller and O'Connor, 2009), whereas in the

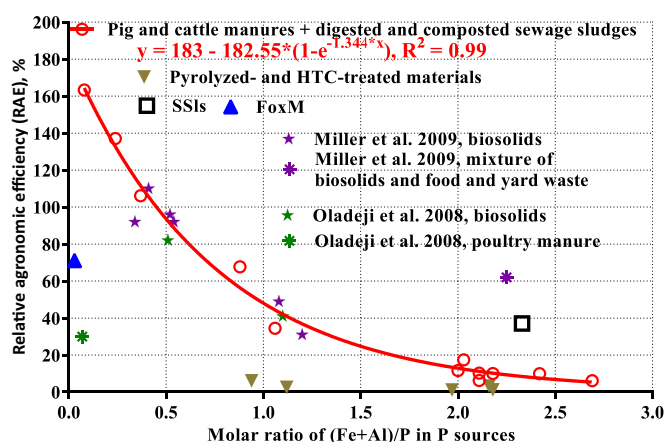


Fig. 3. Relationship between (Fe + Al)/P molar ratio and relative agronomic efficiency (RAE) of different phosphorus (P) sources in the present and previous studies.

other bahiagrass was harvested monthly for six months (Oladeji et al., 2008). This suggests that P uptake in long-term pot trials provides comparable results, as found in our study. In another study, where (Fe + Al)/P molar ratio ranged between 2.8 and 13.0 (Øgaard and Brod, 2016), RAE based on ryegrass P uptake was 2–24% for the first ryegrass harvest

and was correlated negatively with (Fe + Al)/P molar ratio. All these findings show that (Fe + Al)/P molar ratio is a good indicator of RAE for cattle and pig manures and digested sewage sludge. This is supported by the fact that RAE was either decreased or increased, as (Fe + Al)/P molar ratio of PS-EF and SS-G either increased or decreased compared

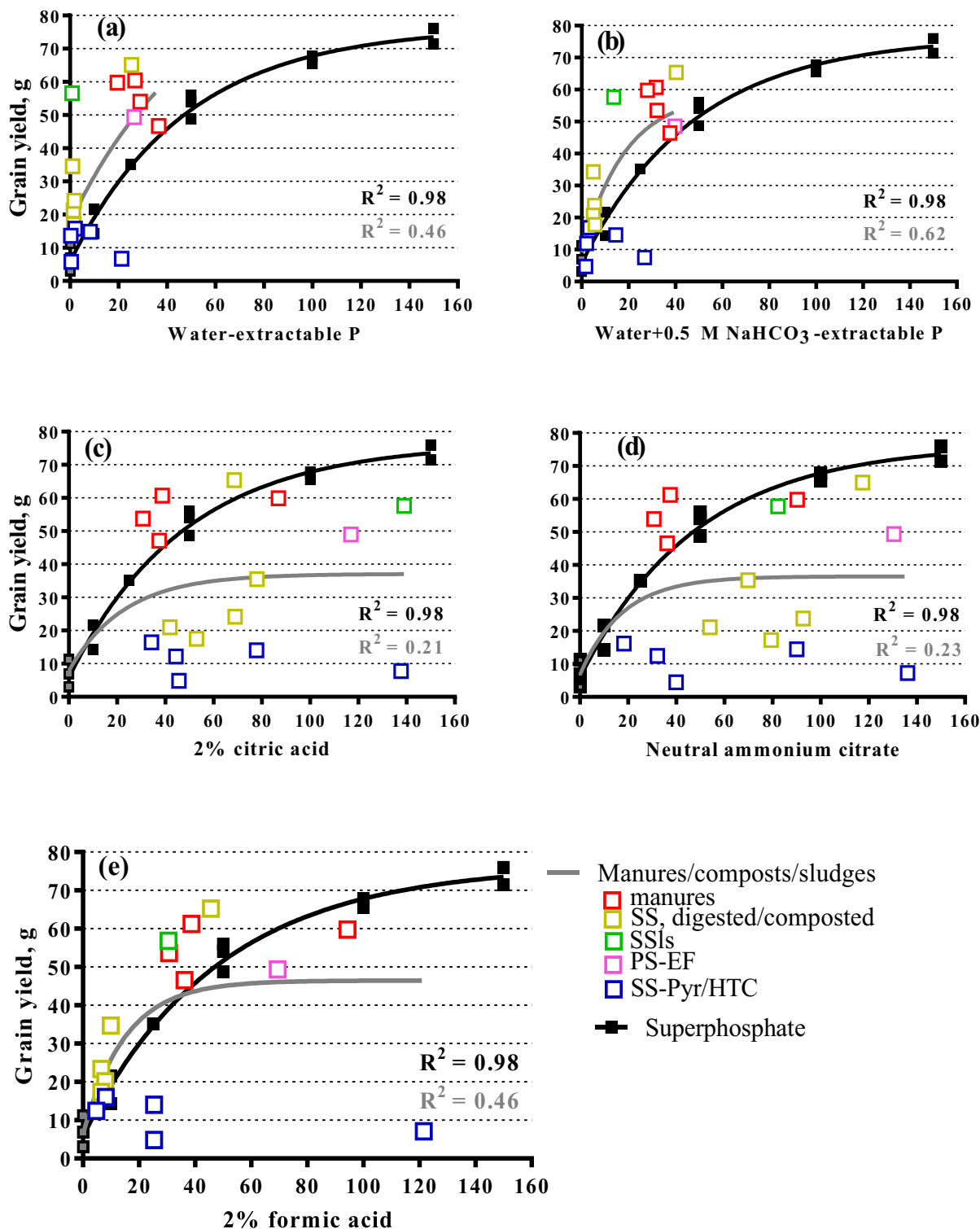


Fig. 4. Relationship between bioavailable phosphorus (P) content in organic P sources, determined with different extraction methods from total P, and barley grain yield in pot experiments. Bioavailable P content was estimated with extraction efficiency of water (a), water+0.5 M NaHCO₃-extractable P (b) according to the Hedley fractionation scheme, 2% citric acid (c), neutral ammonium citrate (d), and 2% formic acid (e), from the total P and proportionated to P amount applied in the pot experiments. Values in x-axes as mg kg⁻¹ soil. Black curves show the yield response of superphosphate in three consecutive growing seasons (reference).

with PS and SS-H or SS-T residues, respectively. Our results also show that Fe has a greater impact than Al, as Fe/P molar ratio explained RAE almost as well ($R^2 = 0.97$; $y = 186.8 - 178.5 * (1 - e^{-2.419*x})$) as (Fe + Al)/P molar ratio. This is further supported by the observation that when plotting Fe/P molar ratios of eight biosolids studied by Miller and O'Connor (2009) and Oladeji et al. (2008), four of which had higher Al/P than Fe/P molar ratio and one equal ratios, together with those in our study, Fe/P-molar ratio still predicted RAE well, with $R^2 = 0.91$ (Fig. A.4).

However, for FoxM, SSIs, and thermochemically treated sewage sludges, RAE did not correlate with (Fe + Al)/P molar ratio (Fig. 3). In FoxM, the acid-soluble P fraction probably mainly originated from bones in the animals' diet (Ylivainio et al., 2008) and was not bound to Fe. Poultry manure, which also had a high Ca content, showed a similar correlation between RAE and (Fe + Al)/P molar ratio (Oladeji et al., 2008) as FoxM in this study (see Fig. 3). In SSIs, lime stabilization of sewage sludge clearly increased acid-soluble P at the expense of the 0.1 M NaOH-extractable fraction, as also shown by Øgaard and Brod (2016). The lime probably turned part of the Fe-bound P into relatively easily soluble calcium phosphate, which was plant-available in the slightly acidic experimental soil. Krogstad et al. (2005) also showed that lime stabilization of sewage sludge increased P bioavailability. In thermochemically treated sewage sludge the RAE was reduced, while the proportion of 0.1 M NaOH-soluble P decreased and that of acid-soluble increased (Fig. 1). Upon heating, P was evidently transformed into a more calcitrant form (Thomsen et al., 2017) which was less available to the barley plants (Robinson et al., 2018).

The conventional extraction methods intended to indicate P bioavailability and solubility in fertilizer materials estimated RAE of sewage sludge-based materials poorly. In particular, citric acid and neutral ammonium citrate extraction performed poorly for both digested and thermochemically treated sewage sludge-based P sources (Fig. 4). The citric acid results are in line with findings in other studies (Delin, 2016). Formic acid was better than citric acid or neutral ammonium citrate in indicating RAE, for sewage sludges with high (Fe + Al)/P molar ratio in particular. However, formic acid also overestimated RAE for thermochemically treated materials, especially PS-EF-HTC (Fig. 4). Similarly, Wang et al. (2012) concluded that formic acid was better than citric acid or neutral ammonium citrate for predicting P availability in biochars. While mild extractants (water and 0.5 M NaHCO₃) predicted P bioavailability better than citric acid, neutral ammonium citrate, or formic acid, these extractants underestimated RAE, especially in SSIs and FoxM, supporting the conclusion that acid-soluble P in these materials is converted to plant-available form in slightly acidic soils. Similar observations were made in a previous study evaluating RAE for FoxM based on ryegrass, where RAE improved during a 3-year growth trial (Ylivainio et al., 2008). The long-term P fertilizing efficiency of digested or composted sewage sludge with high (Fe + Al)/P molar ratio is questionable. Solubility tests underestimated the RAE of manures in our study, especially when RAE was above 100%, supporting the view that chemical composition and especially organic matter content and quality may be influential in improving the RAE of organic materials.

4. Conclusions

RAE of various nutrient-rich organic residues was determined from barley grain yield in pot experiments over three consecutive growing seasons, in order to optimize their use as P fertilizer from crop production point of view. The results showed that manures are good P sources for crops, whereas the P fertilizer value of digested and composted sewage sludges is reduced by the use of P precipitation chemicals and should be only used in amounts that fulfil water quality criteria. RAE of cattle and pig manures, and of digested and composted sewage sludges, was predicted best ($R^2 = 0.99$) by their (Fe + Al)/P-molar ratio, which varied from 0.08 to 2.69. With calcium phosphate-based P sources, lime-stabilized sewage sludge, and fox manure, a similar pattern in RAE was not observed and availability for crops is probably

controlled by soil pH. Common solubility tests with 2% citric acid, neutral ammonium citrate, and 2% formic acid generally underestimated or overestimated RAE. Pyrolysis and HTC treatment reduced RAE of sewage sludge, independent of (Fe + Al)/P-molar ratio, indicating formation of less bioavailable P sources.

Livestock feeding strategy and the technology used for treating nutrient-rich residues strongly affected RAE, causing it to vary from 1% to 189%. Sustainable future use of finite P resources for production of P fertilizers to support global food production will require accurate knowledge of crop P requirements for optimal yield. Non-optimal fertilizer use can increase soil P status, resulting in P leaching to surface waters, or decrease soil P status, resulting in lower crop yields due to P deficiency. Optimal use of both mineral and recycled P fertilizers would thus secure the P fertilizer supply for food production and reduce the environmental impact.

CRedit authorship contribution statement

Kari Ylivainio: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Visualization, Writing – original draft. **Alma Lehti:** Data curation, Investigation, Writing – original draft. **Johannes Jermakka:** Funding acquisition, Investigation, Methodology, Writing – review & editing. **Hanne Wikberg:** Investigation, Methodology, Writing – review & editing. **Eila Turtola:** Conceptualization, Writing – review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.145618>.

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