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Phosphorus in Manure and Sewage Sludge More Recyclable than in Soluble Inorganic Fertilizer

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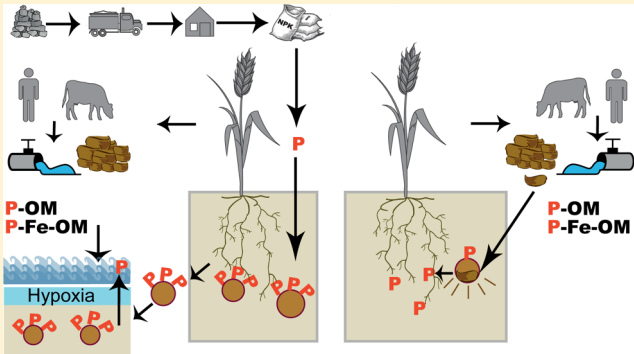
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⑤ *Supporting Information*

ABSTRACT: Phosphorus (P) flow from deposits through agriculture to waterways leads to eutrophication and depletion of P reserves. Therefore, P must be recycled. Low and unpredictable plant availability of P in residues is considered to be a limiting factor for recycling. We identified the determinants for the plant-availability of P in agrifood residues. We quantified P in Italian ryegrass (*Lolium multiflorum*) and in field soil fractions with different plant availabilities of P as a response to manure and sewage sludge with a range of P capture and hygienization treatments. P was more available in manure and in sludge, when it was captured biologically or with a moderate iron (Fe)/P (1.6), than in NPK. Increasing rate of sludge impaired P recovery and high Fe/P (9.8) prevented it.

Anaerobic digestion (AD) reduced plant-availability at relevant rates. The recovery of P was increased in AD manure via composting and in AD sludge via combined acid and oxidizer. P was not available to plants in the sludge hygienized with a high calcium/P. Contrary to assumed knowledge, the recyclability of P in appropriately treated residues can be better than in NPK. The prevention of P sorption in soil by organic substances in fertilizers critically enhances the recyclability of P.

1. INTRODUCTION

Securing a food supply for an increasing global population is one of the greatest challenges of our time, as climate, biodiversity, and aquatic ecosystems are endangered[1,2] and mineral and fossil resources are being depleted. The efficient use of agrifood residues for energy and nutrients represents an important part of a solution.[3,4] Phosphorus (P) is a finite resource that is a key element in terrestrial and aquatic eutrophication. However, the limited, unpredictable, or unknown P availability for plants in residues, compared with soluble fertilizers, is perceived as a hinder for recycling.[5,6]

There is increasing scarcity of virgin P reserves[7] while P fertilizers still are in demand even in the industrial world.[8] The key role of P in terrestrial and aquatic eutrophication, as well as the ongoing paradigm shift toward recycling[9,4] and recovery from the accumulated reserves, "the agricultural legacy",[10−12] have brought the plant availability of P in residues into the focus.[6] Because most P flows within agrifood systems,[13,14] recycling agrifood residues indeed is critical for this nutrient. Among agrifood residues, animal manure often contains the major share of P, while sewage sludge is spatially concentrated, making it readily available in large quantities.[15] The leaching of P from manure of the spatially concentrated animal production and from sewage-originated P precipitates in landscaping over the long-term has focused additional attention on the necessity of recycling P in these residues.

Efficient P recycling is only possible through transformations at number of societal levels. Breaking up the spatial separation of cropping and animal husbandry or locating animal houses close to heat demand for facilitating a comprehensive energy recovery[15] would enhance the feasibility of efficiently using the nutrients in manure. Avoiding mixing sewage with high and low contaminant risks would enable safer use of more sewage sludge. While these shifts would require synchronized actions throughout the agrifood systems, immediate progress can be made through appropriate technological choices. The safety for humans and the environment by these choices has been extensively addressed through research and regulation. In contrast, major knowledge gaps remain regarding recovery of P from current agrifood residues. Because of insufficient empirical information, using residue P is often perceived as detrimental toward the temporal and spatial precision.[5,16] Consequently, an advanced understanding of the nutrient cycling processes subsequent to application of the residue P to soil, of the effects that various treatments of the materials have on the processes,[4] and of the determining factors is needed to develop guidelines that could incentivize the recovery of P.[4,6]

Table 1. Fertilizers and Rates of Application (AD = anaerobic digestion; P = phosphorus; Fe = iron; OLR = organic loading rate; HLR = hydraulic retention time)

| Fertiliser	Origin	P capture	Hygienisation	C/N	C/P	Rate g_{fw} per pot 1	2	3	P_{tot} mg per pot 1	2	3
Manures											
Man	Liquid dairy manure, Finland			13	70	34.4	68.9	300	25.0	50.0	218
Man AD	Liquid dairy manure, Finland		AD, mesophilic process 37 °C, OLR 3 kgVS m^{-3} d^{-1}, HRT 26 d	5.9	39	43.7	87.3	475	19.1	38.1	207
Man ADComp	Liquid dairy manure, Finland		AD, dewatered 7-8 DM%, closed composting (ManAD:peat:straw 1:1:0,3, v:v:v) 2 wk 40-45°C, maturing 5 wk	28	113	87.3	175	365	48.6	97.3	204
Sludges											
S1	Sewage, Plant 1	Secondary treatment, Fe-coagulant, Fe/P 1.6	Primary and secondary treatment sludge, dewatered using rotating sieve	8.3	20	87.0	157	394	200	362	905
S2 DirAD	Sewage, Plant 2	Primary treatment, direct, Fe-coagulant, Fe/P 9.8	AD, dewatered	7.9	16	49.7	263	657	186	985	2 462
S3 BioAD	Sewage, Plant 3	Biological P removal, Fe/P 0.2	AD, dewatered	6.4	13	5.62	11.3	29.3	38.8	77.6	202
S4 BioADStr	Sewage, Plant 4	Biological P removal, Fe/P 0	AD, dewatered, struvite $MgNH_4PO_4*6H_2O$ from reject water	0.9	0.4	0.70	2.15	3.50	64.0	196	320
S1 AD	Sewage, Plant 1	Secondary treatment, Fe-coagulant, Fe/P 1.6	AD, dewatered	7.4	8.5	21.0	68.9	172	212	695	1 738
S1 ADComp	Sewage, Plant 1	Secondary treatment, Fe-coagulant, Fe/P 1.6	AD, dewatered, tunnel composting (S1 AD:bricks:peat, 1t:2m^3:1m^3, w:v:v) 2 wk	9.0	13	28.5	76.3	191	218	584	1 460
S1 ADKem	Sewage, Plant 1	Secondary treatment, Fe-coagulant, Fe/P 1.6	AD, KemiCond: H_2SO_4, H_2O_2, NaOH, dewatered using centrifuge	7.2	11	48.0	66.7	167	223	310	776
S1 ADLime	Sewage, Plant 1	Secondary treatment, Fe-coagulant, Fe/P 1.6	AD, dewatered, CaO 80 kg t^{-1}, tractor mixed	8.1	9.8	23.5	131	327	210	1 170	2 926
References											
NPK: NPK1, NPK2, NPK3	NH_4NO_3; $K_2HPO_4*3H_2O$; KCl					1.43; 0.37; 0.39	3.57; 0.92; 0.97	5.71; 1.47; 1.55	50.0	125	200
Control: 0, NK, NPK0.5	NH_4NO_3; $K_2HPO_4*3H_2O$; KCl					0; 0; 0	0.71; 0; 0.31	0.71; 0.18; 0.19	0	0	25.0
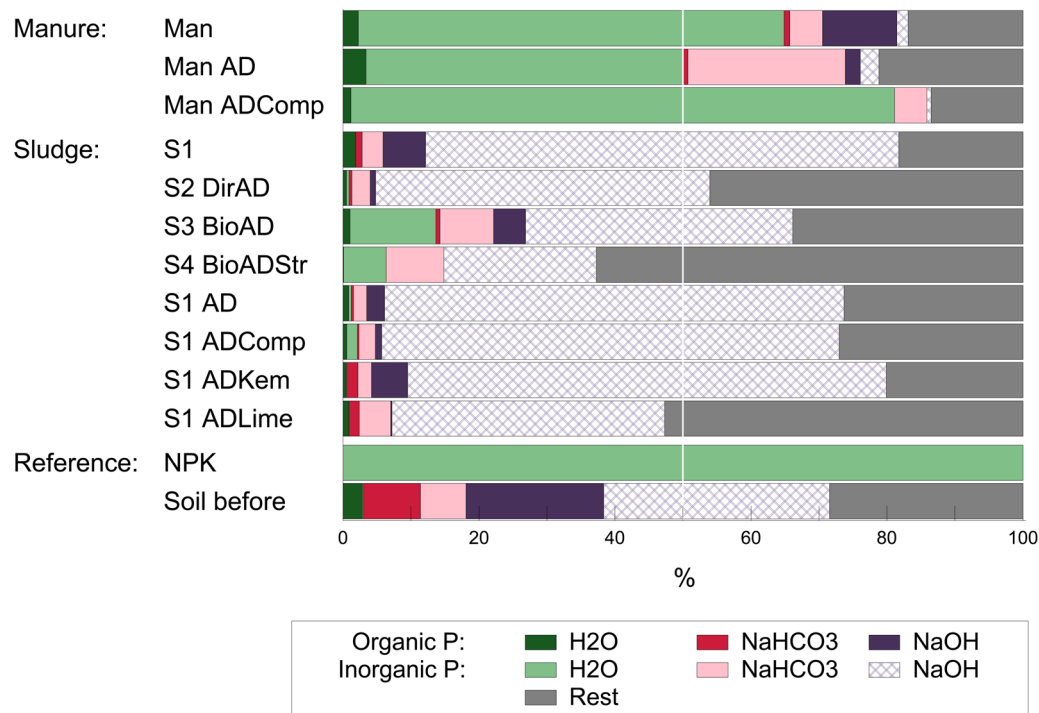
Figure 1. P composition of the soil and fertilizers. Proportions of fertilizer phosphorus (P) (0.2 g per pot) in the seven P fractions and the corresponding proportions of soil P before fertilization.

The availability of P to plants can be either enhanced or reduced, depending on the chemicals used to capture P in sewage, the hygienization method, and the applied amount.[17] The determining factors are not well understood. The capture of P in sewage using iron (Fe) coagulants is a treatment employed to stop P from entering waterways that raises particular concerns for its impact on the availability of P to plants.[6] Manure is the best known organic fertilizer, and anaerobic digestion (AD) used to extract energy and enhance the hygiene of organic solid wastes with or without a subsequent composting is in many aspects mature.[18] However,

while the use of these techniques is rapidly expanding, the impact on the plant availability of P in manure and sewage is not known. This knowledge is needed to implement the rethinking of P management,[19] to explore the options to recycle materials, and to neutralize fixation sites.

The present study explores the relative recyclability of P in manure and sewage in comparison with NPK, as well as how to treat the residues to enhance recyclability. The current treatments to capture P in sewage and to hygienize manure and sewage sludge were compared in terms of the proportions of P in plant and soil. To facilitate the detection of the

underlying mechanisms, a pot experiment with field soil was conducted where a broad range of amounts applied also indicate the effects of accumulation, there is little buffering by bulk soil, and prevention of uncontrolled P losses is possible. The following question was posed: How recyclable is P in agrifood residues, and what determines the recyclability?

2. MATERIALS AND METHODS

2.1. Fertilizers. Sewage sludge, dairy manure, and a soluble NPK compound were compared, as well as various treatments to capture P from sewage and to ensure hygiene of sewage sludge and manure (Table 1, Figure 1). The sewage origins and treatments were selected to cover the entire range of European practices. The sewage sludge-based fertilizers originated from three North European wastewater treatment plants that used a different P removal method each. The manure-based fertilizers were acquired from a single origin. A series of sewage sludge-based fertilizers was prepared with sludge from one of the wastewater treatment plants to ensure that the treatments could be compared. This wastewater treatment plant was a secondary treatment plant that used Fe precipitation, adhering to practices common among North European large-scale plants. In addition, struvite was precipitated from the reject water from the sewage from a fourth plant used in this study. The NPK compound (Table 1) served as the control to represent soluble inorganic fertilizers that are currently the dominant P source in agriculture. The experiment included also a hygienization treatment of AD sludge with NH_3 2.9% $dm_{sewage\ sludge}^{-1}$ and H_2SO_4 for a preliminary investigation. However, the results of this treatment, which is not applied in practice, are not reported because it increased the soil conductivity to a critically high level, obviously inhibiting nitrification and halting microbial activity altogether at higher rates hindering P release from the organic fertilizer.

The sewage sludges and struvite were sampled at the start of December 2011. The sewage sludge for preparing S1 ADKem was sampled on February 7, 2012, due to a failure during the first treatment process. Liquid dairy manure originating from an MTT Agrifood Research Finland research farm operated with modern European husbandry practices was sampled with and without AD on November 14, 2011. The AD manure was composted from November 23, 2011, to January 5, 2012 (Table 1). All of the fertilizers were stored in closed containers at +5 °C until the experiment was established on February 14−16, 2012.

2.2. Pot Experiment. The plant availability of P in the fertilizers was studied in a pot experiment by statistically modeling the proportions of P in the plants and in the soil at the end of the experiment. Three different application rates were set for each fertilizer to achieve comparable plant P uptake rates across the fertilizers (Table 1). These rates were selected based on the results of a preliminary pot trial. To ensure that the nitrogen (N) and potassium (K) would not limit the P uptake, they were supplied in excess. N was supplied at 100, 200, 500, and 800 mg $(kg_{dw})^{-1}$, and K was supplied at 66, 132, 330, and 528 mg $(kg_{dw})^{-1}$ for each P rate, respectively. With the organic fertilizers, the three lowest rates for both N and K were used. Analytical grade ammonium nitrate (NH_4NO_3), potassium chloride (KCl), and (for NPK treatments only) dipotassium phosphate ($K_2HPO_4\cdot3H_2O$) were applied. The experiment was designed using information regarding the variations in the light and other conditions in the growth chambers. The experiment had a factorial alpha design with five complete replicates and seven blocks of six fertilizer by fertilizer rate combinations

within each replicate. Each fertilizer level occurred twice in each block.

The soil for the experiment was collected on September 7, 2011, from a 5−25 cm surface layer of a field that had been under grass for more than five years. Soil was sieved through a 5 mm screen to remove organic residues and stored at +2 °C. The soil had a low content of plant-available P and consisted of clay 3.8%, silt 11.4%, and sand 84.8% (fine sand 48.2%, sand 32.8%, coarse sand 3.9%). The soil (2.5 kg_{dw} per pot) was carefully mixed with the fertilizers except for a layer of 0.3 kg in which the seeds were sown to avoid any negative effects induced by fertilization on germination. Italian ryegrass (*Lolium multiflorum* Lam.) was sown at 50 seeds per pot.

The soil mixture was maintained at 70% water holding capacity. The lighting was provided by 36 W fluorescent lamps for plants (Model Osram fluora). The photosynthetic flux in the growth chamber was 280 μmol m^{-2} s^{-1} at plant height with a 16/8 h light/dark cycle. The air temperature was 21/15 °C. The daily humidity ranged from 50% to 90%, and the CO_2 concentration varied from 290 to 490 ppm. The plants were harvested twice, on March 19 and April 10 (regrowth), approximately 4 and 8 weeks after sowing, respectively. The shoots were cut 2 cm above the soil surface and dried at 60 °C.

2.3. Fertilizer Analyses. The dry matter content of the fertilizers was determined by drying at 105 °C, and the laboratory compacted bulk density was determined for 1 L of soil (EN 13040). Water extractions were performed using moist samples at 1:5 (v/v) (EN 13652) or 1:60 (w/w), shaking for 1 h. The suspensions were centrifuged for 15 min at 3500 rpm, passed through a 2 μm filter, and stored in closed polyethylene bottles until analysis for pH, conductivity, and soluble P. After 1:5 and 1:60 H_2O extractions, the samples were dried at 37 °C and passed through a 2 mm sieve.

A modified Hedley fractionation of P[20,21] was sequentially performed. The fractionation consisted of four extractions with 60 mL for 16 h, using H_2O (4 and 16 h), 0.5 M $NaHCO_3$ (pH 8.5), 0.1 M NaOH, and 1 M HCl, at 1:60 (w/w). After shaking with 1 g of dry fertilizer, the solution was centrifuged for 15 min at 3500 rpm and filtered through a 0.2 μm membrane for the determination of inorganic P. An unfiltered subsample was autoclaved for 30 min at 120 °C to release any organically bound P, except for the last extraction with 1 M HCl. The filtered and autoclaved extracts were stored in closed polyethylene bottles until the analyses of inorganic and total P were conducted. The extracts were analyzed using the molybdenum blue color method using a Shimadzu UV/vis spectrophotometer 120-02 (882 nm).

Solubilities for Al, Ca, Fe, and P were determined using 0.029 M ammonium oxalate extraction (1:20; w/w), and Al, Ca, Fe, and P were measured by inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Jarrell Ash IRIS Advantage, USA). Acid ammonium acetate (pH 4.65, 0.5 M) extractable (1:10) P was determined using a Skalar autoanalyzer on the extracts that had been passed through a 2 μm filter and stored in closed polyethylene bottles. The P extractable in neutral ammonium citrate was determined from 1 g of fertilizer using 100 mL of citrate at 65 °C. After leaching P with water at 1:200, ammonium citrate extractable P was estimated as the difference between total P and P determined from the solid after filtration.[22]

The total P, Ca, Fe, Al, and heavy metal (Cd, Cu, Zn, Mn, Pb, Hg, As, and Se) contents were determined from Aqua regia extraction (EN 13346 Sludges and EN13650 Soil improvers and

growing media). The total C was measured using the Dumas method (LECO CN-2000) from a dry sample.

The chloride content was analyzed from a 1:5 (v/v) water extract using a Skalar autoanalyzer. To assess phytotoxicity and maturity of the fertilizers, seed germination, root length (EN 16086-2:2011 applied),[23] and CO_2 production in a closed bottle test (Evira 7405) were determined for pure wet samples or samples mixed with 30% of substrate.[24]

2.4. Plant and Soil Analyses. The plant samples were prepared using wet digestion, involving dissolution in heated HNO_3. The P concentrations were measured with ICP-OES. The soil was analyzed before the experiment using the same analytical methods as for the fertilizers with the exception of the total N, which was measured using the Dumas method (LECO CN-2000). After the experiment, the soils from all of the pots were analyzed for electrical conductivity, pH, and P_{H2O} from a 1:5 extract (CEN 13652). A simplified sequential Hedley fractionation for the dried samples at 1:60 (w/w) H_2O, $NaHCO_3$, and $NaOH$ extractions was performed, and the total P in the extract (not distinguishing organic and inorganic P) was determined.

P of the four mutually exclusive soil fractions with potentially plant-available P^{20} and plant P uptake at the end of the experiment was summed and the sum, i.e., potentially plant-available P ($P_{\text{potentially plant-available}}$, g per pot) = plant P uptake + soil $P_{H2O\ 1:5}$ + soil $P_{H2O\ 1:60}$ + soil P_{NaHCO3} + soil P_{NaOH} was used in statistical modeling. Both fertilizer P and soil P before fertilization (same soil in every pot within each replicate) are included in $P_{\text{potentially plant-available}}$. Four discrepant observations were excluded from the modeling because they were regarded as suspect measurements and would have had a pronounced effect on the results (Supporting Information Figure S1). To investigate the fate of P for the fertilizers, the proportions of $P_{\text{potentially plant-available}}$ found in plant and in the four soil fractions were analyzed separately by employing generalized linear mixed models with the logit link function, and each proportion was assumed to have a beta distribution. The use of a beta distribution for modeling proportions was proposed, e.g., by Gbur et al.[25] The models were fitted using maximum likelihood estimation based on a Laplace integral approximation method.[25]

To take account of the experimental design, replicate effects and block effects nested within replicates were included as random variables in the models. The relationship between each proportion and $P_{\text{potentially plant-available}}$ was modeled using polynomials. The most complex model for the relation was a second-order polynomial with separate intercepts and linear and quadratic coefficients for each fertilizer. The model had the following form:

$$\text{logit}(\mu_{ijk}) = \alpha_i + \beta_i P_{ijk} + \gamma_i P^2{}_{ijk} + r_j + b_{k(j)} \tag{1}$$

where μ_{ijk} and P_{ijk} denote the mean proportion and the $P_{\text{potentially plant-available}}$ for fertilizer i in block k of replicate j, respectively, and $\text{logit}(\mu_{ijk}) = \ln[\mu_{ijk}/(1 - \mu_{ijk})]$; α_i is the intercept, β_i is the linear coefficient, and γ_i is the quadratic coefficient for fertilizer i. The replicate effects (r_j) were assumed to be distributed independently and normally with means of zero and a constant variance. The distributional assumptions of the random block effects ($b_{k(j)}$) were similar, and both effects were also assumed to be independent of one another. The mean proportion for each fertilizer (μ_i) can be solved from eq 1 as a function of P as follows:

$$\mu_i = [1 + \exp(-\alpha_i - \beta_i P_{ijk} - \gamma_i P^2{}_{ijk})]^{-1} \tag{2}$$

Sequential "type 1" Wald F-tests with the denominator degrees of freedom calculated using the containment method[26] were used to assess the need to have a quadratic term and separate coefficients for the fertilizers in the models. For all proportions of P there was evidence of varying coefficients among the fertilizers indicating nonparallel first- or second-order polynomials for the fertilizers on the logit scale. However, based on the comparisons of the estimated linear and quadratic coefficients,[27] and on a measure pseudo-R^2 of the explained variation,[27] the number of the coefficients could be diminished by dividing the fertilizers into groups such that the coefficients could be considered homogeneous within the groups and different between the groups. After finding an adequate model for each proportion of P, the mean proportions for the fertilizers and the 95% confidence intervals for the means were estimated on the basis of the models at 0.8 g P per pot. Also the preplanned comparisons among the fertilizers were made at this P level using two-sided Wald t tests. The P level was selected by taking into account the ranges of the observations for the fertilizers. The statistical analyses were performed by the GLIMMIX procedure in version 9.3 of the SAS/STAT software.[26]

The agreement of the final models with the data was checked graphically. Systematic departures from the models were assessed by plotting studentized residuals against the linear predictor, and the adequacy of the link function was checked by plotting logit-transformed proportions against the linear predictor.[25] Furthermore, the fit of each model to the data was verified by presenting the models together with the scatter diagrams of the data (e.g., Supporting Information Figure S1).

The statistical analysis of the temporal development of the plant P availability was based on a general linear mixed model,[26] where the difference in plant P uptake between the first and second harvest was a response variable, fertilizer, fertilizer level, and their interaction were the fixed effects, and replicate, block, and experimental error were the random effects. To take account of the increasing variance when increasing the fertilizer level, unequal residual variances were allowed for the three fertilizer rates. The model was fitted by using the restricted maximum likelihood (REML) estimation method. The deviations of the mean differences between the harvests from zero were tested using two-sided t-type tests. The analysis was performed by the MIXED procedure in version 9.3 of the SAS/STAT software.[26]

3. RESULTS

3.1. Fate of P. To get a comprehensive view of the differences in the fate of P among the fertilizers, they were compared in terms of the mean proportions of $P_{\text{potentially plant-available}}$ in plant and in the four soil fractions at the fixed amount of 0.8 g P per pot. Fixing the denominator in the proportion of plant P uptake, for example, indicates that if the mean proportion is higher for fertilizer A compared to fertilizer B, also the mean plant P uptake is higher for A than for B. (At 0.8 g P per pot the mean P uptake = (mean proportion of P in plant %/100) × 0.8 g P per pot).

3.1.1. Plant. The relationship between the $P_{\text{potentially plant-available}}$ and the proportion of P taken up by the plants was approximately linear for all fertilizers on the logit scale and could be modeled using regression lines. Furthermore, the fertilizers could be divided into three groups based on their
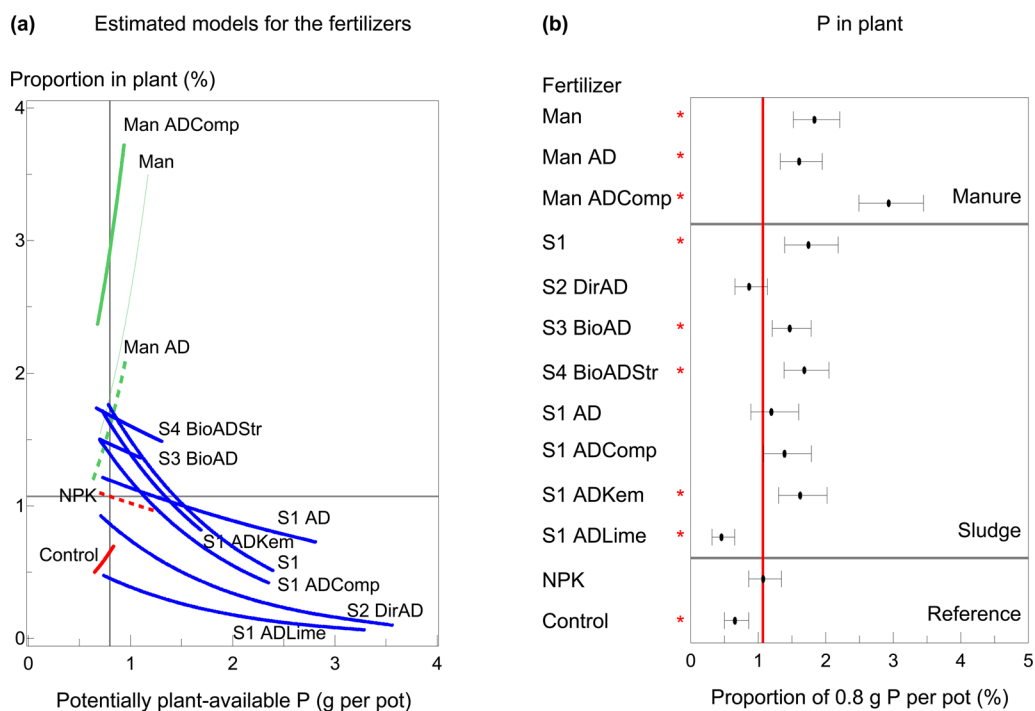
(a) Estimated models for the fertilizers   **(b)**   P in plant

Figure 2. Comparison of plant availability of phosphorus (P) among the fertilizers. (a) Model-based mean proportion of potentially plant-available P in plants at various P amounts at the end of the experiment. The vertical reference line corresponds to 0.8 g P per pot, and the horizontal reference line shows the mean proportion of 0.8 g P for NPK. (b) Model-based mean proportions of 0.8 g P per pot (dots) and 95% confidence intervals for the means (bars). The vertical reference line corresponds to the mean proportion for NPK. The statistically significant differences compared to NPK are marked with asterisks ($p < 0.02$). For S1 ADComp v. NPK, $p = 0.08$.

Table 2. Test Results for the Paired Comparisons of Fertilizers in Terms of the Proportion of Potentially Plant-Available Phosphorus (P) in the Plant at the End of the Experiment[a]

Comparison	df	t-value	P-value
Residue			
Manure v. sewage sludge: Man - S1	154	0.4	0.69
P capture			
Direct: S1 AD - S2 DirAD	154	1.78	0.08
Biological: S1 AD - S3 BioAD	154	-1.35	0.18
Struvite: S1 AD - S4 BioADStr	154	-2.38	0.02
Hygienisation			
AD of manure: Man - Man AD	154	1.25	0.21
AD of sewage sludge: S1 - S1 AD	154	2.28	0.02
Composting of manure: Man AD - Man ADComp	154	-6.17	<0.001
Composting of sewage sludge: S1 AD - S1 ADComp	154	-0.87	0.39
Acid and oxidiser: S1 AD - S1 ADKem	154	-1.88	0.06
Lime stabilisation: S1 AD - S1 ADLime	154	4.44	<0.001

[a]The potentially plant-available P was fixed at 0.8 g per pot for each fertilizer.

estimated slopes so that the slopes were approximately homogeneous within groups and different between groups. The final models with fertilizer-specific intercepts but just three different slopes were transformed to the original scale in which the models are nonlinear (Figure 2, Supporting Information Figure S1). The proportion of $P_{\text{potentially plant-available}}$ found in the plant increased nonlinearly when increasing the amount of $P_{\text{potentially plant-available}}$ for both the manures and the control (0, NK, NPK0.5) (Figure 2). For the sewage sludges, the proportion of P in the plant tended to decline with increased P amounts. The negative relation was weak for the biologically captured P in S3 BioAD and in struvite (S4 BioADStr), as well as for the AD sewage sludge (S1 AD) and NPK (NPK1, NPK2, NPK3) (Figure 2).

The mean proportion of $P_{\text{potentially plant-available}}$ in the plant was for manures and lower amounts of sewage sludges with biologically captured P or with a moderate Fe/P higher than for NPK, struvite (S4 BioADStr) performing best among sewage sludges (Figure 2). Direct precipitation using a high Fe/P (S2 DirAD) led to a low proportion of P in the plant. The AD reduced the proportion of $P_{\text{potentially plant-available}}$ found in the plant with manure. The reduction in the proportion did not depend on the P amount, but the reduction in plant P uptake was clearly the higher the amount. The AD reduced the proportion of P in the plant also at the lowest amounts of sludge, but at high amounts, the plant-availability of P was increased by AD (Figure 2, Table 2). The mean proportion of $P_{\text{potentially plant-available}}$ in the plant was highest for composted manure (Man ADComp), but in the AD sewage sludge not increased by composting (Figure

2, Table 2). An acid and oxidizer treatment (S1 ADKem) increased the proportion of P in plant, whereas sludge hygienized with lime reduced the proportion and the plant P uptake below that of the control (Figure 2).

The higher the proportion of $P_{potentially\ plant-available}$ in the plant and the plant P uptake, the higher also the growth tended to be (Supporting Information Figure S2). Regarding the temporal development of the plant P uptake, the results of the fertilizer comparisons were quite similar to the results of the comparisons for proportions in the plant: the higher the P proportion for a fertilizer, the faster the P uptake for that fertilizer also was (Supporting Information Figure S3). The exception was the acid and oxidizer treatment (S1 ADKem), which was beneficial to P proportion in plant but slowed the P uptake compared to NPK (Supporting Information Figure S3).

3.1.2. Soil. At the end of the experiment, the differences among the fertilizers in the mean proportions of the relatively readily extractable soil fractions (i.e., P_{H2O} and P_{NaHCO3} vs P_{NaOH}) of the $P_{potentially\ plant-available}$ were generally similar to the differences among the fertilizers in the mean proportion of $P_{potentially\ plant-available}$ in plant. The exception was that the proportions of the readily extractable P were lower than for NPK for sewage sludges and further reduced by hygienization (Supporting Information Figure S4). At the amounts higher than 0.8 g P per pot the differences between the fertilizers were more pronounced. Especially the mean proportion in P_{NaHCO3} was higher and the mean proportion in P_{NaOH} lower for manures, references and sewage sludges with P captured biologically (S3 BioAD, S4 BioADStr), whereas the opposite was true for the rest of the sewage sludges.

Composted manure (Man ADComp) and struvite (S4 BioADStr) produced the highest mean proportions in P_{H2O} and the lowest proportions in P_{NaOH} relative to the other fertilizers (Supporting Information Figure S5). However, composted sludge (S1 ADComp) had a higher mean proportion of the $P_{potentially\ plant-available}$ in P_{NaOH} and a lower one in P_{NaHCO3} than S1 AD at low amounts of sludge. AD had no clear impact on the fate of P in soil. The proportion of P in $P_{H2O1:60}$ tended to increase with increasing amount for Control, NPK, manures, and S4 BioADStr and decline for the rest of sewage sludges (Supporting Information Figure S5). The same pattern was observed for P_{NaHCO3}, although the P proportion in this fraction also increased for the S3 BioAD and S1 with increasing P amount.

3.2. Determinants. No single dominant variable explained the differences in plant availability of P across the fertilizers.

3.2.1. P Composition of the Fertilizers. The proportion of P_{H2O} in the fertilizers was related to high proportion of $P_{potentially\ plant-available}$ in plant, with the exceptions of water-soluble NPK (small proportion of P in plant) and the acid and oxidizer (S1 ADKem; low P_{H2O} proportion but relatively high proportion of P in plant) (Figures 1 and 2). For manures containing a relatively high proportion of P in water-extractable fractions, a greater mean proportion of P was also found in water-extractable fractions in soil at the end of the experiment than for sewage sludges that contained less P_{H2O} (Figure 1,Supporting Information Figures S4 and S5). NPK with fully water-extractable P was an exception: the proportion in soil $P_{H2O1:5}$ was clearly the smallest for NPK at lower P amounts (Supporting Information Figure S5). The organic fractions of P in P_{H2O} and in P_{NaOH} in the fertilizers were also positively associated with proportion of P taken up by the plant. The molar ratios Fe/P and Al/P in the applied fertilizer per pot were

highest for the sewage sludge with direct precipitation of P (S2 DirAD) (arithmetic means 7.8 and 0.9, respectively), which had little plant-available P, and the ratios were lowest (arithmetic means between 0 and 0.2), along with NPK, for manure and struvite (S4 BioADStr), which had high P availability. The molar ratio $Ca_{Aqua\ regia}/P_{Aqua\ regia}$ was highest for lime-stabilized AD sewage sludge (S1 ADLime; arithmetic mean 4.75) and $Ca_{(NH4)2C2O4}/P_{(NH4)2C2O4}$ for composted manure (Man AD-Comp; arithmetic mean 0.03).

3.2.2. Other Factors. At the end of the experiment, at 0.8 g $P_{potentially\ plant-available}$ per pot, the high mean proportion of P in the plant for a fertilizer tended to accompany a high mean soil pH (Supporting Information Figure S6). The exceptions were especially the control and S2 DirAD as well as S1 AD and S1 ADLime to a lesser extent; they had a lower mean proportion of P in the plant than expected based on the magnitude of soil pH. Mean conductivity at 0.8 g $P_{potentially\ plant-available}$ per pot was not related to the mean proportion of P in the plant among the fertilizers. At this P level, the mean conductivity in the soils was lowest (0.7 mS cm^{-1}) for S1 AD and highest for NPK and Man AD (3.4−3.5 mS cm^{-1}) (Supporting Information Figure S6).

Chloride ions (mg kg$_{dw}^{-1}$ soil) were observed in the manures (ranges Man 180−990, Man ADComp 230−1100, Man AD 200−1200) more than in the sewage sludge (150−900) and NPK (190−740). Among the potentially phytotoxic metals, the most abundantly observed elements were Zn, Cu, and Mn (mg kg$_{dw}^{-1}$ soil) in the sewage sludge (ranges 0.02−27.6, 0.01−9.96, and 0.04−14.7, respectively); these elements were present at rates many times higher than in the manures (ranges 0.23−2.69, 0.04−0.46, and 0.17−2.32, respectively). In the maturity test for the organic fertilizers, the highest CO_2 production, which reflects a low maturity, was evident for S1, S1 ADKem, Man, and Man AD. Germination occurred only with composting (Man ADComp, in S1 ADComp to a lesser extent) as well as with biological precipitation of P in sewage (S3 BioAD).

4. DISCUSSION

4.1. Generality and Validity of the Findings. Dairy manure and sewage sludge cover the range of plant-availability of P in agrifood residues,[28] and the sewage sludge used covers the range of the current wastewater processes in Europe. The Fe/P molar ratios in P capture in sewage varied between 0.49 and 9.8, covering the European range up to the highest ratio used in Norway only; the Fe/P 1.6 is representative for Northern Europe. The corresponding ratios for 10 random European plants average 0.89, with a median of 0.81 (max. 2.2, min. 0.03) (primary source). The manure and sludge treatments applied are currently the most commonly used. Regarding the amounts used, the rate allowed in Finland for establishment of grassland with a "poor" soil P supply is within the range used for all the fertilizers, corresponding to the lowest rate for most of them. The sandy P-deficient soil ensured that the fertilizer properties were the primary determinants of P behavior.[29] Because NK was supplied in excess, no nutrient deficiency was identified, and the responses by P uptake and growth were similar. Consequently, the differences in plant P can be attributed to the plant-availability of fertilizer P. A controlled pot experiment with a wide range of application rates was required to detect the mechanisms and the probable impacts in a cumulative use, but the practical significance of the differences among organic fertilizers can only be confirmed in long-term experiments in the field.[30]

4.2. Determinants of Recyclability of P. *4.2.1. Manure, Sewage Sludge, and NPK.* The higher recovery of P in manure at higher rates relative to the sewage sludge is due to the water-extractability of the manure P.[31,21] Only a small fraction of P in the sludge was extractable by water. The fully water-extractable inorganic P in NPK was, however, rapidly retained by iron oxides and hydroxides in the low-P soil. In the organic residues, P may be mineralized in step with plant uptake and/or be protected by organic substances from sorption to sparingly available forms, even in the long term.[32,33,17] In addition, the high conductivity and low pH in the soil caused by NPK has obvious negative effects on the plant P uptake.

In contrast, Huang et al.[17] and Frossard et al.[33] observed a lower use of sludge P by ryegrass in pots than P derived from a water-soluble fertilizer. These disparities may be attributed to differences in the soils or in the sewage treatments. Phytotoxic concentrations of chlorides or heavy metals have been observed,[34,35] and the reported metal concentrations were 10 to 100 times higher than in the present study. A review of the recent literature by Singh and Agrawal[36] concluded that in adequately sludge-amended soil, the crop yield is generally greater than that of well-fertilized controls.

4.2.2. P Capture in Sewage. The precipitation procedures were crucial for the plant-availability of P. The biological P removal, previously found to generate bioavailable P,[29] and the secondary precipitation treatment by a Fe-coagulant (Fe/P 1.6) found to adsorb P onto freshly formed Fe-hydroxides,[37] were both superior to direct precipitation (Fe/P 9.8) regarding P recycling. Fe/P 9.8 led also to the highest (though not critical) concentrations of potentially phytotoxic metals. Even an adverse effect on the plant-availability of soil P has been observed, emphasizing the dosing when promoting the recyclability of P.[17,37]

4.2.3. Hygienization of Manure and Sewage Sludge. The decomposition of organic substances by AD increased the sorption of P, as also observed by Frossard et al.[33] for sludge. The conductivity increased by AD in manure contributed to the reduced plant-availability. The marked enhancement in the plant-availability of P in the AD manure through composting, as also observed by Mata-Alvarez et al.,[18] is explained by the increased proportion of water-extractable inorganic P that remains protected from sorption by the organic humic and fulvic acids formed by composting. The less clear positive impact of composting on AD sewage sludge at high application rates may be an implication of complexation of the substances with metals released by AD,[38] as indicated by the increase in the soil P_{NaOH}. The lime stabilization practiced in some European countries retained P as an amorphous Ca precipitate at high pH values.[17,37]

4.3. Rate and Time Dependence. The soil conductivity may explain the negative rate effect of AD on the recyclability of P in manure and of NPK. The rate-induced decrease in plant-availability was clearest if sewage P was captured by Fe coagulants in accordance with the findings of Huang et al.[17] For the lime-stabilized sludge, the added Ca and high pH (still at the end of the experiment at the highest rate) most likely precipitated the soil P, as indicated by a lower plant P uptake than for the unfertilized control. The slower P release induced by hygienization apart from composting indicates that a longer-term study might find different P availabilities.[30] Consequently, the impact of rate, duration, and cumulation of agrifood residue applications deserve critical attention.

4.4. Role of Organic Matter. Organic substances are an important determinant for P recovery from residues in soils that sorb P.[39,40] Organic amendments in soil with high P content can even lead to net desorption[41,42] through competition between the dissolved organic carbon, humic, and fulvic acids and P for soil sorption sites. The direct release of P through decomposition in pace of plant uptake may play an even greater role[39,40] in protecting P from sorption. These factors seem to explain the positive association between the organic fractions and plant-availability of P in the fertilizers. Research is needed to elucidate the relation of plant-availability and susceptibility of P toward leaching during the cumulative use of fertilizers. The factors that determine which combination provides the highest recovery with the least nutrient leaching must be understood.

The assumed knowledge regarding the limited recyclability of P in agrifood residues and the importance of water-extractability as the key determinant are not supported by our findings. While the function of organic matter in preventing P sorption is grounded on rigorous theory, the quantitative significance of this function for the overall bioavailability of P such as highlighted by our results appears to be generally underestimated. Our results indicate important potential of recycled organic residues for counteracting the "P legacy"[11] both in field soils and in the sediments of water systems which are major drivers of eutrophication.[43,44] Even small quantities of organic substances in fertilizers play a substantial indirect role through hindering sorption. The plant-availability of P in agrifood residues, if properly treated, is superior to that of soluble inorganic fertilizers. Technologies for enabling recycling of sewage P currently exist. The efficient use of the recyclable residue P should be incentivized while minimizing problematic compounds in sewage upstream to enable the full benefits from the recyclability of residue P.

ASSOCIATED CONTENT

ⓈSupporting Information

Six figures illustrating relationships of $P_{potentially\ plant-available}$ and proportion of P in plant (Figure S1); relation of plant dry weight, plant P uptake, and the proportion of $P_{potentially\ plant-available}$ in plants (Figure S2); temporal development of P uptake (Figure S3); fate of P for each fertilizer at 0.8 g P per pot (Figure S4); relationships of $P_{potentially\ plant-available}$ and proportion of P in soil fractions (Figure S5); proportion of $P_{potentially\ plant-available}$ in plant against pH and conductivity in soil at 0.8 g P per pot (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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