

Greenhouse Evaluation of Struvite and Sludges from Municipal Wastewater Treatment Works as Phosphorus Sources for Plants

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Sewage sludge obtained by a conventional aerobic activated sludge process (CSS), P-rich sewage sludge from an enhanced biological P removal process (PRS), and struvite (MgNH₄PO₄•6H₂O) recovered from an anaerobic digester supernatant using a low-grade MgO byproduct from the calcination of natural magnesite as a Mg source (STR) were evaluated as P sources for plant growth. For this purpose, a greenhouse pot experiment was conducted using a P-deficient loamy sand soil and perennial ryegrass (*Lolium perenne* L.) as the test crop. The P sources were applied at rates equivalent to 0, 9, 17, 26, 34, and 44 mg/kg P. Single superphosphate (SUP) was used as reference for comparison with the other P sources. The results obtained indicated that STR was as effective as SUP in increasing the dry matter yield and supplying P to ryegrass. Compared to SUP and STR, PRS and especially CSS exhibited less agronomic effectiveness as P sources, which may be attributed, at least partially, to greater soil P fixation because of the larger amount of Fe incorporated with these materials.

KEYWORDS: Enhanced biological P removal; *Lolium perenne*; phosphorus sources; relative agronomic effectiveness; ryegrass; sewage sludge; struvite; superphosphate

INTRODUCTION

Sewage sludge, the main byproduct derived from wastewater treatment, represents a valuable resource for land application, capable of supplying organic matter and a range of plant nutrients, particularly N and P (I). However, many studies have shown that a prolonged addition of sewage sludge to soil, especially in cases where the application rates are based on agronomic N requirements, results in increased total and available soil P, often to values well in excess of crop needs (2–5). Overapplication of P in the form of sewage sludge may increase P losses through runoff and leaching processes, thus endangering surface and groundwater quality (6-9).

Wastewater treatment processes can influence the amount and availability of P in sewage sludge (4, 10, 11). Of particular interest is the so-called enhanced biological P removal (EBPR), which is an extension of conventional secondary biological treatment based on the selective enrichment of microorganisms with a high capacity to accumulate polyphosphate inside their cells (12). The EBPR process consists of recirculating microbial biomass and influent wastewater through anaerobic and aerobic zones. Basically, during the anaerobic phase, microbes residing in the activated sludge applied as an inoculum deplete organic matter from the wastewater, accumulate storage biopolymers

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(i.e., internal polymers, mainly polysaccharides and lipids, which are synthesized from different substrates and degraded when there is a need for energy and external substrates are depleted), and release soluble phosphates from the sludge (13). When conditions change to aerobic, polyphosphate-accumulating microorganisms, by the use of storage biopolymers as energy and C sources, remove inorganic phosphate from wastewater. Polyphosphate-accumulating organisms are selectively enriched within the activated sludge, and the removal of P is enhanced (13). The sewage sludge produced after the EBPR process is thus richer in P than that from a conventional activated sludge process, in which activated sludge is simply seeded into incoming wastewater and the mixture stirred in an aeration tank (12).

Phosphorus can be recovered at municipal wastewater treatment works from the supernatant from anaerobic sludge digestion through the crystallization of struvite, an ammonium magnesium phosphate mineral with the formula MgNH₄PO₄· $6H_2O$ (*12, 14, 15*). Struvite precipitates spontaneously in wastewater treatment environments where high concentrations of soluble P and ammonium are present, which can cause significant operating difficulties (*16*). If formation and collection are controlled, struvite might have potential in the fertilizer market and, at the same time, would help to alleviate stringent restrictions for the land application of sewage sludge based on the potential environmental effects of P on water quality (*12, 14, 15*).

Table 1. Main Chemical Properties (± Standard Errors of Three Laboratory Replicates) of the Single Superphosphate (SUP), Struvite (STR), Conventional Sewage Sludge (CSS), And P-Rich Sewage Sludge (PRS) Used in the Greenhouse Experiment^a

| property | SUP | STR | CSS | PRS |
|--------------------------------|----------------|-----------------|-----------------|-----------------|
| pH | ND | ND | 7.1 ± 0.1 | 7.0 ± 0.1 |
| electrical conductivity (dS/m) | ND | ND | 3.2 ± 0.1 | 5.4 ± 0.1 |
| oxidable C (g/kg) | ND | ND | 243.1 ± 5.1 | 174.2 ± 3.2 |
| total N (g/kg) | ND | 44.4 ± 1.1 | 36.0 ± 1.5 | 52.3 ± 0.9 |
| P (g/kg) | 79.0 ± 0.7 | 103.9 ± 0.3 | 7.4 ± 0.1 | 18.2 ± 0.4 |
| K (g/kg) | 1.41 ± 0.07 | 0.77 ± 0.02 | 2.82 ± 0.14 | 3.55 ± 0.03 |
| Ca (g/kg) | 170.9 ± 0.2 | 12.0 ± 0.3 | 26.0 ± 0.4 | 34.2 ± 0.3 |
| Mg (g/kg) | 2.0 ± 0.1 | 131.0 ± 0.1 | 3.5 ± 0.1 | 5.9 ± 0.1 |
| total Fe (mg/kg) | 864 ± 105 | 1806 ± 122 | 9167 ± 167 | 7300 ± 100 |
| total Mn (mg/kg) | 3.2 ± 0.1 | 140.0 ± 1.0 | 90.0 ± 3.1 | 136.3 ± 1.2 |
| total Zn (mg/kg) | 151.0 ± 5.8 | 18.6 ± 2.2 | 468.3 ± 6.7 | 615.3 ± 8.4 |
| total Cu (mg/kg) | 15.7 ± 1.1 | 7.4 ± 0.9 | 178.2 ± 4.5 | 397.4 ± 7.9 |
| total Pb (mg/kg) | <0.2 | <0.2 | 33.1 ± 4.4 | 36.6 ± 7.4 |
| total Cd (mg/kg) | 7.3 ± 0.3 | <0.2 | <0.2 | <0.2 |
| total Cr (mg/kg) | 81.1 ± 2.7 | 4.4 ± 3.9 | 16.8 ± 3.4 | 69.6 ± 2.6 |
| total Ni (mg/kg) | 13.7 ± 0.7 | 11.2 ± 0.2 | 17.9 ± 0.4 | 36.8 ± 0.5 |
| | | | | |

^a ND, not determined.

However, current technologies used for this purpose are expensive, mainly because of the high cost of chemical inputs needed. In particular, anaerobic digester supernatants tend to be rich in ammonium and phosphates but deficient in Mg, so supplementation of Mg is required (*12, 17, 18*). Recent results obtained on the pilot plant scale by the research group operating in the Centro de Ciencias Madioambientales, Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain, indicate that the use of low-grade MgO-containing byproducts of the magnesite industry as a Mg source, with respect to commercial reagent-grade chemicals such as MgO or MgCl₂, provides a cost-effective way to recover struvite at municipal wastewater plants (*19–21*).

Concerns about soil enrichment with P and potential loss following repeated and long-term application of sewage sludge to agricultural fields emphasize the need to understand how wastewater treatment processes affect P phytoavailability in this material relative to inorganic fertilizers (11, 22). Further, much of the recent literature on struvite recovered from wastewater has been concerned with its production, but there are few reports on its agronomic effectiveness (23). In particular, an examination of the potential agronomic benefits of P recovery as struvite from the supernatant from anaerobic sludge digestion using lowgrade MgO byproducts from the magnesite industry as a lowcost Mg source is still needed. Accordingly, the objective of this work was to evaluate the agronomic effectiveness of three materials from municipal wastewater plants, including sewage sludge obtained from a conventional aerobic activated sludge process (CSS), P-rich sewage sludge from an EBPR plant (PRS), and struvite recovered by the CSIC pilot process (STR), as P sources for ryegrass by means of a pot experiment in a greenhouse. To reach this objective, single superphosphate (SUP), a common P fertilizer that is generally considered to be fully plant-available (24), was used as a reference for comparison with the other P sources.

MATERIALS AND METHODS

Phosphorus Sources and Soil. The SUP was purchased from Fertiberia (Madrid, Spain). The STR sample was recovered by the CSIC pilot process (19–21) from an anaerobic digester supernatant using low-grade MgO byproducts from the calcination of natural magnesite as a Mg source. The anaerobic digester supernatant was collected from the EBPR plant located in Navalcarnero (Madrid, Spain), which is managed by Canal de Isabel II, and the low-grade MgO byproduct was supplied by Magnesitas Navarras, S.A. (Navarra, Spain). Samples of CSS and

PRS were collected from the municipal wastewater treatment plants located in Arroyo del Soto and Navalcarnero (Madrid, Spain), respectively, both managed by the Canal de Isabel II. The CSS was the sludge cake product obtained by a conventional aerobic activated sludge process followed by anaerobic digestion, whereas the PRS was produced by an anaerobic–anoxic–aerobic activated sludge process for EBPR followed by anaerobic digestion.

The principal chemical properties of the P sources were determined by conventional methods (25) in a triplicate analysis of each sample as follows: dry matter content was determined by heating overnight at 105 °C; the pH of the sewage sludges was measured in water suspensions obtained at a sludge-to-water ratio of 1:2.5; electrical conductivity of the sewage sludges was measured on water extracts at a sludge-to-water ratio of 1:5; oxidable C of the sewage sludges was measured by dichromate oxidation and subsequent titration with ferrous ammonium sulphate; total N content was determined by the Kjeldahl procedure, and the total contents of P, K, Ca, Mg, Fe, Mn, Zn, Cu, Pb, Cd, Cr, and Ni were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after the digestion of an oven-dried sample in a nitric acid and perchloric acid mixture. Details of the P sources are shown in **Table 1**.

A surface soil sample was collected from the top layer (Ap horizon, 0 to 20 cm depth) of a Typic Haploxeralf (26) in the experimental farm "La Higueruela" located in Santa Olalla (Toledo, Spain). The soil sample was analyzed by conventional methods (27, 28) in triplicate as follows: humidity was determined on a 105 °C basis; sand, silt, and clay contents were analyzed by pipette analysis following dispersion by sodium hexametaphosphate; pH was measured in water suspensions at a soil-to-water ratio of 1:2.5; electrical conductivity was measured on an aqueous extract of saturated soil paste; total organic C content was determined by dichromate oxidation followed by titration with ferrous ammonium sulphate; total N content was obtained by the Kjeldahl method; available P content was determined by the Bray method; available K, Ca, and Mg contents were determined by ICP-AES in 1 M ammonium acetate soil extracts at a soil-to-solution ratio of 1:10, and total contents of Fe, Mn, Zn, Cu, Pb, Cd, Cr, and Ni were determined by ICP-AES after the digestion of an oven-dried sample in nitric and perchloric acids. The mean values and standard errors measured on the soil sample are listed in Table 2.

Pot Experiment in Greenhouse. A greenhouse experiment was conducted using perennial ryegrass (*Lolium perenne* L. cv. Onyx) as the test crop. Single superphosphate, STR, CSS, and PRS were thoroughly mixed with 10 kg of air-dried, 2-mm-sieved soil in plastic pots at rates equivalent to 9, 17, 26, 34, and 44 mg/kg P (equivalent to 60, 120, 180, 240, and 300 kg/ha P_2O_5 assuming a soil bulk density of 1.5 kg/L), on the basis of the total P content of the material. The P sources differed in physical form, so to ensure a fair comparison, all materials were air-dried at room temperature and ground to pass a 0.5 mm sieve prior to being applied. A control treatment which received

Table 2. Main Chemical Properties (\pm Standard Errors of Three Laboratory Replicates) of the Soil Used in the Greenhouse Experiment

| property | value | property | value |
|-----------------------------------|-----------------------------------|----------------------|--------------|
| sand (g/kg) | 770 ± 2 | available Ca (mg/kg) | 390 ± 3 |
| silt (g/kg) | 190 ± 2 | available Mg (mg/kg) | 59 ± 2 |
| clay (g/kg) | 40 ± 3 | total Fe (mg/kg) | 4408 ± 256 |
| texture | loamy sand | total Mn (mg/kg) | 83.2 ± 2.4 |
| pН | 5.7 ± 0.1 | total Zn (mg/kg) | 10.2 ± 0.2 |
| electrical conductivity (dS/m) | $\textbf{2.01} \pm \textbf{0.09}$ | total Cu (mg/kg) | 2.9 ± 0.5 |
| total organic C (g/kg) | 2.5 ± 0.1 | total Pb (mg/kg) | <0.2 |
| total N (g/kg) | 0.30 ± 0.01 | total Cd (mg/kg) | <0.2 |
| available P (mg/kg) | 12 ± 1 | total Cr (mg/kg) | <0.2 |
| available K (mg/kg) | 110 ± 2 | total Ni (mg/kg) | <0.2 |

Table 3. Amounts of P as Single Superphosphate (SUP), Struvite (STR), Conventional Sewage Sludge (CSS), and P-Rich Sewage Sludge (PRS); N as Ammonium Sulfate; and K as Potassium Sulfate Supplied to Each Treatment in the Greenhouse Experiment

| | | (mg/kg) | | | | (mg/kg) | |
|-----------|----|---------|------|-----------|----|---------|------|
| treatment | Р | Ν | K | treatment | Ρ | Ν | K |
| control | 0 | 214 | 36.0 | CSS1 | 9 | 170 | 32.6 |
| SUP1 | 9 | 214 | 35.8 | CSS2 | 17 | 131 | 29.5 |
| SUP2 | 17 | 214 | 35.7 | CSS3 | 26 | 88 | 26.1 |
| SUP3 | 26 | 214 | 35.5 | CSS4 | 34 | 49 | 23.0 |
| SUP4 | 34 | 214 | 35.4 | CSS5 | 44 | 0 | 19.2 |
| SUP5 | 44 | 214 | 35.2 | PRS1 | 9 | 188 | 34.2 |
| STR1 | 9 | 210 | 35.9 | PRS2 | 17 | 165 | 32.7 |
| STR2 | 17 | 207 | 35.9 | PRS3 | 26 | 139 | 30.9 |
| STR3 | 26 | 203 | 35.8 | PRS4 | 34 | 116 | 29.4 |
| STR4 | 34 | 200 | 35.7 | PRS5 | 44 | 88 | 27.4 |
| STR5 | 44 | 195 | 35.7 | | | | |

no P was included. The total number of treatments was 21, and these were replicated three times in a randomized block design giving 63 pots.

The amounts of N and K required to provide all treatments with 214 mg/kg N and 36 mg/kg K (equivalent to 638 and 130 kg/ha of N and K₂O, respectively) were supplied by variable additions of reagentgrade ammonium and potassium sulfates, taking into account the N and K provided by the P sources (**Table 3**). All P sources were added before sowing. The additions of ammonium and potassium sulfates were made before sowing, except in the case of the treatments with SUP and STR, where half of the amount of N was applied before sowing and the other half after the third harvest. Nitrogen fertilization was split into two applications for SUP- and STR-amended soils to better simulate the behavior of N in the organically amended soils (i.e., the progressive mineralization of organic N during the experiment). All treatments were thus provided with N and K levels in excess of ryegrass requirements. This experimental design was intended to isolate P as the only growth-limiting nutrient.

Ryegrass was seeded on the soil surface at a rate of 60 g m⁻², equivalent to 4.1 g per pot (approximately 100 seeds). The pots were irrigated daily with deionized water during the entire experiment. The ryegrass was harvested at 25, 42, 58, 78, 95, and 115 days after sowing. The ryegrass samples were dried at 65 °C, weighed for yield determinations, and then ground to pass a 0.5 mm sieve before chemical analysis for total P, N, K, Ca, and Mg contents by ICP-AES after digestion in a nitric acid and perchloric acid mixture (25). Nutrient uptake by ryegrass was calculated by multiplying the dry matter yield by the nutrient content. Cumulative dry matter yield and nutrient uptake by ryegrass were determined by combining the six cuts.

Data Analysis. Statistical analysis was performed using SPSS 14.0.1. for Windows (Statistical Product and Service Solutions Inc., Chicago, IL). Data from dependent measures (dry matter yield and P, N, K, Ca, and Mg uptake by ryegrass) were subjected to three-way analyses of variance. Phosphorus source and P rate nested within P source were treated as fixed independent variables and blocks as a random effect.

 Table 4.
 Analysis of Variance for Effects of P Source, Rate (P Rate

 Nested within P Source), and Block on Dry Matter Yield of Ryegrass and

 P and N Uptake^a

| | | yield of ryegrass | | P uptake | | N uptake | |
|-------------------------|----|-------------------|---------|----------|-----------|----------|----------|
| source of variation | df | MS | F ratio | MS | F ratio | MS | F ratio |
| P source | 3 | 0.227 | 8.012* | 0.187 | 30.963*** | 20.014 | 18.126** |
| P rate(P source) | 12 | 0.051 | 1.514 | 0.013 | 1.892 | 3.488 | 3.384** |
| Block | 2 | 0.100 | 4.505 | 0.009 | 2.130 | 1.361 | 1.856 |
| P source \times block | 6 | 0.028 | 0.836 | 0.006 | 0.848 | 1.104 | 1.071 |
| P rate \times block | 8 | 0.020 | 0.599 | 0.028 | 0.003 | 0.483 | 0.468 |

^a df, degrees of freedom; MS, mean square. *, **, and ***, significant at the 0.05, 0.01, and 0.001 levels, respectively.

 Table 5.
 Analysis of Variance for Effects of P Source, Rate (P Rate

 Nested within P Source), and Block on K, Ca, and Mg Uptake^a

| | | K uptake | | Ca uptake | | Mg uptake | |
|-------------------------|----|----------|----------|-----------|-----------|-----------|---------|
| source of variation | df | MS | F ratio | MS | F ratio | MS | F ratio |
| P source | 3 | 7.853 | 10.867** | 0.492 | 27.400*** | 0.005 | 1.319 |
| P rate(P source) | 12 | 0.710 | 0.952 | 0.025 | 1.783 | 0.004 | 1.104 |
| Block | 2 | 1.308 | 2.672 | 0.044 | 1.715 | 0.011 | 2.793 |
| P source \times block | 6 | 0.723 | 0.968 | 0.018 | 1.291 | 0.004 | 0.965 |
| P rate \times block | 8 | 0.357 | 0.478 | 0.029 | 2.078 | 0.004 | 1.079 |

^a df, degrees of freedom; MS, mean square. ** and ***, significant at the 0.01 and 0.001 levels, respectively.

Further, the effects of P sources within rates and P rates within sources were analyzed with repeated one-way analysis of variance, followed by the Bonferroni test at the 0.05 level for separation of means when variances were equal according to Levene statistics.

The relationship between dry matter yield or P uptake and the rate of P applied for all P sources was evaluated using regression procedures as described by Prochnow et al. (29-31). Three response functions (linear, semilog, and square root) were tested:

$$Y_i = \beta_0 + \beta_i X + \varepsilon_i, \quad X \ge 0 \tag{1}$$

$$Y_i = \beta_0 + \beta_i \, \ln X + \varepsilon_i, \quad X \ge 1 \tag{2}$$

$$Y_i = \beta_0 + \beta_i X^{1/2} + \varepsilon_l, \quad X \ge 0 \tag{3}$$

where Y_i is dry matter yield in grams per kilogram or P uptake in milligrams per kilogram obtained with source *i*, *X* is the rate of P applied in milligrams per kilogram, β_i is the slope of the response function for source *i*, β_0 is the intercept, and ε_i is the error term of the fitted model. By using a dummy variable, which took the value of 1 for the P source being considered and 0 for other sources, a combined regression analysis resulted in a common intercept and a single value of the root mean square of error (rmsE) and correlation coefficient (*r*) for the four regression equations (one for each P source). The one representing the lowest rmsE and the highest *r* value was chosen to calculate the relative agronomic effectiveness for each P source *i* (RAE_{*i*}), which is defined as:

$$RAE_i(\%) = (\beta_i / \beta_{SUP}) \times 100 \tag{4}$$

where β_i is the slope of the response function of the P source *i* tested and β_{SUP} is the slope of the response function of SUP. This expression ranks the P sources with respect to SUP according to their agronomic potential to produce a yield response (24).

RESULTS AND DISCUSSION

Yield and Nutrient Uptake by Ryegrass. The analysis of variance reveals that the dry matter yield and the uptake of N, K, and especially P and Ca by ryegrass are significantly affected by the P source, whereas only N uptake is significantly affected by the P rate (**Tables 4** and **5**). The effects of the block and the interactions between the P source and block and the P rate and block are not significant for all the parameters examined (**Tables 4** and **5**).



Figure 1. Dry matter yield and nutrient uptake by ryegrass as affected by sources (SUP, superphosphate; STR, struvite; CSS, conventional sewage sludge; and PRS, P-rich sewage sludge) and rates of P applied. Error bars indicate standard errors. Within the same P rate, different lowercase letters indicate statistically significant differences according to the Bonferroni test at the 0.05 level. Within the same P source, different uppercase letters indicate statistically significant differences according to the Bonferroni test at the 0.05 level.

The dry matter yield and nutrient uptake by ryegrass as affected by the sources and rates of P applied are shown in **Figure 1**. With increasing P levels in the form of SUP and STR, the dry matter yield and N, K, and Ca uptake remain almost constant or increase slightly, whereas the P and Mg uptake tend to increase significantly. Effects were similar for PRS with an increase in the rate of P applied, with the exception of the slightly smaller increases of P and Mg uptake (not significant in the case of Mg uptake), and the significant increase of Ca uptake. In contrast to the results obtained for SUP, STR, and PRS, the application of CSS causes a significant increase of dry matter yield and N and K uptake, a significant increase of

Mg uptake at lower rates of addition, and a very marked increase of Ca uptake and induces no significant P uptake response to increasing P levels.

The yield decline with an increase in the rate of CSS applied may be attributed to several adverse effects on plant growth. In particular, according to Senesi and Plaza (*32*), the application of organic amendments, especially if not sufficiently stable or mature, may induce microbial immobilization of the available N with serious N deficiencies in crops, an introduction of phytotoxic organic compounds, and a production of ammonia at levels that can injure plant roots. Further, the continued active decomposition of unstable and immature organic matter in soil

Table 6. Regression Analysis for the Linear, Semilog, and Square Root Models Describing the Relation between Dry Matter Yield of Ryegrass (DMY) or P Uptake and Rate of P Applied^a

| | linear | | sen | nilog | square root | | |
|----------------------|----------|-----------|----------|-----------|-------------|-----------|--|
| | DMY | P uptake | DMY | P uptake | DMY | P uptake | |
| β ₀ | 1.7467 | 0.5001 | 1.7467 | 0.5001 | 1.7467 | 0.5001 | |
| β _{SUP} | 0.0065 | 0.0142 | 0.0630 | 0.1298 | 0.0387 | 0.0811 | |
| β_{STB} | 0.0069 | 0.0134 | 0.0641 | 0.1224 | 0.0398 | 0.0764 | |
| $\beta_{\rm CSS}$ | -0.0048 | 0.0046 | -0.0285 | 0.0465 | -0.0207 | 0.0283 | |
| β _{PBS} | 0.0015 | 0.0100 | 0.0196 | 0.0935 | 0.0112 | 0.0580 | |
| observations | 63 | 63 | 60 | 60 | 63 | 63 | |
| rmsE | 0.1711 | 0.0833 | 0.1752 | 0.0778 | 0.1735 | 0.0735 | |
| r | 0.6237 | 0.8664 | 0.6067 | 0.8688 | 0.6098 | 0.8981 | |
| MS | 1.1371 | 1.2799 | 1.0371 | 1.0813 | 1.0871 | 1.3757 | |
| F ratio | 38.84*** | 183.63*** | 33.79*** | 178.55*** | 36.12*** | 254.44*** | |

 ${}^{a}\beta_{0}$, common intercept. β_{SUP} , β_{STR} , β_{CSS} , and β_{PRS} , slope for single superphosphate, struvite, conventional sewage sludge, and P-rich sewage sludge, respectively. RMSE, root mean square of error. *r*, correlation coefficient. MS, mean square. ***, significant at the 0.001 level.

subtracts O_2 from root respiration and nitrification processes with the formation of phytotoxic compounds such as nitrites and sulfides. Metal toxicity, which is often regarded as a major limitation for the land application of sewage sludge (22), may be feasibly excluded because of the small quantities applied with CSS (**Table 1**).

The lack of a significant response of P uptake by ryegrass to increasing amounts of P added with CSS may be feasibly attributable to the yield decline in CSS-amended soils. This result contrasts with the positive response measured for PRS and especially SUP and STR. Differences in P uptake among the P sources may also be due to the relative larger amount of Fe applied with PRS and especially with CSS, compared with the amounts applied with SUP and STR (Table 1). Iron is capable of fixing P in sewage sludge by sorption (33). Specific sorption (mainly by Fe and Al oxides) is the major reaction mechanism of P in sandy soils (33–35). Thus, applying sewage sludges containing a large amount of Fe could be expected to increase P sorption and reduce P bioavailability in soil. Despite the dominance of inorganic P forms in sewage sludges (36–38), organic P mineralization rates may also affect phytoavailability (4).

Relative Agronomic Effectiveness. Table 6 shows the bestfit parameters generated from the analysis of experimental data of dry matter yield and P uptake by ryegrass as a function of the P rate applied using the linear, semilog, and square root models. The large *r* values and the small rmsE's indicate that the three models fit well (P < 0.001) to the experimental data sets, as it was previously demonstrated in other works on different P sources (29–31). However, it appears from the regression analysis that the linear model describes slightly better than the others the relationship between the dry matter yield and P rate, and that the square root model describes slightly better the relationship between the P uptake and P rate.

The experimental values of dry matter yield and P uptake as a function of the P rate and the best-fit lines for each P source are shown in **Figure 2**. The slopes of the linear model describing the relationship between dry matter yield and P rate increase in the order CSS < PRS < SUP < STR. However, the slopes for SUP, STR, and PRS are not statistically different from each other, whereas the slope for CSS is significantly larger than those for SUP and STR (**Figure 2a**). Further, the slopes of the square root model describing the relationship between P uptake and P rate for SUP and STR are much larger than the slope for CSS, which is, in turn, smaller than that for PRS (**Figure 2b**).

The RAEs of STR, CSS, and PRS with respect to SUP (100%) in terms of the dry matter yield of ryegrass and P uptake calculated with the slopes of the linear and square root equations,



Figure 2. Experimentally determined values (dots) and model-derived regressions (lines) of dry matter yield (a) and P uptake (b) by ryegrass as a function of the sources (SUP, superphosphate; STR, struvite; CSS, conventional sewage sludge; and PRS, P-rich sewage sludge) and rates of P applied. P sources followed by the same lowercase letter are not statistically different from each other in the slope of the response function according to the Bonferroni test at the 0.05 level.

respectively, are shown in **Figure 3**. The RAE values of STR are 120% for dry matter yield (**Figure 3a**) and 94% for P uptake (**Figure 3b**) (relative to SUP), thus indicating a very efficient use of this P source by ryegrass. Similar to the results of the slopes of the response functions, the RAE value for dry matter yield of PRS, although being much smaller (11%), is not



Figure 3. Relative agronomic effectiveness (RAE) of the superphosphate (SUP), struvite (STR), conventional sewage sludge (CSS), and P-rich sewage sludge (PRS) in increasing dry matter yield (a) and P uptake (b) by ryegrass. Error bars indicate standard errors. Different lowercase letters indicate statistically significant differences according to the Bonferroni test at the 0.05 level.

statistically different from that of STR at the 0.05 level. In contrast, the value of CSS is statistically smaller (-78%) (**Figure 3a**), which may be attributed to the several adverse effects of CSS on plant growth discussed above. For P uptake, the RAE values of CSS (35%) and PRS (71%) are significantly smaller than that of STR (**Figure 3b**), probably due to, at least in part, a greater soil P fixation as a result of the higher amount of Fe incorporated with PRS and especially with CSS. These results are in general agreement with a number of studies in showing that, although the soil P content usually increases when sewage sludges are applied, they are often less effective sources of bioavailable P than fertilizers (3). According to de Haan (39), plant availability of P in sewage sludge varies from 10 to 100% of that in soluble fertilizers.

As a whole, the results obtained in this study indicate that STR recovered by the CSIC pilot process from an anaerobic digester supernatant using a low-grade MgO byproduct from the calcination of natural magnesite can be as effective as SUP in increasing dry matter yield and supplying P to ryegrass. Compared to SUP and STR, PRS and especially CSS feature less agronomic effectiveness as P sources, which may be attributed, at least partially, to a greater soil P fixation because of the relatively larger amount of Fe incorporated with these materials. On these bases, the CSIC pilot process may represent an economically advantageous way to produce a P source attractive to the fertilizer market. Struvite recovery from the supernatant from anaerobic sludge digestion would also help to alleviate stringent environmental restrictions for the land application of sewage sludge that require low levels of P. However, it should be pointed out that the present results were obtained in a greenhouse pot experiment, and more research is needed to evaluate the agronomic effectiveness of STR in field trials, especially for long-term effects and using other test crops.

ABBREVIATIONS USED

CSIC, Consejo Superior de Investigaciones Científicas; CSS, conventional sewage sludge; df, degrees of freedom; EBPR, enhanced biological P removal; ICP-AES, inductively coupled plasma atomic emission spectroscopy; MS, mean square; ND, not determined; PRS, P-rich sewage sludge; rmsE, root mean square of error; *r*, correlation coefficient; RAE, relative agronomic effectiveness; SUP, single superphosphate; STR, struvite.

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