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Dolomite Phosphate Rock-Based Slow-Release Fertilizer for Agriculture and Landscapes

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Most soils in Florida are very sandy, and water-soluble fertilizers (WSF) are subjected to leaching loss. Alternate fertilization is a promising practice to reduce such loss. Dolomite phosphate rock (DPR), which contains calcium, magnesium, and phosphorus, is potentially useful for agricultural production and landscaping plants. In this study, DPR fertilizers were developed from mixing of DPR material and N-viro soil. A typical agricultural soil (Alfisol) in Florida was used for greenhouse studies, and ryegrass and citrus seedlings were tested. The DPR fertilizers appeared superior to WSF for the growth of ryegrass based on dry-matter yield and nutrient concentrations in plant; however, it was not evident in citrus seedlings. DPR fertilizers were effective in raising pH (by 3 units) and electrical conductivity of acidic sandy soils and increasing soil organic matter, total nutrients, and available nutrients. The concentrations of copper, lead, and zinc in the plant tissues were less than toxicity limits.

Keywords Nutrient availability, phosphorus, pot experiment, slow-release fertilizers

Introduction

Phosphorus (P) deficiency is a major constraint to crop production in tropical and subtropical acidic soils, and P fertilizers are required to sustain optimum plant growth (Zapata and Zaharah 2002). Phosphate rock (PR) was reported to be as effective as water-soluble superphosphate but more cost-effective for correcting P deficiencies in these soils (Rajan et al. 1991; Wright et al. 1991). Sinclair et al. (1993) stated that the advantage of reactive PR over soluble P fertilizer for permanent pastures was its lower price and not greater nutrient-use efficiency. Yeates and Clarke (1993) found that application of sulfur-fortified, partially acidulated PR was more useful in lowering P leaching losses than superphosphate on the basis of equal production of dry matter. Increases in pH and exchange [calcium (Ca) and magnesium (Mg)] after dolomite phosphate rock (DPR) application are two important factors in DPR dissolution and timing of DPR application in acidic sandy

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soils (He et al. 2005). The use of such unconventional P fertilizers can enhance nutrient efficiency and increase crop yield with relative economic benefit as compared with conventional P fertilizers (Chien, Prochnow, and Cantarella 2009).

In Florida, 37% of the soils are acidic with pH below 6.0 and 47% are identified as medium to low in P content [Potash and Phosphate Institute / Potash and Phosphate Institute of Canada (PPI/PPIC) 1998]. Their small holding capacity for water and nutrients [especially nitrogen (N) and P] often causes a dramatic increase in P concentration in surface runoff water (Yang et al. 2008). Water-soluble phosphate application to citrus groves and annual pastures growing on acidic sandy soils of the coastal areas of south Florida is of great concern because of eutrophication in water bodies. Alternative fertilization strategies such as slow-release P fertilizers are of benefit in reducing the impacts of fertilization on water quality. The phosphate industry in Central Florida produces significant amounts of DPR, such as reject pebbles, phosphatic clays, and oversize debris. These materials (especially DPR) are high in available Ca, Mg, and P contents (He et al. 2004) and therefore potentially useful for agricultural production and plant landscaping. The objective of this study was to test the agronomic effectiveness of DPR fertilizers for pasture using ryegrass as an indicator plant and for horticultural crops using citrus as an indicator plant.

Materials and Methods

DPR Fertilizers

The DPR fertilizers were manufactured by mixing DPR materials with N-viro soil at the ratios of 20%, 30%, 40%, 50%, 60%, and 70% (dry-weight basis) and incubating for 2 months at room temperature and optimal soil moisture (70% field holding capacity). At the end of the designated time, the mixtures were air dried and stored prior to use. The basic properties of the DPR materials, N-viro, and Alfisol soil are described in Table 1. The concentrations of macro- and micronutrients and related properties of the DPR fertilizers are presented in Tables 2 and 3.

 Table 1

 Chemical properties of DPR, N-viro soil, and the soil used in this study

Properties	DPR material	N-viro	Alfisol
pH (H ₂ O)	7.25 ± 0.864	11.7 ± 1.13	5.64 ± 0.368
EC (μ S cm ⁻¹)	866 ± 76.9	2200 ± 135	405 ± 25.4
Total C (g kg^{-1})	27.0 ± 2.56	71.7 ± 6.21	6.94 ± 0.981
Total N (g kg ⁻¹)	0.168 ± 0.094	4.93 ± 0.912	0.364 ± 0.056
Total P (g kg^{-1})	105 ± 9.38	4.80 ± 0.458	ND^*
Mehlich 3 P (mg kg $^{-1}$)	890 ± 84.3	ND	79.7 ± 6.23
Olsen P ($mg kg^{-1}$)	310 ± 23.6	ND	ND
Total Ca (g kg ⁻¹)	298 ± 38.6	ND	ND
CCE (%)	15.3 ± 1.64	ND	ND
Total Mg (g kg ⁻¹)	11.7 ± 3.38	ND	ND
$Cu (mg kg^{-1})$	14.5 ± 2.15	ND	3.67 ± 0.434
$\operatorname{Zn}\left(\operatorname{mg}\operatorname{kg}^{-1}\right)$	79.4 ± 12.3	ND	3.02 ± 0.512
$B (mg kg^{-1})$	26.1 ± 8.45	ND	0.125 ± 0.031

Notes. ND, not determined; CCE, calcium carbonate equivalent. Data were presented as mean \pm standard deviation.

pH, electrical conductivity (EC), and macronutrient concentrations in the DPR fertilizers with varying proportions of DPR Table 2

Mixed roportion (%)			υ <u>Մ</u>	E) DE	b) NE	TD (A	Olean D	M.	3-extractab	M3-extractable elements ^a	(mg kg ⁻¹)	(1	KCl-extrac	$\begin{array}{c} KCI-extractable \ \mathrm{N}^{b} \\ \mathrm{(mg \ kg^{-1})} \end{array}$
PR N-Viro	- bH	CCE (%)	cm^{-1}	kg^{-1}	kg^{-1}	kg^{-1}	$(g kg^{-1})$	Ь	K	Ca	Mg	Fe	NH4-N	NO ₃ -N
80	9.20 ±	32.7 ±	4676 ±	61.2 ±	3.62 ±	25.1 ±	126 ±	27.5 ±	4184 ±	65648 ±	646 ±	3493 ±	16.2 ±	2.50 ±
	0.02	0.340	10.6	1.30	0.28	2.35	4.10	0.046	81.2	613	16.5	10.7	0.050	0.092
70	$9.29 \pm$	$29.2 \pm$	$4500 \pm$	$56.4 \pm$	$3.11 \pm$	$35.2 \pm$	$120 \pm$	$35.4 \pm$	$3602 \pm$	$56286 \pm$	$512 \pm$	$3545 \pm$	$13.5 \pm$	$1.95 \pm$
	0.01	1.45	48.8	1.94	0.31	4.21	6.44	3.08	73.3	2331	18.8	18.3	0.417	0.354
09	$8.77 \pm$	$31.9 \pm$	$3695 \pm$	54.3 ±	$2.60 \pm$	$45.4 \pm$	$112 \pm$	$37.4 \pm$	$3235 \pm$	$49325 \pm$	± 000	$3200 \pm$	$33.4 \pm$	$2.52 \pm$
	0.02	0.510	83.4	3.45	0.003	3.74	1.89	0.482	118	234	4.16	61.0	1.29	0.127
50	$8.52 \pm$	$33.4 \pm$	$3265 \pm$	$50.0 \pm$	$2.07 \pm$	$52.8 \pm$	$110 \pm$	$32.9 \pm$	$2808 \pm$	$48323 \pm$	$602 \pm$	$2978 \pm$	$56.5 \pm$	$4.18\pm$
	0.01	6.32	24.0	3.53	0.30	4.28	1.23	2.86	118	1066	16.1	8.79	1.12	0.148
40	$8.59 \pm$	$29.4 \pm$	$3068 \pm$	47.0 ±	1.71 土	± 9.59	$116 \pm$	$43.9 \pm$	$2143 \pm$	44588±	549 ±	$3221 \pm$	$50.7 \pm$	$2.98 \pm$
	0.01	0.470	24.7	96.0	0.248	5.61	2.76	2.19	104	401	0.198	9.77	2.90	0.028
30	$8.19 \pm$	$29.6 \pm$	2747 ±	$41.5 \pm$	$1.24 \pm$	$75.7 \pm$	148 土	47.5 ±	$1762 \pm$	$41923 \pm$	570 ±	$3289 \pm$	$46.7 \pm$	$2.69 \pm$
	0.01	0.343	19.1	5.06	0.090	5.38	3.39	2.11	105	436	1.12	47.0	0.884	0.057

^aM3 extractable means available elements extracted with Mehlich 3 reagent. ^bKCl extractable means available N extracted with 2 M KCl solution. Notes. CCE, calcium carbonate equivalent; TC, total carbon; TN, total N; and TP, total P.

Concentrations of micronutrients and heavy metals in the DPR fertilizers with varying proportions of DPR

	Zn	0.028 22.3 ± 0.199	$0.165 18.4 \pm 0.637$	$0.131 18.5 \pm 0.073$	$0.112 19.6 \pm 0.302$	$0.202 17.2 \pm 0.039$	0.044 15.7 ± 0.144
	Pb	10.3 ± 0.028	10.1 ± 0.165	9.48 ± 0.131	9.78 ± 0.112	9.22 ± 0.202	9.08 ± 0.044
M3-extractable elements ^{a} (mg kg ^{-1})	Cu	28.6 ± 0.592	23.6 ± 0.939	19.9 ± 0.057	17.6 ± 0.455	14.8 ± 0.062	11.4 ± 0.135
M3-extractable	Mo	3.48 ± 0.056	3.49 ± 0.066	3.17 ± 0.033	3.23 ± 0.063	3.00 ± 0.056	2.72 ± 0.037
	Mn	13.1 ± 0.114	11.1 ± 0.487	10.2 ± 0.070	10.9 ± 0.159	10.2 ± 0.085	9.94 ± 0.005
	В	22.9 ± 0.247	19.2 ± 0.805	18.0 ± 0.299	16.4 ± 0.364	13.7 ± 0.426	11.0 ± 0.272
Mix proportion (%)	N-Viro	80	70	09	50	40	30
Mix pr	DPR	20	30	40	50	09	70

^aM3 extractable means available elements extracted by Mehlich 3 reagent.

Greenhouse Experiments. The pretreated DPR fertilizers were used as P slow-release fertilizers in Alfisol and applied at a rate of 100 mg available P per kg soil. The total weight of each soil-amendment mixture was 2.50 kg (oven-dry basis). Nitrogen [200 mg N kg $^{-1}$ as ammonium nitrate (NH₄NO₃)] and potassium [200 mg K kg $^{-1}$ as potassium sulfate (K₂SO₄)] were also added. For the control, no chemical fertilizer or DPR fertilizer was applied; for chemical fertilizer treatment (CF), P was supplied as dipotassium hydrogen phosphate (K₂HPO₄) at 100 mg P per kg soil. After the amendment and soil moisture was adjusted to 70% field holding capacity, the soils were incubated at room temperature for 21 days before plants were grown.

Two plant species were tested in this study: ryegrass (Lolium Perenne) representing pasture crops in the area and citrus (Citrus Reticulata Blanco) representing horticultural plants. About 80 ryegrass seeds were sown into each pot evenly. There were three replications for each treatment, and all the pots were placed in the greenhouse with a randomized complete block experimental design. Thinning was performed to establish 50 healthy seedlings per pot 1 week after germination. Water was added daily to maintain proper soil moisture for the plants to grow. One-month-old citrus seedlings (Smooth Flat Seville, a common rootstock for citrus) were purchased from M & M Inc. (Fort Pierce, Fl.). The seedlings in potting medium were fed with only deionized (DI) water (without any fertilizers) for 1 month before they were transplanted to the pots. Each pot contained one seedling. There were three replications for each treatment, and all the pots were placed in the greenhouse following a randomized complete block experimental design. After 2 months of growth, the shoot and root of plants were separately harvested. After washing with tap water, rinsing with DI water, and oven drying (70 °C for 72 h), the plant samples were weighed for dry biomass. The oven-dried samples were ground using a Wiley mill to pass a 0.4-mm sieve for the determination of total organic carbon (TOC), total N (TN), P, K, Ca, Mg, and trace metals including copper (Cu), lead (Pb), and zinc (Zn). Simultaneously, subsamples of the soils were collected from each pot and analyzed for available nutrients, macro- and micro elements, and related soil quality properties including pH, electrical conductivity (EC), and TOC.

Physical and Chemical Analysis

Nutrients and Metal Concentrations in Plant. Portions of the plant samples (0.4 g each) were digested with 5 ml of concentrated nitric acid (HNO₃) / hydrogen peroxide (H₂O₂). The concentrations of P, Ca, Mg, K, and trace metals in the digested samples were determined using inductively coupled plasma–optical emission spectrometry (ICP-OES, Ultima, J.Y. Horiba Group, Edison, N.J.). The TOC and TN in plant samples were determined using a C/N analyzer (Vario MAX CN Macro Elemental Analyzer, Elemental Analysen system GmbH, Hanau, Germany).

Characterization of Cultivated Soil after Plant Harvest. The pH of cultivated soil samples was measured using a pH/conductivity meter (model 220, Denver Instrument, Denver, Col., USA) following U.S. Environmental Protection Agency (EPA) method 150.1; it was measured in DI water at the solid/water ratio of 1:1. Electrical conductivity (EC) of soil samples was determined at the solid/water ratio of 1:2 using the pH/conductivity meter following EPA method 120.1.

The TOC and TN in the cultivated soil were determined using the C/N analyzer. Available P in soil was determined used the method of Olsen and Sommers (1982). Available nutrients and metals in soil and mixture samples were measured by extracting the

samples with Mehlich 3 (M3) solution at a solid to solution ratio of 1:10 (Mehlich 1984). The extracts were filtered through a 0.45-µm membrane. Subsamples of the filtrate were acidified and analyzed for the concentrations of dissolved P and metals [Ca, Mg, K, boron (B), iron (Fe), manganese (Mn), molybdenum (Mo), Cu, Pb, and Zn] using the ICP-OES.

Results and Discussion

Characterization of DPR fertilizers

DPR material had 105 g kg⁻¹ of total P, which is more than 20 times of that in N-viro soil (Table 1). DPR material had lower TOC, TN, pH, and EC as compared with N-viro. The soil (Alfisol), a representative agricultural soil in the Indian River area, had a low pH, TOC, and available nutrients (Table 1). The DPR fertilizer, manufactured from DPR and N-viro mixed at varying ratios, demonstrated varying chemical properties that were associated with DPR or N-viro. The pH, EC, TOC, TN, and M3-extractable K, Ca, B, Mn, Mo, Cu, Pb, and Zn decreased with increasing DPR amendment ratio (Tables 2 and 3), suggesting that the N-viro was their main source in the DPR fertilizer. Total P, M3 P, and KCl-extractable NH₄-N were each positively correlated with DPR amendment ratio (Table 2), suggesting that DPR was their main contributor. Olsen P, accounting for 0.2-0.5% of TP (Table 2), varied in the range of 110–148 mg kg $^{-1}$. Available N (KCl-extractable NH₄-N + NO₃-N) in DPR fertilizers accounted for 0.05–0.4% of TN (Table 2), indicating a large portion of N in DPR fertilizers was the organic form. However, calcium carbonate equivalent (CCE), M3extractable Fe, and KCl-extractable NO₃-N were mainly associated with N-Viro (Table 2). Of the six developed DPR fertilizers, those with low DPR amendment ratios (<30%) had high values of pH (>9.0), EC (>4,000 μ S cm⁻¹), total C (TC) (>55 g kg⁻¹), TN (>3.0 g kg⁻¹), available P (>120 mg kg⁻¹), and M3-extractable nutrients Ca (>55,000 mg kg⁻¹), $K (>3,600 \text{ mg kg}^{-1})$, Fe $(>3,500 \text{ mg kg}^{-1})$, B $(>19 \text{ mg kg}^{-1})$, Mn $(>11 \text{ mg kg}^{-1})$, and Mo (>3.4 mg kg⁻¹) (Tables 2 and 3), which could benefit crop growth in acidic sandy soils.

Effects of DPR Fertilizers on Dry-Matter Yield

Both DPR fertilizers and chemical fertilizer had favorable effects on the growth of pasture plant (ryegrass) and horticultural crop (citrus). However, DPR fertilizers were superior to chemical fertilizers in increasing the dry biomass of pasture plant (Figure 1). In particular, DPR fertilizers containing 20% and 30% DPR materials increased the dry biomass of pasture by about 110% and 95%, respectively, as compared with chemical fertilizer (Figure 1). There was no difference in the biomass production of citrus seedlings between DPR fertilizers and chemical fertilizer, though both increased production of citrus seedlings, as compared with the control. Even though DPR fertilizers and chemical fertilizer had no difference in the biomass production of citrus seedlings, both of them were superior to the control (without DPR or chemical fertilizer) for the biomass production of citrus seedlings.

Effects of DPR Fertilizers on Plant Nutrition

Plant nutrients are essential to plant growth and crop yield. The agronomic effectiveness of a fertilizer is also reflected in nutrient levels in plant tissue. As shown in Figure 2, DPR fertilizers were as effective as chemical fertilizer in maintaining adequate N levels in the shoot and root of citrus seedlings. Similar results were obtained with ryegrass (Figure 2). The C/N ratios in the shoot and root of ryegrass, varying in 40–65, demonstrated an increasing

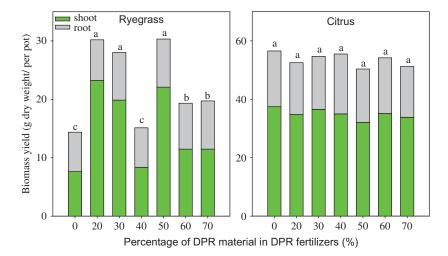


Figure 1. Dry-matter yields of shoot and root of ryegrass and citrus as affected by DPR fertilizers of different formulas: 0, water-soluble chemical fertilizer; 20–70%, percentages of DPR materials contained in DPR fertilizers (color figure available online).

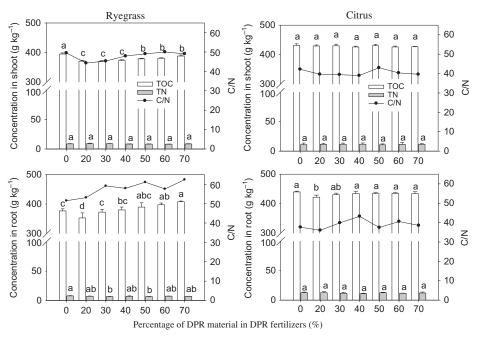


Figure 2. Total N concentration and C/N ratio in ryegrass and citrus plant as affected by DPR fertilizers of different formulas: 0, water-soluble chemical fertilizer; 20–70%, percentages of DPR materials contained in DPR fertilizers.

tendency with elevating DPR materials in the DPR fertilizers; a similar tendency could be observed in the citrus seedlings (Figure 2). Therefore, the effectiveness of DPR fertilizers for supplying N for ryegrass and citrus seedlings was comparable to water-soluble chemical fertilizers.

Both ryegrass and citrus seedlings had greater Ca concentrations in the plant tissues with DPR fertilizers than chemical fertilizers (Figure 3). Application of DPR fertilizers generally resulted in greater Ca concentration in shoot and greater Ca, K, and Mg concentrations in root of ryegrass and more K in shoot and more Ca in root of citrus seedlings (Figure 3). Even though P in ryegrass shoot and root decreased with increasing DPR application rates, it was within the normal range for plant growth (Figure 3). However, concentrations of P in the shoot and root of citrus seedlings were not differentiated between

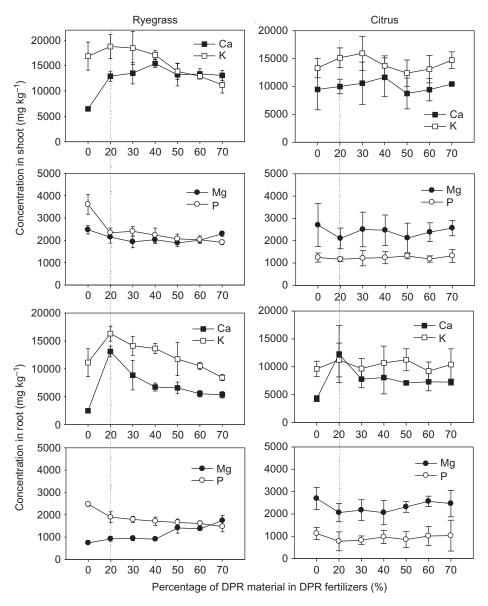


Figure 3. Concentrations of Ca, K, Mg, and P in ryegrass and citrus shoot and root as affected DPR fertilizers of different formulas: 0, water-soluble chemical fertilizer; 20–70%, percentages of DPR materials contained in DPR fertilizers.

applications of DPR fertilizers and chemical fertilizers (Figure 3), which indicated that DPR fertilizers can offer comparable P for the growth of citrus seedlings to that of P in chemical fertilizer. Correlation analyses revealed significant positive relations of M3-extractable Ca and K in ryegrass-cultivated soil with their respective concentrations in the shoot and root of ryegrass (P < 0.01). Even though M3-extractable P and Mg did not, Olsen P in soil did demonstrate significantly positive correlations (P < 0.01) with P concentration in the shoot and root of ryegrass. Therefore, DPR fertilizers (especially those containing 20–30% DPR materials), rich in Ca, Mg, K, and P, can be a good source of these nutrients for ryegrass plants.

Uptake of heavy metals in plant tissues was dependent on cultivar. Both plants had greater concentrations of heavy metals (Cu, Pb, and Zn) in root than in the shoot; in some treatments, concentrations of Pb in the shoot of ryegrass and citrus seedlings were less than its detection limit (Tables 4 and 5). Copper was not different among varying DPR fertilizer applications except for that in ryegrass root, in which DPR fertilizer containing 20% DPR materials resulted in greater Cu concentration (Table 4). The DPR fertilizer application resulted in less Zn uptake in the two plants except for citrus shoot (Table 5). The concentrations of Pb were not discriminated in the ryegrass root, but increased in citrus seedling root with increasing DPR materials in DPR fertilizers (Table 5). These results suggested that application of DPR fertilizers did not increase the uptake of Cu, Pb, and Zn in ryegrass and citrus seedlings as compared with chemical fertilizer.

Effects of DPR Fertilizers on Soil Quality

Application of DPR fertilizers significantly raised soil pH from 4.68 to 7.48 in ryegrass cultivated soil and from 5.42 to 8.15 in citrus cultivated soil, gains of about 3 units over those from chemical fertilizer application (Figure 4). Such amelioration is potentially favorable for plant growth in acidic sandy soils in south Florida. This suggests that DPR fertilizers are superior to water-soluble P fertilizer for neutralizing soil acidity in sandy soils. Acidic sandy soil is supposed to dissolve DPR material, whereas release of Ca and Mg from DPR material can neutralize soil acidity; therefore, soil pH and exchangeable Ca/Mg are highly related to the dissolution of DPR fertilizers (He et al. 2005). Thus, soil pH was negatively correlated with M3-extractable P (P < 0.01) but positively with M3-extractable Ca (P < 0.01) and Mg (P < 0.05) in the ryegrass and citrus cultivated soil.

Application of DPR fertilizers, especially those containing 20% DPR materials, rapidly increased electrical conductivity (EC) in soils because of input of water-soluble salts (such as Ca, Mg, K etc.; Table 2). However, the EC values were still within the normal range for crop production (200–1200 μ S cm⁻¹, Agriculture Solutions LLC 2007). After cultivation of ryegrass and citrus seedlings, the EC in soils applied with chemical fertilizer dropped to less than 200 μ S cm⁻¹; however, those applied with DPR fertilizers still maintained greater EC (>200 μ S cm⁻¹) (Figure 4). This suggested the slow release feature of DPR fertilizers in soils.

The DPR fertilizers generally increased soil organic-matter content because they contain 27 to 72 g kg⁻¹ organic C (Table 1), which is needed for the low organic-matter sandy soils. The TOC content in DPR fertilizers generally decreases with increasing proportions of DPR material, with the greatest TOC in the DPR fertilizer containing 20% DPR material (Table 2), suggesting that N-viro soil was the main contributor of organic matter in the DPR fertilizers. This could be because biosolids are a major component for the production of N-viro soil (Sourcewatch 2010). In addition, the ryegrass-growing soils receiving DPR fertilizers generally had more total and available nutrients including Ca, K, Mg, P, B, Mn,

Concentrations of heavy metals in ryegrass plants (mg kg⁻¹) receiving different DPR fertilizers Table 4

root	Zn	71a $71.3 \pm 5.05a$	$45.5 \pm 3.07b$	$ 7a + 45.1 \pm 7.99bc $	19a 41.6 ± 5.37 bcd	$45.9 \pm 3.26b$	35.8 ± 2.27 cd	28a $34.8 \pm 6.03d$
Ryegrass root	Pb	$3.98 \pm 1.71a$	$5.36 \pm 2.22a$	$2.69 \pm 2.17a$	$1.91 \pm 1.19a$	$2.33 \pm 1.43a$	$3.49 \pm 1.05a$	$5.35 \pm 2.28a$
	Cu	27.9 ± 2.68 ab	$38.7 \pm 10.7a$	$26.3 \pm 2.68b$	$30.8 \pm 3.25ab$	35.2 ± 7.98 ab	$28.4 \pm 3.09ab$	$24.4 \pm 4.91b$
	Zn	47.0 ± 1.19a	$30.1 \pm 0.684b$	$35.6 \pm 3.65b$	$33.8 \pm 2.34b$	$34.9 \pm 7.75b$	$34.7 \pm 1.64b$	$34.4 \pm 4.72b$
Ryegrass shoot	Pb	<dl b<="" td=""><td><df b<="" td=""><td>0.073 ± 0.285a</td><td>$0.463 \pm 1.57a$</td><td><dl b<="" td=""><td>$0.613 \pm 0.590a$</td><td><dl b<="" td=""></dl></td></dl></td></df></td></dl>	<df b<="" td=""><td>0.073 ± 0.285a</td><td>$0.463 \pm 1.57a$</td><td><dl b<="" td=""><td>$0.613 \pm 0.590a$</td><td><dl b<="" td=""></dl></td></dl></td></df>	0.073 ± 0.285 a	$0.463 \pm 1.57a$	<dl b<="" td=""><td>$0.613 \pm 0.590a$</td><td><dl b<="" td=""></dl></td></dl>	$0.613 \pm 0.590a$	<dl b<="" td=""></dl>
	Cu	$18.3 \pm 15.4a$	$13.2 \pm 3.31a$	$23.3 \pm 10.7a$	$23.4 \pm 3.25a$	$23.2 \pm 3.69a$	$23.0 \pm 13.9a$	$21.5 \pm 4.20a$
Percentage of DPR	fertilizers (%)	0^a	20	30	40	50	09	70

Notes. DL, detection limit; STDEV, standard deviation. ^aWater-soluble chemical fertilizer.

Concentrations of heavy metals in citrus plants (mg kg^1) receiving different DPR fertilizers Table 5

Percentage of DPR		Citrus shoot			Citrus root	
fertilizers (%)	Cu	Pb	Zn	Cu	Pb	Zn
0^{a}	$12.6 \pm 6.12a$	$0.223 \pm 0.387a$	49.4 ± 18.7a	39.5 ± 17.3a	$0.020 \pm 0.035c$	$67.3 \pm 11.4a$
20	$10.1 \pm 3.50a$	$0.810 \pm 1.40a$	$40.3 \pm 3.75a$	$40.3 \pm 23.9a$	$2.21 \pm 1.13c$	$43.7 \pm 11.4b$
30	$11.9 \pm 5.94a$	$0.807 \pm 1.40a$	$47.0 \pm 10.4a$	$26.4 \pm 6.03a$	$1.20 \pm 1.12c$	$44.9 \pm 11.3b$
40	$15.8 \pm 8.75a$	<dl b<="" td=""><td>$51.1 \pm 7.26a$</td><td>$23.5 \pm 10.2a$</td><td>$2.47 \pm 2.28c$</td><td>$46.8 \pm 14.3ab$</td></dl>	$51.1 \pm 7.26a$	$23.5 \pm 10.2a$	$2.47 \pm 2.28c$	$46.8 \pm 14.3ab$
50	$8.89 \pm 1.20a$	<dl b<="" td=""><td>$43.3 \pm 6.18a$</td><td>$39.7 \pm 6.52a$</td><td>3.47 ± 1.66bc</td><td>51.0 ± 11.4ab</td></dl>	$43.3 \pm 6.18a$	$39.7 \pm 6.52a$	3.47 ± 1.66 bc	51.0 ± 11.4 ab
09	$13.8 \pm 5.57a$	<dl b<="" td=""><td>$43.0 \pm 4.73a$</td><td>$32.9 \pm 15.2a$</td><td>6.45 ± 3.76ab</td><td>$38.3 \pm 9.13b$</td></dl>	$43.0 \pm 4.73a$	$32.9 \pm 15.2a$	6.45 ± 3.76 ab	$38.3 \pm 9.13b$
70	$12.1 \pm 3.60a$	$0.590 \pm 0.858a$	$48.1 \pm 2.17a$	$27.9 \pm 10.1a$	$7.34 \pm 1.13a$	$47.6 \pm 9.29ab$

Notes. DL, detection limit; STDEV, standard deviation. "Water-soluble chemical fertilizer.

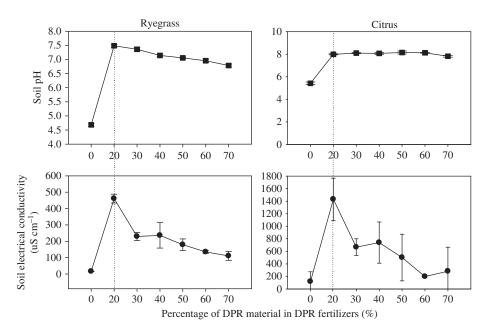


Figure 4. Soil pH and electrical conductivity (EC) after ryegrass and citrus harvest as affected by DPR fertilizers of different formulas: 0, water-soluble chemical fertilizer; 20–70%, percentages of DPR materials contained in DPR fertilizers.

Mo, Cu, and Zn than those treated with water-soluble chemical fertilizer (CF) (Figure 5 and Table 6). The phenomenon was more evident in the DPR fertilizer that contained 20% DPR material (Figure 5 and Table 6). Similar results were observed in the citrus-growing soils except for Cu (Figure 5 and Table 7), suggesting that DPR fertilizers can last longer in the soils, supplying nutrients with a slow-release feature, and are superior to chemical fertilizers for the acidic sandy soils.

Discussion

Previous studies demonstrated the advantages of DPR materials as P fertilizer over watersoluble P fertilizers in slow release time, less loss of P in leaching, neutralizing soil acidity, and abundant Ca, Mg, and micronutrients (He et al. 2005; Chen et al. 2006; Yao et al. 2007). These advantages are also observed in this study (Table 1; Figures 4 and 5); however, some benefits, such as pH, EC, TOC/TN, and M3-extractable K and Ca, seemed more from N-viro than from DPR (Table 2). This observation agreed with that of Yao et al. (2007), who stated that the N-viro soil had a greater effect on pH and EC than the DPR. The DPR fertilizers used for this study consisted of DPR material and N-viro soil; the latter is wastewater sludge with an alkaline admixture, containing not only bioorganic material but also minerals (Sourcewatch 2010). Therefore, the mixing proportion of DPR material and N-viro soil in the DPR fertilizers played an important role in the nutrition functions of DPR fertilizers. Yao et al. (2007) suggested that 20-30% of DPR material in the DPR fertilizers was optimal for radish growth based on plant biomass and uptake of Ca, Mg, and P. This applies to the case of ryegrass in this study but not citrus seedlings (Figure 1). This may be because biomass accumulations of radish and ryegrass are greater in leaves than in root (Figure 1). Because C and N are more effective than P to the biomass accumulation of

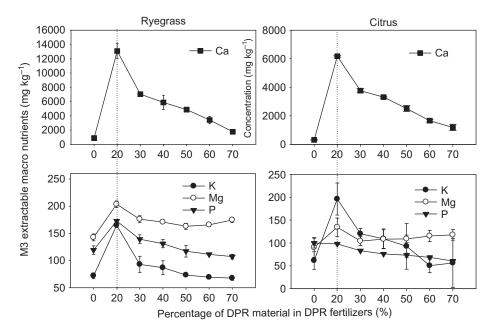


Figure 5. M3-extractable Ca, K, Mg, and P in soils after ryegrass and citrus harvest as affected by DPR fertilizers of different formulas: 0, water-soluble chemical fertilizer; 20–70%, percentages of DPR materials contained in DPR fertilizers.

leaves and the greatest TOC and TN contents were measured in DPR fertilizers containing 20–30% of DPR material (Table 2), the greatest biomass yield in ryegrass was expected in such treatments (Figure 1).

Soil properties, such as pH, EC, and organic matter, can greatly affect the availability of Ca, Mg, and P in DPR-amended soils (Hammond, Chien, and Mokwunye 1986; Wright, Baligar, and Belesky 1992; Chien and Menon 1995). Positive correlations were observed among soil pH, EC, and M3-extractable Ca (P < 0.01) and Mg (P < 0.01) in both soils cultivated with ryegrass and those with citrus seedlings, indicating the effectiveness of DPR fertilizers in improving soil quality. However, M3-extractable P was different from M3 Ca and Mg. It demonstrated no relation with soil pH but had a positive relation with soil EC (P < 0.01) in ryegrass-cultivated soil, whereas it showed a negative correlation with soil pH (P < 0.01) but not with EC in citrus-seedling-cultivated soil. This may hint at the effect of residue of culture media from citrus seedlings. Soil TOC had positive correlations with M3-extractable Ca (P < 0.01), Mg (P < 0.01), and P (P < 0.01) both soils with ryegrass and soils with citrus seedlings. This corroborated that organic matter can enhance the dissolution of PR in soils (Kirk and Nye 1986), which can be further supported by the elevated TOC in DPR fertilizers with increasing N-viro proportion (Table 2). However, on the other hand, elevation of soil pH and EC with DPR fertilizer application was accompanied by an increase in M3-extractable heavy metals (Cu, Pb, and Zn) in ryegrass-cultivated soil. This can be proved by the positive correlations (P < 0.01) of soil pH and EC with M3-extractable heavy metals. Therefore, there could be concerns regarding Pb and Zn release in the ryegrass-cultivated soils; however, this was not the case for Cu in the citrus-seedling-cultivated soils.

The agronomic effectiveness (such as plant nutrition and yield) of PR depends on PR reactivity, soil properties, and crop species (Smalberger et al. 2010). Previous study

M3-extractable nutrients and heavy metals in soils after ryegrass harvest (mg kg⁻¹) as affected by DPR fertilizers of different formulas Table 6

Percentage of							
DPR material in							
DPR fertilizers							
(%)	В	Fe	Mn	Mo	Cu	Pb	Zn
0^a	<dl d<="" td=""><td>$588 \pm 57.7a$</td><td>$30.0 \pm 0.586b$</td><td>3.43 ± 0.058d</td><td>$7.93 \pm 0.289b$</td><td>$11.2 \pm 0.000c$</td><td>$9.07 \pm 0.252e$</td></dl>	$588 \pm 57.7a$	$30.0 \pm 0.586b$	3.43 ± 0.058 d	$7.93 \pm 0.289b$	$11.2 \pm 0.000c$	$9.07 \pm 0.252e$
20	$0.667 \pm 0.116a$	$512 \pm 20.1b$	$33.8 \pm 1.40a$	$4.07 \pm 0.058a$	$9.40 \pm 0.300a$	$14.4 \pm 0.416a$	$13.7 \pm 0.252a$
30	$0.233 \pm 0.058b$	$482 \pm 24.2 bc$	$31.0 \pm 1.72b$	$3.73 \pm 0.153b$	$8.37 \pm 0.404b$	$12.7 \pm 0.625b$	$11.7 \pm 0.529b$
40	0.133 ± 0.116 bc	$467 \pm 22.2 \text{bc}$	$31.5 \pm 0.289b$	$3.80 \pm 0.000b$	$8.23 \pm 0.058b$	$12.8 \pm 0.116b$	$10.9 \pm 0.473c$
50	$0.033 \pm 0.058c$	$417 \pm 56.3c$	$30.1 \pm 0.961b$	3.67 ± 0.153 bc	$7.77 \pm 0.289b$	$11.9 \pm 0.529c$	10.2 ± 0.569 d
09	<dl d<="" td=""><td>464 ± 27.0bc</td><td>$30.6 \pm 0.379b$</td><td>3.63 ± 0.058bc</td><td>$7.70 \pm 0.100b$</td><td>$11.6 \pm 0.153c$</td><td>9.80 ± 0.173de</td></dl>	464 ± 27.0 bc	$30.6 \pm 0.379b$	3.63 ± 0.058 bc	$7.70 \pm 0.100b$	$11.6 \pm 0.153c$	9.80 ± 0.173 de
70	<df d<="" td=""><td>$488 \pm 42.9 \text{bc}$</td><td>$30.0 \pm 1.10b$</td><td>3.50 ± 0.100cd</td><td>$7.97 \pm 0.651b$</td><td>$11.2 \pm 0.529c$</td><td>$9.33 \pm 0.586e$</td></df>	$488 \pm 42.9 \text{bc}$	$30.0 \pm 1.10b$	3.50 ± 0.100 cd	$7.97 \pm 0.651b$	$11.2 \pm 0.529c$	$9.33 \pm 0.586e$

Notes. DL, detection limit; STDEV, standard deviation. "Water-soluble chemical fertilizer.

M3-extractable nutrients and heavy metals in soils after citrus harvest (mg kg⁻¹) as affected by DPR fertilizers of different formulas

Percentage of DPR material in DPR fertilizers (%)	В	F	Mn	Мо	Cu	Pb	Zn
0^a	<dl e<="" td=""><td>330±13.2a</td><td>2.93 ± 1.14ab</td><td>$0.033 \pm 0.006d$</td><td>$3.12 \pm 0.493a$</td><td>$1.09 \pm 0.070e$</td><td>$3.16 \pm 0.78b$</td></dl>	330±13.2a	2.93 ± 1.14ab	$0.033 \pm 0.006d$	$3.12 \pm 0.493a$	$1.09 \pm 0.070e$	$3.16 \pm 0.78b$
20	$1.217 \pm 0.199a$	$248 \pm 6.08d$	$1.07 \pm 0.541b$	$0.297 \pm 0.012a$	3.72 ± 0.705 a	$2.01 \pm 0.061a$	$5.30 \pm 0.041a$
30	$0.673 \pm 0.081b$	$251 \pm 6.00d$	$0.870 \pm 0.423b$	$0.157 \pm 0.012b$	$2.53 \pm 0.520a$	$1.54 \pm 0.036b$	$4.01 \pm 0.070b$
40	0.570 ± 0.165 bc	$243 \pm 12.9d$	$1.26 \pm 0.327b$	$0.137 \pm 0.006b$	$2.81 \pm 0.330a$	1.29 ± 0.038 cd	$3.99 \pm 0.142b$
50	0.410 ± 0.125 cd	265 ± 20.2 cd	$2.02 \pm 1.24b$	$0.143 \pm 0.015b$	$3.25 \pm 1.99a$	$1.41 \pm 0.085c$	4.30 ± 1.21 ab
09	0.203 ± 0.060 de	282 ± 6.66 bc	$4.26 \pm 2.04a$	$0.153 \pm 0.006b$	$3.73 \pm 0.196a$	$1.35 \pm 0.101c$	4.27 ± 1.02 ab
70	$0.053 \pm 0.092e$	$296 \pm 19.6b$	$1.04 \pm 1.14b$	$0.093 \pm 0.031 \mathrm{c}$	$2.97 \pm 0.920a$	1.17 ± 0.100 de	$3.53 \pm 9.17b$

Notes. DL, detection limit; STDEV, standard deviation. "Water-soluble chemical fertilizer.

suggested that sole application of compost, PR, or dolomite to soil did not affect the yield of cotton or maize or the contents of N, P, and K in plants; however, combination of compost with DPR material improved soil fertility (including N, P, and S) (Koulibaly et al. 2009). Therefore, the responses of plant growth and yield are dependent on the characteristics of DPR and N-viro soil, as well as their mixing proportion and soil properties. Amendment of N-viro soil provided a large amount of Ca and K in the soils (Table 2, Figure 5), resulting in increased uptake of Ca and K in plant tissues, especially in ryegrass (Figure 3). Similar results were reported by Yao et al. (2007). The M3-extractable P in ryegrass-cultivated soils treated with DPR fertilizers (especially those containing 20–30% DPR material) was greater than those treated with chemical fertilizer (Figure 5); however, P concentration was greater in the shoot and root of ryegrass treated with chemical fertilizer, indicating soluble P is more readily available to ryegrass.

Uptake of heavy metals by plants is a long-term concern. Soil amendments were widely applied to reduce heavy-metal toxicity to plants (Bolan and Duraisamy 2003). Studies showed that DPR fertilizer contained small amounts of heavy metals and therefore could result in accumulation of these heavy metals in plants (Javied et al. 2009). Other studies demonstrated that PR application is effective in immobilizing Pb in loam soil (Ma and Rao 1999). Perennial ryegrass (Lolium perenne L.), a pasture plant, is frequently cultivated for revegetation in metal-contaminated land because of its ability in accumulating moderate to high levels of metals (Pichtel and Salt 1998; Arienzo, Adamo, and Cozzolino 2004). Therefore, high Cu and Zn contents in the shoot and root of ryegrass were reported even though biosolids were incorporated in the Alfisol, and such accumulation was in connection with the labile fractions of Cu and Zn in the soils (Ahumada et al. 2009). Copper in the shoot and root of ryegrass (Table 4) were comparable to the reported range of 15–40 mg kg⁻¹ (Bolton 1975), but Cu in the root of ryegrass was close to the toxic limit (30 mg kg⁻¹, Leeper 1972). Lead in ryegrass was far less than the leaf tissue toxicity limit (30–100 mg kg⁻¹) (Mendez and Maier 2008). Zinc in ryegrass was less than 100 mg kg⁻¹ in healthy perennial ryegrass (Mackenzie and Purves 1975) and far less than the toxic limit (500 mg kg⁻¹, Leeper 1972). The M3-extractable Cu, Pb, and Zn had poor correlations with their respective concentrations in the shoot and root of ryegrass, indicating that M3 extraction is not an adequate indicator of metal bioavailability in DPR fertilizers. Copper, Pb, and Zn in the DPR fertilizers were mainly from biosolidscontaining N-viro soils (Table 3); therefore, there were still some correlations of metal concentration in the ryegrass (especially Cu in ryegrass root) with N-viro application rate in DPR fertilizers (Table 4). Biosolids, as a main composition in N-viro soil (Sourcewatch 2010), was supposed to reduce heavy-metal uptake in plants when applied in soils; however, this is not the case for ryegrass (Ahumada et al. 2009; Table 4). Application of DPR fertilizers changed soil properties such as pH and EC, thus affecting heavy-metal uptake by ryegrass and citrus seedlings. Furthermore, Cu and Pb in the root of ryegrass were 1.2-3.0 and 4-40 times greater than those in the shoot (Table 4), which agreed with the observation of Santibanez, Verdugo, and Ginocchio (2008). Variation of Pb [<detection limit (DL) \sim 0.810 mg kg⁻¹] in the shoot of citrus seedlings (Table 5) was smaller than that previously reported in citrus leaves (<DL ~5.90 mg kg⁻¹; Menti et al. 2006). However, Cu and Zn contents in the shoot of citrus seedlings (Table 5) were greater than those in citrus leaves $(3.00-9.40 \text{ and } 13.7-46.5 \text{ mg kg}^{-1}, \text{ respectively}; \text{ Menti et al } 2006).$ Compared with the toxicity limits of Pb (10-20 mg kg⁻¹; Chapman 1966; Pettygrove and Asano 1984) and Zn (100–200 mg kg⁻¹; Chapman 1968; Pettygrove and Asano 1984) in citrus, both Pb and Zn contents in the shoot and root of citrus seedlings in this study were far less (Table 5). A 70-day column-leaching study demonstrated that the maximum concentrations of Cu, Pb, and Zn in leachate from the DPR-amended soils were less than the drinking water quality guidance limits of Florida Department of Environmental Protection (data not shown). These results demonstrated that the concentrations of Cu, Pb, and Zn in citrus seedlings receiving DPR fertilizers were in the safety range.

Conclusions

The DPR fertilizers can raise soil pH and EC, soil organic matter, and total and available nutrients when applied in acidic sandy soils. The DPR fertilizers appear superior to water-soluble fertilizer for the growth of ryegrass and citrus in term of both dry-matter yield and nutrient concentrations in plants; however, their agronomic effectiveness is dependent on cultivar and proportion of DPR material in the DPR fertilizers. DPR fertilizers with lower proportions of DPR material (20–30%) appeared to be optimal in supplying nutrients for plant growth with minimal environmental impacts of metals Cu, Pb, and Zn.

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