

“Demonstration of Water Quality Best Management Practices for Beef Cattle Ranching in the Lake Okeechobee Watershed”

Task # 6: Selection and Evaluation of Soil Amendments to Reduce Edge-of-Field P Losses.

Introduction

The use of soil amendments is one of several best management practices (BMPs) to reduce edge-of-field P losses, which can impair water quality. Soil amendments are intended to reduce P concentrations in soil solutions and, thereby, reduce P available for various loss mechanisms, including runoff and leaching. Numerous amendment studies have been conducted throughout Florida over the years by several investigators (e.g., Allen, 1988; Anderson, 1995; Alcordo, et al., 2001; Matichenkov et al., 2001), utilizing a wide variety of amendments. Interpreting the results of these studies is complicated by the wide variety of amendments, amendment rates, soils, P sources, and P loss mechanism(s) investigated. The purpose of our work was to conduct a systematic evaluation of numerous soil amendments using standardized protocols to provide directly comparable results upon which to judge amendment effectiveness. The protocols included standard total elemental analysis of each amendment, short-term lab equilibrations, small column leaching studies, and simulated rainfall studies. Amendments were applied to a composite soil, representing multiple samples of surface soil from the expected field demonstration site on the Beaty Ranch. Amendments included water treatment residuals (Fe-, Al-, and Ca-based WTRs), industrial by-products produced or marketed in Florida (slag, silica-rich, and humate materials), and agricultural amendments (lime and gypsum).

Amendment Selection Criteria

Best management practices to reduce P impacts on water quality can be categorized into methods that: 1) Reduce P inputs, 2) Increase P retention by soil, 3) Reduce P solubility in soil, and 4) Remove P from water escaping the watershed soils before the P-laden water reaches a significant water body. This project focused on reducing soluble P concentrations in the soil solutions of watershed soils using methods 2 and 3, but a permanent solution to P management will likely have to involve a multi-faceted approach (all methods). To be effective, such methods must permanently immobilize P in the soils, not merely delay P mobility. Thus, practices (e.g., use of soil amendments) that alter soil properties to increase P retention or reduce P solubility must also decrease P release (desorption). Further, such alterations must be expected to be permanent, less the P be re-solubilized (mobilized) in the future under normal environmental conditions.

Best management practices must also be matched to the chemical, physical, and hydrologic characteristics of the problematic watershed. Thus, if the soils of the watershed are not already impacted by P (high in soluble P) but are expected to receive large inputs of P (e.g., via surface applications of manure), amendments or other practices that seek to reduce P inputs and/or the solubility of the P inputs can be effective. If the soil is already impacted and high concentrations of soluble P exist throughout the soil

profile, practices that only increase P retention in the zone of incorporation may be ineffective at reducing P losses from other parts of the soil profile. Fine-textured soils may promote P retention and slow P leaching, but encourage surface runoff of soluble or particulate P. Flat, coarse-textured soils may minimize surface runoff, but may allow significant P leaching to ground waters. The presence of slowly permeable layers (e.g., spodic horizons), particularly if shallow in the profile, can alter the hydraulic characteristics of even coarse-textured soils and promote “sub-surface runoff”, or surface runoff in high water table periods (e.g., rainy season). The choice of amendment to use is influenced by all these factors and, thus, is complex. This complexity confounds extrapolation of laboratory studies designed to accentuate one P retention (or P loss) mechanism to the multitude of field conditions possible. Practical considerations such as amendment availability, rate necessary, and cost must also be included. Further, other contaminants (e.g., trace elements, excessive salinity or acidity/alkalinity) in amendments must be considered so solving the “P problem” does not lead to other water quality or soil/plant problems.

Previous Approaches (examples)

1. Reduce the solubility of P added in land-applied wastes.
 - a. Surface waste/amendment applications
Moore and colleagues (e.g., Moore et al., 2000; Moore and Miller, 1994; Shreve et al., 1995) have done extensive work that documents effective control of P solubility by Al added to poultry manure. Sufficient addition of Al sulfate (alum), to yield a 1:1 molar ratio of Al to P in the manure, significantly reduced P solubility and dramatically reduced P in runoff from manured sites.
 - b. Incorporated waste/amendment applications
Elliott et al. (2001) co-applied Al treated water treatment residuals (Al-WTR) with several biosolids, fertilizer, and two manures. They demonstrated almost complete control of P leaching through Florida sands initially low in P, regardless of P source because soluble P levels were dramatically reduced in the soil/amendment mixtures.
2. Increase soil retention of P
 - a. Increased P adsorption
Laboratory studies (O’Connor et al., 2002) showed that Al-WTRs adsorb large amounts of P, and that poorly P-sorbing Florida soils could be made to adsorb significantly more P when they were amended with modest amounts of Al-WTRs. The P retained by Al-WTR or Al-WTR-amended soils was essentially irreversibly bound, barring unrealistic changes in environmental conditions (very low pH). Iron-based WTRs, or salts, can also effectively sorb P, but P release can occur under reducing conditions (Ann et al., 2000a,b).

Surface applications/incorporation of Al-WTRs were much less effective in controlling P leaching in another Florida sand that was already impacted by long-term manure additions (Lane, 2002). Soluble P

concentrations were high below the zone of amendment incorporation, contributing to P loss, and high soluble organic carbon concentrations appeared to reduce P binding to the WTR.

b. Increase soil solid phase control

Soil retention of P can also be increased by causing secondary solid phases (precipitates) of P to form. The process chemistry is similar to that used to remove P from municipal wastewaters (Jenkins and Hermanowicz, 1991). Whereas P solubility in acid systems is typically amenable to control with Fe and Al (to cause insoluble Fe- and/or Al-P compounds to form), high pH soils typically limit P solubility via precipitation of various Ca-P compounds (Allen, 1988; Anderson, 1995). Soils of south Florida impacted by heavy manure applications often exhibit high pH values (≥ 7), despite low natural soil pH values of 4.5 to 5.5. Thus, heavily manure-impacted soils can be more amenable to P control through the use of Ca-containing amendments (e.g., lime, gypsum) than to control with Fe- or Al- containing amendments. However, if the high soil pH values revert to the natural low soil pH values, the solubility of Ca-P compounds is predicted to increase and P would be released.

Choice of amendment and amendment rates

For this study, the choice of amendments and amendment rates to evaluate was influenced by both chemical and historical considerations. Initially, practical considerations of ready availability, application practicality, and cost were ignored. Refinements to the list of amendments for further evaluation, however, involved practical considerations.

1. Chemical considerations

As described above, P solubility is generally limited by Fe and Al in acid soils and by Ca in high pH soils. Thus, sources of Fe and Al as well as sources of Ca (or high pH) were evaluated. The rates of each amendment were roughly based on the presumed chemistry of the resulting (insoluble) metal salts. Thus, P precipitated as insoluble Fe- and/or Al-phosphates (e.g., strengite = FePO_4 ; variscite = Al PO_4) usually have molar ratios of Fe (or Al) to P of 1:1. The P concentration (moles) to be immobilized can be chosen as soluble P or, more commonly, total P in the soil. The concentration (moles) of metal (Fe or Al) needed to react with the P should be based on the “reactive” metal concentration in the amendments. Total metal concentrations in amendments other than soluble metal salts typically overestimate the concentration of metal truly available for reaction with P. O’Connor and Elliott (2001) showed that amorphous (oxalate extractable) metals in Fe and Al amendments better described amendment reactivity toward P than total metal content.

The ratio of metal (Ca) to P in the host of Ca-phosphates that can precipitate in soils varies widely. A common assumption, however, is that P will eventually be

found in various apatite mineral forms, in which the Ca:P molar ratio is 5:3 [e.g., hydroxyapatite = $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$]. Total Ca and P concentrations (moles) are typically used to calculate the amount of amendment (Ca source) necessary to react with P in the soil. Sometimes, the soil is assumed sufficient to supply the necessary Ca, but soil pH must be raised to values where the solubility of Ca-P is low (pH values >7). In this case, the liming value of the amendment and the initial soil pH is considered, rather than the Ca concentration of the amendment.

2. Historical considerations

In this context, historical considerations refer to previous studies (published and unpublished) in which various rates of various amendments have been utilized. Particular attention was paid to literature (or results) generated by Florida investigators.

An excellent discussion of the use of chemical soil amendments to control P in Florida, specifically the Lake Okeechobee watershed, is given by Allen (1988). He calculated amounts of Ca-based amendments needed to control P losses from dairies assuming ideal chemistries (target Ca:P molar ratio of 5:3), but noted the possible interference of such soluble constituents as Mg and organic C on precipitation kinetics and purity of the solid phases formed. Greater quantities of Ca are necessary in such situations. Allen (1988) called for detailed soil chemistry studies to verify the calculations and to quantify interferences and actual reaction rates and reaction products.

Anderson et al. (1995) conducted lab incubations (equilibrations) with manure-loaded soils (Spodosols) amended with Ca-, Fe- and Al-salts, alone or in combination, under both aerobic and anaerobic conditions. Amendment rates were targeted to include metal:P molar ratios indicative of pure metal-P solids, but included rates on either side of the “ideal” rate necessary to attain the target ratios. Gypsum (CaSO_4) rates were 0, 4, 8, and 16 g kg^{-1} soil; FeSO_4 and $\text{Al}_2(\text{SO}_4)_3$ rates were 0, 50, 100, 250, and 1000 mg Fe (or Al) kg^{-1} soil; and CaCO_3 rates (not given) were chosen as the amounts necessary to raise the pH values of individual soils to 7-7.5. Anderson et al. (1995) concluded that lime could be an effective amendment if sufficient material was added to raise (and maintain) soil pH values in the 7-7.5 range. Iron and Al salts effectively increased soil retention of P, but the authors expressed concern about possible Al toxicities and cost of both metal salts. Anderson et al. (1995) favored gypsum as a soil amendment, especially in anaerobic systems and in Spodosols heavily impacted by dairy manure. Gypsum rates as great as 100 mg kg^{-1} soil were effective, although there were unexplained impacts on soil microbial activity at the highest rate.

Alcordero et al. (2001) conducted greenhouse leaching studies with Ap, E, and Bh horizons of beef cattle pasture soil (Immokalee series) amended with additional P fertilizer and a single Ca rate (800 kg Ca ha^{-1}) added as gypsum or lime products. No justification was given for the Ca rate and final soil pH values were not in the

7-7.5 range identified as useful by Anderson et al. (1995). A Ca loading of ~ 2.4 g Ca kg^{-1} soil can be calculated for the Alcordo et al. (2001) treatment, which is similar to the 8 g gypsum kg^{-1} soil (~ 2 g Ca kg^{-1} soil) rate of Anderson et al. (1995). Alcordo et al. (2001) found no benefit of gypsum products in reducing P leaching, but significant benefits of lime.

Rechcigl et al. (2000) evaluated limestone and gypsum as amendments in a field study to reduce P leaching and runoff from beef cattle pastures. Amendments were applied at 2 and 4 Mg ha^{-1} , roughly equivalent to 500 and 1000 kg Ca (from gypsum) ha^{-1} and 800 and 1600 kg Ca (from lime) ha^{-1} . The field rates were, thus, similar to the greenhouse rates used by Alcordo et al. (2001). Rechcigl et al. (2000) reported reduced soil water P concentrations in both the gypsum and lime treatments, but no effect on P concentrations in runoff. Boruvka and Rechcigl (2003) reported that lime was more effective than dolomite or gypsum at increasing P retention by the Ap horizon of a Spodosol (initial pH 4.3), but noted that the effect must be accompanied by an increase in soil pH (≥ 7) to increase P retention.

Stout et al. (2000) applied gypsum (10 and 20 g kg^{-1} soil) to 3 manure-impacted soils from Pennsylvania, and evaluated the impact on surface runoff of P. Gypsum significantly reduced runoff P in grass-covered runoff boxes (where dissolved P predominated), but failed to reduce dissolved P in runoff from bare soil (where particulate P predominates). Leaching losses of P were not evaluated.

Several industrial by-products (e.g., coal combustion by-products, steel processing sludge, bauxite mining residuals, and fertilizer production slag) have been examined as amendments to control P solubility in soil (Peters and Basta, 1996; Stout et al., 1998; Stout et al., 2000; Matichenkov et al., 2001; and Callahan et al., 2002). Amendment rates typically ranged from 5 to 80 g amendment kg^{-1} soil, simulating field application rates of about 3 to 50 Mg ha^{-1} . Effectiveness and practicality varied with application rate, soil condition (pH), and P control mechanism investigated. Only the Matichenkov et al. (2001) study was conducted using Florida soils and will be detailed here.

Matichenkov et al. (2001) evaluated Si-rich materials both for their abilities to increase soil retention of P and to improve Bahiagrass growth. Only the retention impacts are addressed here. Amendments included a slag by-product of the electric production of P fertilizer and Pro-Sil, a by-product of steel processing. Both amendments were applied to Florida soils at the equivalent of 10 Mg ha^{-1} (estimated to = 5 g amendment kg^{-1} soil). Effects of the slag material on (increased) P retention and (decreased) P leaching were marginal, whereas the effects of Pro-sil were dramatic.

Elliott et al. (2002) conducted lab equilibration and column leaching studies with various water treatment residuals (WTRs) produced in Florida. Applications of WTRs, notably the Fe- and Al-WTRs, to Florida soils that sorbed P poorly

increased P retention and decreased P leaching. Amendment rates examined varied from 0.1 to 10% by weight, but practically effective rates were typically 1 to 5% by weight (1 to 50 g WTR kg⁻¹ soil, and ~20 to 100 Mg amendment ha⁻¹). Brown and Sartain (2000) conducted greenhouse studies with a Fe-WTR (Vigiron) applied at 2.5% by weight to golf green mix (85% sand), and studied impacts on Bermuda grass growth and fertilizer-P leaching. Leaching of P was minimal in the presence of Fe-WTR, with no impacts on grass growth or nutrition.

dinoSoil™ (Leonardite, an oxidized form of lignite) has been championed as an amendment to improve soil quality and plant growth and to retard soil P loss (M. Hougland, personal communication, 2003). Rates as low as 1000 lbs per acre of dinoSoil (0.05% by weight) are recommended.

3. Final Selection

Based on the chemical and historical considerations described above, 10 materials were selected for evaluation as amendments at various rates of application (Table 1). The list included two Fe-“humates” (a Fe-WTR, “Vigiron”) and a Ti-mine waste (Fe-“humate”), two Al-WTRs, one Ca-WTR, a coal combustion slag, a Si-rich material (Pro-sil), a Leonardite material (dinoSoil), and two agricultural materials (lime and gypsum). All materials are produced or marketed in Florida, and most have been evaluated to some degree by Florida researchers as amendments for P-impacted soils or waters. Amendment rates were initially chosen to represent wide ranges that encompassed rates reportedly effective at controlling P solubility/mobility. The list of amendments and range of amendment rates was expected to narrow as amendment effectiveness was tested in the various standardized protocols. Ultimately, only 1 or 2 amendment/amendment rate combinations will be recommended for field scale evaluation.

Table 1. Amendments and amendment rates selected for evaluation.

Amendment	Source	Rates		
		g material kg ⁻¹ soil	% by wt.	T/A*
Fe-WTR	Vigiron, Tampa, FL	0, 1, 5, 10,50,100	0 to 10	0 to 100
Fe-“humate”	Dupont, Starke, FL	“	“	“
Al-WTR	Manatee County, FL	“	“	“
Al-WTR	Okeechobee, FL	“	“	“
Pro-sil	Pro-Chem (PA)	0, 1, 2.5, 5, 10, 25	0 to 2.5	0 to 25
Coal slag	Nutrasource, Tampa, FL	0, 1, 5, 10, 50,100	0 to 10	0 to 100
Gypsum	Nutrasource, Orlando, FL	“	“	“
Ca-WTR	Bradenton, FL	0, 0.5, 1, 2, 5, 10	0 to 1	0 to 10
Lime	Franklin Minerals, Ocala, FL	“	“	“
dinoSoil	Leonardite (Texas)	0, 1, 5, 10, 50,100	0 to 10	0 to 100

*Approximated assuming uniform mixing with soil to a depth of 15 cm and a bulk density of 1.3 g cm⁻³, which yields 10³ tons of soil per “acre-furrow-slice”.

Standardized Protocols

Amendment and soil analyses

Amendments were air-dried and ground to pass a 2-mm sieve, and then digested using EPA Method 3050B (USEPA, 1995). Digests were analyzed for P, Fe, Al, Ca, Mg, Mn, S, Cu, As, Se, and Mo using inductively coupled plasma spectrometry (ICP) or graphite furnace atomic absorption spectrometry (GFAA). Percent solids, pH, and % organic matter were determined on materials “as is” (at their native moisture contents) using standard methods (Hanlon et al., 1997; Sparks, 1996). Carbon and N contents of the materials were determined by combustion at 1010 degrees Celsius using a Carlo Erba NA-1500 CNS analyzer. Detailed P chemistry of the materials was determined using sequential analysis (Chang et al., 1983), Mehlich-1 extraction (Hanlon et al., 1997), and oxalate extraction for P, Fe, and Al (McKeague et al., 1971). All analyses were conducted in triplicate, and in accordance with typical QA/QC procedures, which included use of certified standards to verify methods.

Similar analyses were conducted on soil from the expected field site (Beaty Ranch). Soil samples were randomly collected from 10 locations within the field site from the 0-15 cm depth and thoroughly mixed to yield a “composite” soil for use in the protocols involving soil. In addition to the analyses identified above for the amendments, the soil was analyzed for water extractable P using a 1:10 soil:water suspension equilibrated for 24 h, followed by filtration (0.45 micron), and P analysis by a colorimetric method (Murphy and Riley, 1962).

Selected properties of the amendments are given in Table 2. Total elemental analyses are, in general, consistent with values expected for the various materials. Thus, the two Al-WTRs contain elevated total Al contents, the Fe-WTR is high in total Fe, and the Ca-sources (Ca-WTR, gypsum, and lime) contain abundant Ca. The Fe-“humate” from Dupont contains ~10 times more Al than Fe, and the total Fe concentration of the Dupont material is only about ¼ that of the Fe-WTR. The coal slag contains abundant Fe and Al, suggesting that it may serve to immobilize P primarily through reactions with Fe and Al. The slag also has a low pH (3.69), which could affect the pH of poorly buffered soils when applied at high rates. Pro-sil is championed as a Si-rich material, but it also contains appreciable total Fe and Al (~5% by weight), and Ca (~24%), which are expected to influence P solubility. The Pro-sil material we received had an extraordinarily high pH (>11), whereas data provided by the producer suggest the pH is 7.6, but that the pH can vary within piles (B. Ande, 2003, personal communication). A material pH of >11 could be problematic if the liming value of the material was not considered in land application practices, particularly if the material was applied as surface applications to acid-tolerant (“acid-loving”) plants like Bahiagrass. Bahiagrass growth can be severely impacted when soil pH values exceed ~7. The dinoSoil material reportedly contains abundant “humates” in combination with aluminosilicate clay (montmorillonite). The total analysis of Table 2 confirm the high total Fe and Al concentrations expected for aluminosilicate clay, but an organic matter content (as measured by loss on ignition) of only ~8%. The low pH of the dinoSoil material could alter the pH of poorly buffered soil if the material was applied at high rates. All

amendments contain some P, but the total concentrations are usually low and none exceeded 3.12 g kg^{-1} (~0.3%).

Table 2. Selected properties of amendments.

Form	Total Elemental (g kg^{-1} , unless otherwise noted)												% Solids	% Org Matter (LOI)	pH ‡
	C (%)	N (%)	C:N	Fe	Al	Ca	Mg	P	Mn	S	Cu	Zn			
†M-Al-WTR	12.7	0.60	21.1	2.97	78.1	1.09	0.24	2.79	0.04	7.26	0.06	0.02	80.6	26.4	5.04
†O- Al-WTR	19.0	1.17	16.2	5.33	145	5.91	2.43	1.91	0.05	10.5	<0.01	<0.01	9.00	39.0	6.82
Fe- WTR	12.4	0.81	15.2	232	5.04	22.0	0.63	3.12	0.60	4.48	0.48	0.03	77.9	24.8	6.07
Ca- WTR	11.6	0.07	161	0.37	0.60	321	8.61	0.03	0.01	1.08	<0.01	<0.01	99.6	1.92	8.88
Coal slag	26.5	0.31	86.6	88.6	49.7	11.4	2.25	0.27	0.14	40.6	0.08	0.44	93.5	37.4	3.69
Pro-sil	0.85	0.03	29.3	33.5	15.2	240	56.8	0.12	8.22	0.80	0.04	0.04	99.4	1.76	11.3
Dupont	32.2	0.59	54.1	4.85	49.0	0.20	0.49	1.02	0.02	4.67	0.02	0.01	66.3	52.6	3.59
Gypsum	0.80	0.06	13.1	0.50	0.86	267	1.38	0.19	0.01	195	<0.01	<0.01	77.8	1.73	8.30
Lime	11.9	0.06	199	0.50	0.35	347	2.58	0.45	0.03	0.05	<0.01	<0.01	92.8	0.58	8.92
dinoSoil	2.68	0.14	19.6	41.9	66.6	10.2	7.93	0.17	0.35	14.0	0.03	0.09	91.3	7.83	3.63

†M-Al- WTR = Manatee County Al- WTR; O-Al-WTR = Okeechobee Al- WTR

‡ At solid: solution ratio of 1: 2

Additional phosphorus characterization data for the amendments are given in Table 3. The sequential analysis data suggest that little of the total P in any amendment is readily soluble (KCl-extractable values $< 3 \text{ mg kg}^{-1}$) and Mehlich-1-extractable values $< 10 \text{ mg kg}^{-1}$. Much of the sequentially extracted P was found in the HCl fraction (Ca and Mg-associated “forms”) and the residue fraction (non-labile “forms”).

This distribution is expected for the Ca-dominated amendments (gypsum, lime, and Ca-WTR). The lack of dominance of NaOH-Pi (Fe and Al-associated P “forms”) in the Fe and Al-WTRs may appear incongruent, but likely reflects the addition of liming agents to promote Fe- or Al-hydroxyoxide formation in drinking water treatment operations and the recalcitrance of P residues to extraction by the less stringent reagents that characterize the various “forms” of solid-P.

Table 3. Phosphorus characterization of amendments.

Form	Sequentially extracted P (mg kg ⁻¹)						Mehlich-1 P (mgkg ⁻¹)	Oxalate Extractable (g kg ⁻¹) ‡			PSI § (%)
	KCl	NaOH Pi	NaOH Po	HCl	Residue	Sum		P	Fe	Al	
†M- Al- WTR	2.07 ± 0.11	397 ± 10	105 ± 1	2200 ± 110	301 ± 69	3000 ± 189	8.1 ± 0.1	3.02 ± 0.02	3.32 ± 0.05	109 ± 3.8	2.39
†O- Al- WTR	2.86 ± 0.32	66.9 ± 8.8	80.7 ± 4.3	195 ± 12	1680 ± 5	2030 ± 6	0.2 ± 0.0	0.61 ± 0.01	0.78 ± 0.00	73.7 ± 1.9	0.72
Fe- WTR	0.56 ± 0.15	320 ± 3	354 ± 113	857 ± 70	2010 ± 73	3540 ± 32	5.4 ± 0.2	0.90 ± 0.00	76.2 ± 1.0	1.28 ± 0.02	2.07
Ca-WTR	1.71 ± 0.22	1.59 ± 0.07	1.28 ± 1.28	0.98 ± 0.08	46.8 ± 0.1	52.4 ± 1.7	0.1 ± 0.0	0.02 ± 0.00	0.39 ± 0.01	0.51 ± 0.01	2.56
Coal slag	2.16 ± 0.22	30.0 ± 2.3	0.92 ± 0.92	135 ± 6	197 ± 18	365 ± 15	3.3 ± 0.0	0.07 ± 0.00	27.6 ± 1.4	6.49 ± 0.02	0.33
Pro-sil	1.16 ± 0.11	1.27 ± 0.08	0.08 ± 0.08	1.76 ± 0.18	69.7 ± 1.8	74.0 ± 1.9	0.1 ± 0.0	0.03 ± 0.00	28.3 ± 0.7	4.11 ± 0.03	0.16
Dupont	1.87 ± 0.11	141 ± 0	0.00 ± 0.00	521 ± 7	247 ± 12	911 ± 5	5.7 ± 0.0	0.64 ± 0.03	2.76 ± 0.18	27.4 ± 0.4	1.93
Gypsum	2.07 ± 0.11	0.00 ± 0.00	0.25 ± 0.00	135 ± 5	42.7 ± 0.5	180 ± 5	9.0 ± 0.2	0.10 ± 0.02	0.19 ± 0.01	0.04 ± 0.01	65.7
Lime	1.95 ± 0.00	2.01 ± 0.17	0.00 ± 0.00	145 ± 17	314 ± 21	463 ± 4	0.6 ± 0.0	0.22 ± 0.00	0.05 ± 0.00	0.01 ± 0.00	497
dinoSoil	0.71 ± 0.16	44.8 ± 0.0	150 ± 2	20.5 ± 0.3	63.5 ± 2.1	280 ± 2	10.9 ± 0.0	0.12 ± 0.00	2.48 ± 0.03	2.21 ± 0.03	2.91

† M-Al-WTR = Manatee Al-WTR; O-Al-WTR = Okeechobee Al-WTR

‡ At solid: solution ratio of 1:60

§ Phosphorus saturation index [(oxalate P/oxalate Fe + oxalate Al)*100]; elemental concentrations in moles.

Oxalate-extractable P, Fe, and Al values were used to characterize the extent to which amendment total P (and Fe and Al) was associated with amorphous Fe and Al hydroxyoxides (McKeague et al., 1971). In almost all amendments, amorphous Fe and Al solids (and associated P) appear to constitute about 1/3 to 1/2 of total elemental contents, indirectly confirming the prevalence of recalcitrant (residue fraction) P-solids. The exception is the Manatee Al-WTR in which essentially all of the total P, Fe, and Al is oxalate-extractable. The data suggest that the Fe and Al in Manatee-Al-WTR should be highly labile (reactive) toward soluble P in soils. The phosphorus saturation index (PSI) has been suggested as an *a priori* measure of lability of P in solids and a measure of likely P-sorption capacity of the solid (Elliott et al., 2002). Materials with very low PSI values are expected to have large P-sorption capacities; very large PSI values are associated with materials of limited P-sorption and even P release. The index applies only to materials dominated by Fe and Al hydroxyoxides, so values for Ca-dominated materials are not meaningful. Using this concept (PSI), the Okeechobee Al-WTR is identified as a likely good sorbent for P, but the Manatee Al-WTR and Vigiron Fe-WTR are also identified as potentially useful P-sorbents.

Some trace elements (Cu and Zn) were analyzed by normal ICP techniques in the total elemental digests (Table 2). Additional trace elements of significant environmental concern (As, Se, and Mo) were determined using techniques (GFAA, hydride generation, etc.) with lower detection limits. Results of these analyses are given in Table 4. The intent was to identify potential trace element contamination problems that could arise from adding significant amounts of the amendments to agricultural land. Arsenic (As),

selenium (Se), and molybdenum (Mo) are common constituents of industrial wastes, and As and Mo are of particular concern in Florida.

Trace metal concentrations have been identified for “exceptional quality (EQ)” biosolids (Epstein, 2003), which have no limitations to land application. The EQ limits for As and Se are 41 and 36 mg kg⁻¹, respectively. There currently is no EQ value for Mo, but O’Connor et al. (2001) suggested a value of 40 mg kg⁻¹. Such EQ materials may be land applied at rates comparable to the amendment rates examined herein. Ceiling concentrations of trace metals in biosolids represent the maximum trace metal concentrations in biosolids that can be land-applied. Ceiling concentrations for As, Se, and Mo are 75, 100, and 75 mg kg⁻¹, respectively. Most amendments had As, Se, and Mo concentrations well below even the criteria for EQ biosolids, so the amendments are expected to represent minimal trace element risk to humans, animals, or the environment even when the amendments are land-applied at high rates.

Table 4. Trace metal analysis of amendments.

Source	Form	Total Elemental (mg kg ⁻¹)		
		As	Se	Mo
Manatee County	Al- WTR	9.48	1.72	19.7
Okeechobee Utilities Auth.	Al- WTR	12.5	2.32	< 2.21
Vigiron	Fe- WTR	43.9	2.32	70.8
Bradenton, FL	Ca- WTR	0.32	0.06	0.28
Nutrasource	Coal slag	51.3	22.4	173
Pro Chem	Pro-sil	1.36	3.83	41.8
Dupont	Dupont	1.77	13.3	< 0.30
Nutrasource	Gypsum	0.11	2.77	1.65
Franklin Minerals	Lime	1.92	0.78	0.62
dino-Soil	Leonardite	15.9	1.03	< 0.23

Exceptions include Vigiron (Fe-WTR), the coal combustion slag, and possibly Pro-sil. Arsenic concentrations in Vigiron and the coal combustion slag exceed EQ standards, but not the ceiling concentrations. The selenium concentration in Vigiron was low, but the Mo concentration exceeded EQ standards, and approached the ceiling concentration. Special attention to environmental concerns (As) and animal health issues (Mo) are apparently appropriate if Vigiron is used as a soil amendment, especially at high rates of application. Selenium concentrations in all amendments were generally low, but the value for the coal combustion slag (22.4 mg kg⁻¹) is noteworthy. The coal combustion slag also contains Mo at a concentration (173 mg kg⁻¹) that exceeds both EQ and ceiling concentrations for biosolids. A biosolids containing this much Mo could not be legally land-applied at any rate. The trace element content of the coal combustion slag appears to eliminate it as a viable soil amendment. Pro-sil contains a relatively high Mo concentration (41.8 mg kg⁻¹), which dictates careful monitoring of pasture grass Mo concentrations if Pro-sil is applied at high rates. The high pH of Pro-sil (Table 2) can be expected to exacerbate the Mo hazard if sufficient Pro-sil is applied to raise soil pH above pH 7 (O’Connor et al., 2001).

Selected properties of the composite soil representing the surface 15 cm depth from the Beaty Ranch are given in Table 5. Soil maps suggest the site soil could be classified as either the Immokalee (sandy, siliceous hyperthermic, Arenic Alaquods) or the Myakka series (sandy, siliceous hyperthermic, Aeric Alaquods). The composite soil is slightly acidic, low in organic matter, and reflects years of manure-P input in elevated readily soluble (KCl-, water-, and Mehlich-1- extractable) P values (Table 5). The PSI for the soil suggests that the amorphous Fe and Al hydroxyoxides in the soil are nearly saturated with P, and that little additional P-retention capacity on these solids exists.

Table 5. Selected properties of Beaty Ranch composite soil.

Source	Form	pH †	EC μS/cm	% Org Matter (LOI)	Sequentially extracted P (mg kg ⁻¹)						Total P	Mehlich 1 P	Water P	Oxalate Extractable (mg kg ⁻¹) ‡			PSI § (%)
					KCl	NaOH Pi	NaOH Po	HCl	Residue	Sum				(mg kg ⁻¹)			
Beaty Ranch	soil	6.40 ± 0.00	76.5 ± 1.9	2.3 ± 0.1	12.3 ± 0.3	50.1 ± 1.5	49.1 ± 1.8	73.1 ± 1.7	17.1 ± 0.2	202 ± 5.4	209 ± 4.3	116 ± 3.4	8.29 ± 0.10	129 ± 7.8	10.7 ± 2.4	135 ± 8.4	80.4

† At solid:solution ratio of 1:2

‡ At solid:solution ratio of 1:60

§ Phosphorus saturation index [(oxalate P/oxalate Fe + oxalate Al)*100]; elemental concentrations in moles.

Lab equilibration study

A lab equilibration (incubation) study was conducted on the composite Beaty soil and amendments. Multiple rates of each amendment (Fig. 1) were added to the soil along with sufficient background electrolyte to achieve a 1:2 solids:solution ratio. The suspensions were reacted for 40 h on an orbital shaker (250 rpm). Amendment effectiveness was evaluated by comparing the amount of soluble P remaining in the solution phase of the equilibrated suspension to that in the control suspension (no added amendment). Results are given in Fig. 1, where the percent of soluble P remaining in solution is plotted as a function of the amendment treatments. The initial P in the control sample was 3.25 mg kg⁻¹ soil.

The Fe-humate material derived from Ti mine waste (Dupont) sorbed the least P compared to all other treatments (Fig.1). This material also reduced the pH of the suspension to 4.48 at the highest application rate (10%) compared to a pH of 6.15 for the control. The other Fe-humate material (Vigiron Fe-WTR) was more effective at increasing P sorption, particularly at rates ≥5% (Fig. 1), and had little impact on the pH of the suspension. The Okeechobee Al- WTR was very effective at sorbing P, with < 10% (<0.3 mg P kg⁻¹) of the original P left in solution for all rates ≥ 0.5%. The Manatee Al- WTR was less effective than the Okeechobee Al-WTR, and rates ≥ 5.0% were required to reduce the original P in solution to < 15% of the original. Although the Okeechobee Al-WTR appears to offer outstanding sorptive capacity, it has limitations due to its low solids content (9%), which could complicate material transportation and handling.

The Pro-sil material reduced soluble P effectively, with < 20% of the original P being left in solution when amendment rates were ≥ 1.0%. However, this material impacted suspension pH, increasing pH one unit at the 0.1% amendment rate and four units at the

2.5% rate. The coal slag material had a smaller impact on pH, reducing pH one unit at the 10% amendment rate, while reducing the original amount of P in solution to < 5% of the initial value at amendment rates $\geq 5\%$. Coal slag was the most effective material for reducing soluble P of all the materials investigated when applied at high rates. However, at the 10% amendment rate, this material increased the EC (soil salinity) to $3360 \mu\text{S cm}^{-1}$, which is double that of the control ($1560 \mu\text{S cm}^{-1}$). The increase in EC for dinoSoil was comparable to that of the coal slag material, with an EC value of $3540 \mu\text{S cm}^{-1}$ for the 10% amendment rate. The pH decrease with increasing rates for dinoSoil was also comparable to the coal slag material, reducing pH one unit at the 10% amendment rate. However, dinoSoil did not sorb P as effectively as the coal slag; $\sim 11\%$ of the original P was left in solution at the 10% amendment rate.

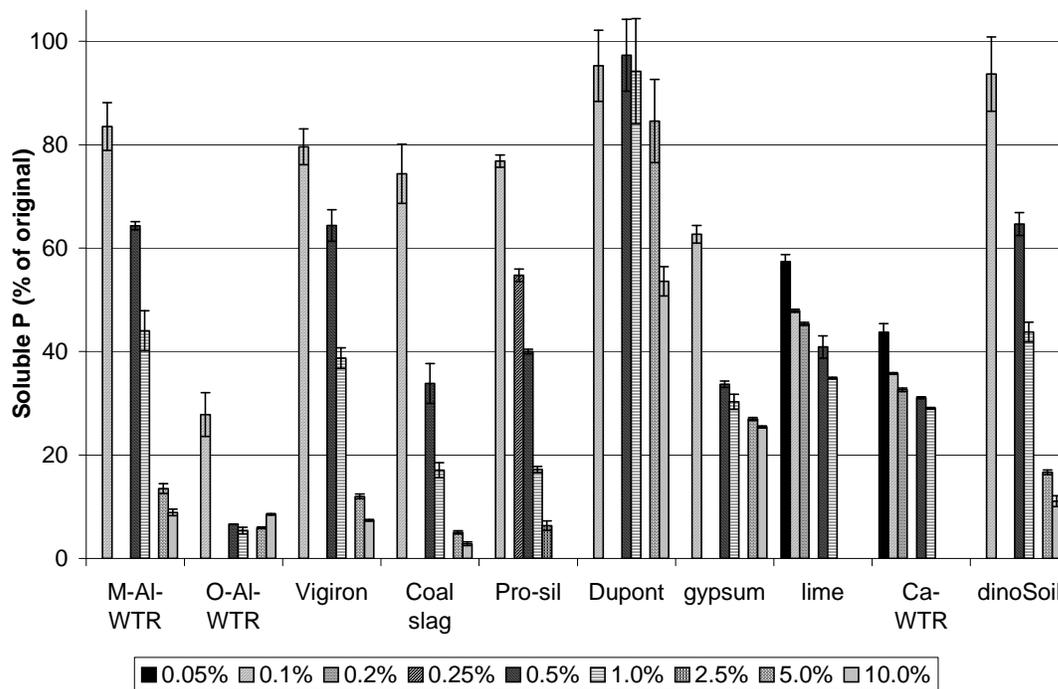


Figure 1. Percent of initial soluble P in solution after 24 h reaction. Amendment rates (key) are % by weight.

Gypsum caused a large increase in suspension EC; at the 0.5% amendment rate, the EC was $3800 \mu\text{S cm}^{-1}$, and at the 10% amendment rate, the EC increased to $4640 \mu\text{S cm}^{-1}$. Such elevated soil salinities could impair grass growth. No amendment rate of gypsum reduced soluble P below 25% of the initial concentration.

The lime and Ca-WTR produced similar results for both soluble P reduction and impact on suspension pH. The Ca- WTR consistently sorbed slightly more P than agricultural lime at the same amendment rate. The 1.0% rate of Ca- WTR reduced the amount of soluble P to $\sim 30\%$ of the initial P concentration. Neither amendment raised the pH of the system above pH 7.00 at the greatest (1.0%) amendment rate tested.

Results from the lab equilibration study suggested that no further work with the Fe-“humate” from Dupont was necessary. Agricultural lime and the Ca-WTR gave essentially the same results, so the lime material was dropped from further study. The Fe- and Al-based materials were clearly the best at reducing soluble P in the Beaty soil, especially at rates of 5% or more. Other materials (other than Dupont and lime) were maintained in the testing for completeness.

Small column leaching study

The small column study was designed to evaluate amendment effectiveness at reducing P leaching in a controlled laboratory setting. Soil used in the columns was the composite material collected from the Beaty Ranch. Soil (320 g) was packed into PVC columns (5 cm diameter x 17 cm long) to a depth of 13 cm at a bulk density of $\sim 1.26 \text{ g cm}^{-3}$. Columns were equipped with a 2 cm drainage hole at the base, covered with screening to block soil loss. The study included 75 columns (8 amendments x 3 rates x 3 replicates + 3 controls). Amendments and amendment rates utilized are given in Table 6. Sixty mL of tap water (adjusted to pH 5) was added to each column, and allowed to infiltrate before amendments were applied to the soil surface. Columns were supported on racks, and loosely covered with clear plastic wrap to reduce moisture loss. The amended columns sat for 4 days before the first leaching event. Tap water (pH 5) equivalent to ~ 5 cm irrigation was added to each column weekly for a total of 8 weeks (~ 40 cm equivalent total), and resulted in a total of ~ 8 pore volumes of leachate being collected. Leachate was collected and its volume recorded. Leachate was analyzed for pH, EC, and soluble reactive P (Murphy and Riley, 1962) within 24 h of collection.

Table 6. Small column leaching study amendments and rates (by weight.).

Amendment	Rate (%)
Manatee Al-WTR	1.0, 5.0, 10.0
Okeechobee Al-WTR	0.1, 0.25, 0.5
Vigiron	1.0, 5.0, 10.0
Ca-WTR	0.1, 0.5, 2.0
Coal slag	0.5, 1.0, 5.0
Pro-sil	0.5, 1.0, 2.5
gypsum	0.5, 2.0, 10.0
dinoSoil	0.1, 1.0, 10.0

Amendment effectiveness in this study was quantified as the amount of P cumulatively leached in the 8 leachings, compared to the mass of P leached in the control treatment. Amendment impacts on leachate pH and EC were also of concern (data not presented).

Amendment impact on leachate pH was minor, and all leachate pH values were within ~0.3 pH units of the control, which averaged about 7.4. Leachate EC (a measure of leachate salinity) was generally unaffected by amendments, except for the highest rate (10%) of dinoSoil and most of the gypsum treatments. Gypsum is the most soluble of the amendments evaluated and was expected to furnish soluble Ca^{++} for reaction with soluble P throughout the column (Anderson et al., 1995). Most leachate EC values for the gypsum treatments were about 4 times (~2500 $\mu\text{S cm}^{-1}$) the value for the control throughout the leaching study. Only the smallest gypsum treatment (0.5%) resulted in smaller leachate EC values (~1500 $\mu\text{S cm}^{-1}$) in the last few leaching events. The elevated and constant EC values suggest that gypsum was able to maintain a relatively constant Ca^{++} activity and a constant potential for precipitation of Ca-P solid.

Leachate P concentrations (data not shown) in the gypsum treatments were nearly constant (~10 $\mu\text{g L}^{-1}$) for each leaching event, also suggesting solid phase control of P solubility. Control treatment leachate soluble P concentrations averaged ~30 $\mu\text{g L}^{-1}$ until leaching #8, when it decreased to ~20 $\mu\text{g L}^{-1}$. There was a correspondingly relatively constant reduction in the total mass of P leached in the gypsum treatments (Fig. 2). Gypsum was the most effective amendment in reducing P leaching loss, averaging ~35% of that lost from the controls. Other Ca-source amendments (e.g., Ca-WTR, Pro-sil, and coal slag) were not as effective, presumably because of limited solubility at the high pH of the soil.

The Al-WTRs were largely ineffective at controlling P leaching loss, but the Fe-WTR was superior to the Al-WTRs (Fig.2). Because the WTRs (surface applied) were not in direct contact with the majority of soluble P in the soil, effectiveness was limited by amendment solubility (releasing soluble Fe or Al) to react with soluble P beneath the zone of application. Direct adsorption of P onto the WTRs was minimized in the leaching protocol used herein. Very different results were observed when the Manatee Al-WTR was applied (surface or mixed with surface) to the surface of a P-deficient soil that was then loaded with P as fertilizer, poultry manure, or biosolids as surface applications (O'Connor and Elliott, 2001). Soluble P mobilized by leaching irrigations then passed through reactive sites on the Al-WTR or Al-WTR-amended soil, and leachate soluble P was significantly reduced (minimally, 50%) at Al-WTR rates of $\geq 2.5\%$ (O'Connor and Elliott, 2001). Thus, Al-WTR can effectively reduce loss of soluble P added subsequently to, or in immediate contact with, amendment, but is much less effective at reducing loss of soluble P not in contact with the amendment. dinoSoil was about as effective as the Fe-WTR, and only reduced P loss by ~40% at the greatest application rate (Fig. 2).

Limited analyses of the selected leachates for trace elements (As, Mo, Se) revealed insignificant leaching of the potentially troublesome metals (data not presented).

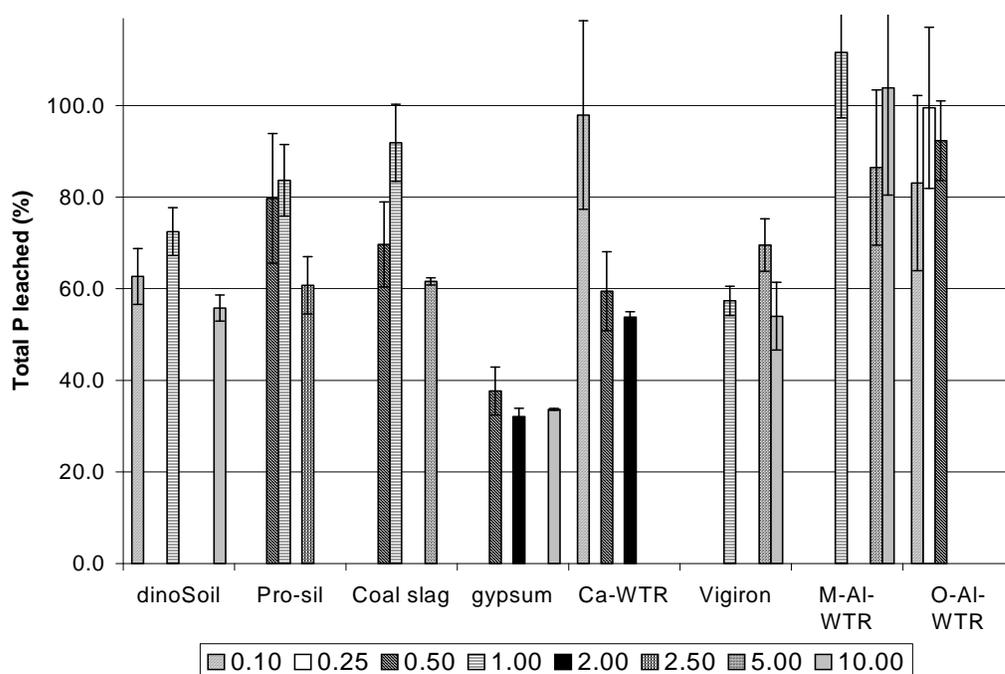


Figure 2. Percent P leached (100% = P leached in control) after 8 pore volumes of leachate. Amendment rates (key) are % by weight.

Simulated rainfall study

The final protocol used to evaluate amendment effectiveness was a simulated rainfall study using equipment and procedures specified by the National P Project protocol (National Phosphorus Research Project, 2001). The protocol specifies dimensions of runoff boxes (1 m long, 20 cm wide, and 7.5 cm deep), rainfall intensity (7.1 cm h^{-1} , ~equivalent to a 10-y, 24-h rain, applied from a height of 3 m above the soil surface), and soil packing and surface slope (3 degrees). The design was modified slightly in our experiments to quantify leaching of P in addition to runoff P by adding a second box under the first in a double-decker design. This design allowed collection of runoff and leachate simultaneously.

Air-dried soil was added to the top box and tapped to produce a depth of 5 cm and a bulk density of 1.4 g cm^{-3} . The soil was wetted to near field capacity and allowed to sit for 24 h. Amendments were surface-applied at the chosen rates (Table 7), and the boxes allowed to sit for another 48 h before beginning the first rainfall event.

Rainfall was applied using a TeeJet™ HH-SS50WSQ nozzle. The nozzle was ~3 m above the soil surface during rainfall events. The operating pressure was ~4 psi, and produced a discharge of $\sim 210 \text{ cm sec}^{-1}$ (7.1 cm h^{-1}). Tap water was adjusted to pH 5 with 1M HCl to mimic rainfall pH in Florida. Runoff was collected for 30 min after runoff began for each box. Following the completion of the first runoff cycle, the boxes were

stored on racks for 48 h before the second cycle began. The same pattern was followed for a third rainfall event.

Table 7. Rainfall simulator study amendments and rates (% by weight.).

Amendment	Rate (%)
Manatee Al-WTR	1.0 and 2.5
Okeechobee Al-WTR	0.1 and 1.0
Vigiron	1.0 and 2.5
Ca-WTR	0.1 and 1.0
Pro-sil	0.5 and 1.0
Gypsum	0.1 and 1.0
dinoSoil	1.0

The collected runoff from each box was weighed, and a 1 L sub-sample collected under constant vortex to promote uniformity of the sample. A second portion of the runoff sample was filtered (0.45 μm) using a vacuum pump to obtain ~100 mL sub-sample. The leachate sample was thoroughly mixed and sub-sampled (250 mL) for later analysis. All samples were refrigerated until P analyses were performed, usually, the next day. Filtered runoff samples were analyzed for pH, EC, soluble reactive P (SRP), and total dissolved P (TDP) (Eaton et al., 1995). Analyses performed on the sediment-laddened runoff samples included pH, EC, total and volatile solids, total P (Eaton et al., 1995), and biologically available P (BAP) (Pierzynski, 2000). Soluble P, pH, and EC were measured on leachate samples. All P analyses were conducted using the ascorbic acid method (Murphy and Riley, 1962).

Total average runoff volumes ranged from 16.1 to 24.3 L (Fig. 3), with the dinoSoil treatment yielding the greatest volume. DinoSoil contains montmorillonite clay and, when applied at the 1% rate, created a nearly impervious layer that sealed the soil surface.

There was no leachate from 2 of the 3 replicates of the dinoSoil treatments, confirming the sealing of the soil surface suggested by the runoff data. The average leachate volumes for the other treatments ranged from 3.2 to 7.6 L (Fig. 4). In most cases, leachate volumes tended to decrease as amendment rates increased, except for Pro-sil treatments where leachate volume increased with amendment rate.

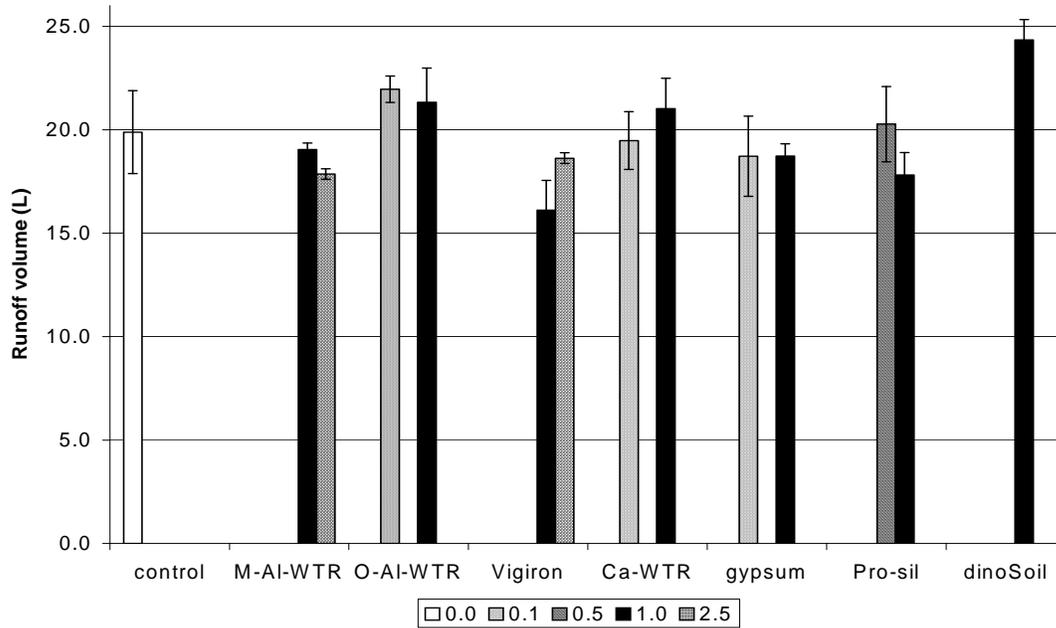


Figure 3. Total runoff volume (L) collected from three rainfall events. Amendment rates (key) are % by weight.

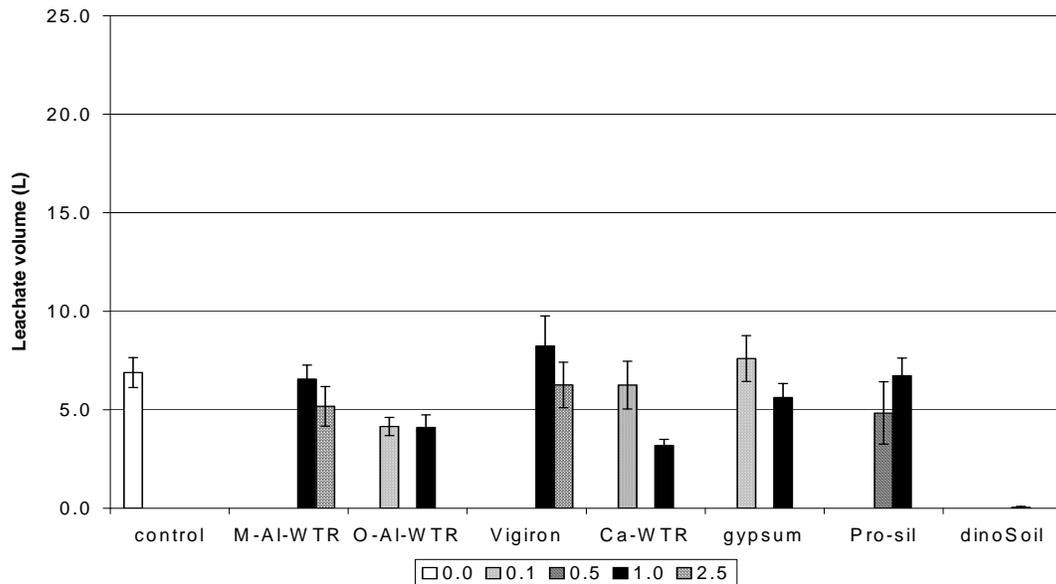


Figure 4. Total leachate volume (L) collected from three rainfall events. Amendment rates (key) are in % by weight.

The average runoff SRP in the control was 0.63 mg P, and the range for the treated soils was 0.18 to 2.14 mg (Fig. 5). All amendments applied at 1% reduced runoff SRP compared to the control, with the exception of the gypsum treatment. dinoSoil reduced runoff SRP by >60%, and both Al-WTRs reduced runoff SRP by ~50%. The Ca-WTR and Vigiron (Fe-WTR) reduced runoff SRP by ~40%, and Pro-sil reduced runoff SRP by

~20% compared to the control. Data for runoff total dissolved P (TDP) were similar to the runoff SRP data, and are not presented. The similarities suggest little contribution of organic P (detected in TDP, but not runoff SRP) to soluble P in runoff.

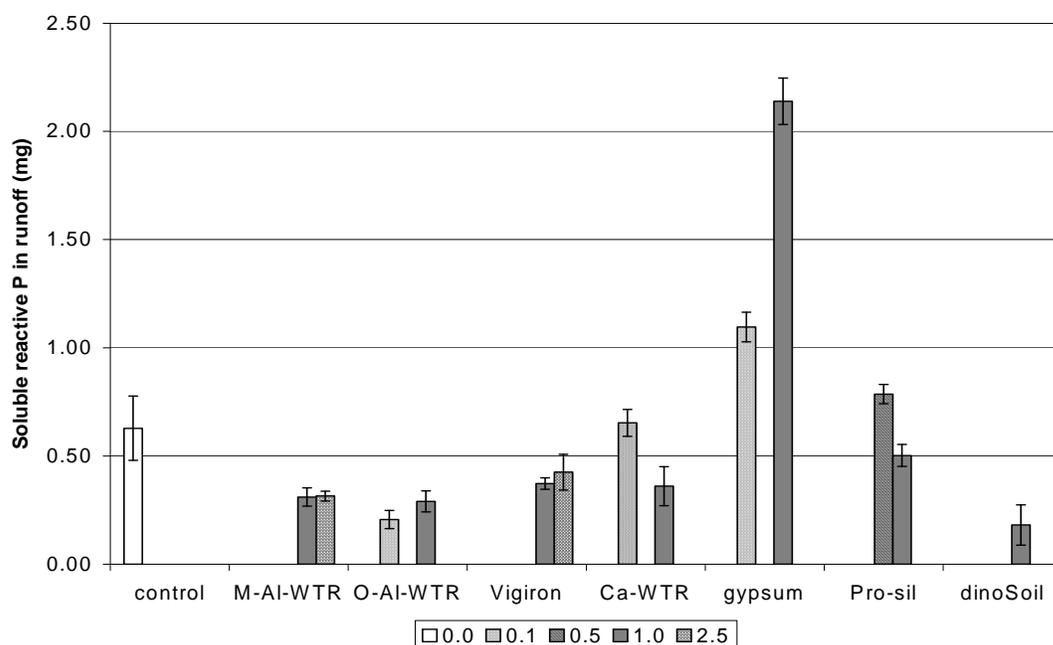


Figure 5. Soluble reactive P in runoff (mg, total of 3 rainfall events). Amendment rates (key) are in % by weight.

Runoff total P (soluble + particulate P) in the control was 14.3 mg P, and the range for the amendment treatments was 3.1 to 65.6 (Fig. 6). The greatest value was measured for dinoSoil, reflecting the easily transported colloidal nature of the material and its inherent total P content (Table 1). The two Al-WTRs, Vigiron, and Pro-sil effectively reduced runoff total P.

Phosphorus extracted by the Fe-strip method is referred to as biologically available P (BAP), as it has been correlated with algae-available P in runoff and sediments. Values of BAP, thus, should represent environmentally significant P better than total runoff P, as total runoff P includes non-labile P. The amount of runoff BAP in the control was 1.8 mg P, and ranged from 0.23 to 4.9 mg P for the amendments (data not shown). The dinoSoil BAP value was dramatically lower than runoff total P, suggesting that much of the runoff total P was non-labile. The two WTRs were again the most effective in reducing BAP compared to the control, although Pro-sil (~59%), Vigiron (~45%), and dinoSoil (~45%) were also effective.

Soluble reactive P (SRP) in the leachate from the control was 6.6 mg P, compared to SRP values in the amendment treatments, which ranged from 3.6 to 9.4 mg P (Fig. 7). The Ca-amendments (gypsum and Ca-WTR) and Vigiron (at the 1% rate) were the most effective amendments in reducing leachate SRP. dinoSoil allowed minimal leaching and SRP in the leachate, but promoted excessive surface runoff via its sealing effect on the soil. The

two Al-WTRs and Pro-sil were largely ineffective at controlling leachate soluble P, especially at the common 1% amendment rate.

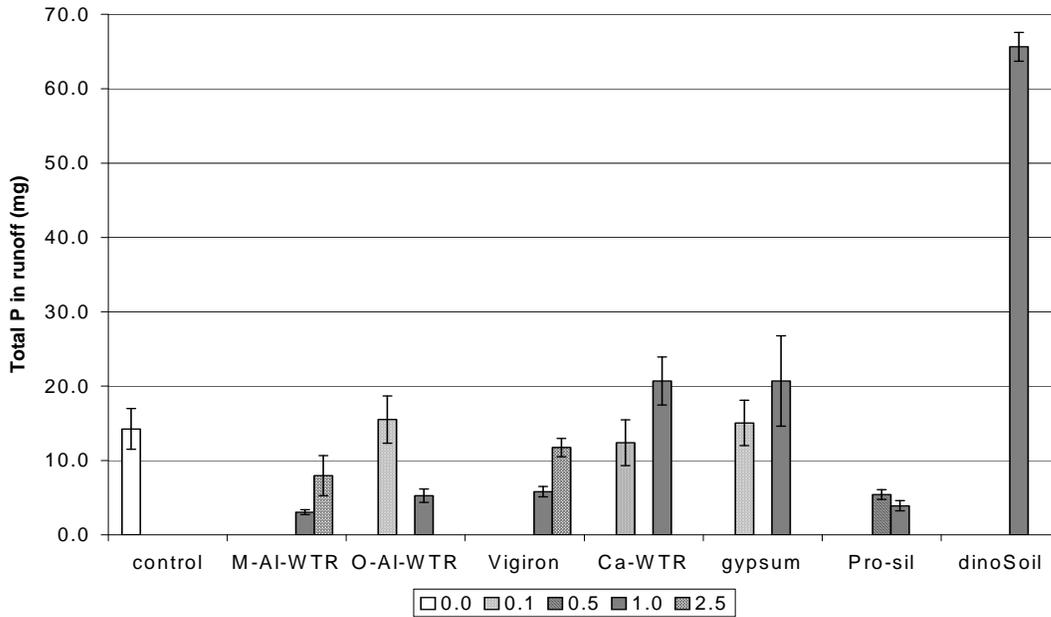


Figure 6. Total P in runoff (mg, total of 3 rainfall events). Amendment rates (key) are in % by weight.

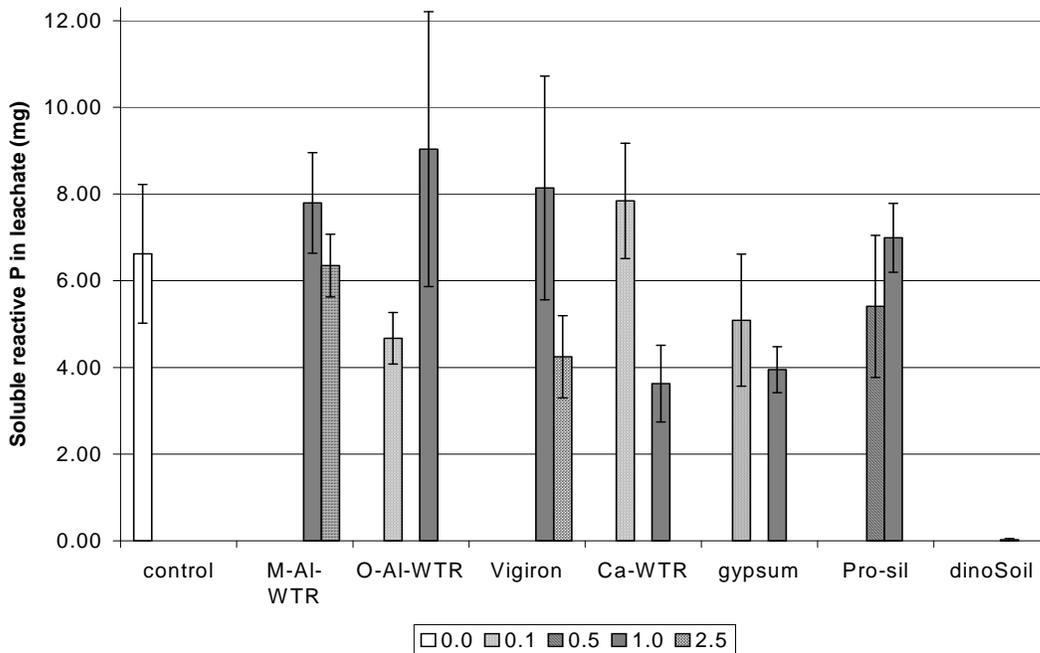


Figure 7. Soluble reactive P in leachate (mg, total of 3 rainfall events). Amendment rates (key) are in % by weight.

The various runoff and leachate parameters were statistically analyzed using a ranking scheme intended to identify the most effective treatment(s). The rankings and associated LSD values for each parameter ranking are given in Table 8. The total column tallies ranking points for all parameters measured in both runoff and leachate. The Total ranking identifies the two WTRs and dinoSoil as the best amendments. The LSD analyses for individual runoff P parameter rankings generally confirm the superiority of the three amendments as well, although only dinoSoil significantly reduced leachate P compared to the control. Recall that dinoSoil essentially sealed the soil surface so little rainfall infiltrated and, thus, minimized leaching. There was minimal effect of amendment rate among the Al-WTRs; however, the low rate of Okeechobee Al-WTR (0.1%) was about as effective as either Al-WTR applied at 1%, or the Manatee Al-WTR applied at 2.5%.

Table 8. Rankings and associated LSD values for various P parameters.

Amendment	rate	leachate	runoff				Total
		SRP	SRP	TDP	TP	BAP	
	%						
control	0.0	9ab	10cde	11cd	9bc	12bc	51(12)*
M-Al-WTR [†]	1.0	11ab	4fg	4efg	1e	2g	22(1)
M-Al-WTR [†]	2.5	8ab	5fg	3fg	6cde	3fg	25(4)
O-Al-WTR [†]	0.1	5b	2g	2fg	11bc	4fg	24(2t)
O-Al-WTR [†]	1.0	14a	3fg	6efg	3de	1g	27(5)
Vigiron	1.0	13ab	7fg	8def	5de	8def	41(10)
Vigiron	2.5	4bc	8ef	10cd	7cd	11cd	40(8t)
Ca-WTR	0.1	12ab	11cd	9de	8cd	10cd	50(11)
Ca-WTR	1.0	2bc	6fg	5efg	13b	9cde	35(7)
Pro-sil	0.5	7ab	12c	12bc	4de	5efg	40(8t)
Pro-sil	1.0	10ab	9def	7def	2e	6efg	34(6)
gypsum	0.1	6ab	13b	13b	10bc	13b	55(13)
gypsum	1.0	3bc	14a	14a	12b	14a	57(14)
dinoSoil	1.0	1c	1g	1g	14a	7def	24(2t)

*cumulative points (actual ranking). Note lower cumulative points represents less P loss.

[†] M-Al-WTR = Manatee Al-WTR; O-Al-WTR = Okeechobee Al-WTR

Selection Summary

Ten materials (Table 1) were selected initially for evaluation as possible amendments to control soluble P in Beaty Ranch soil. A series of evaluation protocols allowed deselecting most amendments and identified the one or two amendments worthy of field investigation. A summary of the pertinent criteria used to select or deselect amendments is given below:

1. DuPont Fe-"humate" - deselected because of minimal P sorption capacity (Fig.1).
2. Coal slag - despite good adsorption and leaching control properties, the material is deselected because of troublesome trace element contents,

especially Mo and As (Table 4), and because the rates of coal slag required for P control could detrimentally affect soil pH and EC.

3. Pro-sil - despite effective P sorption, effective leaching control, and moderate runoff control, the material is deselected because the rates required for P control can raise soil pH excessively which, when combined with a moderately high Mo content, could create an undesirable soil environment for pasture grass growth and grass quality that may threaten livestock health (molybdenosis).
4. Gypsum - very effective at controlling P leaching, but ineffective at P sorption and P runoff control. Also deselected because rates necessary for P control may result in soil salinity incompatible with good pasture grass growth.
5. Lime and Ca-WTR – behaved essentially the same in all protocols. Likely effective in initially acid soils requiring pH adjustment, but not in soils with pH values ≥ 7 , where lime solubility is limited. Because the pH of the Beaty Ranch field site is already 6.4, little (or no) liming agent would be recommended (for most pasture grasses) and low rates of amendments are expected to be ineffective. Both liming agents are, thus, deselected for field evaluation.
6. Vigiron (Fe-WTR) - moderately effective at sorbing P and reducing leaching, but only fair in controlling P runoff. Deselected because it contains moderately high concentrations of Mo and As, and may release immobilized P under reducing conditions.
7. dinoSoil - high rate (1%) slightly effective at sorbing P and reducing leaching, but a top performer in runoff simulations. High cost (~\$145/T), however, likely makes the amendment impractical for large scale use.
8. Manatee and Okeechobee Al-WTRs - effective P sorbers, but ineffective at controlling P leaching when soluble P is below the zone of amendment incorporation. Very effective at controlling P leaching when soluble P is made to contact WTRs (amendment incorporation, or soluble P added after amendment addition). The Al-WTRs dominated the best materials in runoff simulations. The Okeechobee material was uniformly better when applied at 1%, whereas the Manatee material requires rates $\geq 2.5\%$. The Okeechobee material is locally available, but its low solids content (~9%) create handling and transportation problems. Total annual production of the Okeechobee residual is estimated at only 250 to 300 Mg (~tons), which limits its use to minimal acreage at the 1% (10 T/A) rate. Relatively high rates (~25 T/A) of the Manatee material are needed to be effective, but the material's dry condition makes handling/application easy, and large quantities of the material are available (~4000 Mg/y). Thus, we recommend field evaluation of the Manatee Al-WTR at the 2.5% rate; the material should be surface applied on one plot and incorporated (to 5 cm) on the other plot.

Literature Cited

Allen, L.H., Jr. 1988. Dairy-siting criteria and other options for wastewater management on high water-table soils. *Soil Crop Sci. Soc. Florida Proc.* 47:108-127.

Alcordero, I.S., J.E. Rechcigl, and R.C. Littell. 2001. Greenhouse evaluation of lime and gypsum materials for reducing phosphorus leaching in a Spodosol. Final report to the South Florida Water Management District. (No. C-10201)_.

Anderson, D.L., O.H. Tuovinen, A. Faber, and I. Ostrokowski. 1995. Use of soil amendments to reduce soluble phosphorus in dairy soils. *Ecological Engineering.* 5:229-246.

Ann, Y., K.R. Reddy, and J.J. Delfino. 2000a. Influence of chemical amendments on phosphorus immobilization in soils from a constructed wetland. *Ecological Engineering.* 14: 157-167.

_____, _____, and _____. 2000b. Influence of redox potential on phosphorus solubility in chemically amended wetland organic soils. *Ecological Engineering.* 14: 169-180.

Brown, E., and J.B. Sartain. 2000. Phosphorus retention in United States Golf Association (USGA) greens. *Soil Crop Sci. Soc. Florida Proc.* 59:112-117.

Boruvka, L., and J.E. Rechicgl. 2003. Phosphorus retention by the Ap horizon of a Spodosol as influenced by calcium amendments. *Soil Sci.* 168:699-706.

Callahan, M.P., P.J.A. Kleiman, A. N. Sharpely, and W.L. Stout. 2002. Assessing the efficacy of alternate phosphorus sorbing soil amendments. *Soil Sci.* 167:539-547.

Chang, A.C., A.L. Page, F.H. Sutherland, and E. Grgurevic. 1983. Fractionation of phosphorus in sludge affected soils. *J. Environ. Qual.* 12: 286-290.

Elliott, H.A., G.A. O'Connor, P. Lu, and S. Brinton. 2002. Influence of water treatment residuals on phosphorus solubility and leaching. *J. Environ. Qual.* 31:1362-1369.

Eaton, A.D., L. S. Clesceri, and A. E. Greenberg (eds.). 1995. Standard methods for the examination of water and wastewater. American Public Health Association. Washington, D. C.

Epstein, E. 2003. Land Application of Sewage Sludge and Biosolids. Lewis Publishers. Boca Raton, FL.

Hanlon, E. A., J. S. Gonzalez, and J. M. Bartos. IFAS extension soil testing laboratory (ESTL) and analytical research laboratory (ARL) chemical procedures and training manual. 1997.

Jenkins, D., and S.W. Hermanowicz. 1991. Principles of chemical phosphate removal. In. Phosphorus and Nitrogen removal from Municipal Wastewater: Principals and Practices. 2nd Ed. Ed. R. Sedlak. New York, N.Y. Lewis Publishers.

Lane, C.T. 2002. Water treatment residuals effects on phosphorus in soils amended with dairy manure. M.S. Thesis, Univ. FL., Gainesville, FL 32611-0510.

McKeague, J.A., J.E. Brydon, and N.M. Miles. 1971. Differentiation of forms of extractable iron and aluminum in soils. *Soil Sci. Soc. Am. Proc.* 35:33-38.

Matichenkov, V.V., D.V. Calvert, and E.A. Bocharnikova. 2001. Effect of Si fertilization on growth and P nutrition of bahiagrass. *Soil Crop Sci. Soc. Florida Proc.* 60:30-36.

Moore, P.A., Jr., and D.M. Miller. 1994. Decreasing phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. *J. Environ. Qual.* 23:325-330.

Moore, P.A., Jr., T.C Daniel, and D.R. Edwards. 2000. Reducing phosphorus runoff and inhibiting ammonia loss from poultry manure with aluminum sulfate. *J. Environ. Qual.* 29:37-49.

Murphy, J., and J. P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27:31-36.

O'Connor, G.A., R.B. Brobst, R.L. Chaney, R.L. Kincaid, L.R. McDowell, G.M. Pierzynski, A. Rubin, and G.G. Van Riper. 2001. A modified risk assessment to establish molybdenum standards for land application of biosolids. *J. Environ. Qual.* 30:1490-1507.

O'Connor, G.A., and H.A. Elliott. 2001. Co-application of biosolids and water treatment residuals. Final report. FL Dept. Environ. Protection. (No. S 3700 206296).

O'Connor, G.A., H.A. Elliott, and P. Lu. 2002. Characterizing water treatment residuals phosphorus retention. *Soil Crop Sci. Soc. Florida Proc.* 61:67-73.

Peters, J.M., and N.T. Basta. 1996. Reduction of excessive bioavailable phosphorus in soils using municipal and industrial wastes. *J. Environ. Qual.* 25:1236-1241.

Pierzynski, G. M. (ed.). 2000. Methods of phosphorus analysis for soils, sediments, residuals, and waters. Southern Cooperative Series Bulletin 396. United States Department of Agriculture, Cooperative State Research, Education and Extension Service.

Rechcigl, J.E., A.B. Bottcher, R.C.Littell, I.S. Alcorido, and L.Boruvka, 2000. Evaluating limestone and gypsum for reducing P leaching and runoff from beef cattle forage. Annual Progress Report. (Mar 1999 – Jan 2000). South Florida Water Management District Contract No. C-10201.

Shreve, B.R., P.A. Moore, Jr., T.C. Daniel, D.R. Edwards, and D.M. Miller. 1995. Reduction of phosphorus in runoff from field-applied poultry litter using chemical amendments. *J. Environ. Qual.* 24:106-111.

Sparks, D.L. 1996. *Methods of soil analysis: chemical methods*. Soil Sci. Soc. Am. Book Series (Part 3). Soil Sci. Soc. Amer., Inc., Madison, WI.

Stout, W.L., A.N. Sharpely, and J. Landa. 2000. Effectiveness of coal combustion by-products in controlling phosphorus export from soils. *J. Environ. Qual.* 29:1239-1244.

_____, _____, and H.B. Pionke. 1998. Reducing soil phosphorus solubility with coal combustion by-products. *J. Environ. Qual.* 29:111-118.

USEPA .1995. *Process design manual: land application of sewage sludge and domestic septage*, EPA/625/R-95/001, Office of R & D, Cincinnati, Ohio.