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Apatite Control of Phosphorus Release to Runoff from Soils of Phosphate Mine Reclamation Areas

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Abstract Phosphorus (P) in runoff can pose a water quality risk in phosphate mine reclamation areas. High dissolved P (DP) concentrations (about 0.4–3.0 mg L^{-1}) in runoff from these areas and high equilibrium P concentrations for the soils led us to hypothesize that P release is controlled by dissolution of apatite rather than by desorption mechanisms. Objectives were to (a) verify via chemical- and solid-state assessments that P in the reclamation soils is mainly in the form of apatite and (b) examine evidence that DP concentrations in runoff water from these soils is controlled by apatite dissolution. Soil analyses included total P (TP), P sorption isotherms, P fractionation, mineralogy, and P distribution by particle size classes. Runoff samples were chemically characterized and modeled for speciation. Results showed high TP concentrations and the presence of apatite. The Ca- and Mg-bound P accounted for about 95% of TP. Runoff samples were undersaturated with respect to apatite. A strong relationship between calculated apatite specific surface area and measured DP concentration in water extracts is supportive of other evidence that apatite dissolution is a major factor controlling P release from these soils. Data indicate that these soils will be a long-term P source rather than sink. Results are applicable to other phosphate mine reclamation sites and illustrate the need to account for compositional differences between reconstructed soils on reclaimed mining sites and their indigenous soil analogues.

Keywords Dissolved phosphorus ·
Specific surface area · Apatite · Dissolution ·
Reclamation area · Surface runoff

1 Introduction

Phosphorus (P) carried in surface runoff from agricultural lands has been studied extensively and

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identified as a non-point source pollutant of surface water. Loading of P in runoff is heavily influenced by soil properties and land management practices (He et al. 2003). Soil properties that typically affect P dynamics in soil solution include particle size distribution, organic matter and metal oxide content, and pH (Sharpley et al. 1981; Vadas and Sims 2002). In addition, rainfall intensity, runoff duration, and water/soil ratio also influence desorption/diffusion of soil P to runoff water in agricultural lands (McDowell and Sharpley 2001; Storm et al. 1988).

Mechanisms controlling P release from soils rich in geologic P (Wang et al. 1989) may deviate from mechanisms typical for soils enriched with fertilizer P. Geologic P can be abundant in anthropogenic soils of reclaimed phosphate mining areas. The main mineral in Florida's P-rich deposits ("phosphate rock") is carbonate–fluorapatite (CFA, also called francolite), a form of apatite in which there is significant substitution of CO_3^{2-} for PO_4^{3-} (McClellan and Lehr 1969; Van Kauwenbergh et al. 1990). A typical formula for CFA is $Ca_{9.62}Na_{0.273}Mg_{0.106}(PO_4)_{4.976}(CO_3)_{1.024}F_{2.41}$ (Hanna and Anazia 1990), although variations in degree of carbonate and other substitutions have been reported (McClellan and Lehr 1969; Regnier et al. 1994; Schuffert et al. 1990). The dissolution rate of CFA is mainly affected by soil pH, concentrations of P and Ca (Babare et al. 1997; Chien and Menon 1995; Guidry and Mackenzie 2003), moisture content, and particle size (He et al. 2005). The influence of particle size stems from its inverse relation to specific surface area (SSA) in conjunction with dissolution being a surface-controlled process. Dissolution of apatite minerals would ensue immediately upon contact with runoff water. Thus, once runoff occurred in the mining lands, they would be potential sources contributing dissolved P (DP) into water bodies.

High DP concentration (0.4–3.0 mg L^{-1}) has been measured in runoff from two reclaimed phosphate mining sites in Florida (Kuo 2007). This high DP concentration contributes DP loading of 0.28–2.2 kg ha^{-1} $year^{-1}$ from runoff of 610–1,300 m^3 ha^{-1} $year^{-1}$ at these two sites with different soil properties and slopes during the dry season 2006. The average DP concentration in the upper Peace River at the Bartow sub-basin has been declining from 18 to 1.2±1.9 mg L^{-1} due to the changes in mining practices (DEP 2006; Southwest Florida Water Management District 2001) between 1965 and 2005. However, total P (TP) concentration is still higher than the US Environmental Protection Agency (USEPA) criterion of TP concentration (0.01 mg L^{-1}) discharging into a river (Mueller et al. 1995; USEPA 2000).

Soils of these reclaimed sites were constructed from a mixture of materials exhumed, elutriated, mixed, etc. during mining operations. Therefore, their composition potentially deviates from that of indigenous soils. The reclaimed soils have very high P concentrations, but very low clay, Fe, and Al concentrations (Kuo 2007). These conditions along with high DP concentrations in runoff water led to the suspicion that dissolution of residual geologic apatite (CFA) is controlling P release from these soils, rather than P adsorption and desorption processes that typically control the fate of P in soils of the southeastern USA coastal plain (Harris et al. 1996).

The objectives of this study were to (a) verify via chemical- and solid-state assessments that P in the mine reclamation soils is mainly in the form of apatite (most likely CFA) and (b) examine evidence that DP concentrations in runoff water from these soils is controlled by CFA dissolution.

2 Materials and Methods

2.1 Field Sampling

Water and soil samples analyzed in this study were collected from a phosphate mining reclamation site near Bartow, FL. Two experimental sites (A and B) representative of the range of conditions in the area (slopes, surface runoff, lengths, soils) that were 3 km apart were chosen. There are eight runoff plots in each site (Fig. 1). The width of each plot is 3.3 m. The lengths of these plots include 40, 14.4, 13.6, and 5.9 m. The average slopes of site A and site B were 2.0% and 4.3%, respectively. Sixteen soil samples to a depth of 2 cm were collected from each site. This depth was considered adequate to capture the depth of soil–runoff interactions (Sharpley 1985). Soils were examined and photographed "as is" under a dissecting microscope.

Runoff water samples were collected at each trough (Fig. 1) by an automatic water sampler (ISCO 6712, Teledyne Isco, Inc, Lincoln NE) using a flow-weighted sampling. The flow rate was measured from a standard 6-in. (15.24 cm) HS flume (Brakensiek et

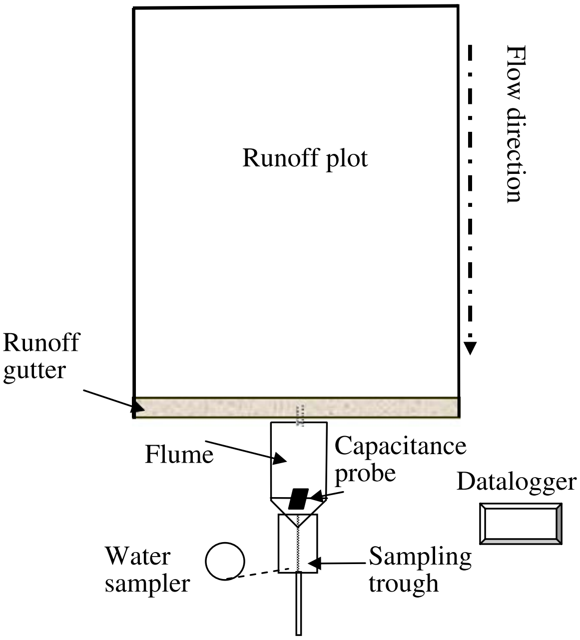

Fig. 1 Runoff plot used to collect runoff water in Bartow, FL

al. 1979). A capacitance probe was inserted vertically in each flume throat to measure the flow stage (Kuo 2007). The datalogger stored the flow stage every minute during a runoff event and converted it automatically into runoff flow rate through flume rating curves. The datalogger then sent sampling pulses to the ISCO 6712 automatic water sampler based on changes in accumulated runoff volume to collect runoff water samples. Runoff samples were then kept in cold storage (4°C) and transported to the laboratory for analysis.

2.2 Soil Chemical Properties

Soil samples were collected from the top 2 cm depths of each site since this zone has the greatest interaction between soil and runoff water. All samples were air-dried and then sieved using a 2.0 mm mesh sieve. Soil pH was measured in a 1:1 mixture of soil/water using a pH meter (pH/Cond 340i/Set, WTW, Germany). Soil organic carbon (OC) was measured by the Walkley–Black oxidation procedure (Nelson and Sommers 1982). The TP in each particle size class, Mehlich-1 extraction, P sorption isotherms, and P fractionation on the whole soil were conducted to investigate the P dynamics in the soil. Details of these analyses are as follows.

2.2.1 Mehlich-1 Extraction

A combination of HCl and H_2SO_4 acids (Mehlich 1953) with a 1:4 (soil/extractant) ratio was used to extract P from soils. The suspension was shaken for 5 min and filtered through Whatman no. 42 filter paper. Mehlich-1 extraction can dissolve Al- and Fe-phosphates as well as P adsorbed on colloidal surfaces in soils. Mehlich-1 extraction works well for most acidic, low cation exchange capacity soils, which are prevalent in the SE USA.

2.2.2 P Sorption Isotherms

Phosphate sorption was measured by using 2 g of soil sample with 20 mL of 0.05 M KCl solution containing 0, 1.5, 4.5, 8.5, 15, and 50 mg[P] L^{-1} in a 50 mL centrifuge tube, respectively. Each tube with suspension was shaken for a 2-h period, which was set to represent a typical time of soil–water contact during a rainfall event. After centrifugation at 5,000 rpm for 15 min, the supernatant was filtered through a 0.45 μm membrane filter. The amount of P adsorbed by soil was determined by the difference between the initial and final concentration of P in the solution. Four replicates of each concentration for both sites are measured.

2.2.3 P Fractionation

The sequential extraction procedure, following the method of Nair et al. (1995), distinguishes six forms of P (Fig. 2). After the supernatant of one extraction was removed, the tube and soil were re-weighed, and the next extracting solution was added to the tube. All of the supernatants were filtered through 0.45 μm membrane filters and refrigerated at 4°C until analysis.

2.2.4 TP in Each Particle Fraction

Particle size fractionation was conducted by sieving and centrifugation using a procedure based on one described by Jackson and Tanner (1947). Samples were initially saturated with Na to promote dispersion. This was accomplished by placing 20 g of soil in a 250 mL centrifuge bottle, adding 1 N NaCl to 250 mL volume, shaking, centrifuging, and decanting supernatant. These steps were repeated twice more, after which samples were rinsed free of salt using repeated washings with deionized water until the supernatant appeared turbid.

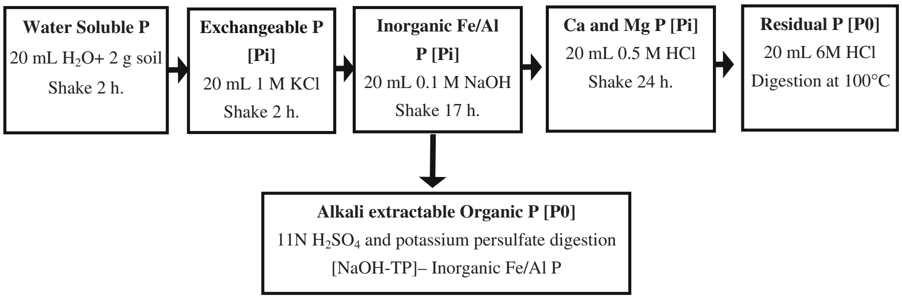

Fig. 2 Scheme of phosphorus fractionation of reclaimed phosphate mining soils

Sand (>37 μm) was then separated from silt and clay particles by wet sieving. The soil in the bottle was washed into a 37-μm mesh sieve using pH=9.5 water. The <37 μm material was collected into centrifuge bottles to separate silt (2–37 μm) and clay (<2 μm) by centrifugation using time and gravity forces based on principles of Stokes law (Jackson 1969). Sand was further fractionated by sieving into particle sizes of 37 to 106 μm and 106 to 250 μm. The soil in each particle class was measured for the TP. The TP was determined by ashing and HCl (6 N) digestion (Anderson 1976). All extractions of P were analyzed using the molybdate blue method of Murphy and Riley (1962).

2.2.5 Solid State Assessments

Samples were examined by X-ray diffraction (XRD) for mineral identification and by X-ray fluorescence (XRF) spectrometry to determine the relative concentrations of elements. Samples were prepared for XRD by grinding to a powder (<50 μm particle size) and side packing into cavity mounts, designed to minimize preferred orientation (Harris and White 2008). They were scanned from 2–40° 2θ on a computer-controlled X-ray diffractometer equipped with stepping motor and graphite crystal monochromator. A computer-controlled XRF spectrometer equipped with 12-position autosampler and silicon drift detector was used for XRF analysis of 4 g sample aliquots.

2.3 Phosphate Solubility Equilibria

Runoff water samples randomly collected from both sites in June 2006 were used for chemical speciation modeling and evaluation with respect to solubility of CFA, fluorapatite (FAP), and hydroxyapatite (HAP). Concentrations of Ca^{2+}, Fe^{2+}, Mg^{2+}, Al^{3+}, K^+, Na^+, Cu^+, Mn^{2+}, and Zn^{2+} were measured following 0.45-μm filtration using atomic absorption spectrometry (Varian 220FS, Varian Australia Pty Ltd, Mulgrave Victoria, Australia). The concentrations of F^-, NO_2^-, NO_3^-, $H_2PO_4^{3-}$, SO_4^{2-}, and Cl^- were analyzed using ion chromatography (Dionex LC20 Chromatography Enclosure, Dionex, CA). Ionic strength of solutions were calculated from equation, $I=0.013$ EC (Griffin and Jurinak 1973), where EC is expressed in millisievert per centimeter. The pH was measured directly from a pH electrode (pH/Cond 340i/Set, WTW, Germany). Ionic activities of solution components were calculated using the Visual MINTEQ equilibrium speciation program (version 2.50; Department of Land and Water Resources Engineering 2006).

Solubility products (K_{sp}) for HAP, FAP, and CFA, respectively, were based on the following formulas:

$$Ca_{10}(PO_4)_6OH_2$$

$$Ca_{10}(PO_4)_6F_2$$

$$Ca_{10}(PO_4)_5(CO_3)F_2$$

The K_{sp} for HAP of $10^{-116.6}$ as determined by McDowell et al. (1977) was used in calculating the HAP solubility line in this paper. In most natural systems, apatite contains F^- (FAP or CFA) instead of OH^- (HAP), resulting in lower solubility. The K_{sp} for FAP of $10^{-121.2}$ as reported by Driessens (1982) was used for the FAP line. Calcium apatite is often found in a non-stoichiometric form which may explain the range in K_{sp} values reported in the literature (e.g., $K_{sp}=10^{-114}$– 10^{-119} for HAP and $K_{sp}=10^{-121}$–10^{-122} for FAP; McConnell 1973; Elliott 1994). The K_{sp} of CFA varies depending on the degree of CO_3 substitution from FAP (Jahnke 1984). CFA with the maximum CO_3 substitution (~6.5 wt.% or ~1 mol CO_3 per formula weight) has the highest solubility ($K_{sp}=10^{-107.5}$) among the CFA specimens evaluated. We used this K_{sp} in the calculation of the CFA solubility

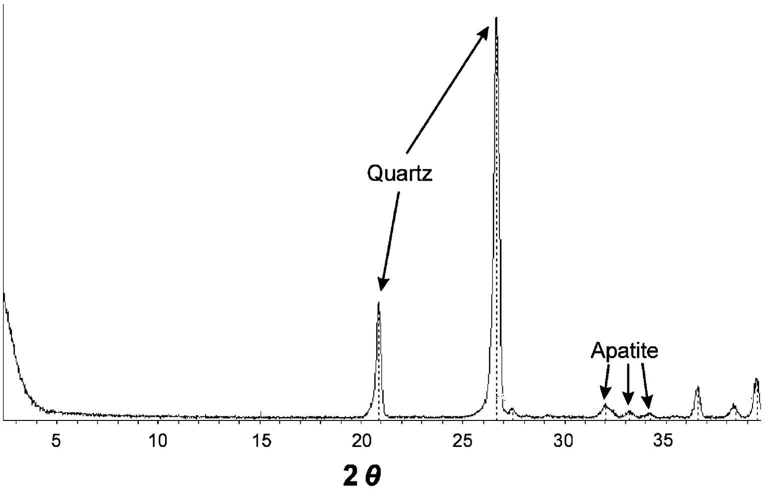

Fig. 3 Powder X-ray diffraction pattern of soil sample from site B, showing peaks for apatite

line. The mean activities of Ca^{2+} (pCa^{2+}=4.7) and F (pF=5.56) were used to develop the diagram.

2.4 Approach for Calculating CFA SSA

The release of P from soils to runoff should relate closely with the SSA of apatite if it is acting as a primary controller of P flux. The SSA of a phase within a porous medium relates to its size and shape. We observed under light microscopy that apatite particles ranged from spheroidal to slightly ellipsoidal. For modeling purposes, we presumed a CFA composition for apatite since it is the dominant form in the phosphate ore. We calculated the CFA SSA using the following equations that take particle shape as well as size into account:

$$\mathrm{SSA}_{(\mathrm{sp})} = \frac{\text{surface area}(\mathrm{m}^2)}{\text{weight of particle}(\mathrm{g})} = \frac{4\pi(d/2)^2}{(4/3)\pi(d/2)^3\times10^6\times\rho_{\mathrm{CFA}}} = \frac{6\times10^{-6}}{\rho_{\mathrm{CFA}}\times d} \tag{1}$$

where $\mathrm{SSA}_{(\mathrm{sp})}$ is SSA of a sphere (square meter per gram), respectively, d is the particle diameter (meter), and ρ_{CFA} is the particle density of CFA (gram per cubic centimeter), which can be calculated from following equation:

$$\rho_{\mathrm{CFA}} = \frac{(\text{Molecular Weight})\times Z}{(\text{Cell Volume}\times 0.60225)} \tag{2}$$

where ρ_{CFA} is particle density of CFA (gram per cubic centimeter), Cell Volume is in cubic angstroms, Z is in formula units per cell, Molecular Weight is in gram per mole, and 0.60225 is the Avogadro constant divided by (1.0×10^{24}).

If a uniform size distribution of spherical particles between particle diameters d_1 and d_2 (meter) is assumed, the average CFA SSA ($\overline{\mathrm{SSA}_{\mathrm{CFA}}}$, square meter per gram) can be calculated as (Storm et al. 1988):

$$\overline{\mathrm{SSA}_{\mathrm{CFA}}} = \frac{6\times10^{-6}}{\rho_{\mathrm{CFA}}(d_2-d_1)}\ln\left[\frac{d_2}{d_1}\right] \tag{3}$$

Table 1 Elemental composition of soil samples from both sites examined by X-ray fluorescence (XRF)

Site	Main compounds in soil samples (%)							
	Si	P	Ca	Al	K	Fe	Ti	Mn
A	41.3±4.4	5.8±0.3	12.4±1.3	9.2±1.5	0.8±0.2	1.5±0.3	0.3±0.1	0.02±0.001
B	54±7.4	3.8±0.5	7.5±1.8	8.7±5.1	1.08±0.4	0.7±0.2	0.3±0.1	0.01±0.003

Data are average ± standard deviation values of four samples within each site

Table 2 Concentration of designated soil phosphorus fractions (units = milligram per kilogram)

Site	Water	KCl	Fe– and Al–P	Organic-P	Mg– and Ca–P	Residual-P	TP
A	17.7±3.8	12.6±1.7	233±76	292±127	18,500±2750	188±50	19,270±2,890
B	23.7±3.2	9.7±6.1	296±91	437±144	20,100±2,550	166±44	21,050±2,720

Data are average ± standard deviation values of 14 samples within each site

The SSA of CFA (square meter per gram) in a soil sample can be calculated from:

$$\mathrm{SSA}_{\mathrm{CFA}} = \sum_{i=1}^{n} \left(\frac{\text{Particle size}(i) \times \text{P concentration ion}(i)}{0.158} \right) \times \overline{\mathrm{SSA}_{\mathrm{CFA}}}(i) \tag{4}$$

where Particle size (i) is the mass fraction of soil particles representing a given size range (i), P concentration (i) is the P concentration within a given particle size range (i) in milligram per kilogram, $\overline{\mathrm{SSA}_{\mathrm{CFA}}}(i)$ is the SSA of CFA for a given particle size range (i) in square meter per gram, which can be calculated from Eq. 3, and 0.158 is the P fraction per unit weight of CFA calculated from the formula of CFA ($Ca_{9.62}Na_{0.273}Mg_{0.106}(PO_4)_{4.976}(CO_3)_{1.024}F_{2.41}$; Hanna and Anazia 1990).

We tested whether the calculated CFA SSA correlated with the release of P from the soils studied. The P release from soil was evaluated experimentally, as follows: 2 g of soil with 20 mL deionized water in a 50-mL centrifuge tube was shaken for 15 min (soil–water contact time), after which the pH was measured. The contact time was selected based on approximate anticipated field contact determined from the hydrograph and the hyetograph for the sites evaluated (Kuo 2007); it is short enough to assure undersaturation of CFA over the entire interval. Mixtures were then centrifuged at 5,000 rpm for 5 min, and the supernatant was filtered through a 0.45-μm membrane filter. The DP concentration in this experiment was determined and compared to calculate $\mathrm{SSA}_{\mathrm{CFA}}$ (Eq. 4).

3 Results and Discussion

3.1 Soil Properties

Physical and chemical properties did not vary appreciably between sites, with slightly acid pH (mean values are 6.09 and 6.37 at site A and B, respectively) and relatively low OC (mean values are 0.76% and 1.70% at site A and B, respectively). The soil textures were sandy; at least 94% of soil particles were greater than 37 μm in size (Kuo 2007). Chemical extractions and P fractionation confirm a very high TP concentration and a dominance of Ca–P. A form of fluorapatite in the samples was confirmed by XRD (Fig. 3). This apatite is likely CFA since that form has been well documented in phosphoritic deposits from which the material used to construct the remediated soils was derived (Van Kauwenbergh et al. 1990; Hanna and Anazia 1990; Guidry and Mackenzie 2003). Results of XRF (Table 1) showed the main elements to be Si, Ca, Al, P, K, and Fe. Quartz is the main mineral in the soils, accounting for the dominance of Si. The second most abundant element is Ca, a major component of apatite. The TP concentrations range from 1.7% to 2.3% at the two sites (Table 2). These very high P concentrations result from the residual apatite. The P sequential fractionation of soils (Table 2) from both sites is also consistent with a dominance of Ca- (and/or Mg-) bound P (approximately 95% of TP). Mean Mehlich-1 P concentration (Table 3) at sites A and B is 849 and 1,192 mg kg^{-1}, respectively. The major Mehlich-1 extractable element was Ca. The mean molar concentration ratios of P/Ca are 0.44 and 0.55 at site

Table 3 Results of Mehlich-1 extraction (±standard deviation)

Site	*N*	Fe (mg kg^{-1})	Al (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})	P (mg kg^{-1})	P/Ca (%)
A	18	4.46±0.66	88.9±30.6	1,986±226	98±35	849±142	55±4
B	10	13.4±2.3	103±49	3,580±140	138±52	1,190±86	43±3

N number of soil samples analyzed within each site

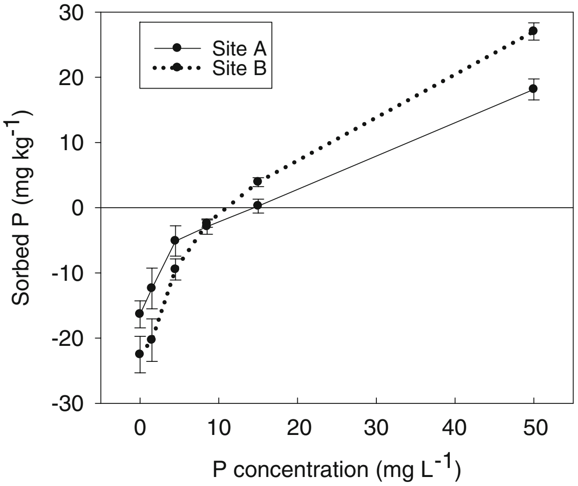

Fig. 4 P sorption isotherms of reclaimed phosphate mining soil samples in sites A and B (shaken for 2 h). Each concentration has four replicates; the error bar represents standard deviation

B and site A, respectively. The molar ratio of P/Ca (0.52) in the formula of CFA is in this range.

Results of P sorption isotherms (Fig. 4) confirm a high equilibrium P concentration at zero net P sorption (EPC_0) for soils from both sites (approximately 11–15 mg L^{-1}). If the P concentration of runoff is less than the EPC_0, then there would be a net release of P from the soil. Thus, only runoff DP concentration greater than 11 mg L^{-1} would result in net P sorption to soil particles. In effect, these soils are an environmental P source rather than a sink.

Total P concentrations and calculated apatite mass fractions were higher in the finer particle size ranges (Table 4). Particles smaller than 37 μm contain about 3.1% P. The concentrations between classes 0<2 μm and 2–37 μm were not significantly different. Coarser particles (250–2000 μm) contain about 1.6% P. The higher P concentration found in finer size fractions relates to a greater abundance of apatite in these fractions, possibly reflecting the predominant particle size of apatite in the ore body. Alternatively, apatite may have been sorted via elutriation or comminuted during the mining process.

3.2 Results of Phosphate Solubility Equilibria

Concentrations of cations and anions, along with pH, EC, and ionic strength of runoff samples (Table 5), were used to model chemical speciation for runoff samples. Using K_{sp} values reported in the literatures for HAP, FAP, and CFA (McDowell et al. 1977; Driessens 1982; Jahnke 1984), a phosphate-mineral solubility diagram was plotted to show the relationships between $\log H_2PO_4^{2-}$ and pH. Such diagrams are particularly useful for depicting relative stability of phosphate compounds and minerals in soils at various pH values (Olsen and Khasawneh 1980). Results indicate that all forms of apatite would be undersaturated in the runoff water (Fig. 5). High Ca-bound P based on P fractionation and Mehlich-1 extraction corroborates equilibrium modeling indications that the high DP concentration in runoff water relates to CFA dissolution.

Table 4 P concentrations, weight fraction of apatite based on CFA composition, and SSA of CFA per gram soil in different particle size classes

Site	0.051~2 (μm)	2~37 (μm)	37~100 (μm)	100~250 (μm)	250~2,000 (μm)
	P concentrations (mg kg^{-1}) in each particle size class (μm)[a]				
A	30,810±2,320	29,860±1,970	21,040±2,270	18,600±1,840	16,330±1,650
B	31,570±2,030	30,410±1,980	23,980±1,860	19,850±1,600	16,630±1,220
	Weight fraction of CFA (g[CFA] g[S]$^{-1}$) in each particle size class[b]				
A	0.1947±0.0147	0.1887±0.0125	0.1330±0.0144	0.1176±0.0117	0.1032±0.0105
B	0.1995±0.0128	0.1922±0.0125	0.1516±0.0118	0.1255±0.0101	0.1051±0.0077
	SSA of CFA (m^2[CFA] g[S]$^{-1}$) in each particle size class per gram soil [b]				
A	0.70760±0.05327	0.03037±0.00201	0.00392±0.00042	0.00135±0.00013	0.00024±0.00002
B	0.72506±0.04660	0.03093±0.00202	0.00446±0.00035	0.00144±0.00012	0.00024±0.00002

Data are average ± standard deviation values of eight samples within each site. (Assuming spherical particle shape)

[a] P concentrations (milligram per kilogram) in each particle size class are measured data

[b] Weight fraction of CFA and SSA of CFA are calculated

Table 5 Concentrations of ions, pH, EC, and ionic strength of runoff samples collected in June 2006

Sample ID	pH	EC ($mS\ cm^{-1}$)	Ionic strength	F^{1-} ($mg\ L^{-1}$)	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Cl^{1-}	Ca^{2+}	Mg^{2+}	Fe^{2+}	Al^{3+}	K^{1+}	Na^{1+}	Cu^{1+}	Mn^{2+}	Zn^{2+}
A1	5.81	21	0.00027	0.39	0.17	0.43	1.45	2.36	12.83	1.13	0.26	0.01	0.11	0.22	1.17	0.00	0.01	0.01
A2	6.01	17	0.00022	0.21	0.16	0.25	1.33	1.91	10.60	0.98	0.24	0.00	0.08	0.24	0.82	0.00	0.01	0.03
A3	6.09	13	0.00017	0.65	0.14	0.21	1.43	1.55	8.06	0.69	0.15	0.01	0.01	0.14	1.02	0.01	0.01	0.02
A4	5.97	17	0.00022	0.08	0.16	0.20	0.97	1.90	10.86	0.51	0.30	0.01	0.12	1.42	0.91	0.01	0.01	0.09
A5	4.86	15	0.00020	0.07	0.11	0.18	1.01	1.67	9.96	0.28	0.17	0.00	0.22	1.42	0.85	0.02	0.02	0.10
A6	4.81	14	0.00018	0.06	0.14	0.17	0.95	1.52	10.66	0.26	0.14	0.01	0.19	1.13	0.90	0.02	0.02	0.09
B1	6.10	28	0.00036	0.36	0.28	0.26	4.92	1.17	9.64	2.01	1.27	0.46	1.23	2.06	1.01	0.03	0.02	0.08
B2	6.20	35	0.00046	0.35	0.33	0.39	5.35	1.38	10.29	2.05	1.25	0.39	1.27	2.34	1.13	0.03	0.02	0.08

A site A, *B* site B

3.3 Relation Between CFA SSA and DP Concentration

A strong relationship between the calculated CFA SSA and measured DP concentration (R^2=0.93; Fig. 6) is supportive of evidence presented herein that CFA dissolution is a major factor controlling P release from these soils. The pH value of these eight samples is ranged from 5.96 to 6.20 with a mean of 6.11. Assumptions such as uniform distribution within each particle size class result in uncertainty in absolute accuracy of the CFA SSA calculation based on Eq. 4. However, the relative SSA values serve as a valid indicator that P release from the soils is related to CFA SSA.

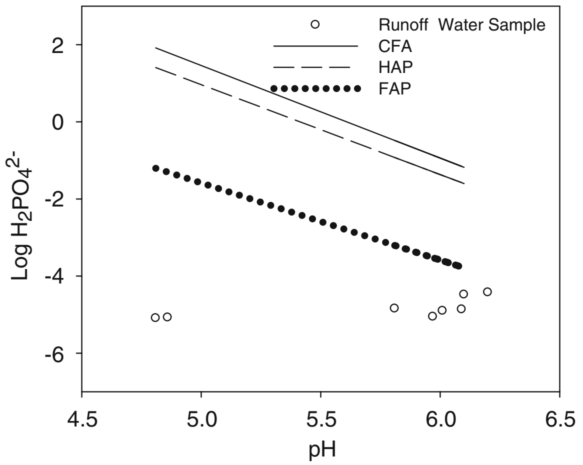

Fig. 5 Phosphate-mineral solubility as related to the log $H_2PO_4^{2-}$activity to pH in soil solutions of runoff water samples collected from reclaimed phosphate mining soil areas

4 Conclusions

Phosphorus in soils constructed from sand tailings at the remediation sites was in the form of apatite, as indicated by XRD and corroborated by XRF elemental analysis and chemical fractionation. Results of this study supported the hypothesis that release of P from the soils was primarily from apatite dissolution rather than desorption from metal oxides that is more typical of soils of the region. The DP concentration in a batch experiment is closely related to the calculated CFA SSA. Results show that these soils are a P source rather than sink. Findings are applicable to other phosphate mine reclamation sites and illustrate the need to account for compositional differences be-

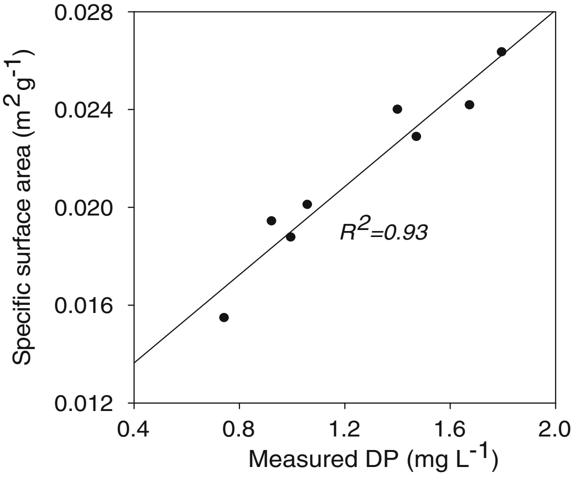

Fig. 6 Relationship between calculated specific surface area (SSA) of carbonate–fluorapatite (CFA) and measured dissolved P (DP) concentrations of solutions shaken with reclaimed phosphate mining soil samples for 15 min

tween reconstructed soils on reclaimed mining sites and their indigenous soil analogues. The high DP loadings in runoff from these soils, along with any related water quality effects, are likely to persist given the abundance and solubility of apatite and the lack of P sorbing components. These results should be considered in the choices made for soil reconstruction material at phosphate mining sites.

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