Journal of
Bioremediation & Biodegradation

Aajjane, et al., J Bioremed Biodeg 2014, 5:4
DOI: 10.4172/2155-6199.1000229

Research Article Open Access

Availability of Three Phosphorus Fertilizers to Corn Grown in Limed Acid-Producing Mine Tailings

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Rec date: Sep 21, 2013, **Acc date:** May 23, 2014, **Pub date:** May 28, 2014

Abstract

Liming can modulate phosphorus (P) availability to plants growing in acid-forming media. The objectives of this study were to determine the effects of lime and phosphorus rates on corn (*Zea mays* L.) grown under greenhouse conditions on an acid-producing mine tailing, and to evaluate P desorption from the mine tailing after harvest. The acid-sulfide tailing (pH 2.65) collected from the Solbec-Cupra mine in Quebec was limed using $CaCO_3$ to theoretical pH values of 5 (11 g/kg), 6 (17 g/kg) and 7 (30 g/kg) prior to corn production. Phosphorus was thoroughly mixed with the tailing at rates of 0, 22.4, 44.8 and 89.6 mg P/kg. Commercial peat-shrimp waste compost; a commercial bone flour fertilizer and reagent-grade KH_2PO_4 were used as P sources. Corn (*Zea Mays* L. cv. 'Pride 1122') was grown for 50 days after emergence. After harvest, the mean tailing pH values varied from 4.20 to 7.20. Dry matter yield of plant tops was significantly affected by lime and phosphorus treatments. Corn yields were significantly correlated with pH, salinity index (electrical conductivity of aqueous extracts) and ammonium acetate-extractable Ca and Mg. In all P treatments, the highest yield was obtained with plot receiving 44.8 mg P/kg and lime rate to achieve pH 6 (17 g of $CaCO_3$/kg). In general, mineral composition of the tops did not show toxic accumulation of trace metals. The P extracted by Na_2EDTA from some tailing samples was a time-dependent process. Results from another P desorption study indicated that the amounts of DTPA-TEA-$CaCl_2$ (pH 7.3) extractable substrate P increased with temperature. The DTPA-extracted P data from the 30 tailing samples over a period of 1 to 48 hours were best described by an empirical first-order-rate equation using $t^{0.5}$ instead of t as the time variable. Liming and P fertilization were determinant factors for the growth of corn in acid sulfide tailings.

Keywords: Phosphorus avalilability; $CaCO_3$; EDTA; Greenhouse study; *Thiobacillus ferrooxidans*

Introduction

The reclamation and revegetation of abandoned sulfide tailing impoundments is afflicted by the generation of acidic mine drainage waters [1] under aerobic conditions [2], thus producing poor vegetation stands. Dant [3] found that phosphorus was one of the most limiting plant nutrients in some minesoils. Sencindiver et al [4] showed that corn yields were higher on phosphatic clay-treated minesoils than one minesoil treated with monocalcium phosphate.

It is known that P availability in limed acid soils depends on pH and P fixing capacity [5]. It has been reported that pH is an important factor in P release from rock phosphate-pyrite mixtures. Although P fertilization has been found essential for good revegetation of coal mine spoils, the fertilizer requirement should be enhanced in limed acid tailing.

The objectives of this study were to determine the effects of lime and phosphorus on corn grown on a highly acid-producing mine tailing, and to examine the P desorption characteristics of the tailing after harvest.

Materials and Methods

The Solbec-Cupra Mine, operated from 1962 till 1970, is a polymetallic ore mine located 80 km North East of the city of Sherbrooke, Quebec, Canada. Acidic sulfidic oxidized tailings were collected in the 0-25 cm upper layer, air-dried in the laboratory and crushed to the original size range. Subsamples were limed using reagent-grade $CaCO_3$ to theoretical pH values of 5 (11 g/kg), 6 (17 g/kg) and 7 (30 g/kg) prior to corn production. Phosphorus was thoroughly mixed with the tailing samples at rates of 0, 22.4, 44.8 and 89.6 mg P/kg. Commercial peat-shrimp wastes compost, a commercial bone flour and reagent-grade KH_2PO_4 were used as P sources. The treatments were arranged in a randomized complete block design with three replications. All treatments received N, K, Zn, Cu, Mn, B and Mo fertilizers. After fertilization, the substrates were watered to field moisture capacity using distilled water and allowed to equilibrate for 4 days before planting. Each pot contained 1 kg of mine tailing. Five seeds of corn (*Zea mays* L. cv. 'Pride 1122') were planted and subsequently thinned to two seedlings per pot 5 days after emergence. Distilled water was added daily. After 50 days of growth, plant tops and roots were harvested and separated. Plant samples were dried at 70°C, ground to 2 mm and oxidized with HNO_3. Plant nutrients and heavy metals in acid extracts were analyzed by plasma emission spectroscopy.

After harvest, mine tailing samples were air-dried and crushed to the original size prior to analysis. The chemical properties of tailing samples and P desorption in relation to temperature and extration time was determined following standard methods as described by Carter [6]. The dissolution of tailing P in EDTA solution over a period of 1 to 14 days was also investigated for some tailing samples. EDTA-extractable P could be considered a source of labile P related to crop response [7]. In another P desorption study, reaction rate of P desorption was evaluated for each cultivated tailing sample using DTPA-TEA-$CaCl_2$ (pH 7.3) as extracting solution and 1, 12, 24 and 48 hours as extraction time. The DTPA method was used to minimize the dissolution of $CaCO_3$ [8] during the extraction in all limed tailing samples. Tailing pH was determined in distilled water using a tailing to solution ratio of 1:1. Electrical conductivity was measured after mixing 30 g of tailing with 30 mL of distilled water. Other analysis included the followings: Mehlich 3-extractable nutrients (P, Ca, Mg, K), ammonium acetate-extractable Ca, Mg and K, acid ammonium oxalate-extractable Fe and P, Na_2EDTA-extractable and DTPA-extractable Fe and P. Phosphorus was determined calorimetrically and metal cations were determined by atomic absorption spectrophotometry. Analysis of variance was conducted using the General Linear Model (GLM) statistical programme of the SAS package [9]. Linear correlation and regression analyses were used to determine the effect of chemical properties of the growing media on corn growth.

Results

Greenhouse study

Substrate properties as affected by liming and P source are presented in Table 1. The pH was the most affected. The smallest yield was obtained at the lowest lime application rate (Ca_1). The ANOVA of treatment effects on top yield indicated significant main effects and a significant lime x P source interaction (Table 2). The lime effect was quadratic and the P rate effect was linear. The effect of P source on corn growth is presented in Table 3. In all $CaCO_3$ treatments, the significantly highest yield was obtained with plot receiving PSC. In general, lime application and P source stimulated corn growth.

		P availability indexes (%)[c]				Dry matter yields (g/pot)	
Sources of P[a]	$CaCO_3$ rates[b]	Mehlich 3	Oxalate	EC[d] (dS/cm)	Tailing pH	Tops	Roots
MKP	Ca1	41.9	3.2	2.26	4.2	5.06	3.12
	Ca2	49.5	2.5	2.3	6.35	14.8	8.31
	Ca3	37.5	3	2.21	7.2	13.25	6.57
PSC	Ca1	42	3.4	2.32	5.55	15.78	8.78
	Ca2	48.7	3	2.29	6.5	17.04	10.92
	Ca3	42	3.2	2.54	7.16	15.31	9.46
BF	Ca1	37.9	2.9	2.01	4.83	9.32	5.9
	Ca2	42.6	2.4	2.28	5.88	15.53	8.92
	Ca3	32.7	3.3	2.34	7.14	14.03	8.44

Table 1: Chemical properties of tailing samples as affected by the rate application of calcium carbonate and three sources of phosphorus [a]MKP: KH_2PO_4; PSC: peat-shrimp wastes compost; BF: peat flour. Rate of P application: 22.4, 44.8 and 89.6 mg P/pot (same for all P sources); [b]Ca1 , Ca2 and Ca3: 11, 17 and 30 g of $CaCO_3$/pot, respectively; [c]Expressed as percentage of tailing total P content; [d]Electrical conductivity of the tailing aqueous extract

Sources	Degrees of freedom	F values
Main effect		
$CaCO_3$ rate (Ca)	2	37.42^{***}
Linear		38.81^{***}
Quadratic		33.29^{***}
Source of P (P)	2	33.33^{***}
P rate (R)	2	06.85^{***}
Linear		09.36^{**}
Quadratic		NS
Interactions		
Ca x P	4	9.90^{***}
Ca x R	4	NS
P x R	4	NS
Ca x P x R	8	NS

Table 2: Analysis of variance on the influence of calcium carbonate (CaCO3), P source and P rate on dry matter yield of the above ground portion of corn grown on a sulfide tailing under greenhouse conditions **, ***: significant at P<0.01 and P<0.001, respectively; NS, non-significant at P<0.05

CaCO3 rate[z] (g/pot)		Corn top yield (g/pot)[y]
Ca_1	Peat shrimp wastes compost (PSC)	15.78a
	Bone flour (BF)	11.09ab
	Monopotassium phosphate (MKP)	5.99b
Ca_2	PSC	17.04a
	MKP	14.79b
	BF	15.53b
Ca_3	PSC	15.31a
	BF	14.70b
	MKP	13.25b

Table 3: Effect of P source at three rates of $CaCO_3$ on dry matter yield of corn tops under greenhouse conditions [z]Treatments are described

in Table 1; [y]The values followed with a same letter are not significantly different at P<0.05 according to Waller-Duncan test

The maximum yield is obtained at intermediate liming (Table 1). There was a highly significant correlation (P<0.001) between P uptake by corn and both tailing pH (r=-0.786) and oxalate-extractable Fe (r=0.762). In general, heavy metal cations (Zn, Cu, Fe and Mn) in corn tissues decreased with lime rate (data not shown).

The Mehlich 3 solution used as a soil test for available-plant P level in Quebec extracted higher amounts of tailing P (P_{M3}) than the acid ammonium oxalate method (P_{ox}) (Table 1). The amount of P_{M3} varied from 32.7 to 49.5% of total P with an average of 42%. Inclusion of independent variables that met the 0.500 significance level for entry into multiple linear regression, e.g. P_{M3}, P_{M3}/total P ratio, and Mehlich-3 extractable Ca and Mg increased the R^2 value to 63.9%.

Laboratory experiment

The evolution of P extracted by EDTA in some tailing samples is presented in Figure 1. In general, the amounts of extractable P were higher in BF-treated samples than in PSC-or MKP-treated tailings. The results of the evolution of P-EDTA extracted in treated tailings samples after 1 and 14 days are show in Table 4.

In another series of experiments, the amounts of P extracted by DTPA-TEA-$CaCl_2$ (DTPA) increased nonlinearly with extraction temperature (Figure 2), indicating that P desorption by DTPA was an endothermic reaction.

Samples treated by	Day 1	Day 14
PSC	27%	66%
BF	20.10%	56.20%
MKP	16%	81%

Table 4: Evolution of P-EDTA extracted in treated tailings samples after 1 and 14 days

PSC: commercial peat-shrimp wastes compost; BF: commercial bone flour; MKP: reagent-grade KH_2PO_4

Discussion

Greenhouse study

The greenhouse study shows that lime and P applications stimulated the growth of corn tops and roots. Maximum yield was obtained at intermediate rates. The effect of liming was more pronounced than P source, as indicated by the highly significant positive correlation between corn yield and tailing pH. Many workers [1,10,11] showed the benefit of liming acid mineral soil or acid mine tailing. The effects of low pH on plant growth could also produce nutritional imbalances [5] and influence the solubility of P compounds. Phosphates may be fixed into less soluble states as iron and aluminium phosphates, especially at low pH [5]. After heavy liming, soluble phosphates could become less available to plants due to chemical precipitation as calcium phosphates on carbonate surfaces [5]. As a result, the interaction between P source and lime rate is related to the influence of pH on P availability. Non-significant correlations between corn yield and total P or P_{ox} indicated that only a small proportion of the P fixed on metal-oxide surfaces accounted for the variation in corn yield. Top yield was significantly higher in PSC-treated tailing than in MKP- or BF-treated tailing samples (Table 3). Hountin et al. [12] also found that application of the same commercial PSC with lime to an acid loamy sand soil maintained high yield of barley and soil fertility. Crop response to compost could be attributable to supplemental nutrients supplied by the compost.

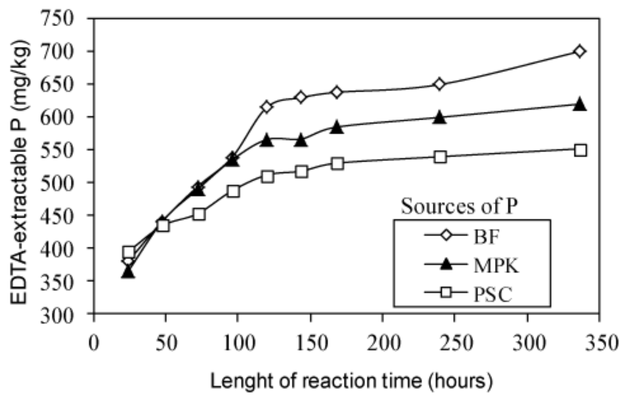

Figure 1: Effect of extraction time on the release of EDTA-extractable P from tailing samples fertilized with monopotassium phosphate (MPK), commercial peat-shrimp wastes compost and bone flour (BF)

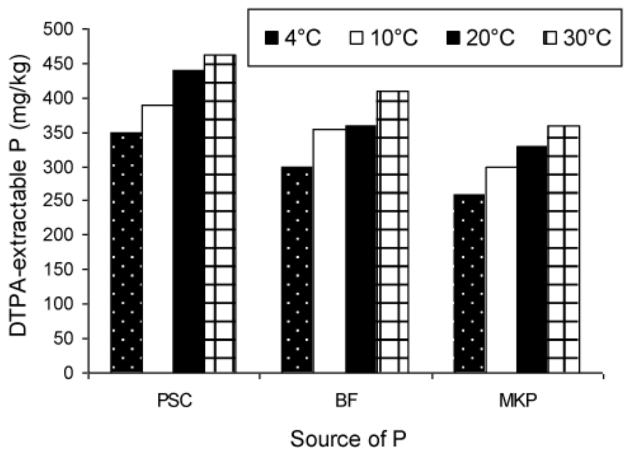

Figure 2: Phosphate desorbed by DTPA as a function of extraction temperature in tailing samples receiving commercial peat-shrimp wastes compost (PSC), commercial bone flour (BF) and reagent-grade KH_2PO_4 (MPK)

Laboratory experiment

Alexander and Robertson [13] suggested that EDTA-extractable P derives mainly from Fe and Al compounds present in soils. Hence, P desorption by EDTA provides an index for the release of readily-extractable P in sulfide tailings rich in Fe compounds. The graphs of EDTA-P released from the sulfide tailing as a function of extraction time follow a parabolic shape (Figure 1). Thus, the recovery of

Citation: Aajjane A, Karam A, Parent LE (2014) Availability of Three Phosphorus Fertilizers to Corn Grown in Limed Acid-Producing Mine Tailings. J Bioremed Biodeg 5: 229. doi:10.4172/2155-6199.1000229

inorganic P was time-dependent, as also found in many reports on the effect of extraction time on P desorption in mineral soils. As illustrated in Figure 1, the higher amount of extracted P was observed with BF, due possibly to mineralisable organic P compounds.

For mineral soils, Beaton et al. [14] found that the rate of dissolution of pellets containing 15 mg of P prepared from water-soluble P fertilizers increased markedly as extraction temperature was increased from 5° to 35°C. Numerous reports indicated that the optimum growth conditions for common microorganism species in the sulfide tailings such as *Thiobacillus ferrooxidans* is 30°C [15]. In general, the release of DTPA-extractable P in relation to temperature from tailing samples increased in the following order: MKP<BF<PSC (Figure 2). The activity of microorganisms involved in the decomposition of organic P into inorganic P or in the oxidation of iron sulfide into P-fixing iron hydroxide could be stimulated as temperature rose from 4° to 30°C. Despite those opposite reactions, the amount of DTPA-extracted P was highest in the temperature range of 20° to 30°C over all treatments.

In order to be useful, a desorption kinetic model must fit the data and yield parameters related to plant response. The kinetics of P desorption from agricultural soils was described by various kinetic models [16] such as:

First-order reaction: $\ln C = \ln C_0 + kt$ (1)

Second-order: $1/C = 1/C_0 - kt$ (2)

Elovich-type equation: $\ln C = a + b\ln t$ (3)

Two-constant rate equation: $\ln C = \ln k + b\ln t$ (4)

Parabolic diffusion law: $C = C_0 + kt^{0.5}$ (5)

Modified first-order desorption model: $\ln C = \ln C_0 + kt^{0.5}$ (6)

Where C is desorbed P concentration in mg/L (same for all models); t is extraction time in hours (same for all models); C_0, a, b and k are empirical constants estimated by the least squares method. The R^2 and the standard error of estimate (SE) were used as criteria for comparing the equations with respect to the goodness of fit [16].

The modified first-order equation (6) provided the best fit, followed by the two-constant rate model (4) (Table 5). The slope varied among treatments due to variations in surface reactivity for various P compounds in cultivated tailing samples. Sharpley [17] related Elovich P desorption parameters to extractable Al and $CaCO_3$ in acidic and calcareous soils, respectively. The k values of the modified first-order model (6) was correlated to P_{M3} (r=0.394, P<0.05), indicating that k values could depend on labile P levels. The k values were negatively correlated to top yield (r=-0.336, P<0.05) and root yield (r=-0.326, P<0.05). On the other hand, C_0 values were positively correlated with dry matter of corn tops (r=0.385, P<0.05) and root yield (r=0.460, P <0.05). Hence, corn yield may be predicted from P desorption measurements in acidic mine tailings.

Conclusion

Our study showed that lime and P applications stimulated the growth of corn tops and roots. Also, the yield obtained with the organic amendments and experiment of P-desorption by EDTA allows concluding that the recovery of inorganic P was time-dependent. In addition, the activity of microorganisms involved in the decomposition of organic P into inorganic P or in the oxidation of iron sulfide into P-fixing iron hydroxide could be stimulated as temperature rose from 4° to 30°C, like that was shown with the use of the DTPA in the P-desorption reactions. Thus, the best model to describe of P-desorption kinetic was:

$\ln C = \ln C_0 + kt0.5$

Where C is desorbed P concentration in mg/L; t is extraction time in hours; C_0, a, b and k are empirical constants estimated by the least squares method. Hence, corn yield may be predicted from P desorption measurements in acidic mine tailings.

Calcium and phosphorus deficiency in acid mine tailing are limiting plant growth. Application of $CaCO_3$ at a rate of 17 g/kg in order to maintain a pH range between 6 and 6.5 during cultivation would be required for optimal plant growth. Managing acid sulfide tailing for crop production requires that plant tolerance to acidity be weighed against the cost of lime and organic materials.

Source of P[z]	Sample no	Elovich		First-order		Second-order		Two-constant rate		Parabolic diffusion		Modified first-order	
		R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE
MKP	4	0.729	0.49	0.984	0.074	0.909	0.125	0.969	0.131	0.919	0.267	0.987	0.066
	5	0.789	0.4	0.886	0.222	0.75	0.299	0.96	0.147	0.923	0.242	0.958	0.135
	7	0.76	0.547	0.974	0.092	0.901	0.1	0.928	0.176	0.941	0.27	0.989	0.059
	10	0.782	0.195	0.963	0.112	0.871	0.335	0.756	0.196	0.952	0.091	0.998	0.028
PSC	14	0.681	0.526	0.989	0.059	0.933	0.107	0.9	0.09	0.883	0.319	0.967	0.104
	16	0.715	0.661	0.992	0.048	0.937	0.063	0.825	0.242	0.911	0.369	0.978	0.078
	17	0.574	0.543	0.967	0.087	0.956	0.062	0.604	0.326	0.816	0.356	0.857	0.181
	20	0.793	0.928	0.939	0.155	0.817	0.097	0.512	0.302	0.95	0.457	0.994	0.05
BF	22	0.8	0.47	0.921	0.198	0.775	0.277	0.93	0.166	0.951	0.232	0.991	0.068

	24	0.827	0.407	0.927	0.173	0.815	0.209	0.945	0.165	0.974	0.158	0.996	0.041
	26	0.94	0.135	0.806	0.268	0.701	0.413	0.937	0.161	0.984	0.07	0.951	0.134
	29	0.589	0.756	0.985	0.101	0.901	0.248	0.918	0.136	0.81	0.514	0.948	0.192

Table 5: Summary of R^2 values and standard error of estimates (SE) of six kinetic models for desorption of P by the DTPA-TEA-$CaCl_2$ solution (pH 7.3) from representative cultivated tailing samples

^{z}MKP=monopotasium phosphate (KH_2PO_4); PSC=peat-shrimp wastes compost; BF=bone flour

Acknowledgement

The financial assistance provided by the National Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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