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Full Length Research Paper

The effect of paper mill sludge on chemical properties of acid soil

Mohammadi A. Torkashvand

Islamic Azad University-Rasht Branch, Rasht, Iran. E-mail: Torkashvand@iaurasht.ac.ir.
Tel: 0098-131-4247058, 09125137128. Fax: 0098-131-4223621.

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The effect of paper mill lime sludge as acid soil amendment in an experimental study was investigated. Sludge used contained 58.4% calcium carbonates plus a small amount of heavy metals. An incubation study was conducted with an acid soil for up to 90 days and the treatments included various amounts of sludge. Results indicated a promising potential for paper mill sludge to be used as an inexpensive source of available lime for correction of soil acidity.

Key words: Acid soil, paper mill lime sludge, soil amendment.

INTRODUCTION

Amelioration of acid soils with liming materials is a common practice (Quoggio et al., 1995), but other materials are also used as acid soil amendment, such as gypsum, phosphate rocks (He et al., 1996) and some industrial byproducts (Abbaspour et al., 2004, Franco-Hernandes and Dendooven, 2006). About 30% of the world's arable soils are acidic (VonUexkull and Mutert, 1995) characterized by an excess of H^+, Al^{3+} and Mn^{2+} and lack (deficiencies or unavailabilities) of certain mineral elements, particularly calcium (Ca), magnesium (Mg) and phosphorus (P). Acid soils are deleterious to plant growth (Foy, 1992). The most common management practice to ameliorate acid soils is the surface application of lime and other calcareous materials (Bolan et al., 2003). The main aim of soil liming is to neutralize acidic inputs and recovering the buffering capacity to the soil (Ulrich, 1983).

Applications of industrial wastes as fertilizer and soil amendment have become popular in agriculture. Paper mill sludge is produced as a by-product of paper production that disposal of this material presents a problem for the mill (Mahmood and Elliot, 2006). Disposal by land filling, the most common disposal method, is costly and faces increasingly stringent environmental regulations (Feldkinchner et al., 2003). Lime sludge is the solid waste produced as part of the process that turns wood chips into pulp for paper. The major component of lime mud is calcium carbonate ($CaCO_3$) and it is estimated that about 0.47 m^3 of lime mud is generated to produce 1 ton of pulp (Wirojanagud et al., 2004).

Land application is one of the several limited methods available to manage solid waste (Schoof and Houkal, 2005) and is more economically and ecologically sound than landfill practice (Zule et al., 2007). For land application of sludges produced from pulp mills, Simpson et al. (1982) reported that combined kraft paper mill secondary sludge-fly ash applied at a rate of 108 metric dry ton ha^{-1} significantly increased the yield of fescue and corn. A 4-year field study in Alberta (Macyk, 1996) recommended an agronomically sound decomposed pulp mill sludge application rate of 40-80 dry ton ha^{-1} for brome grass.

Gaskin and Morris (2004) indicated that lime mud has potential to be used as an agricultural liming material because of its capability to neutralize soil acidity (increase soil pH) and add calcium and magnesium to the soil. Although high moisture content of lime mud creates more shipping and handling difficulties than typical dry agricultural liming materials (Mahmoudkhani et al., 2004), this obstacle can be overcome as sludge dewatering technology improves (Chen et al., 2002; Yin et al., 2004).

The objectives of the present study were then to (1) Determine the effect of paper mill sludge, on pH and EC in an incubation study, and (2) To evaluate the value of the waste as an agricultural lime material. However, it should be noted that results from this controlled laboratory experiment can be different to actual field trials since actual field practice. Also, actual field conditions are under influence from consistently changing weather condition which is dramatically different than this

Table 1. Some properties of the used soil in incubation phase.

Analysis	Amount
pH	6.2
EC (dS/m)	1.1
Total N (%)	0.085
P (mg/kg)	15.6
K (mg/kg)	145.2
Organic matter (%)	0.92
Texture	Clay loam

Table 2. Results of ANOVA taking into consideration treatments effect and time incubation on pH and EC in soils.

Source of change	d. f	F values						
		pH	EC	P	K	Fe	Zn	Mn
treatment	7	171.8**	117.2**	5.43**	4.4**	96.6**	2.6*	15.7**
time	2	35.6**	7.2**	0.55^{ns}	20.4**	12.1**	0.76^{ns}	0.56^{ns}
Treatment × time	1	2.7**	0.72^{ns}	1.46^{ns}	0.49^{ns}	2.4*	0.68^{ns}	0.87ns

** significant at 1% level; * significant at 5% level; ^{ns} is not significantly at 1% level.

laboratory experiment.

MATERIALS AND METHODS

The paper mill sludge was obtained from Pars factory, Khoozestan province, and Chocka-Talesh factory, Guilan province, Iran. Total concentrations of some elements in the mixed paper mill sludge were determined in the extract after digestion of samples with HNO_3 and HCl (Hossner, 1996) for elemental analysis. The amounts in the digests were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES, LEEMAN LABs, Inc.). The sludge pH and EC (Rhoads, 1996) were determined in a 1:2.5 paper mill sludge/water suspension using a Metrohm 320 pH meter and Metrohm 644 conductometer, respectively. The incubation study was conducted with an acid soil collected from the fields beery orchards, Rasht, Iran. Some physical and chemical properties of the soil are shown in Table 1. Soil was air-dried and crushed to pass a 2-mm sieve. Treatments were then applied to 500 g samples of soil and the treated samples were incubated in 1 L plastic containers at field capacity (FC) moisture content for up to 90 days. Sub samples were collected after 1, 30 and 90 days of incubation, air-dried and crushed to pass a 2-mm sieve and stored for chemical analysis. The following treatments were studied:

1. Control, no treatment (L_0).
2. Treated with 0.1, 0.2, 0.5, 1, 2 and 8% W/W dry paper mill sludge ($L_{0.1}$, $L_{0.2}$, $L_{0.5}$, L_1, L_2, L_4 and L_8).

Data were analyzed in a factorial 3×8 completely randomized design. Each treatment was replicated three times. The moisture of the containers was kept near the FC soil moisture content throughout the experiment by periodically weighing and replenishing evaporated water. At each sampling period (1, 30 and 90 days), approximately 50 g of soil was taken from each container to determine pH and EC and AB-DTPA extractable Fe, Mn, Zn, K and P. The concentrations of Fe, Mn and Zn were measured in the extracts by atomic absorption spectrophotometry, K by flame photometry and P by spectrophotometry. Data were analyzed by standard ANOVA procedures using MSTATC and SAS software and significant differences was determined based on P<0.01 level for the least significant difference test.

RESULTS

pH and EC

The chemical composition of the paper mill sludge showed that this compound contained about 58.4% calcium carbonates equivalent and a pH about 13.2 (pH of 1:2.5 dry paper mill sludge/water suspension), and small amounts of Zn, Cu, Cr, Cd and Pb respectively 4.12, 2.35, 7.54, 3.25 and 28.6 $mgkg^{-1}$.

Based on ANOVA results (Table 2), the effect of treatments on soil pH and EC is significant at the 1% level. Table 3 shows the effect of added paper mill sludge on soil pH. Paper mill sludge remarkably increased pH, which was proportional to the application rate of paper mill sludge. Increase in pH was 0.15 units for $L_{0.1}$, 0.88 units for $L_{0.2}$, 1.2 units for $L_{0.5}$, 1.25 units for L_1, 1.59 units for L_2, 2.21 units for L_4 and 2.7 units for L_8 compared to the control (L_0). Results of Table 2 showed that the interaction effect of soil pH and time incubation was significant (P≤0.01). Soil pH initially increased and then decreased under most of the paper mill sludge treatments (Table 4). At the end of incubation time, soil pH declined by 0.42, 0.73, 0.35, 0.80, 0.38, 1.19 units for $L_{0.2}$, $L_{0.5}$, L_1, L_2, L_4 and L_8 treatments compared to the initial pH, respectively. On the base of Table 5, there is a significant difference (P≤0.01) between three incubation

Table 3. The effect of treatments on some chemical properties of soil.

Treatments	pH	EC (dS/m)	P	K	Fe	Zn	Mn
			mg/kg				
L_0	6.04 f	0.37 d	13.1 bc	126.4 a	202.3 a	1.8 c	17.3 a
$L_{0.1}$	6.19 f	0.58 c	11.5 a	125.8 a	191.0 ab	2.1 bc	15.1 ab
$L_{0.2}$	6.92 e	1.08 c	16.0 a	122.6 ab	182.1 b	2.6 ab	14.2 bc
$L_{0.5}$	7.29 d	1.31 c	16.7 a	116.5 abcd	164.7 c	3.0 a	12.6 cd
L_1	7.24 d	1.63 b	15.3 ab	108.5 d	142.5 d	2.6 ab	10.8 de
L_2	7.63 c	1.82 b	16.5 a	113.1 bcd	120.0 e	2.8 ab	9.5 e
L_4	8.25 b	1.96 b	16.0 a	111.3 cd	86.9 f	2.5 ab	9.4 e
L_8	8.74 a	2.76 a	14.3 ab	119.6 abc	87.8 f	2.4 abc	8.4 e

LSD (least significant difference) shows the significant difference (ρ = 0.05) among the different treatments. Values followed by the same letters in each column are not significantly different at the 0.05 level (least significant difference).

Table 4. The effect of treatments and incubation time on some chemical properties of soil.

Treatment	Time	pH	EC (dS/m)	P	K	Fe	Zn	Mn
				mg/kg				
L_0	1	6.12	0.33	13.46	135.3	204.4	1.7	16.6
	2	5.95	0.42	11.5	126.8	207.0	1.9	18.9
	3	6.07	0.37	14.33	117.0	195.4	1.9	16.2
$L_{0.1}$	1	6.28	0.78	11.0	139.2	163.1	2.1	14.2
	2	6.18	0.52	10.16	122.8	202.9	2.3	16.7
	3	6.12	0.45	13.5	115.3	206.8	1.9	14.3
$L_{0.2}$	1	7.14	1.1	16.0	134.6	171.6	2.5	16.9
	2	6.92	1.12	15.5	122.9	177.4	2.4	13.2
	3	6.72	1.04	16.5	110.1	197.1	2.8	12.3
$L_{0.5}$	1	7.71	1.34	16.16	128.5	138.4	2.7	11.6
	2	7.18	1.45	19.0	112.0	169.6	3.6	13.1
	3	6.98	1.13	14.83	108.9	186.0	2.6	13.0
L_1	1	7.45	1.74	15.6	113.1	131.6	3.0	11.2
	2	7.18	1.63	15.33	112.7	140.2	2.1	11.3
	3	7.1	1.54	15.0	99.7	155.6	2.6	9.9
L_2	1	7.98	1.92	14.0	122.4	104.2	3.0	9.7
	2	7.75	1.89	19.66	115.7	117.9	2.9	8.7
	3	7.18	1.67	16.0	101.2	137.7	2.4	9.9
L_4	1	8.46	2.24	16.0	118.0	86.5	2.5	9.4
	2	8.22	1.87	15.66	111.6	85.1	2.7	9.8
	3	8.08	1.78	16.33	104.2	89.1	2.4	8.9
L_8	1	9.43	2.92	14.33	122.5	93.5	2.4	8.4
	2	8.56	2.84	15.5	120.2	87.6	2.8	7.5
	3	8.24	2.53	13.16	116.0	82.1	2.1	9.2

Table 5. The effect of incubation time on soils pH and EC.

Time incubation (day)	pH	EC (dS/m)	P	K	Fe	Zn	Mn
			mg/kg				
1	7.57 a	1.54 a	14.6 a	126.7 a	136.7 b	2.5 a	12.3 a
30	7.24 b	1.46 a	15.3 a	118.1 b	148.9 a	2.6 a	12.4 a
90	7.06 c	1.31 b	14.9 a	109.1 c	156.2 a	2.4 a	11.7 a

times.

According to results in Table 3, paper mill lime sludge increased soil electrical conductivity, 0.71, 0.93, 1.23, 1.45, 1.59 and 2.39 times compared with control treatments in $L_{0.2}$, $L_{0.5}$, L_1, L_2, L_4 and L_8 treatments, respectively. There was not a significant difference between first and second incubation time (Table 5), while EC decreased in third time significantly.

Phosphorus

The use of paper mill sludge amounted 0.2-8% increased AB-DTPA extractable P, but this increase was not significant in 1 and 8% paper mill sludge (Table 3). The time effect and interaction effect of treatment×time was not significant, therefore, AB-DTPA extractable P has only influenced by treatments.

Potassium

The treatments and time effects on AB-DTPA extractable K was significant at 1% level (Table 2). Paper mill sludge decreased AB-DTPA extractable K in L_1, L_2 and L_4 treatments, remarkably (Table 3). Based on Table 4, decreasing trend is observed in AB-DTPA extractable K of treatments during the incubation time. In general, potassium significantly decreased in the second stage than in the first stage and decreased significantly in the third stage as compared with second stage.

Iron

Table 2 shows that the mean effect of treatments on AB-DTPA extractable Fe was significant ($P \leq 1\%$). Paper mill sludge remarkably decreased available Fe, which was proportional to the application rate of paper mill sludge (Table 3). Of course, this decrease in Fe of $L_{0.1}$ treatment than in the control was not significant. Variation trend of available Fe in different times of $L_{0.1}$, $L_{0.2}$, $L_{0.5}$, L_1 and L_2 treatments indicated that Fe has increased during the time, which of course, is not distinct in L_4 treatment (Table 4). In L_8 treatment, Fe decreased during the incubation time.

Zinc

The mean effect of treatments on AB-DTPA extractable Zn was significant at 5% level (Table 2). Paper mill sludge increased available Zn, but the increase in $L_{0.1}$ and L_8 treatments was significant (Table 3). There is not a significant difference between different treatments of paper mill sludge. Zinc concentration was not influence by the incubation time and interaction time and treatment (Tables 4 and 5).

Manganese

Paper mill sludge remarkably decreased AB-DTPA extractable Mn than in the control (Table 3). The decrease in available Mn was higher in the larger amounts of sludge. The incubation time had no effect on manganese concentration (Tables 4 and 5).

DISCUSSION

Paper mill sludge proportional to the application rate increased pH, significantly. Increase in soil pH indicates the usefulness of paper mill sludge as a liming agent for amelioration of acid soils, but further amount of this by-product is not suitable as a soil amendment particularly in primary stages. Similar results was obtained by He et al. (2009) for the use of paper mill lime mud as a liming agent and its effect on soil pH and ryegrass growth. Paper mill lime sludge is a calcareous compound with a high pH that initially increased soil pH, but soil buffering capacity reduced soil pH during the incubation time, although, in an equilibrium system including $CaCO_3$-CaO-H_2O, pH did not increase to more than 8.5. He et al. (2009) used the paper mill lime mud as a liming agent in a laboratory study in rates 0 (L_0), 2.25 (L_1), 9.01 (L_2) and 22.50 (L_4) $tonha^{-1}$ dry weight basis. They concluded that the initial soil pH increase due to the lime mud application dropped in treatments L_1 to L_4 by the end of the 6-week experiment. However, the initial increase in soil pH of L_1 to L_4 decreased as the experiment progressed. Similar phenomenon has been reported by Muse and Mitchell (1995) in an 80 days soil incubation test that initially raised soil pH due to paper mill lime wastes, boiler ash, grit, and dregs decreased rapidly in the first 20 days and remained fairly stable afterward. Soil electrical conductivity increased by the use of paper mill sludge, but this increase in EC did not change the salinity order of soil, consequently, it establish any problem for different crops growth in the lower amount of paper mill sludge.

Soil AB-DTPA-extractable P increased in paper mill sludge treatments, but the time had not effect on P concentration. Phosphorus is an essential plant nutrient, it is indispensable for phospholipids, ATP and nucleic acids synthesis and therefore a deficiency can limit plant growth (Schachtman et al., 1998). High pH values associated with high quantities of Ca probably facilitate precipitation of P as calcium phosphates, thus, limiting the availability of P to the plant. In contrast a similar increase in pH due to lime application, as occured in the present study, may cause some solubilization of P from Fe–P and Al–P complexes, thus, increasing P availability as was suggested by McCants and Woltz (1967). It seems that soil P concentration has increased due to the solubilization of P from Fe–P and Al–P complexes, but it has not changed during the incubation time as the results of an interaction between precipitation and solubilization of P by liming.

The decrease in soil potassium may be due to K fixation. Mohammadi Torkashvand and Sedaghathoor (2007) reported that the use of a calcareous by-product of steel industry as a liming agent reduced K content in an acid soil. They stated that this decrease in soil K might be due to potassium fixation. Al and Fe hydroxides polymers decline in clays interlayer or insoluble compounds, as K alominosilicates are formed consequently increasing K fixation (Malakouti and Afkhami, 1999).

Extractable Fe decreased proportional to the application rate of paper mill sludge. Extractable Fe concentration depends on initial pH of soil. Increase in soil pH to the range of 7.4-8.5 decreased Fe level. It was found that Fe was precipitated as $Fe(OH)_3$ due to the increased pH (Norvell and Lindsay, 1982). Similar results were found by Mohammadi and sedaghathoor (2007) with the use of calcareous converter slag in acid soils. The increase in Fe concentration during the incubation time can be due to the decrease in soil pH.

Increasing zinc concentration in soil can be due to the added Zn by paper mill sludge (the used sludge contains 4.12 $mgkg^{-1}$). The variation of manganese during the time was not significant but it decreased by paper mill sludge treatments that can be due to increasing soil pH and decrease in the solubilization of Mn compounds.

Conclusion

Results indicate a promising potential for paper mill sludge to be used as an inexpensive source of available lime for correction of soil acidity. This, however, needs further studies in the field and with various crops to determine the correct rates and to study the residual and environmental impact of application of this material to the soil.

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