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DETERMINATION OF EFFECTIVE CALCIUM CARBONATE EQUIVALENCE OF PRIMARY DE-INKING PAPER SLUDGES

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SUMMARY: Primary de-inking paper sludge (DPS) is widely used as soil amendments to increase soil pH and nutrient levels in soils. There is little information on the effectiveness of DPS for neutralizing acidity of coarse textured podzolic soils. An incubation experiment was conducted to determine the percentage of effective calcium carbonate equivalence (ECCE) of three primary de-inking sludges (Kingsey Falls, Breaky Fibers and Candiac from Quebec, Canada) added to an agricultural loamy sand incubated for 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 22 weeks. The DPS containing calcium proved to be effective liming materials. The effect of DPS lasted longer acompared to finely ground $CaCO_3$.

Keywords: liming material, lime, soil amendment, neutralization of soil acidity

INTRODUCTION

In Canada, 336 000 Mg of paper sludge and 74 000 of primary de-inking paper sludge (DPS) were recycled as soi amendment in 2010. The application of DPS as amendments to agricultural soils is a common practice (de Vriers and Tiller, 1978; Fierro et al., 1997). Because they contain calcium carbonate DPS may partly substitute agricultural lime to neutralize soil acidity. Liming reduces the availability of toxic elements such as aluminium and adds calcium (Battaglia et al., 2007), enhances biological functioning (Chantigny et al., 1999) and improves physical properties of soils (Chantigny et al., 1999), and soil fertility (Fierro et al., 1997). The efficiency of a liming material depends on its neutralizing capacity, fineness of grinding, chemical composition, and mineralogy (Adams and Barber, 1984). Total calcium carbonate equivalence (TCCE) as estimated by titration method is lime's capacity to neutralize acidity. The effective calcium carbonate equivalence (ECCE) is the fraction of TCCE that reacts with soil acidity during incubation with soil. The aim of this work is to determine ECCE of DPS added to an acid soil.

MATERIAL AND METHODS

Three DPS were collected from Cascade factories (Quebec, Canada): Breaky Fibers, Candiac and Kingsey Falls. The DPS were air-dried, mixed, homogenized and ground to pass through a 2-mm sieve prior to analysis for total C, total N and total Ca. Briefly, Breaky Fibers sludge (BFS) contained 45% organic matter (OM), 0.2% total N and 16.1% total Ca, Candiac sludge (CS) contained 44.0% OM, 0.14% total N and 14.1% total Ca, and Kingsey Falls sludge (KFS) contained 52.0% OM, 0.12% total N and 12.7% total Ca. The pH was 8.0, 7.8 and 8.2 for BFS, CS and KFS, respectively. The total calcium carbonate equivalent (TCCE) (BNQ, 2005) was 45.0, 42.0 and 37.5 for BFS, CS and KFS, respectively.

The soil was a Morin loamy sand, an Orthic Humo-Ferric Podzol (Haplorthod). Subsamples were air dried, then ground to pass through a 2 mm sieve prior to analysis.

Soil pH was determined in deionized water (1:1 ratio) (pH_{water}) and a 0.01 M $CaCl_2$ solution (1:2 ratio) (pH_{CaCl2}). Soil-buffer pH (pH_{SMP}) was determined by mixing 10 mL of soil, 10 mL deionized water and 20 ml Shoemaker-McLean-Pratt (SMP) buffer solution (Shoemaker et al., 1961). The values of pH_{water}, pH_{CaCl2} and pH_{SMP} were 5.1, 4.8 and 5.6, respectively. The content of Mehlich-3-extractable Al was 0.19%.

One thousand-gram of soil (oven-dry basis) was incubated in triplicate for 22 wk with seven levels of reagent-grade $CaCO_3$ (0.0, 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 g kg^{-1} soil) and two rates of DPS equivalent to 2 (Q2) and 4 (Q4) g $CaCO_3$ kg^{-1} soil), respectively, in 1.5-L polypropylene recipients at 23°C. The rates (Q2 and Q4) of DPS (g kg^{-1} soil) were 4.44 and 8.88 for BFS (45% TCCE), 4.76 and 9.52 for CS (42.0% TCCE) and 5.33 and 10.66 for KFS (37.5% TCCE). The water content of the samples was adjusted to 70% of their water holding capacity. Moisture losses during incubation were replenished weekly with de-ionized water. The pH_{CaCl2} of soil samples (oven dried at 105°C) was measured after 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20 and 22 weeks of incubation (t). The ECCE of DPS was derived from the relationship (cubic or quartic polynomial model) between the rates of pure calcium carbonate applied and pH_{CaCl2} after each of the eleven times of incubation. For example, two ECCE values (g $CaCO_3$ kg^{-1} soil) were estimated by determining the pH_{CaCl2} values of Q2 and Q4 for BFS at 2 weeks (Fig. 1). The ECCE values was expressed in percentage using the following equation:

$$ECCE\ (\%) = \frac{Estimated\ ECCE\ (g\ CaCO_3\ kg^{-1})}{Amount\ DPS\ (g\ kg^{-1})} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

The best-fit regression model to predict ECCE after 2 wk of incubation time is cubic as shown in Fig. 1. The pH_{CaCl2} values for BFS at Q2 and Q4 were 5.08 and 5.35, corresponding to ECCE of 0.5 and 1.17 g $CaCO_3$ kg^{-1} soil or 11.3% and 13.2% on DPS basis respectively.

The ECCE (g $CaCO_3$ kg^{-1} soil) increased with incubation time (Fig. 2). After 2 wk of incubation the ECCE was around four times lower than TCCE provided by DPS (i.e., 0.40-0.50 of Q2 of 2.00 g kg^{-1} and 0.93-1.37 compared to Q4 of 4.00 g kg^{-1}).The high organic matter content of DPS (44-52%) seems to reduce the efficiency of DPS calcium carbonate, hence their ECCE, at the beginning of incubation. This is attributable to greater mineralisation of by-product organic matter early in the incubation period (Wang et al., 2011). Indeed, the efficiency of DPS to neutralize soil acidity decreased in the following order: KFS (52% OM) > BFS (45% OM) > CS (44% OM) (Fig. 2). The ECCE of DPS after 2 wk of incubation were 0.40-0.50 for Q1 and 0.93-1.37 for Q2 (Fig. 2) and corresponded respectively to 20-25% and 23-34% of TCCE. These percentages of ECCE increased to 53-63% (for Q1) and 40-43% (for Q2) after 12 weeks and to 100% (for Q1) and 81-92% (for Q2) after 22 weeks. The ECCE doubled and quadrupled after 10 and 20 wk of incubation, respectively.

CONCLUSION

The primary de-inking paper sludges were effective liming materials. Expressed as percentage, the ECCE doubled (from 20-34% to 40-63%) and quadrupled (from 20-34 to 81-100%) after 10 and 20 wk of incubation, respectively. For maximum effectiveness DPS Several months would be necessary to allow sufficient time for DPS to react with soil.

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REFERENCES

Adams F. and Barber S. A. (1984). Liming materials and practices. In: *Soil acidity and liming*, F. Adams, 2nd edn, Agron. Monogr. 12. ASA, CSSA, Madison, WI, pp. 171–209.

Battaglia A., Calace N. Nardi E., Petronio B. and Pietroletti M. (2007). Reduction of Pb and Zn bioavailable forms in metal polluted soils due to paper mill sludge addition: effects on Pb and Zn transferability to barley. *Bioresource Technology*, 98, 2993–2999.

BNQ, Bureau de Normalisation du Québec. (2005). Inorganic soil conditioners- Liming materials from industrial processes. 2nd edn. Standard BNQ0419-090/2005. Québec.

Chantigny M.H., Angers D.A. and Beauchamp C.J. (1999). Aggregation and organic matter decomposition in soils amended with de-inking paper sludge. *Soil Science Society of America Journal*, 63, 1214-1221.

De Vries M. P. C. and Tiller K.G. (1978). Sewage sludge as a soil amendment with special reference to Cd, Cu, Mn, Ni, Pb and Zn— comparison of results from experiments conducted inside and outside a glasshouse. *Environmental Pollution*, 16, 231–240.

Fierro A., Norrie J., Gosselin A., Beauchamp C.J. (1997). Deinking sludge influences biomass, nitrogen and phosphorus status of several grass and legume species. *Canadian Journal of Soil Science*, 77, 693-702.

Shoemaker H. E., McLean E. O. and Pratt P.F. (1961). Buffer methods suitable for determining lime requirement of soils with appreciable amounts of extractable aluminium. *Proceedings of Soil Science Society of America*, 25, 274-277.

Wang N., Xu R. K. and Li J. Y. (2011). Amelioration of an acid Ultisol by agricultural by-products. *Land Degradration and Development,* 22, 513-518.

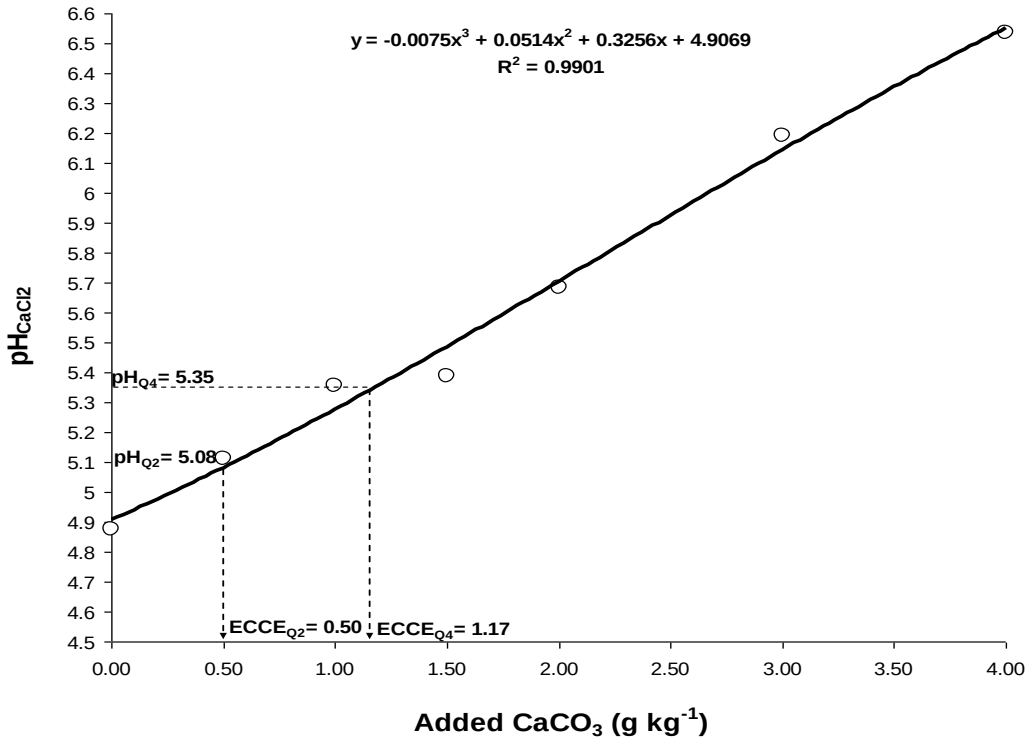

Figure 1. Relationship between $CaCO_3$ added to soil and pH_{CaCl2} of $CaCO_3$-amended soil after two weeks of incubation.

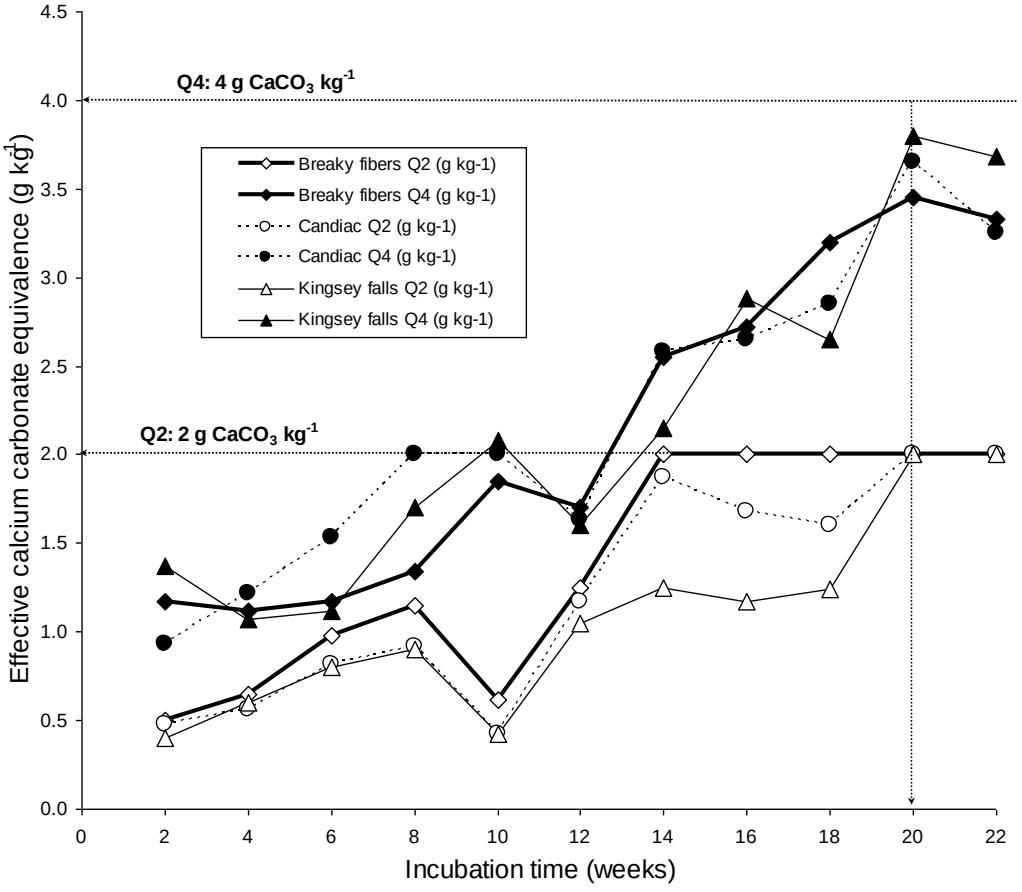

Figure 2. Estimated effective $CaCO_3$ equivalence of DPS as a function of incubation time.