Phosphate fertilizer value of paper mill residuals

STEVEN J. SHIMEK

ABSTRACT: New federal strategies to limit surface water phosphorus loading from agricultural fields may affect many paper mills that are beneficially land-applying wastewater treatment residuals. The phosphate fertilizer value of five paper mill residuals was evaluated in long-term incubation studies to develop data for nutrient planning to address the federal strategies. In four of the five paper mill residuals evaluated, the phosphate fertilizer value was substantially lower than that of commercial fertilizer. The results of the incubation study also found the phosphate fertilizer value in paper mill residuals is dependent on the papermaking and wastewater treatment processes.

Application: The results of this study may help mills evaluate the value of applying mill wastewater residuals to soil.

The farming community has a long history of applying animal manure as a nutrient source. Animal manure typically has a high phosphorus content relative to nitrogen. Applying manure at rates to meet crop nitrogen needs has resulted in an accumulation of excess soil phosphorus. Phosphorus from agricultural fields is considered a major source of the phosphorus affecting surface water quality [1]. To curb the phosphorus loading from agricultural fields, the Natural Resource Conservation Service instituted Nutrient Management Conservation Practice Standard Code 590 [2].

NR 590 identifies two methods of controlling agricultural phosphorus loading to surface waters. One method addresses the loss of phosphorus-entrained sediment associated with erosion. The second method is aimed at limiting the water soluble phosphorus that can leave a field with runoff water.

Research has been conducted to define the relationship of soil test phosphorus to water soluble phosphorus, so that the soil test phosphorus database can be used to predict potential runoff effects [1]. Because this relationship exists, nutrient planners can determine allowable phosphate applications on the basis of soil phosphorus test results and crop phosphorus requirements.

Models have been developed to assist nutrient planners in determining the allowable phosphate application that can be made to agricultural fields and comply with the NR 590 standard. These models require input values for mineral phosphate fertilizer or an equivalent phosphate fertilizer value for organic sources, such as animal manure. Phosphate fertilizer values for atypical organic sources, such as paper mill residuals, are limited.

The annual loading rates of paper mill residuals are generally limited by the nitrogen content of the paper mill residuals and the crop nitrogen demand. However, with the introduction of the NR 590 standard, the annual land application rates may also be limited by phosphorus values. Therefore, it is necessary to determine the phosphate fertilizer value of paper mill residuals so they can be properly managed under the NR 590 standard, similar to animal manure.

Topsoil	Phosphate fertilizer amendment, kg/ha P_2O_5	Soil Test Phosphorus (mg/kg P) Initial	16 Weeks
Loamy sand - 1	410	9	51
Loamy sand - 2	324	8	45
Loam	646	32	101
Silt Loam	164	78	103

I. Phosphate fertilizer amendment and incubation test soil phosphorus results.

Paper mill residuals	Topsoil	Kilograms phosphate amendment, kg/ha P_2O_5	Soil Test Phosphorus, mg/kg P Initial	4 Weeks	16 Weeks	32 Weeks
PMR No. 1	Loamy sand - 1	185	9	10	11	12
PMR No. 1	Loam	370	32	—	39	—
PMR No. 2	Loamy sand - 1	410	9	8	11	17
PMR No. 3	Silt loam	237	78	89	100	117
PMR No. 4	Loamy sand - 2	324	8	14	19	20
PMR No. 4	Loam	646	32	39	43	64
PMR No. 5	Loamy sand - 2	205	8	15	17	—
PMR No. 5	Loam	366	32	39	43	51

II. Paper mill residuals amendment and incubation test soil phosphorus (P) results.

PURPOSE AND STUDY APPROACH

The purpose of this study was to determine the relative phosphate fertilizer value of five paper mill residuals. This was accomplished by completing laboratory incubation studies. The phosphate fertilizer value of the paper mill residuals was determined by comparing the results of soils amended with paper mill residuals to the results of the same soils receiving phosphate fertilizer. The incubation studies with fertilizer were conducted for a period of 16 weeks to represent one growing season. The soils amended with paper mill residuals were incubated for 4-, 16-, and 32-

Paper mill residual	Mill pulp source	Product	Approximate secondary solids content of residuals, g/kg [a]
PMR No. 1	Deinked paper	Tissue	<100
PMR No. 2	Deinked paper	Tissue	<100
PMR No. 3	Bleached hardwood	Paper	200
PMR No. 4	Deinked paper and bleached hardwood	Paper	500
PMR No. 5	Bleached softwood and hardwood	Paper	300

[a] g/kg = grams per kilogram

III. Paper mill pulp source, product, and secondary solids content of residuals.

Topsoil	Associated land application program
Loamy Sand - 1	PMR Nos. 1,2
Loamy Sand - 2	PMR Nos. 4,5
Loam	PMR Nos. 1,4,5
Silt Loam	PMR No. 3

IV. Topsoil samples and associated land application programs.

week intervals, with 16 and 32 weeks representing one and two growing seasons in the service area. We suspected that the availability of phosphorus from the paper mill residuals would increase beyond one growing season.

To confirm laboratory results, the University of Wisconsin Extension established a research plot with one of the paper mill residuals to evaluate the phosphate fertilizer value under field conditions. Results of the field plot study were evaluated and compared to the results of the incubation study results for the paper mill residuals.

Lastly, paper mill residuals were analyzed for aluminum, calcium, and iron content. Research has shown that these metals reduce the availability of phosphorus in soils amended with municipal biosolids, another atypical organic source [3]. A review of the metal results was completed to see how the metals in paper mill residuals may influence the availability of phosphate.

TERMINOLOGY

The agricultural community rates fertilizer on the basis of its phosphate (P_2O_5) content; however, the available phosphorus in soil that results from fertilizer application is measured as elemental phosphorus (P). The available phosphorus determined in agricultural soil tests is based on a weak acid extraction procedure that represents the phosphorus that is likely available to plants. Available phosphorus is also referred to as soil test phosphorus; the terms are used interchangeably.

The agricultural community has developed a relationship between the amount of phosphate fertilizer applied to fields and the resulting soil phosphorus test results. This relationship is referred to as the nutrient buffering capacity of soil [4]. The nutrient buffering capacity is defined in English units as the pounds per acre of phosphate fertilizer that must be applied to a field to raise the soil phosphorus 1 mg/kg. The English unit of pounds per acre is roughly equivalent to kilograms per hectare (kg/ha). The values in this manuscript are reported in kg/ha and can be converted to the English unit by multiplying by 0.9.

METHODOLOGIES

The phosphorus content of the paper mill residuals was determined by Standard Method SM4500-P C (vanadomolybdophosphoric acid colorimetric method) [5]. The paper mill residuals were analyzed for aluminum, calcium, and iron by U.S. Environmental Protection Agency SW-846 Method 6010B [6]. Topsoil samples were analyzed by the University of Wisconsin Soil and Plant Forage Laboratory. The topsoil samples were analyzed for organic matter, pH, and available phosphorus. The available phosphorus was determined using the Bray 1 soil test method [7].

The incubation studies were completed on topsoil samples amended with phosphate fertilizer or paper mill residuals. Three replicates of each topsoil amendment were prepared for each analytical time interval. Topsoil samples were amended with paper mill residuals at rates similar to their respective annual land application rates, which were generally nitrogen-based. Phosphate fertilizer and the phosphate in paper mill residuals were added to the soil samples at the rates summarized in **Tables I** and **II**. The topsoil samples amended with fertilizer or paper mill residuals were thoroughly mixed in plastic containers with at least 250 cubic centimeters of head space. The samples were initially moistened with 50 milliliters of deionized water. Sample containers were sealed and maintained at 21°C (+/-3°C). On 5- to 7-day intervals, the samples were mixed and then opened to allow air exchange. Deionized water was added to samples to maintain moisture near field capacity. Fertilizer-amended topsoil samples were submitted at 16 weeks for analysis of phosphorus. Topsoil amended with paper mill residuals were submitted for analysis of phosphorus at 4, 16, and up to 32 weeks.

The companion field plot study by the University of Wisconsin Extension consisted of a randomly replicated four-treatment trial on silt loam topsoil that was planted with corn, which was harvested for silage.

MATERIALS

Five paper mill residuals (PMR), designated PMR Nos. 1 through 5, consisting of composite samples intended to represent normal operating conditions, were

Paper mill residuals	Total phosphorus, mg/kg	Total phosphate, kg/metric ton [a]	Aluminum, mg/kg	Calcium, mg/kg	Iron, mg/kg
PMR No. 1	3600	8.2	1900	130,000	1000
PMR No. 2	4000	9.2	1800	120,000	1100
PMR No. 3	7500	17.2	6800	35,000	1500
PMR No. 4	6300	14.4	8300	27,000	4100
PMR No. 5	4000	9.2	1200	8200	750

[a] Calculated kilograms of phosphate per metric ton (kg/metric ton).

V. Total phosphorus and phosphate, aluminum, calcium and iron in paper mill residuals.

Topsoil	Initial soil test phosphorus, mg/kg P	Organic matter, %	pH, standard units
Loamy sand - 1	9	2.1	4.7
Loamy sand - 2	8	2.1	5.0
Loam	32	3.8	7.1
Silt Loam	78	2.9	6.4

VI. Phosphorus, organic matter content, and pH of topsoil before amendment.

Paper mill residual	Topsoil	Nutrient buffering capacity of paper mill residuals [a]	
		16 Weeks	32 Weeks
PMR No. 1	Loamy sand - 1	93	62
PMR No. 1	Loam	53	No data
PMR No. 2	Loamy sand - 1	205	52
PMR No. 3	Silt loam	11	6
PMR No. 4	Loamy sand - 2	29	27
PMR No. 4	Loam	58	20
PMR No. 5	Loamy sand - 2	22	No data
PMR No. 5	Loam	37	21

[a] Kilograms per hectare of phosphate fertilizer to raise soil phosphorus 1 mg/kg.

VIII. Nutrient buffering capacity of soils amended with paper mill residuals.

provided by the contributing mills. All five mills had primary clarification and secondary biological treatment. The PMR consisted of combined primary and secondary solids. General characteristics of the mills providing the PMR are identified in **Table III**.

The topsoil samples used for this study represented major soil groups within the service area of the land application programs. The selected topsoil samples included very strongly to strongly acidic loamy sand, a neutral loam, and a slightly acidic silt loam. **Table IV** includes a summary of the topsoil samples and the land application programs they represented.

RESULTS

Table V summarizes the total phosphorus and phosphate, aluminum, calcium, and iron concentrations in the paper mill residuals.

Table VI includes a summary of the analytical results on the topsoil before amendment with fertilizer or paper mill residuals.

Topsoil	Nutrient buffering capacity of fertilizer at 16 weeks [a]
Loamy sand - 1	10
Loamy sand - 2	9
Silt loam	7
Loam	9

[a] Kilograms per hectare of phosphate fertilizer to raise soil phosphorus 1 mg/kg.

VII. Nutrient buffering capacity of soils receiving commercial fertilizer.

Table I summarizes the incubation study results for samples receiving phosphate fertilizer. Table II summarizes the results of the incubation study for samples receiving paper mill residuals.

DISCUSSION

The nutrient buffering capacity of the soils used in this study was calculated for phosphate fertilizer (**Table VII**). Similarly, the nutrient buffering capacity of the soils amended with the paper mill residuals was calculated (**Table VIII**).

A significantly greater amount of phosphate from paper mill residuals is required to raise the soil phosphorus content (Table VIII) as compared to fertilizer (Table VII). The data in these tables can be used to calculate the phosphate fertilizer value of the paper mill residuals. This is done using the following equation:

$$PFV = (PF\ NBC \div PMR\ NBC) * PMR\ P$$

where:

PFV = phosphate fertilizer value, kg/metric ton
PF NBC = phosphate fertilizer nutrient buffering capacity, mg/kg
PMR NBC = paper mill residual nutrient buffering capacity, mg/kg
PMR P = paper mill residual phosphate, kg/metric ton.

Table IX includes the phosphate fertilizer value for the first growing season. Most nutrient management models accept only the phosphate fertilizer value of an organic amendment for the first growing season after application. The phosphate fertilizer value for loamy sand is separated from the loam and silt loam because sand and loamy sand nutrient buffering capacities typically differ from other soil textures.

Table X summarizes the results of the companion field plot study conducted by the University of Wisconsin Extension. Although the soil nutrient buffering capacity was found to be relatively low in the field plot study, the relationship between the treatments receiving fertilizer and those amended with paper mill residuals was similar to the relationship developed in the incubation study. The low nutrient buffering capacity of the silt loam may have been skewed by carry-over of phosphorus from manure applications in previous years [8]. The phosphate fertilizer value calculated from the field plot data is 9.8 kg/metric ton, or 90% of the laboratory results.

Although not substantiated by this study, a portion of the increase in paper mill phosphate fertilizer value over time may be related to mineralization of organic phosphorus in secondary solids. Paper

Paper mill residuals	Total phosphorus of paper mill residuals, mg/kg	Total phosphate of paper mill residuals, kg/metric ton	Phosphate fertilizer value of paper mill residuals, kg/metric ton	
			Loamy sand	Loam or silt loam
PMR No. 1	3600	8.2	0.9	1.4
PMR No. 2	4000	9.2	0.5	—
PMR No. 3	7500	17.2	—	10.9
PMR No. 4	6300	14.4	4.5	2.2
PMR No. 5	4000	9.2	3.8	2.2

IX. Paper mill residuals phosphate and first year phosphate fertilizer value.

Treatment	Initial soil phosphorus, mg/kg	Phosphate added, kg/ha	Phosphate removed as silage, kg/ha	Net phosphate gain, mg/ha	Final soil phosphorus, mg/kg	Nutrient buffering capacity [a]
PMR No. 3	72	160	49	111	99	4.1
Fertilizer	77	160	61	99	120	2.3

[a] Kilograms per hectare of phosphate fertilizer to raise soil phosphorus 1 mg/kg.

X. Field plot results.

mill residuals PMR Nos. 3, 4, and 5 had a secondary solids component exceeding 200 g/kg. Organic phosphorus in amended soil mineralizes much like organic nitrogen [9]. As the organic phosphorus mineralizes, some becomes plant-available. The mineralized organic phosphorus and any initial mineral phosphorus in paper mill residuals are absorbed to mineral soil surfaces or it precipitates, which is referred to as fixation. Havlin, et al. [9] state the fixation of phosphorus in acidic soils is associated with the formation of secondary iron and aluminum minerals or absorption to surfaces of iron and aluminum oxides and clay. In neutral to alkaline soil, the phosphorus precipitates as secondary calcium and phosphorus minerals or it is absorbed onto clay and calcium carbonate. Arai, et al. [10] identified the mineral relationships to phosphorus solubility. They state that the most effective means to reduce labile phosphorus concentrations is to maintain pH near neutral and to have effective absorbents, such as iron and aluminum minerals.

Research by Maguire et al. (2000) has shown that aluminum, calcium, and iron in municipal biosolids limit phosphorus availability. Their work indicates the phosphate fertilizer value of the municipal biosolids is low relative to fertilizer. **Table XI** includes a comparison of phosphorus, aluminum, calcium, and iron in paper mill residuals and municipal biosolids. The phosphorus and metal concentrations in paper mill residuals varies considerably, which is attributed to differences in papermaking and wastewater treatment processes. Several paper mill residuals have calcium and aluminum concentrations that exceed those reported for municipal biosolids, but iron levels are substantially less. This comparison suggests that the findings of Maguire et al. [3] should apply, to some degree, to paper mill residuals. The findings of Arai et al. [10] also help explain the relatively low phosphate fertilizer value of paper mill residuals. The high calcium content of many paper mill residuals will neutralize soil pH, and the aluminum and iron in paper mill residuals are effective phosphorus absorbents.

Paper mill residual	Phosphorus	Calcium	Iron	Aluminum
	mg/kg dry weight basis			
PMR No. 1	3600	130,000	1000	1900
PMR No. 2	4000	120,000	1100	1800
PMR No. 3	7500	35,000	1500	6800
PMR No. 4	6300	27,000	4100	8300
PMR No. 5	4000	8200	750	1200
Typical WI Biosolid [a]	32,000	60,000	21,000	6000

[a] Data for Wisconsin biosolid from 15, "Soils for Management of Organic Wastes and Waste Waters," American Society of Agronomy, 1977 [11].

XI. Phosphorus, calcium, iron, and aluminum concentrations in paper mill residuals used in long-term incubation studies to determine phosphate fertilizer value.

CONCLUSION

Long-term incubation studies were completed to determine the phosphate fertilizer value in paper mill residuals. On a comparative basis, the incubation study results found the phosphate in paper mill residuals did not raise soil phosphorus as much as an equivalent quantity of fertilizer phosphate. The incubation studies found that phosphorus continues to be released from paper mill residuals over two growing seasons. The results varied by papermaking and wastewater treatment processes. Facility specific phosphate availability studies are required to determine phosphate fertilizer value for nutrient planning.

The field plot study results identified a similar relationship of phosphorus fertilizer value in PMR No. 3 as compared to phosphate fertilizer.

The results indicate that laboratory incubation studies provide a good indication of the availability of phosphate from paper mill residuals; however, results from multi-year controlled field experiments should be considered for data verification. **TJ**

ACKNOWLEDGMENTS

The author is grateful to the paper mills that supported this study and those individuals that gave technical guidance, including: John Gilmour, (Gilmour Inc.), F. Andrew Gilbert, (Stora Enso), John Peters (University of Wisconsin Soil and Plant Forage Analysis Laboratory), and Kevin Erb (University of Wisconsin Extension). Also, gratitude goes to Kenneth Williams (University of Wisconsin Extension) for providing results and assisting in the interpretation of data for paper mill residuals PMR No. 3.

LITERATURE CITED

1. Bundy, L., Understanding soil phosphorus (PowerPoint presentation), Department of Soil Science. University of Wisconsin, Madison; 2003. Available at http://www.soils.wisc.edu/extension/teachingmaterials/Understanding_soil_p/show.htm.
2. Natural Resource Conservation Service, Proposed Final Draft—Nutrient Management Code 590. Madison, Wisconsin, 2004.
3. Maguire, R.O., Sims, J.T., and Coale, F.J., Phosphorus fractionation in biosolids-amended soils relationship to soluble and desorbable phosphorus. *SSSA Journal* 64:2018-2024 (2000).

4. University of Wisconsin, *Soil Test Recommendations for Field, Vegetable, and Fruit Crops*, Publication A2809, Madison, Wisconsin, 1998.
5. American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 21st Edition, 2005.
6. US Environmental Protection Agency, Publication SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, 1996.
7. Bray, R.H., and Kurtz, L.T., 1945. Determination of Total, Organic, and Available Forms of Phosphorus in Soils. *Soil Science* 59: 39(1945).
8. Williams, K., personal communication, University of Wisconsin Extension. Antigo, Wisconsin, 2005.
9. Havlin, J., Beaton, J., Tisdale, S., and Nelson, W., *Soil Fertility and Fertilizers—An Introduction to Nutrient Management*. Prentice Hall, Upper Saddle River, New Jersey, 1999.
10. Arai, Y., Livi, K., and Sparks, D., Phosphate reactivity in long-term poultry litter amended southern Delaware sand soils, *SSSA Journal* 69: 616(2005).
11. American Society of Agronomy, *Soils for Management of Organic Wastes and Waste Waters*, Madison, Wisconsin, 1977.

Received: June 23, 2005
Accepted: February 8, 2006

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the April *Solutions! for People, Processes and Paper* magazine (Vol. 89 No. 4).

INSIGHTS FROM THE AUTHOR

In the last decade there has been a movement in the agricultural community to control phosphate applied to farm fields to reduce the effects on surface waters. I was concerned requirements to reduce phosphate loading to agricultural fields would limit land application of paper mill residuals. I completed the research to develop a method to quantify the phosphorus fertilizer value of paper mill residuals, which could be used to properly manage their application under the new requirements.

Researchers have initiated studies of the phosphate contributions of municipal biosolids to farm land and found that only a fraction of the phosphate in the biosolids was recovered by soil tests. They attributed this to fixation to metals, such as calcium, aluminum, and iron. This research also found that only a small percentage of the total phosphate in paper mill residuals was recovered in soil tests, which could be attributed to the same metals.

I found it interesting that most paper mill residuals had a very low phosphate availability and somewhat surprised at the variability of results between facilities.

I think the testing procedure and results will be of value to any paper mill that land applies paper mill residuals, especially those where phosphate controls are already in place.

I believe it would be of interest to evaluate a wider range of papermaking facilities and to provide additional confirmation of laboratory test results with field trials.

Shimek is with STS Consultants, Ltd. Green Bay, Wisconsin. Email Shimek at shimek@stsconsultants.com.

Shimek