

Correlation and Calibration of the SMP Lime Requirement Test with Direct Titration of Soil Acidity

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BACKGROUND

The SMP Buffer method (Shoemaker, et al, 1961) of routinely determining lime requirement on soil samples has been used at the University of Kentucky Soil Testing Laboratory (UKSTL) since the mid-1960's. Initial correlation and calibration for Kentucky soils was a result of incubating several soil samples over a period of time after mixing different rates of lime with them (D.E. Peaslee, 1975, personal communication). During the ensuing years, county agricultural extension agents have raised many questions about recommended lime, based on this initial correlation and calibration. Because of this, we decided to correlate and calibrate routinely determined SMP lime requirements determined by direct titration of some acid soils in Kentucky.

PROCEDURES

Soil samples submitted to the UKSTL during 1991 were reviewed and samples of 25 acid soils representing several areas were selected for use in the study. The series names of these samples are unknown. In addition, 8 samples being used for another study, and whose series name was known, were also included. All samples were air dried, ground, and sieved through a 2mm sieve. Soil water pH was determined by glass electrode in a 1:1 soil:water slurry as outlined in Reference Soil Test Methods for the Southern Region of the U.S. (1983). Exchangeable cations (K, Ca, Mg, and Na) were extracted with Mehlich III solution according to Mehlich (1984) and measured by atomic absorption. Cation exchange capacity (CEC) was determined by the neutral N ammonium acetate method described by Chapman (1965). Base saturation (BS) was determined by expressing the sum of milliequivalents (meq) of K, Ca, Mg, and Na as a percentage of CEC. These data for the 33 soil samples used in the study are summarized in Table 1.

Lime requirements based on the currently used SMP Buffer Test pH and water pH were determined from tables (revised in 1991) contained in the University of Kentucky College of Agriculture's Lime and Fertilizer Recommendations (1994). These tables indicate the amount of aglime with 67% relative neutralizing value (RNV) as outlined by Murdock et al. (1983) recommended to change water pH of a 6 2/3 inch layer of soil assumed to weigh 2 million pounds per acre, to either pH 6.4, 6.6, or 6.8. Lime rates in these tables are rounded up to the nearest 1.0T because of practical considerations.

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Direct titration of each soil for determining lime requirement was performed in duplicate by mixing 5g of air-dried soil with varying amounts of 0.04 N Ca(OH)_2 , bringing the total volume of solution to 40 ml with deionized water, shaking for 4hr (G.W. Thomas, 1992, personal communication) and then measuring pH of this 5g soil:40ml solution slurry. Detailed description of this procedure is given in Appendix 1. This titration curve expressed pH of the soil slurry as a function of different Ca rates supplied by varying rates of 0.04 N Ca(OH)_2 for each sample. The amount of Ca(OH)_2 was carefully determined to provide a base saturation range from pre-existing to 100%, so as to result in a direct reading of soil pH within this range. For constructing the titration curves, soil pH values beyond 7.5 were not plotted since they have no practical application in Kentucky. Linear equations were calculated for the correlation between amounts of Ca added as 0.04 N Ca(OH)_2 to each soil, and the resultant changes in pH. The correlations had r values of 0.98 to 0.99, indicating that the slope of the linear equation could accurately be used to estimate the amount of applied Ca associated with changes in soil pH over the pH range of initial soil pH and pH 7.5. Values for the slope, y intercept, and r are shown for the titration curve for each of the soils in Table 2. Rates of Ca added in the titration procedure were then converted to lime rates based on an RNV of 67%, so that the lime requirement for a desired pH could be read directly from the titration curve. An example of titration results is shown in Table 3, and an example of direct titration of a soil for determining lime requirement is shown in Figure 1, where pH of the 5g:40 ml slurry was plotted against amount of Ca added.

RESULTS AND DISCUSSION

In Figure 1, the amount of Ca has been converted to tons/A of 0.67 RNV aglime. From this plot, a direct measure of lime requirement can be made within the range of the lowest pH shown and pH 7.5. For example, to raise the pH of soil 2 from 4.5 to 5.5 would require 2 tons/A of aglime; from 4.5 to 6.5 would require just over 4 tons/A of aglime. If the pH of soil 2 were 5.5, it would require just over 2 tons/A of aglime to raise it to 6.5.

Lime requirement values determined by both the SMP buffer test and direct titration of all samples are shown in Table 4. Since the UKSTL values are rounded to the nearest 1.0, values obtained by direct titration were also rounded to the nearest 1.0T. Correlation of these two sets of values for amounts of lime required for raising sample pH's from their initial values (Table 1) to pH 6.4, 6.6, and 6.8 is shown in Figures 2-4. Lime requirement recommendations based on current interpretation of the SMP values was about one-third greater than the titrated values for each of the 3 desired target pH's (Table 4). Part of this overestimate is caused by rounding up the tons/acre of lime to the nearest whole number in the routine UKSTL procedure. Additional lime is also built into the current interpretation to account for incomplete mixing and reaction of the lime with the soil.

The slope of the titration curve is the units of pH change per ton of aglime used, from which can be calculated the tons of aglime required per unit change in pH. As shown in Table 2, this ranged from 0.313 to 0.997. This difference is largely related to the magnitude of CEC, as is shown in Figure 5. The higher CEC soils require more aglime per unit change in pH than do the lower CEC soils.

CONCLUSIONS

Compared to determination of LR of acid Kentucky soils over a wide range of CEC and BS by direct titration of soil acidity, LR values based on the current interpretation of the SMP procedure being used by the UKSTL are overestimated by about one-third. Current interpretations were not changed, however, since it was thought that the amount of lime overestimated was justified to compensate for incomplete mixing and reaction in the field as compared to the results from the rigidly controlled direct titration of soil in the laboratory.

REFERENCES

- Chapman, H.D. 1965. Cation exchange capacity. In, *Methods of Soil Analysis Part 2 Chemical and Microbiological Properties*. Am. Soc. Agron., Madison, WI. pp. 894-896.
- Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* 15:1409-1416.
- Murdock, Lloyd, Monroe Rasnake, Ken Wells, and Bill Thom. 1983. Determining the quality of aglime: relative neutralizing value (RNV). AGR-106, Univ of Ky. Coll. of Agric., Lexington, KY.
- Reference Soil Test Methods For The Southern Region of the United States. 1983. Determination of soil pH. Southern Cooperative. Service Bulletin. 289, Univ. of Ga. Coll. of Agric. Exp. Sta. pp. 1-2.
- Shoemaker, H. E., E. O. McLean, and P.E. Pratt. 1961. Buffer methods for determining the lime requirement of soils with appreciable amounts of extractable aluminum. *Soil Sci. Soc. Am. Proc.* 25:274-277.
- University of Kentucky Cooperative Extension Service. 1994. 1994-1995 Lime and Fertilizer Recommendations. AGR-1, Univ. of Ky. Coll. of Agric., Lexington, KY.

APPENDIX I.

The titration procedure required two burettes, one for $\text{Ca}(\text{OH})_2$ stock solution and the other for deionized H_2O . Soil (5g) was weighed and placed in 125ml flasks, and the appropriate aliquot of $\text{Ca}(\text{OH})_2$ was placed in each flask and brought to a final volume of 40ml with H_2O (example soil 1; 0ml $\text{Ca}(\text{OH})_2$ 40ml H_2O in flask 1; 2ml $\text{Ca}(\text{OH})_2$ and 38ml H_2O in flask 2, etc.). Each was duplicated. They were then shaken on an orbital platform shaker for 4hrs, after which pH was recorded using a Beckman Altex Select Ion 2000 pH meter. Lime requirement was calculated by converting $\text{Ca}(\text{OH})_2$ to CaCO_3 and then multiplying the CaCO_3 value by 1.5 to adjust the pure CaCO_3 value to that of 0.67 relative neutralizing value, (RNV).

Procedure

Labware Required

- * Two three-way stopcock and automatic zeroing burets
 - * 125ml flasks
 - * Two 5L carboys with tubulation outlet
 - * Two buret holders
 - * Ascarite
- 1) Weigh reagent grade $\text{Ca}(\text{OH})_2$ to make .04N stock solution (1.482g/1000ml)
 - 2) Mix in oxygen free, cold deionized H_2O
 - 3) Filter with vacuum flask through a #42 Whitman filter paper, and store stock solution in an airtight 5L carboy equipped with ascarite column on air inlet.
 - 4) Titrate the $\text{Ca}(\text{OH})_2$ stock solution for normality using sulfamic acid and phenolphthalein indicator (use normality to calculate the amount of Ca in stock solution)
 - 5) Cover $\text{Ca}(\text{OH})_2$ burets with ascarite filter to prevent CO_2 infiltration
 - 6) Weigh 5g soil into 125ml flask
 - 7) Dispense appropriate aliquots of $\text{Ca}(\text{OH})_2$ and deionized, CO_2 -free H_2O to provide for a total volume of 40ml.
 - 8) Cover flask
 - 9) Shake for 4hrs using an orbital platform shaker
 - 10) Read pH

Table 1. Base data for The 33 soils Tested

Sample no.	Soil Series	County	Water pH	SMP						% Base Sat.
				Buffer pH	-----meq/100g-----					
					CEC	Ca	Mg	Na	K	
1	*	Boone	5.0	6.2	13.04	3.35	1.64	0.09	0.16	40.12
2	*	Boone	4.7	5.8	15.98	3.21	1.74	0.14	0.17	32.92
3	*	Hardin	4.9	6.3	6.99	0.82	0.34	0.03	0.11	18.60
4	*	Fleming	5.3	6.4	19.04	5.90	1.51	0.04	0.42	41.33
5	*	Fleming	5.0	6.3	10.81	2.58	0.63	0.05	0.25	32.47
6	*	Fleming	4.9	6.1	16.80	4.28	1.45	0.05	0.38	36.67
7	*	Harrison	4.9	6.3	17.30	5.78	1.14	0.76	0.43	46.88
8	*	Lawrence	5.4	6.8	5.59	1.21	0.67	0.04	0.16	37.21
9	*	Fleming	5.3	6.5	12.86	3.88	0.63	0.05	0.25	37.40
10	*	Pulaski	4.7	6.0	8.75	1.03	0.39	0.06	0.19	19.09
11	*	Harrison	5.5	6.4	15.19	4.62	0.67	0.08	0.23	36.87
12	*	Harrison	5.6	6.5	15.79	5.02	1.85	0.08	0.43	46.74
13	*	Madison	5.4	6.4	15.68	4.68	2.06	0.04	0.30	45.15
14	*	Laurel	5.5	6.6	12.42	3.77	0.93	0.03	0.57	42.67
15	*	Pulaski	5.0	6.2	14.23	3.42	1.20	0.14	0.44	36.54
16	*	Madison	4.6	6.5	4.73	0.90	0.19	0.02	0.23	28.33
17	*	Madison	4.1	6.3	5.33	0.46	0.12	0.02	0.32	17.26
18	*	Laurel	5.3	6.7	6.52	1.51	0.21	0.06	0.14	29.45
19	*	Cumberland	5.9	6.7	16.27	5.27	1.50	0.02	0.28	43.45
20	*	Bourbon	5.8	6.6	8.37	5.71	0.79	0.04	0.34	82.20
21	*	Breathitt	5.6	6.6	13.74	3.57	2.22	0.12	0.29	45.12
22	*	Perry	5.5	6.6	7.18	2.26	0.43	0.05	0.13	39.97
23	*	Perry	5.9	6.9	11.86	4.56	0.96	0.04	0.11	47.81
24	*	Boone	5.0	6.4	12.27	3.37	1.16	0.11	0.18	39.28
25	*	Hardin	5.6	6.8	8.40	3.38	0.28	0.08	0.17	46.55
26	Falaya	Marshall	5.4	6.8	15.04	3.16	0.50	0.23	0.19	27.10
27	Grenada	Marshall	5.0	6.6	12.90	3.20	0.23	0.14	0.48	31.40
28	Maury	Fayette	6.5	6.8	16.35	6.54	0.64	0.17	0.13	45.70
29	Melvin	McLean	5.2	6.8	11.89	2.79	0.58	0.25	0.09	31.20
30	Pembroke	Warren	5.6	6.6	13.48	3.17	0.29	0.16	0.64	31.60
31	Pope	Breathitt	6.0	6.9	15.65	5.53	0.43	0.16	0.13	39.90
32	Trappist	Nelson	4.4	5.6	17.84	0.75	0.29	0.20	0.22	8.10
33	Zanesville	Caldwell	6.2	7.0	14.39	5.04	0.44	0.33	0.11	41.10

* Soil series unknown

Table 2. Slope, Y intercept, and correlation coefficient (r) values for titration curves

<u>Soil No.</u>	<u>Slope</u>	<u>Y-Intercept</u>	<u>r</u>
1	0.446	5.01	0.998
2	0.451	4.51	0.996
3	0.738	4.32	0.997
4	0.415	5.32	0.988
5	0.469	4.75	0.989
6	0.413	4.47	0.994
7	0.432	5.26	0.989
8	0.926	5.44	0.985
9	0.631	5.36	0.985
10	0.461	4.38	0.992
11	0.409	5.53	0.997
12	0.406	5.74	0.990
13	0.564	5.40	0.995
14	0.426	5.62	0.998
15	0.461	4.57	0.992
16	0.836	4.75	0.988
17	0.675	4.22	0.993
18	0.797	5.32	0.988
19	0.418	5.45	0.999
20	0.361	5.55	0.992
21	0.345	5.63	0.999
22	0.688	5.48	0.992
23	0.578	5.92	0.995
24	0.524	5.29	0.991
25	0.571	5.89	0.988
26	0.726	5.52	0.982
27	0.498	5.17	0.986
28	0.424	6.24	0.995
29	0.997	5.05	0.989
30	0.512	5.51	0.990
31	0.498	5.76	0.993
32	0.313	4.08	0.998
33	0.960	5.97	0.994

Table 3. An example of soil titration (soil no. 2) with 0.04 N Ca(OH)_2 to determine actual lime requirement.

ml added to 5g Soil		pH of Soil/ Solution Mixture		
Ca(OH)_2	Water	Duplicate 1	Duplicate 2	Avg.
0	40	4.50	4.50	4.50
2	38	4.90	5.00	4.95
4	36	5.55	5.60	5.57
6	34	6.30	6.40	6.35
10	30	7.20	7.25	7.22
12	28	7.65	7.65	7.65
14	26	7.95	8.00	7.97
16	24	8.20	8.25	8.22
20	20	8.90	8.85	8.87

Table 4. Comparison of lime requirement (T/A) determined from SMP buffer test and from direct soil titration

Sample No.	Water pH	Tons/A aglime required to raise pH to					
		6.4		6.6		6.8	
		SMP ^{1/}	Titration ^{2/}	SMP ^{1/}	Titration ^{2/}	SMP ^{1/}	Titration ^{2/}
1	5.0	4.0	3.0	5.0	4.0	5.0	4.0
2	4.7	6.0	4.0	7.0	5.0	7.0	5.0
3	4.9	4.0	3.0	5.0	3.0	5.0	3.0
4	5.3	3.0	3.0	4.0	3.0	5.0	4.0
5	5.0	4.0	4.0	5.0	4.0	5.0	4.0
6	4.9	5.0	5.0	6.0	5.0	6.0	6.0
7	4.9	4.0	3.0	5.0	3.0	5.0	4.0
8	5.4	2.0	1.0	2.0	1.0	3.0	2.0
9	5.3	3.0	2.0	4.0	2.0	4.0	2.0
10	4.7	5.0	4.0	6.0	4.0	6.0	5.0
11	5.5	3.0	2.0	4.0	3.0	4.0	3.0
12	5.6	3.0	2.0	3.0	2.0	4.0	3.0
13	5.4	3.0	2.0	4.0	2.0	5.0	3.0
14	5.5	3.0	2.0	3.0	2.0	4.0	3.0
15	5.0	4.0	4.0	5.0	4.0	5.0	5.0
16	4.6	4.0	2.0	4.0	2.0	5.0	3.0
17	4.1	4.0	3.0	5.0	4.0	5.0	4.0
18	5.3	3.0	1.0	3.0	2.0	3.0	2.0
19	5.9	2.0	2.0	2.0	3.0	3.0	3.0
20	5.8	2.0	2.0	3.0	3.0	3.0	4.0
21	5.6	3.0	2.0	3.0	3.0	4.0	3.0
22	5.5	3.0	1.0	3.0	2.0	4.0	2.0
23	5.9	1.0	1.0	2.0	1.0	2.0	2.0
24	5.0	4.0	2.0	4.0	3.0	5.0	3.0
25	5.6	2.0	1.0	2.0	1.0	3.0	2.0
26	5.4	2.0	1.0	2.0	2.0	3.0	2.0
27	5.0	3.0	3.0	4.0	3.0	4.0	3.0
28	6.5	0.0	0.0	1.0	1.0	1.0	1.0
29	5.2	2.0	1.0	3.0	2.0	3.0	2.0
30	5.6	3.0	2.0	3.0	2.0	4.0	3.0
31	6.0	1.0	1.0	1.0	2.0	2.0	2.0
32	4.4	7.0	7.0	7.0	8.0	7.0	9.0
33	6.2	1.0	1.0	1.0	1.0	1.0	1.0
Av.		3.12	2.33	3.67	2.79	4.09	3.24

^{1/} from current recommendation tables

^{2/} rounded to nearest ton.

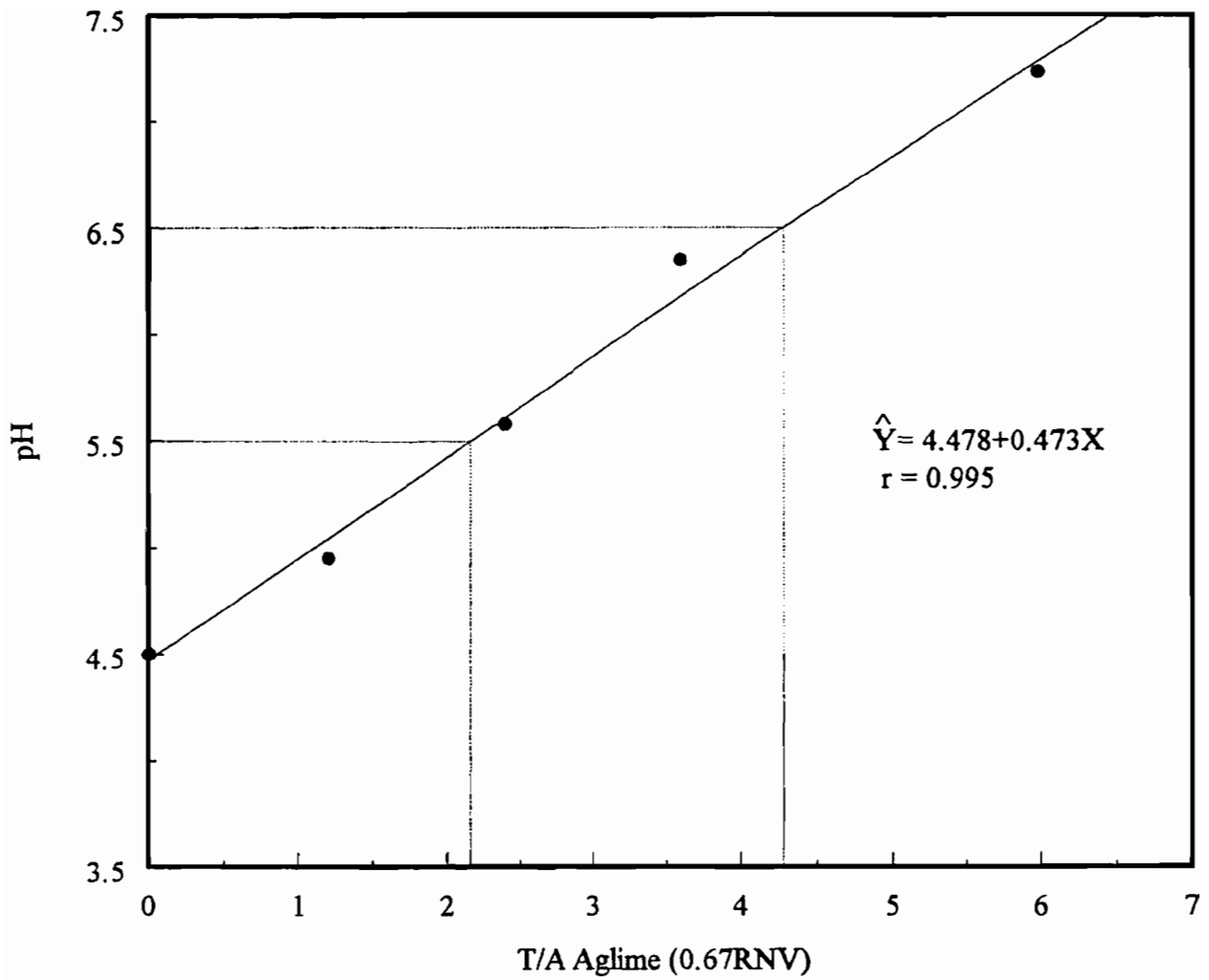


Figure 1. Determination of lime requirement for soil 2 from direct titration with 0.04 N Ca(OH)₂.

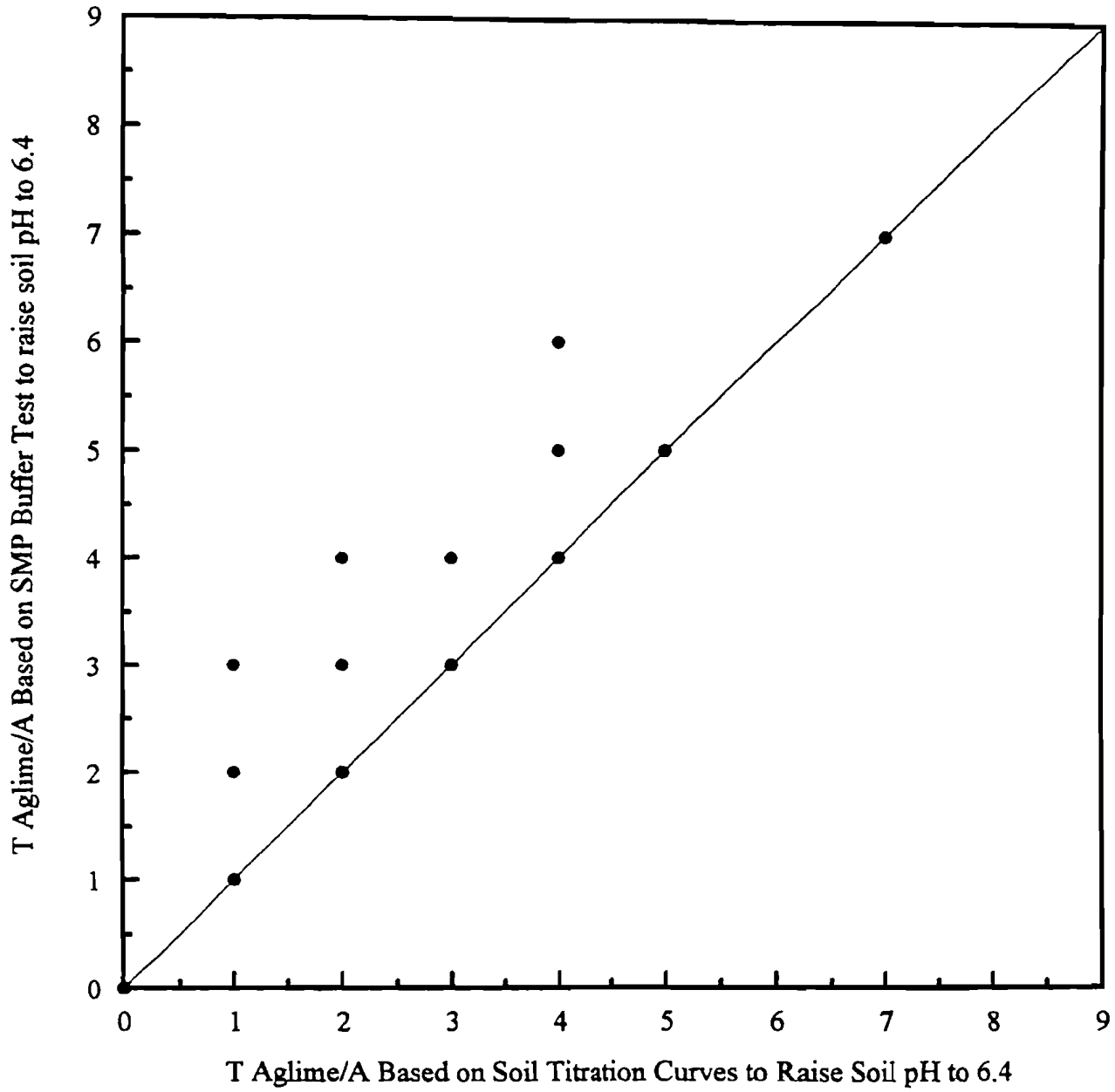


Figure 2. Correlation of SMP buffer test lime requirements with direct titration lime requirements for amounts of aglime required to raise soil pH to 6.4

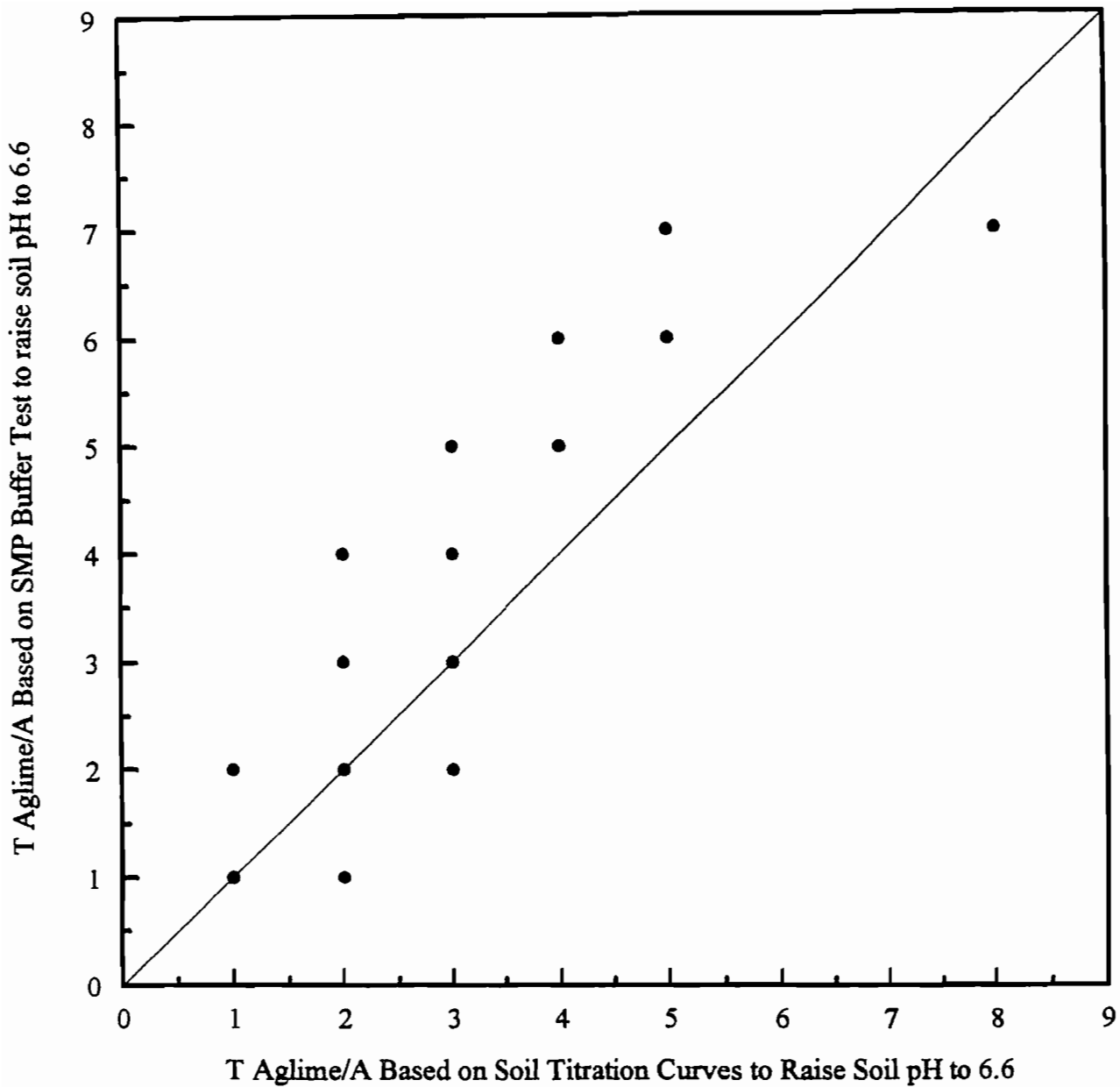


Figure 3. Correlation of SMP buffer test lime requirements with direct titration lime requirements for amounts of aglime required to raise soil pH to 6.6.

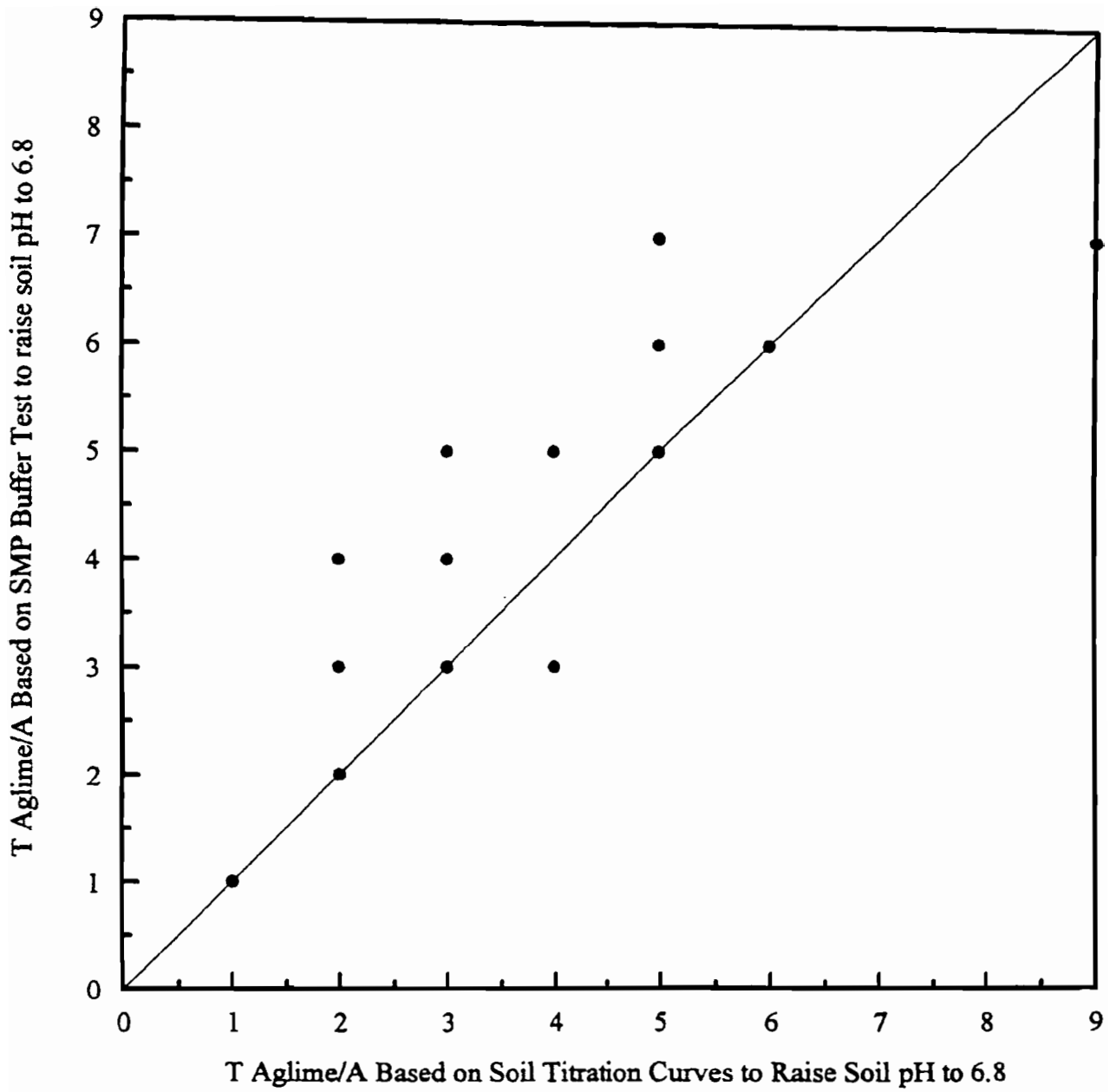


Figure 4. Correlation of SMP buffer test lime requirements with direct titration lime requirements for amounts of aglime required to raise soil pH to 6.8

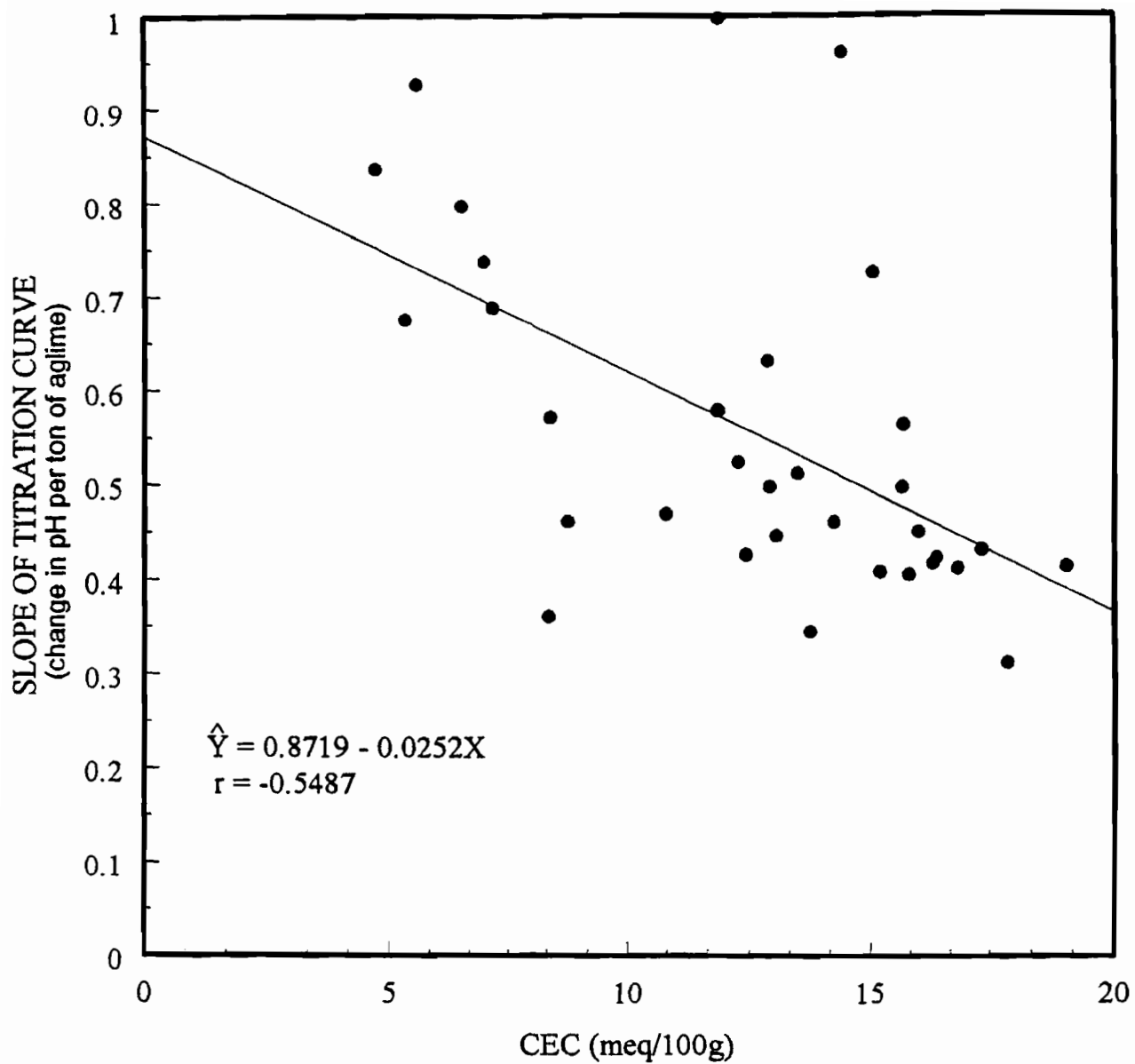


Figure5 . Relationship between change in soil pH per ton of Aglime (slope of the titration curve) and CEC.

**PROCEEDINGS OF THE TWENTY-SIXTH
NORTH CENTRAL EXTENSION-INDUSTRY
SOIL FERTILITY CONFERENCE**

Published for
The North Central Extension-Industry Soil Fertility Conference
by
Potash & Phosphate Institute
700 - 22nd Avenue, South
Brookings, SD 57006
605-697-7149

November 20-21, 1996

St. Louis Westport Holiday Inn
St. Louis, Missouri

Volume 12

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