# A new buffer that imitates the SMP solution for determining potential acidity of Brazilian soils

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## Abstract
A buffer (TSM) was developed to reproduce the behavior of the SMP buffer in the estimate of potential acidity of Brazilian acid soils. This buffer contains four weak bases (TEA, MES, calcium acetate and imidazole) and calcium chloride to control the ionic strength. The efficiency of the new buffer in imitate the SMP was evaluated in twenty one Brazilian soils, whose potential acidity was measured by wet incubation with calcium carbonate, employing treatments 0, 50, 75, 100, 125 and 150% of the potential acidity previously estimate by chemical method. The H+Al measured correspond to the amount of calcium carbonate of the treatment that achieved pH 7, or was obtained by linear interpolation between the treatments below and above pH 7. In the unlimed samples the pH of soil-buffer suspension was determined and these values were plotted against the H+Al measured and fitted by regression for each one of the buffers. The TSM pH values were similar to the SMP ones for the same soils. Thus, the new buffer is a reliable predictor of potential acidity of tropical and subtropical soils and it is able to replace the SMP buffer, with the advantage that it does not contain hazardous substances.

## Key Words
Soil acidity, SMP buffer, liming, hazardous chemicals, tropical soils

## Introduction
The SMP solution, developed by Shoemaker *et al*. (1961) is one of the most employed buffers to evaluate potential acidity of Brazilian soils, since it is suitable for soils with high lime requirements and significant resources of exchangeable aluminum, like those of Southern Brazil, as well as for soils with moderate or low acidity, such as those of Cerrado region. Routine soil testing laboratories usually use SMP method because it is quick, relatively low cost and presents good reproducibility. However, the accuracy of this method must be verified by calibration (soil-lime incubation studies) on the soils routinely tested. The SMP solution contains four chemicals that act as weak bases to buffer the pH (triethanolamine, p-nitrophenol, potassium chromate and calcium acetate), along with calcium chloride to control the solution ionic strength. Among these substances, two are considered hazardous: p-nitrophenol and the chromate ion ($CrO_4^{-2}$), in which the chromium is hexavalent and carcinogenic (USEPA 1998). The immediate effects of human exposure by inhalation, skin contact or ingestion of p-nitrophenol may be headache, nausea, and drowsiness (Huluka 2005). The prolonged exposure to p-nitrophenol should be matter of major concern, especially for operators of soil routine analysis labs. Braunbeck (1989) studied the effect of prolonged exposure of zebra fish to p-nitrophenol. He observed symptoms of degenerative transformation of the liver tissue of 25% of these fishes, following prolonged exposure to 1 mg/l of p-nitrophenol in the water. After the SMP-pH determination these toxic substances remain in the soil suspension residues. Another drawback of SMP method is that the routine use of the glass combined pH electrode to measure the SMP pH promotes the degradation of the electrode reference junction (Hoskins and Erich 2008). In recent years, there is a trend to focus research on the development of more environmentally friendly buffers. A buffer that does not contain hazardous substances, in which imidazole and MES [2-(N-morpholino) ethanesulfonic acid] take the places of p-nitrophenol and chromate, respectively, was developed to mimic the SMP buffer used in some of the USA soils (Sikora 2006). However, the Sikora buffer does not imitate the adapted SMP buffer used in Southern Brazil (Kaminski *et al.* 2007). In this sense, the aim of this work is to develop and test a new solution that mimics the adapted SMP as predictor of potential acidity of soils of tropical and subtropical regions. The new buffer contains some of the bases of the SMP and others of the Sikora buffer, with their concentrations adjusted to give the same buffer capacity of the SMP method.

## Methods

Twenty one unlimed soils samples were collected from the 0-20 cm layer of different physiographic regions of Brazil: eleven from lowlands and seven from highlands of the Rio Grande do Sul state and three from the Cerrado region. Chemical and physical analysis were performed: size distribution of particles, exchangeable $Al^{3+}$ with 1 mol/l KCl solution and organic matter content by wet digestion. These results are presented in Table 1.

**Table 1. General characteristic of unlimed soils.**

| Soil | Clay[1] | Sand[1] | Silt[1] | OM[2] | pH[2] H₂O | Ca[2] | Mg[2] | Al[2] | pH[2] SMP | pH[3] TSM | H+Al[4] |
|------|------|------|------|------|------|------|------|------|------|------|------|
| | ---------------- g/kg ----------------- | | | | | --------- cmo$_c$/kg -------- | | | | | cmol$_c$/kg |
| Lowland | 84 | 689 | 228 | 11 | 4.9 | 1.01 | 0.30 | 0.55 | 6.3 | 6.4 | 6.07 |
| | 293 | 104 | 603 | 36 | 5.0 | 13.2 | 4.25 | 0.15 | 5.9 | 6.1 | 12.17 |
| | 160 | 509 | 331 | 15 | 4.1 | 0.41 | 0.09 | 2.00 | 5.5 | 5.7 | 8.38 |
| | 206 | 215 | 579 | 27 | 4.4 | 5.94 | 1.63 | 0.98 | 5.6 | 5.6 | 11.21 |
| | 195 | 391 | 413 | 17 | 4.4 | 3.34 | 1.14 | 1.38 | 5.8 | 5.8 | 10.73 |
| | 377 | 62 | 561 | 22 | 5.1 | 12.33 | 3.74 | 0.43 | 5.9 | 5.9 | 10.62 |
| | 56 | 782 | 162 | 12 | 4.5 | 0.28 | 0.16 | 0.43 | 6.7 | 6.6 | 4.22 |
| | 59 | 763 | 177 | 13 | 5.4 | 1.59 | 0.77 | 0.00 | 6.8 | 6.7 | 4.02 |
| | 164 | 544 | 292 | 23 | 4.6 | 2.55 | 0.84 | 0.70 | 6.0 | 5.9 | 8.46 |
| | 64 | 776 | 159 | 15 | 4.6 | 1.59 | 0.71 | 0.45 | 6.3 | 6.4 | 4.86 |
| | 139 | 585 | 276 | 18 | 4.4 | 1.71 | 0.79 | 0.88 | 5.9 | 6.0 | 7.13 |
| Highland | 375 | 242 | 383 | 57 | 4.1 | 3.98 | 1.33 | 1.75 | 4.9 | 5.0 | 18.00 |
| | 479 | 175 | 346 | 63 | 4.0 | 2.3 | 1.07 | 3.90 | 4.5 | 4.6 | 28.20 |
| | 497 | 161 | 343 | 82 | 4.4 | 1.49 | 0.83 | 4.65 | 4.4 | 4.4 | 35.95 |
| | 531 | 111 | 359 | 52 | 4.1 | 2.41 | 1.43 | 2.75 | 4.7 | 4.7 | 24.89 |
| | 480 | 172 | 348 | 42 | 4.3 | 1.93 | 1.01 | 3.55 | 4.7 | 4.7 | 19.68 |
| | 544 | 135 | 321 | 58 | 4.0 | 2.55 | 1.69 | 4.03 | 4.5 | 4.5 | 29.64 |
| | 497 | 147 | 356 | 63 | 4.3 | 2.84 | 1.71 | 2.93 | 4.7 | 4.7 | 25.86 |
| Cerrado | 601 | 164 | 235 | 40 | 5.2 | 3.2 | 1.51 | 0.10 | 5.8 | 5.9 | 9.99 |
| | 230 | 730 | 40 | 23 | 5.0 | 1.9 | 0.54 | 0.23 | 6.2 | 6.2 | 6.56 |
| | 293 | 649 | 58 | 29 | 4.9 | 2.48 | 1.09 | 0.30 | 6.0 | 6.0 | 10.41 |

[1]EMBRAPA (1997); [2]Tedesco et al. (1995); [3]TSM buffer; [4]Data from soil incubation results (H+Al measured)

Soil samples (1.00 kg), in quadruplicate, were submitted to the application of increasing doses of calcium carbonate, equivalents to 0, 50, 75, 100, 125, 150% of the potential acidity estimated by chemical method and wet incubated for130 days, with weekly revolving and aeration. Then, soils samples were air dried and grinded, before performing the pH in water and the H+Al measurements.

The adapted SMP solution contains calcium chloride dihydrate ($CaCl_2.H_2O$, 147.01 g/mol) 0.721 mol/l; triethanolamine [$N(CH_2CH_2OH)_3$, 149.19 g/mol] 37.5 mmol/l; ρ-nitrophenol ($O_2NC_6H_4OH$, 139.11 g/mol) 26.2 mmol/l, potassium chromate ($K_2CrO_4$, 194.19 g/mol) 30.9 mmol/l, calcium acetate [$Ca(CH_3COO)_2$, 158.17 g/mol] 12.6 mmol/l. The pH-SMP value is measured in a soil suspension prepared with the volume proportions 1:2:2 (SMP buffer: water: soil) (Tedesco *et al.* 1995). The pH-SMP was determined in unlimed soils and in soils treated with 50% of the potential acidity.

## Results

The developed new buffer, named *Santa Maria* (TSM), was prepared with the following composition: triethanolamine [$N (CH_2CH_2OH)_3$, 149.19 g/mol] 28 mmol/l /; imidazole ($C_3H_4N_2$, 68.08 g/mol) 15.5 mmol/l, MES [2-(N-morpholino) ethanesulfonic acid hydrate] ($C_6H_13NO_4S.H_2O$, 213.25 g/mol) 47.2 mmol/l; calcium acetate [$Ca (CH_3COO)$ 158.17 g/mol] 25.4 mmol/l and calcium chloride dihydrate ($CaCl_2.H_2O$, 147.01 g/mol) 720 mmol/l. The final pH was adjusted to 7.5 with NaOH 40% (w/w). The pH TSM is measured in soil suspension with the same volume proportions above described for the adapted SMP.

Table 1 shows data of unlimed soils. The measured H+Al range from 4.02 to 35.95 cmol$_c$/kg. Organic matter content (OM) vary from 11 to 82 g/kg, with the higher values obtained in highland soils, which are all above 42 g/kg. Exchangeable Al range from zero to 4.65 cmol$_c$/kg, with the lower values corresponding to Cerrado soils (<0.30 cmol$_c$/kg). Therefore, this is a suitable group of soils for this study, since it present a broad range

of soil acidity and physical and chemical characteristics. Currently, most of the agricultural soils have been already limed. For this reason limed soils were included in this study to evaluate the buffers performance in this kind of soil. The liming rate of 50% of the potential acidity was chosen and these data are shown in Table 2.  As expected, lower values of potential acidity were obtained, which range from 1.87 to 22.99 $cmol_c$/kg.

**Table 2. Soil chemical characteristic after lime incubation.**

| Soil | pH $H_2O$[1] | pH SMP[1] | pH TSM[2] | Ca[1] | Mg[1] | Al[1] | H+Al measured[3] |
|---|---|---|---|---|---|---|---|
| | | | | ------------------------ $cmol_c$/kg ------------------------ | | | |
| Lowland | 5.0 | 6.6 | 6.6 | 3.01 | 0.36 | 0.15 | 3.62 |
| | 5.6 | 6.2 | 6.2 | 16.08 | 3.98 | 0.00 | 9.02 |
| | 6.0 | 6.6 | 6.7 | 4.78 | 0.10 | 0.00 | 3.18 |
| | 5.5 | 6.3 | 6.4 | 10.27 | 1.59 | 0.00 | 6.91 |
| | 5.4 | 6.5 | 6.6 | 7.86 | 1.15 | 0.00 | 5.53 |
| | 5.7 | 6.2 | 6.3 | 15.12 | 3.67 | 0.10 | 7.12 |
| | 5.4 | 6.9 | 7.0 | 1.76 | 0.17 | 0.10 | 2.37 |
| | 6.4 | 7.0 | 7.1 | 3.16 | 0.55 | 0.00 | 1.87 |
| | 5.0 | 6.2 | 6.3 | 5.31 | 0.84 | 0.13 | 5.31 |
| | 5.1 | 6.7 | 6.7 | 3.10 | 0.72 | 0.00 | 3.01 |
| | 5.6 | 6.7 | 6.6 | 4.35 | 0.76 | 0.00 | 3.98 |
| Highland | 4.4 | 5.3 | 5.5 | 9.69 | 1.33 | 0.43 | 11.84 |
| | 4.4 | 5.1 | 5.3 | 9.12 | 1.01 | 0.65 | 20.35 |
| | 4.7 | 5.3 | 5.4 | 14.94 | 0.88 | 0.20 | 21.46 |
| | 4.3 | 5.1 | 5.1 | 8.76 | 1.42 | 0.65 | 18.74 |
| | 4.8 | 5.8 | 5.9 | 9.40 | 1.04 | 0.15 | 11.83 |
| | 4.3 | 5.0 | 5.2 | 8.01 | 1.71 | 1.03 | 22.99 |
| | 4.4 | 5.2 | 5.3 | 9.54 | 1.77 | 0.73 | 18.76 |
| Cerrado | 5.7 | 6.1 | 6.1 | 5.06 | 1.44 | 0.00 | 7.53 |
| | 5.9 | 6.7 | 6.7 | 3.97 | 0.47 | 0.00 | 3.41 |
| | 5.6 | 6.3 | 6.4 | 4.82 | 1.00 | 0.10 | 6.91 |

[1]Tedesco et al. (1995); [2] TSM buffer; [3] Data obtained from soil incubation

When a soil sample is put in contact with the buffer solution, a decreasing of pH is observed. For unlimed soils, the obtained values of pH-SMP range from 4.5 to 6.8, while the pH-TSM varies from 4.5 to 6.7. Table 2 shows results obtained for these soils after liming (treatment 50) where these values, as expected, increase: pH-SMP vary from 5.0 to 7.0 and the pH-TSM, from 5.1 to 7.1. A plot of pH-TSM versus pH-SMP, including unlimed and limed (treatment 50) soils, gives a linear relation and the equation pH-TSM = 0.2858 + 0.9596 pH-SMP ($R^2$ = 0.9902). The angular coefficient is close to 1.0 and the linear one is not far from zero, which means that the TSM buffer reproduces quite well the SMP behavior.

Furthermore, from the relation between measured H+Al and pH-SMP or pH-TSM (Figure 1), it is possible to see that the exponential decay of H+Al values as a function of pH is very similar for both buffers.

The replacement of SMP by TSM would avoid the production of around 1,500 litres of hazardous residues of soil analysis per year in Southern Brazil. If this toxic waste containing chromate and p-nitrophenol is drained down the sink it may contaminate water resources. On the other hand, the regulation of its disposal for off-site treatment increases laboratorial costs. The hexavalent chromium present in the chromate ion is carcinogenic (USEPA 1998). The p-nitrophenol ingestion or inhalation can cause headache, nausea, and drowsiness (Huluka 2005) and it was observed abnormal growth of tissues of fishes submitted to prolonged exposure to 1 mg/l  of this compound in water (Braunbeck 1989).

**Conclusion**
The new buffer is a reliable predictor of potential acidity and it is able to replace the SMP buffer, with the advantage that it does not contain hazardous substances, avoiding contamination of water resources with chromate and p-nitrophenol soil analysis residues.  Besides, the lab operator will not undergo the healthy risks of manipulation of chromate and p-nitrophenol, which is especially important at routine analysis labs,

and the replacement of SMP by TSM will not change the laboratorial routine already established.

**References**

Braunbeck T, Storch V, Nagel R (1989) Sex-specific reaction of liver ultrastructure in zebra fish (Brachydanio rerio) after prolonged sublethal exposure to 4-nitrophenol. *Aquatic Toxicology* **14** (3), 185-202.

EMBRAPA (1997) 'Manual of soil analysis methods' (EMBRAPA – SNLCS Publishing: Rio de Janeiro) (in Portuguese).

Hoskins BR, Erich MS (2008) Modification of the Mehlich Lime Buffer Test. *Communications in Soil Science and Plant Analysis* **39**, 2270-2281.

Huluka G (2005) A modification of the Adams-Evans soil buffer determination solution. *Communications in Soil Science and Plant Analysis* **36**, 2005-2014.

Kaminski J, Rheinheimer DS, Santanna MA, Brunetto G, Casali CA, Tiecher T, Toledo JA, Fries H (2007) Determination of soil potential acidity with the Sikora buffer as an alternative to SMP solution. *Proceedings of the 31th Soil Science Brazilian Congress,* Gramado, RS (Brazilian Society of Soil Science) (in Portuguese).

Shoemaker HE, McLean EO, Pratt PF (1961) Buffer methods for determining lime requirement of soils with appreciable amounts of extractable aluminum. *Soil Science Society of America Proceedings* **25**, 274-277.

Sikora FJ (2006) A buffer that mimics the SMP buffer for determining lime requirement of soil. *Soil Science Society of America Journal* **70**, 474-486.

Tedesco MJ, Gianello C, Bissani CA, Bohnen B, Volkweiss SJ (1995) 'Analysis of soil, plants and other materials' (Universidade Federal do Rio Grande do Sul Publishing: Porto Alegre) (in Portuguese).

U.S. Environmental Protection Agency (1998) Toxicological review of hexavalent chromium. CAS No. 18540-29-9. *USEPA*, Washington, DC.
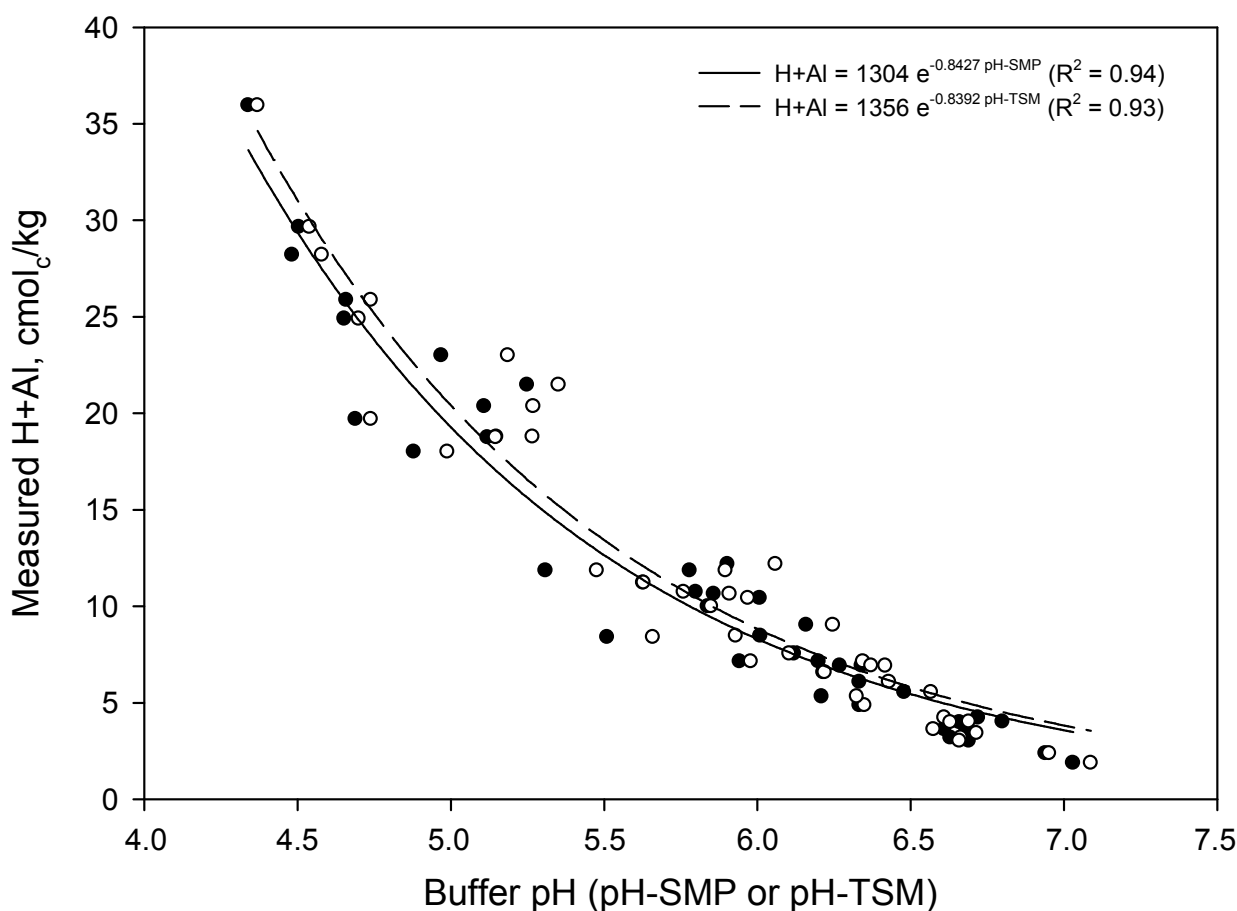
**Figure 1. Relationship between the buffer pH (pH-SMP or pH-Santa Maria) and the potential acidity.**