

NLWRA Theme 5 Project 4c

Acidic Soils and Acidification

Assessment of pH buffer capacity

Final Technical Report and Recommendations

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NLWRA Theme 5 Project 4c: Acidic Soils and Acidification

Technical report on pH buffer capacity assessment

Recommendations

The following recommendations are made on the basis of an assessment of pedotransfer function for predicting pH buffer capacity (pHBC). For surface soils the following pedotransfer functions are suggested according to the availability of data:

If

- if soil organic carbon and clay content are the measured attributes the following equation should be used;

$$\text{pHBC (t CaCO}_3\text{/ha.pH)} = [0.955\text{OC}\% + 0.011\text{Clay}\%] \times 1.2$$

Or

- ECEC and soil organic carbon are the measured attributes the following equation should be used;

$$\text{pHBC (t CaCO}_3\text{/ha.pH)} = [0.310 + 0.282\%C + 0.0546\text{ECEC}(\text{cmol}_e\text{/kg soil})] \times 0.857$$

Or

- if the attributes of exchangeable Al and ECEC are determined the Limeit Model of Helyar should be used (explained below under the Hochman (1989) model);

Or

- in certain cases where organic carbon and field texture are the only attributes, the function of Merry (Merry 2) could be used to predict pHBC.

$$\text{pHBC (t CaCO}_3\text{/ha.pH)} = [0.200 + 0.364\%C + 0.0213\text{FT-Clay}] \times 0.857$$

For subsoils the following recommendations are made:

- if the attributes of exchangeable Al and ECEC are determined the Limeit Model of Helyar should be used (explained below under the Hochman (1989) model);
- if the attributes of clay, silt and OC are determined, the pedotransfer function of Noble et al. (1997) should be considered.

$$\text{pHBC (t CaCO}_3\text{/ha.pH)} = [12.79 - 0.19\text{Clay} - 0.7\text{OC} - 0.03\text{Silt} + 0.74\text{Silt}*\text{OC}] \times 0.06$$

Objectives

1. Undertake an assessment of published laboratory methods for measuring pH buffer capacity (pHBC).
2. Compile and assess published pedotransfer functions and their surrogates used to estimate pH buffering capacity of surface and sub-soil horizons and provide input to ASRIS on the appropriate functions to be used in the compilation of pHBC maps for the aforementioned depth intervals.
3. Assess any other data provided by State representatives associated with the estimation of pHBC for possible use in the development of buffer capacity maps.

Assessment of published laboratory methods for measuring pH buffer capacity.

Lime requirement has been defined as either the amount of lime required to raise soil pH to a predetermined value or in the case of certain tropical soils, the amount of lime required to neutralise aluminium (Al) from the exchange complex (McLean, 1970; Kamprath, 1971; Thomas and Hargrove, 1984). Therefore lime requirement is effectively a product of the change in soil pH (ΔpH) and **buffering capacity** (pHBC) of the soil. The quantity of lime required to achieve these objectives is dependent on the buffering capacity of the soil. The soil pHBC is a measure of the rate of acid or alkali addition per unit change in soil pH (Helyar

and Porter, 1989). Often the pHBC is approximately constant within the pH range 4.5 – 6.0 (Magdoff and Bartlett, 1985) and therefore a single value is used.

Soil pHBC is an intrinsic property of a soil that effectively describes its ability to resist shifts in soil pH. It is generally agreed that this property is a function of soil pH and clay and organic matter content. However, Gillman and Sumpter (1986) observed that in soils of the wet tropics exhibiting variable charge characteristics, consumed approximately 50% of the lime added to raise the pH of a soil suspensions from 4 to 6 was used in generating cation exchange capacity and not in directly increasing soil pH. Consequently, the variable charge nature of certain soils (ie Ferrosols) will have a significant effect on pHBC.

Quantification of soil pHBC is undertaken using several different methodologies that include laboratory and field based assessments some of which are discussed here (Table 1) and elsewhere (Helyar and Porter, 1989). A soil-CaCO₃-moist incubation method to determine pH buffer capacity has been used by Aitken *et al.*, (1990a). Various rates of reagent grade CaCO₃ are dry-mixed with the soil and placed in containers. Soils are brought to field capacity moisture content and maintained at this level for a period of approximately 6 weeks at a constant temperature of 25°C. At the end of this incubation period soils are air dried, sieved to pass a 2mm mesh and the pH determined on a sub-sample. A linear regression function is fitted to the relationship between soil pH (y axis) and the rate of lime added (ie. g CaCO₃/kg soil), x axis. Since buffer capacity is defined as the change in quantity with intensity, the reciprocal of the slope of the regression line is taken as a measure of pH buffer capacity. Whilst this method will result in an adequate approximation of pHBC, it may not take into account the influence of wetting and drying cycles on reactivity of lime and slower buffering processes that take place.

Aitken *et al.* (1990b) undertook an evaluation of various published methods for predicting lime requirement. The laboratory methods evaluated included 1M KCl extractable Al, equilibration of soil:water suspensions with varying amounts of Ca(OH)₂, the Shoemaker, McLean and Pratt (SMP) single-buffer method, the Yuan double-buffer method and the Mehlich single-buffer method. They concluded that extractable Al was a poor predictor of lime requirement to pH_w 5.5. In this respect, the actual amounts of lime required to reduce Al to a predetermined level far exceeded that calculated on the basis of 1 M KCl extractable Al. They observed that buffer methods all correlated well with lime requirement. However, buffer methods that had a high initial buffer pH and a relatively high buffer strength were less well correlated with lime requirement than weaker buffers of lower initial pH. It was concluded that the Mehlich single-buffer method gave the best correlation with lime requirement over the pH ranges assessed. With respect to the batch equilibration of soil:water suspensions containing Ca(OH)₂ they concluded that it gave a reliable assessment but was a relatively time consuming method since it took 7 days to complete the assessment. This latter method and variances of it have been widely used to assess pHBC (Noble *et al.*, 1997; Merry, 1997).

There are several potential errors that are inherent in the estimation of pHBC capacity that have been outlined by Helyar and Porter (1989). For example, the measurement of pH buffer capacity is in general derived from short term laboratory incubation studies that do not take into account the slow pH buffering reactions (ie. the dissolution of solid phases; biological processes) (Ridley *et al.*, 1990). In order to overcome problems associated with short term incubation studies, pH buffering capacity has been determined through field trials where pH changes have been monitored over a long period of time (Helyar *et al.*, 1990). However, errors associated with incomplete dissolution or uneven mixing of lime has been suggested. In addition, acidification may occur on the unlimed treatments at different rates to that of limed treatments (Porter *et al.*, 1995). Clearly the method used to determine pHBC will directly influence the ability to predict the quantity of lime required to neutralize acidity or to achieve a pre-determined pH level. It is generally agreed that short-term equilibration methods may

under estimate buffering capacity and therefore lime requirement. However, it should be borne in mind that pHBC is a dynamic characteristic and therefore any estimated measure is subject to ongoing change. Therefore any estimate through the different methods outlined above should be treated in this light.

Pedotransfer functions used to estimate pHBC.

A pHBC pedotransfer function predicts soil pHBC from easily determined soil attributes. Several pedotransfer functions that predict pH buffer capacity have been proposed in the literature. Whilst these functions use an array of variables to predict buffer capacity, a single unifying function that is effective over a wide range of soil types has yet to be derived. Since pHBC is a function of intrinsic soil properties such as clay content, mineralogy, soil organic carbon, exchangeable Al, pH and cation exchange capacity, it would probably be fortuitous to find a single unifying function. For example, on soils exhibiting variable charge characteristics associated with the presence of sesquioxides, the clay is weakly buffered at pH_0 but is highly buffered on either side of pH_0 . At any pH the buffering capacity increases with specific surface, electrolyte concentration, and valence of the counterion as shown in Figure 1. In addition, clay mineralogy significantly influences pH buffer capacity in that 2:1 clay minerals have a higher permanent charge than 1:1 clay minerals which will influence a soil's ability to resist changes in soil pH.

In an effort to assess published pedotransfer functions for their ability to predict pHBC, several data sets have been gleaned from the literature and individuals for this purpose. It should be pointed out at the outset that the methodology used to measure pHBC differed between data sets and therefore caution should be taken in the interpretation of results. For the purpose of these comparisons the units used to express pHBC are $cmol_c/kg.pH$ unit. The pedotransfer functions that have been assessed in predicting pHBC are as follows:

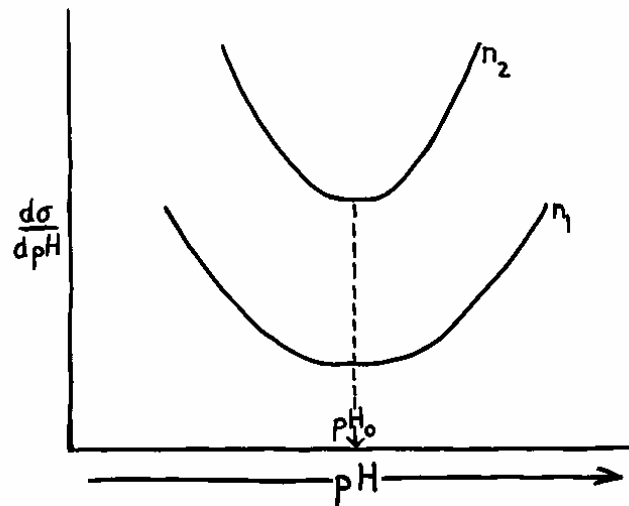


Figure 1. Relationship between buffering capacity and pH in a variable charge system at two electrolyte concentrations (n_1 and n_2). The buffering capacity is the product of the specific surface and the derivative of surface charge density with respect to pH. Adapted from Uehara and Gillman 1981.

1. The Hochman (1989) model: The function relies on the relationship between ECEC and pH. The equation used is as follows:

$$SL_s = (ECEC+f)/(pH-g) \quad (1)$$

Where SL_s slope of the line pH and ECEC and is an index of field buffering capacity ($\text{cmol}_c/\text{kg.pH}$); ECEC is the effective cation exchange capacity ($\sum[\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+ + \text{Al}^{3+}]$); pH is measured in 0.01M CaCl_2 ; f is the ECEC intercept with a value of 0.9568 cmol_c/kg soil; and g is the pH intercept with a value of 2.0428. The function is used in the Limeit model (Hochman *et al.*, 1989) to calculate the laboratory pHBC at the inflection point pH. Hochman arrived at the aforementioned function using exchangeable cations extracted with 0.0125 BaCl_2 (Metson, 1956). In a study using the aforementioned function, Slattery and Coventry (1993) extracted Al with 1 M KCl and exchangeable basic cations with 0.1M $\text{BaCl}_2/\text{NH}_4\text{Cl}$ solution.

In the Limeit model of Helyar (personal communication), the same function is used, however changes in exchangeable Al over the pH range considered are also added to the change in ECEC as calculated using Equation (1). All of the described methods would affect the quantities of exchangeable cations extracted. The method used to measure pH and ECEC changes was field incubation. The method then assumed the pHBC is equal to the change in ECEC plus the change in exchangeable Al over the nominated pH range ($\text{delta cmol}_c/\text{kg} \cdot \text{delta pH}$) (Conyers *et al.*, 2000). That is, all the lime that dissolves is consumed in these reactions and no other reactions are significant. In field experiments all the agricultural grade lime applied is seldom dissolved during the first 12 months after application. Experience in the 500 to 700 mm rainfall zone in southern NSW indicates that about 70%, of a calcitic limestone ground so 100% passed a 0.25 mm sieve, dissolves in 12 months. In this situation the field buffer capacity (lime required to raise the pH by 1 unit 12 months after liming) is the laboratory buffer capacity multiplied by a 'field liming factor' of 1.4.

2. Merry 1: Merry (1997) described a relationship between ECEC and total C as a means of estimating lime requirement. The data set used was derived from 170 South Australian and western Victorian surface soils. pHBC was calculated after equilibration of soil with varying amounts of NaOH over 7 days (Aitken and Moody, 1995). Total carbon was determined using a Leco furnace. The equation is as follows:

$$t \text{ CaCO}_3/\text{ha.pH} = 0.310 + 0.282\%C + 0.0546\text{ECEC}(\text{cmol}_c/\text{kg soil}) \quad (2)$$

$t \text{ CaCO}_3/\text{ha.pH}$ was derived by assuming a 10 cm slice and bulk density of 1.4 g/cm^3 . In the current assessment, $t \text{ CaCO}_3/\text{ha.pH}$.10cm slice has been converted to $\text{cmol}_c/\text{kg.pH}$ by multiplying the value by 1.428. The method used to estimate pHBC was a 7 day incubation with NaOH (Aitken and Moody, 1994).

3. Merry 2: Merry (1997) described a relationship between field texture and total C as a means of estimating lime requirement. The data set used was derived from 170 South Australian and western Victorian surface soils. pHBC was calculated after equilibration of soil with varying amounts of NaOH over 7 days (Aitken and Moody, 1994). Total carbon was determined using a Leco furnace. The equation is as follows:

$$t \text{ CaCO}_3/\text{ha.pH} = 0.200 + 0.364\%C + 0.0213\text{FT-Clay} \quad (3)$$

where FT-Clay is the field texture clay and is assigned the following values:

Field texture class	Assigned clay content (%)
Sand	5
Loamy and clayey sands	8
Sandy loam	15
Loam and silt loams	25
Sandy clay loam	27
Clay and silty clay loams	32
Sandy, silty and light clays	38
Medium and heavy clays	50

In the current assessment, t CaCO₃/ha.pH.10cm slice has been converted to cmol_c/kg.pH by multiplying the value by 1.428.

- Aitken *et al.* (1990a) described a pedotransfer function based on soil clay content and organic carbon (OC) as determined by the Walkley-Black method. The data set used to derive the function consisted of 40 soils from Queensland where the pHBC was determined using a soil-CaCO₃-moist incubation. The equation is as follows:

$$\text{pHBC (g CaCO}_3\text{/kg.pH)} = 0.955\text{OC}\% + 0.011\text{Clay}\% \quad (4)$$

In order to convert pHBC to cmol_c/kg.pH the pHBC was multiplied by a factor of 2.

- Noble *et al.* (1997) derived a pedotransfer based on OC (Walkley-Black), clay and silt content for a range of relatively light textured soils from the semi-arid tropics of northern Australia. The method used to estimate pHBC was a 7 day incubation with NaOH or HCl (Aitken and Moody, 1994). The equation is as follows:

$$\text{pHBC (mmol}_c\text{/kg.pH)} = 6.28 - 0.11\text{Clay} + 3.71\text{OC} - 0.16\text{Silt} + 0.03\text{Silt*Clay} \quad (5)$$

In order to convert pHBC to cmol_c/kg.pH the pHBC was divided by a factor of 10.

Data sets used to evaluate pedotransfer functions:

Several data sets were used to assess the ability of the aforementioned pedotransfer functions to estimate pHBC. These data sets were extracted from the literature as well as from individuals (ie. Drs G. P. Gillman, P. Moody and A. D. Noble). The data sets along with the derived pHBC using the previously described pedotransfer functions, are presented in Table 2-7. As can be seen from these data sets, not all pedotransfer functions could be assessed against measured pHBC due to a lack of data. It should be pointed out that the validity of such a comparison may be questioned since different methodologies were used to measure pHBC in the development of the pedotransfer functions. In the case of the data set from Gillman Ca(OH)₂ short-term equilibration was used to assess pHBC, whilst field incubation of 5 months was used to assess pHBC in the case of the data set from Moody. Noble used a 7 day equilibration using either HCl or NaOH to estimate pHBC.

The pedotransfer functions that used ECEC, namely Merry 1, Hochman and Limeit, were evaluated in 5 of the 6 data sets (Table 8). The excellent agreement between measured pHBC and that predicted using the Merry 1 equation was observed in all sets with r² values ranging 0.75 to 0.88 (Table 8). The slopes of the relationships ranged widely from 0.294 to 0.995 suggesting that in certain cases the pedotransfer function underestimated measured pHBC. It is of note that in the case of the data sets of Hochman *et al* (1992, 1995) that resulted in slopes of 0.995 and 0.862 respectively, measured pHBC was based on field determinations whilst the pedotransfer function of Merry was based on a 7 day equilibration with NaOH in the laboratory (Table 8).

Estimated pHBC using the Hochman pedotransfer resulted in slopes ranging from 0.099 to 1.401 with r^2 values of 0.383 to 0.858 (Table 8). Similarly, the Limeit model resulted in slopes ranging from 0.209 to 1.727 and r^2 values from 0.475 to 0.850 (Table 8). It would appear from these results that the function of Merry which uses ECEC and organic carbon resulted in the best fit of the predicted versus measured pHBC.

The pedotransfer function of Aitken *et al.* 1990 that uses clay content and organic carbon was assessed in 4 of the 6 data sets (Table 8). Slopes of the regression equations ranged from 0.882 to 1.441 with r^2 values of 0.740 to 0.867. The pedotransfer functions of Merry 2 and Noble *et al.* (1997) were only assessed against a single data set and therefore are excluded from consideration.

Whilst it may be argued that the assessment of these pedotransfer functions may be questioned since the methodology used to measure pHBC differed between data sets and therefore would influence the predictive nature of each of these functions, the fact that there is a large degree of agreement between methods is encouraging. It is of note that Ferrosols and Hydrosols were excluded from the assessments in the data set of Aitken *et al.*, 1998 (Table 5) since they resulted in poor fits of the data (Figure 2). This may be ascribed to the variable charge characteristics of these soils and the degree to which these characteristics are expressed. It is therefore suggested that caution should be exercised when using pedotransfer functions to predict pHBC on these soil types.

A comparison of predicted pHBC versus measured for each of the pedotransfer functions listed above over all data sets is presented in Figure 3. It is of note that the Aitken *et al.* (1990) function gave the best fit over the range of data sets used (ie Predicted pHBC = $0.824(\pm 0.214) + 0.833(\pm 0.067)$ measure pHBC; $r^2 = 0.702$). In contrast, the remaining functions resulted in poor relationships between these two parameters over the combined data sets.

In the estimation of pHBC of surface soil horizons, the pedotransfer function used will be entirely dependent on the data source. The following recommendations are made:

- the function of Aitken *et al.* (1998) that uses organic carbon and clay content should be used;
- the function of Merry that uses ECEC and organic carbon should be used in those cases where the aforementioned attributes are available;
- if the attributes of exchangeable Al and ECEC are determined the Limeit Model of Helyar should be used;
- in certain cases where organic carbon and field texture are the only attributes, the function of Merry (Merry 2) could be used to predict pHBC.

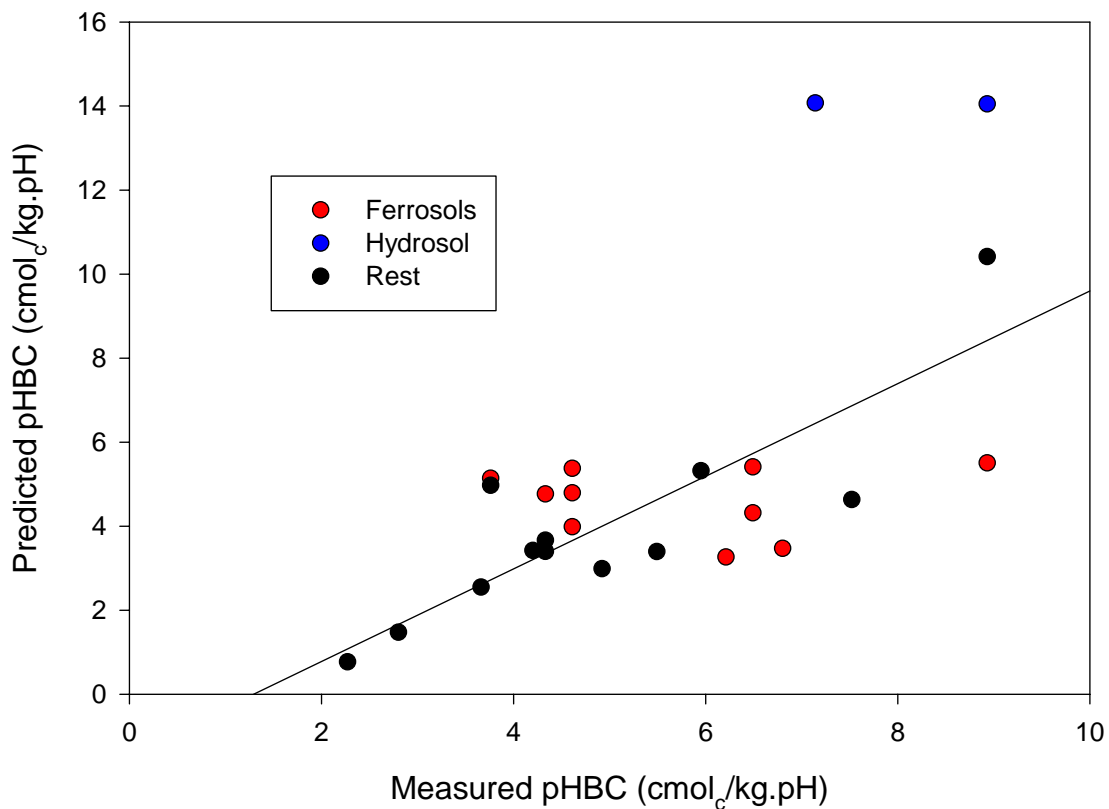


Figure 2. Relationship between measured pHBC and predicted pHBC showing the effect of soil type on the predictive nature of the pedotransfer function. Data from Aitken *et al.* (1998) and the pedotransfer used to predict pHBC was that outlined by Aitken *et al.* (1990).

The equations for estimating pHBC, with units t CaCO₃/ha.pH assuming a bulk density 1200 kg m⁻³ and a depth of 10 cm, are as follows:

Aitken *et al.*, 1990.

Note organic carbon (OC%) is determined by Walkley Black digestion.

$$\text{pHBC (t CaCO}_3\text{/ha.pH)} = [0.955\text{OC}\% + 0.011\text{Clay}\%] \times 1.2$$

Merry 1.

Note that total carbon is used in this equation. Therefore to convert Walkley Black carbon values to total carbon undertake the following conversion:

total carbon (%C) = %OC (Walkley Black) x 1.3 (see comments below regarding conversion factor)

$$\text{pHBC (t CaCO}_3\text{/ha.pH)} = [0.310 + 0.282\%C + 0.0546\text{ECEC}(\text{cmol}_c\text{/kg soil})] \times 0.857$$

Merry 2.

Note that total carbon is used in this equation. Therefore to convert Walkley Black carbon values to total carbon undertake the following conversion:

total carbon (%C) = %OC (Walkley Black) x 1.33 (see comments below regarding conversion factor)

$$\text{pHBC (t CaCO}_3\text{/ha.pH)} = [0.200 + 0.364\%C + 0.0213\text{FT-Clay}] \times 0.857$$

The Limeit model is embedded in an Excel spreadsheet obtainable from Dr K. Helyar.

A recent report for the Australian Greenhouse Office by Skjemstad *et al.* (2000) highlights potential problems associated with the measurement of soil organic carbon undertaken by various laboratories over a prolonged period. They have suggested that conversion factors be used on certain data sets to convert Walkley and Black carbon values to LECO combustion values. The suggested conversion factors are presented below.

Laboratory	Correction Factor	Comments
<u>Queensland</u>		
CSIRO Townsville	1.00	Prior to and including 1968
	1.24	1969 and up to and including 1984
CSIRO Brisbane	1.32	Prior to and including 1968
	1.00	1969 and subsequent years
QDNR	1.34	Prior to and including 1987
	1.07	1988 and subsequent years
<u>NSW</u>		
CSIRO Canberra	1.00	For all years
DLWC	1.13	For all years
<u>Victoria</u>	1.00	For all years
<u>Tasmania</u>		
CSIRO Hobart	1.00	For all years
<u>South Australia</u>		
CSIRO Adelaide	1.00	For all years
<u>Western Australia</u>		
AgWA	1.12	For all years

It is assumed that these conversion factors will be used by the ASRIS to standardize soil organic carbon before proceeding to estimate pHBC.

Subsoil pHBC estimations

With respect to recommendations of suitable pedotransfer functions for predicting the buffer capacity of subsoil horizons, there is little evidence in the literature specifically addressing this aspect. Intuitively pedotransfer functions that rely on soil organic carbon as a variate would over estimate the buffering capacity. Whilst no validation could be undertaken due to a lack of data, it is suggested that the Limeit Model may adequately predict the pHBC of

subsoils based on its mechanistic approach to predicting this attribute. In addition, Noble *et al.* (1997) describe a pedotransfer function for subsoils that is as follows:

$$\text{pHBC (t CaCO}_3\text{/ha.pH)} = [12.79 - 0.19\text{Clay} - 0.7\text{OC} - 0.03\text{Silt} + 0.74\text{Silt*OC}] \times 0.06 \quad (6)$$

It is of note that when compared with equation (5), the weighting on soil organic carbon in the prediction of pHBC is significantly reduced in equation (6). This pedotransfer may have limited use in case where the attributes of clay, OC and silt are available.

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References:

- Aitken, R. L., and Moody, P. W. (1994). The effect of valence and ionic strength on the measurement of pH buffer capacity. *Aust. J. Soil Res.* 32, 975-84.
- Aitken, R. L., Moody, P. W. and McKinley, P. G. 1990a. Lime requirement of acidic Queensland soils. I. Relationships between soil properties and pH buffer capacity. *Aust. J. Soil Res.* 28: 695-701.
- Aitken, R. L., Moody, P. W. and McKinley, P. G. 1990b. Lime requirement of acidic Queensland soils. II. Comparison of laboratory methods for predicting lime requirement. *Aust. J. Soil Res.* 28: 703-715.
- Aitken, R. L., Moody, P. W. and Dickson, T. 1998. Field amelioration of acidic soils in south-east Queensland. I. Effect of amendments on soil properties. *Aust. J. Agric. Res.* 49: 627-637.
- Conyers, M. K., Helyar, K. R. and Poile, G. J. (2000) pH buffering: the chemical response of acidic soils to added alkali. *Soil Sci.* 165: 560-566.
- Gillman, G. P. and Sumpter, E. A. 1986. Surface charge characteristics and lime requirements of soils derived from basaltic, granitic and metamorphic rocks in high-rainfall tropical Queensland. *Aust. J. Soil Res.* 24: 173-192.
- Helyar, K. R. and Porter, W. M. 1989. Soil acidification, its measurement and the processes involved. In 'Soil Acidity and Plant Growth'. (Ed. A. D. Robson.) pp 61-101. Academic Press, Sydney.
- Helyar, K. R., Cregan, P. D. and Godyn D. L. 1990. Soil acidity in New South Wales – Current pH values and estimates of acidification rates. *Aust. J. Soil Res.* 28: 523-537.
- Hochman, Z., Godyn, D. L. and Scott, B. J. 1989. The integration of data on lime use by modelling. In 'Soil Acidity and Plant Growth'. (Ed. A. D. Robson.) pp 265-101. Academic Press, Sydney.
- Kamprath, E. J. 1971. Potential detrimental effects from liming highly weathered soils to neutrality. *Proc. Soil Crop Sci. Soc. Fla.* 31: 200-203.
- Magdoff, F. R. and Bartlett, R. J. 1985. Soil pH buffering revisited. *Soil Sci. Soc. Am. J.* 49: 145-148.
- McLean, E. O. 1970. Lime requirements of soils – inactive toxic substance of favourable pH range? *Soil Sci. Soc. Am. Proc.* 34: 363-364.
- Merry, R. 1997. Estimation of simple lime requirement based on pH buffer capacity measurement and other soil factors. CSIRO Division of Soils Technical Report.
- Metson, A. J. 1956. Methods of chemical analysis for soil survey samples. Soil Bureau Bulletin 12, DSIR, New Zealand, pp. 102-103.
- Noble, A. D, Cannon, M., and Muller, D. 1997. Evidence of accelerated soil acidification under *Stylosanthes*-dominated pastures. *Aust. J. Soil Res.* 35: 1309-1322.
- Ridley, A. M., Helyar K. R., and Slattery, W. J. 1990. Soil acidification under subterranean clover (*Trifolium subterraneum*) pastures in north-eastern Victoria. *Aust. J. Exp. Agric.* 30:195-201.

- Porter, W. M., McLay, C. D. A. and Dolling, P.J. 1995. Rates and sources of acidification in agricultural systems of southern Australia. In R. A. Date et al. (eds). *Plant-Soil Interactions at Low pH: Principles and Management*, 75-83. Kluwer Academic Publishers, The Netherlands.
- Skjemstad, J. O. Spouncer, L. R. and Beech, T. A. (2000). Carbon conversion factors for historical soil carbon data. A consultancy for the Australian Greenhouse Office. CSIRO Land and Water, Adelaide.
- Slattery, W. J. and Coventry, D. R. 1993. Response of wheat, triticale, barley, and canola to lime on four soil types in north-eastern Victoria. *Aust. J. Exp. Agric.* **33**:609-618.
- Thomas, G. W. and Hargrove, W. L. 1984. The chemistry of soil acidity. In 'Soil Acidity and Liming'. (Ed. F. Adams.) pp.3-56. Am. Soc. Agron./Crop Sci. Soc. Am./Soil Sci. Soc. Am.: Madison, Wisconsin.
- Uehara, G. and Gillman G. P. 1981. *The mineralogy, chemistry and physics of tropical soils with variable charge clays*. Westview Press, Boulder, Colorado.

Table 1. Some methods used for estimating pH buffer capacity in Australia.

Cited	Reagent	Dilution (soil:water)	Period of incubation	Temperature	pH method of determination	Comments
Hochman <i>et al.</i> (1992)	Agricultural lime	In field	12 months	Variable	1:5 0.01M CaCl ₂	
Slattery and Coventry (1993)	Dolomitic lime	In field	12 months	Variable	1:5 0.01M CaCl ₂	Predicted lime requirement from Limeit with field based measurements to validate.
Aitken <i>et al.</i> , 1990	CaCO ₃	Laboratory incubation	6 weeks	25°C	1:5 water	
Aitken <i>et al.</i> , 1998	Agricultural lime	In field	5 months	Variable	1:5 water and 0.01M CaCl ₂	
Aitken and Moody, 1994	HCl or NaOH	Laboratory	7 days	25°C	1:5 0.002M CaCl ₂	Ionic strength of equilibrating solution similar to soil solution.
Noble <i>et al.</i> , 1997	HCl or NaOH	Laboratory	7 days	25°C	1:5 0.002M CaCl ₂	Ionic strength of equilibrating solution similar to soil solution.
Merry 1997	HCl or NaOH	Laboratory	7 days	25°C	1:5 0.002M CaCl ₂	Ionic strength of equilibrating solution similar to soil solution.

Table 2. Selected soil chemical and physical data from surface horizons collected in the Dalrymple Shire north Queensland by Noble.

Sample identification; T series	1:5 pHw	OC %	Clay %	Field texture ¹ (%)	Silt %	Measured buffer capacity ² (cmol _c /kg.pH)	Predicted Noble et al. 1997. ³ (cmol _c /kg.pH)	Aitken et al. 1990 ⁴ (cmol _c /kg.pH)	Merry 1997 ⁵ (cmol _c /kg.pH)
8	6.4	0.86	15.00	15	11	1.37	1.26	1.97	1.32
47	6.8	1.06	72.00	50	15	2.80	3.44	3.61	2.52
11	6.8	1.57	29.00	32	16	1.87	2.26	3.64	2.32
59	6.1	0.49	9.00	8	9	1.00	0.94	1.13	0.86
99	6	0.54	21.00	27	7	1.25	1.03	1.49	1.47
145	6.1	0.35	13.00	15	6	0.90	0.84	0.95	0.98
152	6.7	0.50	5.00	8	6	0.81	0.84	1.07	0.87
163	6.5	2.57	31.00	32	30	3.79	3.98	5.59	3.00
168	6.4	1.60	42.00	50	23	2.76	3.62	3.98	2.89
173	6.7	2.01	38.00	27	29	3.52	4.21	4.68	2.47
331	6.5	1.00	22.00	27	10	1.33	1.40	2.39	1.78
335	6	0.53	14.00	15	5	1.12	0.87	1.32	1.10
339	6	1.08	16.00	15	11	1.64	1.36	2.41	1.47
340	6.5	0.64	16.00	15	7	1.40	1.01	1.57	1.17
503	6.39	1.00	7.00	8	6	0.97	1.04	2.06	1.20
507	6.32	0.60	6.00	8	7	1.04	0.90	1.28	0.93
521	6.04	1.30	3.00	5	3	1.56	1.10	2.55	1.32
528	8.29	0.70	27.00	27	16	1.00	1.86	1.93	1.58
533	5.63	1.00	21.00	25	20	1.75	1.99	2.37	1.72
534	5.89	0.70	17.00	15	14	1.32	1.39	1.71	1.21
536	5.88	1.80	14.00	15	20	1.46	1.95	3.75	1.96
542	6.91	0.60	35.00	32	13	1.31	1.81	1.92	1.66
545	5.56	0.20	2.00	5	1	0.77	0.68	0.43	0.57
575	7.5	0.48	43.00	50	17	1.44	2.50	1.86	2.13
579	6.7	2.50	32.00	32	36	3.40	4.60	5.48	2.95
580	6.6	1.70	36.00	32	23	3.25	3.31	4.04	2.41
583	8.2	0.81	24.00	27	9	1.65	1.30	2.08	1.65
M3960	6	0.42	4.00	5	6	0.81	0.80	0.89	0.72
M3974	6.7	0.56	8.00	8	8	0.91	0.92	1.25	0.91

¹Field texture classification as outlined by Merry 1997.

²Buffer capacity determined using methodology of Aitken and Moody 1994.

³Noble et al. 1997:pHBC (cmol_c/kg.pH) = [6.28 - 0.11 x Clay(%) + 3.72 x OC(%) - 0.16 x Silt(%) + (0.03 x Silt(%) x Clay(%))]/10

⁴Aitken et al. 1990:pHBC (cmol_c/kg.pH) = (0.954 x OC(%) + 0.011 x Clay(%)) x 2; equation modified to convert from g CaCO₃/kg.pH to cmol_c/kg.pH

⁵Merry 1997: pHBC (cmol_c/kg.pH) = (0.200 + 0.364 x C(%) + 0.0213 x FT-Clay (%)) x 1.428; where C(%) is total carbon (conversion used to adjust Walkley Black is OC x 1.3); FT-Clay is field texture clay as classified by Merry 1997; equation modified to convert from t CaCO₃/ha.pH to cmol_c/kg.pH.

Table 3. Data from Hochman *et al.* 1995 (Table 4) modified to calculate pHBC using different methods.

Soil	Soil Type	pH _{Ca}	ECEC (cmol _c /kg)	Exch. Al (cmol _c /kg)	C (%) ¹	LRI ² (pH.ha/t)	1/LRI (t CaCO ₃ /ha.pH)	pHBC ³ (cmolc/kg.pH)	Hochman et al., 1989 ⁴	Merry 1997 ⁵	Helyar Limeit ⁶
1	Krasnozem	4.40	10.74	2.52	6.25	0.35	2.84	3.98	4.96	3.80	5.96
2	Chocolate soil	4.71	9.13	0.65	3.28	0.40	2.53	3.54	3.78	2.48	4.32
3	Krasnozem	4.59	11.87	1.24	5.10	0.39	2.57	3.60	5.04	3.42	5.80
4	Yellow podzolic	5.07	10.44	0.09	4.34	0.45	2.24	3.14	3.76	3.00	4.05
5	Grey brown podzollic	4.66	3.45	0.20	1.64	0.99	1.01	1.41	1.68	1.37	1.84
6	Yellow podzolic	4.47	6.34	0.90	2.95	0.53	1.88	2.63	3.01	2.12	3.42
7	Chocolate soil	4.71	8.51	0.87	3.08	0.48	2.10	2.94	3.55	2.35	4.26
8	Yellow podzolic	4.79	9.18	0.52	3.05	0.56	1.79	2.51	3.69	2.39	4.22

¹Assumed that values presented in Table 4 of Hochman are total carbon.

²Lime Responsive Index as determined from field incubated liming trials.

³Conversion of 1/LRI to pHBC; conversion factor is 1.4 x 1/LRI (cmol_c/kg.pH).

⁴pHBC as calculated by Hochman et al., 1989. Calculation is based on the following: pHBC (cmol_c/kg.pH) = (ECEC+2.0428)/(pH_{Ca}-0.9568)

⁵pHBC as calculated by Merry 1997; pHBC (cmol_c/kg.pH) = (0.310 + 0.282 x C(%)) + 0.546 x ECEC(cmol_c/kg) x 1.428.

⁶Helyar Limeit model: Uses as input current pH, ECEC and exchangeable Al. The amount of lime dissolved and reacted required to raise the pH to 5.5.

Table 4. Data from Hochman *et al.* 1992 (Table 2) modified to calculate pHBC using different methods.

Soil	pH _{Ca}	ECEC	Exch. Al	C (%) ¹	LRI ²	1/LRI	pHBC ³	Hochman et al, 1989 ⁴	Merry 1997 ⁵	Helyar Limeit model ⁶
		(cmol _c /kg)	(cmol _c /kg)		(pH.ha/t)	(t CaCO ₃ /ha.pH)	(cmol _c /kg.pH)			
1	4.08	6.07	2.14	1.90	0.73	1.38	1.93	3.45	1.68	3.81
2	4.52	7.48	0.68	1.60	0.89	1.13	1.58	3.41	1.67	3.76
3	5.12	18.75	0.08	1.80	0.50	2.02	2.83	6.40	2.63	6.79
4	4.65	12.47	0.82	3.10	0.47	2.14	2.99	5.15	2.66	5.75
5	4.23	12.05	1.48	2.50	0.60	1.68	2.35	5.95	2.39	6.28
6	4.33	4.77	1.13	4.90	0.48	2.07	2.90	2.50	2.79	2.88
7	4.17	6.48	1.42	2.90	0.79	1.26	1.77	3.50	2.12	3.79
9	4.44	5.24	0.90	1.60	0.79	1.27	1.77	2.59	1.50	2.97
10	4.42	6.57	1.12	2.30	0.65	1.55	2.17	3.17	1.88	3.63
11	4.22	12.47	5.30	6.10	0.39	2.56	3.58	6.17	3.87	7.48

¹Assumed that values presented in Table 4 of Hochman are total carbon.

²Lime Responsive Index as determined from field incubated liming trials.

³Conversion of 1/LRI to pHBC; conversion factor is 1.4 x 1/LRI (cmol_c/kg.pH).

⁴pHBC as calculated by Hochman et al., 1989. Calculation is based on the following: pHBC (cmol_c/kg.pH) = (ECEC+2.0428)/(pH_{Ca}-0.9568)

⁵pHBC as calculated by Merry 1997; pHBC (cmol_c/kg.pH) = (0.310 + 0.282 x C(%)) + 0.546 x ECEC(cmol_c/kg) x 1.428.

⁶Helyar Limeit model: Uses as input current pH, ECEC and exchangeable Al. The amount of lime dissolved and reacted required to raise the pH to 5.5.

Table 5. Data from Aitken *et al.* (1998) presented in Tables 1 and 2.

Site No	Soil type	pH _{ca}	OC	Clay	ECEC	Exch Al	1/slope	Field determined buffer capacity ¹	Hochman et al 1989 ²	Aitken et al. 1990 ³	Merry 1997 ⁴	Helyar Limeit model ⁵
			(%)	(%)	(cmol _c /kg)	(cmol _c /kg)			(cmol/kg/pH)			
1	Ferrosol	3.93	1.0	71	2.9	1.21	4.76	6.80	2.04	3.47	1.19	2.16
3	Ferrosol	4.17	2.4	42	4.2	0.71	6.25	8.93	2.42	5.50	2.03	1.95
4	Ferrosol	3.86	1.2	77	2.4	1.34	3.23	4.61	1.85	3.98	1.26	3.49
9	Ferrosol	4.06	1.1	53	5.4	2.10	4.35	6.21	3.15	3.26	1.44	3.08
11	Ferrosol	4.32	1.5	66	6.5	0.58	4.55	6.49	3.27	4.31	1.73	10.16
15	Ferrosol	4.31	2.1	62	7.7	1.07	3.23	4.61	3.82	5.37	2.14	2.96
20	Ferrosol	4.17	1.7	69	6.0	1.38	3.03	4.33	3.27	4.76	1.80	2.31
21	Ferrosol	4.59	1.9	53	7.9	0.71	3.23	4.61	3.48	4.79	2.05	1.51
22	Ferrosol	4.03	2.0	60	4.7	1.64	2.63	3.76	2.85	5.14	1.86	2.87
23	Ferrosol	4.02	2.2	55	7.5	3.30	4.55	6.49	4.28	5.41	2.18	2.14
13	Hydrosol	3.67	7.0	32	15.6	6.39	5.00	7.14	10.18	14.07	5.32	4.56
24	Hydrosol	4.65	7.0	31	15.4	1.38	6.25	8.93	6.27	14.05	5.31	4.86
2	Kurosol	4.09	1.5	24	7.5	2.47	3.85	5.49	4.13	3.39	1.81	2.56
5	Chromosol	4.79	1.4	34	4.6	0.09	2.94	4.20	2.02	3.42	1.53	3.44
6	Kurosol	4.29	2.3	42	5.1	0.91	4.17	5.95	2.70	5.31	2.04	4.14
7	Kurosol	4.10	2.0	37	4.0	2.16	5.26	7.52	2.41	4.63	1.80	3.56
8	Kurosol	4.04	1.3	23	4.1	1.88	3.45	4.92	2.53	2.98	1.44	3.92
10	Chromosol	4.28	0.3	9	1.4	0.29	1.59	2.27	1.05	0.77	0.71	4.75
12	Kandosol	3.96	1.0	29	3.2	1.34	2.56	3.66	2.17	2.54	1.22	7.26
14	Kandosol	4.12	1.7	7	1.8	0.93	3.03	4.33	1.33	3.40	1.47	2.14
17	Chromosol	3.95	2.2	35	4.4	1.01	2.63	3.76	2.81	4.97	1.94	2.80
18	Kandosol	3.99	1.7	19	2.8	1.59	3.03	4.33	1.93	3.66	1.55	2.82
19	Kurosol	4.24	5.2	22	7.7	3.54	6.25	8.93	3.94	10.41	3.77	1.13
27	Chromosol	4.11	0.6	15	2.3	0.48	1.96	2.80	1.58	1.47	0.94	1.65

¹ pHBC determined on samples collected from field plots 5 months after the application of lime.

² pHBC as calculated by Hochman et al., 1989. Calculation is based on the following: pHBC (cmol_c/kg.pH) = (ECEC+2.0428)/(pH-0.9568)

³ Aitken et al. 1990:pHBC (cmol_c/kg.pH) = (0.954 x OC(%) + 0.011 x Clay(%)) x 2; equation modified to convert from g CaCO₃/kg.pH to cmol_c/kg.pH

⁴ Merry 1997: pHBC (cmol_c/kg.pH) = (0.200 + 0.364 x C(%) + 0.0213 x FT-Clay (%)) x 1.428; where C(%) is total carbon (conversion used to adjust Walkley Black is OC x 1.3); FT-Clay is field texture clay as classified by Merry 1997; equation modified to convert from t CaCO₃/ha.pH to cmol_c/kg.pH.

⁵ Helyar Limeit model: Uses as input current pH, ECEC and exchangeable Al. The amount of lime dissolved and reacted required to raise the pH to 5.5.

Table 6. Data from Gillman for granite derived soils.

Depth	¹ pH _{Ca}	OC	Clay	Exch. Al	ECEC	Measured LR 5.5 ²	Measured Buffer Capacity	Hochman ³	Aitken et al. 1990 ⁴	Merry 1990 ⁵	Helyar Limeit model ⁶
		(%)	(%)	(cmol _c /kg)	(cmol _c /kg)	(cmol _c CaCO ₃ /kg)	(cmol/kg.pH)				
0-10cm	4.17	2.1	33	1.10	2.5	1.86	2.66	1.62	4.73	1.74	1.87
0-10cm	4.17	0.8	26	1.00	1.93	1.00	1.67	1.36	2.10	1.01	1.58
0-10cm	4.06	0.8	17	1.20	1.41	0.84	1.40	1.17	1.90	0.97	1.36
0-10cm	4.11	0.6	34	1.20	1.78	0.92	1.15	1.32	1.89	0.90	1.55
0-10cm	4.62	2.0	15	0.90	2.75	1.58	3.95	1.44	4.15	1.70	2.05
0-10cm	4.71	2.3	15	0.80	2.97	1.46	4.87	1.47	4.72	1.88	2.15
0-10cm	4.06	0.9	25	2.10	2.44	1.36	1.94	1.68	2.26	1.10	2.01
0-10cm	4.17	0.9	19	1.50	2.09	1.22	2.03	1.43	2.13	1.08	1.75
0-10cm	4.45	1.0	12	1.20	1.99	1.04	2.08	1.22	2.17	1.12	1.75
0-10cm	4.11	2.9	8	2.60	3.14	3.14	3.93	1.98	5.71	2.21	2.43
0-10cm	4.53	1.0	16	0.90	2.3	0.74	1.85	1.31	2.26	1.15	1.80
0-10cm	4.30	1.2	9	1.10	1.77	1.22	2.44	1.21	2.49	1.21	1.54

¹pH water converted to pH_{Ca} using Ahern *et al.*, 1995. ie $\text{pH}_{\text{Ca}} = -5.03\text{pH}_{\text{w}} + 0.891\text{pH}_{\text{w}}^2 - 0.043\text{pH}_{\text{w}}^3 + 12.484$.

²Measured lime requirement (LR) to pH 5.5 determined by adding incremental amounts of saturated solution of Ca(OH)₂ to a soil suspension over a 7 day period.

³pHBC as calculated by Hochman *et al.*, 1989. Calculation is based on the following: $\text{pHBC (cmol}_c\text{/kg.pH)} = (\text{ECEC} + 2.0428) / (\text{pH}_{\text{Ca}} - 0.9568)$.

⁴Aitken *et al.* 1990: $\text{pHBC (cmol}_c\text{/kg.pH)} = (0.954 \times \text{OC}(\%) + 0.011 \times \text{Clay}(\%)) \times 2$; equation modified to convert from g CaCO₃/kg.pH to cmol_c/kg.pH.

⁵pHBC as calculated by Merry 1997; $\text{pHBC (cmol}_c\text{/kg.pH)} = (0.310 + 0.282 \times \text{C}(\%) + 0.546 \times \text{ECEC (cmol}_c\text{/kg)}) \times 1.428$; where C(%) is total carbon (conversion used to adjust Walkley Black is OC x 1.3).

⁶Helyar Limeit model: Uses as input current pH, ECEC and exchangeable Al. The amount of lime dissolved and reacted required to raise the pH to 5.5.

Table 7. Data from Gillman for metamorphic derived soils.

Depth	¹ pH _{Ca}	OC	Clay	Exch. Al	ECEC	Measured LR 6 ²	Measured Buffer Capacity	Hochman ³	Aitken et al. 1990 ⁴	Merry 1990 ⁵	Helyar Limeit model ⁶
		(%)	(%)	(cmol _c /kg)	(cmol _c /kg)	(cmol _c CaCO ₃ /kg)	(cmol/kg/pH)				
0-10cm	4.06	1.9	20	1.40	1.88	3.30	2.75	1.41	4.07	1.58	1.63
0-10cm	4.06	2.4	25	2.00	2.80	4.96	3.82	1.86	5.13	1.92	2.18
0-10cm	4.11	1.0	19	1.00	1.21	1.28	1.16	1.05	2.33	1.06	1.23
0-10cm	4.06	1.4	34	2.40	2.64	4.44	3.42	1.78	3.42	1.38	2.14
0-10cm	4.17	2.1	37	1.30	3.37	6.60	5.08	2.03	4.83	1.80	2.32
0-10cm	4.11	2.6	27	1.70	3.45	5.06	3.89	2.13	5.56	2.07	2.45
0-10cm	4.30	0.9	27	1.00	2.21	2.22	1.85	1.40	2.31	1.09	1.71
0-10cm	4.11	0.9	21	1.40	1.69	2.22	1.85	1.28	2.18	1.05	1.53
0-10cm	3.94	2.3	10	2.70	3.00	5.20	3.47	2.09	4.61	1.88	2.38
0-10cm	4.23	1.1	11	1.20	1.80	2.24	2.04	1.26	2.34	1.16	1.56
0-10cm	3.94	1.1	37	3.30	3.82	3.00	2.14	2.52	2.92	1.32	2.87
0-10cm	3.88	3.4	25	6.60	7.40	12.32	7.25	4.56	7.04	2.80	5.13
0-10cm	4.89	1.2	27	0.30	4.31	1.68	2.40	1.85	2.89	1.41	2.24
0-10cm	4.11	1.0	19	1.50	2.23	2.22	2.02	1.54	2.33	1.14	1.82

¹pH water converted to pH_{Ca} using Ahern *et al.*, 1995. ie $\text{pH}_{\text{Ca}} = -5.03\text{xpH}_w + 0.891\text{xpH}_w^2 - 0.043\text{xpH}_w^3 + 12.484$.

²Measured lime requirement (LR) to pH 6 determined by adding incremental amounts of saturated solution of Ca(OH)₂ to a soil suspension over a 7 day period.

³pHBC as calculated by Hochman *et al.*, 1989. Calculation is based on the following: $\text{pHBC (cmol}_c/\text{kg.pH)} = (\text{ECEC} + 2.0428) / (\text{pH}_{\text{Ca}} - 0.9568)$.

⁴Aitken *et al.* 1990: $\text{pHBC (cmol}_c/\text{kg.pH)} = (0.954 \times \text{OC}(\%) + 0.011 \times \text{Clay}(\%)) \times 2$; equation modified to convert from g CaCO₃/kg.pH to cmol_c/kg.pH.

⁵pHBC as calculated by Merry 1997; $\text{pHBC (cmol}_c/\text{kg.pH)} = (0.310 + 0.282 \times \text{C}(\%) + 0.546 \times \text{ECEC}(\text{cmol}_c/\text{kg})) \times 1.428$; where C(%) is total carbon (conversion used to adjust Walkley Black is OC x 1.3).

⁶Helyar Limeit model: Uses as input current pH, ECEC and exchangeable Al. The amount of lime dissolved and reacted required to raise the pH to 5.5.

Table 8. Relationship between measured pHBC and predicted pHBC for a range of pedotransfer functions and selected data sets.

Data set	Pedotransfer function											
	Merry 1	r ²	Merry 2	r ²	Hochman et al., 1989	r ²	Aitken et al., 1990	r ²	Helyar Limeit	r ²	Noble	r ²
Noble			0.705x + 0.455	0.803			1.441x - 0.001	0.867			1.23x - 0.209	0.886
Gillman metamorphic	0.294x + 0.641	0.875			0.459x + 0.497	0.718	0.882x + 0.996	0.856	0.499x + 0.691	0.711		
Gillman granite	0.332x + 0.509	0.808			0.099x + 1.186	0.245	1.027x + 0.483	0.746	0.209x + 1.296	0.636		
Hochman et al. 1992	0.995x - 0.106	0.881			1.401x + 0.815	0.383			1.727x - 0.509	0.475		
Hochman et al. 1995	0.862x + 0.059	0.814			1.227x + 0.041	0.858			1.493x - 0.196	0.850		
Aitken et al. 1998 ¹	0.349x - 0.003	0.752			0.611x + 0.064	0.679	1.102x - 1.424	0.740	0.688x + 0.057	0.666		

¹Analysis excludes Ferrosols and Hydrosols.

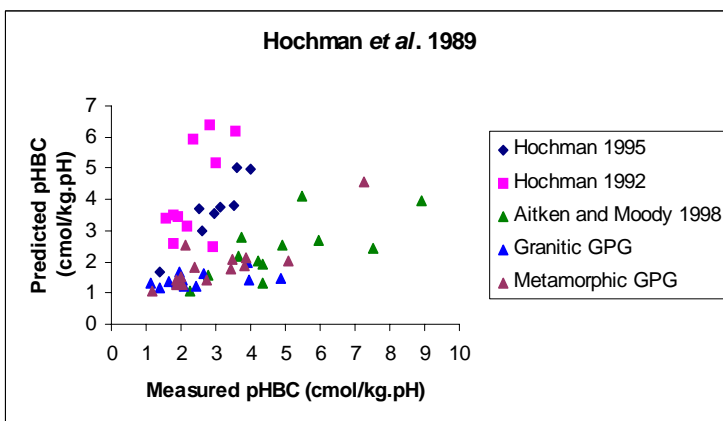
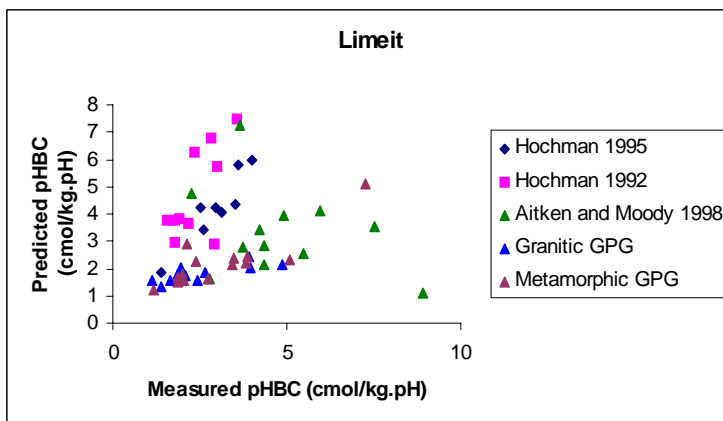
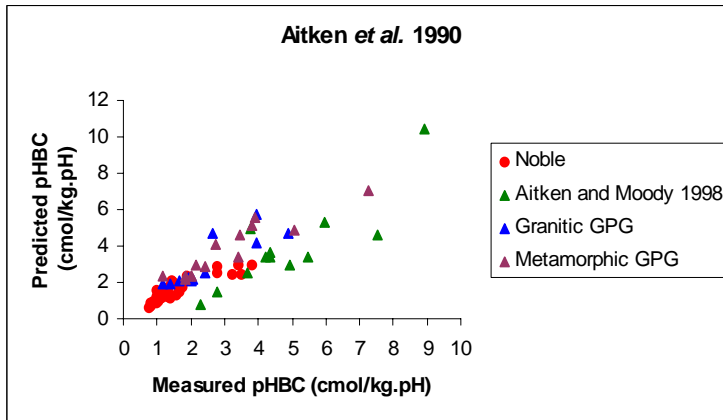
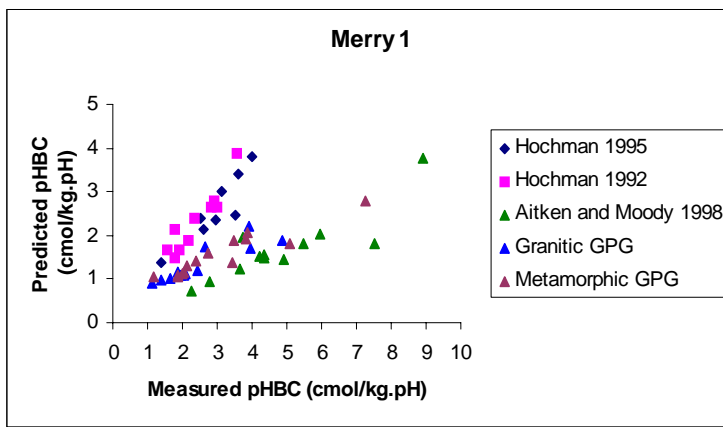


Figure 3. Relationship between predicted and measured pH buffer capacity for each of the pedotransfer functions over all data sets.