Constraining the carbonate system in soils via testing the internal consistency of pH, pCO₂ and alkalinity measurements

Sima Bargrizan1*, Ronald J. Smernik1 and Luke M. Mosley2

Abstract
Inorganic carbon exists in various dissolved, gaseous and solid phase forms in natural waters and soils. It is important to accurately measure and model these forms to understand system responses to global climate change. The carbonate system can, in theory, be fully constrained and modelled by measuring at least two out of the following four parameters: partial pressure (pCO₂), total alkalinity (TA), pH and dissolved inorganic carbon (DIC) but this has not been demonstrated in soils. In this study, this ‘internal consistency’ of the soil carbonate system was examined by predicting pH of soil extracts from laboratory measurement of TA through alkalinity titration for solutions in which pCO₂ was fixed through equilibrating the soil solution with air with a known pCO₂. This predicted pH (pHₐₗ₉) was compared with pH measured on the same soil extracts using spectrophotometric and glass electrode methods (pHₚₑₛₚ and pHₑₑₑₗₑₑ). Discrepancy between measured and calculated pH was within 0.00–0.1 pH unit for most samples. However, more deviation was observed for those sample with low alkalinity (< 0.5 meq L⁻¹). This is likely attributable to an effect of dissolved organic matter, which can contribute alkalinity not considered in the thermodynamic carbonate model calculations; further research is required to resolve this problem. The effects of increasing soil pCO₂ was modelled to illustrate how internally consistent models can be used to predict risks of pH declines and carbonate mineral dissolution in some soils.

Keywords: Soil carbonate system, Internal consistency, Spectrophotometric method, Total alkalinity

Introduction
Concentrations of atmospheric carbon dioxide (CO₂) have increased by 40%, from 280 ppm in 1750 to 400 ppm in 2014 [1]. This increase has been caused by anthropogenic activities, especially burning of fossil fuels which is the main cause of global warming [2]. The soil inorganic carbon system is one of the largest sinks of atmospheric CO₂ and the global C cycle [3], and is vulnerable to anthropogenic perturbations [4]. The partial pressure of CO₂ (pCO₂) in the atmosphere is in equilibrium with the soil surface but deeper soil layers may have higher pCO₂ due to microbial respiration and slow exchange with the atmosphere. Increasing soil pCO₂ as a consequence of the increasing concentrations of atmospheric pCO₂ [5, 6] has demonstrated the participation of soil inorganic carbon systems to global climate change.

Inorganic carbon can occur in different forms in soils including dissolved species (CO₂, carbonic acid, bicarbonate, and carbonate ions), and solid mineral phases (e.g. calcium carbonate, dolomite). Calcium carbonate (CaCO₃) can comprise a major part of some soil systems, particularly in arid and semi-arid areas [7]. Under increased soil pCO₂, soil acidification occurs through carbonic acid formation followed by weak acid dissociation [8]. The weathering (dissolution) of CaCO₃ (calcite and aragonite) in soils arises from either carbonic acid at...
pH > 6 or strong acids at lower pH. Dissolution of solid calcium carbonate at pH > 6.5 [9–11] provides a buffer (provided that it is not exhausted) via an increase in HCO$_3^−$ alkalinity against pH changes in soil [12] caused by acidification processes [13]. As well as pH the assessment of the degree of CaCO$_3$ saturation is crucial for agricultural management due to its influence on chemical and physical soil characteristics such as cation exchange capacity (CEC), porosity, and hydraulic conductivity [14]. The outcome of anthropogenic climate change could be a decrease in CaCO$_3$ mineral saturation status, resulting in dissolution [15–17], a decrease in the pH buffering capacity, and soil acidification.

To give increased confidence in predicting the effects of increased atmospheric pCO$_2$ and risks of soil acidification, accurate characterization of the soil inorganic carbon system [18] is essential. This requires measurement of inorganic carbon system variables such total alkalinity (TA), pH, pCO$_2$ and dissolved inorganic carbon (DIC) [19]. By measuring accurately at least two of these inorganic carbon system parameters it is possible to calculate the remaining parameters using knowledge of carbonate equilibrium constants [20]. If a third carbonate system parameter is measured this enables rigorous checking of the internal consistency of the equilibrium constants of the system and accuracy of measurements [21].

The internal consistency assists in checking if the same outcomes can be obtained through dependent carbon system measurements [22]. The internal consistency of different sets of marine carbonate system measurements and equilibrium constants has previously been demonstrated [18, 23–26]. However, this internal consistency has not been demonstrated yet for the soil carbonate system, and this introduces major uncertainties in our ability to understand acidification risks and response to rising atmospheric CO$_2$ levels. Highly precise analytical measurements of carbonate parameters are a prerequisite for evaluation of the internal consistency of this system [27–31]. This was one of the drivers for our recent development of spectrophotometric pH measurement methods for soil extracts [13, 32] which had previously been proven to provide high precision pH (∼0.01 pH units) in the marine chemistry field [33–38].

The objective of this study was to develop a model for evaluation of the consistency of thermodynamics of the soil carbonate system by calculation of a third parameter from two other parameters. Using a controlled laboratory experiment, we calculated pH of soil extracts equilibrated with a fixed pCO$_2$ and measured total alkalinity (TA) and then compared the results with pH measured through spectrophotometric and glass electrode methods. This study is also unique in terms of the investigation of the internal consistency of the soil carbonate system through the incorporation of state-of-the-art spectrophotometric methods for pH measurement. A further aim of this study was to assess the accuracy of spectrophotometric soil pH measurements against conventional glass electrode pH measurements using the same approach. A modelling approach was then explored as a potential tool for prediction of increasing soil pCO$_2$ and soil carbonate dissolution as a result of global climate change.

### Materials and methods

#### Theory

**Soil pH determination using acid–base equilibria of CO$_2$**

The pH and carbonate equilibria in the soil solution can in theory be determined using Henry’s Law constant for CO$_2$ ($K_h$), the first and second dissociation constants of carbonic acid (H$_2$CO$_3^*$) ($K_1$ and $K_2$) resulting in bicarbonate and carbonate ions, respectively and the water self-dissociation equilibrium constant ($K_w$) [39]:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3^* \quad K_h = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2]} = 10^{-1.47} \tag{1a}
\]

\[
\text{H}_2\text{CO}_3^* = \text{H}^+ + \text{HCO}_3^- \quad K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = 10^{-6.35} \tag{1b}
\]

\[
\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.33} \tag{1c}
\]

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_w = \{[\text{H}^+][\text{OH}^-] = 10^{-14} \tag{1d}
\]

\{\} represents ion activities for the mass action equations with the equilibrium constants given valid at 25 °C and zero ionic strength ($\mu = 0$). The fugacity ($fCO_2$) may be approximated by the partial pressure of CO$_2$(pCO$_2$) in the air as the ideal behavior of CO$_2$ was considered in our study.

The soil pH$_{CO_2}$ is determined using the following equation:

\[
\text{Alkalinity} = C_B - C_A = \frac{K_H f CO_2}{\alpha_0} (a_1 + 2a_2) + \frac{K_w}{[H^+]} - [H^+] \tag{2}
\]

This equation represents experimentally measured alkalinity since it corresponds to the concentration of strong acid required to titrate the solution to the endpoint of bicarbonate. pH can be determined using equation [2] provided that the amounts of acid or base added to the system and pCO$_2$ are known. Equation (2), can be solved iteratively by the bisection method until the left-hand side (alkalinity) equals the right-hand side or via other
numerical methods (see the supplementary information, Additional File 1, for the full derivation of the equation).

**Soil extract preparation**

Nine soils collected from South Australia with a pH range of 6–8 (Table 1) and three replicates of each soil extract (1:1 w/v soil:water) were used in the study for pH measurements (refer to [32] for details).

**Laboratory experimental set up**

A laboratory experiment was conducted in which ca. 25 mL of soil extract was introduced into a custom-made equilibration flask (Fig. 1) which was connected via tubing to a flow-through cell on a double-beam spectrophotometer (GBC UV/VIS 916). The flask was placed on a temperature-controlled water bath adjusted to 25 °C. The temperature in the spectrophotometric cell holder was also kept constant at 25 °C using an installed water thermostat. A pH electrode (Orion SureFlow) was inserted into the flask that had been pre-calibrated with commercially manufactured (Australian Chemical Reagents) standard high ionic strength pH 7 and pH 4 buffers (m ≈ 0.1 mol L⁻¹) at 25 °C.

The soil extracts were equilibrated with a fixed pCO₂ via a gas tube connected to a pure air cylinder (BOC gases) inserted into the top of the equilibration cell (Fig. 1). The pCO₂ in the gas stream was measured using a calibrated LICOR 840a infra-red gas analyser. The air was circulated through the soil solution using slow bubbling for approx. 30 min per sample until the spectra of solution and the electrode pH measurement were stable.

Then for spectrophotometric pH measurement, a sulfonaphthalein indicator depending on the sample pH range (determined by the electrode) was selected and injected into the soil solution. The absorbance spectrum with dye was recorded for the circulating soil extract solution. The absorbance spectrum for the indicator was generated through subtraction of a baseline spectrum of soil solution without indicator dye (refer to [32] for details).

**Alkalinity measurement**

After pH measurement, a measured volume of soil solution and indicator dye was transferred into a separate beaker for alkalinity measurement. Great attention was taken to avoid solution loss by extracting all the solution out of the flow-through cell and connecting tubes. The solution was stirred gently, and initial pH was recorded when a stable reading was obtained, and then titration was conducted using an autotitrator to deliver increments of 0.16 N H₂SO₄ and continued to the end point at pH ≤ 4.5. pH was measured using a glass electrode after each acid addition. Adequate titration points were

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Table 1 Soil physical properties and major ion concentrations in a 1:1 w/v soil:water extract

| Depth, cm | Sand silt clay, % | Major cations and anions Cl⁻ NO₃⁻ SO₄²⁻ Ca²⁺ K⁺ Mg²⁺ Na⁺ meq L⁻¹ |
|----------|-------------------|-------------------------------------------------|
| Monarto 1* | 0–10  | 84.6  | 7.10  | 8.30 | 0.65 | 0.44 | 0.13 | 2.62 | 0.46 | 0.56 | 0.69 |
| Lock siliceous | 0–10  | 95    | 0     | 5    | 0.38 | 2.35 | 0.09 | 3.59 | 0.78 | 0.44 | 0.35 |
| Karoonda   | 0–10  | 97.4  | 0.2   | 2.40 | 0.24 | 0.24 | 0.11 | 0.39 | 0.25 | 0.21 | 0.20 |
| Ngarkat    | 0–10  | 95.80 | 1.0   | 3.20 | 0.18 | 0.04 | 0.05 | 0.25 | 0.11 | 0.17 | 0.21 |
| Lock Horizon B | 0–10 | 97.50 | 2.50 | 0  | 0.20 | 0.34 | 0.14 | 1.40 | 0.11 | 0.54 | 0.60 |
| Modra      | 0–10  | 65    | 5     | 30   | 3.36 | 5.70 | 0.31 | 5.72 | 1.34 | 1.39 | 1.34 |
| Monarto 2* | 0–10  | 93.6  | 1.1   | 3.8  | 0.31 | 0.24 | 0.19 | 0.50 | 0.39 | 0.30 | 0.25 |
| Cowirra    | 0–10  | 41.50 | 18.80 | 39.70 | 4.57 | 0.02 | 35.6 | 25.46 | 1.14 | 14.36 | 9.17 |
| Black point | 10–20 | 72.70 | 9.20 | 18.10 | 2.21 | 0.28 | 0.37 | 2.23 | 0.27 | 0.55 | 2.46 |

*Monarto 1 and Monarto 2 were selected from two locations (Highland and Highway, respectively)*
recorded, ensuring high accuracy. A gran linear extrapolation function was utilized to determine alkalinity for low ionic strength samples [40].

**Laboratory analytical measurements**

Stock solutions of bromocresol purple (BCP) and phenol red (PR) at a total concentration of \(3 \times 10^{-3}\) mol L\(^{-1}\) were used. The absorbance maxima (Abs) of acid and base forms of PR were read at 433 nm, 558 nm (\(\lambda_1\) and \(\lambda_2\)) and BCP at 432 nm, 589 nm (\(\lambda_1\) and \(\lambda_2\)), respectively, using the spectrophotometer Cintral™ software and used for \(R = (\lambda_2\text{Abs.}/\lambda_1\text{Abs.})\) calculation (see [32]). The value for molar absorbance ratios (\(e_1-e_3\)) and pK\(_2\) of indicators used in this study (PR and BCP) are those of [36].

The ionic strength (\(\mu\)) of each soil extract was determined via electrical conductivity (EC, mS cm\(^{-1}\)) measurement using a calibrated conductivity electrode (TPS Glass K = 1.0 Cond Sensor) using the equation

\[
\mu = EC \times 0.0127
\]  

[32, 41, 42].

The concentration of dissolved organic carbon (DOC) in filter soil solutions was also estimated using a spectrophotometer at an absorbance of 250 nm [43] using the regression equation

\[
[DOC] = 33.99 A_{250} + 8.16
\]

[43–45]. Concentrations of major cations (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), K\(^{+}\)) were measured by inductively coupled plasma optical emission spectroscopy (ICPOES) [46] and concentrations of anions (NO\(_3^-\), SO\(_4^{2-}\), Cl\(^-\)) were determined by ion chromatography using a Dionex ICS-2500 system [46] (Table 1).

**Geochemical modelling calculations**

To assess the internal consistency of the soil carbonate system, we compared the soil solution pH (n = 27, pH range of appx. 6–8) calculated from pCO\(_2\) (pH\(_{\text{CO}_2}\)), and alkalinity measurements using Eq. (2), to pH measured using both spectrophotometric (pH\(_{\text{spec}}\)) and glass electrode (pH\(_{\text{elec}}\)) methods. Carbonate system calculations were based on equilibrium constants reported by [39] at zero ionic strength (\(\mu = 0\)) and 25 °C with corrections for variable ionic strength made using the Davies equation.

The geochemical speciation program PHREEQC [47] was used to calculate carbonate mineral (calcite, aragonite, dolomite) saturation states from the fixed pCO\(_2\) and measured alkalinity, measured major ions and also at a range of elevated pCO\(_2\) (to assess the effect of climate change) values.

**Results and discussion**

Measurement and internal consistency of the soil carbonate system

The pH values calculated from pCO\(_2\) and alkalinity (pH\(_{\text{CO}_2}\)) and pH obtained using electrode and spectrophotometric methods (pH\(_{\text{elec}}\) and pH\(_{\text{spec}}\)) are shown in Table 2. An average precision of ca. 0.03 pH units was obtained for three replicate (pH\(_{\text{CO}_2}\)) measurements, which was similar to the recorded precision of measured pH\(_{\text{spec}}\) and pH\(_{\text{elec}}\) values (0.05 pH units) (Table 2). Hence the potential for spectrophotometric pH measurements to provide a higher accuracy for determining the carbonate system parameters (compared to a conventional glass electrode measurement) was not proven in this experiment. This may reflect our very careful pH electrode measurement protocols (e.g., temperature control, electrodes with free-flowing junctions designed for soil). Spectrophotometrically measured pH along with another carbonate system parameter has been the most common and accurate approach to calculate oceanic pCO\(_2\) [23, 26]. This might be particularly important in saline soils where there are difficulties in calibrating glass electrodes to enable accurate measurement.

A plot of the residual of pH\(_{\text{CO}_2}\) minus pH\(_{\text{elec}}\) and pH\(_{\text{spec}}\) (Fig. 2a), shows that calculated pH (pH\(_{\text{CO}_2}\)) was in general higher than the measured pH values (pH\(_{\text{elec}}\) and pH\(_{\text{spec}}\)). There was a good agreement between measured and calculated pH for soil extracts with pH > 7 (Table 2, Fig. 2a) with an average difference of approximately 0.1 pH units. These results show that the soil carbonate system model using the constants of [39] was internally consistent with measurements in pH > 7 extracts. While the internal consistency of the seawater CO\(_2\) system has been previously demonstrated [18, 23, 26, 27, 31], our measurements show it is possible to demonstrate this in soil solutions. This is important as it demonstrates, for the first time to our knowledge, that carbonate system equilibria can be accurately modelled in soils.

However, there was a larger deviation of 0.3–0.8 pH units for those samples with pH ≤ 7 (Table 2, Fig. 2a), which mainly corresponded to soil extracts with low alkalinity of < 0.5 meq L\(^{-1}\) (Fig. 2b). Inconsistencies in the pH-DIC-pCO\(_2\) relationship have been previously explained with regards to the difference between TA

| Soil          | pH\(_{\text{CO}_2}\) (SD) | pH\(_{\text{spec}}\) (SD) | pH\(_{\text{elec}}\) (SD) |
|---------------|------------------------|------------------------|------------------------|
| Lock Siliceous| 7.98 (0.01)            | 8.00 (0.09)            | 7.91 (0.03)            |
| Ngarkat       | 7.08 (0.01)            | 7.03 (0.04)            | 6.79 (0.03)            |
| Monaro 1      | 8.06 (0.01)            | 8.06 (0.03)            | 8.11 (0.04)            |
| Modra         | 7.60 (0.04)            | 7.67 (0.04)            | 7.63 (0.02)            |
| Lock Horizon  | 8.17 (0.03)            | 8.12 (0.04)            | 8.10 (0.04)            |
| Karoonda      | 7.05 (0.06)            | 6.47 (0.08)            | 6.24 (0.14)            |
| Monaro 2      | 7.17 (0.12)            | 6.75 (0.06)            | 6.63 (0.06)            |
| Cowirra       | 7.79 (0.01)            | 7.74 (0.05)            | 7.72 (0.02)            |
| Black point   | 7.94 (0.01)            | 8.04 (0.03)            | 8.04 (0.01)            |
| Average SD    | 0.03                   | 0.05                   | 0.05                   |
through the carbonate model and measured TA concentrations [26]. Measured TA constitutes the contribution of both organic bases [26, 30, 31, 48] and carbonate species. Conversely, calculation of TA via the thermodynamic carbonate model used in this study does not include the contribution of organic bases as they cannot be easily measured. However, in an attempt to determine the source of total alkalinity surplus relative to calculated carbonate, dissolved organic carbon (DOC) for all samples was estimated via spectrophotometric measurements in the UV-range [43] (Table 3). There was little difference DOC among the samples, with all extracts containing approximately 70 mg L$^{-1}$ DOC, except Lock B (33.5 mg L$^{-1}$).

For those samples with low alkalinity $\leq 0.5$ meq L$^{-1}$ the discrepancy between total (Gran, measured

![Fig. 2](image-url)  
*Fig. 2* Difference between pH calculated using carbonate systems and spectrophotometric and electrode pH measurements for different soils against spectrophotometric pH values (a). Difference between calculated and measured pH values as a function of total alkalinity (b).

| Soil          | $T_{A\text{tit}}$ (SD), meq L$^{-1}$ | Estimated DOC, mg L$^{-1}$ |
|---------------|--------------------------------------|---------------------------|
| Lock siliceous| 1.38 (0.05)                           | 74.69                     |
| Monarto 1     | 1.66 (0.03)                           | 78.14                     |
| Ngarkat       | 0.18 (0.01)                           | 62.08                     |
| Modra         | 0.62 (0.05)                           | 68.88                     |
| Lock B        | 2.9 (0.17)                            | 33.50                     |
| Karoonda      | 0.19 (0.01)                           | 70.91                     |
| Monarto 2     | 0.25 (0.03)                           | 73.71                     |
| Cowirra       | 1.06 (0.09)                           | 76.64                     |
| Black point   | 1.28 (0.01)                           | 75.24                     |
alkalinity) and carbonate alkalinity (calculated TA using the model) seems likely to have been caused by the uptake of protons by organic bases (Table 2). To further assess this, the organic alkalinity of soil solutions was estimated from the difference between measured total alkalinity and carbonate alkalinity calculated using the thermodynamic carbonate model (Eq. 2) with the measured spectrophotometric pH and experimentally fixed pCO2 as inputs. The % of organic alkalinity versus total alkalinity shown in Fig. 3 suggests that the low alkalinity soils in general have a much higher proportion of organic alkalinity. Hence it may be preferable to not use alkalinity as a measured parameter for carbonate system calculations in some soils with low alkalinity. Measuring another parameter of the soil carbonate system such as pCO2 or dissolved inorganic carbon (DIC) could be preferable in these soils. Spectrophotometric carbonate ion measurements have recently been developed [49] and may enable precise values that can be used for internal consistency calculations in soils.

Calculation of carbonate mineral saturation states
Calcite, aragonite and dolomite saturation states (mg L\(^{-1}\)) of soil solutions were calculated from non-fixed pCO2 (pH\(_{\text{spec}}\) and TA) and fixed pCO2 (pCO2 and TA) using the geochemical speciation program PHREEQC. There was variability in carbonate mineral saturation states with some over-saturated (SI > 0 at pH\(_{\text{PHREEQC}}\) > 8, suggesting mineral calcite could precipitate from solution) and some under-saturated (SI < 0 at pH\(_{\text{PHREEQC}}\) < 8, suggesting calcite dissolution) (Table 4).

Simulating increasing pCO2 in soil solutions
As noted above soil pCO2 is one of the most important variables governing soil solution pH [50] and this is also influenced by atmospheric pCO2 changes. To indicate the potential application of an internally consistent carbonate system model to assess climate and/or biogeochemical process change effects, we modelled the influence of four elevated soil pCO2 scenarios (1000, 2500, 5000, and 10,000 µatm). Soil pH decreased from 0.4 to 1 pH units as a consequence of increased pCO2 levels from 1000 to 10,000 µatm respectively (Fig. 4). The effect of elevated pCO2 on calcite/aragonite (CaCO3) and dolomite (CaMg(CO3)2) saturation status (calculated using PHREEQC from pH, alkalinity and major ion concentrations) of these soils is shown in Fig. 5. The soils that are initially supersaturated relative to carbonate minerals at current atmospheric pCO2 levels (≈ 400 µatm) transition to undersaturated in the 500–1000 µatm pCO2 range. This is because carbonate ion concentrations have declined due to the lowering of pH (Fig. 4). In contrast the soils that are undersaturated at current atmospheric pCO2 levels (Karoonda, Ngarkat, Modra, Monarto 2) remain undersaturated as expected under elevated pCO2. This suggests that carbonate minerals in some surface soils could be highly vulnerable to dissolution due to global climate change, which could result in large pH

Table 4 Calculated pH (pH\(_{\text{PHREEQC}}\)) and calcite, aragonite and dolomite saturation status using the geochemical speciation program PHREEQC

| Soil         | pH\(_{\text{PHREEQC}}\) | SI-Calcite, Aragonite and Dolomite (pH\(_{\text{spec}}\) and TA) (mg L\(^{-1}\)) | SI-Calcite, Aragonite and Dolomite (pCO2 and TA) (mg L\(^{-1}\)) |
|--------------|--------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------|
| Lock Siliceous | 8.27                     | 0.28, 0.14, –0.20                                                              | 0.54, 0.39, 0.30                                               |
| Monarto 1     | 8.36                     | 0.34, 0.19, 0.14                                                               | 0.62, 0.48, 0.71                                               |
| Ngarkat       | 7.41                     | –2.5, –2.7, –5.20                                                              | –2.20, –2.3, –4.4                                              |
| Modra         | 7.89                     | –0.28, –0.42, –1.04                                                            | –0.06, –0.21, –0.61                                           |
| Lock Horizon  | 8.47                     | 0.25, 0.10, 0.22                                                               | 0.58, 0.43, 0.88                                               |
| Karoonda      | 7.38                     | –2.9, –3.14, –6.12                                                             | –2.09, –2.2, –4.3                                              |
| Monarto 2     | 7.51                     | –2.4923, –2.6361, –5.0855                                                      | –1.7, –1.8, –3.5                                              |
| Cowira        | 8.04                     | 0.35, –0.02, –0.23                                                             | 0.64, 0.17, 0.16                                              |
changes once this buffer is exhausted. It is also important to note that our measurement set-up and models assumed an open system with fixed pCO2. Nevertheless, the internal consistency demonstrated should also apply to a closed system where pCO2 can vary while DIC is fixed.

The soil carbonate system measurement and modelling conducted in this study is an important first step for enabling a better understanding of related soil geochemical processes, in particular risks of inorganic carbonate dissolution due to global climate change. However, it would be important to see if internal consistency can also be demonstrated in situ. For this purpose, field experiments are now suggested accompanied by both spectrophotometric and electrode soil pH measurement methods. The influence of soil respiration, which affects both pCO2 and pH, also needs to be considered in the design of field measurements. Widespread global measurement of soil pH and calcium carbonate states using these methods would appear beneficial to assess the soil system response to climate change.

**Conclusions**

In this study, the internal consistency of the soil carbonate system was assessed using experimental measurements and a thermodynamic equilibrium carbonate system model. The pCO2 was fixed in the experiment by equilibrating the soil solution with air with a known pCO2. Discrepancy of calculated pH from measured pH using spectrophotometric and glass electrode methods was within 0.00–0.1 pH units when alkalinity was > 0.5 meq L\(^{-1}\). This implies accurate prediction of pH from other carbonate system parameters is feasible using inorganic carbon system equilibrium calculations. However, contribution of organic bases appeared to result in errors in the calculated pH for samples with low alkalinity < 0.5 meq L\(^{-1}\). Nevertheless, this appears to be the first time that the internal consistency of soil carbonate system has been demonstrated. This enables a better understanding of soil responses to global climate change. Further development and application of methods for low alkalinity or organic-rich soils, and in situ measurement, is recommended.
Fig. 5  Modelled relationship between calcite, aragonite and dolomite saturation state and soil pCO₂
Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s12932-020-00069-5.

Additional file 1. Includes theory and derivation of equations that underpin soil pH determinations using acid-base equilibria of CO2.

Abbreviations

TA: Total alkalinity; DIC: Dissolved inorganic carbon; pHCO2: Calculate pH using the carbonate model; pHMeq and pHMeq: Measured pH using spectrophotometric and glass electrode methods; DOC: Dissolved organic carbon; pHiCO2: pH calculated by PHREEQC program; EC: Electrical conductivity; TAeq: Alkalinity titration; SD: Standard deviation; BCP: Bromocresol purple; PR: Phenol red.

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Authors’ contributions

SB carried out experiment, data collection, data analysis and interpretation, wrote manuscript and acted as corresponding author. LMM conceived and supervised development of work, data interpretation, manuscript evaluation and correction. All authors read and approved the final manuscript.

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Availability of data and materials

All results of this article are available in the manuscript and figures, and also in the Ph.D. thesis of Sima Bargrizan.

Consent for publication

All authors have consented to publication.

Competing interests

The authors declare that they have no competing interests.

Author details

1 The School of Agriculture, Food and Wine, The University of Adelaide, Waite Campus, Adelaide, SA 5064, Australia. 2 Acid Sulfate Soils Centre, School of Biological Sciences, The University of Adelaide, Adelaide, Australia.

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