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ALKALINITY MEASUREMENTS IN WATER EXTRACTS OF CALCAREOUS SOILS

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Abstract

In soil carbonate solubility studies, it is usually assumed that total alkalinity is equal to inorganic-C alkalinity. Recent studies have raised questions about the validity of this assumption. This study reexamined previously published soil data from grass-oak (*Quercus* spp.) woodlands and deserts to test the hypothesis that total alkalinity is equal to inorganic-C alkalinity. Total alkalinity was measured with strong-acid titration, while inorganic-C alkalinity was calculated from pH and the partial pressure of CO₂ (*p*CO₂) measurements. Within the limits of error, calculated inorganic C alkalinity (*Y*) was equal to measured total alkalinity (*X*) ($Y = 0.01 + 0.998X$, $r^2 = 0.97$). A recommendation was made for overdetermining the state of experimental systems in solubility studies; this allows one to check the internal consistency of experimental measurements, equilibrium constants, and model assumptions.

WHEN MEASURING the solubility of CaCO₃ in calcareous soils, the assumption is generally made that measured total alkalinity is equivalent to inorganic-C alkalinity (Olson and Watanabe, 1959; Marion and Babcock, 1977; Suarez, 1977; Levy, 1981; Suarez and Rhoades, 1982; Inskip and Bloom, 1986). In several recent studies, total alkalinity was separated from inorganic-C alkalinity (Amrhein and Suarez, 1987; Takkar et al., 1987; Reddy et al., 1990); these studies

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indicated that organic anions may, at times, contribute significantly to total alkalinity. If this is true in general, then previously reported studies and their conclusions, especially that soils are generally supersaturated with respect to calcite, will need to be reexamined.

Alkalinity, pH, and *p*CO₂ are not independent variables in pure inorganic C solutions (Olson and Watanabe, 1959; Stumm and Morgan, 1970; Marion and Babcock, 1977). Given any two of the above three variables, it is possible by successive approximations to calculate the third (or unspecified) variable. Therefore, it is possible to theoretically calculate the inorganic-C alkalinity based on pH and *p*CO₂ measurements. The objective of this study was to reexamine previously published data on the solubility of CaCO₃ in calcareous soil suspensions in order to test the hypothesis that total alkalinity is equal to inorganic C alkalinity.

Materials and Methods

This study reexamined data from three previously reported studies. The soils in the Marion and Babcock (1977) study were from near Livermore in northern California and were found under mixed grass and oak woodland. The soils in the Schlesinger (1985) study were from the Mohave Desert near Desert Center, CA. The Marion et al. (1990) study site was the Jornada Experimental Ranch in the Chihuahuan Desert near Las Cruces, NM.

All three studies used the same experimental design and the same computer speciation model. Briefly, 1:5 soil/water suspensions were prepared through which gas of a known CO₂ composition was bubbled at 25°C. In the Marion and Babcock (1977) study, aliquots were centrifuged at 12500 rpm for 10 min after sampling to remove suspended material. In the two later studies, aliquots were filtered sequentially through Whatman glass microfibre (GF/F) (Whatman Ltd., Maidstone, England) and Millipore 0.45-µm (HA) filters (Millipore Corp., Bedford, MA).

Critical to this study are the methods used to determine pH, *p*CO₂, and total alkalinity. The pH was measured in a special cell through which the gas of fixed *p*CO₂ was passed. The pH electrode and meter were calibrated with commercial buffer solutions that were accurate to ±0.02 pH units. In the Marion and Babcock (1977) study, *p*CO₂ was estimated in NaHCO₃ solutions of known composition through which the CO₂ gas (0.90 kPa) was bubbled; this method relies on Na and pH measurements, a charge-balance equation, and the equilibrium constants for H₂CO₃. In the other two studies, CO₂ concentrations were measured by gas chromatography (range 0.040-0.053 kPa). Total alkalinity was measured by titration with standardized HCl. The specific method used by Marion and Babcock (1977) is an adaptation of a procedure to standardize HCl with Na₂CO₃ using a mixed methyl red-bromocresol green indicator to determine the titration endpoint (Blaedel and Meloche, 1963; American Public Health Association, 1985). The soil solution is titrated with standard HCl until the first trace of a color change occurs (green to red, pH ≈ 4.5). At this point, the samples are heated to boil away accumulated CO₂, which causes the solutions to revert to green. After cooling to room temperature, the titration is completed to a sharp endpoint. The possibility that CaCO₃ might precipitate following removal of CO₂ by boiling between the initial and final titrations is unlikely because the initial titration converts an alkaline, predominantly Ca(HCO₃)₂ solution into an acidic, predominantly CaCl₂ solution. In the two later studies, the solutions were titrated to a fixed pH endpoint (4.3).

Solution-phase concentrations were calculated by successive approximations using the Newton-Raphson method

with a computer program that corrected for the presence of ion pairs (Marion and Babcock 1977; Marion, 1991). The convergence criterion was that successive estimates of each constituent had to agree within $\pm 1\%$ for every solution-phase constituent. At each iteration, the ionic strength was reestimated and then used to estimate activity coefficients using the Davies equation (Lindsay, 1979). Ion pairs were considered between the cations, Ca^{2+} , Mg^{2+} , K^+ , and Na^+ , and the anions, HCO_3^- , CO_3^{2-} , and SO_4^{2-} . Stability constants for the ion pairs and H_2CO_3 were taken from Lindsay (1979).

The computer program has three input options requiring a specification of (Option 1) pH and alkalinity, or (Option 2) $p\text{CO}_2$ and alkalinity, or (Option 3) $p\text{CO}_2$ and pH. Given any one of these options plus measurements of total dissolved Ca, Mg, K, Na, Cl, and SO_4 , the program calculates the true ionic concentrations in the solution phase. Copies of this program (on disk), written in TrueBASIC and operating on either a Macintosh or MS-DOS (IBM-compatible) computer in stand-alone versions, are available from the corresponding author.

At present, the computer program in Options 1 and 2 assumes that measured total alkalinity is equivalent to inorganic-C alkalinity, and therefore partitions the alkalinity among the inorganic-C species. If this assumption is incorrect, then the program will overestimate the true inorganic-C concentrations and, as a consequence, overestimate the true ion activity products for CaCO_3 . Given measurements of $p\text{CO}_2$ and pH (Option 3), however, the computer program will calculate the true concentrations of inorganic-C species, which can then be compared with the measured total alkalinity.

Results and Discussion

For the regression of calculated inorganic-C alkalinity on measured total alkalinity (Fig. 1), the intercept of the regression line (0.01) is not significantly different from 0.0, and the slope (0.998) is not significantly different from 1.000; 97% of the variation is accounted for by this regression equation. There are a few data points somewhat far removed from the regression line, but these are probably measurement errors. A few points at low alkalinities from Marion et al. (1990) may be a systematic deviation from the regression line, suggesting that total alkalinity may not always be equal to inorganic-C alkalinity. Overall, however, calculated inorganic-C alkalinity is equal to

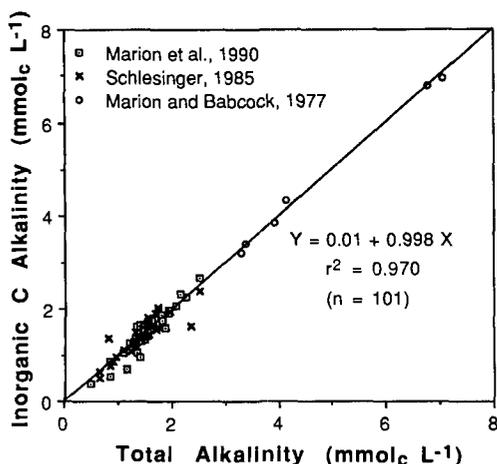


Fig. 1. A comparison between calculated inorganic-C alkalinity and measured total alkalinity from three previous studies.

measured total alkalinity. Recently, in a reevaluation, Suarez et al. (1990) also concluded that total alkalinity was equal to inorganic-C alkalinity.

On the other hand, there are clearly cases where the two measures of alkalinity are not equal. For example, Amrhein and Suarez (1987) examined CaCO_3 solubility in the presence of decomposing plant materials; provisions were made in the analytical methods to separate total and inorganic-C alkalinities. Noncarbonate alkalinities reached values as high as 1.2 mmolc L^{-1} in the latter study. In another study by Reddy et al. (1990), there was a consistent difference between total alkalinity estimated by strong-acid titration and inorganic-C alkalinity estimated from dissolved inorganic C. Takkar et al. (1987) attributed lack of agreement between titratable alkalinity and an independent estimate of dissolved inorganic C to the presence of organic compounds in solution.

Critical to the interpretation of alkalinity measurements is the method used. The end point in the alkalinity titration is not sharp due to the presence of accumulated CO_2 (Blaedel and Meloche, 1963; Stumm and Morgan, 1970; American Public Health Association, 1985). This end point can be sharpened considerably, and accuracy and precision improved, by removing accumulated CO_2 from the solution either by scrubbing with CO_2 -free air during titration or by boiling off the CO_2 prior to final titration. Where accuracy and precision are paramount, provision should be made for removing accumulated CO_2 in the alkalinity titration.

In laboratory experiments with carbonate systems, it is possible to measure or control pH, $p\text{CO}_2$, and alkalinity. To estimate equilibrium aqueous-phase chemical compositions, two of the latter three properties must be known (assuming total alkalinity = inorganic-C alkalinity). Measuring all three properties leads to an overdetermination of the state of the system. This overdetermination allows one to check the internal consistency of experimental measurements, equilibrium constants, and model assumptions. Thirty years ago, there were major uncertainties concerning the validity of pH measurements (Olson and Watanabe, 1959; Jenny, 1961); today the interpretation of alkalinity is in question. These uncertainties can frequently be eliminated by overdetermining the state of experimental systems, as was done in this study by measuring pH, $p\text{CO}_2$, and alkalinity. Where possible in solubility studies, experimental systems should be overdetermined.

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TRANSPORT IN A HORIZONTAL FLOW CHAMBER

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Abstract

A better understanding is needed of the factors that control the fate of chemicals that move laterally in shallow groundwater within fields to tile lines and drainage ditches and from fields to nearby streams or estuaries. A chamber was designed and used to simulate shallow groundwater flow in the field. The chamber, made of Plexiglas with dimensions 120 by 60 by 60 cm, was filled to a depth of 30 cm with sand. A multiport arrangement of 10-mm-diam. holes on a 5 by 5 cm grid on both end walls of the chamber provided a combination for quite uniform solute application at the inlet side, and allowed sampling simultaneously from all ports at the outlet side. As a first approximation, the flow and transport were assumed to be one dimensional, and a convective-dispersive solute-transport model was applied to the Cl breakthrough data of each of the 50 outlet ports in order to quantify the spatial distribution of the dispersion-coefficient values at the outlet plate. Based on the inconsistency observed between measured and estimated pore-water velocities and dispersion coefficients of each of the 50 outlet ports, it appears that the one-dimensional model is not appropriate to adequately characterize transport parameter in this horizontal flow system.

THE FATE of agrochemicals in a shallow phreatic layer that are moving laterally to tile lines through

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riparian zones is increasingly important to environmental studies. A first approximation to modeling and field experimental design for such lateral-flow conditions can be accomplished under laboratory conditions.

In the past, most laboratory-flow studies were designed to examine the vertical movement of water and solutes (Starr and Parlange, 1976; Rao et al., 1980). Studies of horizontal solute transport have been largely limited to unsaturated conditions, or have considered only short soil columns (Elrick et al., 1979; Clothier and Elrick, 1985; Clothier et al., 1988). Here, we present results from an experiment using a laboratory-scale chamber to simulate horizontal flow conditions that might occur in the field.

Materials and Methods

A laboratory chamber was constructed out of 1.2-cm-thick Plexiglas with the dimensions of 120 by 60 by 60 cm (Fig. 1). Six rows of 1-cm-diam. holes were drilled through the 60 by 60 cm end walls of the chamber on a 5 by 5 cm spacing, starting 2.5 cm from the bottom (and corner) of each wall. The holes on the inlet wall were connected to a small manifold (1.5-cm i.d. and 30 cm long) via 3-mm-i.d. vinyl tubing, and connected to a Mariotte siphon apparatus (Klute and Dirksen, 1986). The outlet holes were connected to a Plexiglas sampling plate with the vinyl tubing. This construction provided an opportunity for simultaneous sampling from all the outlet ports at the same pressure head, and control of the pressure potential at the inlet (by the Mariotte apparatus) and the outlet (by adjusting the height of the sampling plate).

A thin layer of cheesecloth was placed on the inside of the perforated inlet and outlet walls to prevent sand from entering the inlet tubes. Water was then added to a sieved sand (<2 mm) to a gravimetric water content of $\approx 30 \text{ g kg}^{-1}$ to minimize particle separation during packing. A known amount of sand, equivalent to a 1.5-cm depth at a ρ_b of $\approx 1.35 \text{ g cm}^{-3}$, was added sequentially to the chamber. Careful tamping between sand additions, followed by scratching of the top of the upper layer, was done to obtain a near-uniform density throughout the chamber. The final depth of the sand was $\approx 30 \text{ cm}$, covering six rows at the inlet and outlet walls. Two pressure transducers were installed at equally spaced distances along the length of the chamber, for head measurements, providing information for calculating the pressure gradient along the chamber (Fig. 1).

A steady-state condition with respect to horizontal water flow was established by maintaining the height of the water level at the inlet side $\approx 2 \text{ cm}$ below the sand surface, and by leveling the outlet tips with the second row at the outlet side (i.e., $\approx 7.5 \text{ cm}$ below the sand surface). This resulted in a hydraulic gradient of $\approx 0.046 \text{ cm cm}^{-1}$ for all 60 outlet ports. No discharge was obtained from Row 1 since it was in the unsaturated zone, and the two end columns were discarded due to possible side-wall effects. The bulk pore-water velocity for the chamber, with the saturated water content (θ) of $0.470 \text{ cm}^3 \text{ cm}^{-3}$ for the saturated sand, was 36.8 cm d^{-1} .

After constant flow was established with distilled water, an 87-h pulse of 0.714 mM CaCl_2 solution was instantaneously added through the inlet manifold. Immediately after switching the connection of the manifold from distilled water to CaCl_2 solution, the manifold was flushed with the CaCl_2 solution. Effluent samples were then collected from the outlet ports at time intervals ranging from 2 to 12 h during

Abbreviations: BTC, breakthrough curves; ρ_b , soil bulk density; θ , soil water content.