

Spatial Variability of CaCO_3 Solubility in a Chihuahuan Desert Soil

G. M. MARION

USACRREL
72 Lyme Rd.
Hanover, New Hampshire 03755

W. H. SCHLESINGER

Botany Department
Duke University
Durham, North Carolina 27706

P. J. FONTEYN

Biology Department
Southwest Texas State University
San Marcos, Texas 78666

Abstract *Spatial variability in CaCO_3 solubility is an important factor in parameterizing simulation models and designing experiments. The objective of this study was to quantify the spatial variability, both horizontal and vertical, in CaCO_3 solubility in a Chihuahuan Desert soil. CaCO_3 solubilities were estimated in 1:5 soil:water suspensions. Soil horizon extracts were generally supersaturated with respect to calcite. The mean (± 1 SE) pIAP(CaCO_3) for the A, B_{k1} , and B_{k2} horizons were 8.03 (0.055), 8.19 (0.019), and 8.26 (0.015), respectively. The differences in pIAP between the A and B horizons (vertical variability) were statistically significant; these differences could be due to organic matter inhibition of calcite precipitation. Supersaturation with respect to calcite and vertical variability in CaCO_3 solubility needs to be explicitly considered in simulation models. The standard errors in pIAP (horizontal variability) were greatest for the A horizons and decreased with increasing soil depth. Given the inherent variability in CaCO_3 solubility, a large sample size is necessary to detect small differences in CaCO_3 solubility for this Chihuahuan Desert soil.*

Keywords CaCO_3 solubility, desert soils, spatial variability, experimental design, simulation modeling.

Introduction

Considerable attention has centered on what controls the solubility of CaCO_3 in soils. The preponderance of evidence indicates that soils are supersaturated with respect to calcite (Olsen and Watanabe 1959, Marion and Babcock 1977, Suarez 1977, Suarez and Rhoades 1982, Inskip and Bloom 1986, Amrhein and Suarez 1987); calcite is the most thermodynamically stable polymorph of CaCO_3 (Lindsay 1979). In calcareous soils, the

Received: October 16, 1989; accepted: March 5, 1990.

solubility of CaCO_3 is a major factor controlling (1) soil pH, (2) acid neutralization reactions, (3) the availability of plant nutrients such as P and Fe, and (4) the mobility of Ca through soils (Dutt *et al.* 1972, Robbins *et al.* 1980, Bohn *et al.* 1985, Marion *et al.* 1985, McFadden and Tinsley 1985).

Despite the obvious importance of CaCO_3 solubility, we were unable to find any soil studies where the spatial variability of CaCO_3 solubility was evaluated within experimental plots. There are a few soil studies where horizontal variability at a larger scale have been reported (Suarez 1977, Inskeep and Bloom 1986). We have found no studies where the vertical variability in CaCO_3 solubility have been reported. A knowledge of spatial variability is particularly important for parameterizing simulation models and designing field experiments. The objective of this paper was to determine the spatial variability (both horizontal and vertical) of CaCO_3 solubility in a Chihuahuan Desert soil.

Methods and Materials

Study Area

Located on the Jornada Experimental Ranch, the study area is part of the Desert Long-term Ecological Research (LTER) program of New Mexico State University. The climate is arid, with mean annual rainfall averaging 210 mm. Vegetation is dominated by creosotebush (*Larrea tridentata* (DC.) Cov.) and snakeweed (*Gutierrezia sarothrae* (Pursh) Britt. & Rusby) (Schlesinger *et al.* 1987).

The soils are located on an alluvial piedmont formed from the monzonite parent materials of Mount Summerford, northernmost peak of the Doña Ana Mountains, located 40 km NNE of Las Cruces, New Mexico. The alluvial material forms the Jornada II geomorphic surface, on which there have been 25,000–75,000 years of soil profile development (Gile *et al.* 1981). Most soils are coarse loamy, mixed thermic Haplargids of the Onite Series. Some profiles show evidence of surface erosion and/or deposition of more recent, Organ sediments. These profiles are classified as Calciorthids in the Whitlock series.

Field and Laboratory Methods

Soil profiles were described in the field with the consultation of Leland Gile (retired) of the Soil Conservation Service. Soil samples (16) were collected from five soil pits that were used for intensive study. These pits were excavated within a 0.15-ha (30 × 50 m) area. In addition to the soil pits, 56 samples were obtained from the recognized horizons in eighteen 0.1-m-diameter soil cores taken in the same area. A total of 72 soil horizons were sampled from 23 soil profiles in the 0.15-ha area.

Samples for bulk density were taken from the walls of the soil pits using a sharpened brass corer of 420-cm³ volume. These samples were dried at 100°C for 24 h and weighed. Additional samples were taken from each horizon for determination of CaCO_3 content (Horton and Newsom 1953), cation exchange capacity using the arid land soils method of Rhoades (1982), and particle size distribution using the hydrometer method with a clay reading at 2.0 h (Day 1965). For samples with <10% clay we found good agreement between the hydrometer method and analyses made with the pipette method by the National Soil Testing Laboratory, Lincoln, Nebraska (unpublished data). CaCO_3

was determined on whole soil, whereas all other analyses were determined on the <2-mm fraction.

Equilibrium between the solid and solution phases was evaluated by equilibrating 40 g of sieved (<2 mm), air-dried soil and 200 mL of distilled water, forming a 1:5 suspension. At the time the soil samples were collected, they were near air-dry; the loss of water from the bulk density samples dried at 110°C was in the range 1–3%. Following the methods of Marion and Babcock (1977), these samples were shaken in 250-mL flasks in a constant temperature (25°C) waterbath for 10 days. Throughout this equilibration, the samples were bubbled with air containing 0.050% CO₂ in a controlled environment chamber in the Duke University Phytotron.

A large soil:water ratio (1:5) was selected for these experiments because this allowed for frequent sampling to establish the equilibrium time, the time at which Ca solubility becomes time-invariant. A preliminary test showed that under the shaking and bubbling regime imposed in these experiments, 10 days were sufficient for equilibration (Fig. 1); between 7 and 24 days, the total dissolved Ca concentrations for individual soil horizons were essentially constant except for one aberrant A horizon measurement at 24 days.

At the end of the equilibration, the 72 samples were filtered sequentially through Whatman glass microfiber (GF/F) and Millipore 0.45- μ m (HA) filters. Each of the 72 samples was analyzed once except for a few quality control samples. Total dissolved Ca, Mg, K, Na, pH, alkalinity (HCO₃⁻ + CO₃²⁻), SO₄²⁻, Cl⁻, and dissolved organic carbon (DOC) were determined in the filtrate. pH was determined on an Orion 701 pH meter using a Ross Combination Electrode while the sample was bubbled with air containing 0.050% CO₂. Total dissolved SO₄²⁻ and Cl⁻ were determined by ion chromatography on a Dionex 2010i system. Total dissolved Ca, Mg, K, and Na were determined with a

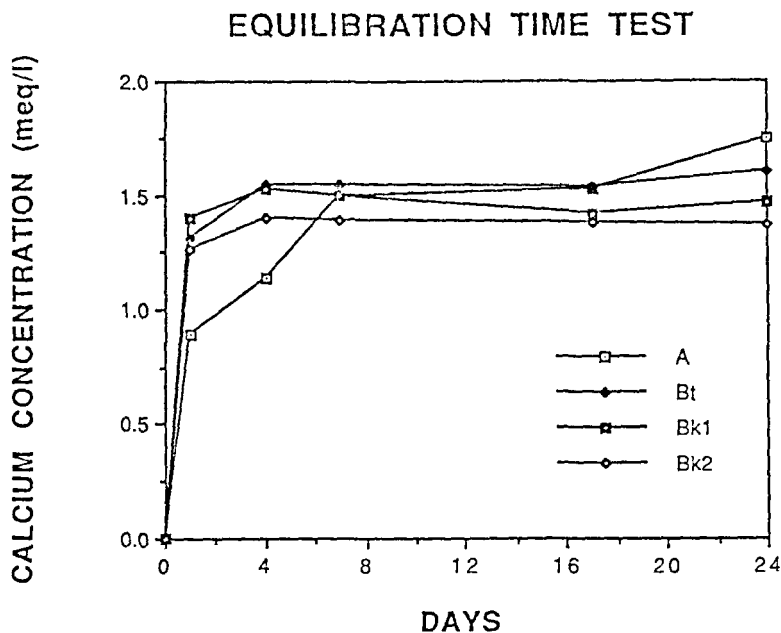


Figure 1. The equilibration time test for the desert soils.

Perkin-Elmer atomic absorption spectrophotometer. Alkalinity was determined by titration with a standardized acid. DOC was measured with an OIC (O.I. Corporation) carbon analyzer.

Solution Phase Activity Calculations

Solution phase activities 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). 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. 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 carbonic acid were taken from Lindsay (1979). The Davies equation was used to calculate ion activity coefficients (Sposito 1981).

The computer program has three input options requiring a specification of (1) pH and alkalinity, (2) P_{CO_2} and alkalinity, or (3) P_{CO_2} and pH. Given any one of these options plus measurements of total dissolved Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , and SO_4^{2-} , the program calculates the true ionic concentrations in the solution phase.

To simplify tabulation of the ion activity products (IAP), the conventional logarithmic transformation was undertaken:

$$p\text{IAP}(\text{CaCO}_3) = -\log[(\text{Ca}^{2+})(\text{CO}_3^{2-})] \quad (1)$$

where parentheses denote activities.

Statistical Analyses

Means, standard errors, and analysis of variance (ANOVA) were conducted using standard statistical techniques (Steel and Torrie 1960). The log-transformed data (Eq. 1) were tested for normality using the Shapiro-Wilk's test (Shapiro and Wilk 1965). A one-way ANOVA was used to test for significant differences among soil horizons. Whenever a significant F value was found in the ANOVA analysis, Tukey's multiple comparison test was used to test the individual means for significant differences.

Results

The Soils

Pit 1 showed a distinct horizon of clay accumulation (B_1) and was classified as a Typic Haplargid; pits 3, 4, and 6 lacked argillic horizons and were Calciorthids (Table 1). Pit 5 showed a lack of horizonation in the upper 18 cm, which consisted of recent alluvial deposition that buried earlier horizons formed in this profile. All horizons contained some CaCO_3 , which increased with depth from a mean of 9.0 g kg^{-1} in the surface horizon. Carbonate was visible as filaments in the B_{k1} horizon that typically extended from 2 to 37 cm in depth. All soil profiles showed stage III carbonate cementation (Gile *et al.* 1981) in a B_{k2} horizon that averaged 37 (± 2.7) cm in depth and 20 cm in thickness. Mean CaCO_3 content of this horizon was 152 g kg^{-1} in the five soil pits (Table

Table 1
A Summary of Physical and Chemical Properties of Soils

Soil Pit	Soil Horizon	Horizon Thickness (m)	Bulk Density (Mg m ⁻³)	Texture (g kg ⁻¹)			Cation Exchange Capacity (cmol(+) kg ⁻¹)	CaCO ₃ Content (g kg ⁻¹)
				Sand	Silt	Clay		
1	A	0.02	1.49	870	78	52	42	5.2
	B _t	0.09	1.57	698	208	94	73	5.4
	B _{k1}	0.33	1.35	618	199	183	74	39.0
	B _{k2}	0.15	1.37	662	179	159	42	170.0
3	A	0.03	1.46	807	128	64	58	1.5
	B _{k1}	0.19	1.52	723	192	85	33	44.7
	B _{k2}	0.28	1.40	657	245	98	14	194.7
4	A	0.04	1.54	733	176	92	96	1.4
	B _{k1}	0.23	1.48	676	233	92	77	44.0
	B _{k2}	0.26	1.21	683	242	75	67	124.6
5	C	0.18	1.56	890	59	51	38	19.3
	B _{k1b}	0.15	1.24	673	245	82	85	94.5
	B _{k2b}	0.10	1.38	627	297	76	46	143.8
6	A	0.05	1.28	803	146	51	60	17.8
	B _{k1}	0.40	1.45	782	175	44	102	40.8
	B _{k2}	0.06	1.36	704	239	58	25	125.8

1). In several pits, localized discontinuities or "pipes" (Gile *et al.* 1981) were seen in the calcic horizon.

The Soil-Water Suspensions

Calcium and alkalinity made up the majority of the cationic and anionic charges in the soil suspensions (Table 2). Concentration of Cl were highest in the B_{k1} horizon. This concentration peak may indicate the mean annual depth of wetting under the current climatic regime (Eisenberg *et al.* 1982); but, Schlesinger *et al.* (1987) report some seasonal fluctuation in soil moisture at 70 cm in the same area. Whereas the concentration of Na in the soil extracts increased with depth, the highest K was found in the surface samples and probably reflects the circulation of K by biota. Similar results were reported by Schlesinger (1985) for soil profiles in the Mojave Desert.

Two tests were made on the internal consistency of the soil suspension data. A charge balance was conducted for the 72 solutions. For these solutions, 8 (11%) were greater than $\pm 10\%$ out of balance, and 3 (4%) were greater than $\pm 20\%$ out of balance. Repeat analyses on a few samples suggest that this charge imbalance was primarily analytical error. The mean (± 1 SE) % difference between cation and anion balances was +3.2 ($\pm 0.9\%$). This slight positive bias is statistically significantly different from 0.0 (the ideal balance). However, a bias of this magnitude is of little practical importance

Table 2
A Summary of Chemical Data of the Water Phase of Soils in 1:5 Soil:Water Suspension

Soil Pit	Soil Horizon	Concentrations (meq L ⁻¹)							Charge Balance (%)	Dissolved Organic Carbon (mM)	pH	pIAP ^a	
		Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Alkalinity	Cl ⁻	SO ₄ ²⁻				(CaCO ₃)	(CaSO ₄)
1	A	0.35	0.10	0.078	0.036	0.47	0.023	0.072	-0.4	0.88	7.72	9.77	8.33
	B _t	1.17	0.14	0.076	0.035	1.20	0.046	0.079	+6.6	0.48	8.18	8.44	7.86
	B _{k1}	1.27	0.22	0.020	0.076	1.40	0.019	0.072	+6.0	0.34	8.31	8.22	7.88
	B _{k2}	1.17	0.29	0.037	0.161	1.37	0.018	0.130	+8.1	0.62	8.24	8.34	7.66
3	A	1.73	0.23	0.115	0.032	1.81	0.013	0.150	+6.2	0.63	8.36	7.95	7.46
	B _{k1}	1.37	0.13	0.038	0.037	1.37	0.221	0.082	-6.3	0.23	8.25	8.26	7.79
	B _{k2}	1.21	0.20	0.018	0.065	1.35	0.022	0.057	+3.9	0.29	8.31	8.25	7.99
4	A	1.38	0.20	0.140	0.032	1.73	0.023	0.052	-3.3	0.06	8.42	8.00	8.00
	B _{k1}	1.35	0.16	0.020	0.065	1.49	0.049	0.075	-1.1	1.02	8.30	8.18	7.84
	B _{k2}	1.20	0.23	0.019	0.074	1.40	0.018	0.076	+1.8	0.29	8.28	8.27	7.88
5	C	1.16	0.10	0.074	0.023	1.29	0.011	0.036	+1.2	0.70	8.22	8.37	8.20
	B _{k1b}	1.45	0.12	0.022	0.091	1.40	0.129	0.072	+5.0	0.57	8.25	8.22	7.83
	B _{k2b}	1.58	0.20	0.024	0.065	1.37	0.010	0.036	+24.3	0.38	8.24	8.21	8.10
6	A	1.78	0.20	0.179	0.021	2.16	0.014	0.038	-1.4	0.93	8.46	7.77	8.05
	B _{k1}	1.40	0.12	0.014	0.083	1.43	0.023	0.060	+6.0	0.42	8.20	8.27	7.92
	B _{k2}	1.20	0.16	0.016	0.061	1.40	0.019	0.039	-1.9	0.32	8.21	8.34	8.16

^apIAP = -log (cation²⁺)(anion²⁻).

given the larger uncertainties in other factors involved in the analyses (e.g., stability constants, pH measurements). Ion activity products were calculated with three input options: (1) pH and alkalinity, (2) P_{CO_2} and alkalinity, and (3) pH and P_{CO_2} . The pH and alkalinity estimate of $p\text{IAP}(\text{CaCO}_3)$ always fell between the other two options; for this reason, the $p\text{IAP}$ data in tables and figures were all based on the pH and alkalinity option. The range of differences in $p\text{IAP}$ between the pH and alkalinity option and the most dissimilar option was 0.01 to 0.09 with a mean of 0.03. These results suggest that the pH, alkalinity, and P_{CO_2} data and the constants relating them were consistent.

All samples were undersaturated with respect to gypsum ($pK_{\text{sp}} = 4.64$, Lindsay 1979) in the 1:5 soil:water suspension; but, most samples were apparently supersaturated with respect to calcite ($pK_{\text{sp}} = 8.48$, Plummer 1982) (Table 2).

Spatial Variability

The difference in $p\text{IAP}(\text{CaCO}_3)$ between soil horizons is a measure of vertical variability. The frequency distributions for $p\text{IAP}(\text{CaCO}_3)$ showed a preponderance of low values for the A horizon (Fig. 2). When the data were summarized by soil horizon and analyzed with an ANOVA analysis, the A horizon had a significantly lower $p\text{IAP}(\text{CaCO}_3)$ than the B horizons (Fig. 3). These data show a statistically significant difference in vertical variability. Excluded in calculating soil horizon $p\text{IAP}(\text{CaCO}_3)$ were B₁, B₃, and C horizons (3 samples) because they were too few in number, samples for which the charge imbalance was greater than $\pm 10\%$ (8 samples), and samples that were undersaturated ($p\text{IAP}(\text{CaCO}_3) > 8.6$, Fig. 2) (5 samples). A total of 14 samples (19%) were excluded for these reasons.

Based on the Shapiro-Wilk's test, it was necessary to exclude the five undersatu-

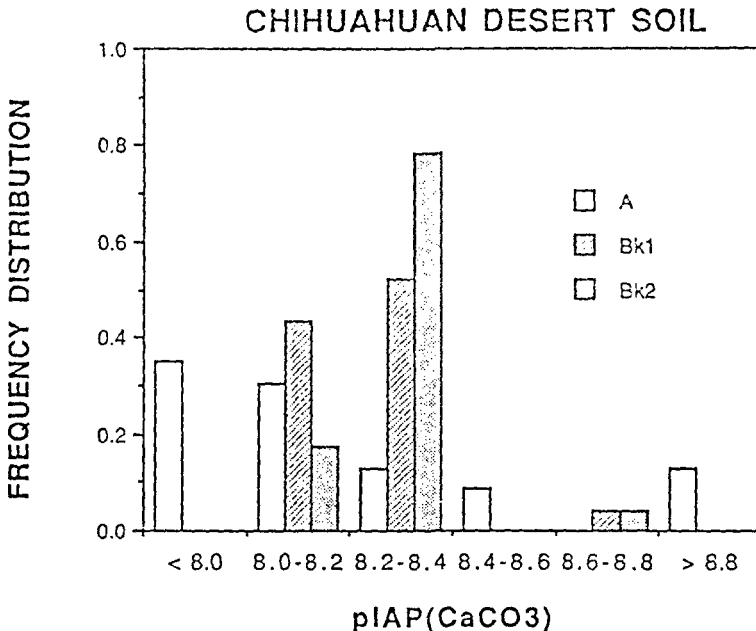


Figure 2. The frequency distributions for the A, B_{k1}, and B_{k2} horizons.

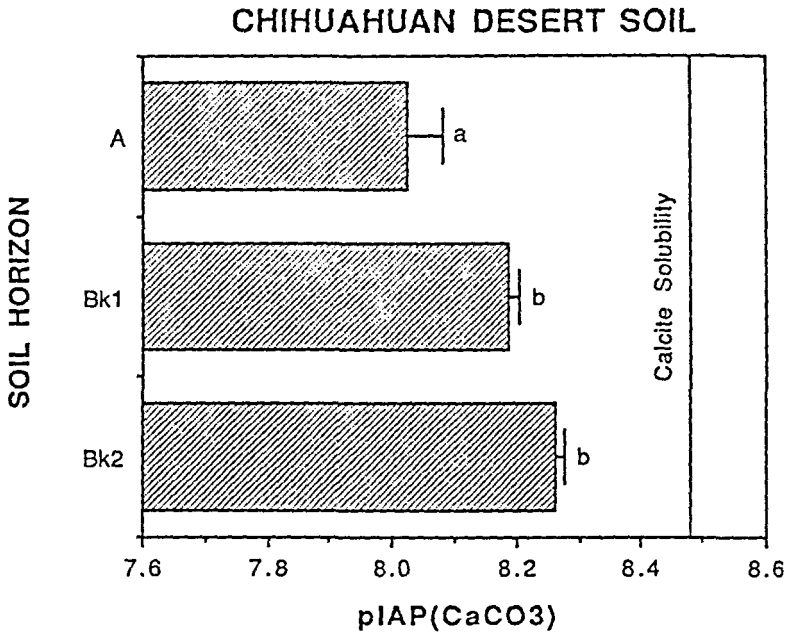


Figure 3. The mean (± 1 SE) $pIAP(CaCO_3)$ as a function of soil horizon. A different lowercase letter implies a statistically significant difference.

rated, outlier values (Fig. 2) in the ANOVA analysis to satisfy the requirement for normally distributed data. The three undersaturated A horizon samples can be excluded for physicochemical reasons because the solubility measurements suggest that $CaCO_3$ was not present based on pH, Ca, and alkalinity measurements and calculated $pIAP(CaCO_3)$ (e.g., see soil pit 1, A horizon, Table 2). Therefore, we did not include these three surface horizons “apparently” lacking $CaCO_3$ in calculating the average $pIAP(CaCO_3)$ for the A horizon. The consequences of excluding the two B horizon samples were minor for both the calculated means (± 0.02) and standard errors (± 0.008).

The magnitude of the standard error is a measure of horizontal variability, which for the A, B_{k1} , and B_{k2} horizons was 0.055, 0.019, and 0.015, respectively. The A horizons showed the greatest horizontal variability (Figs. 2 and 3). The reason for a greater variability in A horizons may be due to the greater instability of this horizon with respect to erosion and/or deposition. It was possible to distinguish eroded surfaces and recent depositional surfaces where soil pits were dug (Table 1); for example, our soil pit 2 was excluded from this analysis because it was clearly an eroded surface. The identification of eroded and depositional surfaces was not possible for the soil core samples; and as a consequence, some A horizon samples may represent either eroded surfaces or more recent deposition. In either case, these horizons may not represent A horizon $CaCO_3$ formed *in situ*.

Discussion

Calcium Carbonate Solubility

Most recent work has shown that soil CaCO_3 is generally supersaturated with respect to pure calcite (Marion and Babcock 1977, Suarez 1977, Suarez and Rhoades 1982, Inskip and Bloom 1986, Amrhein and Suarez 1987), which agrees with our findings (Table 2, Figs. 2 and 3). Inskip and Bloom (1986) attributed calcite supersaturation, up to 40-fold, in Calciaquolls from Minnesota to organic coatings on calcite that inhibited precipitation; this metastable state persisted for the 40 days of their experiments. Amrhein and Suarez (1987) attributed soil calcite supersaturation to the rate of alkalinity production from organic matter decomposition exceeding the rate of calcite precipitation.

Both of the latter two papers suggest that organic matter may be the cause of calcite supersaturation in soils. Although we did not measure soil organic matter in our study, one can reasonably assume that the A horizons contain higher levels of organic matter than the subsurface horizons. The generally higher level of calcite supersaturation in the A horizons than in the B horizons (Figs. 2 and 3) could be due to organic matter inhibition of calcite precipitation.

Organic matter inhibition of calcite precipitation could also account for the "apparent" undersaturation of five samples (Fig. 2). For example, the solubility measurement for the soil pit 1, A horizon sample suggests gross undersaturation (Table 2); on the other hand, there was more than enough CaCO_3 present in this horizon (Table 1) to satisfy the calcite solubility product. In a complex soil system, the solubility product principle may not always accurately reflect the true controls on solubility.

Simulation Modeling

A number of simulation models for CaCO_3 pedogenesis in arid land soils (Arkley 1963, Marion *et al.* 1985, McFadden and Tinsley 1985) and salt movement through calcareous soils (Dutt *et al.* 1972, Robbins *et al.* 1980) have been developed. These models generally assume a uniform soil profile and equilibrium with respect to calcite. Our results demonstrate that the Chihuahuan Desert soil is supersaturated with respect to calcite (Fig. 3), the most thermodynamically stable CaCO_3 polymorph. Furthermore, the CaCO_3 in the A horizon was significantly more soluble than in the B horizons. These results have important implications for simulation modeling. The fact that CaCO_3 solubility is greater than calcite implies that Ca will be more mobile and leach to greater depth in soils under a given climatic regime. Simulation models have been used to draw inferences about soil pedogenesis and previous climatic regimes (e.g., the Pleistocene) (Marion *et al.* 1985, McFadden and Tinsley 1985). Failure to consider spatial variability in CaCO_3 solubility could lead to erroneous inferences about both CaCO_3 pedogenesis and previous climatic regimes. A variable vertical CaCO_3 solubility should be explicitly recognized in simulation models in order to more accurately describe CaCO_3 flux through soils.

Experimental Design

Variability is important in experimental design because it influences sample size. An estimate of the number of replicates (n) required to detect a difference (d) is given by the inequality

$$n \geq \frac{2(t_0 + t_1)^2 s^2}{d^2} \quad (2)$$

where t_0 is the t value associated with a type I error, t_1 is the t value associated with a type II error, and s^2 is an estimate of the sample variance (Steel and Torrie 1960). A type I error occurs when the experimenter rejects the null hypothesis and it is true. A type II error occurs when the experimenter accepts the null hypothesis and the alternative is true. Assuming a probability for a type I error of .05, a probability for a type II error of .20, and $s^2 = .0220$ (from the analysis of variance of $p\text{IAP}(\text{CaCO}_3)$), one can calculate the number of replicates needed to detect a given difference. In this calculation, a completely randomized design with three classes (e.g., soil horizons) was assumed. For $d = 0.1$ and 0.2 , the required replicates were 36 and 10, respectively. The number of replicates increases inversely with the square of the difference (Eq. 2). In our case (Fig. 3), 19 replicates were sufficient to detect a difference of 0.16 at the .05 probability level of a type I error; the calculated sample size to detect a 0.16 difference was 14.

Variation in the horizontal dimension plays an important role in experimental designs through its effect on sample size. Testing scientific hypotheses dealing with soil CaCO_3 solubility should recognize variability *a priori* in designing experiments. Our results demonstrate that many replicates may be necessary to detect small differences in CaCO_3 solubility.

Acknowledgments

We thank Walter Whitford (New Mexico State University) for his hospitality and support during our field work at the Jornada LTER site. We thank Leland H. Gile (retired, Soil Conservation Service) for helping us describe soil profiles. The assistance of Joan Walker in analyzing the soil samples was greatly appreciated. We thank Fiorenzo Ugolini (University of Washington) for analyzing our DOC samples. This work was funded by NSF Grant BSR-8212466 to Duke University.

References

- Amrhein, C., and D. L. Suarez. 1987. Calcite supersaturation in soils as a result of organic matter mineralization. *Soil Science Society of America Journal* 51:932-937.
- Arkley, R. J. 1963. Calculation of carbonate and water movement in soil from climatic data. *Soil Science* 96:239-248.
- Bohn, H. L., B. L. McNeal, and G. A. O'Connor. 1985. *Soil Chemistry*, 2d ed. Wiley, New York.
- Day, P. 1965. Particle fractionation and particle-size analysis, pp. 545-567, in C. A. Black, ed. *Methods of Soil Analysis, Part I*. Am. Soc. Agron., Madison, Wisconsin.
- Dutt, G. R., M. J. Shaffer, and W. J. Moore. 1972. Computer simulation model of dynamic biophysiochemical processes in soils. *Arizona Agricultural Experiment Station Technical Bulletin* 196. Tucson, Arizona.
- Eisenberg, J., J. Dan, and H. Koyumdjisky. 1982. Relationship between moisture penetration and salinity in soils of the northern Negev (Israel). *Geoderma* 28:313-344.

- Gile, L. H., J. W. Hawley, and R. B. Grossman. 1981. Soils and geomorphology in the Basin and Range area of southern New Mexico—Guidebook to the desert project. *Memoir 39, New Mexico Bureau of Mines and Mineral Resources*. Socorro, New Mexico.
- Horton, J. H., and D. W. Newsom. 1953. A rapid gas evolution method for calcium carbonate equivalent in liming materials. *Soil Science Society of America Proceedings* 17:414–415.
- Inskip, W. P., and P. R. Bloom. 1986. Calcium carbonate supersaturation in soil solutions of Calciacquolls. *Soil Science Society of America Journal* 50:1431–1437.
- Lindsay, W. L. 1979. *Chemical Equilibria in Soils*. Wiley, New York.
- Marion, G. M., and K. L. Babcock. 1977. The solubilities of carbonates and phosphates in calcareous soil suspensions. *Soil Science Society of America Journal* 41:724–728.
- Marion, G. M., W. H. Schlesinger, and P. J. Fonteyn. 1985. CALDEP: A regional model for soil CaCO_3 (caliche) deposition in southwestern deserts. *Soil Science* 139:468–481.
- McFadden, L. D., and J. C. Tinsley. 1985. Rate and depth of pedogenic-carbonate accumulation in soils: Formation and testing of a compartment model, pp. 23–41, in D. L. Weide, ed. *Soils and Quaternary Geology of the Southwestern United States. Geological Society of America Special Paper 203*. The Geological Society of America, Boulder, Colorado.
- Olsen, S. R., and F. S. Watanabe. 1959. Solubility of calcium carbonate in calcareous soils. *Soil Science* 88:123–129.
- Plummer, L. N. 1982. The solubilities of calcite, aragonite, and vaterite in carbon dioxide-water solutions between 0 and 90°C, and an evaluation of the aqueous model for the system calcium carbonate–carbon dioxide–water. *Geochimica et Cosmochimica Acta* 46:1011–1040.
- Rhoades, J. 1982. Cation exchange capacity, pp. 149–157, in A. L. Page, R. H. Miller, and D. R. Keeney, eds. *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, 2d ed. American Society of Agronomy, Madison, Wisconsin.
- Robbins, C. W., R. J. Wagenet, and J. J. Jurinak. 1980. A combined salt transport chemical equilibrium model for calcareous and gypsiferous soils. *Soil Science Society of America Journal* 44:1191–1194.
- Schlesinger, W. H. 1985. The formation of caliche in soils of the Mohave Desert, California. *Geochimica et Cosmochimica Acta* 49:57–66.
- Schlesinger, W. H., P. J. Fonteyn, and G. M. Marion. 1987. Soil moisture content and plant transpiration in the Chihuahuan Desert of New Mexico. *Journal of Arid Environments* 12:119–126.
- Shapiro, S. S., and M. G. Wilk. 1965. An analysis of variance test for normality (complete samples). *Biometrika* 52:591–611.
- Sposito, G. 1981. *The Thermodynamics of Soil Solutions*, Oxford University Press, New York.
- Steel, R. G. D., and J. H. Torrie. 1960. *Principles and Procedures of Statistics*. McGraw-Hill, New York.
- Suarez, D. L. 1977. Ion activity products of calcium carbonate in waters below the root zone. *Soil Science Society of America Journal*. 41:310–315.
- Suarez, D. L., and J. D. Rhoades. 1982. The apparent solubility of calcium carbonate in soils. *Soil Science Society of America Journal*, 46:716–722.