CARBON STORAGE IN THE CALICHE OF ARID SOILS: A CASE STUDY FROM ARIZONA

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ABSTRACT

Using data from 91 Arizona soils, I calculated the accumulations of organic- and carbonate-carbon in different soil orders and ecosystem types. Regional accumulations were examined relative to precipitation, elevation, and parent material. The largest accumulations of pedogenic carbonates were found in Aridisols and in areas of desert scrub vegetation, where carbonate-carbon exceeded organic carbon by a factor of > 10. In soils under woodland vegetation, organic carbon accumulations predominated. According to the Arizona data, I estimate that more than 800×10^{15} grams of carbon are stored in the caliche layers of the world's Aridisols and arid Entisols.

INTRODUCTION

On a worldwide basis the amount of carbon in decaying plant litter and in soil organic matter may exceed the amount of carbon in living vegetation by a factor of 2 to 3 (Woodwell et al. 1978). Thus, biogeochemists have recently recognized an important role of soils in the global carbon cycle. Despite the availability of various estimates of the world storage of organic carbon in soils (Bohn 1976; Schlesinger 1977; Meentemeyer et al. 1981; Post et al. 1981), none has attempted to estimate the importance of carbon stored in inorganic form, primarily as calcium carbonate, in soils of arid and semiarid regions of the world. The present paper compares the storage of organic and inorganic carbon in arid soil profiles, using the state of Arizona as an example. This comparison is used to extrapolate a worldwide estimate for the storage of carbon in pedogenic carbonates.

The precipitation of carbonates in the soils of arid and semiarid ecosystems is a worldwide phenomenon (Dregne 1976; Reeves 1976). Although these deposits are best known from the arid regions, where they may strongly influence vegetation patterns (Shreve and Mallery 1933; Hallmark and Allen 1975; Cunningham and Burk 1973), they can be expected in semiarid regions as well (St. Arnaud 1979; Mogen et al. 1959). Secondary carbonate occurs in a variety of forms in soil profiles, ranging from precipitates in the interstitial spaces of the parent material to almost pure, laminated layers of carbonate (Gile 1961; Gile et al. 1966; Flach et al. 1969).

The terminology applied to such deposits has varied widely (Reeves 1976). Highly indurated layers are referred to as *calcrete* or *petrocalcic* horizons, and less-cemented layers are known as *caliche* or *calcic* horizons (Lattman 1973; Dregne 1976).

The deposition process has apparently occurred in arid regions throughout geologic time. Indurated carbonate deposits form the Llano Estacado of Texas, a desert bajada of Pliocene age (Aristarain 1970; Reeves 1970, 1976). Highly indurated deposits of Pleistocene age form the caprock of the Mormon Mesa in Nevada (Gardner 1972). Soil scientists generally concur that carbonate precipitation is also a present-day pedogenic process in desert regions (Buol 1965; Dregne 1976; Jenny 1980). Thus a continuum of age and induration is represented by various deposits called caliche.

The state of Arizona is ideal for a case study of the amount of carbon in carbonate soil deposits. The state includes large areas of the major soil orders of arid regions—Aridisols, Entisols, and Mollisols. There are smaller areas of Alfisols and Vertisols. The vegetation includes regions in the Mojave, Sonoran, and Chihuahuan deserts, large areas of desert grassland and woodland, and moderate areas of chaparral and montane forest. Thus, there is a variety of arid and semiarid ecosystems, as well as clear gradients of increasing precipitation as a function of elevation.

Most compilations of the carbon content (biota and soil) of terrestrial ecosystems of the world have been organized around vegetation units, increasingly so as remote sensing techniques are used to improve estimates of land areas. In contrast, soil data are collected and classified by soil order. Though there is often a strong correlation between the vegetation and soil characteristics of large regions, both vegetation and soil approaches were pursued separately in this paper.

METHODS

Data reported by the Soil Conservation Service (1974) were used to estimate the storage of organic and inorganic carbon in Arizona soils. These data were compiled from several decades of soil mapping and survey throughout the state. Generally for the various horizons comprising a complete soil profile, measurements of soil bulk density, organic carbon, and calcium carbonate equivalent are reported using standard techniques. Bulk density is measured as the ovendry weight of saran-coated clods, for which the volume is measured by displacement in water. Organic carbon is measured by FeSO₄ titration of an acid-dicromate digestion. Calcium carbonate is measured by manometric collection of CO₂ evolved during HCl treatment. These methods have been outlined in detail (Soil Conservation Service 1972). Because dolomite and MgCO₃ are usually of minor importance among pedogenic carbonates (Doner and Lynn 1977), in this paper calcium carbonate equivalent was converted to carbon content by multiplying by 0.12, the mole fraction of carbon in CaCO₃.

Ninety-one of the 189 soil profiles (Soil Conservation Service 1974) reported the necessary data for samples at various depths comprising a complete profile. This subset of profiles was used in the present paper. Unless parent material was encountered at a lesser depth, all profiles were sampled to at least 125 cm. The data for all sites also include additional information regarding precipitation, current vegetation, elevation, and the probable parent material of soil formation. Among soil orders, 56 Aridisols, 14 Mollisols, 13 Entisols, 4 Alfisols, and 4 Vertisols were included. Among vegetation types, 31 desert scrub, 29 desert grassland, 8 woodland, 4 chaparral, and 19 agricultural areas were included.

For this study each profile was classified according to the parent material of soil formation. Soils were classified as basalt- or limestone-derived if there was any mention of these parent

rocks, regardless of their quantitative contribution in soil formation. The remaining soils were classified as mixed alluvial soils; this category includes both acid igneous parent materials (e.g., granite, rhyolite, and quartzite) as well as igneous materials richer in calcium (e.g., andesite).

To estimate the area of the soil orders and of the major vegetation types comprising the state of Arizona, large-scale maps were photocopied and the individual soil and vegetation categories were cut out. These pieces were weighed to the nearest 0.1 mg on an analytical balance and converted to km² based on the weight of pieces of photocopy paper representing known land area. For soils, the North American Sheet of the FAO/UNESCO Soil Map of the World (1975) was used at 1:5 000 000 scale. Yermosols were considered equivalent to Aridisols, Regosols were considered equivalent to Entisols, and Kastanozems were considered equivalent to Mollisols. For vegetation, Kuchler's (1975) map of the Potential Natural Vegetation of the United States was used at a scale of 1:3 168 000. Community numbers 27, 38, 39, 41-44, and 46 were considered desert scrub, numbers 53 and 58 were considered desert grassland, numbers 19, 23, and 31 were considered woodland, number 32 was considered chaparral, and numbers 18, 20, and 21 were considered forest. According to these methods, the total area of Arizona calculated as the sum of soil groups and of vegetation groups agreed with the actual area within 1% in both cases.

RESULTS AND DISCUSSION

For the entire data set, storage of soil carbon as organic matter on a whole profile basis (i.e., to bedrock or ≥1.25 m) averaged 4.9 kg C/m², and storage of soil carbon in carbonate minerals averaged 26.0 kg C/m² (Table 1). Figure 1 shows a frequency histogram for these data. Soils derived from limestone parent materials generally contained more carbonate-carbon than soils derived from basalts and mixed alluvium, though no pairwise comparisons between means for these groups showed a significant difference. The ratio of carbonate-carbon to organic carbon was relatively similar among soils from these three groups, 4.7 to 5.8.

Comparison of soils

Carbon stored in calcium carbonate exceeded carbon stored in organic form by mean factors

TABLE 1 Profile contents of organic and carbonate-carbon in Arizona soils; mean values \pm (2 SE)

Data set	Number of profiles	Organic carbon	Carbonate carbon
T .:			
Entire	91	4.9 (0.5)	26.0 (2.9)
By parent rock			
Basalt	17	4.8 (2.4)	25.5 (13.6)
Mixed alluvium	53	4.2 (0.9)	24.2 (8.6)
Limestone	21	6.6 (1.7)	31.0 (11.0)
By soil & rock			
Aridisol	56	3.4 (0.9)	33.9 (8.4)
Basalt	10	1.5 (1.0)	40.2 (17.9)
Mixed alluvium	40	3.7 (1.1)	30.8 (10.5)
Limestone	6	4.4 (2.6)	44.3 (17.7)
Entisol	13	4.9 (2.1)	11.4 (8.0)
Basalt	1	1.6	0.0
Mixed alluvium	5	3.5 (2.2)	9.1 (9.1)
Limestone	7	6.4 (3.4)	14.6 (13.4)
Mollisol	14	8.8 (1.5)	16.0 (13.9)
Basalt	2	12.2 (1.9)	2.9 (1.1)
Mixed alluvium	6	6.9 (2.0)	0.1 (0.2)
Limestone	6	9.6 (1.7)	36.2 (24.3)
Alfisol	4	6.2 (4.2)	17.7 (24.4)
Mixed alluvium	2	7.8 (6.2)	2.9 (2.6)
Limestone	2	4.6 (6.8)	32.5 (42.6)
Vertisol (basalt)	4	10.4 (0.8)	6.5 (4.0)
By vegetation & rock			()
Desert scrub	31	2.2 (1.2)	31.0 (7.1)
Basalt	8	2.2 (2.6)	29.7 (13.5)
Mixed alluvium	18	1.5 (0.8)	30.5 (10.2)
Limestone	5	5.0 (5.0)	35.0 (14.5)
Desert grassland	29	7.3 (1.2)	22.3 (9.3)
Basalt	2	11.3 (3.6)	7.7 (5.5)
Mixed alluvium	16	6.7 (1.7)	14.6 (9.3)
Limestone	11	7.6 (1.9)	36.0 (17.9)
Chaparral	4	5.2 (1.7)	0.3 (0.5)
Basalt	1	6.0	1.1
Mixed alluvium	3	5.0 (2.2)	0.0 (0.0)
Woodland & forest	8	7.6 (2.7)	5.0 (3.0)
Basalt	3	10.7 (0.6)	4.6 (2.7)
Mixed alluvium	5 5	5.7 (3.4)	4.6 (2.7) 5.2 (4.9)
Agricultural		5.7 (3.4) 4.2 (1.4)	5.2 (4.9) 37.9 (20.8)
Basalt	3	1.2 (0.5)	• •
Mixed alluvium	3 11	, ,	55.3 (55.3)
Limestone	5	4.2 (1.6) 5.9 (3.3)	43.3 (31.7) 15.7 (16.1)

ranging from 1.8 for Mollisols to 10.0 for Aridisols. Only in Vertisols did the mean for organic carbon exceed carbonate-carbon. The mean values for organic carbon (Table 1) were similar, but consistently larger than the mean values reported for soil orders in southern New Mexico: $2.8 \ \text{kg C/m}^2$ for Aridisols, $3.4 \ \text{kg C/m}^2$ for Entisols, and $5.2 \ \text{kg C/m}^2$ for Mollisols (Gile and Grossman 1979).

When these mean values for soil orders were more closely examined, the effect of calcareous parent materials was strongly evident. Within each soil order the mean content of carbonate-carbon in soils derived from limestones exceeded that in soils derived from basalts and mixed alluvium (cf. Lattman 1973). For Alfisols and Mollisols the mean for carbonate-carbon exceeded organic carbon only on limestone-derived

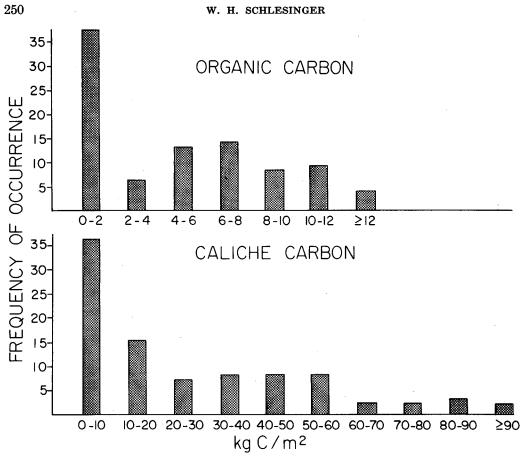


FIG. 1. Frequency distributions for organic carbon (above) and inorganic carbon (below) in 91 Arizona soils. All data are kilograms of carbon per square meter.

TABLE 2
Some linear regressions to predict the profile contents of organic and carbonate-carbon in Arizona soils

Dependent variable	Independent variable	Slope	\mathbf{r}^2	F	
Organic carbon, kg C/m ²	Precipitation, cm	0.23	0.37	52.1°	
	Elevation, m	0.0045	0.46	76.1^{a}	
Carbonate-carbon, kg C/m ²	Precipitation, cm	-1.03	0.13	13.1^{a}	
on basalt	Precipitation, cm	-1.80	0.37	8.8^a	
on mixed alluvium	Precipitation, cm	-0.99	0.13	7.8^{a}	
on limestone	Precipitation, cm	0.02	0.00	0.0	
Carbonate-carbon, kg C/m ²	Elevation, m	-0.0153	0.10	9.4^a	
Organic-carbon, kg C/m ²	Carbonate carbon, kg C/m ²	-0.01	0.01	0.7	
Precipitation, cm	Elevation, m	0.0156	0.81	388.5^{a}	

^a Significant at P < 0.05.

alluvium. For Aridisols and Entisols, carbonatecarbon exceeded organic carbon on most materials, but the tendency was most pronounced on limestone.

Relation of soils to precipitation and elevation

Among the 91 profiles examined, the content of carbon stored as carbonate declined signifi-

cantly with increasing mean annual precipitation, though the correlation was not strong (r = -0.36, Table 2). Because precipitation is highly correlated with elevation among the 91 sites (r = +0.90), it is not surprising that the profile content of carbonate-carbon also declines significantly with increasing elevation (r = -0.31). These observations were more incisive when the

entire data set was subdivided into soils derived from different parent materials. The relation was significant on basaltic and mixed alluvial materials; no relation was seen for limestonederived soils. These relations suggest that the amount of precipitation is an important determinant of the quantity of caliche in noncalcareous alluvium. Past studies have shown strong positive relations between the depth to caliche layers and the depth of the mean annual infiltration of precipitation (Jenny and Leonard 1934; Arkley 1963). The interpretation of such correlations is not straightforward to the extent that present-day soil deposits formed during past climatic regimes that may have included greater rainfall (e.g., Van Devender and Spaulding 1977; Wells 1979). Nevertheless, one might assume that sites throughout Arizona have maintained similar patterns of rainfall relative to one another, even if the total regional quantity was greater. In contrast to the significant correlations for basaltic and mixed alluvium, it is likely that carbonates in alluvium derived from limestone are primarily from parent materials and not the result of pedogenic processes related to precipitation.

Storage of organic carbon in the soil profile increases significantly as a function of precipitation and elevation, presumably as a result of greater primary production and production of plant detritus in forest and woodland ecosystems compared with deserts. Similar relationships have been reported for various temperate-zone mountain ranges (Franz 1976; Hanawalt and Whittaker 1976; Whittaker et al. 1968). There is no significant correlation between organic carbon and carbonate-carbon.

Comparison of vegetation types

Vegetation in Arizona is also related to precipitation and elevation; thus the general patterns for vegetation are similar to those for soils. Carbon stored in pedogenic carbonates greatly exceeded organic carbon in the soils of desert scrub and desert grasslands. For woodland and chaparral soils, the opposite was true. Mean organic carbon was highest in woodlands and lowest in soils under desert scrub. Mean inorganic carbon was lowest in soils under chaparral and highest in desert scrub. These general trends were also evident when the data were examined by parent material group. Within each vegetation type, soils from limestone parent materials had greater carbonate-carbon than soils derived

from basaltic or mixed alluvium. This was strongly evident in desert grasslands.

Agricultural soils

The 19 soil profiles from agricultural lands had a mean content of 4.2 kg/m^2 of organic carbon and 37.9 kg/m^2 of carbonate-carbon (Table 1). The latter is considerably higher than the mean for the entire data set. When one particularly high value, 166.9 kg C/m^2 , is removed, the mean carbonate-carbon in soils under agricultural use is 31.0 kg/m^2 .

Potential changes in carbon storage in agricultural soils are worthy of further investigation. particularly in view of the increasing pressure to cultivate arid lands. Accumulation of calcite in irrigated soils has long been recognized as a problem in arid regions and requires various management approaches (Bower et al. 1968: Mivamoto et al. 1975; Levy 1980). This accumulation is surprising, however, compared with what might be anticipated simply by an extrapolation of the regressions for carbonate-carbon versus mean annual precipitation. Irrigation waters are not simply analogous to greater rainfall. Groundwaters used for irrigation are often supersaturated with respect to CaCO₃ (Suarez 1977), and much irrigation water is drawn from the large rivers in Arizona that drain areas dominated by limestone (e.g., Gila and Colorado Rivers).

Carbon pool estimates

Compared with the carbon stored in sedimentary rocks, carbon in soils is more closely tied to the biogeochemical cycles at the surface of the earth. Soil carbon contents may be altered by man's activities on a rather short time scale (Schlesinger 1982). Both organic and inorganic storages of carbon in soils are important to consider in this context, although the processes of their formation and degradation are different and only partially related.

Using Arizona as a case study of arid regions, these data show the importance of including inorganic forms of soil carbon in any assessment of the total pool of carbon that exists in the pedogenic zone of world soils that might actively exchange carbon dioxide with the atmosphere. Using a classification based on soil areas, there is approximately 5.7 times as much carbon stored in inorganic form as in organic form in Arizona soils (Table 3). Using the vegetation classification, this factor is approximately 4 (Table 4). For the entire state, the pool of organic

TABLE 3

Accumulation of organic and carbonate-carbon in soils classified by soil orders of Arizona

Soil order ^a	A 12	Profile content		Statewide pool	
	Area, km²	Organic kg	Carbonate C/m ²	Organic 10 ⁷ 1	Carbonate mt C
Aridisols	196 700	3.4	33.9	66.9	666.8
Entisols	34 300	4.9	11.4	16.8	39.1
Mollisols	68 100	8.8	16.0	59.9	109.0
				144×10^7	815×10^7
				$= 959 \times 10^7 \text{ mt C}$	

[&]quot;No area of Alfisols or Vertisols on Arizona portion of North America Soil Map (FAO/UNESCO 1975).

TABLE 4

Accumulation of organic and carbonate-carbon in soils classified by vegetation types of Arizona

Vegetation type	Area, km²	Profile content		Statewide pool	
		Organic kg	Carbonate C/m ²	Organic 10 ⁷ 1	Carbonate nt C
Desert scrub	127 800	2.2	31.0	28.1	396.0
Desert grassland	66 400	7.3	22.3	48.5	148.0
Woodland & forest	82 200	7.6	5.0	62.5	41.1
Chaparral	16 300	5.2	0.3	8.5	0.5
				148×10^7	586×10^7
				$=734 \times$	$10^7 \mathrm{\ mt\ C}$

carbon estimated by these two methods is surprisingly similar; carbonate-carbon is larger using the soils classification.

Estimates of the area of the desert ecosystems of the world converge on 2.1×10^9 ha (Ajtay et al. 1979). For instance, Whittaker and Likens (1973) cite 1.8×10^9 ha as desert scrub, with an additional amount undifferentiated in the category of "extreme desert, rock and ice." Thus, desert scrub constitutes 12% of the area of world land vegetation. Higher values are given by Dregne (1976) based largely on the compilations of Shantz (1956), which include some semiarid grassland areas. These values range from 4.2 to 4.9×10^9 ha. Similarly, Dregne (1976, p. 39) gives 1.7×10^9 ha as the area of world Aridisols, 11% of the world soil area. When a soils classification is used, the total area of arid regions in all soil orders is 4.6×10^9 ha, or 31.5% of the world land

Storage of organic carbon in world soils has been calculated as a result of several recent compilations. Schlesinger (1977) suggests a mean organic carbon content of 5.6 kg C/m² for desert ecosystem soils. Post et al. (1981) give values of 1.4 kg C/m² for warm temperate deserts and 9.7 kg C/m² for cool temperate deserts.

According to the former value, the pool of organic carbon in the soil of the world's desert ecosystems ($1.8 \times 10^{13} \mathrm{m}^2 \times 5.6 \mathrm{~kg~C/m^2}$) makes up approximately 7% of the total in the world's soils, $1456 \times 10^{15} \mathrm{~g~C}$ (Schlesinger 1977). Following an analogous approach using a soil classification, Buringh (1982) found that Aridisols contained 2.2% of the organic carbon in soils of the world.

If we assume that the area of Arizona is representative of the diversity of landscapes and soils characteristic of arid and semiarid regions of the world, we can make some preliminary estimates of the importance of carbon in caliche deposits as a pool in the global carbon cycle. When we use 31.0 kg C/m² as the carbonatecarbon content of soils in desert scrub ecosystems (Table 1), their contribution increases from 7 to 33% of a revised total for soil carbon, 2014 \times 10¹⁵ g C, following the vegetation approach. Similarly the carbonate-carbon content of Aridisols, 33.9 kg C/m², and of arid Entisols, 11.4 kg C/m², multiplied by their land areas (Dregne 1976, p. 39) suggests a total storage of 780×10^{15} g C in these soils of the world. Thus, the contribution of desert soils to world storage of carbon in soils increases from 2.2 to 35% of a revised total, 2236×10^{15} g C, including both organic and inorganic forms. These values are conservative because Aridisols, arid Entisols, and desert scrub ecosystems do not represent the total extent of arid and semiarid regions. Moreover caliche and calcrete now occur in regions that were arid under former climatic regimes (Reeves 1976). Although caliche cannot be expected in all arid regions—indeed silcretes can be expected in some areas of Australia (Litchfield and Mabbutt 1962; Stephens 1971)—these preliminary estimates suggest an important role of desert soils in the global carbon cycle.

Where caliche develops in desert alluvial soils derived from limestone rocks, there is probably little net exchange of carbon dioxide with the atmosphere. Over many areas of the southwestern United States, however, noncalcareous alluvium, including high-calcium basaltic parent material, is found. In these areas calcium weathered from parent material and deposited as carbonate in alluvial soil must represent a sink for carbon from the atmosphere—i.e., rainfall in equilibrium with atmospheric CO₂ provides bicarbonate and ultimately carbonate for calcite precipitation (Smith and Drever 1976; Roy et al. 1969), viz.

$$2H_2O + 2CO_2$$

$$\Rightarrow 2H^+ + 2HCO_3^- \Rightarrow 2H_2CO_3 \quad (1)$$

Ca-Al-silicate
$$+ 2H_2CO_3 + H_2O \rightleftharpoons$$

Al-silicate $+ H_4SiO_4 + 2HCO_3^- + Ca^{2+}$ (2)

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$
 (3)

That well-developed caliche is found in areas of the world that are downwind of major sources of eolian material suggests that the atmospheric deposition of calcareous loess may be important (Gardner 1972; Lattman 1973). These observations are concordant with those of Gile (1975), who found nearly equivalent amounts of pedogenic carbonate in alluvial soils from limestone and rhyolite areas. Soil carbonates that are derived from the eolian transport of carbonate loess may not represent an important sink for atmospheric CO₂—viz., limestone weathered by deflation is simply transported to another locale.

In eastern New Mexico, Gile and Grossman (1979) showed that the content and age of caliche layers on various geomorphic surfaces were consistent with the hypothesis of a long-term eolian deposition of calcium as a source material. By dividing profile contents of carbonate-carbon

by the 14C age in buried horizons or by ages derived from geomorphic evidence, they found accumulation rates of 0.12 to 1.44 g C/m²/yr during the late Pleistocene and Holocene. Presumably, these rates are for the integrated accumulation and may have varied considerably during the interval. Similarly, data from Buol and Yesilsoy (1964) suggest accumulation rates ranging from 0.47 to 0.68 g C/m²/vr in southern Arizona. Dating soil carbonates by ¹⁴C is not without difficulty (Williams and Polach 1971; Ku et al. 1979; Margaritz et al. 1981), but these estimates undoubtedly represent the order of magnitude of the rate of fixation of carbon as carbonate in desert soils. The rates are similar in magnitude to the long-term, non-steady-state accumulation of organic carbon in grassland soils, 1 g C/m²/yr (O'Brien and Stout 1978; Schlesinger 1977).

If the typical rate of storage of carbon in pedogenic carbonates deposited in arid regions is $0.5 \text{ g C/m}^2/\text{yr}$, a worldwide storage of $0.23 \times 10^{14} \text{ g C/yr}$ occurs, calculated using 4.6×10^9 ha as the area of desert lands. Net fixation of carbon from the atmosphere by these processes is lower to the extent that this storage is reprecipitated calcite from parent materials and carbonate loess. For comparison, Garrels and Lerman (1981) estimate that the annual transport of calcium in the world's rivers is balanced by the annual net formation of CaCO_3 and other carbonates in the world's oceans. These processes transfer $1.5 \times 10^{14} \text{ g C/yr}$.

Accumulations of pedogenic carbonate in desert soils endow these regions with a greater importance in the global carbon cycle than the amount of soil organic matter, biomass, and proportional land area would otherwise suggest. On a worldwide basis, the carbon pool in caliche and the rate of formation and exchange of carbon between these deposits and the atmosphere need study beyond the present, preliminary estimates. These studies should examine the net storage of carbon in caliche layers vis-à-vis the sources of calcium for these deposits. Experimental studies should address the potential for altered rates of exchange in areas that are being converted to agriculture.

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