The reactivity of carbonates in selected soils from Iran

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Abstract

This study was conducted to characterize the reactivity of carbonates in the surface horizons of 20 soils (Entisols and Aridisols) from Iran. The samples were analyzed for calcium carbonate equivalent (CCE), active calcium carbonate equivalent (ACCE), non-active calcium carbonate equivalent (N.ACCE), carbonate mineralogy and surface area of carbonates (SSA) by N_2 adsorption. The CCEs ranged from 38 to 228 g/kg of soil, with a mean 105.1g/kg of soil. ACCEs ranged from 13.4 to 99.8 with a mean 37 g/kg of soil. About 34% of $CaCO_3$ in the soils were able to react with oxalate .There is a considerable scatter of data about the regression line (R^2 = 0.60) between ACCE and CCE. This observation support the idea that calcium carbonate in the soils does not consist of particles with common particle size distributions. This feature of native carbonates is an important property in determining nutrient elements in calcareous soils. The surface area of carbonates was negatively and significantly correlated with CCE (0.52*, n=20), indicating that with increasing CCE content, surface area decreases. X-ray diffraction (XRD) analysis showed that [$Mg_x Ca_{1-x} (CO_3)$] is the most commonly carbonate in the studied soils. Dolomite was only present in 7 soils.

Key Words
Calcium carbonate equivalent, active carbonate equivalent, calcareous soils.

Introduction
Carbonates, which are common constituents of many soils of arid and semiarid areas, have a marked influence on soil chemical properties, e.g., pH, cation and anion sorption and physical properties, such as soil structure (Delcampillo *et al*. 1992). For this reason, the measurement of calcium carbonate equivalent (CCE) in calcareous soils is common and is useful for the evaluation of soil processes. In some instances, active calcium carbonate reactivity is related more highly than CCE to soil processes or properties. For example, the severity of iron chlorosis (Morris *et al*.1990) and phosphorous sorption in calcareous soils (Samadi and Gilkes 1999). In several countries, the active calcium carbonate equivalent (ACCE) is determined by reaction with 0.1 M NH_4-Oxalate (Drouneau 1942). Soil carbonate can be estimated from the difference in N_2 adsorption of soil and decalcified soil. This surface area was related to phosphate sorption capacity.
The purpose of the present study was to characterize the carbonate reactivities and carbonate surface area of some calcareous soils of the central part of Iran.

Methods
The 20 samples used in this study were collected from the surface horizons (0-30 cm) of Entisols and Aridisols from Gazvine plain, Tehran and Qom provinces in the central of Iran. Soil physical and chemical characteristics were determined according Method of Soil Analysis (Carter and Gregorich 2008).
Calcium carbonate equivalent was determined by acid digestion method. The ACCE was determined with 0.1 M NH_4 Oxalate using a 1:25 soil: ratio, and shaking 2 h at 250 rpm on a reciprocating shaker (Drouineau 1942). To calculate the N2-accessible SA of the CCE, 10-g samples were treated with HOAC-NaOAC (pH 4.75) buffer to remove carbonate. After this treatment, the samples were washed with water until they began to disperse and were freeze dried and weighted. The surface area (SA) of the intact samples and of their decalcified counterparts was then measured by N2 adsorption.
The "apparent" SA of the CCE was calculated using the equation:

$$SSA = A - B(1 - \frac{\%ACCE \ or \ CCE}{100})$$

Where SSA is the SA attributable to the CCE, and A and B are the SSA of the intact and decalcified soil materials, respectively.

Results
The CCE ranged from 38 to 228 g/kg and ACCE1 from 9.9 to 90.6 g./kg and ACCE2 from 14.6 to 99.8 g/kg(Table 1).

Table 1. Values of carbonate calcium equivalents for the studied soils.

Soil No.	CCE (g/kg)	ACCE1 (g/kg)	ACCE2 (g/kg)	$\dfrac{\%ACCE2}{CCE}$	$\dfrac{\%ACCE1}{CCE}$	SSA.CCE (m^2/g)	SSA.ACCE1 (m^2/g)	SSAN.ACCE1 (m^2/g)
1	80	37.2	38.4	48	46.5	157	99	208
2	46	14.9	19.2	41.7	32.4	111	44	143
3	72	26	27.2	37.8	36.1	83	124	61
4	136	60.6	62.6	46	44.6	50	28	68
5	62	43.3	44.5	71.8	70	151	20	450
6	88	15.2	16.1	18.3	17.3	28	36	26
7	98	11.2	13.4	13.7	11.4	127	682	55
8	125	32.2	33.5	26.8	25.8	94	197	58
9	108	19.8	27.8	25.7	18.3	74	141	59
10	228	90.6	99.8	43.8	39.7	79	26	114
11	95	17.4	22.2	23.4	18.3	88	88	88
12	82	39.6	40.8	49.8	48.3	124	13	228
13	38	15.2	27.3	71.8	40	140	110	159
14	94	35.9	40.8	43.4	38.2	102	132	84
15	194	52.8	58.5	30.1	27.2	21	25	19
16	170	50.2	65	38.2	29.5	45	94	25
17	90	21.5	23.5	26.1	23.9	84	39	98
18	48	9.9	14.6	30.4	20.6	403	279	436
19	108	30.9	34.6	32	28.6	49	110	25
20	140	28.5	31.4	22.4	20.3	54	155	28
Mean	105	32.6	37.1	34	31.9	103.2	122	121

ACCE1 is active carbonate calcium equivalent in native soils and ACCE2 is the same property after sieving thorough a 1 mm sieve.

The slope of the regression line between ACCE1 and CCE is 0.60 and for ACCE2 is 0.62, i.e. about 60 % CCE is able to react with Oxalate (Figure 1). As shown in Figure 1, various proportions of CCE are present as ACCE and CCE in the soils indicating that carbonate does not consist of particles with a common particle size distribution. This feature of native carbonate is an important property in determining phosphate and zinc retention (Samadi and Gilkes 1999). X-ray diffraction (XRD) analysis showed that Mg-Calcite is the carbonate most commonly found in the soils (data are not shown). Only in 7 soils was dolomite present.
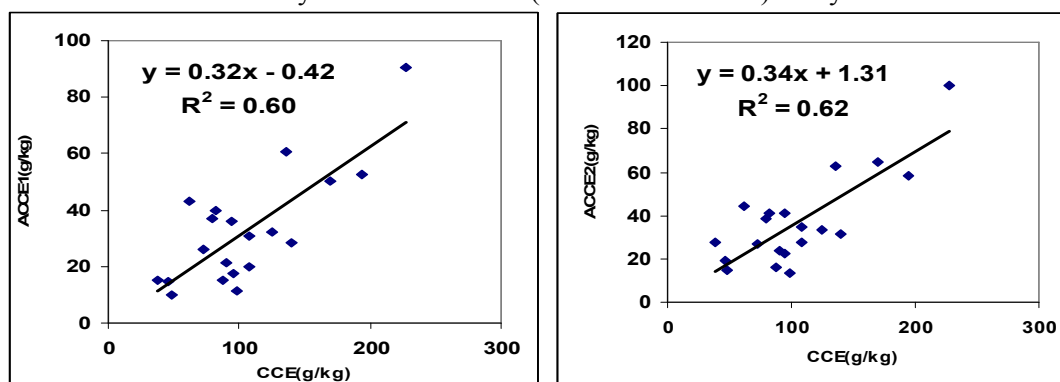
Figure 1. Relationship between active calcium carbonate equivalent and calcium carbonate equivalent.

The calculated SSA of the CCE ranged from 21 to 403 with a mean 103 m^2/g CCE. These values are similar to those found by Holford and Mattingly (1975), but lower than the reported values of Delcampillo *et al.* (1992). Holford and Mattingly (1975) found values up to 500 m^2/g for several soils with about 10 g CCE/kg soil ,but Delcampillo *et al.* (1992) believed that these high values might result from an error in the difference between the SAs of intact and decalcified soil samples, since decalcification could possibly have altered the effective SA of noncarbonated soil components. In this study, it seems that one of soils (soil No.18) was abnormal, so after removing this soil the relationships are better. In these studied soils the SA attributable to the CCE was inversely related to CCE (Figure 2) and positively related to the ACCE/CCE ratio (Figure 3). This result indicates the increasing surface area (decreasing particle size) produced by the progressive dissolution of parent limestone (Delcampillo *et al.* 1992).
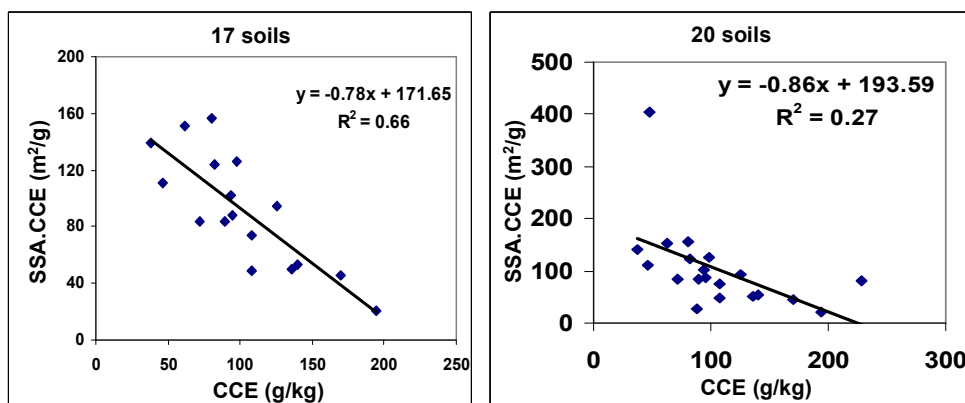
Figure 2. Relationship between SA attributable to the CCE and CCE, in all studied soils (n=20) and after removal of soils no 6, 10 and 18.
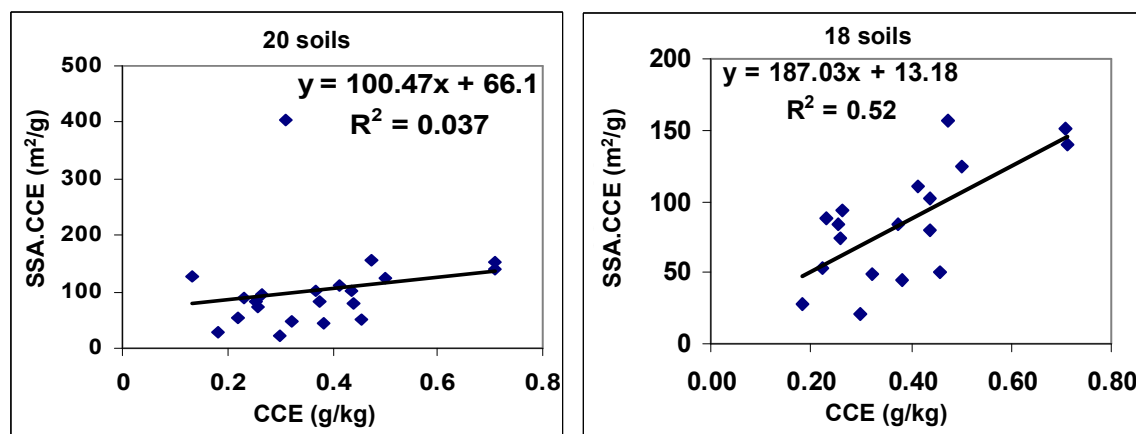

Figure 3. Relationship between SA attributable to the CCE and ACCE/CCE ratio for all the studied soils (no=20) and after removal of two soils (no 7 and 18).

Conclusion

Active calcium carbonate equivalent has been related by many workers with pH buffering and isotopic-exchangeable ions. The ACCE method described in this paper is a fast and provides a good quantitative estimate of reactive soil carbonate. This property should be measured for all calcareous soils of Iran to assist with the better interpretation of soil analysis results.

Acknowledgements

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