Assessment of Soil Inorganic Carbon Content and Its Implications for Accurate Soil Organic Carbon Quantification

1. Background and rationale

We investigated soil organic carbon (SOC) and nitrogen content using the Loss On Ignition method and C/N analyzer, we observed unusually high C/N ratios in several samples, with values exceeding 20 in some treatments. According to literature, healthy agricultural soils have a C/N ratio between 8-15, with values above 20 suggesting potential analytical interference or nitrogen immobilization.

The coastal location of our study site in Niigata presents a particular concern for inorganic carbon interference. Coastal environments are prone to carbonate mineral ($CaCO_3$) accumulation from marine sources, which can inflate apparent organic carbon measurements when using elemental analyzers without acid pretreatment. This interference can lead to overestimation of organic carbon stocks, resulting in incorrect assessments of soil carbon sequestration potential.

2. Objectives

The primary objectives of this study were to: (1) Quantify soil inorganic carbon (SIC) content in sandy coastal agricultural soils under different management practices; (2) Assess the magnitude of potential interference in SOC measurements from inorganic carbon sources; and (3) Provide correction factors for accurate SOC quantification.

3. Soil Inorganic Carbon Analysis

3.1 Materials and equipment

The SIC analysis employed the acid digestion method using the following materials:

- Soil samples: 0.1 g (ground to fine powder)
- 1.2 M HCl: 1 mL per analysis
- Pure air: for dilution and mixing
- 50 mL glass vials: reaction vessels
- 20 mL vacuum vials: for gas collection
- Rubber stoppers: for sealing vials
- 1 mL pipettes: for precise reagent addition
- Gas chromatograph: for CO_2 concentration measurement

3.2 Analytical procedure

The SIC measurement protocol used the following steps:

1. Sample preparation: 0.1 g of ground soil was weighed into 50 mL glass vials (blank controls contained no soil)

2. Acid addition: 1.0 mL of 1.2 M HCl was added to each vial to dissolve carbonate minerals according to the reaction:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow \quad (1)$$

3. Sealing and reaction: Vials were immediately sealed with rubber stoppers and allowed to react completely (approximately 5 minutes)
4. Pressure measurement and dilution: After complete reaction, internal pressure was measured, and 30 mL of pure air was added to dilute and mix the gases
5. Gas sampling: 30 mL of the gas mixture was collected and transferred to 20 mL vacuum vials, taking care to avoid HCl vapor uptake
6. CO_2 quantification: CO_2 concentration (ppm) in the gas samples was determined using gas chromatography

3.3 Calculations

SIC content was calculated using the ideal gas law and the following parameters:

- Room temperature (T): 28°C (301.1 K)
- Atmospheric pressure: 100.85 kPa
- Vial internal pressure (P): measured after reaction (kPa)
- Gas constant (R): 8.314 kPa·L/(K·mol)
- Total gas volume (V_{Gas}): 80 mL (50 mL vial + 30 mL added air)

Calculation steps:

1. CO_2 volume calculation (L):

$$V_{CO_2} = V_{Gas} \times \frac{[Sample\ CO_2\ concentration - Blank\ CO_2\ concentration]}{10^6} \quad (2)$$

2. Moles of CO_2 using ideal gas law:

$$n_{CO_2} = \frac{P \times V_{CO_2}}{R \times T} \quad (3)$$

3. Mass of CO_2 (g):

$$Mass_{CO_2} = n_{CO_2} \times 44.01 \quad (4)$$

4. Mass of carbon in CO_2 (g):

$$Mass_{Carbon} = Mass_{CO_2} \times \frac{12.01}{44.01} \quad (5)$$

5. SIC percentage:

$$SIC = \frac{Mass_{carbon}}{Soil\ mass} \times 100 \quad (6)$$

3.4 Quality control

Quality control measures included:

- Blank controls: Three HCl only blanks to account for background CO_2
- Replicate analysis: Eight replicates per treatment
- Standardized conditions: Consistent temperature, pressure, and timing
- Calibration verification: Regular GC calibration checks

4. Results

4.1 Overview of SIC measurements

A total of 48 soil samples plus 3 blank controls were analyzed for inorganic carbon content. The CO_2 concentrations in the HCl blank controls were low (131.04 to 146.28 ppm), with an average blank value of 140.05 ppm used for background correction.

4.2 SIC content by treatment

4.2.1 Descriptive statistics

The SIC content across all soil samples ranged from -0.00088% to 0.00168% (Figure 1), indicating low and variable inorganic carbon concentrations. The negative values observed in some samples result from CO_2 concentrations below the blank average, suggesting measurement uncertainty at very low SIC levels (Table 1).

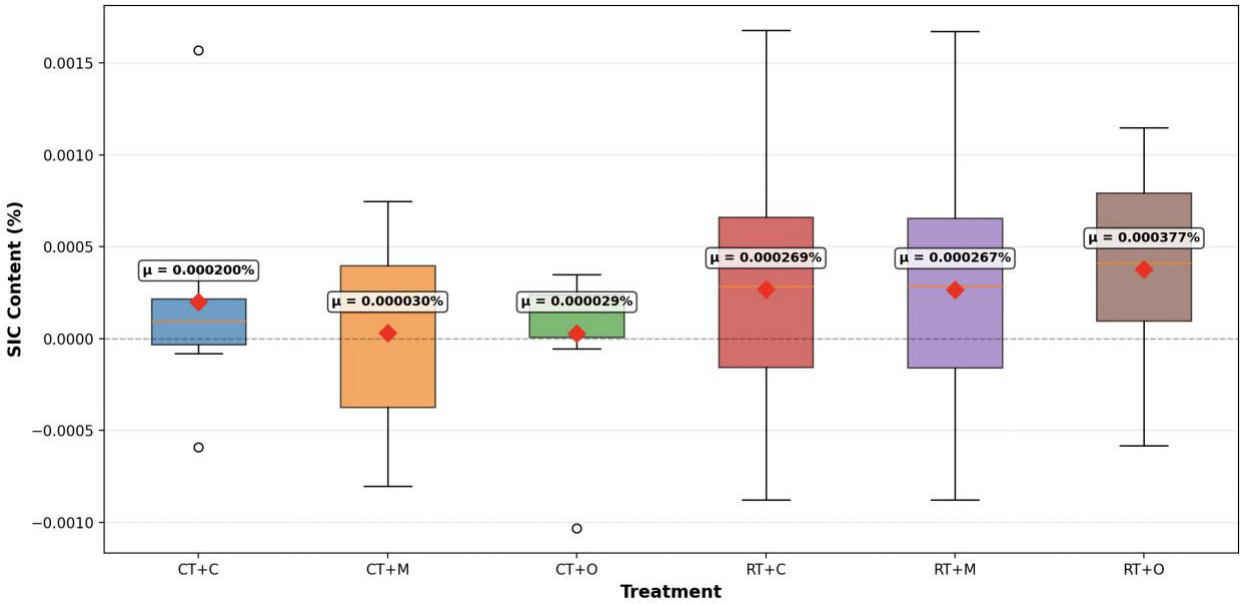

Figure 1. Distribution of soil inorganic carbon content per treatment

Table 1. Soil Inorganic Carbon content summary per treatment

Treatment	Mean SIC	Standard Deviation	Min	Max	Positive samples
CT+C	0.00020	0.0006	-0.0006	0.0016	5/8
CT+M	0.00003	0.0006	-0.0008	0.0008	4/8
CT+O	0.00003	0.0005	-0.0010	0.0004	6/8
RT+C	0.00027	0.0008	-0.0009	0.0017	5/8
RT+M	0.00027	0.0008	-0.0009	0.0017	5/8
RT+O	0.00038	0.0006	-0.0006	0.0012	6/8

One-way ANOVA showed no significant differences between treatments ($F = 0.3748$, $p = 0.863$).

The samples showed very low inorganic carbon content (<0.001%), indicating minimal carbonate presence.