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<https://doi.org/10.5109/16137>

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出版情報：九州大学大学院農学研究院紀要. 54 (2), pp.499-503, 2009-10-29. Faculty of Agriculture, Kyushu University

バージョン：

権利関係：



## Is pH of Greenhouse Soils Measured Adequately?

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(Received June 29, 2009 and accepted July 13, 2009)

We measured the soil pH on fourteen soil samples collected from greenhouses under intensive fertilizer application. All the soil samples contained carbonate, but the pH values measured by conventional method were too low in view of carbonate equilibrium. We examined the effect of the soil to water ratio, shaking time and standing time and found that the pH gradually increased as the standing time was prolonged. It reached a maximum after 192 to 264 h of standing and then decreased. The maximum pH values were fairly close to those that are calculated from the thermodynamic equation based on carbonate equilibrium.

### INTRODUCTION

It is a common understanding that the soil pH is the single most informative quantity that characterizes nature of soils. Soil pH reflect the exchangeable cation composition of soils, controls the mobility of trace elements in soils and greatly affect the microbial and enzymatic activity in soils. From physico-chemical standpoint, the pH of interstitial solution, i. e., soil solution, would be the natural quantity to be measured to get insight into those soil processes. However, sampling soil solution is extremely laborious and time consuming and it is not adequate for the method of routine soil testing. In routine practices, the pH of soil suspension at soil to water ratios (SWR) ranging from 1:1 (Thomas, 1996) to 1:5 (Committee on Soil Testing, 2000; ISO, 2005) is measured and designated as soil pH.

The typical water content of field-moist upland soils is around 0.15 to 0.25 kg kg<sup>-1</sup> and making a suspension from a soil sample inevitably dilute the soil solution retained in its interstices and, in turn, may alter the pH. However the effect of dilution is not as straightforward as might be expected. Davis (1943) showed that the change in soil pH associated with 10-fold dilution was not more than 0.4 unit. Committee on Soil Testing (2000) examined the effect of dilution on the measured pH for some soils and clay minerals and reported that the SWR did not affect the pH significantly in a SWR range from 1:1 to 1:10. Okajima (1981) measured both the soil pH and soil solution pH on several tens of soil samples and found that the difference between the two pHs was mostly less than 0.5 unit. Thus, there is a consensus that the SWR does not significantly affect the measured soil pH and ISO (2005) adopted taking a soil sample with a measuring

spoon accommodating approximately 5 mL instead of weighing.

In contrast to the effect of SWR, there seems to be some disagreement with regard to the time required for equilibration. The Soil Science Society of America recommends 10 min after mixing soil and deionized water at a SWR of 1:1 (Thomas, 1996). Japanese Society of Soil Science and Plant Nutrition, on the other hand, advocated that the standing time should be more than 1 h at a SWR of 1:2.5 (Soil Environmental Analysis Methods Committee, 1997). Japanese Geotechnical Society and ISO adopted in their standards the SWR of approximately 1:5 and the standing times not more than 3 h (Committee on Soil Testing, 2000; ISO, 2005). According to these *de facto* standards, the time for equilibration should be longer than 10 min but no longer than 3 h.

Recently we carried out a series of soil testing on several tens of soil sample collected in greenhouses in Fukuoka prefecture, Japan and found that the prescribed methods for pH measurement are not suitable for equilibrium-pH measurement. All the soil samples contained small amount of free carbonate. Nevertheless, the measured pH values were significantly lower than the values anticipated for calcareous soils. The objective of the present study was to re-examine the effect of standing time on the soil pH determined on soil suspensions.

### MATERIALS AND METHODS

#### Soil samples

Fourteen samples were collected from the Ap horizon of soils in greenhouses in Fukuoka prefecture. The greenhouses were being used for growing tomato, leek, spinach and komatsuna. The collected samples were air-dried and passed through 2-mm screen and stored in plastic bags. As reference soil samples, Ap soil samples from an acidic soil collected in Korea was used.

#### Experimental methods

Basic chemical properties of the soil samples including pH, organic carbon content and exchangeable cation composition were determined by the standard methods (Soil Environmental Analysis Methods Committee, 1977).

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The soil pH was measured at a SWR of 2.5. Carbonate content of the soil samples were determined by the procedure proposed by Wada (1997). Water soluble cations and anions were extracted by shaking with distilled water at a SWR of 1:5 for 24 h. The cations and anions were determined by atomic absorption spectroscopy and ion chromatography.

In the pH measurement, 5.00 g soil samples were taken in plastic centrifuge tubes, mixed with deionized water at SWR of either 1:1, 1:2.5 or 1:5, shaken on a reciprocal shaker for either 15 min., 30 min or 60 min and allowed to stand for up to 700 h. The tubes were uncapped to keep the suspensions oxidative. In cases when the amount of soil available for pH measurement was limited, soil suspensions were prepared in reduced size keeping the SWR. A preliminary experiment showed that the reduced sample size did not affect the pH value even when only 1 g soil was used for preparing suspension. The pH was measured by immersing a glass electrode in supernatant of the soil–water mixtures. An F-24 pH meter combined with Type 6378 glass electrode (HORIBA Co., Kyoto) was used throughout the experiment. Sample

preparation and pH measurement were carried out in a room kept at 25 °C.

The atmospheric CO<sub>2</sub> concentration in the room where pH measurement was carried out was monitored by CO<sub>2</sub> detector tube.

## RESULTS AND DISCUSSION

The basic chemical properties of the soil samples are summarized in Table 1. As shown in the last column of the table, the F104, F206, F214 and F215 samples contained more than 10 cmol kg<sup>-1</sup> of carbonate. Since the CO<sub>2</sub> evolution during the carbonate determination almost completed in 5 min, the carbonate is considered to be mostly calcite. Contrast to the soils from greenhouses, the soils used for comparison were acidic and Al dominated among the exchangeable cations.

Major cation and anion concentrations in the extract obtained at a SWR of 1:5 after 24 h shaking are listed in Table 2. Some soils contain large amount of soluble salts reflecting intensive fertilizer application. The comparison of Table 1 and Table 2 indicate that there is no clear

**Table 1.** Basic chemical properties of soil samples used

Soil	OC*	pH	Exchangeable cation					Carbonate
			Ca	Mg	K	Na	Al	
	%		cmol kg <sup>-1</sup>					cmol kg <sup>-1</sup>
F104	3.08	7.0	30.6	4.3	1.8	0.6	0	30.8
F206	3.22	6.6	11.4	3.7	3.2	1.5	0	36.7
F215	3.94	6.6	28.0	10.1	0.5	0.5	0	22.4
F214	4.85	6.3	29.5	5.2	2.9	0.7	0	12.0
F151	1.88	5.6	19.2	5.6	0.3	0.4	0	7.6
F212	3.41	6.2	27.2	7.3	0.7	0.6	0	7.8
F324	2.60	7.0	21.6	2.7	1.7	0.3	0	4.8
F207	3.86	5.8	13.2	4.3	3.1	1.3	0	3.0
F213	2.81	6.5	21.0	4.5	1.5	1.0	0	2.8
F109	1.43	6.0	14.2	4.1	1.7	1.4	0	2.4
F211	3.28	6.5	17.4	3.2	1.1	0.7	0	1.0
F219	1.97	5.6	13.2	3.8	2.7	0.2	0	0.8
F323	3.80	6.3	12.8	3.0	1.3	0.2	0	0.8
F401	3.20	6.7	20.7	6.0	1.9	0.5	0	0.5
K1	1.58	4.5	1.5	0.6	0.2	0.1	3.2	0

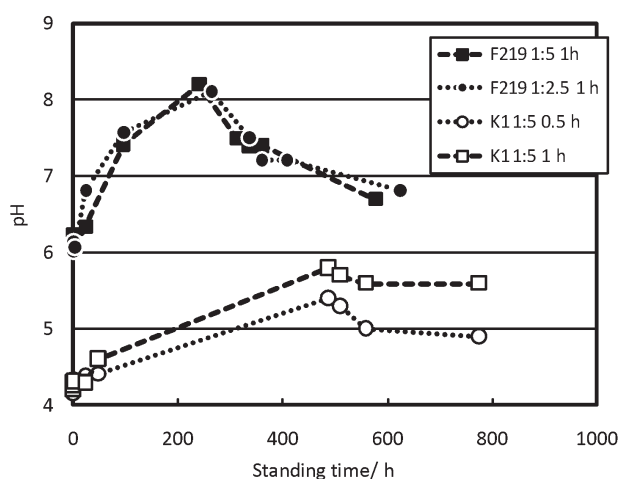
\* organic carbon content

**Table 2.** Major ion concentrations in 1:5 water extracts

	Ca	Mg	K	Na	Cl	SO <sub>4</sub>	NO <sub>3</sub>
	mmol L <sup>-1</sup>						
F104	4.1	1.2	1.0	0.8	0.5	1.9	3.6
F206	2.3	0.7	1.4	0.8	0.5	1.7	0.9
F215	2.9	2.8	0.2	0.6	0.5	1.4	3.1
F214	3.1	1.1	2.0	0.8	0.8	1.1	4.2
F151	3.2	2.2	0.2	0.8	1.2	2.5	2.5
F212	2.9	1.7	0.4	0.6	0.4	2.9	1.2
F324	0.9	0.2	0.4	0.2	0.2	0.8	0.2
F207	2.0	1.1	2.2	0.6	0.7	2.3	2.3
F213	1.2	0.5	0.8	1.2	0.4	0.8	0.7
F109	5.5	2.0	1.6	0.8	1.6	4.0	4.0
F211	1.1	0.4	0.6	0.8	0.3	0.7	0.7
F219	0.6	0.4	0.6	0.2	0.6	0.9	0.9
F323	0.7	0.3	0.6	0.2	0.2	0.2	0.2
F401	0.3	0.1	0.2	0.2	0.1	0.1	0.1

relationship between the carbonate content and soluble salt concentration. The effect of shaking time on the ion concentrations of water extract was examined for selected soil samples. The results indicated that there is no significant effect of shaking time on the ionic concentrations in the extract.

Fig. 1 shows the measured pH values for two soil samples (F219 and K1) as a function of standing time after shaking. For the F109 soil, the pH values measured at SWR of 1:2.5 and 1:5 were plotted against standing time after shaking for 1 h. For the K1 soil the pH values measured at the same SWR of 1:5 but after different shaking time of 0.5 and 1 h were plotted. The pH for the F109 soil gradually increased as the standing time increased up to about 8.1 at a standing time of 264 h and then decreased to about 6.8 after about 600 h. The two plots for the SWR of 1:5 and 1:2.5 almost coincided, suggesting that the SWR does not affect the soil pH. As seen from the congested data points at short standing times, the pH was almost constant within 2 h after shaking. For the K1 soil,



**Fig. 1.** The effect of soil to water ratio and standing time on the measured pH for tow soil samples.

the trend of the pH change was basically similar, i. e., the pH gradually increased as standing time increased and then decreased again. But the increment in pH was not as large as 1 unit. For this soil sample, the pH was almost constant within 24 h after shaking and the shaking time did not virtually affect the pH at least in a short period after shaking. The data for other greenhouse soils behaved in quite a similar way in that they all showed pH maxima at 250–300 h after shaking (Fig. 2).

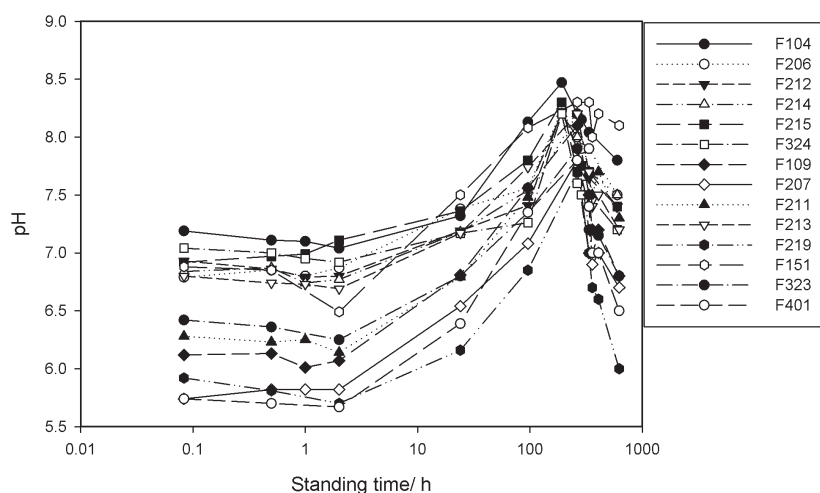
These observations are basically in accordance with those in the preceding studies in that the SWR does not affect pH measurement (Davis, 1943; Committee for Soil Testing, 2000). In addition, the fairly large pH change after prolonged standing time explains why relatively short standing times are recommended for soil pH measurement in the existing standards (Soil Environmental Analysis Committee, 1977; Committee for Soil Testing, 2000; ISO, 2005). Being reproducible and taking short time are important for routine analytical method for soil testing. However, whether obtained values are chemically meaningful or not is other thing. Table 1 shows that the pH values obtained in 2 h after shaking ranged from 6.8 to 7.2 for soils containing significant amount of carbonate (Fig. 2 and Table 1) and they are definitely too low. Thus the conventional method for soil pH measurement is not suitable to obtain chemically meaningful equilibrium pH values.

When a soil solution is at equilibrium with pure calcite, the following equation holds;

$$K_{sp} = (\text{Ca}^{2+}) (\text{CO}_3^{2-}) \quad (1)$$

where  $K_{sp}$  is the solubility product of calcite and the parentheses indicate the thermodynamic activity. The activity of carbonate ion can be related to the activity of hydrogen carbonate ion and carbonic acid through;

$$K_{a1} = \frac{(\text{HCO}_3^-) (\text{H}^+)}{(\text{H}_2\text{CO}_3)} \quad (2)$$



**Fig. 2.** The soil pH measured at a water to soil ratio of 1:2.5 as a function of standing time. Logarithmic scale was used for abscissa to avoid congestion of the plot points.

and

$$K_{a2} = \frac{(\text{CO}_3^{2-})(\text{H}^+)}{(\text{HCO}_3^-)} \quad (3)$$

where  $K_{a1}$  and  $K_{a2}$  are the first and second dissociation constant of carbonic acid. Since the partial pressure of  $\text{CO}_2$  in the air is almost constant, the activity of carbonic acid in the soil solution can be related to the atmospheric partial pressure of  $\text{CO}_2$  through;

$$(\text{H}_2\text{CO}_3) = K_H P_{\text{CO}_2} \quad (4)$$

where  $K_H$  ( $\text{mol atm}^{-1}$ ) and  $P_{\text{CO}_2}$  (atm) are the Henry constant and the partial pressure of  $\text{CO}_2$ . By combining eqs. (2), (3) and (4), the activity of carbonate ion can be related to the partial pressure of  $\text{CO}_2$  in the air;

$$(\text{CO}_3^{2-}) = \frac{K_{a1}K_{a2}K_H P_{\text{CO}_2}}{(\text{H}^+)^2} \quad (5)$$

By substituting eq. (5) into eq. (1) and taking common logarithm of the both side, following equation is obtained.

$$\begin{aligned} \text{pH} = & -\frac{1}{2} (\log K_{a1} + \log K_{a2} + \log K_H + \log P_{\text{CO}_2} \\ & + \log (\text{Ca}^{2+}) - \log K_{\text{sp}}) \end{aligned} \quad (6)$$

In the derivation the negative logarithm of proton activity was set equal to pH. Since  $\log K_{a1} = -6.35$ ,  $\log K_{a2} = 10.33$ ,  $\log K_H = -1.46$ , and  $\log K_{\text{sp}} = -8.35$  (Novozamsky and Beek, 1976), eq. (6) reduces to;

$$\text{pH} = 4.89 - \frac{1}{2} (\log P_{\text{CO}_2} + \log (\text{Ca}^{2+})) \quad (7)$$

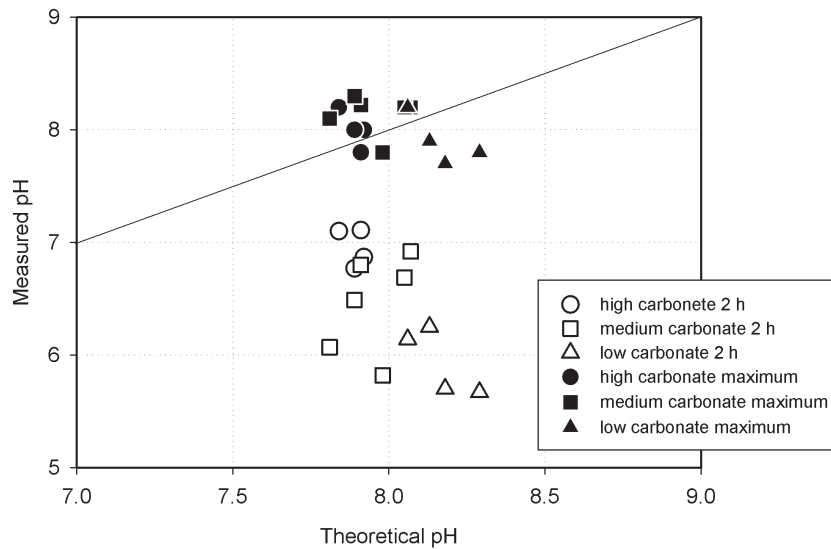
This means that the pH of a soil solution at equilibrium with calcite is solely determined by the  $\text{Ca}^{2+}$  activity and the partial pressure of  $\text{CO}_2$  in which the pH measurement

is carried out. In this experiment the partial pressure of  $\text{CO}_2$  in the room was on average 0.00035 atm. Eq. (7) further reduces to;

$$\text{pH} = 6.62 - \frac{1}{2} \log (\text{Ca}^{2+}) \quad (8)$$

As shown in Table 1, all the soil samples contained free carbonate and the equilibrium pH of the soil solutions at equilibrium with them can be estimated with eq. (8). Since the soil pH plotted in Fig. 2 was measured at a SWR of 1:2.5, the values of the  $\text{Ca}^{2+}$  activity at that SWR are needed to use eq. (1). The major ion concentrations at a SWR of 1:2.5 were estimated from the data shown in Table 2 following the method proposed by Wada *et al.* (2006-a, 2006-b). In this calculation sulfate concentration was estimated in a way similar to those for chloride and nitrate. The activity of  $\text{Ca}^{2+}$  was then calculated with a computer code PHREEQC (Parkhurst and Appelo, 1999) and the equilibrium pH was estimated with eq. (8). The pH measured after 2 h standing was plotted against theoretical pH in Fig. 3. In the same figure, the observed maximum pH was also plotted against the theoretical pH for comparison.

Apparently, the pH values after 2 h standing were lower than the theoretical values by 0.7 to 3 pH units. The difference between the observed and theoretical values were relatively small for soils containing  $>10 \text{ cmol kg}^{-1}$  carbonate than for those with carbonate content  $< 2 \text{ cmol kg}^{-1}$ . The distribution of carbonate particles in a soil sample may not have been uniform and the whole soil may not have been at equilibrium with calcite. If the calcite content in the soil sample is low, it may dissolve during shaking and standing. However, in view of very low solubility of calcite, complete dissolution of  $>10 \text{ cmol kg}^{-1}$  of calcite is not probable. The large downward deviation of the plot points (open circle) for high carbonate content soils strongly suggests that the 1 h shaking and 2 h



**Fig. 3.** The relationship between the measured pH and theoretically predicted pH. The open symbols refer to measured pHs after 2 h standing and closed ones maximum pHs attained after 192–264 h standing.

standing is not enough for equilibration.

Fig. 3 also shows the plots for highest pH values (closed symbols), which were obtained after 192 to 264 h of standing. All these plots scatter around 1:1 line, suggesting that the maximum pH values are close to the theoretical pH values that were calculated under the assumption of the presence of free carbonate. The deviation from the theoretical value was mostly within  $\pm 0.5$  pH units. There is little chemical background in regarding the maximum pH as the equilibrium pH with respect to carbonate dissolution. However, the fact that all the plot points (closed symbols) fell in the vicinity of the 1:1 line deserves further study.

It is well known that soil pH increases as oxidation–reduction potential decreases. In the present study, all the centrifuge tubes used for pH measurement were kept open to allow free access of the air and it is unlikely that reducing condition prevailed in all of them, although soil color turned grayish in some tubes. If it had occurred to some extent, it would have not affected the suspension pH, because the pH is solely determined under the presence of calcite by the  $\text{Ca}^{2+}$  activity and equilibrium  $\text{CO}_2$  pressure (eq. (8)) irrespective of oxidation–reduction condition. During standing after shaking, some of the water evaporated from the suspensions, resulted in lower SWR. However, this would not have affected the pH because, as shown in Fig. 1, the SWR has little effect on pH.

The acidic K1 soil showed gradual but significant pH increase during prolonged standing (Fig. 1). This suggests that the increase in pH is not necessarily a result of slow carbonate equilibration.

The results of the present study strongly suggest that the conventional methods for soil pH measurement, i. e., shaking for <1 h and standing for <3 h, is not adequate to obtain equilibrium pH values for greenhouse soils containing free carbonates. During prolonged standing after shaking, the pH gradually rose and theoretically reasonable values were attained after 192 to 264 h and then dropped. Even if the attained maximum pH values represent the equilibrium with regard to carbonate dissolution, it is not convenient to wait for more than 8 days for pH

measurement. Further studies are needed to improve the method to obtain equilibrium pH values quickly and to understand the mechanism of up and down in pH during prolonged standing.

## ACKNOWLEDGEMENTS

This study was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Society for Promoting Sciences (# 21380048).

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