Research article

Potential Measurement as a Method for Monitoring the Soil Chemical Environment

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Received 8 January 2021 Accepted 19 May 2021 (*Corresponding Author)

Abstract Soil chemical environment (SCE) affects soil degradation and productivity, thus understanding of the temporal changes of SCE is important for obtaining higher soil productivity. Widely used indices of SCE included ion concentration, pH, and redox potential (ORP), but these cannot monitor SCE continuously. Previously, a study proved that continued potential measurement can represent temporal changes in the water quality at the sea floor. However, no report related to monitoring the SCE with continued potential measurement has been found. Therefore, this study proposes a method for evaluating soil ORP using continued potential measurement, and examine the method's validity in representing changes in SCE due to soil reduction, bacteria activation, and soil oxidation. Laboratory experiments were conducted using soils from rice paddy fields. A brush-type carbon electrode was installed in the soil layer that then connected to a reference electrode for measurement of the soil ORP. Different soil conditions were created by mixing the paddy soil with cow manure compost or potassium sulfate. The soil ORP was automatically recorded every 15 min using a voltage meter. The ORP of paddy soil decreased temporally and stabilized at 50 days after the start of the experiment, suggesting that soil reduction occurred over those 50 days. When testing the potassium sulfate-paddy soil mixture, the soil ORP rapidly decreased during the first day after the experiment started. When testing cow manure compost-paddy soil mixture, a larger decrease in soil ORP was observed compared to that in the paddy soil alone. These findings suggest that soil reduction is promoted by adding potassium sulfate or cow manure compost. Among the soil samples tested, there was a range of soil ORPs and trends in the potential decreases. Based on the results of this study, it was found that continued potential measurement is effective in evaluating soil ORP, which represents temporal changes in SCE due to redox reactions after the addition of cow manure compost or potassium sulfate. In addition, the effects of bacteria activation are revealed during continued potential measurement of soil ORP.

Keywords potential measurement, carbon electrode, redox reaction, metabolism reaction, soil reduction, soil oxidation

INTRODUCTION

Soil is a medium for plant growth and is one of the fundamental bases for agricultural productions, thus agricultural productivity is strongly influenced by the use of soil fertilizer (Hatfielf, 2006). Over the last few decades, the relationship between cropping and managing systems and the soil chemical environment (SCE) has been discussed with regard to obtaining higher productivity by preventing soil degradation or erosion. The understanding of SCE is useful for ensuring healthy soil that can sustain crop production and environmentally friendly agriculture (Yan and Hou, 2018).

It has been suggested that the transition from conventional to organic or low-input farming has caused changes in the SCE and the processes related to soil fertility (Clark et al., 1998). As a decline in soil fertility results in a decrease in productivity (Buresh et al., 1997), management of soil fertility and soil health plays an important role in realizing sustainable agriculture (Prasad and Power, 1997). Since chemical reactions and nutrient circulation affect soil fertility, understanding changes in the SCE are essential in facilitating successful, high-productivity organic farming.

To date, parameters such as pH, organic matter contents, phosphorus availability, and cation exchange capacity have been widely used as indices for evaluating SCE. However, their measurements cannot be conducted continuously, thus changes in the SCE over time are underdetermined. Therefore, a method that can continuously monitor SCE is required. Potential measurement is a method that can monitor the redox environment of soil over time. This method may play an important role in organic farming. For obtaining a higher productivity of organic farming, the measuring SCE over time can provide useful information for controlling or improving redox and biological conditions of soils. This method was used by Nagama et al. (2018) when they suggested that water potential measurement can describe changes over time in the water quality at the sea floor. However, no report related to monitoring SCE with continued potential measurement has been found in the literature.

OBJECTIVE

This study was aimed at proposing a method for measuring soil ORP and at examining the method’s validity in representing changes in SCE due to soil reduction, bacteria activation, and soil oxidation. This was done by continued potential measurement to determine changes in the soil ORP of paddy soil. The paddy soil samples studies were pure, mixed with cow manure compost, or mixed with potassium sulfate.

METHODOLOGY

The experimental device comprised a cylindrical bottle with an inner diameter of 120 mm and a height of 150 mm. The bottle was filled with paddy soil to a depth of 20 mm, and a brush-type carbon electrode was placed on the soil layer. Then, another soil layer at a depth of 30 mm was placed on the electrode. Finally, tap water was poured over the soil layers (Fig. 1). The paddy soil was collected during the agricultural off-season from a rice filed in Ebina, Kanagawa, Japan. Approximately 150 mm of the surface soil was collected and transported to the laboratory.

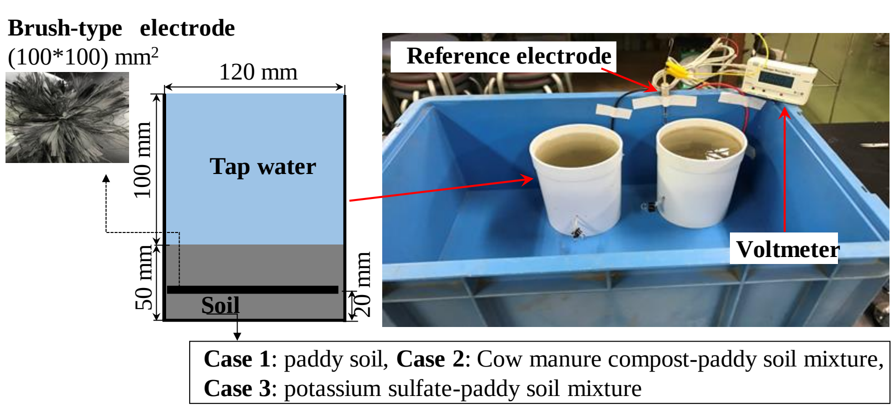

Fig. 1 Experimental device and measurement method

The soil layer was prepared under different conditions to ensure differences in the SCE. For example, certain paddy soil was mixed with cow manure compost, and another mixture had potassium sulfate. The mixing ratio (mass basis) of paddy soil to cow manure compost or potassium sulfate was 9:1. The electrode material was carbon cloth (News Company, PL200-E), which was heated at 500°C for 1 h prior to use to improve its performance, as was suggested by Nagatsu et al. (2014). The heated carbon cloth with a width of 100 mm and a length of 100 mm was separated into fibers to form a brush-type electrode (Fig. 1).

The bottles were then submerged in a container that was filled with tap water (Fig. 1). In the container, the electrode in the soil layer was connected to a reference electrode (Toyo Co., RE-7A) for measuring the electrode potential. This electrode potential was the soil ORP. The potential was recorded automatically every 15 min by a voltmeter (T&D Corp., VR-71). A plastic-coated copper wire was used for all the connections in the measurements.

RESULTS AND DISCUSSION

Accuracy of Potential Measurement

To examine the accuracy of potential measurement, two paddy soil samples were made under the same condition, and the soil ORP measurements of the two samples were compared (Fig. 2). The soil ORP measurements taken during the first day were used because they nearly reflected the electrode potential. As time increases, the SCE may differ from one sample to another, even though they were made under the same condition because soil reduction (organic matter decomposition) may differ.

As demonstrated in Fig. 2, the maximum variance in potential was only +0.004 V (1.33%), indicating this method's high accuracy. Therefore, it can be said that the proposed method, i.e., potential measurement, can accurately represent temporal changes in the SCE owing to redox reactions and bacteria activation in soils.

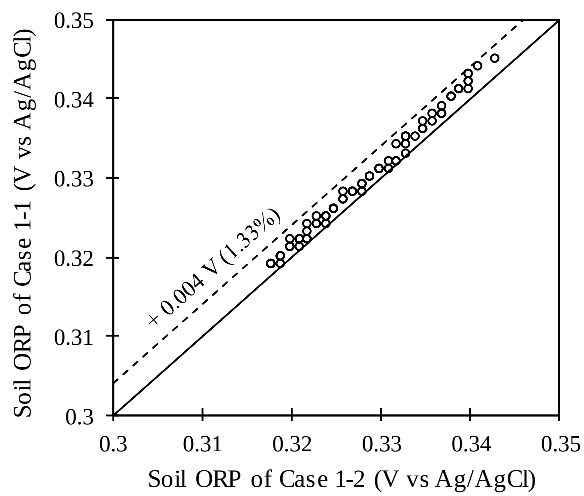

Fig. 2 Comparison of the measured soil ORP from two samples under the same condition

Potential Measurement for Representing Soil Reduction

Fig. 3 illustrates the comparison of temporal changes in soil ORP for each sample. The paddy soil used was in an oxidized state as it was collected during the agricultural off-season. Thus, the initial potential was 0.35 V which then temporally decreased and almost stabilized after 50 days. Approximately two months are required for complete soil reduction.

On day 50, the soil ORPs were −200 mV for the paddy soil, −260 mV for the potassium sulfate-paddy soil mixture, and −475 mV for the cow manure compost-paddy soil mixture. Previously, it was reported that different redox reactions result in a difference in soil ORP (Liesack et al., 2000; Matocha, 2005). Specifically, soil ORP indicates redox reactions occurring in soils. The results of this study indicate that different redox reactions occur because of different soil compositions. Compared with paddy soil alone, a large decrease in soil ORP was observed when potassium sulfate was added to the paddy soil. This was due to the reduction reaction of sulfate in the soil. Since methanogens are present in cow manure, methane production occurred in the paddy soil the manure was mixed with, resulting in a large decrease in soil ORP. In summary, potential measurement is useful for understanding changes in SCE due to redox reactions in soils.

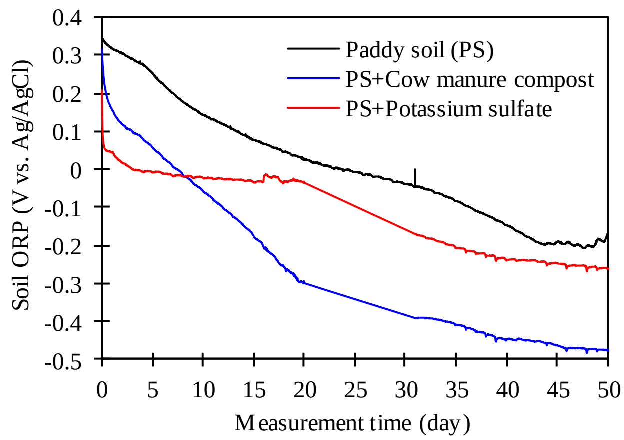

Fig. 3 Comparison of temporal changes in soil ORP

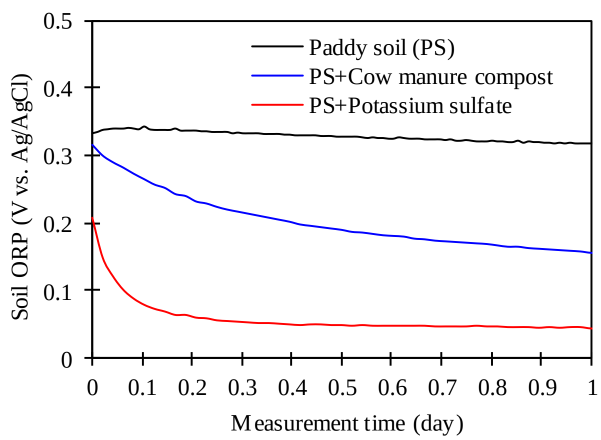

Fig. 4 Comparison of decreasing trends of soil ORP during the first day of the experiment

Potential Measurement for Representing Microbial Activation in Soils

Fig. 4 depicts a comparison of decreasing trends of soil ORP during the first day of the experiment. Interestingly, large differences in decreasing soil ORP were observed during this time. Compared with paddy soil, a large decrease in soil ORP was recorded when the soil was mixed with cow compost manure, and an even larger decrease in soil ORP was recorded when it was mixed with potassium sulfate. These trends depend on the redox reactions occurring at the electrode and possible potential losses due to electron transfer at the electrode surface.

Following the Nernst equation (Eq. 1), the electrode potential (E) depends on the standard potential of redox couple (E^0) and the concentration of ions (logarithm term).

$$E = E^o + (RT/nF) \ln (O_x/ R_e) \quad (1)$$

R is the universal gas constant, T is the temperature in Kelvins, n is the number of electrons transferred in the reaction or half-reaction, F is the Faraday constant, O_x is the activity of the oxidized form, and R_e is the activity of the reduced form.

E^0 value are different between redox couples; for example, E^0 =1.057 V for the $Fe(OH)_3/Fe^{2+}$ redox couple and E^0 =0.303 V for SO_4^{2-}/H_2S. Therefore, large changes of E will be observed when the redox reaction varies from one to another redox couple. Compared with a biological reaction, a chemical reaction occurs rapidly, thus the observed rapid decrease of soil ORP in this study is due to the change of the redox couple from iron reduction in the paddy soil alone to sulfate reduction in the potassium sulfate-paddy soil mixture.

In addition, E depends on microbial activation at the electrode. According to Yamasaki et al. (2018), potential loss (activation loss) occurs during the flow of electrons into an electrode. In a potential measurement, activation loss should be minimized to obtain the equilibrium potential in a short time. Microbial activation at the electrode is one of the methods for minimizing activation loss. Wang et al. (2009) succeeded in improving electrode performance by lowering the potential losses by activating bacteria at the electrode. As seen in Fig. 4, the decrease of soil ORP when cow manure compost was used was larger than that when paddy soil alone was used. This may be explained in that microbial activation occurs in the cow manure compost. Therefore, changes in the redox couple and the benefits of microbial activation in soil can be understood through potential measurement.

Potential Measurement for Representing Soil Oxidation

Measurement did continue after day 50 for the case of using paddy soil alone. Germination was confirmed on day 50. From the measurement taken (Fig. 5), soil ORP started to increase on day 50, indicating the generation of soil oxidation. On day 170, the soil potential reached 0.32 V which is close to the initial potential measurement taken. Additionally. the plant growth had occurred (Fig. 5).

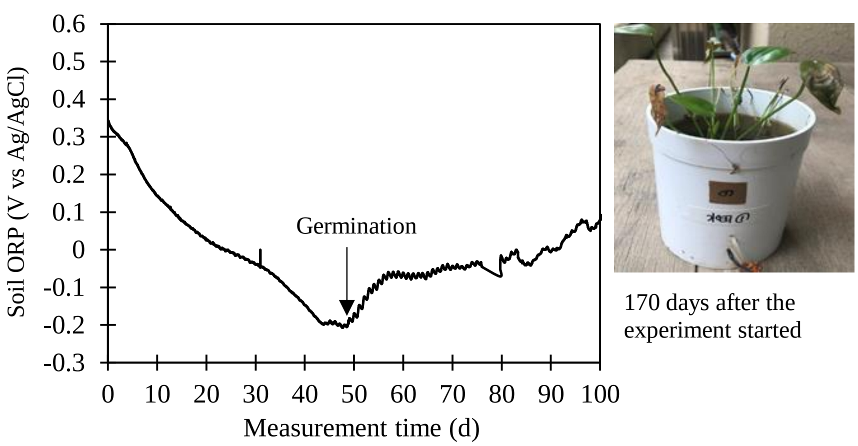

Fig. 5 Changes in soil ORP of paddy soil due to soil oxidation

The increase in soil ORP was caused by soil oxidation owing to the oxygen supply from the overlying water layer. Plant growth may have also facilitated the oxygen supply of the soil layer. As the electrode was placed at a depth of 30 mm from the soil surface, the oxygen supply may have affected these long-term measurement results. In other words, the proposed method of potential measurement may also predict soil oxygen levels.

CONCLUSIONS

In this study, a laboratory experiment was conducted to examine a method for monitoring SCE and to examine its validity in representing changes in SCE due to soil reduction, bacteria activation, and soil oxidation. It was found out that the proposed method, i.e., potential measurement, had high accuracy (with a variance of 1.33%) for representing SCE. A difference in equilibrium soil ORP was observed when mixing different fertilizers with paddy soil, indicating that redox reactions in soils can be predicted through potential measurement. In addition, different trends in decreasing soil ORP were observed, suggesting that chemical and biological reactions in soil can be understood from potential measurement. Finally, soil ORP started to increase on day 50 because of soil oxidation, indicating that potential measurement can predict soil oxygen supply that causes soil oxidation.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the students of the Rural Environmental Engineering Laboratory, Tokyo University of Agriculture, for their efforts in collecting data.

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