



# Reuse of Unavailable Phosphate in Soils Using Solar Cell-Powered Electrokinetic Treatment

**NARONG TOUCH\***

*Faculty of Regional Environment Science, Tokyo University of Agriculture, Tokyo, Japan  
Email: nt207118@nodai.ac.jp*

**TAKAHIKO NAKAMURA**

*Faculty of Regional Environment Science, Tokyo University of Agriculture, Tokyo, Japan*

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**Abstract** Electrokinetic treatment (ET) is widely used for soil remediation, specifically for removing heavy metals from soil. Till date, we have focused on the nutrients released in soils using a solar cell-powered ET, which contributes to increasing the productivity of organic farming. Previously, when a 1.5 V solar cell was used in ET, the release of ammonium ions and the growth of microorganisms were observed. However, no release of phosphate ions was observed. Thus, it is presumed that a 1.5 V solar cell is insufficient to release phosphate in soils. Therefore, this study aims to examine the effects of solar cell voltage on the release of phosphate in soils. In laboratory experiments, an anode (oxidation reaction) and a cathode (reduction reaction) were installed in andosol mixed with cow manure compost, and a 3 or 6 V solar cell was used to produce an electric current between the two electrodes. Sixty-two days after the current generation, the chemical properties of the soil were measured. The results suggest that soil redox conditions can be controlled by changing the solar cell voltage. From the pH distributions, a higher voltage of solar cells was used and a large change in pH was obtained. Furthermore, a decrease in soil redox potential was obtained by increasing the solar cell voltage. From the phosphate distributions, a 6 V solar cell is required to release phosphate in soils. It is recommended that applying ET powered by a 6 V solar cell (potential gradient: 0.12 V/cm) facilitates nutrient release in soils, which is the most important factor in organic farming.

**Keywords** solar cell, voltage, electrokinetic treatment, soil reduction, phosphate, organic farming

## INTRODUCTION

According to the Ministry of Agriculture, Forestry, and Fisheries of Japan, organic farming is a strategy to achieve sustainable agriculture. The government has proposed many countermeasures to facilitate organic farming (MAFF, 2019). Hence, productivity-enhancing technologies and implementation systems are required.

In organic farming, because nutrients are supplied by the decomposition of organic matter, facilitating this decomposition is crucial in providing higher productivity. As the decomposition of organic matter depends on the Soil Chemical Environment (SCE), controlling SCE is imperative in enhancing the productivity of organic farming. According to Yan and Hou (2018), understanding SCE is useful for ensuring healthy soil that can sustain crop production. Therefore, to provide higher productivity in organic farming, a technology that can control the SCE to activate bacterial metabolism for enhancing the decomposition of organic matter is required.

Electrokinetic Treatment (ET) is a technology for generating a low-intensity electrical field between two electrodes buried in soils by applying a direct current or constant voltage (an external power supply). ET has been widely used for a few decades to remove contaminants, such as dyes and heavy metals (Hanay et al., 2009, Almomani and Baranova, 2013). Kim et al. (2010) reported changes in soil pH and electrical conductivity owing to ET application in soil. Additionally, ET can

be used to control SCE. Previously, a battery was used to apply a direct current or a constant voltage, but now a solar system is also used as an external power supply of ET (Liu et al., 2020). However, a large potential gradient, for example, 3-5 V/cm, is commonly applied to soils, which causes large variations in the SCE. This, in turn, influences soil biology, limiting the decomposition of the organic matter.

We thought that by decreasing the potential gradient (i.e., the solar cell voltage), the effects on soil biology could be reduced. As such, in our previous study (Touch and Nakamura, 2022), a 1.5 V solar cell (potential gradient: 0.03 V/cm) was used in ET. Following the application, the release of ammonium ions and the growth of microorganisms were observed, which would also be useful for organic farming. However, no release of phosphate was observed. Thus, a 1.5 V solar cell was insufficient to release phosphate in soils. As increasing the voltage of the solar cell facilitates reactions on the electrode surface in soils, using a higher voltage of the solar cell may cause the release of phosphate.

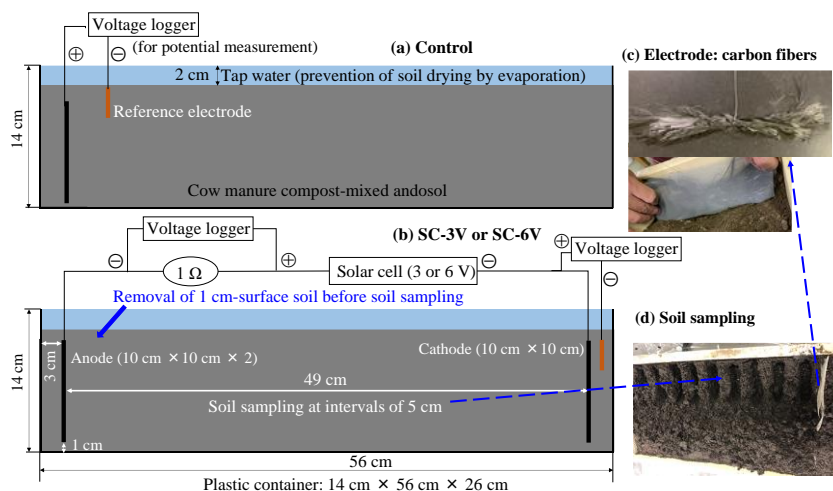
## OBJECTIVE

This study aims to examine the effects of solar cell voltage on the release of phosphate in soils. Specifically, we examined changes in electrode potential by increasing the solar cell voltage, the soil redox conditions (pH and redox potential), and nutrient release following the application of solar cell-powered ET. This was conducted by applying ET to andosol mixed with cow manure compost with a generated electric current for two months.

## METHODOLOGY

### Experimental Procedures and Operations

Commercial products, i.e., dried cow manure compost (fully matured, nitrogen 1.09%, phosphate 2.29%, potassium 2.28%) and andosol (volcanic derived soils with high contents of organic matter and aluminum compounds), were used in laboratory experiments. First, the compost was mixed with andosol at a volume ratio of 47% (generally, 40-60% was used). The mixture was then used in the experiments, which were conducted under three conditions without treatment (Control), treated with a 3 V solar cell (SC-3V), and treated with a 6 V solar cell (SC-6V). For Control, an electrode was installed in the mixture to measure the soil potential continuously (Fig. 1a).



**Fig. 1 Experimental devices and operations**

For SC-3V or SC-6V, two electrodes were installed in the soil layer (Fig. 1b). To generate an electrical current, one electrode was connected to the positive terminal, and the other was connected to the negative terminal of a solar cell (3 V or 6 V) using the circuit shown in Fig. 1b. Different voltages of the solar cells were obtained by connecting a 1.5 V solar cell (Tamiya, 1.5 V-500 mA) in series. An external resistance of  $1 \Omega$  was loaded between the anode and solar cell. The electrode material was carbon cloth (News Company, PL200-E), which was heated at  $500^\circ\text{C}$  for 1 h before using it, as Nagatsu et al. (2014) suggested. The heated carbon cloth with a width of 10 cm and height of 10 cm was separated into fibers to form a brush-type electrode. The electrode was placed in a plastic net (1-mm mesh) and installed in the soil layer (Fig. 1c). The anode surface area was  $0.02 \text{ m}^2$  ( $10 \text{ cm} \times 10 \text{ cm} \times 2$ ), while the cathode surface area was  $0.01 \text{ m}^2$  ( $10 \text{ cm} \times 10 \text{ cm}$ ). A smaller cathode surface area compared with the anode surface was made to obtain a higher reduction at the cathode.

After installing both electrodes, the container was filled with tap water. Consequently, a 2 cm water layer was formed on the soil surface, which can prevent the soil from drying owing to evaporation. The voltage at both terminals of the external resistance was measured every 15 min using a voltage logger (T&D Corp., MCR-4V) to calculate the circuit current according to Ohm's law. The current density was obtained by dividing the current by the surface area of the anode, i.e.,  $0.02 \text{ m}^2$ . The electrode and a reference electrode (Toyo Corp., W-RE-7A) placed in the soil layer were connected to the voltage logger using the circuit shown in Figs. 1a and 1b to measure the electrode potential.

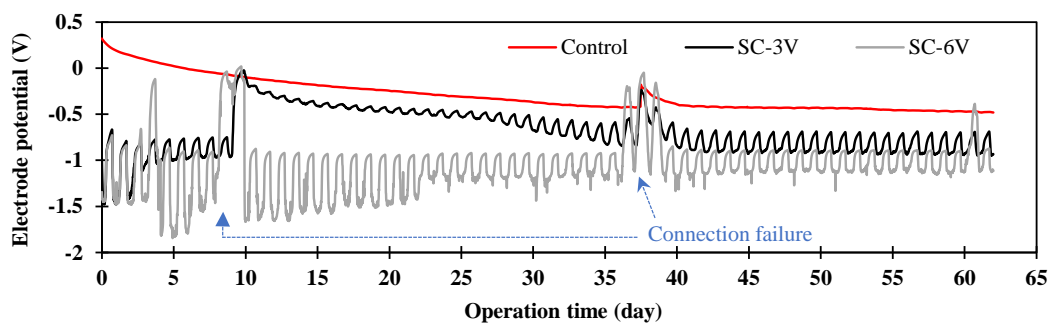
## Analyses

Two months after the experiments started, soil sampling was conducted. The surface soil of 1 cm was removed, and pH and redox potential (ORP) were measured using a pH/ORP meter (Horiba, D-50) at intervals of 5 cm from the anode. Soil samples were collected (Fig. 1d) after pH and ORP measurements. Furthermore, each soil sample was centrifuged at 6000 rpm for 5 min (As One, CN-2060) to extract pore water. Finally, each ion concentration in pore water (phosphate,  $\text{PO}_4^{3-}$ ; ammonium,  $\text{NH}_4^+$ ; potassium,  $\text{K}^+$ ) was measured. The ion concentration was measured using PACKTEST (Kyoritsu Corp., WAK), except for  $\text{K}^+$  concentration which was measured using a  $\text{K}^+$  meter (Horiba, K-11).

## RESULTS AND DISCUSSION

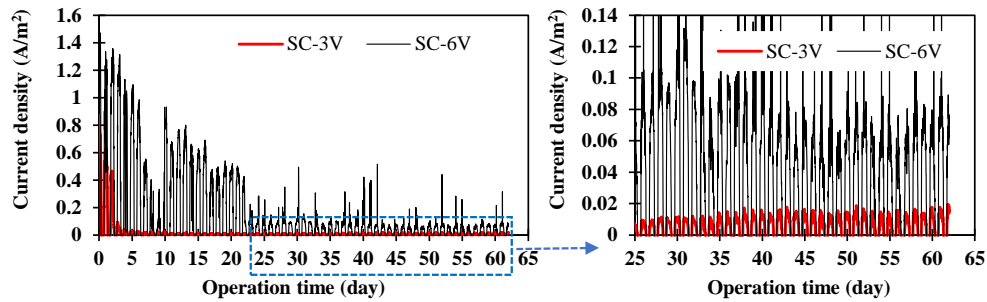
### Variations of Electrode Potential with Different Voltages of Solar Cells

Figure 2 depicts temporal changes in the electrode potential during the experiments. For SC-3V and SC-6V, the electrode potential refers to the potential of the cathode in which a reduction reaction occurs. For Control, the electrode potential decreased temporally, and mostly stabilized at  $-0.48 \text{ V}$  on Day 62 after the experiment started. The low potential was observed because cow manure compost was used, and it took approximately two months for its reduction. On Days 50-60, the peak electrode potential ranged from  $-0.70 \text{ V}$  (night-time) to  $-0.94 \text{ V}$  (daytime) for SC-3V and  $-0.90$  (night-time) to  $-1.14 \text{ V}$  (daytime) for SC-6V.



**Fig. 2 Comparison of electrode potential with and without using the solar cell**

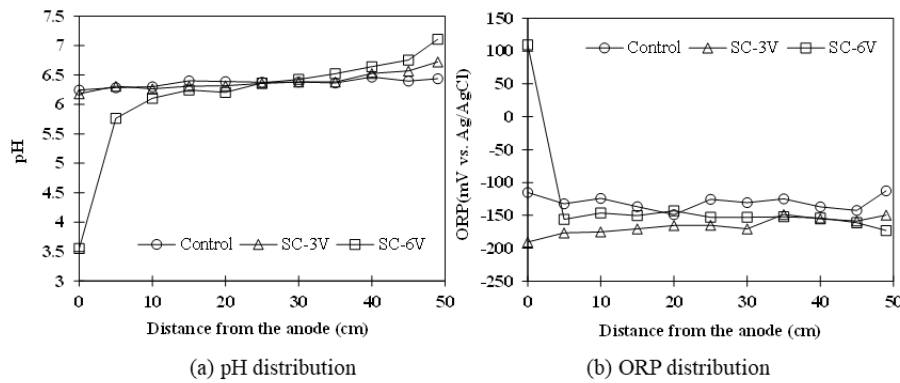
Compared with the Control, more reduction was obtained when a high-voltage solar cell was used, and there was a large decrease in the electrode potential when the solar cell voltage was increased from 3 V to 6 V. This is because the reactions on the electrode are more active owing to an increase in electrical current when the voltage of the solar cell increases. As shown in Fig. 3, the current density was approximately 0.06-1.30 A/m<sup>2</sup> for SC-6V and 0.01-0.61 A/m<sup>2</sup> for SC-3V. The system current can vary using different solar cell voltages, that is, by changing the solar cell voltage, soil reduction can be controlled.



**Fig. 3 Comparison of current densities generated by SC-3V and SC-6V**

### Changes in Redox Conditions at the End of the Experiment

Figure 4 shows changes in pH and ORP due to the current generation at the end of the experiment. In Fig. 4, 0 and 49 cm refer to the soil samples at the anode (oxidation) and cathode (reduction), respectively (SC-3V and SC-6V). In Fig. 4a, the pH at the anode was 6.21 for Control, which decreased to 6.18 for SC-3V and 3.56 for SC-6V. These decreases were caused by oxidation reactions at the anode. However, the pH at the cathode was 6.44 for Control, which increased to 6.72 for SC-3V and 7.11 for SC-6V. These increases were caused by reduction reactions at the cathode. From the pH distributions, a distance of 25 cm from the electrode were influenced by the current generation using a 3 V or 6 V solar cell.



**Fig. 4 Changes in pH and ORP due to current generation at the end of the experiment**

Decreased soil ORP was observed on using a 3 V or 6 V solar cell compared to Control, except at the anode of SC-6V. The soil ORP ranged from -150 to -112 mV for Control and -190 to -150 mV for SC-3V and SC-6V, respectively (Fig. 4b) which disagrees with our previous study (Touch and Nakamura, 2022) that reported an increase in ORP when using a 1.5 V solar cell. By increasing the solar cell voltage, a large decrease in soil ORP can be obtained.

### Nutrient Release Owing to Current Generation

The distributions of ammonium ( $\text{NH}_4^+$ ), phosphate ( $\text{PO}_4^{3-}$ ), and potassium ( $\text{K}^+$ ) are shown in Fig. 5. The release of  $\text{NH}_4^+$  was observed, which parallels our previous study (Touch and Nakamura, 2022). A 1.8- to 2.3-fold increase in  $\text{NH}_4^+$  concentration was observed within 5–20 cm of the anode (Fig. 5a). However, no significant difference was observed between SC-3V and SC-6V at 10–30 cm of the anode, suggesting that a 3 V solar cell is enough to release  $\text{NH}_4^+$  in soils. The increase in  $\text{NH}_4^+$  concentration was low near the cathode compared with that near the anode. This is because of the reduction reactions near the cathode, which induce denitrification. In Particular, the  $\text{NH}_4^+$  concentrations in SC-6V were lower than those of Control within 5 cm from the cathode.

No differences in  $\text{PO}_4^{3-}$  concentration were observed between Control and SC-3V (Fig. 5b), suggesting no release of  $\text{PO}_4^{3-}$  despite using a 3 V solar cell. Interestingly, a 2- to 7-fold increase in  $\text{PO}_4^{3-}$  concentration was observed within 20–45 cm of the anode for SC-6V. Within 15 cm of the anode, no increase in  $\text{PO}_4^{3-}$  concentration was observed. This was because of the release of calcium ions at this distance (Fig. 5c) following the decrease in pH (Fig. 4a), leading to the fixation of  $\text{PO}_4^{3-}$  by the calcium ions. An increase in  $\text{K}^+$  concentration was also observed. Compared with the Control, maximum 1.3-fold (SC-3V) and 1.6-fold (SC-6V) increases in  $\text{K}^+$  concentration were observed within 5-20 cm of the anode (Fig. 5d). However, a smaller increase in  $\text{K}^+$  concentration was observed near the cathode (20-45 cm of the anode), except for the cathode. A decrease in sediment pH induced the dissociation of metal compounds, causing the release of metal ions (e.g.,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ), which can fix  $\text{PO}_4^{3-}$  in littoral sediments (Touch et al., 2017; Touch et al., 2018).

In summary, applying ET powered by a 6 V solar cell can release nutrient compounds in soils, such as  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , and  $\text{K}^+$ . These releases are caused by the enhancement of organic matter decomposition in soils and the decrease in soil pH following ET application.

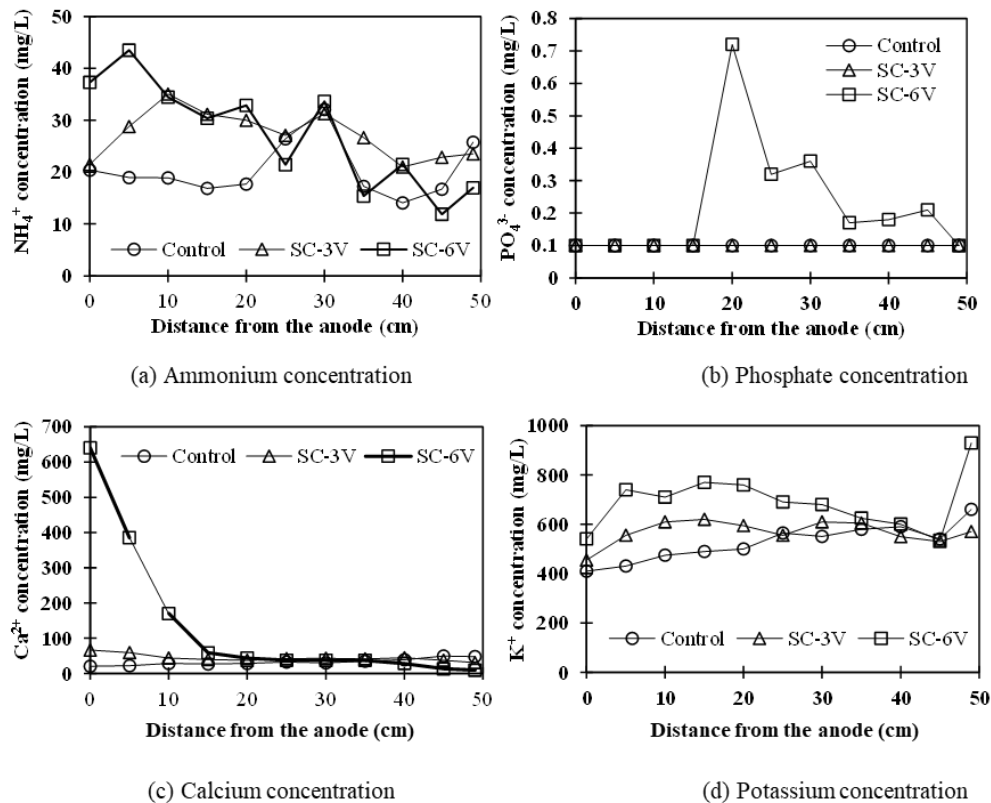


Fig. 5 Comparison of nutrient concentration distributions

## CONCLUSIONS

Laboratory experiments were conducted to examine the effects of solar cell voltage on the release of phosphate in soils. Specifically, we examined changes in the electrode potential by increasing the solar cell voltage, the soil redox conditions (pH and redox potential), and nutrient release after applying solar cell-powered ET to andosol mixed with cow manure compost. The system current increased as the solar cell voltage increased, which effectively induced reactions on the electrode. By changing the solar cell voltage, electrode potential, and soil redox conditions were controlled. From the pH distributions, 25 cm from each electrode was influenced by the application of ET. A larger influence was obtained with a higher voltage of the solar cell. From the ORP distributions, a large decrease in soil ORP was obtained by increasing the solar cell voltage. Hence, soil redox conditions can be varied using solar cells of different voltages. From the  $\text{PO}_4^{3-}$  distributions, a 6 V solar cell is required to release  $\text{PO}_4^{3-}$  in soil. It was also highlighted that decreasing the pH near the anode decreased the  $\text{PO}_4^{3-}$  concentration. Finally, applying ET powered by a 6 V solar cell (potential gradient: 0.12 V/cm) facilitates nutrient release in soils.

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