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ENVIRONMENTAL APPLICATION OF ELECTRICAL DISCHARGE FOR OZONE TREATMENT OF SOIL

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Abstract. In this study, influence of ozone treatment on physical properties of soil was investigated. We used a quartz container for ozone treatment of soil. The amount of soil used for treatment was 100 g. Treating time was 90 minutes. Flow rate of ozone gas was 1.5 L/min. We measured characteristics of soil such as inorganic nutrient ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_4\text{-N}$), $\text{pH}(\text{H}_2\text{O})$, fungi, DNA of soil, and exchangeable bases (Ca, K, Fe, and Al) before and after ozone treatment.

Keywords: ozone treatment, sterilization, soil, nutrient, $\text{pH}(\text{H}_2\text{O})$

ZASTOSOWANIE WYŁADOWANIA ELEKTRYCZNEGO DO OZONOWANIA GLEBY

Streszczenie. W niniejszym opracowaniu, opisano badania wpływu obróbki ozonem na własności fizyczne gleby. Do ozonowania gleby wykorzystaliśmy pojemnik kwarcowy. Ilość gleby poddanej działaniu ozonu wynosiła 100g, a czas oddziaływania 90 minut. Przepływ ozonu wyniósł 1.5l/min. Mierzono właściwości gleby, takie jak nieorganiczne składniki odżywcze ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ i $\text{NH}_4\text{-N}$), $\text{pH}(\text{H}_2\text{O})$, grzyby, DNA w glebie i zasady wymienne (Ca, K, Fe i Al) przed i po poddaniu jej działaniu ozonu.

Słowa kluczowe: ozonowanie, sterylizacja, gleby, substancje odżywcze, $\text{pH}(\text{H}_2\text{O})$

Introduction

Ozone sterilization is one of the most important techniques to ensure the safety of food processing in agriculture. Sterilization of soil using pesticides is one of the effective ways to resist the spread of diseases in the soil. However, contamination such as residual pesticides in the produce and NO_2 in groundwater caused by the overuse of chemicals has become a serious issue in agricultural fields. Therefore alternative sterilization methods are required from the environmental point of view. Recently, ozone has attracted attention as a disinfectant because it has high oxidation energy compared to that of fluorine and does not produce residual toxins. Moreover, it is known that ozone can decompose residual pesticides. There are numerous studies about reactive oxygen species such as ozone and their effects on seeds [10], plants [1, 13, 14], soil [2, 3, 12], residual toxic [8, 9], pathogens, virus [15], and pests [11]. We have proposed the potential of ozone treatment for agricultural soil. Since almost atmospheric discharge plasma in air produce ozone, the effect of ozone should be examined in agricultural application. We have proposed the use of ozone generated by surface barrier discharge plasma into agricultural applications [4–7].

In this study, we developed equipment for the sterilization of soil, which induced a quartz container rotated by a motor. The ozone generator, which uses the surface dielectric barrier discharge, provides a maximum ozone concentration of 78 g/m^3 at a flow rate of 1.5 L/min. We studied the influence of ozone treatment on the physical properties of soil in the container. We investigated the characteristics of soil such as inorganic nutrient content ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_4\text{-N}$), $\text{pH}(\text{H}_2\text{O})$, fungi, DNA of soil, and bases (Ca, Al, Fe, and K) before and after the ozone treatment. Nitrogen is an essential element of proteins and chlorophylls required for the formation of cellular components in plants. The main source of nitrogen for plants is nitrate in the soil solution, which is assimilated by the roots. Organic nitrogen from decaying plant and organisms is converted to ammonia and ammonium. Nitrification from ammonium to nitrate progresses naturally via nitrifying bacteria, such as *Nitrosomonas*, in the soil. The pH of soil is determined in potassium chloride (KCl) or water (H_2O). The $\text{pH}(\text{H}_2\text{O})$ is the pH value in the soil solution. The $\text{pH}(\text{H}_2\text{O})$ of soil solution is also an informative indicator for the growth of crops. It is known that weak acidity and neutrality are suitable for crops. Ozone treatment of soil was performed in a quartz container to prevent the consumption of ozone by the reaction with organic materials except for soil.

1. Experimental methods

Fig. 1 shows the schematic illustration of the ozone treatment system for soil. An ozone generator that uses a surface dielectric barrier discharge provides the maximum ozone concentration of 78 g/m^3 at a flow rate of 1.5 L/min. The generated ozone gas was injected into the soil directly in a quartz container ($1.3 \times 10^{-2} \text{ m}^3$) that performed a rotation function. There was no leakage of gas in this equipment. The gas inside the container was exhausted by a pump at a flow rate of 3.4 L/min. The soil used for ozone treatment was andosol. The amount of andosol used for ozone treatment was 100 g. The temperature of soil was measured with a thermo-couple. Exhaust ozone gas was monitored with an ozone monitor (Iwasaki electric Inc., OZM-700GN). The treatment time was 90 minutes. The ozone dose rate, which is defined as ozone dose weight per unit weight of soil, was 11%. We measured the characteristics of soil such as inorganic nutrient content ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_4\text{-N}$), $\text{pH}(\text{H}_2\text{O})$, fungi, DNA of soil, and bases (Ca, Al, Fe, and K) before and after ozone treatment. Quantities of nitrate, nitrite and ammonium were evaluated using standard indices of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_4\text{-N}$ at mg/kg. Inorganic nutrients were measured by colorimeter method with test reagent (Kasahara Chemical Instruments, NH4NOX-3Z). The amount of DNA was also measured to confirm disinfection effect or the degree of decomposition of organic substances using an electrophoresis method with DNA detector (Nippon Gene, ISOIL).

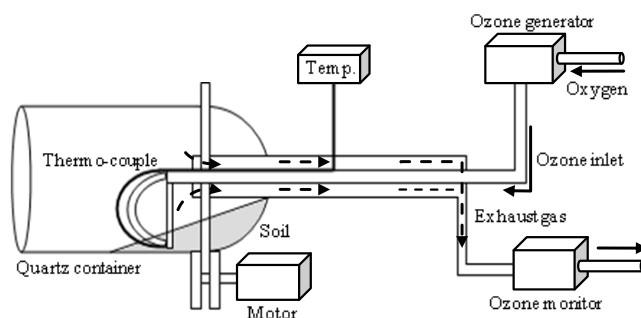


Fig. 1. Schematic illustration of the ozone treatment system for soil

2. Results and discussion

Results of the quantitative analysis of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NH}_4\text{-N}$, and $\text{pH}(\text{H}_2\text{O})$ before and after treatment are presented in Table 1. Content of $\text{NO}_3\text{-N}$ increased twice from original value after treatment, even though the number of nitrate bacteria (2×10^7 /mg) was not changed.

Table 1. Quantitative evaluation of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NH}_4\text{-N}$, and $\text{pH}(\text{H}_2\text{O})$

	Before ozone treatment	After ozone treatment
$\text{NO}_3\text{-N}$ (mg/kg)	9.0	22.5
$\text{NO}_2\text{-N}$ (mg/kg)	0	0
$\text{NH}_4\text{-N}$ (mg/kg)	1.0	50.0
$\text{pH}(\text{H}_2\text{O})$	6.9	4.5
Ca^{2+} (mg/kg)	38.0	285.0

Content of $\text{NH}_4\text{-N}$ increased fiftyfold from original value after treatment, even though the number of nitrate bacteria (8×10^6 /mg) was not changed. However, these were maintained at a constant value with time as shown in Fig. 2 and Fig. 3. The dot line shows the value before treatment. It was revealed that ozone treatment could induce the generation of nitrogen nutrients in the soil due to the strong decomposition power of ozone. Contents of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ increased after treatment, even though the number of nitrite and nitrate bacteria, 8×10^6 /mg and 2×10^7 /mg respectively were not changed. Therefore, we assumed that organic substances were decomposed and ammonium was generated. The following reaction can be considered because of the high oxidation potential of ozone. Ammonium generated by the decomposition of organic substances was oxidized by ozone and nitrite was generated. This oxidation was an exothermic reaction. Nitrite was oxidized by ozone and nitrate was generated. This oxidation was also an exothermic reaction. These results suggest that ammonification and nitrification from organic decomposers in soil is induced by the strong decomposition and oxidation potential of ozone. Since the reaction rate from nitrite to nitrate is faster compared to that for the generation of nitrite, there is no accumulation of $\text{NO}_2\text{-N}$. These ammonification and nitrification processes resulted in the temperature increase of the soil because there are exothermic reactions.

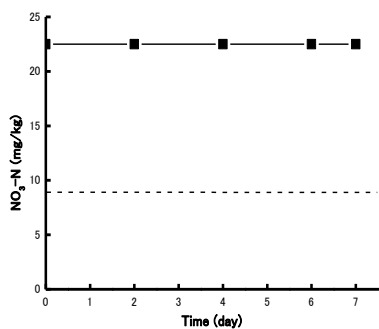


Fig. 2. Shows the change the content of $\text{NO}_3\text{-N}$ with time

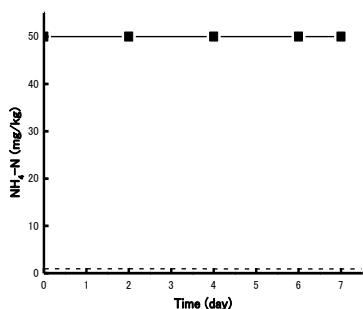


Fig. 3. Shows the change the content of $\text{NH}_4\text{-N}$ with time

The $\text{pH}(\text{H}_2\text{O})$ decreased drastically to the strong acidic region ($\text{pH}(\text{H}_2\text{O}) = 4.5$) just after ozone treatment, which is too acidic for the growth of crops. However, the $\text{pH}(\text{H}_2\text{O})$ value recovered gradually with time as shown in Fig. 4. The dot line shows $\text{pH}(\text{H}_2\text{O})$ value before treatment. This indicated that H^+ ions in the soil solution increased by a factor of hundred after the ozone treatment. However, seven days after the ozone treatment, $\text{pH}(\text{H}_2\text{O})$ almost recovered to the value of optimal range (6.0 to 7.0) which the growth of crops is expected. We considered that basic aluminum was decomposed and aluminum and H^+ ions were generated. It was considered that the buffering function for soil acidity performed after the ozone treatment. Exchangeable positive ions that adsorbed onto the surface of the soil colloid changed the positions with H^+ ions in the soil solution. Subsequently, the $\text{pH}(\text{H}_2\text{O})$ value recovered because of a decrease in H^+ ions in the soil solution. Ca^{2+} ions increased sevenfold from original value after treatment. However, the Ca^{2+} value recovered gradually with time as shown in Fig. 5. The dot line shows Ca^{2+} ions value before treatment. From these results, it was demonstrated that exchangeable positive ions such as Al or Ca and soil nutrients ($\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$) increased by the ozone treatment of soil.

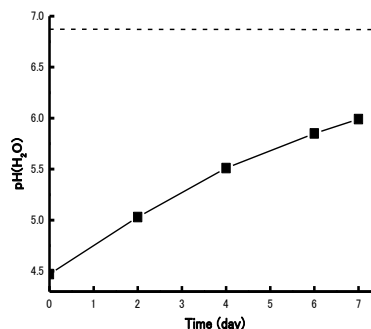


Fig. 4. Recovery curve of $\text{pH}(\text{H}_2\text{O})$ after ozone treatment

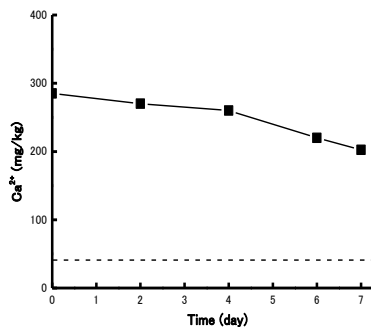


Fig. 5. The content of Ca^{2+} ions changes before and after ozone treatment

The DNA of soil had been decomposed completely by ozone treatment for 90 minutes. as shown in Fig. 6.

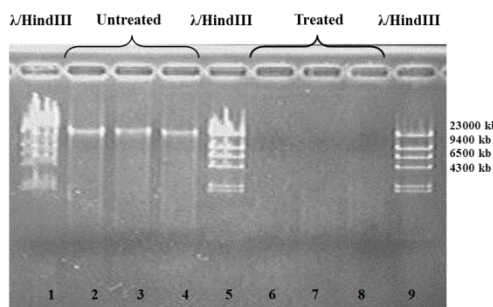


Fig. 6. The change of DNA of soil before and after ozone treatment

We used three samples each for before and after ozone treatment, respectively. The λ /HindIII was used as a DNA fragment length marker (Lanes 1, 5, and 9). Extracted high molecular DNA from ozone treated soil (Lanes 6 to 8) was reduced as compared with untreated samples (Lanes 2 to 4). It shows potential ability of ozone sterilization for soil.

3 Conclusions

In this study, influence of ozone treatment on physical properties of soil was investigated. We used a quartz container for ozone treatment of soil. The contents of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ increased after treatment and subsequently kept a constant quantity. The $\text{pH}(\text{H}_2\text{O})$ decreased drastically to strong acidic region, however, it was recovered via buffering recovery potential of soil. It was revealed that buffering function for soil acidity was still available after ozone treatment. The DNA of soil had been decomposed completely by ozone treatment for 90 min. It shows potential ability of ozone sterilization for soil.

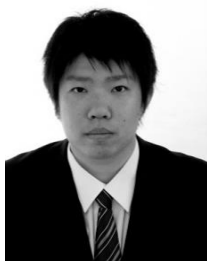
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