

DOI: 10.5604/20830157.1176573

ENVIRONMENTAL APPLICATION OF ELECTRICAL DISCHARGE FOR OZONE TREATMENT OF SOIL

Tomoya Abiru¹, Fumiaki Mitsugi¹, Tomoaki Ikegami¹, Kenji Ebihara², Shin-ichi Aouki³, Kazuhiro Nagahama⁴

¹Kumamoto University, Graduate School of Science and Technology, ²Environment and Energy Laboratory, ³Sojo University, Department of Computer and Information Science, ⁴Sojo University, Department of Applied Microbial Teach

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 decomposed 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).

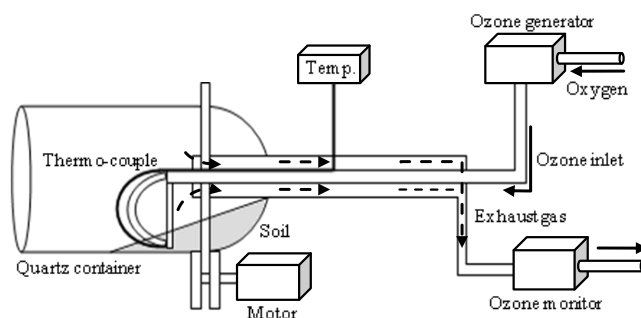


Fig. 1. Schematic illustration of the ozone treatment system for soil

2. Results and discussion

Results of the quantitative analysis of NO₃-N, NO₂-N, NH₄-N, and pH(H₂O) before and after treatment are presented in Table 1. Content of NO₃-N increased twice from original value after treatment, even though the number of nitrate bacteria (2×10⁷/mg) was not changed.

Table 1. Quantitative evaluation of NO₃-N, NO₂-N, NH₄-N, and pH(H₂O)

	Before ozone treatment	After ozone treatment
NO ₃ -N (mg/kg)	9.0	22.5
NO ₂ -N (mg/kg)	0	0
NH ₄ -N (mg/kg)	1.0	50.0
pH(H ₂ O)	6.9	4.5
Ca ²⁺ (mg/kg)	38.0	285.0

Content of NH₄-N increased fiftyfold from original value after treatment, even though the number of nitrate bacteria (8×10⁶/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 NO₃-N and NH₄-N increased after treatment, even though the number of nitrite and nitrate bacteria, 8×10⁶/mg and 2×10⁷/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 NO₂-N. These ammonification and nitrification processes resulted in the temperature increase of the soil because there are exothermic reactions.

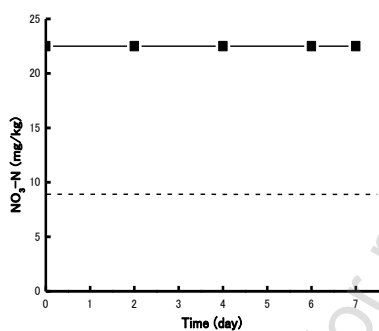


Fig. 2. Shows the change the content of NO₃-N with time

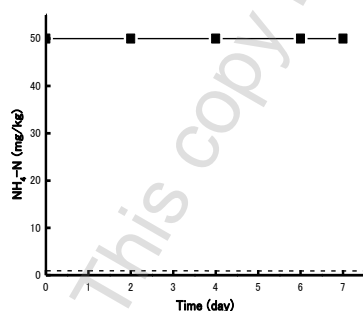


Fig. 3. Shows the change the content of NH₄-N with time

The pH(H₂O) decreased drastically to the strong acidic region (pH(H₂O) = 4.5) just after ozone treatment, which is too acidic for the growth of crops. However, the pH(H₂O) value recovered gradually with time as shown in Fig. 4. The dot line shows pH(H₂O) 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, pH(H₂O) 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 pH(H₂O) value recovered because of a decrease in H⁺ ions in the soil solution. Ca²⁺ ions increased sevenfold from original value after treatment. However, the Ca²⁺ value recovered gradually with time as shown in Fig. 5. The dot line shows Ca²⁺ ions value before treatment. From these results, it was demonstrated that exchangeable positive ions such as Al or Ca and soil nutrients (NO₃-N and NH₄-N) increased by the ozone treatment of soil.

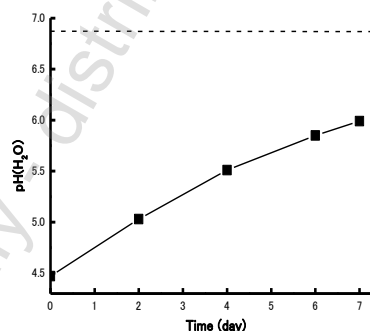


Fig. 4. Recovery curve of pH(H₂O) after ozone treatment

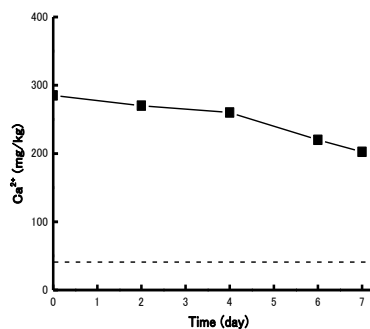


Fig. 5. The content of Ca²⁺ ions changes before and after ozone treatment

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

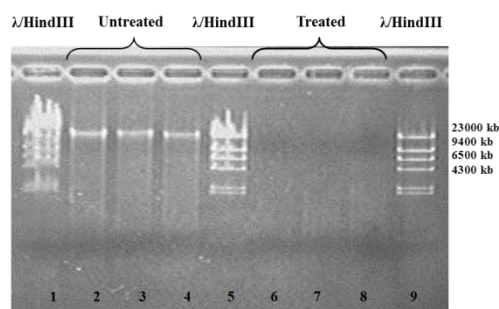


Fig. 6. The change of DNA of soil before and after ozone treatment

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.

References

- [1] Ahsan N., Nanjo Y., Sawada H., Kohno Y., Komatsu S.: Ozone stress-induced proteomic changes in leaf total soluble and chloroplast proteins of soybean reveal that carbon allocation is involved in adaptation in the early developmental stage, *Proteomics*, 10(14), 2010, 2605–2619.
- [2] Alvarez M. G., Poznyak T., Leal E. R., Sanchez C. S.: Anthracene decomposition in soils by conventional ozonation, *Journal of Environmental Management*, 113, 2012, 545–551.
- [3] Cui X. C., Hu J. L., Lin X. G., Wang F. Y., Chen R. R., Wang J. H., Zhu J. G.: Arbuscular mycorrhizal fungi alleviate ozone stress on nitrogen nutrition of field wheat, *Journal of Agricultural Science and Technology*, 15(5), 2013, 1043–1052.
- [4] Ebihara K., Mitsugi F., Ikegami T., Nakamura N., Hashimoto Y., Yamashita Y., Baba S., Stryczewska H. D., Pawlat J., Teii S., Sung T.: Ozone-mist spray sterilization for pest control in agricultural management, *The European Physical Journal Applied Physics*, 61(2), 2013, 1–5.
- [5] Ebihara K., Stryczewska H. D., Ikegami T., Mitsugi F., Pawlat J.: On-site ozone treatment for agricultural soil and related applications, *Przegląd Elektrotechniczny*, 87(7), 2011, 148–152.
- [6] Ebihara K., Stryczewska H. D., Mitsugi F., Ikegami T., Sakai T., Pawlat J., Teii S.: Recent development of ozone treatment for agricultural soil sterilization and biomedical prevention, *Przegląd Elektrotechniczny*, 88(6), 2012, 92–94.
- [7] Ebihara K., Sugimoto S., Ikegami T., Mitsugi F., Stryczewska H. D.: Application of gaseous ozone to agricultural soil sterilization, *Przegląd Elektrotechniczny*, 85(5), 2009, 113–114.
- [8] Ikeura H., Kobayashi F., Tamaki M.: Removal of residual pesticide, fenitrothion, in vegetables by using ozone microbubbles generated by different methods, *Journal of Food Engineering*, 103(3), 2011, 345–349.
- [9] Ikeura H., Kobayashi F., Tamaki M.: Removal of residual pesticides in vegetables using ozone microbubbles, *Journal of Hazardous Materials*, 186, 2011, 956–959.
- [10] Kitazaki S., Koga K., Shiratani M., Hayashi N.: Effects of atmospheric pressure dielectric barrier discharge plasma irradiation on yeast growth, *Materials Research Society Symposium Proceedings*, 1469, 2012, 86–91.
- [11] McDonough M. X., Mason L. J., Woloshuk C. P.: Susceptibility of stored product insects to high concentrations of ozone at different exposure intervals, *Journal of Stored Products Research*, 47(4), 2011, 306–310.
- [12] Msayle N., Ibrahim S.: Treatment of nematodes with ozone gas: A sustainable alternative to nematicides, *Physics Procedia*, 21, 2011, 187–192.
- [13] Olmez H., Akbas, M. Y.: Optimization of ozone treatment of fresh-cut green leaf lettuce, *Journal of Food Engineering*, 90(4), 2009, 487–494.
- [14] Saitanis C. J., Karandinos M. G.: Effects of ozone on tobacco (*Nicotiana tabacum* L.). Varieties, *Journal of Agronomy and Crop Science*, 188, 2002, 51–58.
- [15] Wigginton K. R., Kohn T.: Virus disinfection mechanisms: The role of virus composition, structure, and function, *Current Opinion in Virology*, 2(1), 2012, 84–89.

Tomoya Abiru

e-mail: t-abiru@st.cs.kumamoto-u.ac.jp

Was born in Nagasaki. He received the B.E. degree from Department of Computer Science and Electrical Engineering, Kumamoto University, Kumamoto, Japan, in 2015. He is currently working toward the M.E. degree in Graduate School of Science and Technology. His current research interests include soil sterilization with ozone using surface dielectric barrier discharge.



Assoc. Prof. Fumiaki Mitsugi

e-mail: mitsugi@cs.kumamoto-u.ac.jp

Received his B.E. degree from the Department of Electrical Engineering and Computer Science in 1997, and his M.E. and Dr. (Eng.) degrees from the Graduate School of Engineering of Kumamoto University, in Kumamoto City, Japan, in 1999 and 2002, respectively.

From 2002 to 2007, he worked as a postdoctoral research fellow in electrical engineering at Oita University in Oita City, Japan. From 2007 to 2014, he worked as an Assistant Professor, and he has been working an Associate Professor with the Graduate School of Science and Technology at Kumamoto University since 2014. He has contributed more than 100 papers in international journals and conference proceedings. His research interests include time-resolved observation of discharge plasmas in atmospheric pressure, pressure waves from discharges, laser-solid processes and thin film fabrication, laser ablation in supercritical fluids, optical wave microphone technique, and the applications of ozone for plants, soil, and water.

Prof. Tomoaki Ikegami

e-mail: Ikegami@cs.kumamoto-u.ac.jp

Received the B.E., M.E. and D.E. degrees in electrical engineering from Kyushu University, Fukuoka, Japan in 1978, 1980, and 1989, respectively. From 1980 to 1988, he was a Research Associate with the Faculty of Engineering, Kyushu University. He was a Research Associate from 1988 to 1990, and an Associate Professor from 1990 to 2003 with the Faculty of Engineering, Kumamoto University. Since 2004, he has been a Professor with the Graduate School of Science and Technology, Kumamoto University.



Prof. Kenji Ebihara

e-mail: kankyo@mild.ocn.ne.jp

Received the Dr. Engineering in Electrical Engineering, Kyushu University in 1979. From 1984 to 2007, he was Professor of Kumamoto University and is Professor Emeritus of same University. He has been Director of Environment and Energy Laboratory established in 2009. He is the author of five books, more than 100 journal papers, 120 conference papers, 40 seminar and invited lectures and seven patents. His research interests include ozone sterilization for agriculture and plant growth as well as bio-medical treatment. He has studied on global research project "Development of portable ozone sterilization spray for non-chemical agriculture" under the promotion project for global technology cooperation of the Ministry of Economy, Trade and Industry of Japan.



Prof. Shin-ichi Aouqi

e-mail: aoqui@cis.sojo-u.ac.jp

Was born in Tokyo, in 1957. He received the B.S. in Department of Applied Physics, from University of Electro-Communications, Tokyo, and M.S. degree from University of Tsukuba, Ibaraki, in 1983, and the Ph.D. degree from Kumamoto University, Kumamoto in 2000. He was an Associate Professor from 1997 with the Faculty of Engineering, Kumamoto Institute of Technology (in 2000, change of name to Sojo University). From 2001 to 2002, he was a visiting Professor with Department of Condensed Matter Physics, Royal Institute of Technology (KTH), Sweden. Since 2007, he has been a Professor with Faculty of Computer and Information Sciences, Sojo University. His current research interest includes Plasma and discharge phenomenon and material sciences. He is also interested in bioscience and agriculture based on plasma to agriculture in the next generation.



Assoc. Prof. Kazuhiro Nagahama

e-mail: kazuhiro@bio.sojo-u.ac.jp

Was born in Tokyo, Japan. He received the Ph.D. (Engineering), degree from Kumamoto Institute of Technology, 1992. His thesis was "Ethylene formation by *Pseudomonas syringae*". He is currently an Associate Professor with the Faculty of Biotechnology and Life Science, Department of Applied Microbial Technology, Kumamoto, Japan. His research is focused on the insect-microbial symbiosis for sustainable agriculture.

