博士論文要約（Summary）

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タイトル **Title**	DESIGN AND DEVELOPMENT OF NDIR-BASED N_2O GAS MEASURING DEVICE FOR AGRICULTURAL FIELDS

キーワード Key word（ **NDIR** ）**(gas sensor calibration)** （ **N_2O gas sensor**） **(low-cost gas monitoring) (soil Nitrous Oxide emission) (silicone diffusion cell) (soil gas flux) (silicone diffusion cell) (soil gas diffusivity) (passive gas sampling) (soil gas diffusion coefficient) (soil gas flux simulation)**

Chapter 1

Development of Low-Cost NDIR-Based N_2O Gas Detection Device for Agricultural Soils: Design, Assembly, Calibration Model Validation, and Laboratory Testing

Introduction

Population growth demands an elevated rate of crop production, and the crops' nutrient requirements are accomplished by synthetic fertilizers. Nitrogen (N) fertilizer is an indispensable fundamental component of crop nutrient inputs. Synthetic fertilizers provide nitrogen-based nutrients and subsequently, from animal waste, recycling of crop residues, and biological N fixation by legumes. For the period of the past 159 years, the atmospheric nitrous oxide (N_2O) concentration has expanded from 270 to 323 ppbv due to synthetic fertilizer applications and anthropogenic activities. The N_2O gas contributes to atmospheric warming 298 times more than carbon dioxide. Therefore, the shrinking of N_2O emissions from agricultural fields is significant.

Considering the instrumentation for gas measurement, various types of N_2O gas-metering methodologies (chamber methods, gas chromatography, infrared-based methods, and laser absorption spectroscopy), have been introduced. Specifically, instrument-related circumstances such as the requirement of portable and high precision instruments, expensiveness, and associated maintenance activities limit the gas monitoring activities in agricultural fields and developing countries are the most affected segment. Therefore, the designing and developing of a low-cost portable device for onsite N_2O gas monitoring in agricultural fields will be indispensable.

NDIR technology has been adopted broadly for monitoring CO_2 and CH_4 gas measurements. in agricultural activities, the structural development of NDIR gas sensors has been modified for a wide range of specific gas monitoring purposes. The structural setup of the NDIR incorporates a target gas an infrared light source, holding an optical tube, a specific wavelength filter, and an infrared detector. Since the customizable basic structure of NDIR, the development of a simplified version, and designing a low-cost movable gas measuring device is feasible. Compared to high-precision devices, low-cost and low-precision gas measuring devices can be used for highly concentrated N_2O gas measurements. Also, the concentration of the N_2O gas is higher in the soil atmospheric region than on its surface. Since the higher permeability of silicone material for N_2O gas, it can be used as a sampler to absorb gases in the soil. Since the soil atmosphere contains a higher concentration of N_2O gas than its surface and with the possibility of gas sampling using a silicone diffusion cell, this research aimed to develop a low-cost, portable NDIR-based device for measuring N_2O gas through a submerged silicone diffusion cell. Moreover, to conduct the performance tests for the new device and adopt the developed device for soil gas measurement with a gas diffusion cell.

Materials and methods

The prototype device was designed by assembling the optical system (a separate gas cell of which two edges are covered by optical windows, detector, light source, plano-convex lens) with a microcontroller unit (Pyreos PCB—C8051f350). PYREOS dual-channel pyroelectric detector covered with a bandpass filter (80 nm HPB, 4.525 µm CWL) was used as a detector. Micro-Hybrid MEMS-based infrared radiation source on a TO39 cap was fixed as the light source. The rms values of the detector output and controlling of the IR emitter driver were performed using a PC-installed graphical user interface (GUI- PYREOS). In the performance tests of the device, the first experiment was concerned with basic tests for the calibration model validation and testing of the repeatability and accuracy of the device. The second test was a practical usability test. In the test to determine the best operating frequency of the IR emitter, the respective detector output was recorded by adding five concentration levels of pure N_2O gas (0 – 96.1 ppm) into the N_2 gas-filled gas chamber while changing the IR emitter frequency (from 2 Hz to 10 Hz).

The modified Bear-lambert law was used to determine the gas concentration from the recorded values of the detector output. During the calibration steps, a known concentration (0–2000 ppm) of N_2O gas was injected into an N_2-filled external gas chamber, which was serially connected to the device, and using the calculated gas concentrations of the recorded detector output, the calibration curve was plotted. The repeatability and sensitivity tests for the new device were done by applying known gas concentrations and conducting measurements on each gas level repeatedly six times. Allan deviation test was done to determine the detection limit of the new device, and the device was run at a constant gas concentration level (7.7 ppm) for more than 10 min period, and the data were logged at a speed of 140 Hz. Using the recorded data, the Allan deviation was calculated. since the humidity level in the gas can be affected to the optical path, the absorbance of light energy was measured by changing the humidity levels from 20 % to 90 % in the gas–cell with the instrument running under inserted pure N_2O gas levels (19.2 to 76.8 ppm) at each corresponding humidity level. As a practical usability evaluation test for the new device, a soil N_2O gas measurement test was performed using 1 kg of soil mixed with 0.5 g of $(NH_4)_2SO_4$. The silicone tube was buried in the soil and serially connected with an air circulation pump and the new device for temporal (every 30-minute interval) gas measurement. Similarly, a separate soil gas measuring setup was built and connected with an FTIR device as a reference device and soil gas data were recorded.

Results

The highest detector output (root means square -RMS) values of the detector were observed under 6 Hz of emitter frequency and it was selected for the best operating level for the gas measurement. The fractional absorbance was shown as a curved graph, and it was linearized. The coefficient of determination (R^2) was shown as 0.9999 for the regression analysis of the calculated and measured gas concentrations in the device calibration process. The results of the repeatability tests by regression analysis indicated higher correlation coefficients (>0.9995) for each testing event, and 0.627 of maximum residual standard error was recorded. Therefore, according to the repeatability test results, the embodied simple optical arrangement of the new NDIR gas analyzer can be operated with a higher accuracy level under repeated measurements. According to the maximum deviation of Allan deviations plot, the minimum detection limit was observed as 1 ppm. The results of the humidity-NDIR light absorption tests indicate no change in the fractional absorbance of light against the variations of relative humidity from 20–90%. This fact was confirmed statistically with the results of ANOVA (p-value 0.148 at a 95% confidence interval). In the soil gas measurement test, the pattern of recorded gas level from the new device was similar to the FTIR device output, but the concentration levels were different since the differences of volumes of each gas cell of the new device (320.3 mL) and the FTIR device (500 mL). It was observed that the new device gives results earlier than the FTIR device because of the quick saturation of low-volume gas cell.

Conclusion

The prototype gas measuring device built on two plano-convex lens arrangements in a 59 cm lengthen single path gas cell was successful in obtaining 320.3 ml volume. The best operating frequency of MEMS-based IR source for higher absorbance was obtained as 6 Hz. The arrangement of optics, NDIR sensor, and emitter with MCU was simple and the condition of easy to assemble was also achieved under 2780 USD cost. The device achieved a 1–2000 ppm measurable range, including maximum sensitivity of an 11.87 detector output RMS/ppm at a low concentration (3.87 ppm) of N_2O gas, and the minimum was a 3.38 detector output RMS/ppm at a high concentration (1929 ppm). Therefore, the developed device can also be used for all agricultural settings that emit higher gas levels. The moisture interference test confirmed the no significant impact from air humidity levels on light energy belonging to the wavelength of N_2O gas, and it is useful to operate the device under field conditions without attaching a dryer to the system. The new device demonstrated the advantage of its low-volume gas cell compared to the reference device due to its ability to give an early response at higher gas concentrations from the soil tests. In the tests of the N_2O gas-accumulation rate in the diffusion cell, the gas response time for gas-level saturation in the silicone tube was recorded for the new device as 3–4 h, which was lower than that of the FTIR device-connected system (7–8 h). laboratory soil experiment setup confirmed that the developed device has a great ability to measure the N_2O gas presence in the soil atmosphere through a silicone tube-based submerged diffusion cell.

Chapter 02

Gas Diffusion Analysis Method for Simulating Surface Nitrous Oxide Emissions in Soil Gas Concentrations Measurement

Introduction

Nitrous oxide flux assessment activities in agricultural fields need to be accelerated to control GHG emissions. The operational costs induced by high-precision gas-monitoring devices and the related accessories that are necessary for existing gas-monitoring methodologies are major barriers to achieving the targeted gas emission estimations. Mutually, low-cost N_2O gas-monitoring devices use passive sampling methods to sample the gases in the soil (where there are higher gas levels than on the surface), and numerical simulation approaches can be used to predict gas fluxes in cost-efficient ways. In the first experiment, we developed a low-cost N_2O gas measuring device that can be used to measure the highly concentrated soil gas via a soil-buried silicone diffusion cell. Therefore, this study aimed to test a simulation approach for estimating N_2O flux on the soil surface corresponding to the soil gas concentration measured by a low-cost measuring device that connected to a silicone soil gas sampler.

Materials and methods

The conceptual background of the experiment was mainly based on the soil N_2O gas flux simulation process of the logged soil N_2O levels resolute by a low-cost NDIR device with a diffusion cell (silicone tube) buried in the soil region, where there are higher N_2O gas concentration levels than in its atmosphere. With the diffusion coefficient, the inner N_2O gas intensity of the diffusion cell changes, along with the temporal changes in the soil gas concentration. From the gas concentrations logged in the silicone diffusion cell, the predicted concentrations on temporal variations in the soil N_2O gas concentration were simulated by solving the diffusion equation using the method of implicit finite difference.

The values calculated for N_2O flux on the soil surface (CF) were simulated by solving the diffusion equation (implicit finite difference method) using the six soil gas diffusivity models. To compare the simulated values, the observed surface flux of N_2O gas (MF) was calculated from monitored soil surface emission levels using a high-resolution gas-monitoring device followed by the chamber method. Accordingly, the overall experiment was based on three main steps: (1) the determination of the diffusion coefficient of the silicone membrane; (2) the measurement of the concurrent N_2O gas concentrations in the soil gas and soil surface; and (3) the development of a simulation process to determine the CF values. The resulting values of CF and MF were compared graphically and statistically.

Results

In the simulation output of the gas diffusion test on a silicone membrane, the temporal variation in calculated gas concentrations in both systems matched with the measured values. For the N_2O gas, the diffusion coefficient of the silicone membrane (*Dslcn)* was $1.1 \times 10{-}8$ cm^2/s according to the steps resolved in the difference equations. According to the graphical descriptions, the highest agreement level between the cumulative calculated flux (*CFcu*) and cumulative measured flux (*MFcu*) is shown by soil gas diffusivity models 4 and 5. The results of the accuracy statistical tests (*SMAPE*: symmetric mean absolute percentage error (%), *d*: Willmott's agreement index) for model fitting with *MFcu* also confirm the output of said graphical explanation. Among the tested characteristic-based soil gas diffusivity models for soil water, models 4 and 5 demonstrate lower *SMAPE* (%) values (experiment 1: 8.18%, 10.18%; experiment 2: 10.73%, 8.02%) and higher d values (experiment 1: 0.9996, 0.9994; experiment 2: 0.9992, 0.9997). The independent models for the different soil types (models 1, 2, and 3) showed higher *SMAPE* and lower *d* values for both experiments. Therefore, according to the selected soil category, by considering the common simulation approach for predicting soil surface N_2O flux from the soil gas levels, soil gas diffusivity models 4 and 5 are the most appropriate. The tested method, including the arrangement of its hardware arrangement with the simulation steps, makes it easier to estimate soil N_2O emissions once the gas diffusion coefficients of the silicone membrane and the soil have been determined. Compared to closed-chamber methods, the tested method requires less accessories for gas sampling and circulating and uses low-cost measurement devices. As a passive gas sampling unit, the special characteristics (water repellency, structural stability of the wall, and higher gas permeability) of the silicone diffusion cell allow it to be layered under the soil. This keeps the upper surface free of gas-sampling devices and enables natural soil gas diffusion to the air. Moreover, the gas sampler does not require operating power or intensive maintenance, which allows it to be used for long-term monitoring.

Conclusion

The experiment in the second chapter was focused on the development of a simulation method for predicting the surface N_2O gas flux by measuring the soil gas levels. The measurement of soil gas levels is easy with low-cost devices because of the presence of higher gas levels (approximately ten times) than its surface. Three main steps were followed to test the methodology. First, the diffusion coefficient of the silicone membrane test and found to be $1.1 \times 10{-}8$ cm^2/s by solving a diffusion equation. Second, simultaneous measurements were performed to detect the soil gas as well as surface gas levels. Using the recorded soil gas levels, the surface gas flux was simulated under three steps, and simulated values were validated by the recorded surface fluxes. In the first stage of the simulation, the diffusion coefficient of the silicone membrane was used to predict the variation in the soil N_2O gas level according to the measured N_2O gas concentrations in a silicone diffusion cell by solving the gas diffusion equation via the implicit finite difference analysis method. In the second stage, using soil gas diffusion coefficients from six soil gas diffusivity models, the N_2O gas flux from the soil surface emissions was predicted from the predicted soil gas levels. At the laboratory level, we successfully simulated the cumulative values of the predicted soil surface N_2O flux and confirmed good agreement with the measured cumulative flux graphically and statistically. The overlapping simulated flux and measured flux curves demonstrate how expensive conventional N_2O flux estimation methods can be replaced with the use of low-cost gas monitoring devices for soil gas measurements through the passive sampling cells with gas flux simulation steps. Moreover, field-level studies are needed for the simulation method to be adopted for use in cultivated croplands.