Environmental Science
Processes & Impacts

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Journal:	*Environmental Science: Processes & Impacts*
Manuscript ID:	EM-ART-06-2014-000339.R1
Article Type:	Paper
Date Submitted by the Author:	31-Aug-2014
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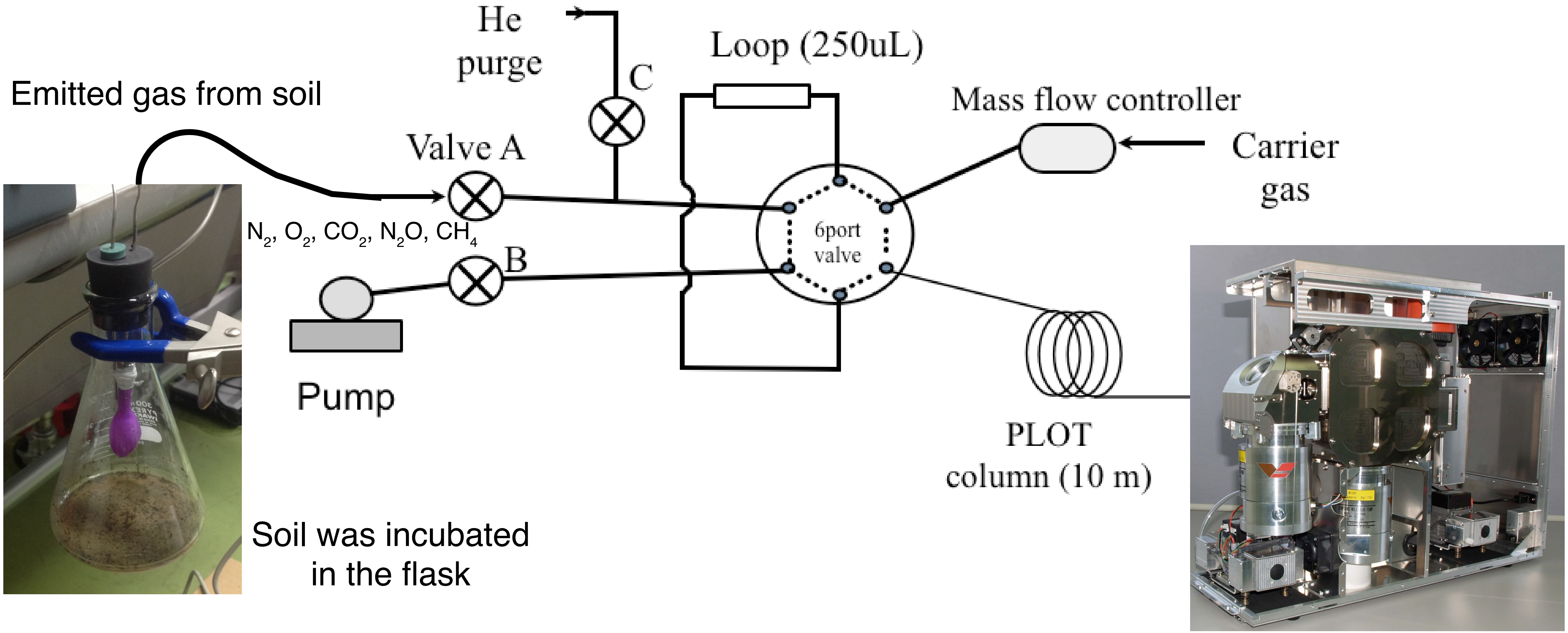

Miniaturized high-resolution TOF mass spectrometer “MULTUM-S II”

Graphical Abstract Anan et al.

Real time monitoring of gases emitted from soils using the Multi-turn Time-of-Flight Mass Spectrometer “MULTUM-S II”

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Abstract

Many miniaturized mass spectrometers used for on-site analysis have been designed and developed recently utilizing a broad range of analyzer platforms. These instruments are expected to have widespread applications covering many fields of interest. In our laboratory, a miniaturized multi-turn time-of-flight (TOF) mass spectrometer “MULTUM-S II” was designed and constructed. The size and weight of the developed “MULTUM-S II” is 45 cm × 23 cm × 64 cm and 36 kg. Irrespective of this small platform, it still boasts a high mass resolution capability of more than 30000. In this study, we attempted to carry out real-time monitoring of gaseous compounds such as N_2, O_2, CO_2, N_2O and CH_4. Using conventional miniaturized mass spectrometers, CO_2 and N_2O cannot be detected simultaneously due to the low mass resolution inherent to these established analyzer designs. Using a new method, “GC/high resolution mass spectrometry” described in this paper, real time monitoring of gases emitted from soils can be achieved. In a soil incubation experiment, CO_2 and N_2O started to increase just after water supplement and these gases varied similarly during the experiment, thus showing that this improved gas analyzing system could monitor short time response of gaseous production in soil.

1. Introduction

In recent years, the increase in greenhouse gases (CO_2, N_2O and CH_4) emitted from soils is becoming a global problem. It is known that these gases as well as N_2, are generated by soil microbial activities [1]. In particular, N_2O is known as one of the most serious greenhouse gases, and is also involved in depressing the stratospheric ozone layer [2]. According to the Intergovernmental Panel on Climate Change [3], warming effects of N_2O and CH_4 are 298 and 25 times, “respectively” greater than that of CO_2. The emissions of gases are affected by the influence of fertilizer N application and environmental factors (precipitation, temperature, wind speed, etc.). In the conventional method of gas sampling and measurement, gases are collected from a sampling chamber, taken to the laboratory, and measured by using gas analyzers [4]. It takes several hours to collect gas samples at the field and measure gas concentrations in the laboratory, so that frequent sampling of the gases to understand production and emission of gases has been labor intensive and difficult. Therefore, on-site gas sampling and fast analysis have been required to elucidate generating mechanisms and determine possible reduction procedures of gases produced from agricultural soils. Conventionally, concentration of N_2O in collected samples is analyzed using a gas chromatograph with an electron capture detector (ECD) [5]. It is difficult to apply gas chromatography using an ECD on the agricultural field because radioisotopes (e.g. ^{63}Ni) are used in these detectors. Current methods utilize an infrared (IR) analyzer to monitor concentration of CO_2 [6] and concentration of CH_4 is measured by a gas chromatograph with a flame ionization detector (FID) [7]. Thus, it is impossible to detect these gases simultaneously in a single analyzer. Due to the varied analyzers and conditions of this measurement technique, complicated systematic errors are an inherent problem. Gas chromatography/mass spectrometry (GC/MS) has the powerful potential to measure a large variety of gases in the agricultural field. In the conventional method of gas analysis, using a gas chromatograph-mass spectrometer [8, 9], the main components of air (e.g. N_2, O_2 and Ar), CH_4, CO_2 and N_2O are separated using a PLOT (porous layer open tubular) column and detected by the mass spectrometer. The schematic illustration of a chromatogram is shown in Fig.1A. Analysis times on a scale of several minutes to detect CH_4, CO_2 and N_2O are a definite disadvantage of this method. In contrast, soil microbial activities are influenced by sudden changes in the environmental conditions, therefore; a higher gas sampling rate is essential. For a chromatographic separation, retention time is directly proportional to the length of a column. We attempted to shorten the measurement time by using a very short column. However, the insufficient chromatographic separation might give rise to overlap of the peaks of CO_2 and N_2O, O (the fragment of O_2) and CH_4 (Fig.1B). Conventional miniaturized mass spectrometers, such as quadrupole mass spectrometers or ion trap mass spectrometers cannot separate these doublets (mass resolution <500), because the nominal mass of N_2O and CO_2 are the same. To separate these gases in the field, it is necessary to introduce a miniaturized mass spectrometer, which has high mass resolving power. Required mass resolution to separate CO_2 and N_2O doublet is larger than 8000 and resolution for doublet O and CH_4 is larger than 1500. Therefore a mass spectrometer with high mass resolving power will provide a significantly reduced measurement time to separate components having the same nominal mass (Fig.1C). In this case, GC separation could still be necessary, because the target gases such as CO_2 and N_2O, (whose concentrations are small), are separated from the main components of air (N_2, O_2) to avoid ion suppression in the EI ion source. In our laboratory, the miniaturized multi-turn time-of-flight (TOF) mass spectrometer with high mass resolving power 'MULTUM-S II' has been developed [10]. In previous work, a combination of a multi-turn TOF mass spectrometer and a gas chromatograph was applied to environmental research [11], and 1 ppb heptachlorinated biphenyl was detected at a resolution of 10000. Using GC-high resolution TOF mass spectrometer, 66 PCB (polychlorinated biphenyl) congeners were detected within 5 min [12]. In this paper, the preliminary results of monitoring gas emitted from soils by using a GC-multi-turn TOF mass spectrometer is reported.

2. Instrumentation

Multi-turn TOF mass spectrometer (MULTUM)

A photograph of MULTUM-S II is shown in Fig.2. The MULTUM-S II consists of an ion source, a multi-turn mass analyzer, a detector, a vacuum system, and an electronic circuit/ control unit. The total size and weight of a MULTUM-S II is 45 cm × 25 cm × 64 cm and 36 kg, respectively. The equipped ionization source is a two-stage acceleration ion source of electron ionization (EI) type introduced by Wiley and McLaren [13]. The mass resolution of the TOF mass spectrometer is proportional to its total flight path length. In order to obtain a long flight path, it is necessary to place the ions in a closed orbit and to pass the ions around the same orbit many times (multi-turn). Our multi-turn system is capable of high mass resolution because of its infinite flight path utilizing perfect space and time focused closed flight orbit [14]. It has high mass resolution capability of (>30000) and high mass accuracy (<2.6 ppm). The detailed discussion about MULTUM-S II was described elsewhere [10].

Gas sampling system

We developed a simple automatic gas sampling system. Figure 3(A) shows a scheme of the gas sampling system to inject a pre-determined amount of gas into the MULTUM-S II periodically. This system consists of a 6-port valve (AU-CF-6, GL Science Inc., Tokyo, Japan), solenoid valves (USB 3-6-1, CKD Corporation, Aichi, Japan), a mass flow controller (SEC-E40, HORIBA STEC, Kyoto, Japan), a 250 μL sampling loop, a diaphragm pump (N84.3ANDC, KNF Neuberger Inc., Trenton, NJ) and a short PLOT column (GS-CARBONPLOT, Agilent Technologies). A certain amount of the gas was injected into the MULTUM-S II by this sampling system and the loss of sample gas was kept to a minimum. Timing of switching for the valves and the pump was controlled using a digital I/O device (USB-6501, National Instruments, TX, USA). The timing chart of gas sampling is shown in Fig.3(B). Before measurements, the solenoid valve B was opened and the sampling loop was evacuated using the diaphragm pump. After closing the solenoid valve B, the solenoid valve A was opened.

Then, the sampling loop was filled with sample gas, the solenoid valve C was opened and purged with high purity He gas (99.9995 %, NERIKI, Hyogo, Japan) to prevent atmospheric contamination. The pressure of purged high purity He gas was 1.02×10^5 Pa. After gas sampling, the 6-port valve was switched to flow the sample to the PLOT column. Ultrapure He gas (99.99995 %, NERIKI, Hyogo, Japan) was used as a carrier gas of the gas chromatograph. The mass flow controller was used to regulate the flow.

Measurement of gas emission from soil

In this study, soil gas emissions were monitored using the gas sampling system. Soil for incubation experiment was collected in a cornfield in Shinhidaka, Hokkaido, Japan. Soil type is classified as Andisol, and its pH, total carbon, total nitrogen, C:N ratio and texture are 5.9, 5.22 %, 0.44 %, 11.9 and sandy clay loam, respectively. Concentrations of ammonium and nitrate are 4.75 mgN/kg, and 76.0 mgN/kg, respectively. In the experiment, 3 g of air-dried soil in the 200 mL Erlenmeyer flask is incubated at an aerobic condition. After 24.5 hours incubation, 2.1 mL water was added to the soils to change the water condition drastically and enhance N_2O and CO_2 production. Using the GC-MULTUM, we performed long term gas monitoring to detect changes of gas concentrations (N_2, O_2, CO_2 and N_2O) emitted from soils. The total duration of measurement was 3 days (before adding water; 1 day, after adding water; 2 days). Before adding water, gas sampling and measurement was carried out every 4 hours. Between 30 min before adding water and 90 min after adding water, gas sampling and measurement was carried out every 5 min. After that, the periodical sampling and measurement was performed (27, 28, 29, 32, 36, 48, 52, 56, 60 and 75 hours). As the headspace gas was taken, the pressure in the headspace was reduced. To maintain constant atmospheric pressure in the headspace, air was injected into the flask. The sample gas was replaced by an equal amount of the air.

Operation of MULTUM-S II

The mass spectrometer 'MULTUM-S II' was used in the 'multi-turn mode' with electron ionization. The block diagram of the timing chart of operation of the MULTUM-S II is shown in Fig.3(C). Ions are injected into the orbiting trajectory by applying voltage to the Injection Electrode, and then the applied voltage to the Injection Electrode is turned off after all ions are injected into the orbiting trajectory. When voltage is applied to the Ejection Electrode, ions exit the orbiting trajectory and are detected by the detector. The switching timing of the Ejection Electrode controls the number of cycles.

GC-MS analysis

The conditions of GC were (i) ion source temperature: 200 °C, (ii) GC interface temperature: 40 °C, (iii) flow rate of He gas: 7.0 cc/min (at constant flow) and (iv) PLOT column: 10 m × 0.32 mm i.d. ; film thickness 3.00 μm.

3. Results and Discussion

Separation of CO_2 and N_2O, O and CH_4

In this experiment, separating the doublets of $^{12}C^{16}O_2^+$ and $^{14}N_2^{16}O^+$, $^{16}O^+$ and $^{12}CH_4^+$ was carried out by using the MULTUM-S II. The mixture of CO_2 and N_2O (49.4 %: 50.6 %) was purchased from DAIHO SANGYO Inc. (Tokyo, Japan). The gas was introduced into the EI ion source via a needle valve. Figure 4 shows mass spectra of the doublet of CO_2 and N_2O by changing the number of cycles. Since both CO_2 and N_2O have same nominal mass of *m/z* 44, CO_2 and N_2O were detected as one peak after 2 cycles (Fig.4(A)). In this cycle, the doublet peak could not be separated due to the low mass resolution (< 400). After 50 cycles, CO_2 and N_2O peaks were separated completely (Fig.4(B)). A mass resolution of 15000 was achieved. The signal intensity at 50 cycles was decreased to 10 % of 2 cycles. Figure 4(C) shows the mass spectrum at *m/z* 16 after 10 cycles. In this spectrum, the peak of $^{12}CH_4^+$ was separated from the peak of $^{16}O^+$. A mass resolution greater than 2000 was achieved, hence using this TOF mass spectrometer with high mass resolving power 'MULTUM-S II', CO_2^+, N_2O^+, $^{16}O^+$ and CH_4^+ can be separated.

Evaluation of gas monitoring system GC-MULTUM

In this experiment, we performed fast GC-high resolution MS to evaluate measurement of CO_2 and N_2O in the air. The atmospheric concentrations of CO_2 and N_2O were 380 ppm and 314 ppb, respectively. The conditions of MULTUM-S II were (i) electron energy; 23 eV, (ii) filament current; 3.6 A, (iii) applied voltage to the detector (ETP secondary electron multiplier 14880, SGE Analytical Science Pty Ltd, Victoria, Australia); 2700 V and (iv) the number of cycles of ion packets; 50. The obtained chromatograms and mass spectrum are shown in Fig.5. In the averaged mass spectrum at the retention time of 36 to 39 sec, CO_2 and N_2O were separated by the mass spectrometer with high mass resolving power. Furthermore, mass chromatograms were extracted using a mass window of ±0.0005 u. In this system, CO_2 and N_2O were detected within 1 min. We found fast GC-high resolution MS could be performed. The limit of detection (LOD) of N_2O was less than 300 ppb with a signal to noise ratio > 2. The linear signal response was evaluated by the measurement of the diluent gas of N_2O. The standard gas of 30 ppm N_2O was purchased from DAIHO SANGYO Inc. The standard gas was diluted in high purity helium from 0.3 ppm to 30 ppm (300 ppb, 3 ppm, 10 ppm and 30 ppm). A sample gas of 250 μL was measured by using the GC-MULTUM. Figure 6 shows the concentration dependence of the peak intensities of N_2O. The linear signal response for MULTUM-S II was shown using diluted N_2O gases. Peak intensities were plotted as a function of the concentration. The linear signal response was $R^2=0.999$. The coefficient of variation (CV) for the standard gas of 30 ppm N_2O was less than 2.3 % (the number of measurements: 30).

Monitoring of gases emitted from soils

Gases emitted from soils were measured to evaluate our developed system for environmental monitoring. The conditions of the MULTUM-S II were (i) electron energy; 60 eV, (ii) filament current 3.6 A (N_2 and O_2) and 4.2 A (CO_2 and N_2O), (iii) applied voltage to the detector; 2700V (N_2 and O_2) and 3300 V (CO_2 and N_2O) and (iv) the number of cycles of the MULTUM; 2 (N_2 and O_2) and 50 (CO_2 and N_2O). Figure 7 shows temporal changes in N_2, O_2, CO_2 and N_2O concentrations. We found steep and large reduction of N_2 and O_2 concentrations after the addition of water (Fig.7(A)). These reductions may be due to dissolution into the water, but a more detailed experiment should be required to understand this variation. The concentrations of N_2 and O_2 decreased and returned to an atmospheric level at 75 hours, indicating the headspace of the incubation system sustained an aerobic condition. The concentration of N_2O increased with increasing the concentration of CO_2 after the water application, reaching a maximum at a concentration of 17 ppm. This result suggests that water is a trigger of CO_2 production and N_2O is affected by CO_2 production. Rewetting of dry soil often induces CO_2 and N_2O flush from soil [16]. Both organic matter decomposition and denitrification emit CO_2 as a result of microbial aerobic and/or anaerobic respiration. Similar change of CO_2 and N_2O concentrations just after adding water, therefore, showed that CO_2 production on rewetting process was closely linked with that of N_2O production even in aerobic condition. Because N_2O production in the process of denitrification requires organic C as an electron donor, N_2O production by denitrification is often correlated with CO_2 production in soil [17]. Thus, our monitoring system could measure the response of CO_2 and N_2O production induced by water supply on a short-time scale. In the future our monitoring system, combined with some closed chamber method or other gas sampling system, could be used for detailed analysis of gas production and emission, especially in the field where the use of large-scale equipment would be prohibitive. This will enable us to more easily understand the mechanisms of material dynamics in environment. Furthermore this methodology could be used to investigate other areas of interest like carbon sequestration. We could envision using our system in a future trial to monitor CO_2 levels on the grounds of a carbon sequestration by plant to analyze this greenhouse gas during specific periods of growing and non-growing seasons. This method could be used to detail photosynthetic efficiency of plant, by comparing the quantities of gas being absorbed and rereleased into the atmosphere during the day. There are many other potential applications including, (but not limited to) monitoring the release of methane from hydrates during deep sea drilling and potential bio photosynthetic monitoring.

4. Conclusion

Using a gas chromatograph-MULTUM-S II, we have demonstrated the ability of simultaneous quantification of the gaseous compounds (CO_2, N_2O) within 1 minute. Using this monitoring system, we achieved real-time monitoring of N_2O, CO_2, N_2 and O_2 emitted from soils. The results indicate this newly developed system can be helpful for elucidating the generating mechanism. In the future, it will be possible to achieve on-site analysis of gaseous compounds using our methodology.

Acknowledgements

This work was supported by a Grant-in-Aid for Young Scientists (A) (21685010) from the Ministry of Education, Culture, Sports, Science and Technology, a supporting program for creating university ventures from the Japan Science and Technology Agency (JST), and Support Program for Osaka University Future Research Initiative Groups. The authors thank Mr. Shinichi Miki and Dr. Hirofumi Nagao of MSI.TOKYO Inc. for their technical support and discussion.

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Figure captions

Fig.1 The schematic of chromatogram. (A) Conventional GC-MS (low mass resolution), (B) fast-GC-MS (low mass resolution), (C) fast-GC-MS (high mass resolution).

Fig.2 (A) Photograph of MULTUM-S II. (B) Schematic of multi-turn part of MULTUM-S II

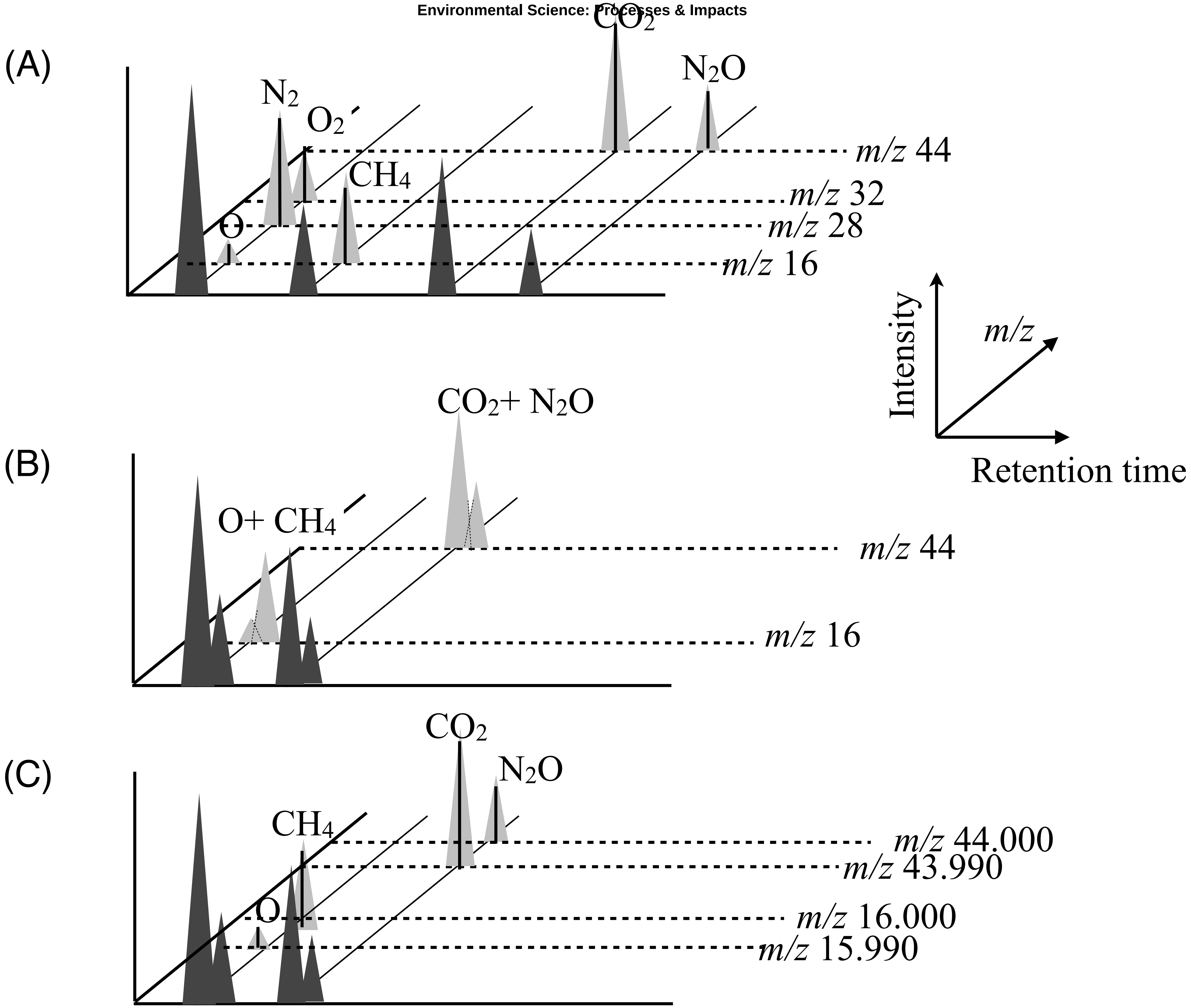
Fig.3 The schematic of developed gas sampling system(A). Timing charts of gas sampling (B) and mass spectrometer (C).

Fig.4 Mass spectrum of $^{12}C^{16}O_2$ and $^{14}N_2{}^{16}O$ doublet after (A) 2 cycles and (B) 50 cycles. Mass spectrum of ^{16}O and $^{12}CH_4$ doublet after 10 cycles (C).

Fig.5 The total ion current chromatogram and mass chromatograms of CO_2 and N_2O in the air (A) and the averaged mass spectrum at the retention time of 36 to 39 sec (B).

Fig.6 The signal response curve of N_2O from 0.3 ppm to 30 ppm.

Fig.7 Temporal changes in N_2 and O_2 (A), CO_2 (B) and N_2O (C) concentrations emitted from soils for 3 days. After 24.5 hours incubation, 2.1 mL water was added to the soils.



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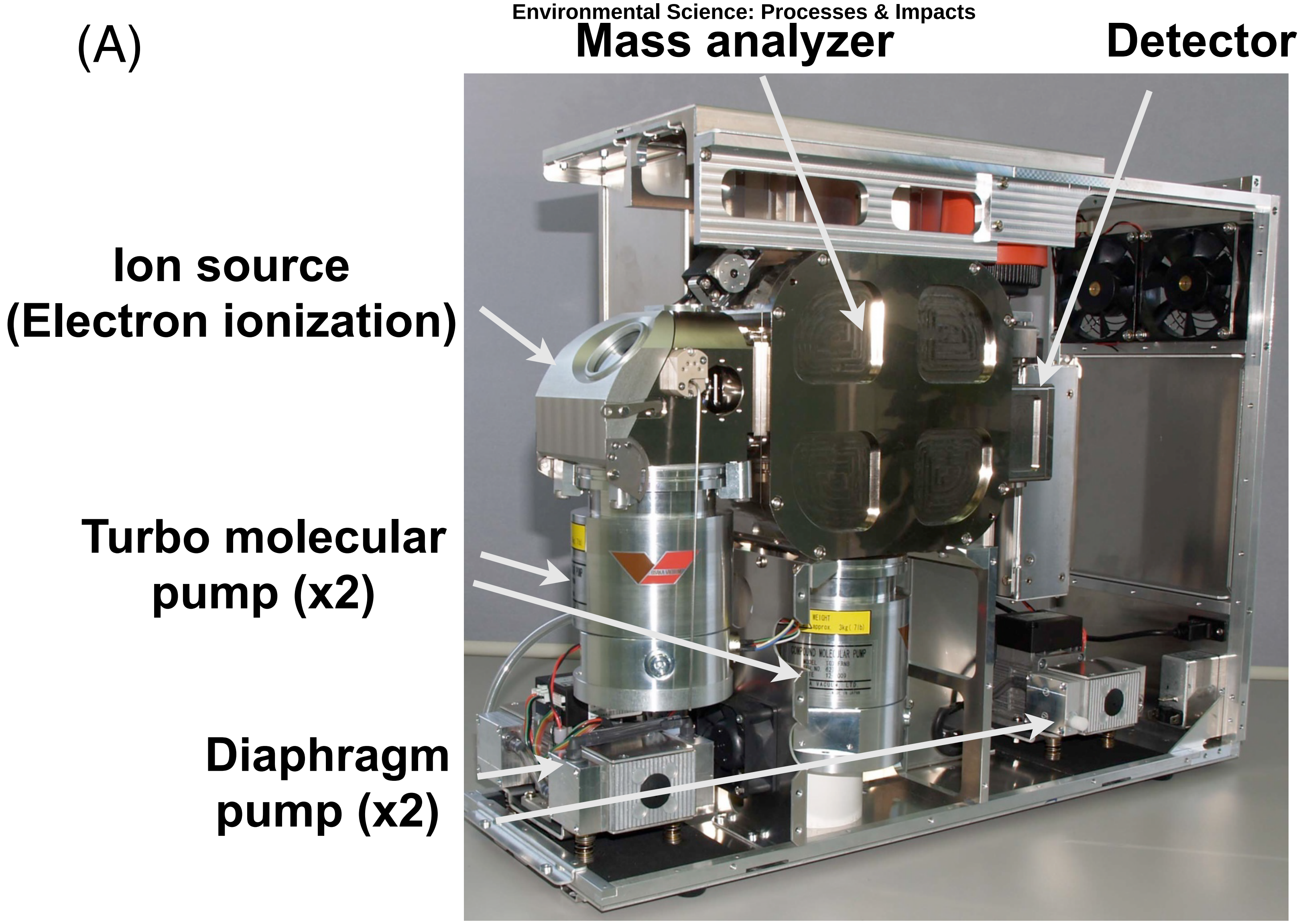

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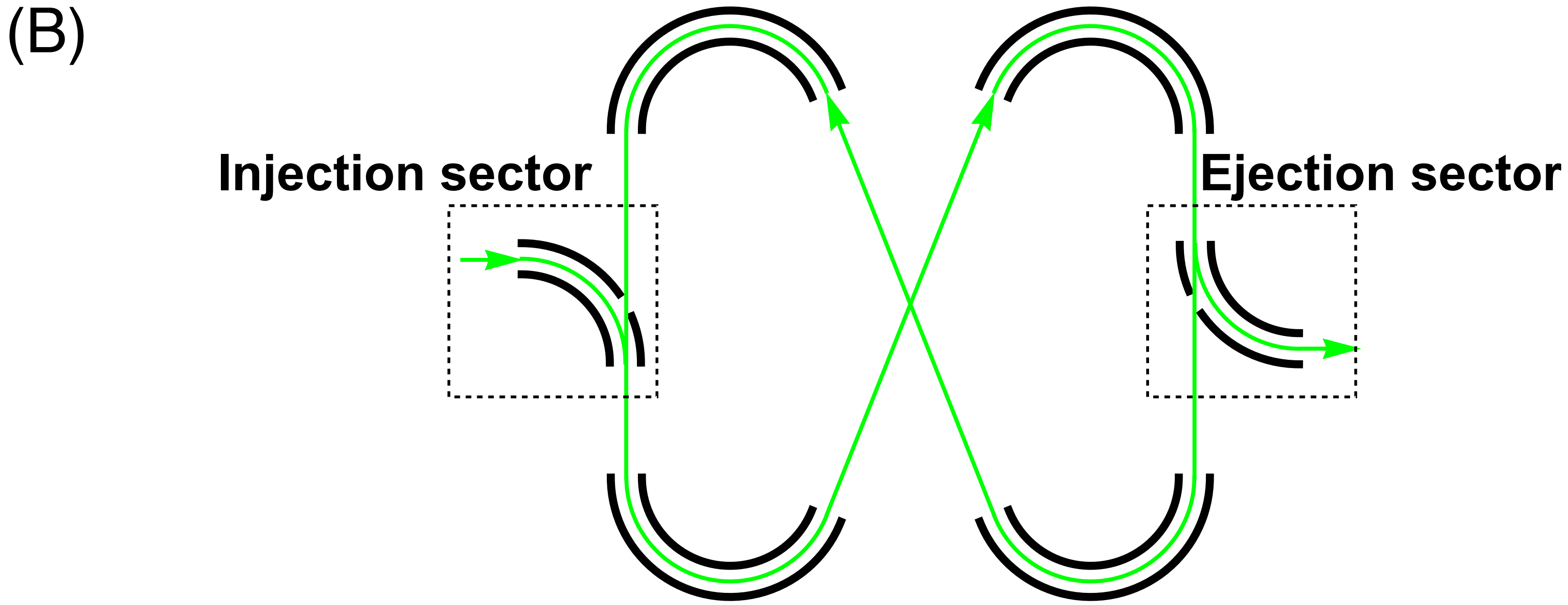

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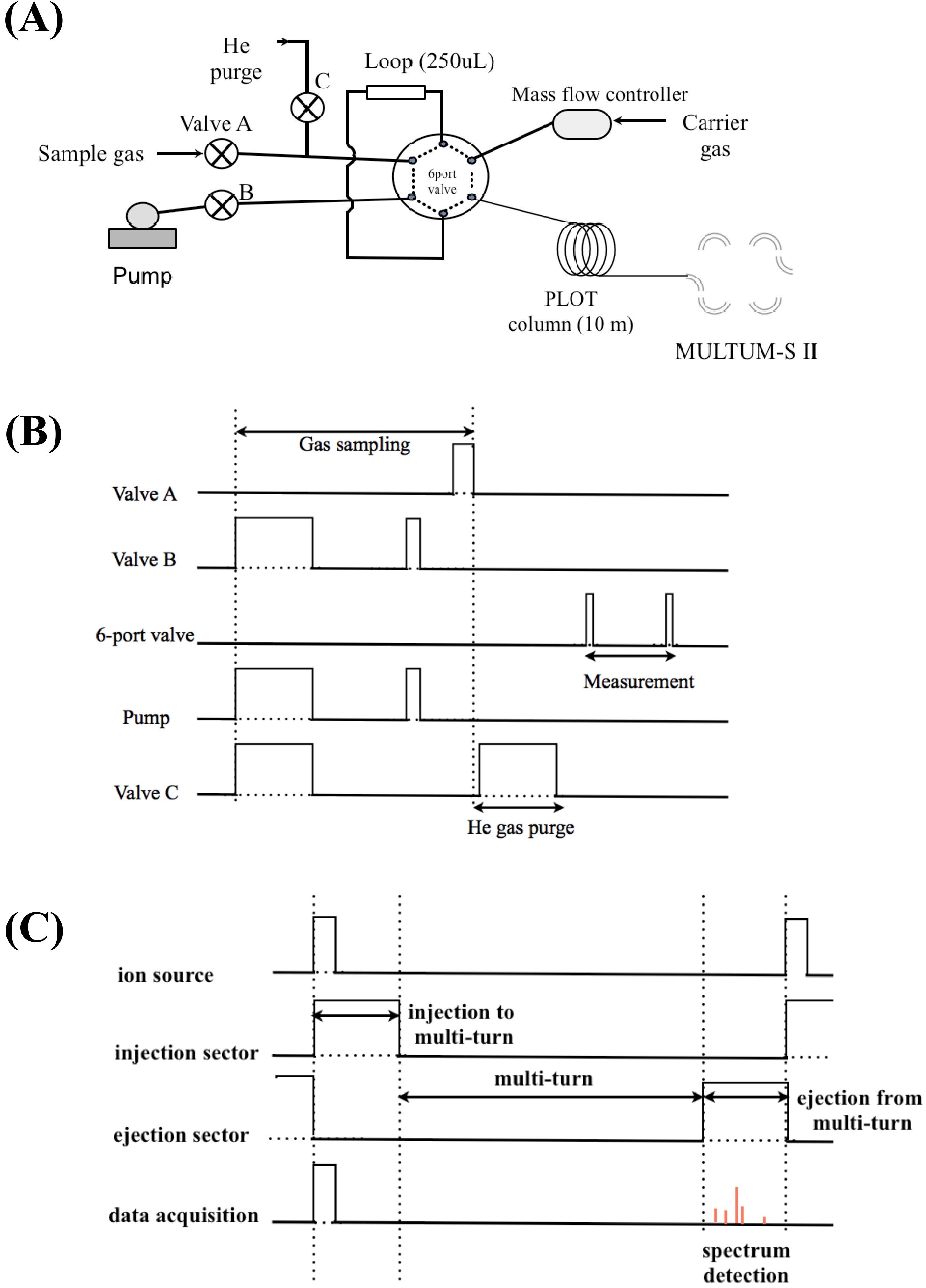

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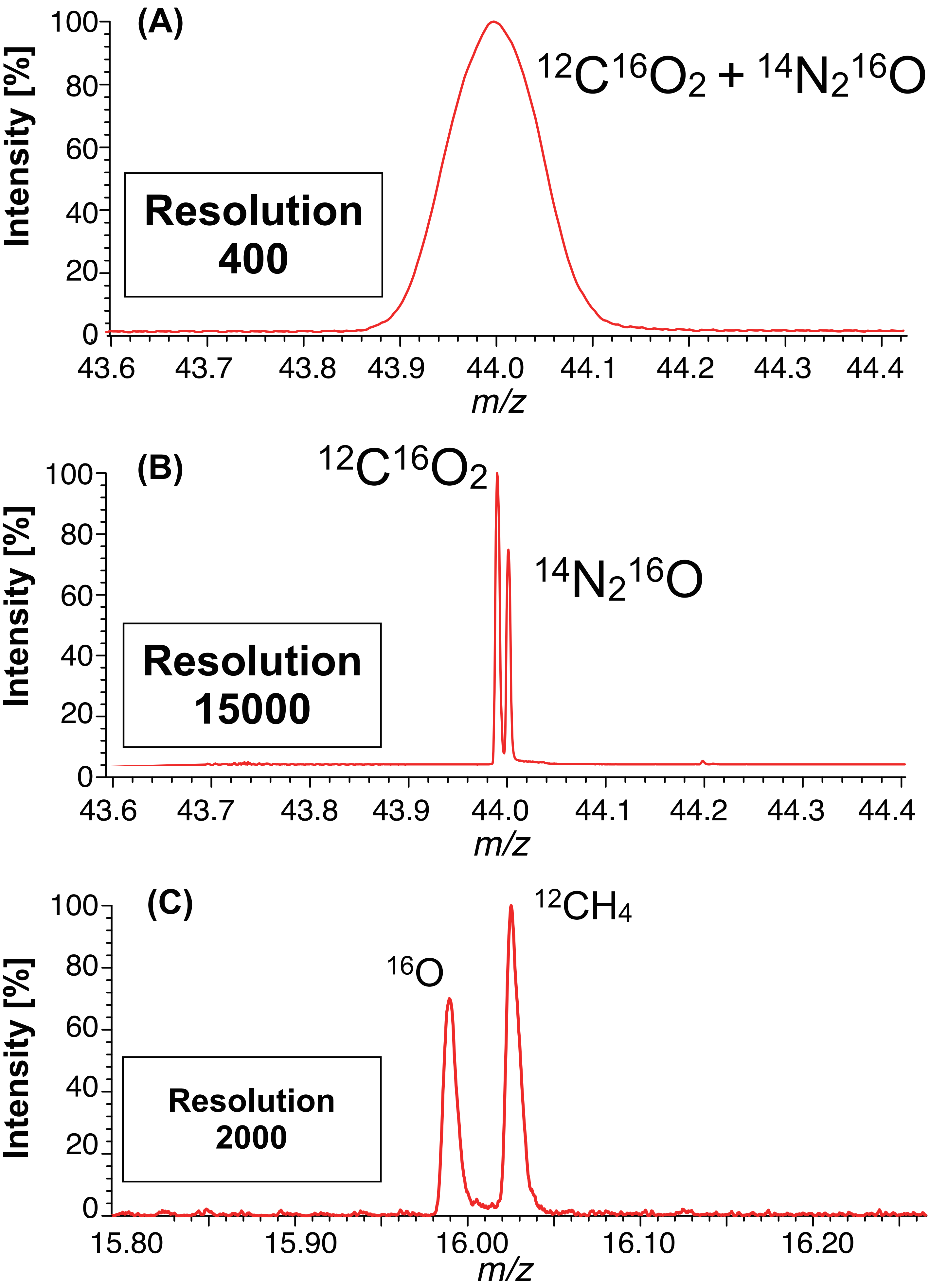

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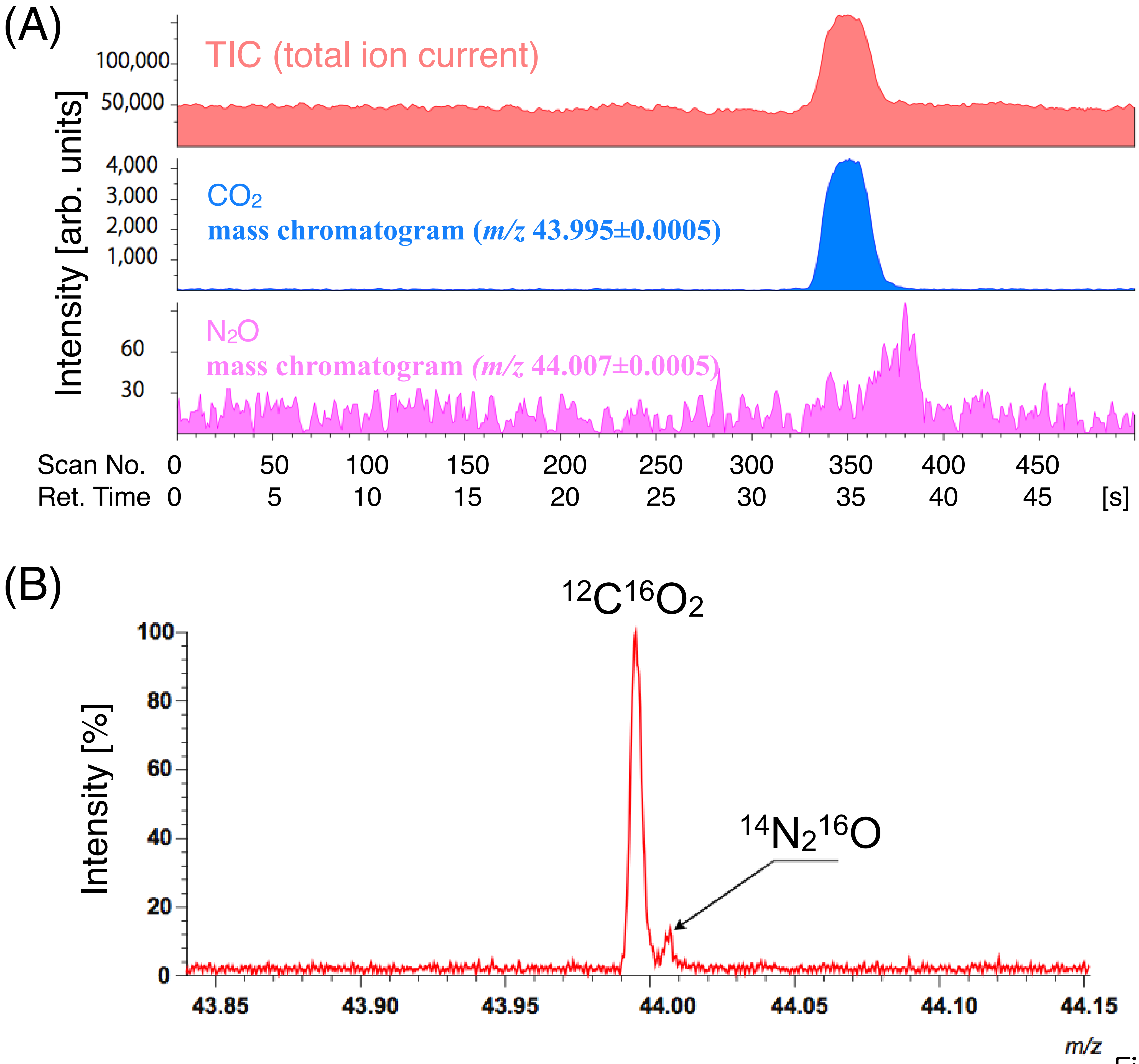

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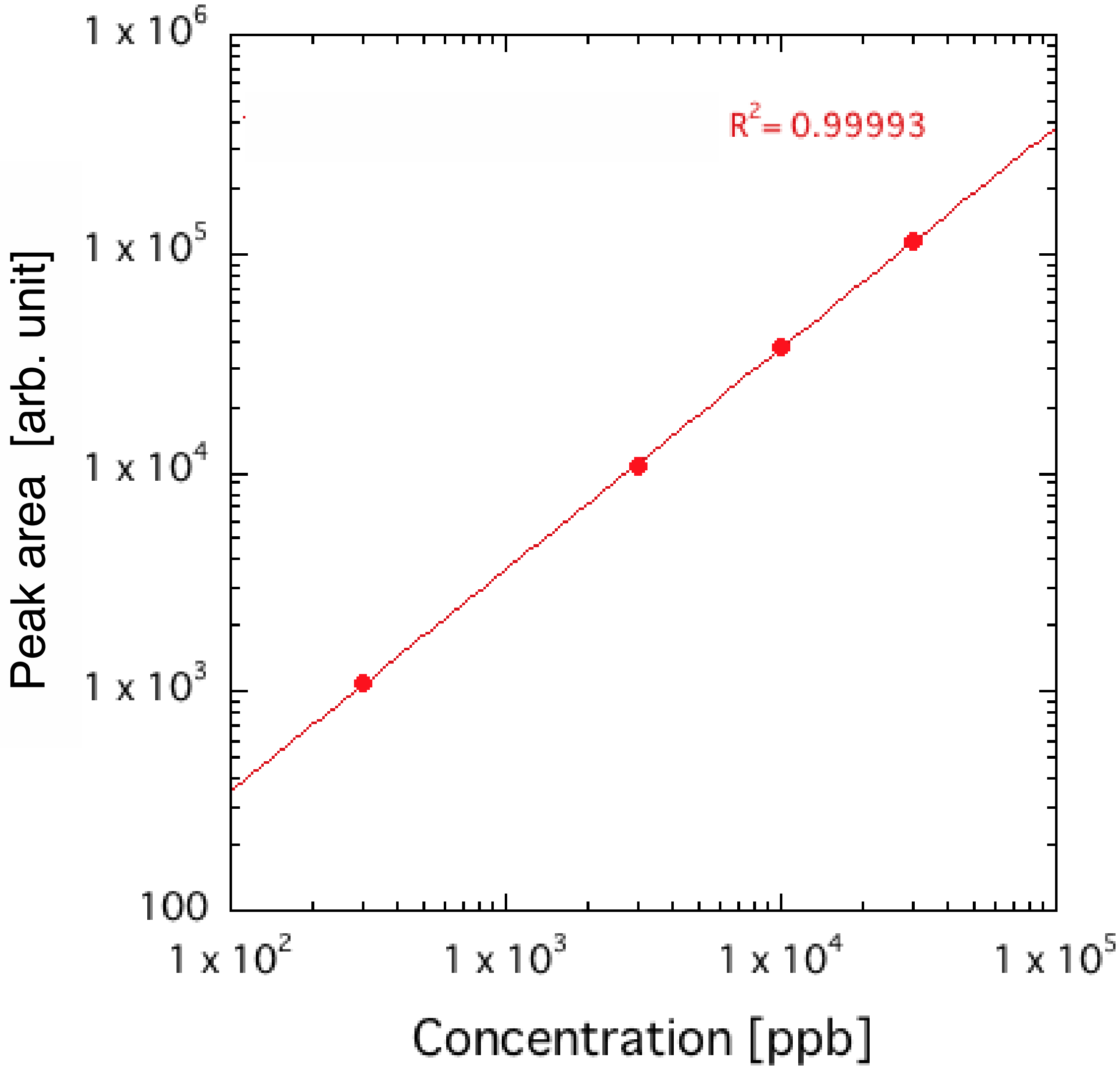

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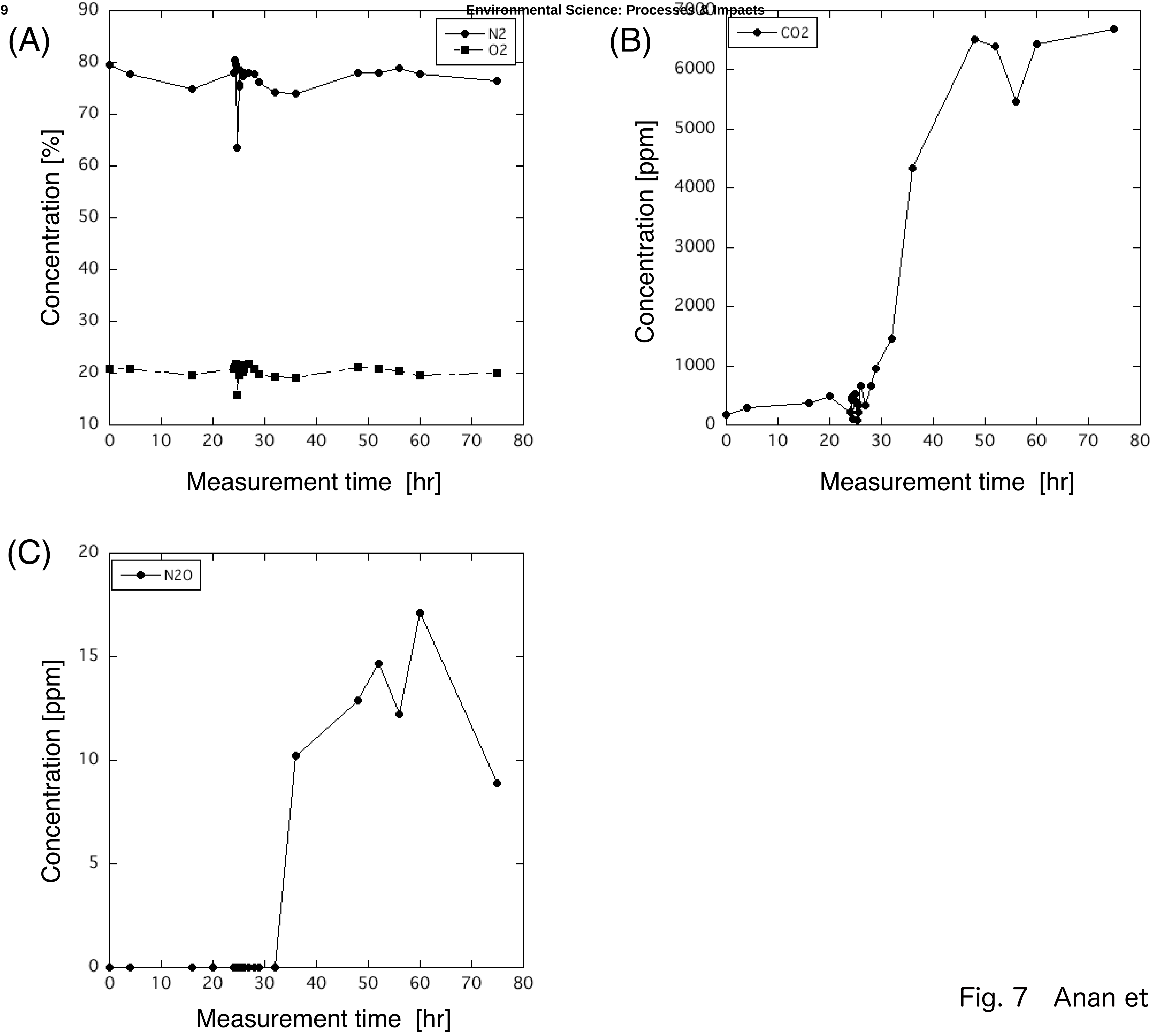

Fig. 7 Anan et al.