RF-062 **Development of Measurement Technique of Trace Gases and Stable Isotope Ratios of Atmospheric CO_2 for CO_2 Flux Partitioning (Abstract of the Final Report)**

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Total Budget for FY2006-FY2007 19,304,000Yen (**FY2007**; 9,307,000Yen)

Key Words Carbon Dioxide, Climate Change, Flux, Future Prospects, Tracer

[Abstract]
We developed a flux-partitioning method using chemical tracers (e.g. stable isotopes of CO_2 and carbonyl sulfide) as additional constraints. The flux partitioning using stable isotopes of CO_2 is based on the imbalance of net flux of the CO_2 isotopes between 'respiration' and 'photosynthesis'. On the other hands, carbonyl sulfide (COS) is decomposed by enzyme CA (carbonic anhydrase) in leaf stomata. The uptake rate of COS is dominantly controlled by stomatal regulation of gas exchange as well as CO_2. Because of this similarity in the control factors for uptake ratio, the net flux of COS is regarded as a possible constraints for the functioning of variations in photosynthetic CO_2 uptake by terrestrial ecosystem.
In current circumstances, the measurements of both CO_2 isotopes and COS fluxes by the EC method is quite difficult due to the limitation of performance of analyzers. In our study, we will measure the fluxes of both CO_2 isotopes and COS by using relaxed eddy accumulation (REA) method coupling with glass-flask sampling and high precision lab-analyses. We established a measurement system for precise determination of atmospheric COS from small amount of sample air. We evaluated that precision of the measurements of CO_2 isotopes and COS were high enough for the REA-based flux observation. We tested the quality change of atmospheric composition in a intermediate storage reservoir made with new-age gas barrier film called Eval. Eval showed excellent permeation-resistance for CO_2. We also established a quality control protocol for high-precision measurement of atmospheric COS.

1. Introduction

For the purpose of determining the CO_2 uptake by terrestrial ecosystem, eddy covariance method

(EC) is used commonly in the world wide tower-flux measurement network. The flux measured by this method is called 'net ecosystem exchange (NEE)'. NEE has the meaning of difference between photosynthetic uptake and respiratory release of CO_2. Both the gross flux have difference in response function against changes in environmental factors, such as temperature and water. Therefore it is important to evaluate the characteristics of variations in both gross CO_2 fluxes individually in the future prediction of CO_2 uptake by terrestrial ecosystem.

2.Research Objective

Separation of NEE into both gross fluxes is most likely done by using an approximate temperature expression of respiratory flux. This approximate expression is based on the assumption that the NEE observed at nighttime equals to the respiratory flux. The photosynthetic uptake of CO_2 is defined as difference between the observed NEE and "respiration" approximated as a temperature-function. Because of its technical simplicity, this approach has provided useful information about climatology of the gross CO_2 fluxes. However, the temperature expression of respiratory flux has several limitations in its application. For example, possible response of respiratory flux against factors other than temperature (water availability, phenology etc) is neglected in this approach. In development of detailed investigation of variability in the gross CO_2 fluxes, it is highly desired to establish new flux-partitioning method.

We are now planning the development of a flux-partitioning method using chemical tracers (e.g. stable isotopes of CO_2 and carbonyl sulfide) as additional constraints. The flux partitioning using stable isotopes of CO_2 is based on the imbalance of net flux of the CO_2 isotopes between "respiration" and "photosynthesis" (e.g. Bowling et al., 2003). On the other hands, carbonyl sulfide (COS) is decomposed by enzyme CA (carbonic anhydrase) in leaf stomata. The uptake rate of COS is dominantly controlled by stomatal regulation of gas exchange as well as CO_2. Because of this similarity in the control factors for uptake ratio, the net flux of COS is regarded as a possible constraints for the functioning of variations in photosynthetic CO_2 uptake by terrestrial ecosystem.

3.Results

We developed flask-sampling system on the basis of Relaxed Eddy Accumulation (REA) method for measuring net flux of stable isotopes of CO_2 and of COS. Methods for high-precision measurements of stable isotope ratios of CO_2 and COS was also developed. COS in air samples was determined by using gas-chromatograph equipped with sulfur-chemiluminescene detector (Figure 1). This detector has selectivity and extremely high sensitivity for sulfur compounds. Those features are suitable for our research objective. Appearance of the REA-based flask sampling system was shown in Figure 2. Analytical precision of atmospheric COS was estimated to be 20ppt (1 standard deviation of 24 replicated measurements) (Figure 3). On current stage, standard error of 10ppt (about 2% of mean atmospheric concentration of COS) was obtained by 4 measurements. We prospected that the analytical precision of atmospheric COS by our system would be improved significantly by modification of chromatogram-processing. Reliable reference gas for atmospheric COS measurement was unavailable and the sulfur-chemiluminescene detector had significant sensitivity fluctuation (Figure 4). Therefore we designed a quality control procedure for atmospheric COS emasurements. We also investigated the optimum experimental configuration of REA-based sampling by simulation based on the real observed micrometeorological data.

References

Bowling, D.R., D.E. Pataki, and J.R. Ehleringer (2003) Critical evaluation of micrometeorological methods for measuring ecosystem–atmosphere isotopic exchange of CO_2, Agric. For. Meteorol., 116, 159-179.

Major Publications

None

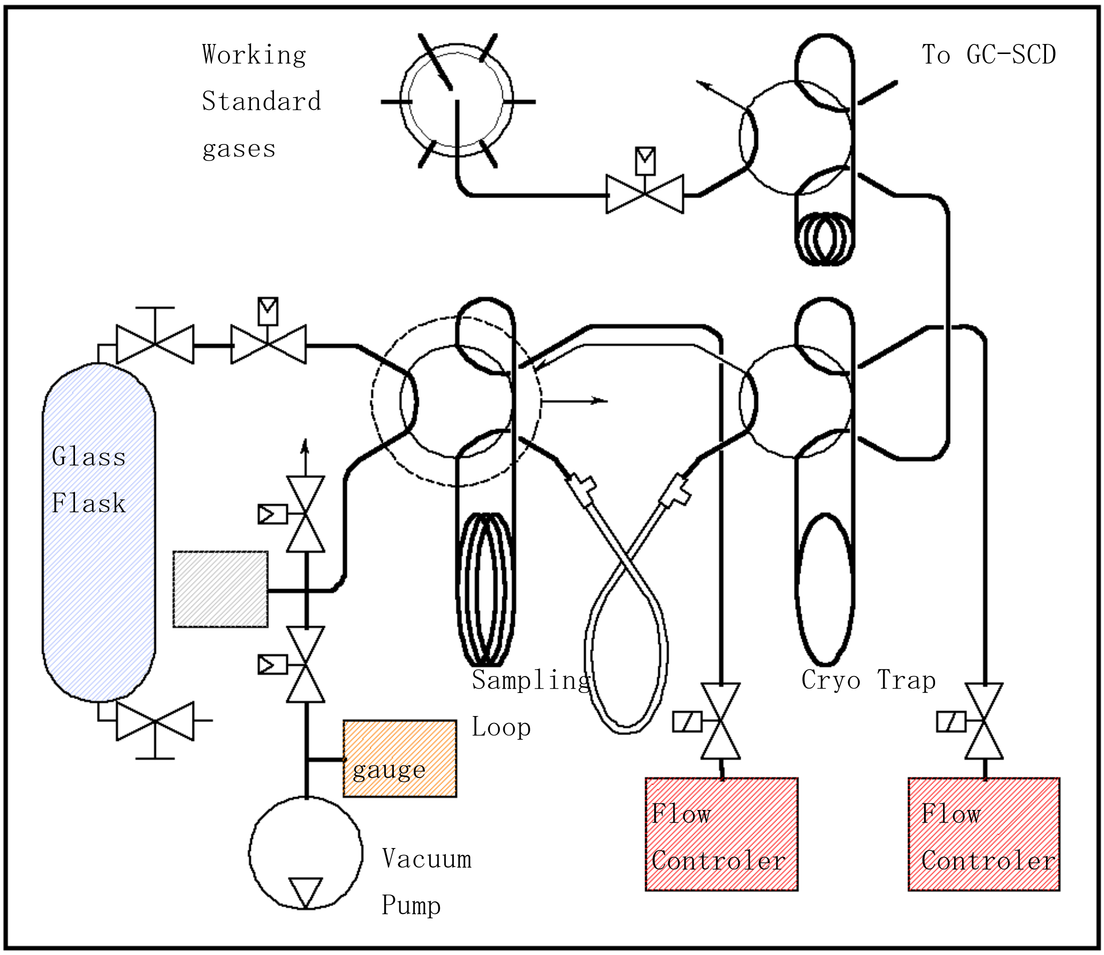

Figure 1 Schematic diagram of COS measurement system

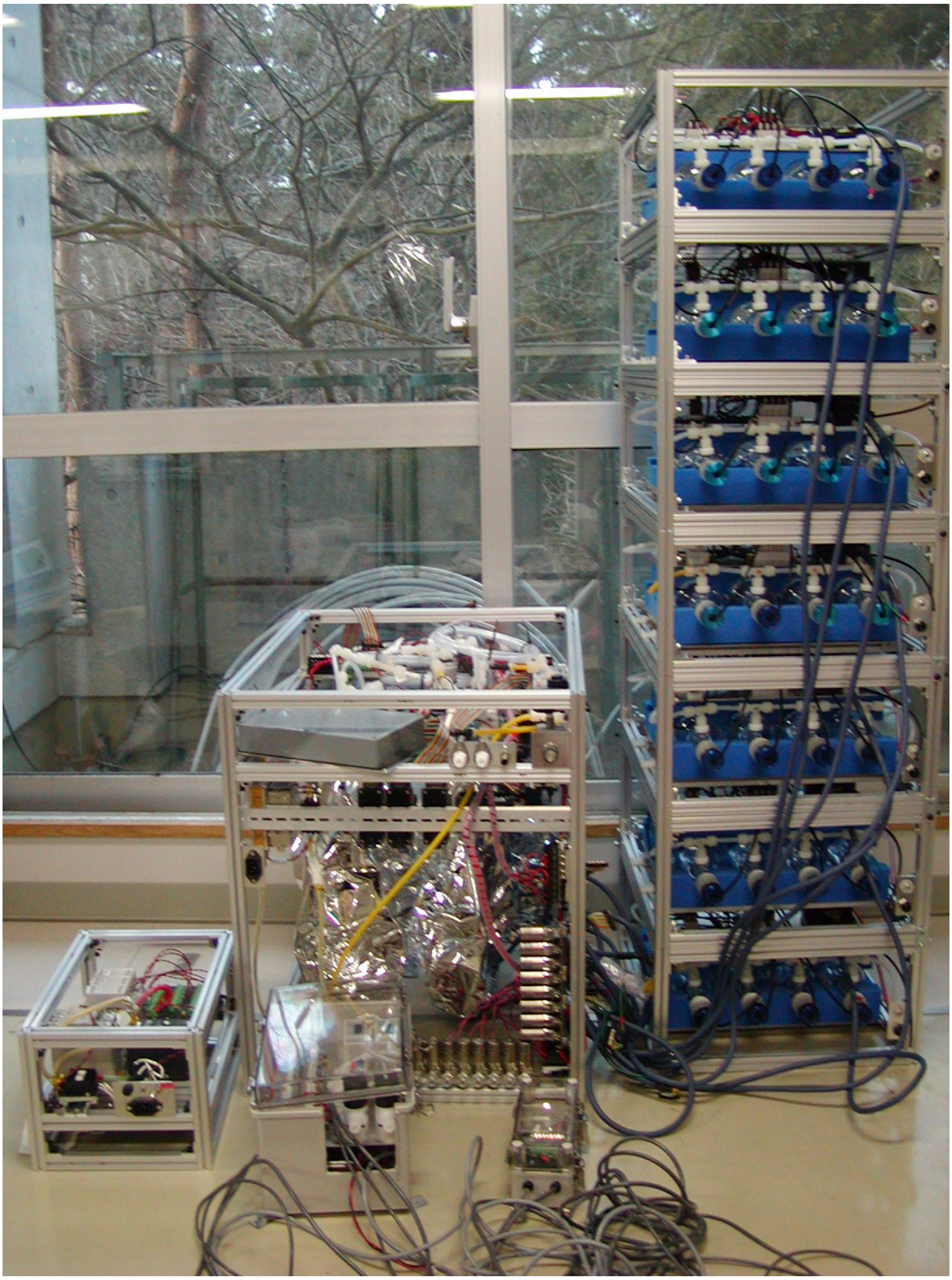

Figure 2 Appearance of Eddy-Accumulation-based sampling system for stand scale fluxes evaluation of CO_2 isotopes and carbonyl sulfide.

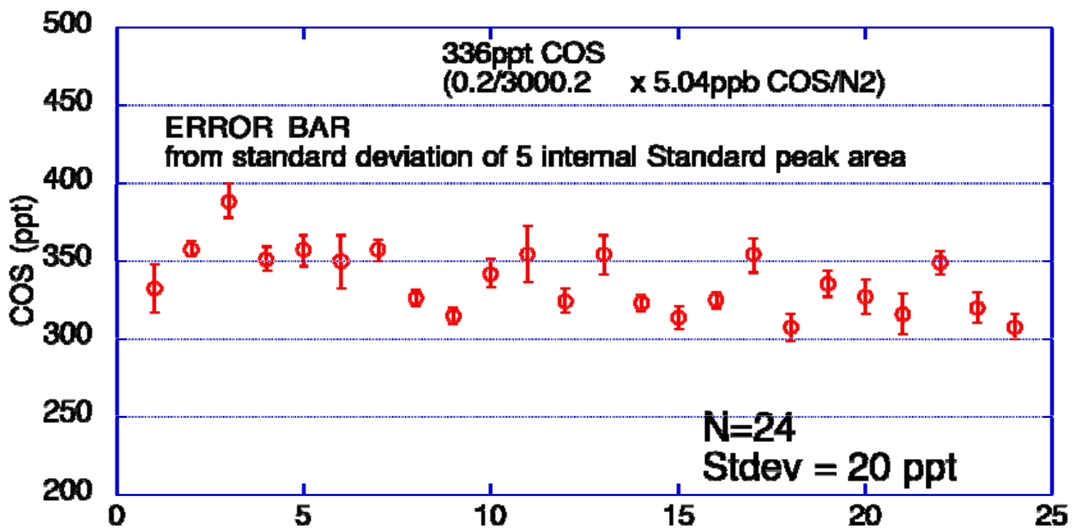

Figure 3 Results of multi-time measurements of single sample. Standard deviation of the COS measurement were 20ppt (N=24).

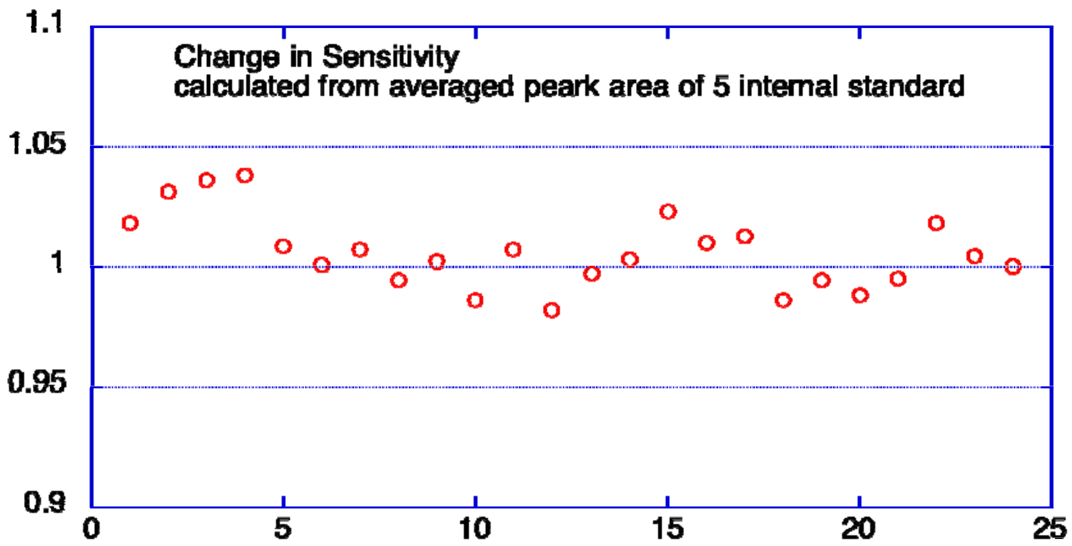

Figure 4 Change in sensitivity of Sulfer Chemiluminescene Detector.