

2.5 Relaxed eddy accumulation (REA) method

The eddy covariance method requires a small number of assumptions for flux observations over the ground surface, thus it is considered to be the most direct flux observation method. When the eddy covariance method is used for flux observations of trace gases such as methane or volatile organic compounds (VOCs), the fluctuating component of the trace gases needs to be measured with a high response time. Such measurements are necessary in order to match the fluctuating vertical wind velocity, w , which is measured by an ultrasonic anemometer thermometer (SAT) usually at a sampling rate of approximately 10 Hz. However, when a gas chromatograph (GC) is used for the analysis of trace gases, the analysis requires a few minutes to a few tens of minutes, and the eddy covariance method cannot be used. In this case, the relaxed eddy accumulation (REA) as outlined by Businger and Oncley (1990) can be used instead.

In the REA method, air samples are collected in two isolated reservoirs. An air sample is collected into one of the two reservoirs according to whether it was sampled with an upward or downward vertical wind velocity (positive w or negative w , respectively). After air samples have been collected over a specified time period, the concentration of the atmospheric trace gas in the air sample in each reservoir is analyzed. Subsequently, the difference in the concentrations of the atmospheric trace gas between the two air samples, $\Delta\rho_g$ [mgm^{-3}], is calculated. The value of the flux, F_c [$\text{mgm}^{-2}\text{s}^{-1}$], can be evaluated by multiplying the value of $\Delta\rho_g$, the standard deviation of w , σ_w [ms^{-1}], and an empirical coefficient b . Thus, the REA method replaces the eddy covariance method when the concentration of a trace gas to be measured is small and the observation calls for the use of a gas analyzer (e.g., GC) that requires some time for concentration analysis.

Measurement principle

The REA method is a variant of the true eddy accumulation method. In flux measurements with the true eddy accumulation method, the flow rate for the atmospheric air sampling is adjusted in proportion to the magnitude of the vertical wind velocity. Over a given length of time, air samples are accumulated in two reservoirs: one for positive (w^+) and one for negative (w^-) wind velocities [ms^{-1}]. This procedure allows evaluation of the time-averaged value of the concentration of the trace gas of interest, ρ_g [mgm^{-3}]. As a true eddy accumulation method, Komori *et al.* (2004) proposed a method that uses syringes connected to a high-speed pulse motor which is synchronized with a pulse generator. In the true eddy accumulation method, the vertical flux of a trace gas, F_g [$\text{mgm}^{-2}\text{s}^{-1}$], is expressed as follows:

$$F_g = \overline{w^+ \rho_g} + \overline{w^- \rho_g} \quad (2.5-1)$$

Because the true eddy accumulation method requires control of the sampling flow rate at a high rate of response, the measuring system becomes complex. On the other hand, the measurement procedure is simplified in the REA method by keeping the sampling flow rate constant. In the REA method, the vertical

flux of a trace gas, F_g , is expressed as follows:

$$F_g = b \cdot \sigma_w \cdot \Delta \rho_g \quad (2.5-2)$$

where $\Delta \rho_g$ is the difference in the average concentration of an atmospheric trace gas between the two sampling reservoirs and σ_w is the standard deviation of w within a specified time period. The variable b is an empirical coefficient and can be determined from other variables such as the sensible heat flux which can be measured with the eddy covariance method. If the value of b for an atmospheric trace gas flux is assumed to be equal to that of the sensible heat flux, the following relationship holds between the sensible heat flux and the coefficient b :

$$\overline{w'T'} = b \sigma_w (T^+ + T^-) \quad (2.5-3)$$

where the left and right sides of the equation represent the sensible heat flux determined from the eddy covariance method and that determined from the REA method, respectively. The variables T^+ and T^- represent the average air temperatures [K] from the times when the values of w are positive and negative, respectively. The above equation can be solved for b as:

$$b = \frac{\overline{w'T'}}{\sigma_w (T^+ - T^-)} \quad (2.5-4)$$

The structure of the system used for the REA method

The system for collecting atmospheric trace gases consists mainly of a SAT, solenoid valves, pumps, a mass flow controller, air sampling reservoirs, a programmable recording device such as a CR1000 (Campbell Scientific, Inc., US) and a PC. According to the sign (positive or negative) of the vertical wind velocity, w , the air sample which has been drawn in near the SAT is sorted into the appropriate reservoir. The air sample is sorted with the use of a solenoid valve (Photo 2.5-1) that is operated at high speed. (Refer to Figs. 2.5-1 and 2.5-2; the red and blue lines indicate the flow paths for the positive and negative values of w , respectively.) The flow rate of the sampled air is controlled by a mass flow controller so that the flow rate can be maintained at a constant value. However, it is critical to set the flow rate low (0.2 Lmin^{-1} or less) to ensure that the sampling rate does not exceed the capacity of the sampling tube. At the same time, in order to avoid the influence of wind velocity fluctuations, the air intake rate needs to be maintained at a constant value (4 Lmin^{-1} or larger), and a bypass needs to be included



Photo 2.5-1 A SAT and an air inlet used in an REA system. (Yamashiro forest hydrology research site)

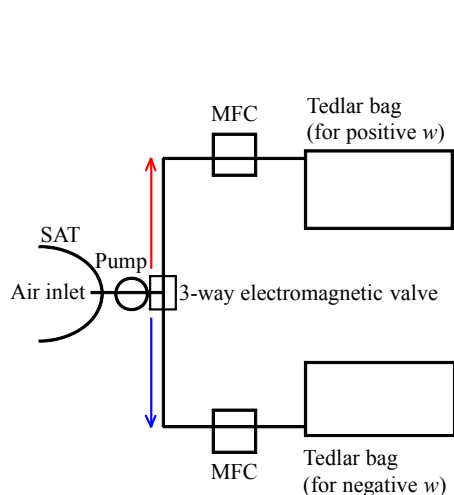


Fig. 2.5-1 Configuration of an REA system for methane.

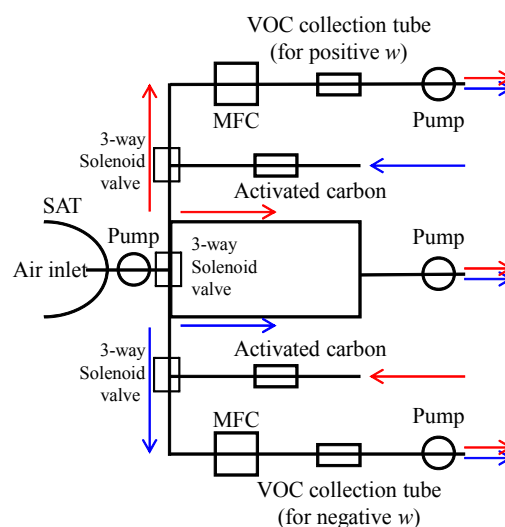


Fig. 2.5-2 Configuration of an REA system for VOCs.

within the measurement system. Additionally, for the purpose of keeping the pressure constant in the system during the solenoid valve switching, the system is equipped with a three-way solenoid valve. When the sampling air inlet is closed, VOC free air that has been filtered through activated-carbon is supplied to the gas sampling tube instead of the sampled air.

A programmable data logger such as the CR1000 is used for 1) controlling the solenoid valves, 2) recording the wind velocities and temperature, and 3) determining the sign (positive or negative) of w according to the moving-average value of w (Photo 2.5-2). In order to exclude the influence of the low-frequency wind-velocity variation, the averaging time for w is selected based on the actual observation conditions, and the averaging time is frequently set to 15 minutes or less. When the averaging time is 15 minutes and the data are recorded at 10 Hz, the sign of w is determined using the moving average of the 9,000 data values up to and including the data value obtained 0.1 seconds before the determination of the sign. In the REA method, a threshold value is sometimes defined for the purpose of eliminating from the analysis the effects of extremely low wind velocities, that is, wind velocities which are lower than the minimum resolution of the data logger or the anemometer. In this case, when the wind velocity is smaller than the threshold value, the trace gas is not stored, but vented out instead (A deadband is set.)

The characteristics of each trace gas are different including its absorptivity, boiling point, and atmospheric lifetime. Therefore, the REA system needs to be configured exclusively for the trace gas to be measured by taking into account its properties and the requirements of the analysis method. For example, large Tedlar bags made of PTFE are often used for storing methane. For storing a VOC such as isoprene or terpene, a reservoir system consisting of multiple air sampling tubes or consisting of canisters is frequently used (Photo 2.5-3). Air sampling tubes are made of stainless steel or glass, are as small as 6 mm in diameter, and are filled with adsorbent. Canisters used for the reservoir system are vacuum vessels made of glass or stainless steel. The reservoir system collects the atmospheric air by automatically switching the flow-path at regular time intervals with the use of programmable relays. The measurement system needs to be designed in

such a way that analysis results of high accuracy can be achieved. Specifically, it is necessary to 1) maintain a constant flow rate at a point as close to the air inlet as possible, 2) sort the air samples with a high-speed response time, and 3) store the air samples by minimizing the effects of degradation by ozone as well as adsorption in the flow path. To meet these requirements, it is useful to block ultraviolet radiation, add an ozone scrubber, and use PTFE materials or heating tubes.

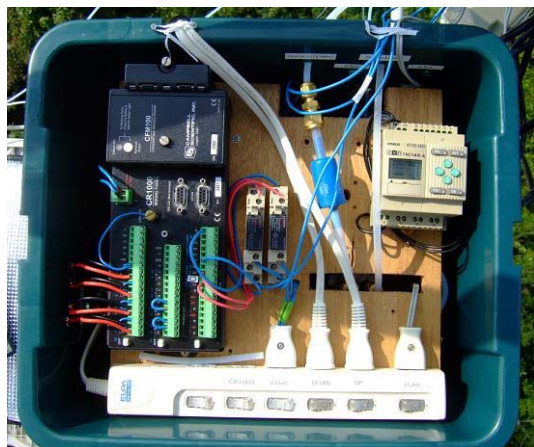


Photo 2.5-2 Control section of a system which is designed for the REA method and uses a CR1000. (Fujiyoshida forest meteorology research site)



Photo 2.5-3 An example of multiple VOC reservoirs (sampling tubes). (Fujiyoshida forest meteorology research site)

Measurement procedure

A typical procedure for trace gas flux measurement is as follows:

- 1) Observation of w with a SAT and calculation of the time-averaged value of w .
- 2) Determination of the sign of w , switchover of the solenoid valves, and recording of the determined sign.
- 3) Automatic exchange of air sampling reservoirs (or on-site automatic analysis of the previously collected air sample during the next sampling period.)
- 4) If on-site automatic analysis is not performed, the air sample reservoirs need to be brought back to a laboratory. After the analysis equipment has been calibrated with the use of a calibration gas, the air samples are analyzed, and the difference in the concentrations of the trace gas is determined between the times with positive values of w and those with negative values of w .
- 5) Calculation of the value of b with the use of the sensible heat flux.

Types of analyzers

Although mainly gas chromatographs have been used for the analysis of trace gasses, other types of analyzers have also been used in recent years. Various types of analyzers that are used for trace gas flux observations are described below.

Gas Chromatograph - Flame Ionization Detector

A gas chromatograph-flame ionization detector (GC-FID) reacts only to carbon compounds other than

CO₂ and CO, and is little affected by other constituents of the air. A highly sensitive quantitative analysis of a trace gas of interest can be made by separating the trace gas from the rest of the air sample with the use of an appropriate column. Advantages of the detector include its simple configuration, low price, high stability, and low operating cost. For the analyses of methane and VOCs, an activated-carbon-packed column and a capillary column are used, respectively. The time required for methane analysis is a few minutes. On the other hand, the analysis time required for VOCs is longer than that for methane. In a temperature programmed analysis in which the column temperature is raised for analyzing the high-boiling-point component, cooling time is also required after the analysis. In qualitative analyses, no information other than the retention time of the separated trace gas can be obtained. Therefore, additional information needs to be acquired from a reference substance and a gas chromatograph - mass spectrometer. Because leakage of the hydrogen gas which is required for the analyses may cause an explosion, safety measures should be taken in advance. These measures include the use of a safety device such as an alarm and an automated ventilator for sufficient ventilation.

Gas Chromatograph - Electron Capture Detector

As a measurement principle, a gas chromatograph - electron capture detector (GC-ECD) depends on the change in the base current which takes place when a chemical compound captures free electrons. GC-ECDs are used for detecting nitrous oxide (N₂O), a greenhouse gas that is regulated by the Kyoto Protocol. Because the atmospheric concentration of N₂O is very low (310 ppb), the analysis of N₂O is affected by the peaks of atmospheric N₂ and O₂. Therefore, the heart-cut technique is adopted to extract the constituents that are eluted at and near the peak of N₂O on the chromatograph, and the extracted constituents are analyzed with the detector. In addition, the GC-ECD is highly sensitive in detecting electrophilic substances such as halide and nitro compounds and is also used for analyzing methyl bromide (CH₃Br) which is subject to regulations under the Montreal Protocol. GC-ECDs can be classified into two types: radioactive and non-radioactive GC-ECDs. Use of the former type requires compliance with laws and regulations concerning the conditions for use and storage of radioactive materials.

Gas Chromatograph - Mass Spectrometer

A gas chromatograph - mass spectrometer (GC-MS) is a highly sensitive analyzer and thus is often used for qualitative and quantitative analyses of atmospheric trace gasses. One of the distinguishing characteristics of a mass spectrometer is that it provides mass spectra that include information on the chemical structure of the trace gas of interest. For the analysis of a trace gas with an extremely low concentration, the gas needs to be pre-concentrated in advance. In VOC flux observations using the REA method, air sampling tubes containing adsorbent are frequently brought back to a laboratory for desorption with a thermal desorption unit. A GC-MS analysis is conducted after the air sample is concentrated by cooling the air sample with a cold trap called a cryofocus trap and heat is added to the air sample. Alternatively, air samples can be brought back to a laboratory with the use of canisters, and the samples can be analyzed after moisture is selectively removed with a three-stage trap. This method has enabled the analysis of alcohols which are water-soluble

constituents and were previously difficult to analyze. The time required for an analysis with a GC-MS is no different from the time required for analysis with a GC-FID which utilizes capillary columns. However, the maintenance cost of a GC-MS is relatively high compared to that of a GC-FID due to the need to replace turbo-molecular pumps.

Soft Ionization Mass Spectrometer

A proton transfer reaction mass spectrometer (PTR-MS) is a type of soft ionization mass spectrometer and ionizes pure water vapor for the primary ion source. The PTR-MS is able to detect alkane, ethylene, propylene, and acetylene, which are characterized by lower affinity for protons than water. The PTR-MS can detect various other organic gases and hydrogen sulfide. When injecting air samples into the PTR-MS, no pre-processing is required for the air samples such as condensation of the trace gas of interest. Quantitative analyses with a PTR-MS are less prone to measurement errors than those with a GC-MS. A PTR-MS is also capable of continuous and high-accuracy analyses and consecutive quantitative measurements of multiple VOCs at intervals of a few seconds. Recently, based on the high response characteristics of a PTR-MS, the disjunct eddy covariance (DEC) technique has been developed (Rinne *et al.*, 2000). This technique conceptually falls between the eddy covariance method which relies on sensors with a fast response time and the REA method. In the DEC technique, atmospheric air sampling periods of less than 1 second are separated in time by intervals of no air sampling. The values of w are recorded, and the air samples are analyzed. This technique aims to include the effect of small-eddy transport by minimizing the sampling time as much as possible. In practical use, virtual disjunct eddy covariance (vDEC) (Karl, 2002) as modified DEC is also commonly used for flux measurement of several compounds.

An ion molecule reaction mass spectrometer (IMR-MS) is another type of soft ionization mass spectrometer. While an IMR-MS is more expensive than a PTR-MS, the former spectrometer is able to analyze any gasses and the sensitivity of the spectrometer is as high as that of a PTR-MS. The IMR-MS uses three gases (Hg, Xe and Kr) as the primary ion sources. Fragmentation (i.e., break-up of molecular ions into smaller pieces due to bond cleavage) occurs more frequently in analyses with an IMR-MS than in those with a PTR-MS, however, an IMR-MS can identify a substance by analyzing the fragments using multiple ion sources. On the other hand, multiple optional ion sources have become available for use in PTR-MSs in recent years, and the differences between an IMR-MS and a PTR-MS have become smaller than earlier.

Tunable Diode Laser Spectrometer

In a tunable diode laser spectrometer (TDLS), two high-reflectance mirrors are set face-to-face in order to obtain an optical path of several kilometers. Within the optical path, laser beams are reflected multiple times, and the attenuation and decay time of the laser intensity are measured. Adjustments for the alignment of the mirrors and the optical source which were required for proper TDLS operations used to be major issues of observations away from laboratories. However, in recent years, these issues have been resolved for some analyzers with the application of optical measures which rely on the use of lenses. Methane analyzers are an example of such analyzers. Regarding the Fast Methane Analyzer DLT-100, (Los Gatos Research, Inc.,

US) due to its structural feature of having a lens, the volume of the analyzer cell is large (408 ml) thus more suitable for REA method compared to eddy covariance. Therefore, air samples need to be drawn in with a large vacuum pump within a short time interval. As for the methane analyzer G2311-f, (Picarro Inc., US), which is designed for the eddy covariance method, the volume of the cell of the analyzer is small, and it is able to measure H₂O and CO₂ simultaneously using another laser spectroscopy, cavity ring down spectroscopy (CRDS). Laser spectroscopy is expected to be applied in studies of uncovering CO₂ - H₂O exchange process using stable isotopes.

Chemiluminescence Analyzer

For the measurements of isoprene and ethylene, analyzers have been developed with a chemiluminescent method. During the operation of an isoprene analyzer, air is introduced into a reaction cell that is filled with gas containing a high concentration of ozone. Ultraviolet radiation (430 nm) which is emitted from the reaction of isoprene with ozone in the cell is selectively filtered and is measured by an electron multiplier. An ethylene analyzer depends on a property of ethylene that its chemical reaction with certain other substances causes long-lasting chemiluminescence. The chemiluminescent emission from chemical reactions with NO and ozone in a mixing chamber is measured. Finally, chemiluminescent methods are susceptible to the effects of substances that interfere with the chemiluminescent reactions.

Deployment

Selection of deployment location

The air inlet of an REA system should be deployed as close to the SAT as possible, however, in such a way that the air inlet does not affect the vertical wind. Furthermore, in order to minimize the time delay in measurements due to the switching of flow paths, the solenoid valves and their switching system should be placed immediately after the air inlet. Sufficiently high suction force is also necessary so that the air inflow rate at the time of suction is not affected by wind velocity fluctuations. For this purpose, a mass flow controller is used to maintain a constant flow rate. Finally, care is necessary to prevent water from entering the analyzer and to prevent water vapor from condensing inside the analyzer.

Tips!

The Campbell CR1000 is equipped with a terminal with a switch for 12 V DC output (SW12 terminal). Because the SW12 terminal can supply up to 900 mA of electric current at a temperature of 20 °C, this terminal can be used for direct control of solenoid valves. On the other hand, the digital I/O ports, C1 through C8, can output only up to 2.0 mA of electric current at 3.5 V, and thus a relay circuit is necessary for using these ports for control. An example of such a circuit is shown in Chapter 5 of the CR1000 Operator's Manual.

Tip 2.5-1