2.2 Open-path CO_2/H_2O gas analyzers

2.2.1 Measurement of fluctuating CO_2 concentration by an open-path gas analyzer

An open-path CO_2 gas analyzer measures the number of CO_2 molecules within the open path of the instrument. Because the CO_2 measurement by the instrument is based on the absorption of infrared energy by CO_2, the attenuation of infrared radiation is the basic output value from the analyzer. The output value is converted to the number of CO_2 molecules per unit volume (CO_2 number density [mol-CO_2m^{-3}]) with the use of the calibration coefficients determined by the manufacturer or the user. Therefore, the user needs to be aware that the physical variable being measured is CO_2 number density rather than the mixing ratio ([ppm] or [mol-CO_2mol-dry-air^{-1}]) which is used to label the calibration gas and also to calculate the fluxes.

The general characteristics of an open-path CO_2 gas analyzer (open-path gas analyzer hereafter) relative to a closed-path gas analyzer (Section 2.3) are as follows: 1) the response time of an open-path gas analyzer to the fluctuating CO_2 is faster; 2) an open-path gas analyzer requires less power; 3) the overall configuration, i.e., the analyzer and its peripheral components, of an open-path gas analyzer is simpler; 4) the volume of the sensor head is larger for an open-path gas analyzer. (The sensor head becomes an obstruction to measurements at the measurement height.); 5) automated calibrations of an open-path gas analyzer are difficult; 6) accurate measurements of air temperature and pressure within the open path are not easily obtained, and also the magnitude of the correction term of the so-called WPL correction (Webb *et al.*, 1980) is larger. Characteristics 1 to 3 are generally considered advantages of an open-path gas analyzer, while characteristics 4 to 6 are generally considered disadvantages.

Types of available open-path gas analyzers

Table 2.2-1 summarizes the major open-path gas analyzers that are available as commercialized products. The measurement principle of all the products is the same, that is, their measurements are based on the infrared absorption characteristics of CO_2 molecules. All the sensors listed in Table 2.2-1 are also equipped with interference filters for the infrared absorption waveband of H_2O molecules. Thus, all the sensors are able to measure the number of H_2O molecules per unit volume (mol-H_2Om^{-3}) simultaneously with that of CO_2. The details of the measurement principle and the structure of typical open-path gas analyzers are summarized in Kohsiek (2000). Kohsiek (2000) also gives the details of the cross sensitivity (see next paragraph) and a method for evaluating the cross sensitivity.

When CO_2 is measured by an open-path gas analyzer, the presence of H_2O changes the infrared absorption characteristics of CO_2 molecules. The effect of H_2O molecules on the measurement of the CO_2

number density (cross sensitivity) needs to be taken into consideration to evaluate the CO_2 number density accurately (Kohsiek, 2000). The control box of the LI-7500 (LI-COR, Inc., US) takes into account the cross-sensitivity (LI-COR, 2004), however, the E-009 (Advanet, Inc., Japan) and the OP-2 (ADC BioScientific Ltd., UK) do not adjust their measurement outputs for the cross-sensitivity. Furthermore, the indoor experiments of Leuning and King (1992) and Leuning and Judd (1996) on the cross-sensitivity of the E-009 showed that the characteristics of the cross-sensitivity of individual instruments vary according to the serial numbers even within the same model. Therefore, when the E-009 or the OP-2 is used for observations, the degree of cross-sensitivity needs to be assessed with indoor experiments such as those of Kohsiek (2000) or from the shape of the co-spectrum (Monji, 2003).

Table 2.2-1 Open-path CO_2 gas analyzers.

Model	**Manufacturer**	**Path length**	**Outside dimensions*** (diameter and length)**	**Weight***	**Output signal**
LI-7500	LI-COR	12.5 cm	6.5×30 cm	0.75 kg	0-5 V, RS-232C, SDM**
E-009***	Advanet	20 cm	11×45.5 cm	-	–5 ~ 5 V
OP-2	ADC	Multiple folded path (20 cm×4)	7.6×37 cm	1.1 kg	–5 ~ 5 V

* Outside dimension and weight are those of the sensor head

** Synchronous Device for Measurement communication protocol of Campbell

*** This product has been discontinued.

A commercially available open-path gas analyzer usually consists of a sensor head, a control box, a power supply unit and a mountable calibration tube. Furthermore, accessories such as instrument-specific software are available for some of the commercially available open-path gas analyzers. When selecting an open-path gas analyzer, the user needs to take into consideration the cable lengths because the length of the cable between the sensor head and the control box as well as the length of the cable for the output signals of the measured values are limited in some models of open-path gas analyzers. Regarding the LI-7500, the value of the time lag of the output signal and the deployment method of the analyzer vary among its product model which can be identified by the serial number. When the LI-7500 is selected for use, the user needs to be aware of its serial number in order to address these issues. (See Appendix 2.2-1 for details.)

Advanet, Inc., of Japan, was one of the first companies to commercialize open-path gas analyzers in 1985 with the E-009 series. For many years the E-009 series was very popular and used in multiple field observations. After LI-COR introduced the LI-7500 in 2000, the number of LI-7500 users gradually increased. Currently (as of 2008), the LI-7500 is becoming the world-wide *de facto* standard instrument.

Tips!

Manufacturers do not always notify users of the latest information related to open-path gas analyzers such as version upgrades of the firmware. Users are advised to visit the manufacturers' websites every 3 to 6 months to check for the latest information on the instruments.

Tips 2.2-1

Measurement method

(1) Method of deploying an open-path gas analyzer

Two factors are considered important when an open-path gas analyzer is deployed: 1) the open-path gas analyzer needs to be deployed in such a way that it does not interfere with the measurements made by the ultrasonic anemometer thermometer, SAT; and 2) the distance between the open-path gas analyzer and the SAT should be minimized in order to minimize the loss of fluxes in the high frequency range. Often, these two factors are at odds with each other. For the deployment of an open-path gas analyzer, the characteristics of the individual observation site, e.g., the prevailing wind direction and the range of expected wind directions, also need to be taken into consideration. Therefore, no standard or formulated method of deployment exits. Here, an example of a deployed open-path gas analyzer will be introduced in order to elucidate the principles of deploying an open-path gas analyzer.

Method for deploying sensor head

Photo 2.2-1 shows an open-path gas analyzer that was deployed by a research group from the National Institute for Agro-Environmental Sciences (NIAES). If the configuration of a SAT is not rotationally symmetrical, the SAT needs to be deployed with the open section (front plane) pointed into the prevailing wind direction. When an open-path gas analyzer is deployed, it should not be placed behind the SAT structure. The open-path gas analyzer should also be mounted on the side of the SAT sensors that is downwind of the prevailing wind. In other words, the mounting position of the open-path gas analyzer needs to be selected in such a way that air parcels passing the open-path gas analyzer only occasionally flow through the SAT. This goal is most easily achieved for observation sites at which the wind direction remains relatively constant.

Tips!

It is advised that an open-path gas analyzer not be mounted behind the structure of a SAT and be mounted at some distance away from and behind the "measurement paths" of the SAT. Refer to Photo2.2-1 or Figure 3 (p.5) of the operator's manual from Campbell. (Campbell, 2006)

Tips 2.2-2

Photo 2.2-1 An example of a deployed open-path sensor (LI-7500, LI-COR). (Mase paddy flux site) A SAT (DA-600, SONIC CORPORATION, Japan) can be seen behind the open-path sensor. Because the prevailing wind direction of this site is easterly to southerly, the open section of the SAT is pointed to the south at this site. With this set up, the influence of the LI-7500 on the wind velocity measurements is small even when the wind is easterly. (Easterly wind blows from the back to the front through this photo.) Occurrence frequencies of northerly (from the back side of the DA-600) and westerly (from the direction of the LI-7500) winds are low at this observation site.

Alternatively, Campbell Scientific, Inc., US recommends that an open-path gas analyzer to be mounted horizontally underneath the measurement paths of the SAT (Campbell, 2006). With this method, the influence of the open-path gas analyzer on the wind velocity measurement is small. Therefore, this method is considered effective for SAT measurements at observation sites with a large variation in wind direction. However, when the wind direction is parallel to the measurement path of the horizontally mounted open-path gas analyzer, the sensor head of the analyzer interferes with the analyzer's measurement. This measurement interference reduces the valid range of wind directions for the open-path gas analyzer, which is considered a disadvantage of the horizontal mounting of an open-path gas analyzer. Furthermore, the frequency response characteristics of the co-spectra, i.e., fluxes, from the horizontal mounting method and the methods for correcting flux losses at high frequencies are both currently limited. (Refer to Appendix 2.2-2 for flux losses at high frequencies.)

Sensor separation distance

The ideal separation distance between the open-path gas analyzer and the SAT is 15 to 20 cm, and no larger than 30 cm. The sensor separation distance needs to be at least 15 cm. Otherwise, the influence of the sensor head on the wind velocity measurement becomes large. When the sensor separation distance is larger than 30 cm, the flux losses at high frequencies become large (particularly for an ecosystem with a small canopy height such as a grass field), and the uncertainty increases for the flux loss correction.

The sensor separation distance is defined as the distance between the center of the open-path gas analyzer measurement path and that of the SAT measurement path. When the sensor separation distance is measured, in addition to the value of the sensor separation distance, the following information needs to be recorded: the north-south as well as the east-west distance [cm] between the center of the open-path gas analyzer measurement path and that of the SAT measurement path. (Alternatively, the bearing of the position of the open-path gas analyzer can be recorded with respect to the center of the SAT measurement path.) The set of information described here will be required for correcting the flux loss at high frequencies and/or quality-controlling the data. If the centers of the measurement paths are situated at different heights, this information should also be recorded. Because of limited research on the topic, our understanding is currently limited on flux loss due to the vertical separation distance between the centers of the measurement paths, e.g., the frequency response characteristics of co-spectra and the method for correcting for flux loss. However, future research may require flux loss correction and lead to appropriate methods for correcting the flux losses due to sensors installed at different heights.

When an open-path gas analyzer is calibrated, the sensor head needs to be temporarily removed from and placed back into its deployment location. Therefore, it is recommended that the sensor head is mounted in such a manner that the position of the analyzer with respect to the SAT remains unchanged before and after the calibration. The advantages of such a mounting method include that the characteristics of flux losses remain the same between pre- and post-calibration and that the measurement of the sensor separation distance does not have to be repeated.

Method for securing the sensor head and installation angle

In addition to the cautions related to the SAT as discussed above, the method for securing the sensor head and the installation angle of an open-path gas analyzer need to be considered for its installation. Because vibrations of the sensor head at certain frequencies will influence the measurements of an open-path gas analyzer (LI-COR, 2004), the open-path gas analyzer needs to be secured in such a way as to inhibit sensor head vibrations.

Tips!

The sensor head of an LI-7500 is equipped with a mounting post and a bolt for installation (LI-COR, 2004). However, the use of the mounting post and bolt is insufficient to secure the open-path gas analyzer firmly. To ensure a secure mounting, it is advisable to use additional parts such as the crossover Nu-Rail fitting as in Campbell (2006), a cross-over plate as in Photo 2.2-1 or a U-bolt.

Tips 2.2-3

The installation angle of the sensor head of an open-path gas analyzer can be classified into 4 options: 1) vertical, 2) slightly tilted (10 to 15 degrees), 3) tilted, and 4) horizontal. The author recommends “2) slightly tilted” among these options. The advantages of a slightly tilted installation angle can be summarized as follows:

1. Flow disturbance related to the measurement by the open-path gas analyzer is small. (Accurate measurements are possible for any wind direction.)

2. Rain water can run off easily. (Little rain water accumulates on the lens that is located at the end of the measurement path.)
3. The frequency response characteristics due to path-length averaging are well understood. (For the frequency response characteristics, the sensor head can be considered to be oriented vertically in an approximate sense.)
4. If an LI-7500 is used for observation and the analyzer can be assumed to be vertically oriented, the correction formula due to instrument surface heating of Burba *et al.* (2008) is applicable. (Refer to Appendix 2.2-3 for the issue of instrument surface heating.)

The disadvantages of installing an open-path gas analyzer with a slightly tilted are the following:

5. When wind flows from the open-path gas analyzer to a SAT, the SAT measurement is disturbed. (This disadvantage can be minimized if the open-path gas analyzer is installed by taking into consideration the prevailing wind direction.)
6. When an LI-7500 that was manufactured prior to the one with serial number 0282 is used, direct solar radiation influences the measurement. (Refer to Appendix 2.2-1.)

If an open-path gas analyzer is installed vertically (option 1), rain drops tend to accumulate on the lens. If an open-path gas analyzer is installed with a tilt or horizontally (options 3 and 4, respectively), the interference of the analyzer on the SAT measurement is small if the analyzer and SAT are positioned appropriately. With these installation methods, the instrument surface heating can also be reduced. However, the frequency response characteristics of both the spectra and co-spectra from a tilted or horizontal open-path gas analyzer remain unknown, and the ability to correct flux losses at high frequencies becomes limited (Appendix 2.2-4).

(2) Method for recording output signals

When output signals are analog-recorded in voltage, the output signals may be contaminated by noise, and low-pass and/or digital filters are applied to remove the noise as necessary. For recording the data output from an LI-7500, the use of the Synchronous Device for Measurement (SDM) communication protocol of Campbell is highly recommended. Unlike analog recording, recording with the SDM communication protocol avoids the issue of noise. The SDM communication protocol also allows the simultaneous recording of the operation status of the analyzer. One of the recorded variables that represents the operation status is the Automatic Gain Control (AGC). The value of AGC changes according to the presence of objects, e.g., dirt and pollen, that are adhered to the lenses and interfere with the measurements in the measurement path. The AGC data are particularly useful for quality-controlling the acquired data.

When output signals are recorded, caution must be exercised on compensating for the time lag of the signal output. After measurements are made by the sensor head of an LI-7500, they are processed in the control box. This measurement processing requires time, which causes a time lag in outputting the data. The duration of the time lag varies according to the specified output format. The product manual for the LI-7500 (LI-COR, 2004) provides the following time lags for signal output: 0.240 seconds for signal output in voltage and 0.186 seconds for sampling with SDM and RS-232C. With the LI-7500 software, the time lag can be increased in increments of 0.0065 seconds. Consider the case in which the output signal is recorded in the SDM format with a time interval of 0.1 seconds. If the time lag is increased by 17 units (0.0065 seconds × 17 = 0.1105 seconds), the total time lag of the output signal becomes 0.297 seconds (0.186 seconds + 0.1105 seconds), which corresponds to three data values (0.297 seconds / 0.1 seconds). Therefore, if the time lag of the SAT is zero, the data from the SAT and from the LI-7500 can be synchronized (almost perfectly) by shifting the time series of data from the LI-7500 forward by three values. (The remaining slight mis-synchronization, 0.3 seconds –0.297 seconds = 0.003 seconds, is considered sufficiently small to be neglected for most sites.) To summarize, when an LI-7500 is used for observation, the time lag of the signal output needs to be adjusted according to the signal output format, the time lag of the SAT, and the data recording interval so that the total mis-synchronization within the system becomes sufficiently small.

No descriptions of the time lag of the output signals are provided in the product manuals for the E-009 or the OP-2. When these open-path gas analyzers are used, the time lag should be considered equal to zero. Alternatively, cross-correlation can be used to estimate the time lag. Calculate the cross-correlation coefficient of the output signals from the SAT and those from the analyzer as a function of the time lag. The time lag at which the cross-correlation coefficient reaches the maximum value is used as the time lag of the output signals of the open-path gas analyzer with respect to the SAT. The use of the latter approach implicitly includes a partial correction of flux losses due to the sensor separation in the along-wind direction. Therefore, when this estimation approach is adopted, caution is necessary to avoid over-correcting flux losses in the course of the flux calculation.

The time lag of the output signal influences the flux calculation significantly at sites at which the contribution of the co-spectra at high frequencies to the total flux is large, e.g., grassland. The issue of the time lag of the output signal needs to be addressed especially for those sites.

(3) Maintenance

The maintenance of an open-path gas analyzer is relatively easy. During regular visits to the observation site, it is advisable to follow the instructions below:

1. Using the display panel of the sensor and/or the data recorder, make sure that the signal output is within the normal range. When the signal output is abnormal, one of the following may be the cause of the abnormal values:
    - Dirt and/or dust accumulated on the lenses located at the end of the measurement path (see instruction 2 below)
    - Loose connections of cables or signal wires
    - Trouble with the power and voltage supplies
    - Blown fuse
    - Abnormality in the environment surrounding the control box (e.g., high temperature or water intrusion)

- Broken cables or signal wires
- Deterioration of desiccant or other chemicals (if they are in use)

In addition to the possible causes above, if an LI-7500 is used for the measurement, the sensor diagnosis information should also be checked. (When SDM is used, check “Diagnostic value”. The diagnosis information can also be checked by connecting the sensor to a PC with the designated software.)

2. Clean the lenses (remove dirt and/or dust accumulated on the lenses) on the measurement paths with water and Kimwipes (Kimberly-Clark Corporation, US) or other cleaning tissues. Even when the lenses look clean, accumulated fine dirt or dust particles may be influencing the measurement. Regardless of whether dirt or dust is apparent on the lenses, it is advisable to clean the lenses regularly at a rate of once every 10days to once a month. (Refer to Appendix 2.2-5 for the effect on the measurement of dirt or dust on the lenses.) Finally, application of water repellent such as Rain-X (Pennzoil-Quaker State Company, US) on the lenses is recommended.

(4) Measurement of the absolute magnitude of CO_2 number density

The absolute magnitude of CO_2 number density (time-averaged value) is required to calculate CO_2 fluxes from the data acquired by an open-path gas analyzer. An open-path gas analyzer can measure the absolute magnitude of CO_2 number density. However, because the measurement path of an open-path gas analyzer is exposed to the atmosphere, the lenses located at the end of the measurement path can easily accumulate dirt and dust. The dirt or dust accumulated on the lenses influences the measurement of the absolute magnitude of CO_2 number density. (See Appendix 2.2-5 for reference.) Thus, if possible, it is desirable to measure the absolute magnitude of CO_2 number density (or CO_2 mixing ratio) with a closed-path analyzer. Because the measurement with a closed-path analyzer is intended for the evaluation of the time-averaged values of the absolute magnitude of CO_2 number density, an analyzer with a relatively slow response time can be used. However, make sure to select an analyzer that can provide reliable values of the absolute magnitude of CO_2 number density. If the use of a closed-path analyzer is not feasible, the use of a humidity sensor such as the HMP45 manufactured by Vaisala, Oyj., Finland can be used instead as proposed by Serrano-Ortiz *et al*. (2008). In this method, the time-averaged values of the atmospheric water vapor content obtained from the humidity sensor are compared to those obtained from the open-path gas analyzer. From this comparison, the amount of dust and dirt on the lenses is estimated, and the offset in the absolute magnitude of CO_2 number density measured by the open-path gas analyzer can be corrected.

Calibration

As discussed in the beginning of this section, the variable measured by an open-path gas analyzer is CO_2 number density [mol-$CO_2$$m^{-3}$]. On the other hand, the unit of mixing ratio [ppm] is usually used to label the cylinder that contains the CO_2 gas used for calibration. (Refer to Appendix 2.2-6.) Therefore, in order to calibrate an open-path gas analyzer, the mixing ratio of CO_2 in the calibration cylinder needs to be first converted into units of CO_2 number density with the use of the temperature and pressure within the sample cell. The obtained value of the CO_2 number density is compared to the output value from the open-path gas analyzer to determine the offset value and sensitivity of the analyzer. The calibration tube for the LI-7500, which is an accessory for the LI-7500, is equipped with a thermistor, thus the above-mentioned unit conversion for the CO_2 gas in the cylinder can be easily made using the data from the pressure meter inside the control box. (If a separate pressure meter is available, the measurement of the pressure inside the calibration tube can also be made.) If an E-009 or OP-2 is used for observation, a temperature sensor can be attached inside the calibration tube. (Alternatively, the temperature sensor can also be attached to the outside wall of the calibration tube.) The temperature measured by the temperature sensor and the pressure near the calibration tube (or a constant pressure value, e.g., 101.3 kPa) are used for the unit conversion for the concentration of the CO_2 gas in the cylinder.

Frequency of calibration is an important factor to consider. The CO_2 flux observational group of NIAES has extensive experience in using the open-path gas analyzers listed in Table 2.2-1. When all factors are considered together along with the knowledge acquired from experience, the CO_2 flux observational group recommends the following frequencies for calibration: once every month to three months for the E-009 and the OP-2; once or twice a year for the LI-7500. The change in the calibration coefficients with time for each of the three analyzers is provided in Ono *et al*. (2003) and Ono *et al*. (2007). When the user has become familiar with the calibration procedure of an open-path gas analyzer, only 5 to 6 hours are necessary to complete the entire calibration procedure including the warming-up time for the analyzer prior to calibration. In this case, the open-path gas analyzer can be taken back to the laboratory in the evening for calibration. After completing calibration during the night, the analyzer can be brought back to the observational site for re-installation the next morning. In contrast, if the user is not yet familiar with the calibration procedure, multiple attempts may be necessary to carry out the entire procedure and calibration may take up to 1 to 2 days. During the calibration period, no data can be collected in the field. Therefore, the timing of calibration should be planned in advance in order to avoid time periods during which flux data are necessary.

Cleaning of the lenses located at the end of the measurement path is at least as important as the frequency of calibration. (Refer to “Measurement Method (3) Maintenance” and Appendix 2.2-5.) The offset due to dirt or dust accumulated on the lenses is generally larger than the changes in offset and calibration coefficients of the individual analyzer, particularly for the LI-7500, thus the lenses of the analyzer need to be cleaned periodically.

Here, (1) the equipment necessary for calibration and (2) the procedure for calibration will be discussed. The discussions will assume the use of an LI-7500 and will include calibration for H_2O. Subsequently, (3) calibration of an E-009 and an OP-2 will be discussed. In this section, the sensitivity is defined as the ratio of the change in the indicated quantity (output value) to the change in the measured quantity (the value of the mixing ratio of CO_2 in the calibration cylinder). The units of sensitivity are non-dimensional or $V(\text{mol-}CO_2 m^{-3})^{-1}$. In addition, the offset is defined as the value (output value) indicated at the time of zero-gas supply. The units of offset are ppm, $\text{mol-}CO_2 m^{-3}$ or volts.

(1) Equipment required for calibration

Standard gas for calibration

For calibration, three cylinders with the following concentrations of CO_2 are required: 0 ppm, i.e., zero-CO_2 gas, approximately 300 ~ 350 ppm, and approximately 500 ~ 700 ppm. (Cylinders with more than 3 different CO_2 concentrations can also be used. In this case, make sure to include cylinders with at least the following 2 different CO_2 concentrations: 0 ppm and approximately 500 ~ 700 ppm or 400 ~ 500 ppm for studies in forests.) The concentration of H_2O in the standard gas is usually zero, thus the above-mentioned cylinders with the standard gas for CO_2 can also be used as zero-H_2O gas. As for the balance gas, the use of an air balance is recommended over the use of pure nitrogen.

Tips!

CO_2 standard gas is a gas that has been certified for a specific concentration. All other gases besides CO_2 are called balance gases. Common balance gases include nitrogen (N_2 balance) and air (air balance). For CO_2 concentration measurements in the atmosphere, it is advisable to use a CO_2 standard gas in which air is used as the balance gas. This choice is recommended because the absorption characteristics of infrared radiation by the gas mixture vary according to the balance gas.

Tips 2.2-4

Zero-CO_2 and zero-H_2O gases can also be produced with chemical scrubbers. A number of chemical scrubbers are considered appropriate for producing zero gases, and their characteristics are summarized in LI-COR (2003). LI-COR (2003) recommends a combination of soda lime and magnesium perchlorate for removing CO_2 and H_2O from the air to produce zero gases. (The air needs to pass through the chemicals in the correct order: the soda lime first and subsequently the magnesium perchlorate.)

Pressure regulator

It is recommended to use a pressure regulator with two adjustment screws that can adjust the gas pressure from the cylinder to approximately 0.1 MPa (= 1.1 $\mathrm{kgfcm^{-2}}$ or 15 psi). Prepare tube fittings appropriate for the tubing to be used for calibration.

Tubing

Tubing that is made of fluoroethylene resin such as Teflon and is either 6 mm or 1/4 inch in the outer diameter is frequently used for calibration. Choose appropriate tube lengths to facilitate ease of use. Minimize the length of the tubing for H_2O calibration to avoid condensation inside the tubing.

Flow meter

Select a flow meter that can measure a flow rate of approximately 1 $\mathrm{Lmin^{-1}}$ and allows flow rate adjustment at an increment of approximately 0.1 $\mathrm{Lmin^{-1}}$. A float-type flow meter is frequently used for calibration.

Dew-point generator

A dew-point generator is usually used for H_2O calibration. In the field of research flux observations, the LI-610 portable dew-point generator manufactured by LI-COR is used as the *de facto* standard dew-point generator. The LI-610 is already equipped with a floating-ball flow meter; therefore connect the LI-610 directly to the calibration tube with a length of tubing. (It is better to avoid including a flow meter between the LI-610 and the calibration tube as the inclusion of a flow meter increases the likelihood of condensation or leakage within the system.)

Other equipment

Other equipment required for calibration includes the following: the calibration tube for the LI-7500; a PC running the software for the LI-7500 analyzer, LI7500.exe (hereafter referred to as “LI-7500 software”); and a serial cable to connect the control box to the PC. When the pressure inside the calibration tube is measured, a barometer will also be required. (For this measurement, a regular barometer used for meteorological observations such as the PTB210 manufactured by Vaisala is sufficient.)

(2) Calibration procedure

The procedure for calibrating an LI-7500 that has been in operation at an observational site is explained below. Based on the purpose of individual stages of calibration, the entire calibration procedure can be roughly classified into 3 steps, which will be referred as Step 1, Step 2, and Step 3. In this subsection, precautions regarding the preparation and the entire procedure for calibration will be discussed first. Subsequently, the work sequence within each step will be explained.

Preparations and important reminders for the calibration procedure

1. If the equipment necessary for calibration can be taken out to the observational site, calibration can potentially be conducted outdoors. However, outdoor calibration is subject to changes in the external environment during the calibration and other uncertain factors that influence the calibration results. Therefore, the user is advised not to calibrate the LI-7500 outdoors and to calibrate it indoors instead by removing the sensor head and control box from the observation stand.
2. Make sure that there is no leakage at the tubing junctions when connecting the tubing to the calibration equipment. When zero-CO_2 gas is flowing through the sensor head and tubing junctions, breath on these parts to ensure there is no leakage. i.e., ensure that the CO_2 output does not change.
3. Check the AGC output on the PC when the calibration tube is not mounted on the analyzer. Subsequently, place the calibration tube on the analyzer and make sure that the value of AGC does not change. (If the mounting position of the calibration tube is inappropriate, the value of AGC will increase.) The value of AGC also needs to be checked immediately after the initiation and before the cessation of calibration gas supply to ensure that the calibration tube is not misaligned. While H_2O gas

is supplied, despite an appropriate mounting of the calibration tube, the value of AGC can increase by approximately 10 compared to the value of AGC without the calibration tube.

4. The flow rate of the calibration gas should be set to 0.5 ~ 1.0 Lmin^{-1}. Adjust the flow rate after the initiation of the calibration gas supply. Also make sure to check the flow rate before shutting off the calibration gas supply.
5. The CO_2 reading should stabilize in less than 5 to 10minutes after the initiation of the calibration gas supply. In the case of H_2O, 10 to 30 minutes (or sometimes longer) are required for the reading to stabilize after the calibration gas supply has been initiated. The stabilization of the H_2O reading frequently requires some time especially when zero-H_2O gas is supplied subsequent to supplying calibration gas that contains H_2O.
6. For analysis, use the data that are acquired in the last 1 to 3 minutes of the calibration gas supply and during which the output value is stable.
7. In the course of H_2O calibration, make sure that the dew-point temperature is always at least 3 to 5 °C lower than the ambient air temperature. This dew-point temperature setting is necessary to avoid condensation inside the tubing.
8. Occasionally, the output of the LI-7500 suddenly changes by a few ppm after the passage of some time (approximately 5 min to 1 hour) following the initiation of calibration gas supply. The change in the output of the LI-7500 is accompanied by a change in the cooler voltage of the LI-7500. During calibration (particularly in Step 2), closely monitor the output displayed on the PC to make sure that no sudden change occurs in the output.
9. The sensor head of the LI-7500 analyzer is internally equipped with two plastic bottles, containing soda lime and magnesium perchlorate that keep the detector free of CO_2 and H_2O. The product manual (LI-COR, 2004) recommends that the bottles be recharged with fresh chemicals once a year. After recharging, the analyzer needs to be operated for at least 4 hours in warm-up mode. It has been the experience of the CO_2 flux observational group of NIAES that the chemicals degrade at a slow rate and replacing the chemicals once every 2 to 3 years is sufficient. The group has also found that the analyzer needs to be operated in warm-up mode for 1 to 3 days to achieve a stable zero output after exchanging the chemicals.
10. After the completion of calibration, apply water repellant (e.g., Rain-X) on the lenses located at the ends of the measurement path to prevent adhesion of rain drops.

The individual steps of calibration

Step 1

The objective of Step 1 is to check the sensitivity and offset of the LI-7500 as it was operated at the observational site. The calibration gases required for Step 1 are zero gas and one or more concentrations of span gas for both CO_2 and H_2O.

Supply calibration gas to the open-path gas analyzer and check the sensor output. This procedure is performed on the analyzer while its condition is left the same as it was at the observational site, that is, before any cleaning is performed on the lenses located at the ends of the measurement path. To avoid removing the accumulated dirt and dust from the lenses, supply the CO_2 gas first and then the H_2O gas. This procedure determines the sensitivity and offset of the LI-7500 in its condition from the observational site as well as the degree of dirt and dust accumulation on the lenses. While the sensitivity drift of the analyzer is usually less than 1 ~ 3 %, thus small, the offset of the instrument can be as large as approximately 10 ppm.

Subsequently, clean the lenses with water and Kimwipes. When the lenses are completely dry, supply the calibration gas again and check the sensor output. At this time, either CO_2 or H_2O gas can be supplied first. This procedure determines changes in the sensitivity and offset of the LI-7500 itself. These changes are small under usual circumstances (sensitivity drift: less than 1 ~ 3 %; offset change: a few ppm).

Step 2

The goal of Step 2 is to modify the calibration coefficients stored in the control box of the LI-7500. This procedure is identical to the calibration procedure discussed in Section 4 “Calibration” of the product manual (LI-COR, 2004).

Because Step 2 modifies the calibration coefficients Z and S that are stored in the control box, both before and after Step 2, make sure to record the old and new values of these two coefficients either in a field notebook or on a PC in case these values are needed in the future. After recording the old values of the coefficients, supply zero-H_2O and CO_2 gases to the calibration tube. When the output stabilizes, perform zero adjustments on the H_2O and CO_2 channels with the use of the LI-7500 software. The zero adjustments are performed for H_2O first and then for CO_2. Next, a span adjustment is performed on the H_2O channel. For this adjustment, provide H_2O gas to the calibration tube from the dew-point generator. (The dew-point temperature setting should be 3 to 5 °C lower than the ambient air temperature.) When the output reaches a steady value, span the H_2O sensor using the LI-7500 software controls. Finally, the CO_2 sensor is spanned. Supply CO_2 gas of high concentration (500 ~ 700 ppm for analyzers used over farmland and grassland and 400 ~ 500 ppm for analyzers used over forests) to the calibration tube. When the output is stabilized, span the CO_2 sensor with the LI-7500 software controls.

In Step 2, zero calibration needs to be performed prior to span calibration. Because the presence of H_2O influences the CO_2 output, H_2O calibration should be performed prior to CO_2 calibration as a precaution. (The gas used for CO_2 calibration contains no H_2O, thus the order of calibration should not influence the calibration results in principle. However, a large offset may exist in the H_2O channel, thus it is recommended that calibration of the H_2O channel be performed first.)

Step 3

Step 3 consists of two sub-objectives: 1) checking the calibration coefficients stored in the control box that were modified in Step 2 (that is to check if Step 2 is finished successfully or not); and 2) performing a set of calibrations to be used as a reference in Step 1 of the next round of calibration in the future.

In Step 3, as in Step 1, the CO_2 and H_2O outputs are checked after supplying zero gas and more than one kind of appropriate span gas to the calibration tube of the LI-7500. If the calibration in Step 2 has been carried out properly, the difference between the stated value of the concentration of the calibration gas and the output of the LI-7500 will be small. (For CO_2, the difference should be smaller than 1 ppm; for H_2O, the difference in dew-point temperature should be less than 0.2 ~ 0.3 °C.)

When the calibration gas used in Step 2 is re-used in Step 3, the difference between the stated value of the concentration of the calibration gas and the output of the LI-7500 is expected to be small. However, when a calibration gas other than that used in Step 2 is used in Step 3, the difference between the stated value of the concentration of the calibration gas and the output of the LI-7500 will sometimes be large. For example, consider the case in which a calibration gas of 700 ppm is supplied in Step 2 and a calibration gas of 350 ppm is supplied in Step 3. In this case, the difference between the concentration of the calibration gas and the output of the LI-7500 can sometimes become as large as 1 ppm.

When the difference between the concentration of the supplied calibration gas and the output of the LI-7500 becomes large (as a rough guide, more than 2 ~ 4 ppm for CO_2 and more than 0.2 ~ 0.5 °C in dew-point temperature for H_2O), repeat Step 2 and Step 3.

(3) Calibration of the E-009 and OP-2

In principle, the E-009 and OP-2 do not require modification of the calibration coefficients stored in the analyzers. (While the gain of both open-path gas analyzers can be adjusted in the control box, the analyzers are usually used without adjusting the gain.) Accordingly, only the calibration procedure equivalent to Step 1 for the LI-7500 needs to be performed regularly to determine the sensitivity and offset of the analyzer. The preparations and important reminders for the calibration procedure and the procedure outlined in Step 1 for the LI-7500 are all applicable for the E-009 and the OP-2. However, the following cautions are also important.

Although calibration tubes are available as accessories for both open-path gas analyzers, the calibration tubes are not equipped to measure temperature or pressure for converting the units of the calibration gas concentration, unlike the LI-7500. Therefore, a thermocouple or a thermistor needs to be used to measure the temperature inside the calibration tube (or the temperature of the wall of the calibration tube). As for the pressure, measured values near the calibration tube are desirable, however, the use of a constant such as 101.3 kPa is acceptable as an approximation. Both open-path gas analyzers undergo changes in their sensitivities in environments with extremely low air temperatures (Miyata and Mano, 2002). When the open-path gas analyzers are used outside the temperature range stated in the product manual, the sensitivity and the temperature-dependency of the offset needs to be investigated prior to usage. (This caution is also applicable to the LI-7500.)

The product manual of the E-009 (Advanet, 1996) calls for a flow rate of about $5\mathrm{Lmin}^{-1}$ for the calibration gas.

The OP-2 is equipped with a temperature sensor inside the sensor head. Temperature data can be output from the sensor, however, these data are intended to calibrate the drift of the CO_2 and H_2O outputs. Thus, it is advisable to avoid using these data as approximations of the temperature inside the calibration tube. (Use a separate temperature sensor instead to evaluate the temperature inside the calibration tube.) The product manual for the OP-2 (ADC, 2003) calls for at least 3-point calibration for H_2O as the H_2O output is expressed in a quadratic expression.

Finally, application of the calibration results to the observational data is considered. Over a period of observation, the sensitivity and offset of an open-path gas analyzer sometimes change significantly. In this case, the method of application of the calibration results to the observational data needs to be considered.

Because the change in the sensitivity of the analyzer influences the flux (co-variance) calculation, the sensitivity change cannot be taken lightly. If CO_2 number density (mixing ratio) data have been simultaneously collected with a closed-path analyzer, the time-averaged values of these data can be compared to those of the CO_2 number density from the open-path gas analyzer. The result of the comparison can sometimes be used to evaluate the temporal change in sensitivity. If no CO_2 number density (mixing ratio) data are available from a closed-path analyzer (or an evaluation of the temporal change in sensitivity was not possible from the comparison), choose either of the following methods: 1) apply the new value of the sensitivity since a particular date chosen by the investigator; and 2) adjust the data using a mathematical operation that is based on the initial and final values of sensitivity over the period under consideration. (See below.) In the former method, if an incidence such as a power outage occurred that would change the sensitivity of the analyzer, the investigator should consider adjusting only the data collected after the incidence. If no such incidence occurred, adjust the data collected after the most recent calibration or after the mid-date between the previous and present calibrations. In the latter method, two further options can be considered. In the first option, the average of the two values of sensitivity is used to adjust the collected data. In the second option, the value of sensitivity can be calculated by distributing the difference between the two values of sensitivity in proportion to the time elapsed (number of days) between the latest calibration and the one before. However, there is no obvious solution for adjusting the collected data if no information on the change of sensitivity with time is available. Determine the sensitivity to be applied for data adjustment by taking the magnitude of sensitivity change and the length of the observational period into consideration.

Changes in the offset value have no impact on the calculation of co-variance, therefore, as long as CO_2 number density (mixing ratio) has been measured additionally by a closed-path analyzer, the flux calculation will not be influenced by the change in the offset values. If no closed-path CO_2 analyzer data are available, compare the H_2O output by the open-path gas analyzer to the water vapor content measured by a separate humidity sensor. From this comparison, the temporal change in the offset value of the CO_2 data can sometimes be evaluated. (Refer to "Measurement method (4) Measurement of the absolute magnitude of CO_2 number density" or Appendix 2.2-5.) If none of the above-mentioned methods can be used, follow a procedure similar to that for adjusting data for the change in sensitivity of the open-path gas analyzer.

Tips!

If the calibration results (sensitivity and offset) change significantly over a specific observational period, calculate the flux values with both sets of calibration results to evaluate the difference in the flux values caused by the difference in calibration results. It is also advisable to plot the relationship between the calculated flux values and a meteorological factor (e.g., the relationship between solar radiation and CO_2 flux). This plot sometimes reveals a change in both the flux values and the meteorological factor after a particular time, which helps the investigator determine the time period in which the changes in the sensitivity and offset values occurred.

Tips 2.2-5

2.2.2 Measurement of fluctuating H_2O concentration by an open-path gas analyzer

The measurement of water vapor (H_2O) by an open-path gas analyzer relies on the infrared absorption characteristics of H_2O molecules for the measurement principle. One advantage of the use of this measurement principle is that it allows a simultaneous measurement of CO_2 with an interference filter that transmits radiation with particular frequencies. Accordingly, open-path H_2O/CO_2 infrared gas analyzers (referred to as an "open-path IRGA" hereafter) are currently (as of 2008) the most commonly used analyzers in the field of research flux observations. Other factors that make open-path IRGAs the number one choice for H_2O flux (i.e., latent heat flux) observations are their widespread availability and the abundance of information on using them for measurements and flux calculations.

In addition to open-path IRGAs, open-path ultraviolet gas analyzers are also open-path H_2O gas analyzers. The measurement principle of open-path ultraviolet gas analyzers is based on the ultraviolet absorption characteristics of H_2O molecules. Thermocouples are also sometimes used for measuring H_2O although they are not strictly open-path gas analyzers. However, the use of these non-IRGA instruments is not widespread, and some aspects of these instruments are not well-suited for long-term continuous observation. Except for cases with special research objectives and needs that call for the use of non-IRGA instruments, an open-path IRGA is recommended for constructing a new observation system.

Types of available analyzers

Open-path gas analyzers are the collective term for gas analyzers for which the measurement sections for the sample gas are exposed (open) to the atmosphere. Ordinarily, as the measurement principle, open-path gas analyzers utilize the absorption characteristics of particular wavelengths of radiation by gaseous molecules (e.g., H_2O and CO_2). Specifically, the infrared source situated at the end of the measurement path emits a well-defined amount of infrared radiation to a detector that is situated at the other end of the measurement path. The infrared radiation measured by the detector provides a measurement of the attenuation of the infrared radiation over the measurement path (between the infrared source and the detector). This measurement is then used to calculate the number density of gaseous molecules in the measurement path. In general, the response time of open-path gas analyzers is shorter than that of closed-path gas analyzers. Open-path gas analyzers are able to sample data at rates as high as 10 to 20 Hz, allowing accurate measurements of the fluctuating number density of gaseous molecules. However, because the measurement path is exposed to the atmosphere, the infrared source and detector of an open-path gas analyzer are subject to influences from the ambient environment. Therefore, open-path gas analyzers are not well-suited for stable and accurate measurements of the absolute magnitude of the number density of gaseous molecules.

Open-path gas analyzers for H_2O measurements can be classified into open-path IRGA and open-path ultraviolet gas analyzers according to the wavelengths of radiation used. As described in the beginning of this section, open-path IRGA are able to measure H_2O and CO_2 simultaneously and are the main gas analyzers used for flux observations at the present time. Unless there exist specific reasons for choosing ultraviolet gas analyzers, the use of open-path IRGAs recommended for H_2O flux observations. H_2O flux measurements are also possible with thermocouples. Though it is not strictly open-path gas analyzer, the methodology that involves the use of thermocouples will be introduced briefly in this section. The characteristics of each type of sensor are summarized below.

(1) Infrared gas analyzers

Refer to the section on CO_2 measurement (Section 2.2.1 "Measurement of fluctuating CO_2 concentration by an open-path gas analyzer") for the methods of deployment, maintenance, and calibration as well as for the characteristics of open-path IRGAs. Information on commercially available open-path IRGAs can also be found in the same section.

(2) Ultraviolet gas analyzers

The measurements of open-path ultraviolet gas analyzers are based on the ultraviolet absorption characteristics of H_2O. According to the particular wavelengths of ultraviolet radiation (Lyman-alpha radiation) or the radiation source (Krypton tube) that is used for these analyzers, open-path ultraviolet gas analyzers are also called Lyman-alpha hygrometers or Krypton hygrometers. H_2O molecules absorb ultraviolet radiation more readily than infrared radiation. Therefore, the path length of an open-path ultraviolet gas analyzer can be shortened to a few cm, and the spatially-smoothed values of H_2O measured by an open-path ultraviolet gas analyzer are higher in resolution than those measured by an open-path IRGA. (The path length of the KH20 manufactured by Campbell (see next paragraph) is about 1 cm, which is one tenth to one twentieth of the path length of an open-path IRGA.) Some research requires the use of a short measurement path length, for example, for evaluating the turbulence transport and dissipation rate within a plant canopy. In this case, an open-path ultraviolet gas analyzer is frequently chosen for use. The disadvantages of open-path ultraviolet gas analyzers include the short lifetime of the radiation source and the large temporal variation of the calibration coefficients that are required for converting the ultraviolet attenuation into H_2O number density. Accordingly, open-path ultraviolet gas analyzers cannot be operated over a long time period (on the order of years) without investing a significant amount of labor. Finally, when H_2O measurements are made by open-path ultraviolet gas analyzers, corrections are required for the cross-sensitivity of H_2O and O_2 on the measurements. Details of the required corrections are discussed in van Dijk *et al.* (2003).

As of now, the KH20 manufactured by Campbell is one of the open-path ultraviolet gas analyzers that are available for purchase. The price of the instrument is about 1.1 to 1.2 million yen (available through TAIYO KEIKI Co., Ltd., Japan as of November, 2008), less expensive than the open-path IRGAs that are discussed in Section 2.2.1 “Measurement of fluctuating CO_2 concentration by an open-path gas analyzer”. Therefore, the KH20 is an appropriate choice when a system needs to be constructed only for H_2O flux observations with a relatively low budget. The use of a KH20 is also appropriate for research which requires a short measurement path length as mentioned earlier. (However, the reader is reminded that a KH20 is not well-suited for long term continuous measurements.)

Refer to Section 2.2.1 for the deployment method of an ultraviolet open-path gas analyzer as it is the same as that for an open-path IRGA. For the calibration method and maintenance of ultraviolet open-path gas analyzers, refer to the product manuals.

(3) Thermocouples

Unlike open-path gas analyzers, thermocouples can be used to directly measure H_2O in the atmosphere by the sensing element of the instrument itself. There are two methods for measuring H_2O with thermocouples. One method uses a thermocouple psychrometer, and the other method uses the combination of a SAT and a thermocouple.

Measuring H_2O with a thermocouple psychrometer

A pair of dry-bulb and wet-bulb thermocouples, i.e., a thermocouple psychrometer, can be constructed with fine wires 50 ~ 100 μm in diameter (fine-wire thermocouples) to measure the air temperature. The difference in air temperature measured by the pair of thermocouples is used to evaluate H_2O concentration. A number of combinations of metals can be used to construct thermocouples. They include the combinations of copper-constantan, chromel-constantan, and chromel-alumel. Although construction of high-quality finished thermocouples may be difficult at first, thermocouples can be constructed in-house and at low cost by users. For methods of constructing thermocouples, refer to Section 3.3 “Air temperature”, 森林立地調査法 (*Handbook of forest environmental survey - environmental measurement in forest-*, 1999 [in Japanese]), and 農業気象の測器と測定法 (*Instruments and measurement techniques in agricultural meteorology*, 1988 [in Japanese]). Other advantages of the use of a thermocouple psychrometer include the following: 1) the temperature measurement is highly accurate; 2) the measured value is not subject to the effect of line averaging because of the small sensing elements of the thermocouple psychrometer; and 3) a thermocouple psychrometer has little influence on the wind velocity measurement of a SAT. On the other hand, the following are disadvantages of the use of thermocouple psychrometers: 1) thermocouple psychrometers are not well-suited for long-term observations because of the significant effort required for maintenance; and 2) corrections are required on the measurements by the dry-bulb and wet-bulb thermocouples due to the difference in the response characteristics between the two types of thermocouples (Tsukamoto, 1986). Therefore, the use of thermocouple psychrometers is appropriate when an observational system is constructed for a short-term measurement at low cost.

Measuring H_2O with a thermocouple and a SAT

As discussed in Section 2.1 “Ultrasonic anemometer thermometers (SATs)”, the temperature measured by a SAT is the sonic virtual temperature that includes the influence of H_2O in the atmosphere. Therefore, if the air temperature is measured by another instrument, the concentration of H_2O in the atmosphere can be calculated from the difference between the sonic virtual temperature and the measured air temperature. The air temperature can be measured by tungsten resistance wires, platinum wires, or thermistors as well as 25 ~ 50 μm diameter thermocouples. In theory, as long as the sonic virtual and actual air temperatures are measured with high accuracy, H_2O fluxes can also be measured accurately. The present method has been adopted for short-term observational studies (e.g., Hanafusa *et al*., 2005). However, no long-term observational study (of more than a few months) based on this method has been reported in the literature. In some cases, H_2O fluxes estimated from the difference between the sonic virtual and actual air temperatures differ from those estimated from other methods (e.g., Gunji *et al*., 2008; Matsuoka and Hayashi, 2008). The combined use of a SAT and a thermocouple or another temperature sensor for the estimation of H_2O fluxes is currently under investigation and development. Thus, the present method cannot be recommended as a method for H_2O flux measurements at the present time (as of 2008).

2.2.3 Recent progress in addressing the effect of surface heating of open-path analyzers as of 2011

Both the knowledge and technology of open-path analyzers have progressed remarkably. Three years have passed since this chapter was initially prepared in 2008. In the meantime, three new models of analyzers that have overcome measurement difficulties, specifically the effect of instrument surface heating on the CO_2 flux measurement, have been brought to market and are available for purchase today (2011). In this newly added subsection, the recent progress in addressing the effect of the surface heating of an open-path analyzer will be briefly described, and the three new models together with their individual characteristics will be introduced.

As discussed in Appendix 2.2-3, the effect of surface heating of an open-path analyzer is an issue in which the open-path analyzer becomes a heat source, creating errors in the CO_2 flux measurements due to errors in the estimate of the sensible heat flux. Specifically, the effect of instrument surface heating causes the sensible heat flux measured within the measurement path of the open-path analyzer, H_{op} [Wm^{-2}], to deviate from that measured by a SAT, H [Wm^{-2}]. The presence of this deviation ($\Delta H = |H - H_{op}|$) is becoming commonly recognized in the field of flux observation (refer to Appendix 2.2-7) as a result of past research findings including: 1) downward CO_2 flux observed by open-path analyzers even during periods with no photosynthetic activity (Harazono *et al*., 2000); 2) results based on comparisons of CO_2 fluxes observed by open-path analyzers to those observed by closed-path analyzers (H does not have to be taken into consideration) (e.g., Hirata *et al*., 2005); and 3) findings from measurements of air temperature fluctuations within the measurement paths of open-path analyzers (e.g., Grelle and Burba, 2007; Ono *et al*., 2008). An equation based on an instrument surface heat balance analysis has been proposed to evaluate ΔH, that is, as a correction method, although it is limited to a specific open-path analyzer (LI-7500) (Burba *et al*., 2008; Heusinkveld *et al*., 2008). The correction method proposed by Burba *et al*. (2008) is intended to be versatile so that it can be easily applied to previously-acquired data as well as newly-acquired data. However, the equations used in this method were derived for vertically deployed open-path analyzers, and there remain some uncertainties arising from some of the simplifying assumptions. While the correction method proposed by Heusinkveld *et al*. (2008) requires iterative calculations, it takes into account the latent heat term which evaluates the amount of water condensed on the lenses at the ends of the measurement path, the difference between the temperature of the measurement path of the SAT and that of the open-path analyzer, and other factors. This method is applicable for open-path analyzers that are deployed either horizontally or vertically. (However, the method is not applicable to analyzers which are deployed with a tilt, a commonly adopted deployment style for flux observations.) In the session titled "Barriers in Flux Measurements" at AsiaFlux Workshop 2009, discussions were held on the effect of instrument surface heating with Dr. Burba, one of the investigators who have proposed a correction method for this effect. In this session, it was brought up that the correction term may underestimate the necessary correction in a low-temperature environment (a brief summary of the content of the discussion is reported in Ohkubo *et al*., 2009). In the Workshop, a simulation study was presented, indicating that the correction term of Burba *et al*. (2008) overestimates the necessary correction in high wind speed conditions (Ono *et al*., 2009). Currently, there is no agreement on the method for evaluating ΔH. Amiro (2010), for example, calculated the cumulative CO_2 flux for two cases, that is, using the correction term as is and using the correction term reduced by 50 %, and compared the two values. Furthermore, the effect of instrument surface heating, that is, the difference between the air temperature within the measurement path of an open-path analyzer and the actual air temperature becomes large in a low temperature environment. (Burba *et al*. (2005) showed that the temperature difference can become 4 °C or 10 ~ 12 °C at an air temperature of –10 °C.) Therefore, in practice, the correction method of Burba *et al*. (2008) is applied only to data colleted at air temperatures below 0 °C (or below –10 °C), or alternatively, missing values are assigned to these data (Mkhabela *et al*., 2009; Amiro, 2010). As discussed above, it has become commonly acknowledged that conventional measurements with open-path analyzers are subject to the effect of instrument surface heating, however, this issue is being handled on a trial and error basis as of today (2011).

In parallel with the efforts to clarify the effect of instrument surface heating by researchers, efforts have been made by manufacturers to address the effect by improving existing open-path analyzers. In order to address the effect of instrument surface heating (non-zero ΔH), the following three measures are considered effective, and three new models were brought to market in 2010 based on the second and third measures.

The first measure, instead of aiming to minimize or eliminate ΔH, calculates CO_2 flux from the directly measured value of H_{op} rather than the value of H. Grelle and Burba (2007) placed a fine-wire thermometer of 0.1 mm diameter (fine-wire Platinum Resistance Thermometer) on one of the support rods of the measurement path of an LI-7500 in order to measure the air temperature fluctuations within the measurement path. The CO_2 flux calculated with the sensible heat flux from this thermometer (H_{op}) agrees well with that evaluated from a closed-path analyzer (LI-6262, LI-COR), suggesting that this measure is effective for addressing the effect of instrument surface heating. This measure, which utilizes a fine-wire thermometer (or a thermocouple), is applicable for other conventional open-path analyzers in addition to the LI-7500. Furthermore, the thermometer can be installed by an investigator, and the system can be constructed at a relatively low cost. However, this measure is not well-suited for stable continuous observations extending over a long period as, being made of fine-wires, the sensing element of the thermometer deteriorates with age and is easily damaged by high speed winds and rainfall. Such disadvantages of this measure are probably among the reasons that no analyzer models based on this measure are commercially available at the present time.

The second measure is based on the notion of minimizing ΔH as much as possible. ΔH is generated as a result of the open-path analyzer being a heat source, which is attributable mainly to heat generation from the interior of the analyzer; or; longwave or shortwave radiation striking the analyzer, or both. While heating by the former cause can be reduced by cutting down the power consumed by the analyzer, heating by the latter cause (radiation) can be reduced by adjusting the analyzer configuration (specifically, for example, by cutting down the area that receives radiation). With this in mind, LI-COR has produced the LI-7500A as a successor to the LI-7500. The LI-7500A is equipped with an internal temperature setting function, allowing the temperature to be set either at 5 °C or 30 °C according to the air temperature (LI-COR, 2011a). By adjusting the temperature setting appropriately for summer, winter, and other seasons, the analyzer can be operated with a power consumption of 12 W in the normal air temperature range (–20 to 40 °C). (The analyzer can also be operated at a minimum power consumption of 8 W, depending on the conditions. For details, contact the distributors.) Campbell has developed an open-path analyzer, the EC150, which can be used together with the CSAT3, the SAT available from the same corporation. Operation of the EC150 requires low power consumption (4.1 W at a temperature of 25 °C). The analyzer outputs measured values which have been corrected for the temperature change inside the analyzer. Optically, the analyzer is designed to reduce the radiation effect. Because the analyzer is also slim, it causes less disturbance to the wind velocity field, thus the sensor separation distance between the SAT and the analyzer can be reduced. (The sensor separation distance is 6 cm when used together with the CSAT3.) When CO_2 flux is evaluated with an open-path analyzer, high frequency flux loss (see Appendix 2.2-2) is generally most attributable to sensor separation. Therefore, the slimmer analyzer not only reduces the effect of instrument surface heating on the flux measurement, but also reduces the magnitude of the flux loss correction term (that is, reduction of uncertainties). Furthermore, the EC150 is equipped with a feature to enhance water vapor evaporation subsequent to rainfall and diminish water condensation on the lenses at the ends of the measurement path with the use of heaters. This feature reduces the occurrence of missing values in the data acquired by the analyzer.

Finally, the third measure addresses the effect of instrument surface heating without the need to use H in the process of CO_2 flux calculations. H is the temperature fluctuation term that is required in the mass conservation equation for dry air (Webb *et al*., 1980) and does not have to be considered for closed-path measurements because air temperature fluctuations become attenuated in the course of drawing the sample air. (However, because the degree of attenuation is influenced by factors such as tube configuration, tube length, and drawing rate, the combination of these factors needs to be selected appropriately. For details, refer to Clement *et al*., 2009). LI-COR has created a new product, the LI-7200, by covering the measurement path of the LI-7500A with a PVC hood, which is low in temperature conductivity and allows little water to adhere, and thus converting the instrument into a closed-path analyzer. With the combined use of an LI-7200, a pump exclusive for the LI-7200, and a flow rate control unit, CO_2 flux can be calculated using the calculation procedure for closed-path analyzers, that is, without using H. Conventional closed-path analyzers tend to be complex in terms of the configuration of the system because they are required to be installed indoors or in shelters to address the influence of rainfall and changes in the surrounding environment (particularly temperature). However, the open-path analyzer LI-7500A was adopted for the basic measurement component of the LI-7200. Because the pump and flow rate control unit of the analyzer are also designed to be weather-resistant, despite being a closed-path analyzer, the LI-7200 can be deployed outdoors. The design of the LI-7200 reduces missing data during a rainfall event, and as reported by Nakai *et al*. (2011), it also allows evaluation of the pressure correlation term, which contributes to the CO_2 flux (Webb *et al*., 1980; Lee and Massman, 2011). These features are advantages of the LI-7200. However, caution is necessary because water vapor (H_2O) fluctuations, in a similar manner to air temperature fluctuations, become attenuated in the process of drawing sample air. Because the suction tube of the LI-7200 is short, the attenuation of water vapor fluctuations inside the tube is smaller for this model than for other models of closed-path analyzers, that is, approximately 10 % of the signal is attenuated (LI-COR, 2011b). Nonetheless, this value cannot be neglected, and adequate corrections are necessary for the attenuated water vapor fluctuations. Incidentally, Campbell initiated the sale of a closed-path analyzer, the EC155, which possesses features similar to those of the LI-7200.

As discussed above, the measurement theory and hardware technology in the field of CO_2 flux measurements with an open-path analyzer are in the process of advancement. Therefore, users need to pay attention to announcements from manufacturers as well as published papers so that newly acquired knowledge can be incorporated into ongoing observations.

Appendix 2.2-1: Serial number-specific characteristics of the LI-7500 (LI-COR)

Ever since the LI-7500 became commercially available in 2000, LI-COR has been continuously modifying and improving the product. Therefore, precautions are necessary at the time of calibration and measurement for LI-7500 with certain serial numbers. These precautions are briefly summarized below. Because the product will likely continue to be modified in the future, it is advisable to visit the web site of LI-COR regularly to check the latest information.

(1) For all serial numbers

Upgrade the firmware for the control box (LI-7500 Instrument Embedded Software), the PC software (LI7500.exe), and obtain the latest product manual for the LI-7500. The latest versions (as of Nov. 2008) of the firmware, PC software and product manual are Ver. 3.0.1, Ver. 3.0.2, and Rev. 4, respectively.

(2) LI-7500s manufactured prior to serial number 75H/B-0282

When an LI-7500 manufactured prior to the one with serial number 75H/B-0282 is exposed to direct solar radiation, it affects the ends of the paths of the analyzers and changes the output (LI-COR, 2002). To avoid this effect, the sensor head of the LI-7500 needs to point north in the northern hemisphere and also needs to be tilted according to the latitude of observation. For example, for an observation at 35°N, tilt the sensor head by about 35 degrees to the north. For an observation at 40°N, tilt the sensor head by about 30 degrees to the north.

(3) LI-7500s distributed earlier than around July 2003

The firmware for the control box with version numbers Ver.1.0.0 ~ 2.0.4 is used for LI-7500s that were distributed earlier than around July 2003. The time lag of the output signal programmed in the firmware is different from that given in the product manual. (LI-COR refers to this discrepancy in the time lag as timing error.) This timing error can be eliminated by upgrading the firmware to Version 3.0.0 or later versions.

(4) LI-7500s manufactured after serial number 75H/B-0370

As a result of improvements in the main circuit in the control box, LI-7500s manufactured after the one with serial number 75H/B-0370 can be used at low air temperatures (down to –40 °C). As long as the calibration coefficients can be transferred properly, LI-7500s can be used for measurements even if the serial numbers of the sensor head and the control box do not match. However, the coefficients determined for a combination of the main circuit of a control box manufactured before the above-mentioned improvement and a sensor head cannot be used for a combination of the main circuit of a control box manufactured after the improvement and a sensor head, and vice versa. Therefore, when the sensor head that was used with the old-version (new-version) control box is transferred to the new-version (old-version) control box, calibration needs to be performed for the new combination of sensor head and control box. LI-COR recommends that calibration be performed, prior to the measurements, on the sensor head combined with the control box when the serial numbers differ between the sensor head and the control box (even when the type of control box itself remains the same before and after the change in combination). Refer to pp. 3–18 ~ 3–20 of the product manual for the LI-7500 (Rev. 4) (LI-COR, 2004) for details on changing the sensor head.

Appendix 2.2-2: High frequency flux loss

When the measurement sensor for the vertical wind velocity and that for a scalar quantity (CO_2 in the present section) are separated by some distance, the sensor separation changes the cospectral shape (frequency response characteristics). Numerous observations and studies have been conducted on the effect of the sensor separation in the horizontal plane (horizontal direction) on the cospectral shape, and satisfactory methods for correcting the change in the cospectral shape have been established (e.g., Moore, 1986; Massman, 2000). However, the influence of vertical separation between the two sensors on the frequency response characteristics is not fully understood. When flux loss due to the vertical separation of the sensors is corrected, a technique such as the band-path method which is often applied for flux measurement with a closed-path analyzer (e.g., Watanabe *et al.*, 2000) should be adopted. The methods for correcting flux loss due to the sensor separation described here are discussed in the analysis edition of the present manual.

Appendix 2.2-3: The influence of heating by the open-path gas analyzer on flux calculation

When CO_2 fluxes are calculated using data collected by an open-path gas analyzer, the correction term for air density fluctuations (dry air flux) needs to be evaluated (Webb *et al.*, 1980). (For details of the Webb correction, refer to the analysis edition of the present manual.) The Webb correction requires evaluation of air temperature fluctuations within the measurement path of the open-path gas analyzer (sensible heat flux, H_{op}). In the past, H_{op} was assumed to be the same as the sensible heat flux measured by the SAT. However, in recent years, it has been reported that the difference between the two sensible heat fluxes ($\Delta H = |H_{op} - H|$) cannot be neglected for the Webb correction (e.g., Burba *et al.*, 2008; Ono *et al.*, 2008). The magnitude of the introduced error depends on the magnitude of ΔH not that of H. (That is, the issue arises regardless of the absolute magnitude of H.)

The non-zero value of ΔH originates from the open-path gas analyzer itself being the source of heating of the air within the measurement path. The instrument can be heated due to its internal electronics or by solar radiation. Burba *et al.* (2008) proposed a correction method for ΔH for vertically-deployed LI-7500s. Thus, the correction method is not applicable for LI-7500s that are deployed other than vertically. The same method is also not applicable to other open-path gas analyzers although they are also likely subject to the heating issue. The issue of an open-path gas analyzer being the source of heating remains under investigation as of today (2008), and journal articles associated with the topic continue to be published (e.g., Heusinkveld *et al.*, 2008.) Thus, investigators are advised to keep up with the latest research trends and future announcements by the manufacturer.

Appendix 2.2-4: Issues associated with horizontally deployed open-path gas analyzers

The value of the CO_2 number density measured by an open-path gas analyzer is that within the measurement path. Accordingly, when the measurement path length is 20 cm, CO_2 number density variations occurring at a length scale smaller than 20 cm are averaged. When an open-path gas analyzer is deployed vertically, CO_2 number density variations occurring at a length scale smaller than 20 cm in the vertical direction are averaged. Numerous studies have been conducted on the smoothing of CO_2 number density fluctuations measured by open-path gas analyzers mounted vertically, thus the smoothing effect can be evaluated and/or corrected. When an open-path gas analyzer is deployed horizontally, CO_2 number density variations occurring at a length scale smaller than 20 cm in the horizontal direction are averaged. In the vertical direction, CO_2 number density variations occurring only at very small length scales are averaged. For this case, there exists little research in the literature on the smoothing of CO_2 number density fluctuations, and no appropriate method is currently available for evaluating and/or correcting the smoothing effect.

Appendix 2.2-5: Influence of dirt and dust accumulated on the lenses of the open-path gas analyzer on CO_2 number density measurements

When dirt and dust accumulate on the lenses of an open-path gas analyzer (LI-7500), the CO_2 and H_2O outputs are offset (Serrano-Ortiz *et al.*, 2008). According to Serrano-Ortiz *et al.* (2008), when the outputs with dust-induced offsets are used to calculate fluxes, the errors on the calculated fluxes become large when evaluating the long term (e.g., yearly) cumulative flux values. To minimize such errors, the following actions are considered effective: 1) measure the absolute magnitude of CO_2 number density (mixing ratio) with a closed-path analyzer; 2) compare the H_2O output from the open-path gas analyzer to that measured by a humidity sensor. Apply the result of this comparison to correct the CO_2 output; and 3) clean the lenses at the end of the measurement path regularly. Although the discussions of Serrano-Ortiz *et al.*(2008) are strictly valid only for LI-7500s, it is likely that dirt and dust on the lenses of other open-path gas analyzers also induce offsets in the CO_2 and H_2O outputs. Thus, the above-mentioned actions may be necessary when data are collected by other open-path gas analyzers.

Appendix 2.2-6: Density and mixing ratio

CO_2 mass density is defined as the mass of CO_2 that is included in a unit volume of air. CO_2 mixing ratio is expressed as the ratio of CO_2 mass density, ρ_{c} [$\mathrm{kgm^{-3}}$], to dry air density, ρ_{d} [$\mathrm{kgm^{-3}}$], that is,

$$\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{d}}} = \frac{m_{\mathrm{c}}}{m_{\mathrm{d}}} \frac{p_{\mathrm{c}}}{(p-e)} \qquad \text{(A2.2-1)}$$

where m_{c}: molecular weight of CO_2 [$\mathrm{kgmol^{-1}}$], m_{d}: molecular weight of dry air [$\mathrm{kgmol^{-1}}$], p: atmospheric pressure [Pa], e: water vapor pressure [Pa], p_{c}: partial pressure of CO_2 [Pa]. The partial pressure of CO_2, p_{c} is related to CO_2 concentration as $p_{\mathrm{c}} = \rho_{\mathrm{cc}} p \times 10^6$, where ρ_{cc} is the CO_2 concentration [$\mathrm{\mu molmol^{-1}}$].

Appendix 2.2-7: Literature which reports a negligible effect of instrument surface heating on open-path analyzer measurements

Some literature such as Giasson *et al*. (2006) and Haslwanter *et al*. (2009) reported that the effect of instrument surface heating on the flux measurements by an open-path analyzer is negligibly small. At the observation site of Giasson *et al*. (2006), winter CO_2 flux indicating absorption of CO_2 by the ecosystem, which is caused by the effect of instrument surface heating, was not observed. Amiro (2010) suggested that high wind speeds might have reduced the effect of instrument surface heating, leading to the results observed by Giasson *et al*. (2006). Specifically, concurrent with the cooling of the instrument directly by the wind, H_{op} / H_{body}, the ratio of H_{op} (see Appendix 2.2-3) to the sensible heat flux generated at the instrument surface, H_{body} [$\mathrm{Wm^{-2}}$], might have decreased with increasing wind speed, an effect reported by Ono *et al*. (2009).