Water vapor density effect on measurements of trace gas mixing ratio and flux with a massflow controller

Xuhui Lee
School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut

Abstract. One configuration in measurements of trace species in the atmosphere uses a massflow controller to regulate airflow through a device that traps the species of interest. Because the flow controller is calibrated with dry air, correction should be made to account for the density effect of water vapor in the ambient air. A common type of massflow controller regulates the flow by measuring temperature difference along a heated tube. It is shown that for these units the true mixing ratio \( s_c \) (ratio of mass of trace species \( c \) to mass of dry air) is related to the apparent mixing ratio \( S_c \) (measurement before correction), as \( s_c = (1 + 1.85r)S_c \), where \( r \) is water vapor mixing ratio of the ambient air, typically varying in the range 0–0.04. Correction should also be made to the surface-air flux measured with such an apparatus in conjunction with micrometeorological flux gradient or relaxed eddy accumulation method and flux chambers; this involves a correction term proportional to surface evaporation rate and for some measurement configurations the same scale factor \( (1 + 1.85r) \) as for \( s_c \). Examples are given for gaseous mercury to illustrate the magnitude of these corrections. No correction is needed if moisture is removed from the airstream before it enters the massflow controller.

1. Introduction

One configuration in measurements of trace species in the atmosphere is to draw the ambient air through a device that traps the species of interest at a flow rate regulated by a massflow controller [e.g., Nie et al., 1995; Kim and Lindberg, 1994]. The trapped material is subsequently released to an analytical instrument for determination of its mass, which is converted to density or mixing ratio given the known flow rate and trapping time. Because the flow controller is usually calibrated with dry air, the measurement will be in error if correction is not made to account for the density effect of water vapor present in the ambient air. (Some manufacturers perform the calibration with nitrogen and provide a table of correction factors for other gases including dry air.) The objective of this paper is to quantify this density effect by considering the operating principle of massflow controller and thermodynamic theory. Specifically, we are concerned with a common type of massflow controller that regulates the flow by measuring heat transfer in the boundary layer or near the wall of a heated tube (Figure 1; FMA series, Omega, Stamford, Connecticut; Tyran General models, Torrance, California; MKS Instruments, Andover, Massachusetts; 800 series, Sierra Instruments, Carmel Valley, California). The method established here can be easily extended to other types of massflow controller [DeCarlo, 1984].

2. Mixing Ratio

Let \( Q \) be the apparent mass flow rate (reading given by the massflow controller with calibration for dry air) in units of \( \text{m}^3\text{s}^{-1} \). Because measurements with a massflow controller are referenced to standard temperature \( T_o \) and pressure \( P_o \) (STP), the proper definition of an apparent (dimensionless) mixing ratio is

\[
S_c = \frac{m_c}{Q} \left( \frac{P_o}{R_T T_o} \right),
\]

where \( m_c \) is mass of species \( c \) collected by the trapping device over time interval \( \delta t \), in units of kilograms, and \( R_T \) is the ideal gas law constant for dry air. (The reader should be aware that the apparent mixing ratio defined by (1) is not the same as the ratio of mass of \( c \) to mass of moist air.) Because the massflow controller is usually calibrated with dry air, correction should be made to obtain the true volume flow rate of moist air \( Q_m \) at STP and in units of \( \text{m}^3\text{s}^{-1} \). The correction is given by

\[
Q_m = \frac{\rho_c C_{pm}}{\rho_d C_{pd}} Q,
\]

where \( \rho_d \) and \( \rho_m \) are densities of dry air and moist air at STP, respectively, and \( C_{pd} \) and \( C_{pm} \) are specific heat of dry air and moist air at constant pressure, respectively [Omega, 1992; DeCarlo, 1984]. Using the following relationship [Emanuel, 1994]

\[
C_{pm} = (1 + 0.85r)C_{pd},
\]

and the ideal gas law, (2) becomes

\[
Q_m = \frac{R_m}{(1 + 0.85r)R_d} Q,
\]

where \( R_m \) is the ideal gas law constant for moist air and \( r \) is water vapor mixing ratio. It follows from (3) that the total mass of moist air that has passed through the trapping device and flow controller over time \( \delta t \) is (in units of kg)

\[
m_m = \rho_m Q_m \delta t = \frac{\rho_o Q \delta t}{1 + 0.85r}.
\]

By definition, the mass of dry air that has passed through the trapping device over time \( \delta t \) is (in units of kg)

\[
m_d = m_m(1 + r).
\]
Combining (1), (4), and (5), we obtain the true (dimensionless) mixing ratio of species \( c \) in the ambient air

\[
s_c = \frac{m_c}{m_d} = (1 + r)(1 + 0.85r)s_c,
\]

(6)

Mixing ratio of water vapor in the air varies in the range 0–0.04, and (6) shows that the correction factor can be as high as 7%. This correction should be made in situations where atmospheric moisture shows large variations, as in studies that attempt to contrast atmospheric moisture between the terrestrial ecosystems and the atmosphere [Slemr et al., 1985]. The moisture effect is believed to be one of the factors contributing to the seasonal pattern of lower TGM concentration in summer than in winter [Slemr and Scheel, 1998; Lee et al., 2000; Ames et al., 1998].

3. Flux Observation

3.1. Flux With Micrometeorological Methods

The trapping device/massflow controller can be used to measure the vertical gradient of \( c \) for determination of surface-air flux as in the flux-gradient relationship

\[
f_c = \frac{\partial s_c}{\partial z},
\]

(7)

where \( f_c \) is the vertical eddy flux of \( c \) in units of kg m\(^{-2}\) s\(^{-1}\) and positive (negative) if the surface is a source (sink), \( \rho_a \) is dry air density at actual temperature and pressure, \( K \) is eddy diffusivity, and \( z \) is height [Webb et al., 1980]. Substituting (6) into (7) yields

\[
f_c = (1 + 1.85r)F_c + 1.85s_cE_c,
\]

(8)

where \( F_c \) is the apparent flux of \( c \)

\[
F_c = \frac{\partial s_c}{\partial z},
\]

(9)

and \( E \) is water vapor flux

\[
E = \frac{\partial r}{\partial z}.
\]

Equation (8) indicates that correction of flux for the water vapor effect involves the same scale factor as for \( s_c \) and an additional term proportional to the evaporation rate. The evaporative effect is eliminated with the gaseous mercury flux, an important but poorly understood pathway of mercury between the terrestrial ecosystems and the atmosphere [Lindberg et al., 1998]. At a typical annual mean evaporation rate of 0.015 g m\(^{-2}\) s\(^{-1}\) at midlatitudes [Black et al., 1996; Lee et al., 1999; Wilson and Baldocchi, 2000] and TGM mixing ratio of 2.1 pg g\(^{-1}\), the second term on the right-hand side of (8) is equal to 0.2 ng m\(^{-2}\) hr\(^{-1}\), or an annual total of 1.7 \( \mu \)g m\(^{-2}\), which is of the order of 10–20% of some reported wet deposition values [Fitzgerald et al., 1991; Sorensen et al., 1994; Hoyer et al., 1995; Burke et al., 1995]. The correction can be an order of magnitude higher than this at times of high TGM concentrations or when evaporation is vigorous (e.g., in summer months).

The above density correction formula differs from that proposed by Webb et al. [1980]. The difference exists mainly because in the work by Webb et al. [1980] the concentration of \( c \) is measured at actual temperature and pressure while a massflow controller automatically presents the measurement at STP. No additional Webb correction should be performed if flux is computed from (8). Neither Webb nor the above correction is necessary if water vapor is removed from the air stream before it enters the trapping device. In some situations, addition of a water vapor filter may interfere with the efficiency of the trapping device; filtering of water vapor downstream of the trapping device and upstream of the flow controller will also eliminate the density effect.

It can be shown that (8) also holds for flux measured with the relaxed eddy accumulation method. In a related study, Pattey et al. [1992] extended the work of Webb et al. [1980] and derived a density correction formula for flux measured with this method. Once again for the reason given above, their expression is different from (8).

3.2. Flux With Chambers

3.2.1. Closed chamber. We consider an air-tight closed chamber whose flow rate is maintained by a flow controller (Figure 2). Air within the chamber is well mixed. The apparent flux of \( c \) is given by
where $m_{\text{do}}$ and $m_{\text{d}}$ are lateral dry air mass flow at the outlet (or in the interior) and at the inlet, respectively, in units of kg s$^{-1}$. It follows from (4), (5), and (15) that

$$
\dot{m}_{\text{do}} = \frac{\rho_d}{1 + 1.85r_o} (Q_b + Q_2). 
$$

Using (6) and (17), (18) becomes

$$
f_c = [(1 + 1.85r_o)s_{\text{co}} - (1 + 1.85r)S_c]m_{\text{do}}/A,
$$

$$
f_c = (1 + 1.85r_o)(S_{\text{co}} - S_c)m_{\text{do}}/A + 1.85(r_o - r)S_c m_{\text{do}}/A. 
$$

Combining (16), (19), (20), and (21), we obtain the true flux for the dynamic chamber

$$
f_c = F_c + 1.85S_c E. 
$$

Once again, (22) calls for correction for the influence of evaporation within the chamber, but unlike the closed chamber system or micrometeorological methods, the scale factor $(1 + 1.85r)$ does not appear here.

A variant of the chamber design shown in Figure 3 is to replace the traps by inline infrared gas analyzers that measure the true mixing ratios $s_c$ and $s_{\text{co}}$ directly, that is, $s_c = S_c$ and $s_{\text{co}} = S_{\text{co}}$. A common practice is to use (16) to compute the flux. This, however, will result in error because the flow rate maintained by massflow controllers MC2 and MC3 is influenced by water vapor. It can be shown that the proper formula for computing the true flux with this hybrid chamber design is

$$
f_c = \frac{\rho_d(s_{\text{co}} - s_c)(Q_b + Q_2)}{(1 + 1.85r_o)A}. 
$$

4. Conclusions

1. We have discussed the density correction procedure for a common type of massflow controller that regulates the flow by measuring temperature difference along a heated tube. For other types of controller, (2) and (6) are not applicable, and new correction methods should be established.

2. When applying the above correction, the reader should follow the definition of apparent mixing ratio (equation (1)) and the appropriate definition of apparent flux (equation (9) for flux gradient or relaxed eddy accumulation method, (10) for closed chambers, and (16) for open chambers).

3. No additional density correction [e.g., Webb et al., 1980] is necessary once the above correction has been done. Neither Webb nor the above correction is necessary if water vapor is removed from the airstream before it enters the massflow controller.

4. The above correction should not be applied in cases where the mixing ratio or flux is determined without using the flow rate value provided by the massflow controller. A case in point is a closed chamber shown in Figure 2 but with the traps replaced by an inline gas analyzer that can detect the true mixing ratio. However, caution should be exercised with the hybrid dynamic chamber design discussed in section 3.2.
References


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X. Lee, School of Forestry and Environmental Studies, Yale University, 370 Prospect Street, New Haven, CT 06511. (xuhui. lee@yale.edu)

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