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

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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; Tylan 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 m^3 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

$$S_c = \frac{m_c}{Q\,\delta t}\bigg/\left(\frac{P_o}{R_d T_o}\right), \tag{1}$$

where m_c is mass of species c collected by the trapping device over time interval δt, in units of kilograms, and R_d 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 m^3 s^{-1}. The correction is given by

$$Q_m = \frac{\rho_d C_{pd}}{\rho_m C_{pm}} Q, \tag{2}$$

where ρ_d and ρ_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

$$Q_m = \frac{R_m}{(1 + 0.85r)R_d} Q, \tag{3}$$

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 δt is (in units of kg)

$$m_m \equiv \rho_m Q_m \delta t = \frac{\rho_d Q\,\delta t}{1 + 0.85r}. \tag{4}$$

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

$$m_d = m_m/(1 + r). \tag{5}$$

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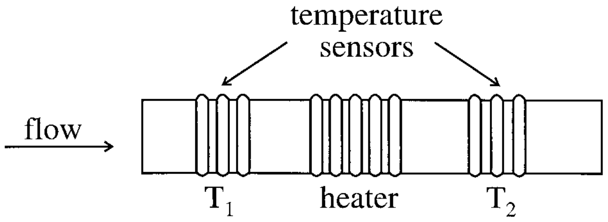

Figure 1. Flow meter in which boundary layer of the flow is heated by an external source. The flow rate is proportional to $\rho c_p(T_2 - T_1)$, where ρ and c_p are density and specific heat at constant pressure of the fluid, respectively [*DeCarlo*, 1984].

Combining (1), (4), and (5), we obtain the true (dimensionless) mixing ratio of species c in the ambient air

$$s_c \equiv \frac{m_c}{m_d} = (1 + r)(1 + 0.85r)S_c,$$
$$s_c \equiv \frac{m_c}{m_d} \simeq (1 + 1.85r)S_c. \tag{6}$$

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 s_c in winter and summer, in tropical versus polar latitudes, and in marine and continental climates, or in studies of profiles extending from the atmospheric boundary layer to the free atmosphere. As an example, the correction can be as large as 0.2 ng m^{-3} at a typical total gaseous mercury (TGM) concentration of 2.5 ng m^{-3} STP (mixing ratio 2.1 pg g^{-1} [*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

$$f_c = -\rho_a K \frac{\partial s_c}{\partial z}, \tag{7}$$

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), ρ_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

$$f_c = (1 + 1.85r)F_c + 1.85S_cE, \tag{8}$$

where F_c is the apparent flux of c

$$F_c = -\rho_a K \frac{\partial S_c}{\partial z}, \tag{9}$$

and E is water vapor flux

$$E = -\rho_a K \frac{\partial r}{\partial z}.$$

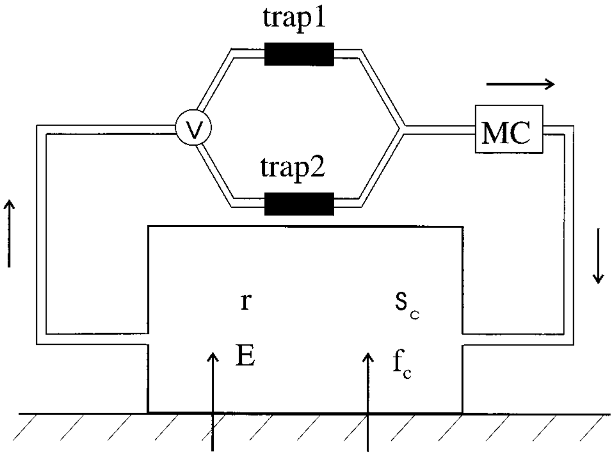

Figure 2. Schematic of a closed chamber system. Time rate of change of concentration c is determined by alternating the flow between traps 1 and 2 via three-way valve. The flow is controlled by massflow controller MC.

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 can be illustrated 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 μg 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 airstream 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

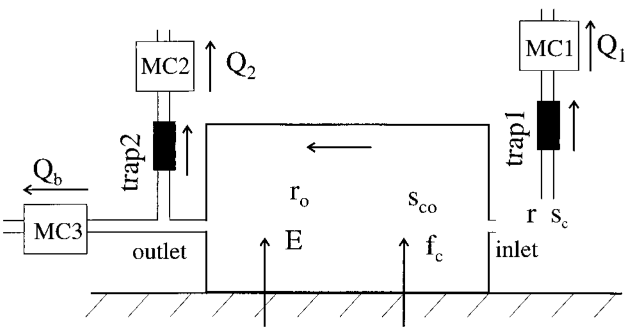

Figure 3. Schematic of a dynamic, open chamber system. Airstreams are controlled by three massflow controllers (MC1, MC2, and MC3) of the same type.

$$F_c = \frac{\rho_a V}{A}\frac{\partial S_c}{\partial t}, \tag{10}$$

where V is the chamber volume and A is the chamber base area. To derive the true flux f_c, we note that the conservation of mass of dry air, c, and water vapor requires

$$0 = \partial M_d/\partial t, \tag{11}$$

$$Af_c = \partial(M_d s_c)/\partial t, \tag{12}$$

$$AE = \partial(M_d r)/\partial t. \tag{13}$$

Equation (11) holds because dry air flux from the surface is zero. Substituting (6) into (12) and making use of $M_d = \rho_a V$ (total dry air mass within the chamber) and (10), (11), and (13), we obtain the true flux of c

$$f_c = (1 + 1.85r)F_c + 1.85S_cE. \tag{14}$$

This equation is identical to (8) with the exception that r and S_c are measured within the chamber. Correction for the evaporative effect is also proposed for a leaky chamber by *Licor, Inc.* [1997] who assume that the escape of air from their chamber is fully compensated by evaporation.

3.2.2. Dynamic chamber. Figure 3 is the sketch of a typical dynamic chamber. Air near the inlet is sampled by trap 1 at a flow rate controlled by massflow controller MC1. The flow stream at the outlet is split into two parts, a base flow at a rate Q_b controlled by MC3 and a sampling flow at a rate Q_2 controlled by MC2. Samples collected by trap 2 represent conditions within the chamber because air is assumed to be uniformly mixed. According to (3), the total mass flow rate of moist air at the outlet is

$$Q_{mo} = \frac{R_{mo}}{(1 + 0.85r_o)R}(Q_b + Q_2), \tag{15}$$

where subscript o denotes variables at the outlet (identical to those in the interior of the chamber). The apparent flux is given by

$$F_c = \rho_d(S_{co} - S_c)(Q_b + Q_2)/A, \tag{16}$$

where S_c and S_{co} are apparent mixing ratios of c from traps 1 and 2, as defined by (1).

At steady state the conservation of mass of dry air, c, and water vapor requires

$$0 = \dot{m}_{do} - \dot{m}_d, \tag{17}$$

$$Af_c = s_{co}\dot{m}_{do} - s_c\dot{m}_d, \tag{18}$$

$$AE = r_o\dot{m}_{do} - r\dot{m}_d, \tag{19}$$

where $\dot{m}_{do}$ and $\dot{m}_d$ 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

$$\dot{m}_{do} \simeq \frac{\rho_d}{1 + 1.85r_o}(Q_b + Q_2). \tag{20}$$

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

$$f_c = [(1 + 1.85r_o)S_{co} - (1 + 1.85r)S_c]\dot{m}_{do}/A,$$

$$f_c = (1 + 1.85r_o)(S_{co} - S_c)\dot{m}_{do}/A + 1.85(r_o - r)S_c\dot{m}_{do}/A. \tag{21}$$

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

$$f_c = F_c + 1.85S_cE. \tag{22}$$

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_{co} directly, that is, $s_c = S_c$ and $s_{co} = S_{co}$. 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

$$f_c = \frac{\rho_d(s_{co} - s_c)(Q_b + Q_2)}{(1 + 1.85r_o)A}. \tag{23}$$

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.

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