

**Chemical sensor
resolution
requirements**

M. D. Rowe et al.

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Chemical sensor resolution requirements for near-surface measurements of turbulent fluxes

M. D. Rowe^{1,*}, C. W. Fairall², and J. A. Perlinger¹

¹Michigan Technological University, Houghton, MI, USA

²NOAA/ESRL, Boulder, CO, USA

*now at: US Environmental Protection Agency, Grosse Ile, MI, USA

Received: 7 September 2010 – Accepted: 5 October 2010 – Published: 20 October 2010

Correspondence to: M. D. Rowe (rowe.mark@epa.gov)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Businger and Delany (1990) presented an approach to estimate the sensor resolution required to limit the contribution of the uncertainty in the chemical concentration measurement to the flux measurement uncertainty to 10% for eddy covariance, gradient, and relaxed eddy accumulation flux measurement methods. We describe an improvement to their approach to estimate required resolution for the covariance method. In addition, we provide data to support selection of a form for the dimensionless scalar standard deviation similarity function based on observations of the variance of water vapor fluctuations from recent field experiments. We also redefine the atmospheric parameter of Businger and Delany in a more convenient, dimensionless form. To make the expression convenient for gas transfer applications, we introduce a “chemical parameter” based on the gas transfer (piston) velocity. Finally, we provide examples in which the approach is applied to measurement of carbon dioxide, dimethylsulfide, and hexachlorobenzene fluxes. The information provided here will be useful to plan field measurements of atmosphere-surface exchange fluxes of trace gases.

1 Introduction

In recent decades, significant developments in technologies and methods for direct measurement of turbulent atmosphere-surface exchange fluxes have been achieved. These measurements are of interest with respect to climate change, atmospheric chemistry, hydrology, and ecology. Eddy covariance is usually the method of choice if a fast-response (10 Hz) sensor is available, for example in the case of carbon dioxide (McGillis et al., 2004) and dimethylsulfide (Blomquist et al., 2006, 2010). Current methods to measure atmospheric trace gas fluxes for which fast response sensors are not available include gradient methods, such as the modified Bowen ratio method (Walker et al., 2006; Perlinger et al., 2005, 2008), and relaxed eddy accumulation REA (Bowl-
ing et al., 1999; Businger and Oncley, 1990; Park et al., 2010); for these methods,

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



chemical concentration measurements requiring accumulation times of up to an hour or so may be used, limited by the time of stationarity of the flux. With ongoing interest in application of these methods to additional gases, over a range of atmospheric conditions, and with new sensor technologies, it is necessary to predict the sensor resolution required to achieve a given resolution under a given set of conditions.

Businger and Delany (1990), hereafter referred to as BD90, presented an analysis of sensor resolution, R , required to make chemical flux measurements to an estimated 10% uncertainty. Their results took the form

$$R = 0.1 \overline{w'c'} AP_x \quad (1)$$

where the factor 0.1 represents the 10% uncertainty requirement, $\overline{w'c'}$ the flux of the scalar C , and AP_x the “atmospheric parameter” describing the uncertainty associated with the flux method x (either covariance, cov, gradient, g , or relaxed eddy accumulation, r). A full list of symbols with SI units is given in Appendix A. Note that R has the same units as C . In the flux expression, w' represents turbulent variations of vertical velocity and c' turbulent fluctuation of the chemical (scalar) of interest; the overbar denotes a time average. For example, for covariance the atmospheric parameter is given as

$$AP_{\text{cov}} = \frac{\sigma_c}{u_* |c_*|} = \frac{\phi_\sigma(z/L)}{u_*} \quad (2)$$

where σ_c is the standard deviation of C , u_* the friction velocity, $c_* = (-\overline{w'c'}/u_*)$ the chemical flux scaling parameter, and ϕ_σ the similarity function for the dimensionless scalar standard deviation ($\sigma_c/|c_*|$), which is a function of sensor height, z , and the Monin-Obukhov stability length, L . For measurements over water, z is measured upward from the surface. For measurements over land $z-d$ is used in place of z , where d is the displacement height of the canopy (e.g., Kaimal and Finnigan, 1994, p. 68). For simplicity of notation, $d=0$ is used hereafter. BD90 arrived at Eq. (2) by specifying

**Chemical sensor
resolution
requirements**

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



that the resolution for covariance measurements should be 10% of σ_c .

$$R = 0.1 \sigma_c = 0.1 \frac{|\overline{w'c'}|}{u_*} \phi_\sigma(z/L) \quad (3)$$

Similar expressions for gradient and REA methods were obtained by specifying that the resolution should be 10% of the mean gradient or 10% of the mean REA reservoir difference.

Here we offer several suggested improvements to the BD90 formulations. First, we suggest an improved approach to specifying the resolution limits for the covariance method. We have also redefined AP_x by removing the factor u_* . Finally, we present data to support selection of a form for $\phi_\sigma(z/L)$ based on observations of the variance of water vapor fluctuations from recent field experiments. BD90 used temperature observations, which they pointed out are poorly defined near neutral stability, because water vapor flux and variance observations were not available.

2 Modifications to the approach of BD90

2.1 Atmospheric parameter redefined

We have redefined the atmospheric parameter by removing the factor u_* . In contrast to Eq. (1),

$$R = 0.1 \frac{|\overline{w'c'}|}{u_*} AP'_x \quad (4)$$

In our opinion, the u_* variable is better included with the flux term since $\overline{w'c'}/u_*$ has a weak wind speed dependence; thus, the atmospheric parameter also has a weak wind speed dependence. Defined this way, AP'_x is unitless, in contrast to AP_x , which has SI units of s m^{-1} .

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.2 Modified covariance resolution requirement

Our revised treatment of covariance flux resolution requirements follows from the expression for the uncertainty in the mean value of C computed over time interval T (Blomquist et al., 2010)

$$\delta(\bar{C})_T = \frac{2}{\sqrt{T}} \left[\sigma_{c1}^2 \tau_1 + \sigma_{c2}^2 \tau_2 \right]^{1/2} \quad (5)$$

Here we have considered only two possible sources of variance for C ; we assume the sources are independent so the variances sum. Note we allow a different time scale and variance for each process. The first process is the turbulent fluctuations described above. For surface-layer turbulence processes, the turbulent flux drives variance in the variables that is easily computed from Monin-Obukhov similarity theory

$$\sigma_{c1} = \left| \frac{\overline{w'c'}}{u_*} \right| \phi_\sigma(z/L) \quad (6)$$

The second process is the band-limited white noise of the sensor, σ_{wn} .

Because we are estimating the covariance flux with high-speed measurements that resolve most of the frequency components that contribute to the flux, the relevant time scale for the turbulence process is the integral time scale associated with the turbulent fluctuations. In the surface layer, this time scale can be estimated from the frequency, f_m , corresponding to the *peak* in the vertical velocity or scalar variance spectral density or, alternatively, the $w - c$ cospectrum

$$\tau_1 = \tau_{wc} = 1/(2\pi f_m) \quad (7)$$

We can also compute the integral time scale in the case of band-limited white noise. The noise could be simply electronic noise or Poisson counting statistics from a photon detector. Band-limited white noise is characterized by a constant variance-spectral value from 0 to a maximum frequency (Nyquist frequency), f_x :

$$\phi_{\text{wn}}(f) = \phi_{\text{wn}} = \sigma_{\text{wn}}^2 / f_x \quad f < f_x \quad (8a)$$

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$$\phi_{\text{wn}}(f) = 0 \quad f > f_x \quad (8b)$$

The integral time scale for white noise is (Blomquist et al., 2010)

$$\tau_{\text{wn}} = \frac{1}{4f_x} \quad (9)$$

Substituting this expression into Eq. (5)

$$\delta(\bar{C})_T = \frac{2}{\sqrt{T}} \left[\sigma_{c1}^2 \tau_1 + \sigma_{\text{wn}}^2 / (4f_x) \right]^{1/2} \quad (10)$$

We now specify the 10% condition as follows: the white noise of the sensor cannot account for more than 10% of the total uncertainty in \bar{C} (or, equivalently, the uncertainty in the covariance flux of C , assuming that the wind speed measurement is relatively noise-free). We specify this by requiring that adding a small white noise term will increase the uncertainty by 10%. The uncertainty without noise is obtained from Eq. (10) by neglecting the σ_{wn}^2 term; thus the ratio of the uncertainty with noise to the uncertainty without noise is

$$\frac{\left[\sigma_{c1}^2 \tau_1 + \sigma_{\text{wn}}^2 / (4f_x) \right]^{1/2}}{\left[\sigma_{c1}^2 \tau_1 \right]^{1/2}} = 1.1 = \left[1 + \sigma_{\text{wn}}^2 / (4f_x \sigma_{c1}^2 \tau_1) \right]^{1/2} \approx 1 + \frac{1}{2} \sigma_{\text{wn}}^2 / (4f_x \sigma_{c1}^2 \tau_1) \quad (11)$$

If we equate R with σ_{wn} , then this condition applied to Eq. (11) is

$$\sigma_{c1}^2 \tau_1 = 10R^2 / (8f_x) \quad (12)$$

or

$$R = 0.1 \sigma_{c1} \sqrt{80 \tau_1 f_x} = 0.1 \left| \frac{w'c'}{u_*} \right| \phi_\sigma(z/L) \sqrt{80 \tau_1 f_x} \quad (13)$$

**Chemical sensor
resolution
requirements**

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Note that Eq. (13) is similar to Eq. (3) except for the additional factor of $\sqrt{80\tau_1 f_x}$. For example, if the signals are digitized at 10 times a second (Nyquist frequency $f_x = 5$ Hz), this factor is on the order of 40 for measurements at a height of 20 m. This criterion implies direct covariance measurements require about 40 times less resolution for fast sensors used in flux estimates than that suggested by BD90. BD90 assumed a worst case scenario in which the noise is well correlated with c' , whereas we assume white noise that is not correlated to c' . Note that Eq. (12) is also related to the “figure of merit” for covariance measurements defined by Lenschow and Kristensen (1985) for sensors that obtain concentration through counting statistics (e.g., a photon detector or aerosol size spectrometer). In their Eq. (28), they take the ratio of error variance contributed by uncorrelated noise to that contributed by atmospheric variability.

3 Atmospheric stability dependence of σ and τ

In order to apply Eq. (13), it is necessary to estimate the scalar standard deviation and integral time scale. In this section, we present data to support selection of a form of the stability-dependent scalar standard deviation similarity function, and then substitute the similarity relationships into Eq. (13) to yield a form that is useful in field experiments.

3.1 Updated similarity function for the standard deviation of a scalar

In surface-layer scaling theory, the dimensionless standard deviation of a scalar due to turbulent fluctuations is defined through Eq. (6), where

$$\sigma_c/c_* = \phi_\sigma(z/L) = Af_c(z/L) \quad (14)$$

Here A is a dimensionless constant with a value set so that $f_c(0) = 1.0$. Panofsky and Dutton (1984) present mixing arguments (p. 170–171) that

$$f_c(z/L) = \phi_c(z/L) \quad (15)$$

where

$$\phi_c(z/L) = \frac{\kappa z}{c_*} \frac{\partial \bar{C}}{\partial z} \quad (16)$$

is the stability function for the dimensionless mean gradient of a scalar.

Another approach to parameterize the scalar variance is to use the variance budget equation; neglecting the turbulent transport term, the net production of variance is a balance of gradient generation and dissipation (Edson and Fairall, 1998)

$$\frac{D(\overline{c'^2})}{Dt} = -2\overline{w'c'} \frac{\partial \bar{C}}{\partial z} - N_c = 0 \quad (17)$$

where N_c is the rate of dissipation of the variance of C via turbulent mixing and molecular viscosity. We can represent N_c through the turbulent mixing/dissipation time scale

$$N_c = \overline{c'^2} / \tau_{cD} = \sigma_c^2 / \tau_{cD} \quad (18)$$

Using Eqs. (16), (17), (18) and the definition of c_* , we find

$$\frac{\sigma_c^2}{c_*^2} = \frac{2u_*}{\kappa z} \tau_{cD} \phi_c \quad (19)$$

We use the standard deviation of the vertical velocity, σ_w , and its corresponding similarity function, f_w (Kaimal and Finnigan, 1994, p. 16), to define the mixing time scale

$$\sigma_w = 1.25u_* f_w(z/L) \quad (20a)$$

$$f_w(z/L) = [1 + 3|z/L|]^{1/3} \quad z/L < 0 \quad (20b)$$

$$f_w(z/L) = 1 + 0.2(z/L) \quad z/L > 0 \quad (20c)$$

$$\tau_{cD} \cong \frac{\kappa z}{\sigma_w} = \frac{\kappa z}{1.25u_* f_w(z/L)} \quad (20d)$$

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Substituting Eqs. (20a–d) into Eq. (19) and combining constants into one empirical parameter yields

$$\frac{\sigma_c}{c_*} = A \left[\frac{\phi_c(z/L)}{f_w(z/L)} \right]^{1/2} \quad (21)$$

Observations of temperature variance from the Kansas experiment (Kaimal and Finnigan, 1994) indicate that Eq. (15) is reasonable for unstable conditions ($z/L < 0$), but the stability dependence of f_c for stable conditions ($z/L > 0$) is much weaker than that of ϕ_c . Observations of temperature and humidity variance over land consistently show that in unstable conditions, ϕ_σ is well represented by

$$\phi_\sigma = A(1 - Bz/L)^{-1/3} \quad z/L < 0 \quad (22)$$

with values of A of 3 to 4 and B 20 to 35. For example, Andreas et al. (1998) found $A = 3.2$ and 4.1 for temperature and humidity, respectively, with $B = 28.4$; Choi et al. (2004) give $A = 3.7$ and 3.5 for temperature and humidity, respectively, with $B = 34.5$ and 32.7 ; Blomquist et al. (2010) suggest $A = 3.0$ and $B = 20$.

Observations for stable conditions are more problematic because the turbulent fluxes are small and a near-constant flux surface layer may be shallow. Over the ocean stable conditions are associated with fog and water condensation that interferes with sensors (especially optical fast humidity sensors). For temperature there is also infrared radiative heat transfer in strong vertical temperature gradients that may upset the scaling relationships. The Surface Heat Budget of the Arctic (SHEBA) field program offers a one-year set of observations of fluxes from 5 levels of sonic anemometers (Grachev et al., 2003). These data indicate ϕ_σ for potential temperature increases weakly with z/L . However, when z/L exceeds about 2 the five levels no longer collapse to a single value – indicating that similarity scaling is breaking down. Andreas et al. (1998) also found weak stability dependence for $0 < z/L < 1$.

Published observations of dimensionless scalar variance over the ocean are sufficiently rare that we include results for humidity variance from two ship-based field

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



programs: the New England Air Quality Experiment (NEAQS) and the Stratus07 field program. NEAQS was conducted on the NOAA R/V *Ronald H. Brown* in the Gulf of Maine in the summer of 2004. Details of the observations are reported by Fairall et al. (2006). The Stratus07 project was also conducted on the *Brown* off the coast of Chile in 2007 (see DeSzoek et al., 2009). Velocity and temperature turbulence were measured with sonic anemometers and fast humidity fluctuations were measured with near-infrared absorption hygrometers – hardware, ship motion correction, and processing details are reported by Fairall et al. (2006).

Observations of dimensionless scalar variance are plotted in Fig. 1, and compared to several mathematical representations. Individual hourly observations from Stratus07 show an excellent fit with land-derived unstable stability functions (Fig. 1, left panel). The Stratus07 field program had large sea-air humidity contrast (about 5 g kg^{-1}), the latent heat flux was substantial (about 85 W m^{-1}), and there was essentially no precipitation so it was ideal to measure the humidity variance and the scaling parameters (unstable conditions dominated). We chose the NEAQS field program because stable conditions dominated. However, fog, precipitation and internal boundary layers associated with offshore flow were common. Sea-air humidity contrast was modest (about 2.5 g kg^{-1}) and so were the latent heat fluxes (about 25 W m^{-1}). Individual hourly observations from NEAQS had about ten times the scatter of those from Stratus07, so we averaged the data in bins of z/L . Bulk z/L values (computed with COARE 3.0) were used to avoid artificial correlation. The results for the stable NEAQS averages are shown in Fig. 1, right hand panel. Also shown in the figure are points digitized from the line in BD90 Fig. 1, three of the mathematical representations discussed above, and the stable SHEBA results for temperature variance. The unstable observations are consistent and imply a neutral value for ϕ_σ between 3.0 and 4.0. Humidity observations on the stable side imply a constant value or a weak increase with increasing stability. For subsequent calculations, we selected the functions of Andreas et al. (1998, 5.9a, b) as the closest approximation to the data.

**Chemical sensor
resolution
requirements**

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.2 Incorporation of similarity functions into the resolution expression for covariance

We can add detail to Eq. (13) using stability functions for σ_{c1} from Andreas et al. (1998) and for τ_1 from Blomquist et al. (2010). Each of the key variables is expressed in terms of scaling variables and a dimensionless stability dependence, $f(z/L)$, scaled to have a value of 1.0 at $(z/L) = 0$:

$$\sigma_{c1} = \left| \frac{\overline{w'c'}}{u_*} \right| \phi_\sigma(z/L) = \left| \frac{\overline{w'c'}}{u_*} \right| A f_c(z/L) \quad (23a)$$

$$\tau_1 = b \frac{z}{U_r} f_\tau(z/L) \quad (23b)$$

where $A = 3.2$ (Andreas et al., 1998). The coefficient b is fairly uncertain but is near 3. Here we use $b = 2.8$ (Blomquist et al., 2010). U_r is the mean wind speed relative to the sensor (not corrected for platform motion). The stability functions are

$$f_\tau(z/L) = [\min(5, \max(0.5, 1 + 0.6z/L))]^{-1} \quad (24a)$$

$$f_c(z/L) = [1 + 28.4 |z/L|]^{-1/3} \quad z/L < 0 \quad (24b)$$

$$f_c(z/L) = 1 \quad z/L > 0 \quad (24c)$$

where Eqs. (24b, c) are equivalent to Andreas et al. (1998, Eq. 5.9a, b). We substitute Eq. (24) into Eq. (13) to obtain the expression for sensor resolution required to limit at 10% the contribution of sensor noise to uncertainty in flux measured by eddy covariance.

$$R = 0.1A \left| \frac{\overline{w'c'}}{u_*} \right| f_c(z/L) \sqrt{80b \frac{zf_x}{U_r} f_\tau(z/L)} = 4.8 \left| \frac{\overline{w'c'}}{u_*} \right| f_c(z/L) \sqrt{\frac{zf_x}{U_r} f_\tau(z/L)} \quad (25)$$

4 Results and discussion

4.1 Comparison of required sensor resolution for three flux measurement methods using the redefined atmospheric parameter

For the modified atmospheric parameters described by Eq. (4) we have

$$AP'_{cov} = 48 \sqrt{\frac{zf_x}{U_r}} f_c(z/L) \sqrt{f_r(z/L)} \quad (26a)$$

$$AP'_g = (\sqrt{2}\kappa)^{-1} [\ln(z_2/z_1) - \Psi_c(z_2/L) + \Psi_c(z_1/L)] = (\sqrt{2}\kappa)^{-1} G \quad (26b)$$

$$AP'_r = \frac{u_*}{\sqrt{2}b_{th}\sigma_w} = \frac{1}{1.8b_{th}f_w(z/L)} \quad (26c)$$

Equations (26b and c) follow from the derivation of BD90 except that a factor of $\sqrt{2}$ is applied to the uncertainty in concentration measurement to account for the fact that BD90 set R equal to $\delta(\Delta C_{12})$, while here R is set equal to $\delta(C)$. Here $\kappa = 0.4$ is the von Kármán constant, z_2 and z_1 are the two heights for the gradient measurement, Ψ is the stability function for the dimensionless vertical profile of a scalar (from COARE 3.0), and b_{th} the three-reservoir REA calibration coefficient (a function of the threshold used for the up/down reservoirs). In Eq. (26b), G is introduced as shorthand notation for the stability term in square brackets.

Figure 2 shows examples of AP'_x values for a typical ship-based application. Here we have used $U_r = 8 \text{ m s}^{-1}$, $z = 18 \text{ m}$. For the gradient method, a typical ocean, ship-based installation with $z_2 = 18 \text{ m}$ and $z_1 = 10 \text{ m}$, and a lake or land-based installation with $z_2 = 10 \text{ m}$ and $z_1 = 1 \text{ m}$, are considered. For REA, two values of b_{th} were considered: $b_{th} = 0.36$ for the method of Businger and Oncley (1990) with a threshold of $0.6\sigma_w$, and $b_{th} = 0.21$ for the asymmetrical hyperbolic REA method of Bowling et al. (1999) with a hole size of 1.10 (see their Table 1). Of the three flux measurement

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



methods, eddy covariance has the least stringent requirement for sensor resolution over the full range of stability. However, if a fast-response sensor is not available for the chemical of interest, it is necessary to consider the gradient or REA method. Of these two, gradient is a favorable choice for stable conditions, while REA may have a less stringent resolution requirement under unstable conditions, depending on selection of the threshold for REA, or hole size for HREA, that determine the value of b_{th} .

4.2 Predicted sensor resolution requirements for air-water gas exchange measurements of specific chemicals

It is useful to recast Eq. (4) in the language of air-water gas transfer by using the standard transfer velocity, k , approach

$$\overline{w'c'} = \alpha_c k_c \Delta C \quad (27)$$

where α_c is the dimensionless solubility of C and $\Delta C = C_w/\alpha_c - C_a$ is the water-air difference in concentration at specified reference depth and height. Thus

$$R = 0.1 \alpha_c \frac{k_c}{u_*} |\Delta C| AP'_x \quad (28)$$

or, in a dimensionless form normalized to the water-air concentration difference

$$\frac{R}{|\Delta C|} = 0.1 CP_c AP'_x \quad (29a)$$

$$CP_c = \alpha_c \frac{k_c}{u_*} \quad (29b)$$

where CP_c is a “chemical parameter” that has minimal dependence on atmospheric variables.

Values of CP_c for chemicals having a range in solubility were calculated using COARE 3.0 for neutral stability, $U_{10} = 11 \text{ m s}^{-1}$, $u_* = 0.4 \text{ m s}^{-1}$. The programs of Johnson (2010) were used to estimate Sc and temperature-dependent solubility at 20°C for

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



fresh water using data compiled by Sander (1999). Solubility for additional compounds was obtained elsewhere: Hg(0) (Sanemasa, 1975), HgCl₂ and Hg(OH)₂ (Lindqvist, 1985), and 8-2 fluorotelomer alcohol (Hilal et al., 2004, SPARC On-Line Calculator <http://ibmlc2.chem.uga.edu/sparc/>, accessed 7 August 2010). CP_c varies over four orders of magnitude for the range of chemicals considered, mainly as a function of solubility. Schmidt numbers vary over a much more limited range than solubility (Fig. 3). Chemicals that are more water soluble (higher values of α_c) have higher values of CP_c , and thus a less restrictive sensor resolution is required for a given value of AP'_x . Note that CP_c levels off at high solubility where the transfer becomes limited by the atmospheric resistance. An estimate of required sensor resolution for a given chemical, flux measurement method, and stability can be obtained by reading values from Figs. 2 and 3, and use of Eq. (29) for air-water exchange. For land-based applications, Fig. 2 can be used with Eq. (4).

We consider a simple case for measurement of CO₂ and DMS at a height of 18 m, wind speed 8 m s⁻¹, $u_* = 0.28$ m s⁻¹, $f_x = 5$ Hz, and neutral stability ($z/L = 0$). From Fig. 2, we find $AP'_{cov} = 161$ for covariance. From Fig. 3, we find $CP_c = 1.7 \times 10^{-4}$ for CO₂ and $CP_c = 1.8 \times 10^{-3}$ for DMS (DMS is more soluble than CO₂). For CO₂ we have $R/\Delta C = 0.0027$ and for DMS we have $R/\Delta C = 0.029$. This case for DMS is from Blomquist et al. (2010), where $\Delta C = 2.0$ ppbv, which yields $R = 50$ pptv. Their sensor has a white noise level of 4 pptv²/Hz, which, at $f_x = 5$ Hz, corresponds to a resolution of 6.3 pptv. Thus, sensor noise makes a negligible contribution to uncertainty in covariance DMS flux estimates with their device (see their Fig. 8). The situation is not as favorable for CO₂. If we use a typical commercial sensor with resolution of 0.2–0.3 ppm, then we need $\Delta C > 100$ ppm to obtain < 10% contribution of sensor noise to the flux uncertainty. Most of the open ocean has $\Delta C < 20$ ppm. Open-ocean CO₂ flux measurements require almost an order of magnitude improvement in fast CO₂ sensors to meet the requirement.

For an additional example, Perlinger and Rowe (2008) measured hexachlorobenzene (HCB) flux over Lake Superior as a function of downwind fetch from shore on 14

**Chemical sensor
resolution
requirements**

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



July 2006 using the modified Bowen ratio gradient method assuming a turbulent diffusion coefficient equal to that of sensible heat with samplers at $z_2 = 10$ and $z_1 = 1$ m. At the 15-, 30-, and 60-km fetch stations, $z/L = 0.12, 0.70, 1.03$, $|\Delta C| = 70, 50, 40 \text{ pg m}^{-3}$, and from Fig. 2 $AP'_g = 5, 9, \text{ and } 11$, respectively. Figure 3 gives CP_c of 4.3×10^{-3} for HCB. Application of Eq. (29) gives $R = 0.1, 0.2, \text{ and } 0.2 \text{ pg m}^{-3}$ for the three stations, respectively. Perlinger and Rowe (2008) estimated an overall method precision of 9% from duplicate measurements, or ca. 5 pg m^{-3} , indicating that greater method precision is required to reduce the contribution of sensor resolution to uncertainty in the flux measurement to $< 10\%$ using this method.

4.3 Random noise/resolution contributions, flux uncertainty, and time averaging

In their original treatment BD90 did not explicitly consider averaging time of the observations which may lead to some confusion in the interpretation of flux uncertainty versus the fraction of uncertainty contributed by noise and/or sensor resolution. Sample length must be addressed to explicitly account for uncertainty in covariance flux measurements. For example, Blomquist et al. (2010) state the uncertainty in covariance flux measurements as

$$\delta(\overline{w'c'})_T = \sigma_w \delta(\overline{C})_T = \frac{2\sigma_w}{\sqrt{T}} [\sigma_{c_1}^2 \tau_1 + R^2 / (4f_x)]^{1/2} \quad (30)$$

Here it is clear that, while the resolution may contribute some fraction to the uncertainty, the total error can be reduced to an arbitrary limit by increasing the averaging time. Alternatively, an ensemble of data may be assembled and individual 1-h observations may be grouped (say, by wind speed) and averaged. The sampling uncertainty of a typical 1-h covariance flux estimate of a well-resolved scalar (such as water vapor) is on the order of 25% (Fairall et al., 2003; Blomquist et al., 2010). Thus, approximately six independent flux estimates could be averaged and the uncertainty of the average flux would be on the order of 10% (i.e., $25\%/\sqrt{6}$). On the other hand, suppose

Chemical sensor resolution requirements

M. D. Rowe et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

a sensor with poor resolution is used and the total uncertainty for a 1-h observation is increased substantially. For example, consider the case for CO₂ with a sensor resolution of 0.30 ppm in conditions where ΔC = 20 ppm, as discussed above. From Eq. (30) we estimate the flux uncertainty for a 1-h sample would be increased to 66%. Now we would require almost 45 independent observations to be able to compute an average flux with uncertainty of 10%.

An error analysis shows that the gradient method has some major differences compared to the covariance method. Consider the basic gradient flux equation from BD90

$$\overline{w'c'} = -\frac{\kappa u_*}{G} \Delta C_{21} \quad (31)$$

where ΔC₂₁ is concentration difference between heights z₂ and z₁. An error expansion of Eq. (31) yields

$$\left(\frac{\delta(\overline{w'c'})_T}{(\overline{w'c'})_T} \right)^2 = \left(\frac{\delta u_*}{u_*} \right)^2 + \left(\frac{\delta G}{G} \right)^2 + \left(\frac{\delta(\Delta C_{21})}{\Delta C_{21}} \right)^2 \quad (32)$$

Unlike the covariance flux, the uncertainty in the gradient flux also depends on the uncertainty of the determination of u_{*} and the factor G which may involve uncertainties in empirical stability functions and the estimate of z/L. (Note that for the modified Bowen ratio gradient approach mentioned in the example above, the first two terms on the right-hand side in Eq. (32) are replaced by $\left(\frac{\delta(\overline{w'\theta'})_T}{(\overline{w'\theta'})_T} \right)^2$ and $\left(\frac{\delta(\Delta\theta_{21})}{\Delta\theta_{21}} \right)^2$, respectively, where θ represents potential temperature. In this case it is unnecessary to estimate u_{*} and G and their associated uncertainties.) The uncertainty in the concentration difference is

$$(\delta(\Delta C_{21}))^2 = 2(R^2 + \sigma_{c1}^2 \tau_1/T) \quad (33)$$

This closely resembles Eq. (10) for covariance fluxes except now the resolution term characterizes the instrumental/analytical precision in the 1-h average concentrations

**Chemical sensor
resolution
requirements**

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Chemical sensor
resolution
requirements**

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(e.g., the 9% variability for HCB in the duplicate samples quoted by Perlinger and Rowe, 2008), so it is not divided by T . If T is sufficiently long the second term is negligible, and, if uncertainty in u_* and G are neglected, Eq. (32) reduces to BD90's original equation. For the modified Bowen ratio example above the second term in Eq. (33) will be less than R^2 when T is greater than 1 s, so the error in 1-h samples is dominated by the precision of the chemical analysis. For example, the measurement precision in this case (5 pg m^{-3}) is larger than the atmospheric variability (σ_c about 1 pg m^{-3}), so sampling variability does not contribute significantly to uncertainty. Even if these numbers ($R = 0.2\sigma_c$) were reversed atmospheric variability would be negligible for a 1-h average. Ensemble averaging can be used to reduce uncertainty for the gradient method in the same way as described for eddy covariance.

5 Conclusions

An updated and improved approach was described to estimate the required sensor resolution to limit to 10% the contribution of the sensor to uncertainty in micrometeorological atmosphere-surface exchange flux measurements using eddy covariance, gradient, and relaxed eddy accumulation methods. A change was made to the approach presented by Businger and Delany (1990), which results in a less stringent resolution requirement for eddy covariance than was estimated by their approach. The stability functions used to predict dimensionless standard deviation of a scalar caused by turbulent fluctuations were compared to water vapor measurements from recent field experiments. For $z/L < 0$, there was good agreement between existing functions and the data, while for $z/L > 0$ the various data sets do not agree. The functions proposed by Andreas et al. (1998) were selected as the best approximation to the data. The empirical functions and figures presented here can be used to consider the feasibility of flux measurement methods for planned field experiments.

List of symbols with SI units

b	empirical coefficient [-]
b_{th}	three-reservoir REA calibration coefficient [-]
c'	turbulent fluctuation of scalar C [kg m^{-3}]
c_*	chemical flux scaling parameter ($-w'c'/u_*$) [kg m^{-3}]
f	frequency [s^{-1}]
$f_c(z/L)$	similarity function for dimensionless scalar standard deviation [-]
f_m	frequency corresponding to the peak in the vertical velocity or scalar variance spectral density, or, alternatively, the $w - c$ cospectrum [s^{-1}]
$f_w(z/L)$	similarity function for vertical wind velocity standard deviation [-]
$f_\tau(z/L)$	similarity function for scalar integral time scale [-]
f_x	maximum frequency of band-limited white noise (Nyquist frequency) [s^{-1}]
u_*	friction velocity [m s^{-1}]
w'	turbulent variations of vertical velocity [m s^{-1}]
$\overline{w'c'}$	vertical turbulent flux of scalar C [$\text{kg m}^{-2} \text{s}^{-1}$]
x	subscript indicating flux measurement method (either cov = covariance, g = gradient, or r = relaxed eddy accumulation) [-]
z	distance upward from the surface [m]. For land-based measurements, $z - d$ is used in place of z , where d is the displacement height of the canopy.
z_2, z_1	upper and lower heights above the surface in gradient flux measurement [m]
A, B	empirical coefficients [-]
AP'_x	BD90 atmospheric parameter for flux measurement method x [$\text{m}^{-1} \text{s}$]
AP'_x	redefined atmospheric parameter [-]

**Chemical sensor
resolution
requirements**

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



C	concentration of scalar C [kg m^{-3}]
$\delta(C)$	uncertainty in C [-]
ΔC	water-air concentration difference in C at specified reference depth and height [kg m^{-3}]
ΔC_{12}	concentration difference between heights z_2 and z_1 in a gradient measurement or reservoirs 1 and 2 in an REA measurement [kg m^{-3}]
CP_c	chemical parameter for C [-]
G	stability function for the gradient method [-]
L	Monin-Obukhov stability length [m]
N_c	rate of dissipation of the variance of C [$\text{kg m}^{-3} \text{s}^{-1}$]
R	sensor resolution required to conduct chemical flux measurement to an estimated 10% uncertainty [kg m^{-3}]
Sc	Schmidt number [-]
T	integral time period of a measurement [s]
U_r	mean wind speed relative to the sensor at the sensor height [m s^{-1}]
α_c	dimensionless solubility (liquid over gas) of chemical C [-]
θ	potential temperature [K]
κ	von Kármán constant, assumed to have a value of 0.4 [-]
k_c	air-water transfer velocity of scalar C [m s^{-1}]
σ_c	standard deviation of C [kg m^{-3}]
σ_{c1}	standard deviation of C associated with turbulent fluctuations [kg m^{-3}]
σ_{c2}	standard deviation of C associated with sensor white noise [kg m^{-3}]
σ_w	standard deviation of vertical wind velocity [m s^{-1}]
σ_{wn}	standard deviation of white noise in measurement of C [m s^{-1}]
τ	integral (decorrelation) time scale [s]
τ_1, τ_{wc}	integral time scale of turbulent fluctuations in c [s]
τ_2, τ_{wn}	integral time scale associated with white noise in measurement of C [s]

Chemical sensor resolution requirements

M. D. Rowe et al.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


τ_{cD}	turbulent mixing/dissipation time scale for variance of C [s]
$\phi_c(z/L)$	similarity function for the dimensionless scalar mean gradient [–]
ϕ_{wn}	variance spectral density of band-limited white noise in C measurement [(kg m ⁻³) ² s]
$\phi_\sigma(z/L)$	similarity function for the dimensionless scalar standard deviation [–]
$\Psi(z/L)$	similarity function for the dimensionless scalar vertical concentration profile [–]

Acknowledgements. C. Fairall's contributions are supported by the NOAA Health of the Atmosphere Program and the NOAA Climate Observations Division.

References

- 5 Andreas, E. L., Hill, R. J., Gosz, J. R., Moore, D. I., Otto, W. D., and Sarma, A. D.: Statistics of surface-layer turbulence over terrain with metre-scale heterogeneity, *Bound.-Layer Meteorol.*, 86, 379–408, 1998.
- Blomquist, B. W., Huebert, B. J., Fairall, C. W., and Faloon, I. C.: Determining the sea-air flux of dimethylsulfide by eddy correlation using mass spectrometry, *Atmos. Meas. Tech.*, 3, 1–20, doi:10.5194/amt-3-1-2010, 2010.
- 10 Blomquist, B. W., Fairall, C. W., Huebert, B. J., Kieber, D. J., and Westby, G. R.: DMS sea-air transfer velocity: Direct measurement by eddy covariance and parameterization based on the NOAA/COARE gas transfer model, *Geophys. Res. Lett.*, 33, 1–4, 2006.
- Bowling, D. R., Delany, A. C., Turnipseed, A. A., and Baldocchi, D. D.: Modification of the relaxed eddy accumulation technique to maximize measured scalar mixing ratio differences in updrafts and downdrafts, *J. Geophys. Res.*, 104, 9121–9133, 1999.
- 15 Businger, J. A. and Delany, A. C.: Chemical sensor resolution required for measuring surface fluxes by three common micrometeorological techniques, *J. Atmos. Chem.*, 10, 399–410, 1990.
- 20 Businger, J. A. and Oncley, S. P.: Flux measurement with conditional sampling, *J. Atmos. Oceanogr. Technol.*, 7, 349–352, 1990.
- Choi, T., Hong, J., Kim, J., Lee, H., Asanuma, J., Ishikawa, H., Tsukamoto, O., Zhiqui, G., Ma, Y., Ueno, K., Wang, J., Koike, T., and Yasunari, T.: Turbulent exchange of heat, water vapor,

24428

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- and momentum over a Tibetan prairie by eddy covariance and flux variance measurements, *J. Geophys. Res.*, 109(D21), D21106.1–D21106.12, doi:10.1029/2004JD004767, 2004.
- DeZoeke, S. P., Fairall, C. W., and Pezoa, S.: Ship observations of the tropical Pacific Ocean along the coast of South America, *J. Climate*, 22, 458–464, 2009.
- 5 Edson, J. and Fairall, C.: Similarity relationships in the marine atmospheric surface layer for terms in the TKE and scalar variance budgets, *J. Atmos. Sci.*, 55, 2311–2338, 1998.
- Fairall, C. W., Bradley, E. F., Hare, J. E., Grachev, A. A., and Edson, J. B.: Bulk parameterization of air-sea fluxes: updates and verification for the COARE Algorithm, *J. Climate*, 16, 571–591, 2003.
- 10 Fairall, C. W., Bariteau, L., Grachev, A. A., Hill, R. J., Wolfe, D. E., Brewer, W. A., Tucker, S. C., Hare, J. E., and Angevine, W. M.: Turbulent bulk transfer coefficients and ozone deposition velocity in the International Consortium for Atmospheric Research into Transport and Transformation, *J. Geophys. Res.*, 111(D23), D23S20.1–D23S20.19, doi:10.1029/2006JD007597, 2006.
- 15 Grachev, A., Fairall, C., Persson, P., Andreas, E., Guest, P., and Jordan, R.: Turbulence decay in the stable Arctic boundary layer, Seventh Conference on Polar Meteorology and Oceanography and Joint Symposium on High-Latitude Climate Variations, Hyannis, MA, 2003,
- Hilal, S. H., Carreira, L. A., and Karickhoff, S. W.: Prediction of the solubility, activity coefficient, gas/liquid and liquid/liquid distribution coefficients of organic compounds, *QSAR Comb. Sci.*, 23, 709–720, 2004, SPARC On-Line Calculator <http://ibmlc2.chem.uga.edu/sparc/>, accessed 7 August 2010.
- 20 Johnson, M. T.: A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas, *Ocean Sci. Discuss.*, 7, 251–290, doi:10.5194/osd-7-251-2010, 2010.
- 25 Kaimal, J. C. and Finnigan, J. J.: *Atmospheric Boundary Layer Flows*, Oxford University Press, New York, NY, 289 pp., 1994.
- Lenschow, D. and Kristensen, L.: Uncorrelated noise in turbulence measurements, *J. Atmos. Oceanic Technol.*, 2, 68–81, 1985.
- Lindqvist, O.: Atmospheric mercury – a review, *Tellus*, 37B, 136–159, 1985.
- 30 McGillis, W. R., Edson, J. B., Zappa, C. J., Ware, J. D., McKenna, S. P., Terray, E. A., Hare, J. E., Fairall, C. W., Drennan, W., Donelan, M., DeGrandpre, M. D., Wanninkhof, R., and Feely, R. A.: Air-sea CO₂ exchange in the equatorial Pacific, *J. Geophys. Res.*, 109, C08S02, doi:10.1029/2003JC002256, 2004.

- Panofsky, H. A. and Dutton, J. A.: Atmospheric Turbulence: Models and Methods for Engineering Applications, John Wiley and Sons, New York, NY, 397 pp., 1984.
- Park, C., Schade, G. W., and Boedeker, I.: Flux measurements of volatile organic compounds by the relaxed eddy accumulation method combined with a GC-FID system in urban Houston, Texas, Atmos. Environ., 44, 2605–2614, 2010.
- 5 Perlinger, J. A., Tobias, D. E., Morrow, P. S., and Doskey, P. V.: Evaluation of novel techniques for measurement of air-water exchange of persistent bioaccumulative toxicants in Lake Superior, Environ. Sci. Technol., 39, 8411–8419, 2005.
- 10 Perlinger, J. A. and Rowe, M. D.: Atmospheric transport and air-water exchange of hexachlorobenzene in Lake Superior, Organohalogen Compounds, 70, 598–601, 2008.
- Sander, R.: Compilation of Henrys Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3): online available at: www.henryslaw.org, 1999, access 18 June 2010.
- 15 Sanemasa, I.: The solubility of elemental mercury vapor in water, B. Chem. Soc. Jpn., 48, 1795–1798, 1975.
- Walker, J. T., Robarge, W. P., Wu, Y., and Meyers, T. P.: Measurement of bi-directional ammonia fluxes over soybean using the modified Bowen-ratio technique, Agr. Forest Meteorol., 138, 54–68, 2006.

**Chemical sensor
resolution
requirements**M. D. Rowe et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Chemical sensor resolution requirements

M. D. Rowe et al.

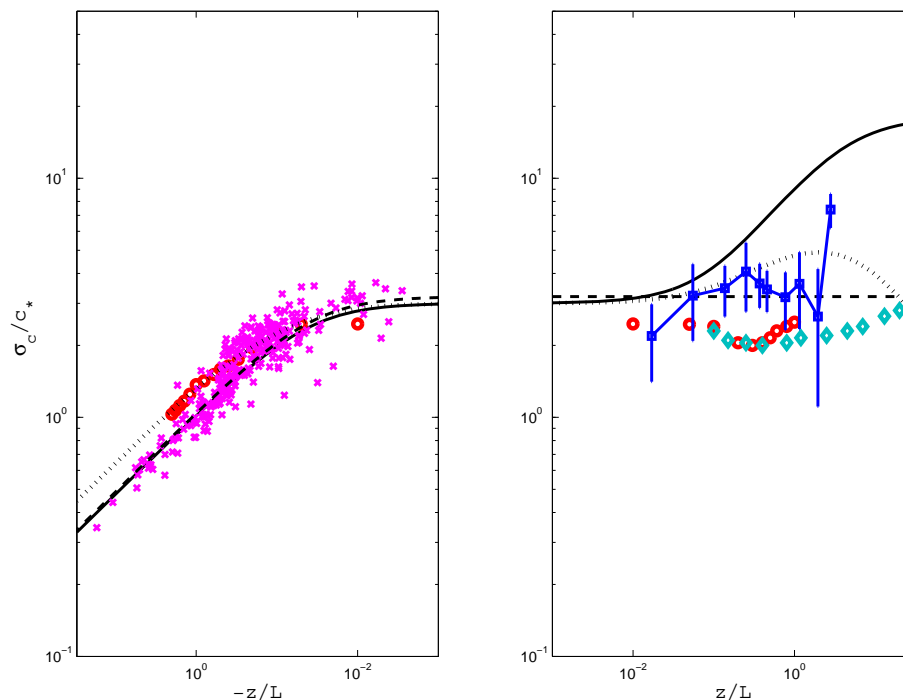


Fig. 1. Dimensionless scalar standard deviation versus stability, z/L : left panel, unstable conditions ($z/L < 0$) and right panel, stable conditions ($z/L > 0$). Lines are mathematical representations: solid – Blomquist et al. (2010, Eqs. 26a, b); dashed – Andreas et al. (1998, Eq. 5.9a, b, $C = 3.2$), and dotted – Eq. (21) with the COARE3.0 gradient function and Eq. (20). The magenta x's are hourly data from Stratus07; solid circles – digitized from BD90 Fig. 1; Diamonds – data from SHEBA; and squares – data from NEAQS.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

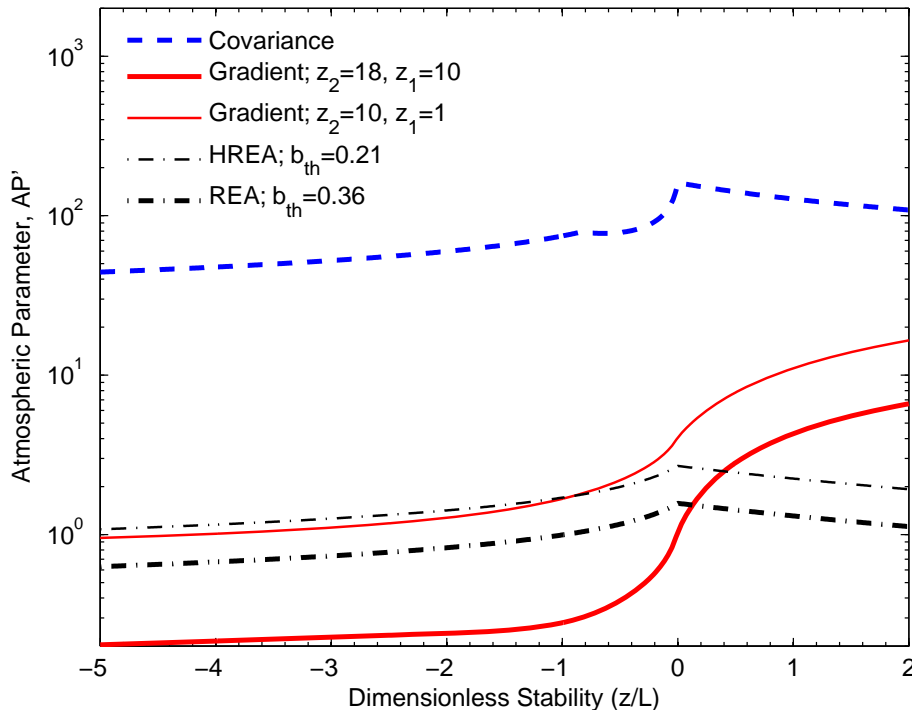



Fig. 2. Comparison of the required sensor resolution as a function of stability for three flux measurement methods as indicated by the redefined atmospheric parameter, AP'_x . Wind speed is 8 m s^{-1} and instrument height is 18 m for covariance and (H)REA methods. Two cases are shown for the gradient method: For the gradient method, a typical ocean, ship-based installation with $z_2 = 18 \text{ m}$ and $z_1 = 10 \text{ m}$, and a lake or land-based installation with $z_2 = 10 \text{ m}$ and $z_1 = 1 \text{ m}$, are considered.

Chemical sensor resolution requirements

M. D. Rowe et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Chemical sensor resolution requirements

M. D. Rowe et al.

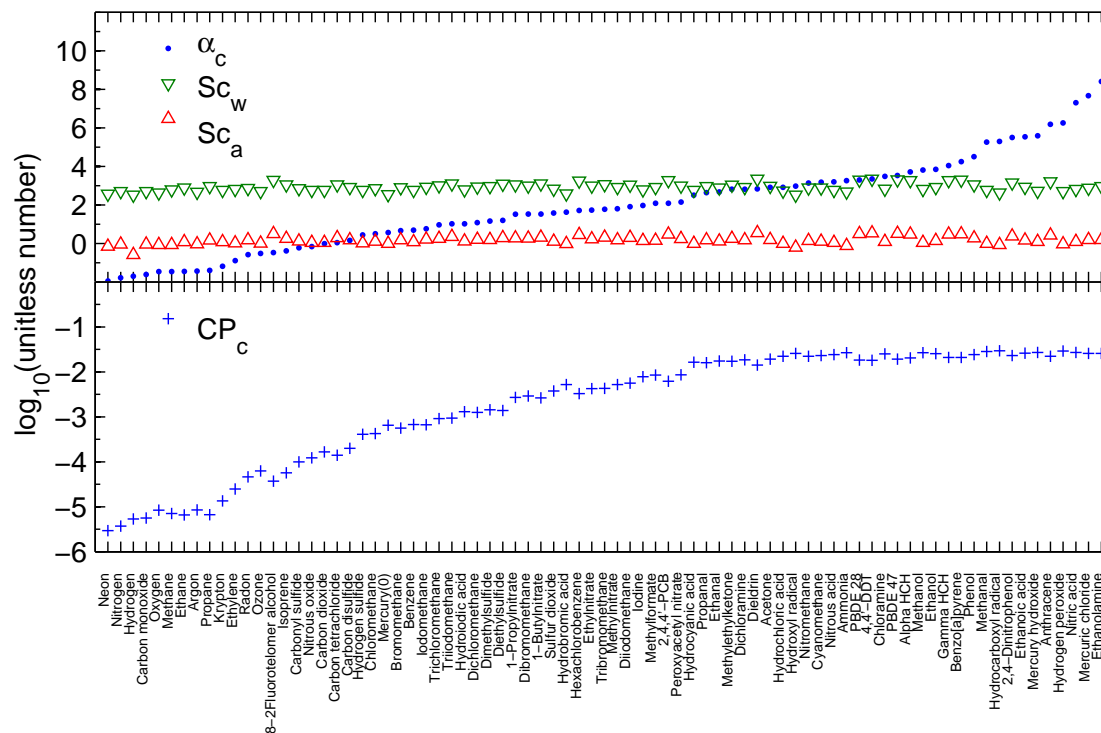


Fig. 3. The chemical parameter, CP_c , computed as in Eq. (29b), for chemicals having a range in solubility at 20 °C. For information about values of the other parameters used in computing these CP_c values, see the text. CP_c can be multiplied by AP'_x from Fig. 2 to obtain the required sensor resolution for a given flux measurement method and specified stability. Solubility and air- and water-side Schmidt numbers are shown for comparison.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

