

Supplement of

Comparison of VOC measurements made by PTR-MS, Adsorbent Tube/GC-FID-MS and DNPH-derivatization/HPLC during the Sydney Particle Study, 2012: a contribution to the assessment of uncertainty in current atmospheric VOC measurements

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Supplementary Information

S.1 Measurement Uncertainty Analysis

The uncertainty analysis of these measurement proceeds via the mathematical model, here called the measurement equation, for the measurement following the Guide to Expression of Uncertainty in Measurement and the law of propagation of uncertainty (JCGM, 2008b) also known as the error propagation equation (Bevington and Robinson, 1992; Harris, 2003). All uncertainties in this analysis are expanded uncertainties with a coverage factor $k = 2$. The associated level of confidence of the uncertainty interval is typically 95%.

The equation for propagation of uncertainty for a measurement equation:

$x = f(u, v, \dots)$ is:

$$\sigma_x^2 = \sigma_u^2 \left(\frac{\partial x}{\partial u}\right)^2 + \sigma_v^2 \left(\frac{\partial x}{\partial v}\right)^2 + 2\sigma_{uv} \left(\frac{\partial x}{\partial u}\right) \left(\frac{\partial x}{\partial v}\right) \dots$$

In this equation and subsequent uncertainty interpretations, variances are represented as population values. In the calculations the experimentally determined variances are used.

In this analysis, based on a knowledge of the measurement procedure, some uncertainties are set as random and can be diminished by multiple observations, whereas others are fixed. We assume that all errors evaluated here are uncorrelated.

This analysis involves more detail than is normally documented for air quality measurement uncertainty as presented in ISO 20988 (ISO, 2007).

The atmospheric units used for VOCs are parts per billion by volume (10^{-9} v/v) for the purpose of making this analysis compatible with most current studies of VOCs. The SI unit is mole fraction.

S1.1 PTR-MS Measurement Uncertainty

The basic equation for measurement by the PTR-MS includes the following terms:

- C mixing ratio in gas phase of compound measured
- I signal intensity (normalized cps)
- F flow rate in the calibration system (mL min^{-1})

With subscripts

- s the reference gas standard in the cylinder
- a ambient
- z zero mode
- d dilution (flow)

The measurement equation for PTR-MS is:

$$C_a = \frac{C_s}{(I_s - I_z)} \times \frac{F_s}{(F_s + F_d)} \times (I_a - I_z)$$

Equation S1

Represent

$$I_s - I_z \text{ by } I_s^1$$

$$I_a - I_z \text{ by } I_a^1$$

$$F_s + F_d \text{ by } F_d^1$$

Calculate the uncertainties

$$\sigma_{I_s^1}, \sigma_{I_a^1}, \sigma_{F_d^1}, \sigma_{C_s}, \sigma_{F_s}$$

Substitute in the following equation:

$$\sigma_{C_a}^2 = \sigma_{C_s}^2 \left(\frac{C_a}{C_s}\right)^2 + \sigma_{F_s}^2 \left(\frac{C_a}{F_s}\right)^2 + \sigma_{I_a^1}^2 \left(\frac{C_a}{I_a^1}\right)^2 + \sigma_{I_s^1}^2 \left(\frac{C_a}{I_s^1}\right)^2 + \sigma_{F_d^1}^2 \left(\frac{C_a}{F_d^1}\right)^2$$

Equation S2

For the purposes of this analysis, C_a was represented by the mean VMR (ppbv) of the dataset, and I_a^1 and by the median zero corrected ion signals (ncps) of the sample data set.

We assumed:

$I_s^1, I_a^1, \sigma_{I_a^1}$ and $\sigma_{I_s^1}$ were determined from the daily calibration, ambient and zero measurements.

F_s, F_d^1 and $\sigma_{F_d^1}, \sigma_{F_s^1}$ were determined from multiple calibrations, performed before and after the field campaign, of the mass flow controllers which were used to control the flows of the dilution (F_d) and calibration gas standards (F_s).

The combined standard uncertainty, with coverage, $k = 2$, for an individual measurement is derived from Equation S2..

The combined standard uncertainty, with coverage, $k = 2$, for the mean value of a set of N measurements is derived from Equation S3.

$$\sigma_{C_a}^2 = \sigma_{C_s}^2 \left(\frac{C_a}{C_s}\right)^2 + \sigma_{F_s}^2 \left(\frac{C_a}{F_s}\right)^2 + \sigma_{F_d^1}^2 \left(\frac{C_a}{F_d^1}\right)^2 + \frac{\sigma_{I_a^1}^2 \left(\frac{C_a}{I_a^1}\right)^2 + \sigma_{I_s^1}^2 \left(\frac{C_a}{I_s^1}\right)^2}{\sqrt{N}}$$

Equation S3

S1.2 AT-VOC Measurement Uncertainty

The basic equation for measurement by the AT-VOC method includes the following terms:

- C mixing ratio in gas phase of compound measured
- A peak area
- V volume, V_m molar volume, V_i = volume measured by instrument under ambient conditions
- P pressure
- T temperature
- M mass, M_s molecular mass of a compound

With subscripts

- s the reference gas standard in the cylinder, standard temp and pressure,
- a ambient

l	loop
m	molecular or standard conditions
i	instrument output
r	replicate measurements

The equation for mass injected from the loop per standard injection is:

$$M_l = (V_l \times P_l \times T_s \times M_s \times C_s) / (V_m \times P_s \times T_l) \quad \text{Equation S4}$$

The mass in an ambient sample is:

$$M_a = M_l \times A_a / A_s \quad \text{Equation S5}$$

where

A_a is the peak area of the ambient sample minus the average of the peak areas in the blanks.

A_s is the peak area of the calibration sample

Volume of an ambient sample under standard conditions

$$V_a = (V_i \times P_a \times T_s) / (P_s \times T_a) \quad \text{Equation S6}$$

The equation for concentration calculation is:

$$C_a = M_a \times V_m / (V_a \times M_s) \quad (\text{units mixing ratio}) \quad \text{Equation S7}$$

This can be expanded by substitution.

$$C_a = (C_s \times V_l) \times \left\{ \frac{P_l}{A_s \times T_l} \right\} \times \left\{ \frac{T_a \times A_a}{V_i \times P_a} \right\} \quad (\text{units mixing ratio}) \quad \text{Equation S8}$$

The uncertainty in the VOC measurement can be calculated from the uncertainties of the 3 terms on the RHS of Equation B5. The first is the uncertainty in the standard injection, the second the uncertainty in replicate measurements of the standard, and the third the uncertainty in the measurement of replicate ambient measurements. In the case of AT-VOC measurements there were two occasions when 8 sets of sampling equipment were run simultaneously and analysed on the same equipment. The repeatability of these measurements, $\sigma_{C_r}^2$, incorporates all uncertainties due to the third term on the RHS of Equation B5 and is used for such in the uncertainty analysis. Note that in the case of C₈ aromatics allowance is made for the fact 3 peak areas (ethyl-benzene; m- + p-xylene; o-xylene) are used not one as with other compounds.

The combined standard uncertainties uncertainty, with coverage, k = 2, for an individual measurement is derived from Equation S9.

$$\sigma_{C_a}^2 = \sigma_{C_s}^2 \left(\frac{C_a}{C_s} \right)^2 + \sigma_{A_s}^2 \left(\frac{C_a}{A_s} \right)^2 + \sigma_{V_l}^2 \left(\frac{C_a}{V_l} \right)^2 + \sigma_{T_l}^2 \left(\frac{C_a}{T_l} \right)^2 + \sigma_{P_l}^2 \left(\frac{C_a}{P_l} \right)^2 + \sigma_{C_r}^2 (C_a)^2$$

Equation S9

The combined standard uncertainty, with coverage, k = 2, for the mean value of a set of N measurements is derived from Equation B6.

$$\sigma_{C_a}^2 = \sigma_{C_s}^2 \left(\frac{C_a}{C_s} \right)^2 + \sigma_{A_s}^2 \left(\frac{C_a}{A_s} \right)^2 + \sigma_{V_l}^2 \left(\frac{C_a}{V_l} \right)^2 + \sigma_{T_l}^2 \left(\frac{C_a}{T_l} \right)^2 + \sigma_{P_l}^2 \left(\frac{C_a}{P_l} \right)^2 + \frac{\sigma_{C_r}^2 (C_a)^2}{\sqrt{N}}$$

Equation S10

S1.3 DNPH-VOC Measurement Uncertainty

The basic equation for measurement by the DNPH method follows USEPA Method TO11A and includes the following terms:

Ca	concentration in gas phase of compound measured
Cs	concentration of standard in liquid phase
A	peak area
V	volume, V_s volume of standard injection
P	pressure
T	temperature
M	mass

With subscripts

s	the reference gas standard in the cylinder, standard temp and pressure, molecular mass
a	ambient
m	molecular or standard conditions

The instrument response factor determined from a standard injection is RF_s

$$RF_s = \frac{(A_s - A_z)}{C_s} \quad (\text{units area/mass/unit volume}) \quad \text{Equation S11}$$

The mass in an ambient sample is (ng):

$$M_a = \frac{(A_a - A_z) \times V_e}{RF_s} \quad (\text{units mass}) \quad \text{Equation S12}$$

Where A_a is the mass in the sample minus the average mass in the blanks; V_e is the acetonitrile extract volume.

By substitution:

$$M_a = \frac{(A_a - A_z) \times C_s \times V_e}{(A_s - A_z)} \quad \text{Equation S13}$$

Volume of an ambient sample under standard conditions (nL)

$$V_a = \frac{M_a}{M_s} \times (RT_a) \times \frac{P_s}{P_a} \quad \text{Equation S14}$$

The equation for concentration (ppbv) calculation is:

$$C_a = V_a / V_{\text{sample}} \quad \text{Equation S15}$$

Where V_{sample} is the total volume of air sampled (L).

The measurement equation for DNPH-VOC is:

$$C_a = \frac{C_s \times R \times P_s}{M_s} \times \frac{1}{(A_s - A_z)} \times \frac{T_a}{(P_a \times V_{\text{sample}})} \times [V_e \times (A_a - A_z)] \quad \text{Equation S16}$$

Note in the first term in the RHS only C_s is a variable and has uncertainty and this is associated with the standard. The second term on the RHS is associated with standard injections, the third term is associated with the volume of the ambient sample and the fourth term associated with ambient sampling.

Represent

$$A_s - A_z \text{ by } A_s^1$$

$$A_a - A_z \text{ by } A_a^1$$

Calculation of the uncertainties:

$$\sigma_{C_a}^2 = \sigma_{C_s}^2 \left(\frac{C_a}{C_s}\right)^2 + \sigma_{A_s^1}^2 \left(\frac{C_a}{A_s^1}\right)^2 + \sigma_{C_r}^2 \left(\frac{C_a}{C_r}\right)^2$$

Equation S17

The combined standard uncertainty, with coverage, $k = 2$, for a single measurement is derived from Equation S17.

The combined standard uncertainty, with coverage, $k = 2$, for the mean value of a set of N measurements is derived from Equation S18.

$$\sigma_{C_a}^2 = \sigma_{C_s}^2 \left(\frac{C_a}{C_s}\right)^2 + \sigma_{A_s}^2 \left(\frac{C_a}{A_s}\right)^2 + \frac{\sigma_{C_r}^2 \left(\frac{C_a}{C_r}\right)^2}{\sqrt{N}}$$

Equation S18