Atmospheric
Measurement
Techniques

Measuring OVOCs and VOCs by PTR-MS in an urban roadside microenvironment of Hong Kong: relative humidity and temperature dependence, and field intercomparisons

Long Cui[1], Zhou Zhang[2], Yu Huang[3,4], Shun Cheng Lee[1], Donald Ray Blake[5], Kin Fai Ho[6], Bei Wang[7], Yuan Gao[1,8], Xin Ming Wang[2], and Peter Kwok Keung Louie[9]

[1]Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University,
Hung Hom, Hong Kong, China
[2]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry,
Chinese Academy of Sciences, Guangzhou, China
[3]Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences,
Xi'an, China
[4]State Key Lab of Loess and Quaternary Geology (SKLLQG), Institute of Earth Environment,
Chinese Academy of Sciences, Xi'an, China
[5]Department of Chemistry, University of California, Irvine, CA, USA
[6]School of Public Health and Primary Care, The Chinese University of Hong Kong,
Shatin, Hong Kong, China
[7]Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong,
Hong Kong, China
[8]Department of Civil Engineering, Chu Hai College of Higher Education,
New Territories, Hong Kong, China
[9]Hong Kong Environmental Protection Department, Revenue Tower, 5 Gloucester Road,
Wanchai, Hong Kong, China

Correspondence to: Shun Cheng Lee (ceslee@polyu.edu.hk)

Abstract. Volatile organic compound (VOC) control is an important issue of air quality management in Hong Kong because ozone formation is generally VOC limited. Several oxygenated volatile organic compound (OVOC) and VOC measurement techniques – namely, (1) offline 2,4-dinitrophenylhydrazine (DNPH) cartridge sampling followed by high-performance liquid chromatography (HPLC) analysis; (2) online gas chromatography (GC) with flame ionization detection (FID); and (3) offline canister sampling followed by GC with mass spectrometer detection (MSD), FID, and electron capture detection (ECD) – were applied during this study. For the first time, the proton transfer reaction–mass spectrometry (PTR-MS) technique was also introduced to measured OVOCs and VOCs in an urban road-side area of Hong Kong. The integrated effect of ambient relative humidity (RH) and temperature (T) on formaldehyde measurements by PTR-MS was explored in this study. A Poly 2-D regression was found to be the best nonlinear surface simulation ($r = 0.97$) of the experimental reaction rate coefficient ratio, ambient RH, and T for formaldehyde measurement. This correction method was found to be better than correcting formaldehyde concentrations directly via the absolute humidity of inlet sample, based on a 2-year field sampling campaign at Mong Kok (MK) in Hong Kong. For OVOC species, formaldehyde, acetaldehyde, acetone, and MEK showed good agreements between PTR-MS and DNPH-HPLC with slopes of 1.00, 1.10, 0.76, and 0.88, respectively, and correlation coefficients of 0.79, 0.75,

0.60, and 0.93, respectively. Overall, fair agreements were found between PTR-MS and online GC-FID for benzene (slope = 1.23, $r = 0.95$), toluene (slope = 1.01, $r = 0.96$) and C_2-benzenes (slope = 1.02, $r = 0.96$) after correcting benzene and C_2-benzenes levels which could be affected by fragments formed from ethylbenzene. For the intercomparisons between PTR-MS and offline canister measurements by GC-MSD/FID/ECD, benzene showed good agreement, with a slope of 1.05 ($r = 0.62$), though PTR-MS had lower values for toluene and C_2-benzenes with slopes of 0.78 ($r = 0.96$) and 0.67 ($r = 0.92$), respectively. All in all, the PTR-MS instrument is suitable for OVOC and VOC measurements in urban roadside areas.

1 Introduction

Volatile organic compounds (VOCs), which are important precursors of tropospheric ozone and secondary organic aerosols (SOAs) (Sillman, 2002), can be emitted from multiple anthropogenic sources (e.g., vehicular emissions, industrial emissions, and solvent usage) and biogenic sources (Watson et al., 2001; Atkinson and Arey, 2003). VOCs also have adverse impact on human beings (von Schneidemesser et al., 2010; Lelieveld et al., 2015). As one of the most densely populated cities in the world, Hong Kong has over 7.2 million people and more than 699 540 registered vehicles in an area of $1104\,km^2$ as of December 2014 (Hong Kong Transport Department, 2014). Special attention has been paid to the characteristics of roadside VOCs and their impacts on the local air quality of Hong Kong during the past years (Lee et al., 2002; Ho et al., 2004; Guo et al., 2007; Louie et al., 2013; Ling and Guo, 2014). Previous studies have shown that vehicular emissions are one of the major contributors to ambient VOCs in Hong Kong (Guo et al., 2007). Lau et al. (2010) found that 31–48 % of ambient VOCs in Hong Kong were generated by vehicle- and marine-vessel-related sources in 2002–2003, and the percentage increased to 40–54 % in 2006–2007.

In order to investigate urban roadside VOCs in Hong Kong, multiple sampling and analytical techniques were used, such as offline 2,4-dinitrophenylhydrazine (DNPH) cartridge sampling followed by high-performance liquid chromatography (HPLC) analysis for oxygenated volatile organic compounds (OVOCs); online gas chromatography (GC) with flame ionization detection (FID); and offline canister sampling followed by GC with mass spectrometer detection (MSD), FID, and electron capture detection (ECD) for VOCs (Ho et al., 2013; Cheng et al., 2014; Ou et al., 2015). These techniques, however, can be impacted by their relatively low sampling resolution that may lead to the underestimation or overestimation of ambient OVOC and VOC concentration levels (Wisthaler et al., 2008; Jobson et al., 2010; Wang et al., 2014). Moreover, since there is no single

technique that can measure all OVOCs and VOCs simultaneously, different kinds of sampling and analytical techniques are usually used to obtain the measurements of these species (Wisthaler et al., 2008; Ambrose et al., 2010; Jobson et al., 2010; Warneke et al., 2011a).

Proton transfer reaction-mass spectrometry (PTR–MS) is a relatively novel method that can fulfill online measurements of OVOCs and VOCs at trace levels in ambient air. Proton transfer enables soft ionization of chemical species that have a higher proton affinity (PA) than that of the reagent species (i.e., H_2O). PTR-MS does not need any sample treatment such as drying and/or precondensation like gas chromatographic analysis, and it is available for monitoring OVOCs which are quite difficult to quantify from canister samples. Hence, PTR-MS has recently been widely used in atmospheric chemistry research (de Gouw and Warneke, 2007; Jobson et al., 2010). PTR-MS has been used in China for environmental studies throughout the years (Wang et al., 2014, 2016). But PTR-MS was firstly used in an urban roadside microenvironment of Hong Kong to measure ambient OVOCs and VOCs in this study.

Formaldehyde (HCHO) is one of the most abundant OVOCs in Hong Kong. The lifetime of HCHO in the boundary layer is estimated to be only several hours when photolysis and its reaction with OH radical occur with sunlight. Because HCHO is carcinogenic (Kerns et al., 1983), it is one of the OVOCs of most interest in urban areas. Only offline DNPH cartridge sampling analyzed by HPLC has previously been used to determine the level of ambient formaldehyde in Hong Kong (Ho et al., 2002; Guo et al., 2004; Louie et al., 2013; Cheng et al., 2014). PTR-MS was introduced to measure ambient concentrations of formaldehyde continuously in this study. HCHO can be protonated by the following Reaction (R1):

$$HCHO + H_3O^+ \rightarrow HCHO \cdot H^+ + H_2O, \tag{R1}$$

$$HCHO \cdot H^+ + H_2O \rightarrow HCHO + H_3O^+. \tag{R2}$$
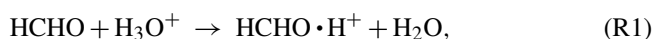
However, because the proton affinity (PA) of formaldehyde ($170.4\,kcal\,mol^{-1}$) is just slightly higher than that of water ($165.2\,kcal\,mol^{-1}$), the backward Reaction (R2) of protonated formaldehyde with H_2O can lead to an underestimation of HCHO by PTR-MS (Hansel et al., 1997). Jobson and McCoskey (2010) found that the sensitivity to HCHO can be improved by removing water vapor from the air sampling inlet. Correction for absolute humidity (AH) effects on HCHO measurement by PTR-MS was further discussed by Vlasenko et al. (2010). However, the previous studies did not fully discuss the effect of ambient relative humidity (RH) and/or temperature (T) separately and integratively on HCHO measurements by PTR-MS. In addition, few studies have reported intercomparisons between PTR-MS and DNPH-HPLC during field studies, especially in urban roadside areas.

In this study, PTR-MS was applied in Hong Kong to measure ambient OVOCs and VOCs coupled with other mea-

surement techniques. The effect of ambient conditions (RH and T) on OVOC and VOC measurements by PTR-MS is discussed in this paper. Detailed comparisons of PTR-MS, DNPH-HPLC, online GC-FID, and offline canister sampling followed by GC-MSD/FID/ECD for OVOC and VOC measurements at an urban roadside site in Hong Kong are conducted.

2 Methodology

2.1 Field sampling site

An urban roadside station, Mong Kok (MK) air quality monitoring station (AQMS), was chosen as the field sampling site in this study. This sampling site, which is one of the three roadside monitoring stations established by the Hong Kong Environment Protection Department (HKEPD), is located in a mixed commercial and residential area with heavy daily traffic in Hong Kong. Briefly, MK AQMS is the best representative of the roadside environment in Hong Kong, and more detailed information can be found elsewhere (Chan et al., 2002; Lee et al., 2002). The field study was conducted in May, August, and November 2013 and February, May, and August 2014 to cover the seasonal variations of traffic-related pollutants.

2.2 PTR-MS

A commercially available PTR-MS instrument (PTR-QMS 500, IONICON Analytik GmbH, Innsbruck, Austria) was used in this study. The PTR-MS instrument has been described in detail elsewhere (Lindinger et al., 1998; de Gouw et al., 2003; de Gouw and Warneke, 2007). Briefly, PTR-MS mainly consists of a discharge ion source, a drift tube, and a quadrupole mass spectrometer. In this study, H_3O^+ was utilized as the reagent ion, the drift tube was operated at 2.2 mbar pressure, and the electric field was maintained at 600 V difference. The E/N (E stands for the electric field strength, and N stands for the air density inside drift tube) value in the drift tube was kept at 136 Townsend (Td). The electric field maintains a controlled ion velocity in the drift tube so that the clustering of water ions can be reduced. The PTR-MS inlet system and the drift tube were maintained at 60 °C to minimize wall losses.

The PTR-MS instrument was located in a shelter with an air-conditioning system at the MK station. The inlet was located about 2 m above the ground. A $1/8''$ Teflon line was used as a sample line. The sample air was pumped at a flow rate of 75 mL min^{-1}, with an estimated residence time of 2 s in the inlet line. An in-line particulate filter (4.7 mm Teflon membrane filter assembly, Whatman Inc., Clifton, NJ, USA) was used to prevent particles from entering the instrument.

An Ionimed mixed-VOC gas standard (IONICON Analytik GmbH, Innsbruck, Austria) was used for PTR-MS calibration in this study. Seventeen species were contained
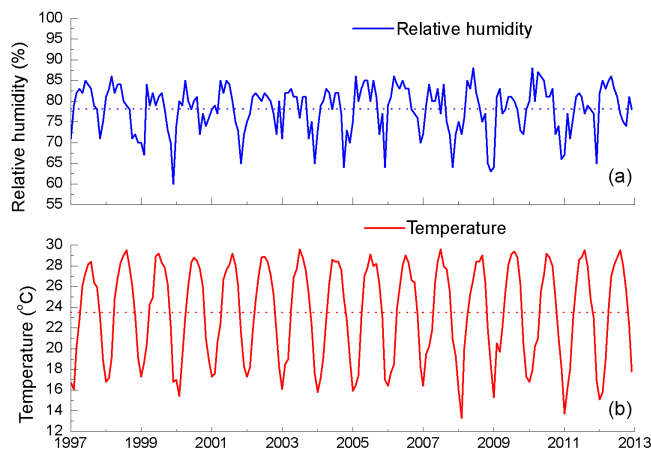

Figure 1. Statistics of relative humidity and temperature of Hong Kong from 1997 to 2012; dashed lines represent the average levels of RH and T (data were obtained from the Hong Kong Observatory).

in the gas standard, namely formaldehyde, methanol, acetonitrile, acetaldehyde, ethanol, acrolein, acetone, isoprene, crotonaldehyde, 2-butanone, benzene, toluene, o-xylene, chlorobenzene, α-pinene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene with mixing ratios about 1 ppm for each compound. Standard VOC gas mixtures (Supelco TO-14 Calibration Mix) were used for determining the transmission curve of the PTR-MS instrument. Zero air was generated by a gas calibration unit (GCU) (IONICON Analytik GmbH, Innsbruck, Austria) with a VOC scrubber installed inside the GCU. Background level was determined by zero air with the frequency of half an hour each day. The relative humidity and temperature of inlet gas were controlled by adjusting the humidification chamber and a dew point mirror inside the GCU. Ionimed mixed-VOC gas standard was diluted with four different ratios (0.08, 0.06, 0.04, and 0.001) to calibrate the PTR-MS. Calibrations were done every 6 days to ensure the accuracy of PTR-MS. The relative humidity and temperature of inlet gas for calibration were set at 80 % and 25 °C, respectively, according to the average level (RH = 78.2 % and T = 23.5 °C) of ambient air in Hong Kong from 1997 to 2012 (shown in Fig. 1; data were obtained from the Hong Kong Observatory, http://www.hko.gov.hk/cis/climat_.htm). The accuracy and the measurement precision of the PTR-MS were 3–20 and 1.6–10.0 %, respectively.

The accuracy of each species measured by PTR-MS was determined by the percentage difference between measured mixing ratio and actual mixing ratio based on calibrations every 6 days during the whole campaign. The quantification precision was determined by the experimental standard deviation of the respective mass signal intensity at a constant volume mixing ratio (about 1 ppbv in this study) (Graus et al., 2010). The limit of detection (LOD) was determined as the 3σ uncertainty of the 5 min background measurements.

Table 1. Detection limit, accuracy, precision, and total uncertainty of the PTR-MS for individual VOCs in gas standard.

Component	m/z	LOD (pptv)	Accuracy	Precision	Uncertainty
Formaldehyde	31	296	11.9 %	3.1 %	12.3 %
Methanol	33	162	5.3 %	2.7 %	5.9 %
Acetonitrile	42	17	7.4 %	2.0 %	7.7 %
Acetaldehyde	45	101	3.0 %	1.7 %	3.4 %
Ethanol	47	237	19.9 %	10.0 %	22.3 %
Acrolein	57	23	11.8 %	2.4 %	12.0 %
Acetone	59	31	4.2 %	1.7 %	4.5 %
Isoprene	69	40	18.0 %	3.4 %	18.3 %
Crotonaldehyde	71	25	15.5 %	2.1 %	15.6 %
2-Butanone	73	18	6.3 %	1.6 %	6.5 %
Benzene	79	12	4.6 %	1.8 %	4.9 %
Toluene	93	30	7.1 %	2.0 %	7.4 %
o-Xylene	107	25	7.4 %	1.7 %	7.6 %
α-Pinene	137	29	9.9 %	2.2 %	10.1 %
Dichlorobenzenes	147	21	7.8 %	2.7 %	8.3 %
Trichlorobenzenes	181	96	10.0 %	3.3 %	10.5 %

Table 2. Summary of detection limit, accuracy, and precision of different techniques used in this study.

Method	Measured parameters	LOD (pptv)	Accuracy	Precision
PTR-MS	OVOCs and VOCs	12–296	3–20 %	1.6–10.0 %
DNPH-HPLC	OVOCs	20–450	1–15 %	0.5–10.0 %
Online GC-FID	VOCs	15–1186	5–20 %	1.2–10.1 %
Offline GC-MSD/FID/ECD	VOCs	1–10	1–5 %	0.5–5.0 %

The total uncertainty for each species can be determined by the geometric sum of the accuracy and precision (Eerdekens et al., 2009). The LOD, accuracy, precision, and total uncertainty for each species measured by PTR-MS are listed in Table 1. Table 2 is a summary table in which the LOD, accuracy, and precision for PTR-MS and the other three techniques described in following sections are shown.

2.3   DNPH-HPLC

Twenty-four-hour (00:00–23:59) OVOC samples were collected by an ATEC Model 2200 automated sampler (Atmospheric Technology, Malibu, CA, USA) once every 6 days in each sampling month. An ozone scrubber (Sep-Pak; Waters Corporation, Milford, MA) was used to remove ozone during carbonyl sampling with 2,4-dinitrophenylhydrazine cartridges (Waters Sep-Pak DNPH-Silica, Milford, MA). The flow rate was regulated at $0.7 \, \mathrm{L \, min^{-1}}$ by a mass flow controller. Cartridge samples were analyzed according to the United States Environmental Protection Agency (USEPA) Method TO-11A (USEPA, 1999).

A HPLC system (Perkin Elmer Series 2000, MA, USA) coupled with an ultraviolet (UV) detector operating at 360 nm was used for chemical analysis. The column for separation was a $4.6 \times 150 \, \mathrm{mm}$ Hypersil ODS 5 m reversed phase column (Alltech, Deerfield, IL) at room temperature

(Huang et al., 2011). The mobile phase consisted of two solvent mixtures: (A) 6 : 3 : 1 ($v/v/v$) water–acetonitrile–tetrahydrofuran and (B) 4 : 6 (v/v) water–acetonitrile. The gradient program was 80 % A/20 % B for 1.5 min, followed by a linear gradient to 50 % A/50 % B for 8 min, and finally 100 % B for 10 min. The flow rate was $2.0 \, \mathrm{mL \, min^{-1}}$ throughout the run. All solvents and water used were HPLC grade (Duksan Pure Chemicals Co., Ltd, Gyeonggi-do, Korea) and Milli-Q grade, respectively. The calibration curve was established by five concentration points covering the levels of interest. One calibration standard was run for every 10 samples to ensure the stabilization of the instrument. Carbonyls were identified and quantified by their retention times and peak areas of the corresponding calibration standards (Cheng et al., 2014). Formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, 2-butanone, i-/n-butyraldehyde, benzaldehyde, i-valeraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde were detected by this method. The detection limits for target carbonyls were below 0.45 ppbv. The accuracy was 15 % or better, which was determined by measuring the recovery of a spiked sample. Sample precision is measured by the analysis of ambient duplicate samples, and the precision of the measurements was less than 10 %.

2.4 Online GC-FID

An online GC-FID analyzer (Syntech Spectras GC 955, Series 600/800, the Netherlands), which consists of two separate systems for detection of C_2–C_5 and C_6–C_{10} hydrocarbons was used to collect VOC speciation data continuously from May 2013 to August 2014. All the online GC-FID data used in this study were measured by the HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). Data quality was assured by strict quality assurance and quality control (QA/QC) procedures. Weekly calibrations were conducted by using NPL standard gas (National Physical Laboratory, Teddington, Middlesex, UK). More details about the online GC-FID system can be found from previous studies in Hong Kong (Xue et al., 2014; Ou et al., 2015). The C_2–C_{10} hydrocarbon species included ethane, ethene, ethyne, propane, propene, *n*-butane, *i*-butane, 1-butene, *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, *n*-pentane, *i*-pentane, 1-pentene, *trans*-2-pentene, *n*-hexane, 2-methyl pentane, *n*-heptane, *n*-octane, *i*-octane, benzene, toluene, ethylbenzene, *m,p*-xylene, *o*-xylene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. Sampling resolution for the online GC-FID analyzer was 30 min, and hourly averaged data were used for further analysis. The accuracy and precision of the measurements were 5–20 and 1.2–10.1 %, respectively. The accuracy of each species measured by online GC-FID was determined by the percentage difference between measured mixing ratio and actual mixing ratio based on weekly span checks and monthly calibrations. The precision was based on the 95 % probability limits for the integrated precision check results (Ling et al., 2013; Lyu et al., 2016).

2.5 Offline GC-MSD/FID/ECD

Twenty-four-hour (00:00–23:59) VOC samples were collected using 2 L electropolished, conditioned stainless-steel canisters and an ATEC Model 2200 automated sampler (Atmospheric Technology, Malibu, CA) once every 6 days in each sampling month. All canisters used in this study were pre-cleaned and evacuated by the Rowland–Blake group at the University of California, Irvine (UCI). Detailed information of the preparation and pre-conditioning of the canisters can be found elsewhere (Blake et al., 1994; Simpson et al., 2010). After sampling, canisters with air samples were sent back to the laboratory at UCI for VOC analysis by a GC-MSD/FID/ECD system within 1 week of collecting the canister samples. Complete analytical details are given in Colman et al. (2001). Briefly, the sample flow is split into five streams, with each stream chromatographically separated on an individual column and sensed by a single detector, namely (1) FID with a DB-1 column (60 m; ID: 0.32 mm; film: 1 mm); (2) FID with PLOT (30 m; ID: 0.53 mm) + DB-1 (5 m; ID: 0.53 mm; film: 1 mm) columns; (3) ECD with a Restek 1701 column (60 m; ID: 0.25 mm; film: 0.50 mm); (4) ECD with DB-5 (30 m; ID: 0.25 mm;

film: 1 mm) + Restek 1701 (5 m; ID: 0.25 mm; film: 0.5 mm) columns; and (5) MSD with a DB-5ms column (60 m; ID: 0.25 mm; film: 0.5 mm). This technique was used to measure 55 C_1–C_{10} VOCs, including all those measured by the online GC-FID. The accuracy of the VOC measurements was 5 % or better; replicate runs of the calibration standards yielded a measurement precision that ranged from 0.5 to 5 % (Colman et al., 2001; Ling and Guo, 2014; Lyu et al., 2016).

3 Results and discussion

3.1 Effect of ambient RH and *T* on PTR-MS measurement

As described in the Methodology section, four-point calibrations were conducted to get the calibration curves. The experimental reaction rate coefficient (k) of each compound was obtained by the original input k value (typically 2.0×10^{-9} cm^3 s^{-1}) multiplied by the slope of the measured concentration to the diluted concentration of standard gas, because the volume mixing ratio (VMR) of each species is inversely related to its reaction rate coefficient (k) (see Eq. 1) (de Gouw and Warneke, 2007). Experimental k values of selected VOC and OVOC species were obtained under different ambient conditions, and RH ranged from 25 to 100 %, while T ranged from 5 to 25 °C through this method.

$$\text{VMR} = \frac{\mu_0 N_0}{\text{k}L} \times \frac{E}{N^2} \times \frac{I_{\text{RH}^+} \times \text{TR}_{\text{H}_3\text{O}^+}}{I_{\text{H}_3\text{O}^+} \times \text{TR}_{\text{RH}^+}}, \tag{1}$$

where VMR is the volume mixing ratio (ppbv); μ_0 is the reduced mobility (cm V^{-1} s^{-1}), N_0 is the gas number density at standard pressure (1 atm) and temperature (273.15 K), k is the reaction rate coefficient (10^{-9} cm^3 s^{-1}), L is the length of the drift tube (9.3 cm in this study), E is the electric field strength (V m^{-1}), N is the air density in the drift tube (m^{-3}), I is the numbers of detected ions (cps), and TR is the transmission factor of respective ions.

Figure 2 shows the effect of ambient RH on the sensitivity and experimental k value of HCHO and benzene. The temperature of inlet air was kept at 25 °C during the series of various RH tests. A significant decrease (about 40 %) of sensitivity and calibrated k value was found when the RH of inlet air increased from 25 to 100 % for HCHO (m/z 31). However, the sensitivity and experimental k value of benzene (m/z 79) did not vary much, while the RH of inlet air changed with a variance of less than 5 %. The variation patterns of sensitivity and experimental k value for the other species were similar to benzene. Therefore, only benzene is plotted to represent other species in the gas standard. HCHO was found to have lower sensitivity (less than 2.0 ncps ppbv^{-1}) than benzene (about 20 ncps ppbv^{-1}), since the backward reaction of protonated formaldehyde with H_2O is not negligible, and the ratio between the forward and backward reaction was determined to be about 6000 by Spanel
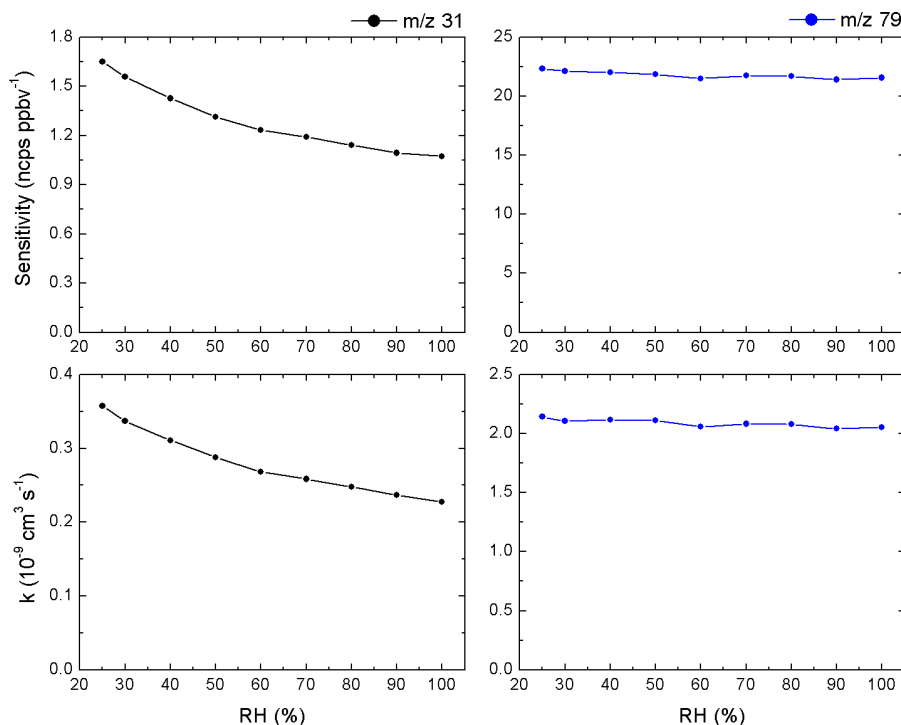
Figure 2. The effect of ambient RH on sensitivity and experimental k value of HCHO (m/z 31) and benzene (m/z 79).

and Smith (2008). Beauchamp et al. (2013) used a similar mixed gas standard for PTR-MS calibration; low sensitivity of HCHO was also found below 2 ncps ppbv^{-1} when the RH ranged from 20 to 100 %. Moreover, strong nonlinear dependence on RH for HCHO was found by Beauchamp et al. (2013), and the sensitivity of HCHO significantly decreased by about 50 % when the RH of inlet air increased from 20 to 100 %, which is comparable to this study. The effect of ambient temperature on sensitivity and experimental k value of HCHO and benzene is plotted in Fig. 3 under different RH. Both the sensitivity and experimental k value significantly dropped by 30–40 % when the temperature of inlet air increased from 5 to 25 °C. Both sensitivity and experimental k value maintained a relatively stable level (variance less than 5 %) for benzene when the temperature of inlet air was changed under the given RH, and the same for the other species in the standard gas excluding HCHO. A quadratic polynomial fit was found to be the best-fit model ($r^2 > 0.98$) for the experimental k value of HCHO with a single variable (RH or T of inlet air). Because the RH and T of inlet gas for calibration were set at 80 % and 25 °C, respectively, $R_{(RH,T)}$ (the ratio of k value under given ambient conditions to the experimental k value under 80 % and 25 °C) was chosen to explore the integrated effects of ambient RH and T on experimental k value. Poly 2-D regression, which used a binary quadratic equation, was found to be the best nonlinear surface simulation of $R_{(RH,T)}$, ambient RH, and T for HCHO in this study, and the following equation (Eq. 2) shows the

relationship between them:

$$R_{(RH,T)} = \tag{2}$$
$$r_0 + a \cdot RH + b \cdot T + c \cdot RH^2 + d \cdot T^2 + f \cdot RH \cdot T,$$

where $R_{(RH,T)}$ is the ratio of experimental reaction rate under given RH and T to calibrated reaction rate under 80 % and 25 °C, RH is the relative humidity of inlet gas/air, and T is the temperature of inlet gas/air.

The constant term r_0 and coefficients a, b, c, d, and f as well as the correlation coefficients of all species in the gas standard are listed in Table 3. The difference of $R_{(RH,T)}$ was within 10 % for all species except HCHO (m/z 31) when the condition of inlet air changed within the controlled range for RH (25–100 %) and T (5–25 °C). The $R_{(RH,T)}$ for formaldehyde differs significantly because of humidity effects on HCHO measurement by the PTR-MS. Excellent correlation was found between $R_{(RH,T)}$, ambient RH, and T for HCHO (m/z 31) with a correlation coefficient of 0.97. The relationship between these three factors is plotted in Fig. 4.

The relationship of experimental k value and AH in sample air for HCHO is plotted in Fig. 5. The best simulation ($r = 0.92$) was found following the function $k_{(AH)} = 0.0007 \cdot AH^2 - 0.0568 \cdot AH + 1.8139$, where $k_{(AH)}$ stands for the experimental k value of HCHO and AH stands for the absolute humidity in sample air. Figure 6 shows the comparison between concentrations of HCHO measured during the campaign at MK after correction by $R_{(RH,T)}$ and $k_{(AH)}$ separately. Good agreement during the field sampling for HCHO
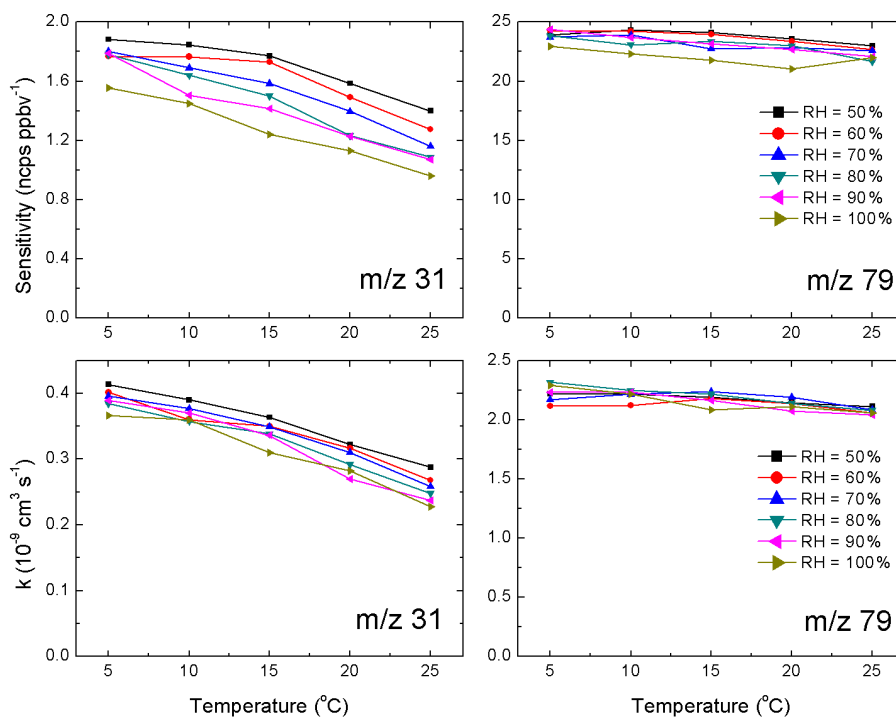
Figure 3. The effect of ambient temperature on sensitivity and experimental k value of HCHO (m/z 31) and benzene (m/z 79) under different RH.

Table 3. Poly 2-D simulation results of different species in gas standard for the PTR-MS.

| Component	m/z	r	Value					
			r_0	a	b	c	d	f
Formaldehyde	31	0.97	1.63E+00	−3.81E−03	1.92E−02	5.10E−05	−6.41E−04	−3.76E−04
Methanol	33	0.68	9.43E−01	1.16E−03	−6.16E−04	−7.23E−06	−8.01E−05	2.44E−05
Acetonitrile	42	0.72	9.77E−01	6.82E−04	−1.63E−03	−3.01E−06	−3.62E−05	1.80E−05
Acetaldehyde	45	0.70	1.04E+00	−5.07E−04	−3.97E−03	1.24E−06	4.83E−07	3.74E−05
Ethanol	47	0.67	1.16E+00	−3.30E−03	−1.83E−02	−6.65E−06	1.67E−04	2.35E−04
Acrolein	57	0.74	9.94E−01	−4.42E−04	−5.98E−03	−1.47E−06	2.32E−05	8.29E−05
Acetone	59	0.77	1.04E+00	−6.97E−04	−2.27E−03	6.21E−06	−4.00E−05	2.17E−05
Isoprene	69	0.92	1.00E+00	−1.38E−03	−8.82E−03	7.97E−06	1.13E−04	9.88E−05
Crotonaldehyde	71	0.79	8.69E−01	2.03E−03	−2.91E−04	−7.67E−06	−2.55E−05	1.57E−05
2-Butanone	73	0.74	9.77E−01	6.06E−04	−1.20E−03	−2.06E−06	−4.10E−05	1.41E−05
Benzene	79	0.81	1.03E+00	−3.93E−04	5.65E−03	1.17E−05	−1.53E−04	−6.35E−05
Toluene	93	0.84	1.03E+00	1.91E−04	4.66E−03	7.32E−06	−1.67E−04	−5.62E−05
o-Xylene	107	0.86	1.03E+00	1.06E−03	2.15E−03	−1.75E−06	−1.05E−04	−4.56E−05
α-Pinene	137	0.76	9.60E−01	1.56E−03	3.61E−03	−3.53E−06	−1.01E−04	−4.75E−05
Dichlorobenzenes	147	0.74	1.08E+00	6.93E−04	4.18E−03	2.16E−06	−1.56E−04	−7.19E−05
Trichlorobenzenes	181	0.55	8.66E−01	5.20E−03	1.18E−02	−2.23E−05	−2.91E−04	−1.23E−04
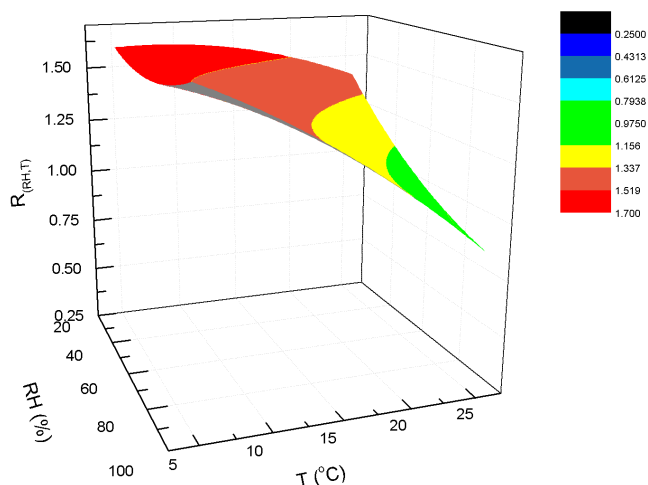
Figure 4. Simulation of experimental reaction rate coefficient, ambient relative humidity (RH), and temperature (T) for HCHO (m/z 31).
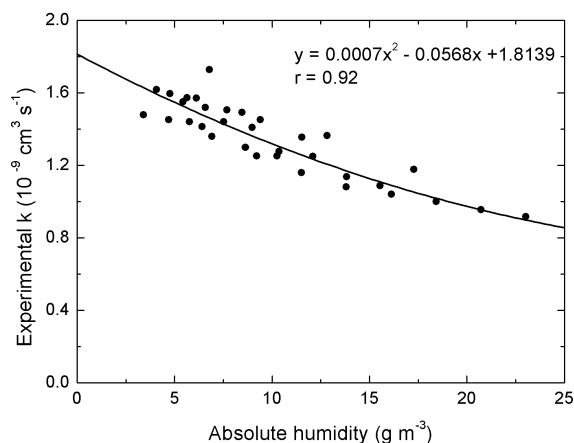

Figure 5. Experimental k value of HCHO (m/z 31) as a function of absolute humidity in sample air.

was found between the above two correction methods, with a slope of 1.02 and a correlation coefficient of 0.99 (as shown in Fig. 6).

A relationship between the normalized detection sensitivity, S (ncps ppbv^{-1}), of HCHO and its humidity dependence at a certain E/N condition was stated by Inomata et al. (2008) as follows:

$$S = \frac{m}{n} \cdot \frac{a}{[H_2O]_{sample} + b} \cdot \frac{1}{88.0}, \qquad (3)$$

where m is the detection sensitivity of HCHO by direct introduction (ncps ppbv^{-1}), n is the detection sensitivity of HCHO by dynamic dilution (ncps ppbv^{-1}), a and b are fitting parameters obtained from the simulation equation $y = a/(x + b)$ for the signal intensity of HCHO, and
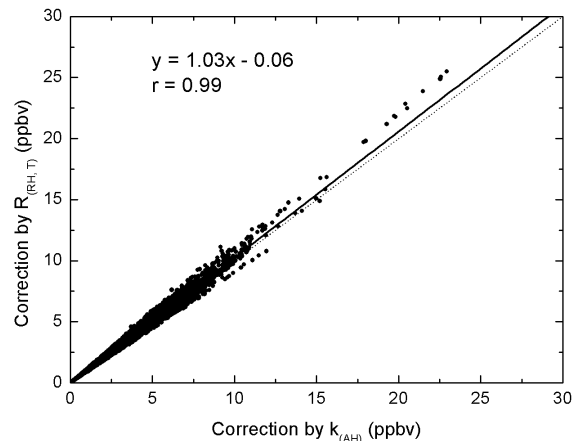

Figure 6. Linear regression of two correction methods for HCHO concentrations during the field study at MK in Hong Kong.

$[H_2O]_{sample}$ is the water vapor concentration in sample air (mmol mol^{-1}).

Ion counts are divided by 88.0 because the humidity dependence was measured with HCHO of 88.0 ppbv in the dynamic dilution method in this study. The relationship of the signal intensity of HCHO and the water vapor concentration in sample air is plotted in Fig. 7. Simulated fitting parameters, a and b, are 5404 ± 72 (ncps mmol mol^{-1}) and 26 ± 0.4 (mmol mol^{-1}), respectively. The value of m/n is 1.09 in this study, and it is about 1.2 times that of the $(k_a/k_{-a})/a$ value. This result agrees with the study of Inomata et al. (2008). Hence, the normalized detection sensitivity of HCHO in this study can be determined as a function of the water vapor concentration in sample air as Eq. (4).

$$S = \frac{67.18}{AH_{sample} + 26.04} \qquad (4)$$

Figure 8 shows the comparison of the measured detection sensitivity of HCHO and the normalized detection sensitivity obtained from Eq. (4). Good agreement was found between the measured detection sensitivity and the normalized detection sensitivity of HCHO with a slope of 1.18 ± 0.01 ($r = 0.998$). Since the normalized detection sensitivity of HCHO was 1.18 times that of the measured detection sensitivity, lower HCHO concentration will be obtained by using the normalized detection sensitivity with a percentage of about 15.3 %.

3.2 PTR-MS vs. DNPH-HPLC

Daily averaged PTR-MS data were used to compare the ambient OVOC measurements by PTR-MS and by DNPH-HPLC. As shown in Fig. 9, good linear correlations were found for formaldehyde, acetaldehyde, and MEK, with correlation coefficients of 0.79, 0.75, 0.93, respectively, and with slopes of 1.00 ± 0.10, 1.10 ± 0.33, and 0.88 ± 0.058, respectively. For acetone, the slope is 0.76 ± 0.23 (PTR-MS to
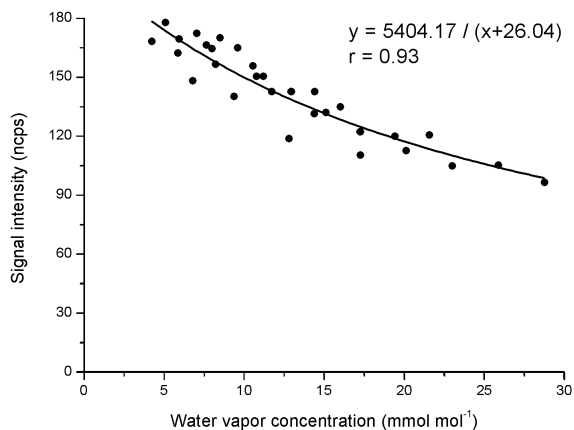
Figure 7. The relationship of the signal intensity at m/z 31 and the water vapor concentration in sample air.

Figure 8. Linear regression of the measured detection sensitivity of HCHO and its normalized detection sensitivity by water vapor concentration in sample air.

HPLC) with a correlation coefficient of 0.60. Concentrations of HCHO measured by the PTR-MS in Fig. 9b were the corrected data by the Poly 2-D regression of RH and T. Since the conditions of inlet air for calibration were set at RH $= 80\%$ and $T = 25\,°C$, which were close to the average level of ambient air in Hong Kong from 1997 to 2012 (shown in Fig. 1), uncorrected concentrations of HCHO measured by PTR-MS were only slightly lower than those by DNPH-HPLC with a percentage of 8.0 % ($r = 0.68$). Corrected concentrations of HCHO by absolute humidity in sample air also correlated well with those by DNPH-HPLC (slope $= 0.91$, $r = 0.77$), because of the excellent correlation between these two different correction methods discussed above. However, correction for HCHO concentrations by Poly 2-D regression of RH and T, which has a better slope than the others, is a better choice. Moreover, it is easy to measure RH and T of ambient air for further correction of HCHO data by PTR-MS in practice.

Wisthaler et al. (2008) reported the intercomparison between PTR-MS and DNPH-HPLC in an atmosphere simulation chamber; good agreement was found between PTR-MS and DNPH-HPLC while ambient air was introduced into the chamber, but the concentration of HCHO measured by DNPH-HPLC was less than that by PTR-MS, which could be caused by some interferences for the DNPH-HPLC method or the varying performance of the KI ozone scrubber. Overestimation of DNPH-HPLC for HCHO in the presence of NO_2 was also reported by Herrington and Hays (2012), because NO can be oxidized to NO_2 in the upstream ozone scrubber, and NO_2 will react with DNPH to form 2,4-dinitrophenyl azide (DNPA), which has similar chromatographic properties to the formaldehyde-DNP-hydrazone. Hence, the intercept of -0.03 for HCHO intercomparison between PTR-MS and DNPH-HPLC in this study may be explained by the interference of NO_2 because of the high NO_x levels at the roadside sampling site.

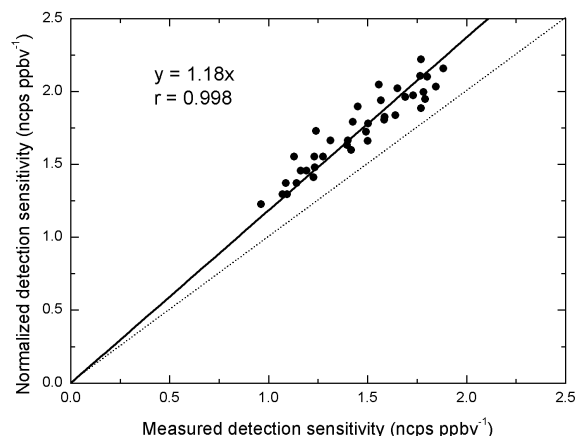Low acetaldehyde collection efficiencies (CEs), ranging from 1 to 62 %, were found by Herrington et al. (2007) for the typical 24 h sampling period, which can lead to the underestimation of acetaldehyde by the DNPH-HPLC method. And this artifact is consistent with the result for acetaldehyde intercomparisons in this study. It was found that ketone (acetone and MEK) concentrations determined by the DNPH-HPLC method could be underestimated by 35–80 % under high-RH ($> 50\%$) conditions when the temperature is about $22\,°C$ (Ho et al., 2014). This DNPH issue could explain the 12 % difference between PTR-MS and DNPH-HPLC for MEK and the relatively bad agreement for acetone in our study.

3.3 PTR-MS vs. online GC-FID

Hourly data were used to conduct intercomparison between PTR-MS and online GC-FID. Because the ion signal at m/z 107 reflects C_2-benzenes (the sum of p-xylene, m-xylene, o-xylene, ethylbenzene, and benzaldehyde) (de Gouw and Warneke, 2007), C_2-benzenes measured by online GC-FID were compared with the ion signal at m/z 107 of PTR-MS. Time series concentrations of benzene, toluene, and C_2-benzenes measured by PTR-MS and online GC-FID are plotted in Fig. 10. Excellent correlation was found for toluene, with a slope of 1.01 ± 0.01 and a correlation coefficient of 0.96. Good linearities were observed for benzene and C_2-benzenes between PTR-MS and online GC-FID, with correlation coefficients of 0.92 and 0.96, respectively. However, the concentration of benzene detected by PTR-MS was 65 % higher than that by online GC-FID, and the concentration of C_2-benzenes detected by PTR-MS was 17 % lower than that by online GC-FID. The significant difference of benzene detected by PTR-MS and online GC-FID could mainly be due to the fragments from ethylbenzene and propylbenzene to m/z 79. Rogers et al. (2006) stated an equation (Eq. 5) to calculate the contributions from ethylben-
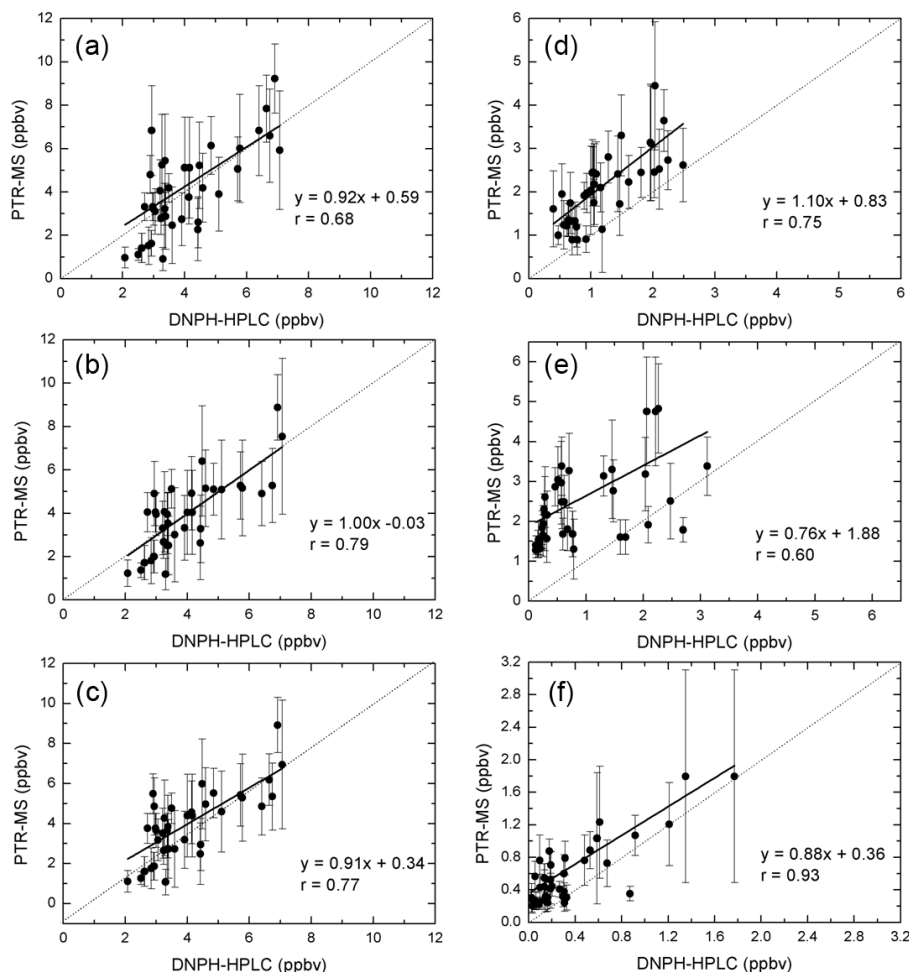
Figure 9. Intercomparison between ambient OVOC measurements by PTR-MS and by DNPH-HPLC during the field study at MK in Hong Kong: **(a)** formaldehyde without correction, **(b)** formaldehyde corrected by $R(\text{RH}, T)$, **(c)** formaldehyde corrected by $k(\text{AH})$, **(d)** acetaldehyde, **(e)** acetone, and **(f)** MEK. Linear regression fits are indicated by the solid black line. Error bar stands for the standard deviation of 24 h averaged PTR-MS data. Dashed line is the 1 : 1 line for reference.

zene and propylbenzene to m/z 79:

$$[\text{benzene}] = [\text{M79}] - \frac{S_{\text{ethylbenzene}}}{S_{\text{benzene}}} \text{BF}_{\text{ethylbenzene}}[\text{ethylbenzene}]$$
$$- \frac{S_{\text{propylbenzene}}}{S_{\text{benzene}}} \text{BF}_{\text{propylbenzene}}[\text{propylbenzene}], \quad (5)$$

where [benzene] is the volume mixing ratio of benzene, [M79] is the volume mixing ratio of m/z 79, [ethylbenzene] is the actual volume mixing ratio of ethylbenzene, [propylbenzene] is actual volume mixing ratio of propylbenzene, S_x/S_{benzene} is the ratio of the ionization efficiencies, and BF is the fraction of m/z 79 ion product that each produces upon ionization.

Since propylbenzene was not measured in this study, only ethylbenzene was used to correct the concentrations of benzene and C_2-benzenes measured by PTR-MS following

Eqs. (6) and (7): propylbenzene to m/z 79.

$$[\text{Benzene}] = [\text{M79}] - 0.2235[\text{M107}], \quad (6)$$
$$[C_2 - \text{benzenes}] = 1.2235[\text{M107}], \quad (7)$$

where [C_2-benzenes] is the volume mixing ratio of C_2-benzenes and [M107] is the volume mixing ratio of m/z 107.

Time series of benzene, toluene, and C_2-benzenes results obtained by online GC-FID and PTR-MS during the sampling period were plotted in Fig. 10. Figure 11a and c shows the correlation between corrected concentrations of benzene and C_2-benzenes based on Eqs. (6) and (7) for PTR-MS and their measured concentrations by online GC-FID at MK AQMS. The agreement between the two different sampling techniques for benzene is better after correction by Eq. (6) with a slope of 1.23 ± 0.01 and a correlation coefficient of 0.95. Excellent agreement (slope $= 1.02 \pm 0.01$, $r = 0.96$) between the two different sampling techniques for
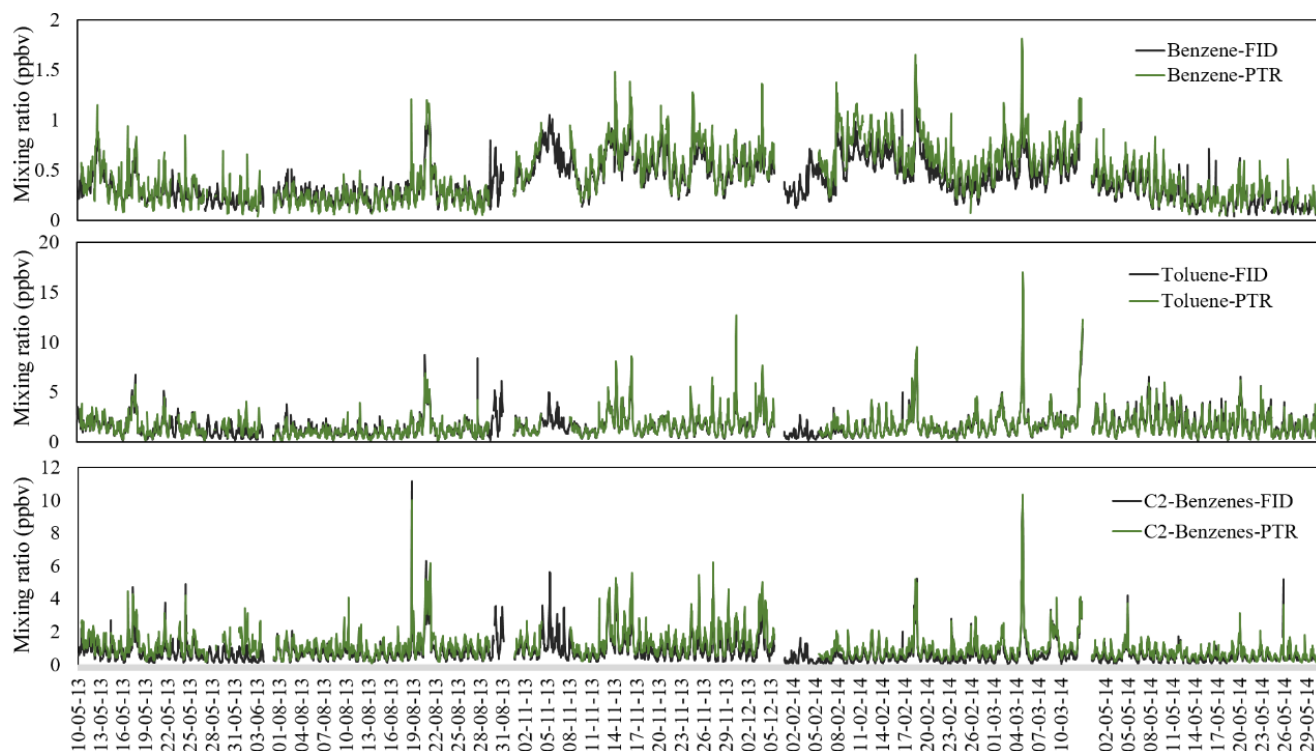
Figure 10. Measurement results for benzene, toluene, and C_2-benzenes obtained during the field study at MK in Hong Kong. The black lines show the online GC-FID data, and the green lines show the PTR-MS results.

C_2-benzenes is achieved using the corrected concentrations of C_2-benzenes by PTR-MS. Since the toluene-to-benzene ratio is one of the key indicators for determining VOC sources and C_2-benzenes are related to vehicular emissions and solvent usage, accurate measurements are required in studies on source apportionment of ambient VOCs. The two equations above (Eqs. 6 and 7) could offer a good correction method for the concentrations of benzene and C_2-benzenes measured by PTR-MS in an urban roadside area of Hong Kong.

3.4 PTR-MS vs. offline GC-MSD/FID/ECD

The intercomparison between the PTR-MS data averaged over the 24 h canister sampling interval and offline GC-MSD/FID/ECD analysis of the canisters is displayed in Fig. 12. Corrected concentrations of benzene and C_2-benzenes by the PTR-MS were used for comparison. Acceptable linear regressions were found for benzene, toluene, and C_2-benzenes between the PTR-MS and the offline GC-MSD/FID/ECD with correlation coefficients of 0.62, 0.96 and 0.92, respectively. However, the mixing ratios of toluene and C_2-benzenes measured by PTR-MS were lower than those measured by offline canister samples with percentages of 22 and 33 %, respectively. The maximum offsets from the 1 : 1 line were usually found at high concentrations, which could be mainly caused by the different sampling time reso-

lution for each sample of the PTR-MS and canister samples. The canister samples were 24 h samples with constant flow, while PTR-MS detected a total group of 17 different species with a 30 s cycle. From previous studies on comparison between the PTR-MS and the GC-MSD/FID/ECD, the slope for toluene ranged 0.52–1.18, and the slope for C_2-benzenes ranged 0.58–3.20 (Kato et al., 2004; Christian et al., 2004; de Gouw et al., 2003; Warneke et al., 2001), so PTR-MS and offline GC-MSD/FID/ECD analysis were comparable for aromatic hydrocarbon measurements in this study.

3.5 Comparison with other studies

Intercomparisons between PTR-MS and other alternative technologies are summarized in Table 4. Most studies were conducted in urban areas, suburban areas, coastal areas, forested areas, or the free troposphere. Overall, most of the slopes of PTR-MS to alternative methods agreed to within less than the PTR-MS measurement accuracy of 20 %.

Few studies have conducted intercomparisons between PTR-MS and alternative methods for OVOCs (e.g., HCHO, acetaldehyde, acetone, and MEK). Even fewer studies have investigated intercomparison between PTR-MS and DNPH-HPLC. In most studies, a differential optical absorption spectroscopy (DOAS) instrument and Hantzsch monitor were usually used to measure ambient HCHO. Good agreement was found between PTR-MS and DOAS in both moun-

Table 4. Intercomparisons between PTR-MS and alternative methods in this study and the comparison with previous other studies.

| Compound	m/z	Alternative method	Slope	Intercept (ppbv)	r	Sampling area type	Reference
Formaldehyde	31	MAX-DOAS	1.01	−0.02	NA	mountain area	Inomata et al. (2008)
		DOAS	1.17	NA	0.84	urban area	Warneke et al. (2011b)
		Hantzsch	1.35	NA	0.74	urban area	Warneke et al. (2011b)
		DNPH-HPLC	NA	NA	NA	in chamber	Wisthaler et al. (2008)
		DNPH-HPLC	1.00	−0.03	0.79	urban roadside area	This study
Acetaldehyde	45	PIT-MS	1.25	NA	0.87	in chamber	Warneke et al. (2011a)
		online GC-MS	1.56	−0.17	0.93	on ship	de Gouw et al. (2003)
		DNPH-HPLC	NA	NA	NA	in forest	Müller et al. (2006)
		DNPH-HPLC	1.10	0.83	0.75	urban roadside area	This study
Acetone	59	AP-CIMS	1.18	0.06	0.94	in flight	Sprung et al. (2001)
		online GC-MS	1.00	−0.05	0.98	on ship	de Gouw et al. (2003)
		online GC-MS/FID	1.03	−0.44	0.90	urban area	Wang et al. (2014)
		DNPH-HPLC	NA	NA	NA	in forest	Müller et al. (2006)
		DNPH-HPLC	0.76	1.88	0.60	urban roadside area	This study
MEK	73	online GC-MS	2.51	0.02	0.95	on ship	de Gouw et al. (2003)
		offline canister	0.85	0.06	NA	in flight	de Gouw et al. (2006)
		online GC-MS/FID	1.39	−0.18	0.89	urban area	Wang et al. (2014)
		DNPH-HPLC	0.88	0.36	0.93	urban roadside area	This study
Benzene	79	offline canister	0.82	0.11	0.91	suburban area	Warneke et al. (2001)
		online GC-MS	1.12	0.00	0.96	on ship	de Gouw et al. (2003)
		online GC-ITMS	0.85	0.00	0.97	suburban area	Kuster et al. (2004)
		online GC-QMS	0.97	0.00	0.92	suburban area	Kuster et al. (2004)
		online GC-FID	0.82	0.03	NA	suburban–urban area	Kato et al. (2004)
		offline canister	0.96	0.07	0.98	urban area	Rogers et al. (2006)
		offline canister	1.08	0.01	0.87	in flight	de Gouw and Warneke (2007)
		offline canister	1.05	−1.16	0.65	urban area	Jobson et al. (2010)
		DOAS	1.22	0.39	0.61	urban area	Jobson et al. (2010)
		online GC-MS/FID	0.80	0.07	0.96	urban area	Wang et al. (2014)
		online GC-FID	1.23	−0.03	0.95	urban roadside area	This study
		offline canister	1.05	−0.03	0.62	urban roadside area	This study
Toluene	93	offline canister	1.18	−0.07	0.96	suburban area	Warneke et al. (2001)
		online GC-MS	1.08	0.01	0.99	on ship	de Gouw et al. (2003)
		online GC-ITMS	0.91	0.00	0.98	suburban area	Kuster et al. (2004)
		online GC-QMS	0.81	0.10	0.95	suburban area	Kuster et al. (2004)
		online GC-FID	0.52	0.16	NA	suburban–urban area	Kato et al. (2004)
		offline canister	0.99	0.02	0.99	urban area	Rogers et al. (2006)
		offline canister	0.88	0.00	0.90	in flight	de Gouw and Warneke (2007)
		offline canister	0.94	−0.43	0.66	urban area	Jobson et al. (2010)
		DOAS	0.60	0.81	0.55	urban area	Jobson et al. (2010)
		online GC-MS/FID	0.94	0.05	0.99	urban area	Wang et al. (2014)
		online GC-FID	1.01	0.02	0.96	urban roadside area	This study
		offline canister	0.78	0.19	0.96	urban roadside area	This study
C_2-benzenes	107	online GC-MS	3.20	0.01	0.98	on ship	de Gouw et al. (2003)
		online GC-ITMS	1.02	0.00	0.97	suburban area	Kuster et al. (2004)
		online GC-FID	0.58	0.00	NA	suburban–urban area	Kato et al. (2004)
		offline canister	0.86	0.00	0.91	in flight	de Gouw et al. (2006)
		offline canister	1.31	−0.40	0.99	urban area	Rogers et al. (2006)
		offline canister	0.86	−0.01	0.91	in flight	de Gouw and Warneke (2007)
		offline canister	0.91	0.18	0.61	urban area	Jobson et al. (2010)
		DOAS	0.59	0.04	0.58	urban area	Jobson et al. (2010)
		online GC-MS/FID	0.87	0.09	0.98	urban area	Wang et al. (2014)
		online GC-FID	1.02	0.31	0.96	urban roadside area	This study
		offline canister	0.67	0.38	0.92	urban roadside area	This study

NA – not available
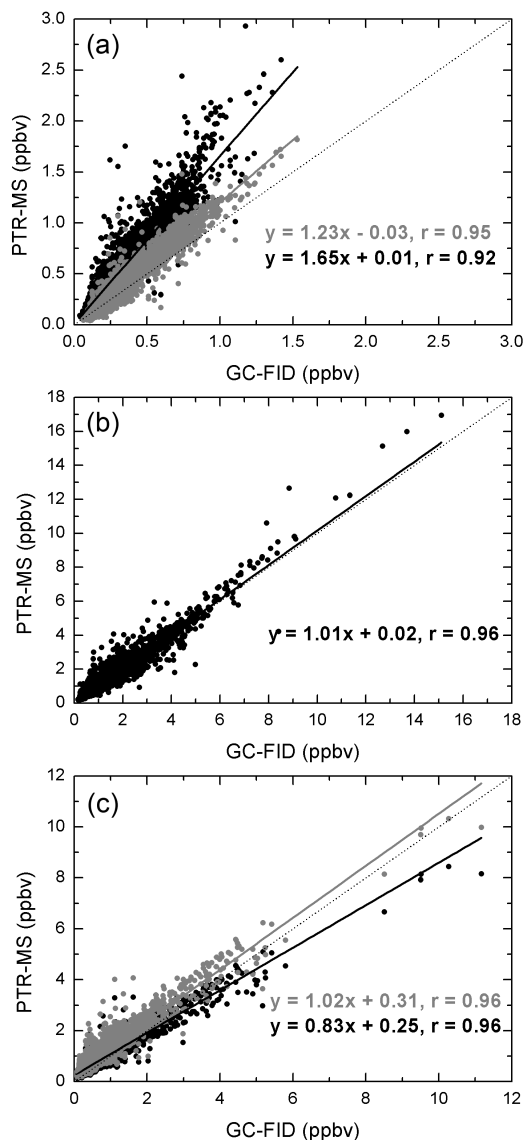
Figure 11. Intercomparison between ambient aromatic hydrocarbon measurements by PTR-MS and by online GC-FID during the field study at MK in Hong Kong: **(a)** benzene, **(b)** toluene, and **(c)** C_2-benzenes. Original data are plotted in black dots; grey dots represent the corrected data based on Eqs. (6) and (7). Linear regression fits for original and corrected data are indicated by the solid black line and the solid grey line, respectively. Dashed line is the 1 : 1 line for reference.

Figure 12. Intercomparison between ambient aromatic hydrocarbon measurements by PTR-MS (corrected based on Eqs. 6 and 7) and by offline canister measurements using GC-MSD/FID/ECD during the field study at MK in Hong Kong: **(a)** benzene, **(b)** toluene, and **(c)** C_2-benzenes. Linear regression fits are indicated by the solid black line. Error bar stands for the standard deviation of 24 h averaged PTR-MS data. Dashed line is the 1 : 1 line for reference.

tain areas (slope = 1.01) (Inomata et al., 2008) and urban areas (slope = 1.17) (Warneke et al., 2011b). HCHO measurement by DNPH-HPLC was compared to PTR-MS in an atmosphere simulation chamber by Wisthaler et al. (2008), and significant lower HCHO levels by DNPH-HPLC were observed in dry synthetic air because of hydrazine-to-hydrazone conversion. Proton-transfer-reaction mass-spectrometry (PIT-MS), atmospheric pressure chemical ionization mass spectrometry (AP-CIMS), and GC-
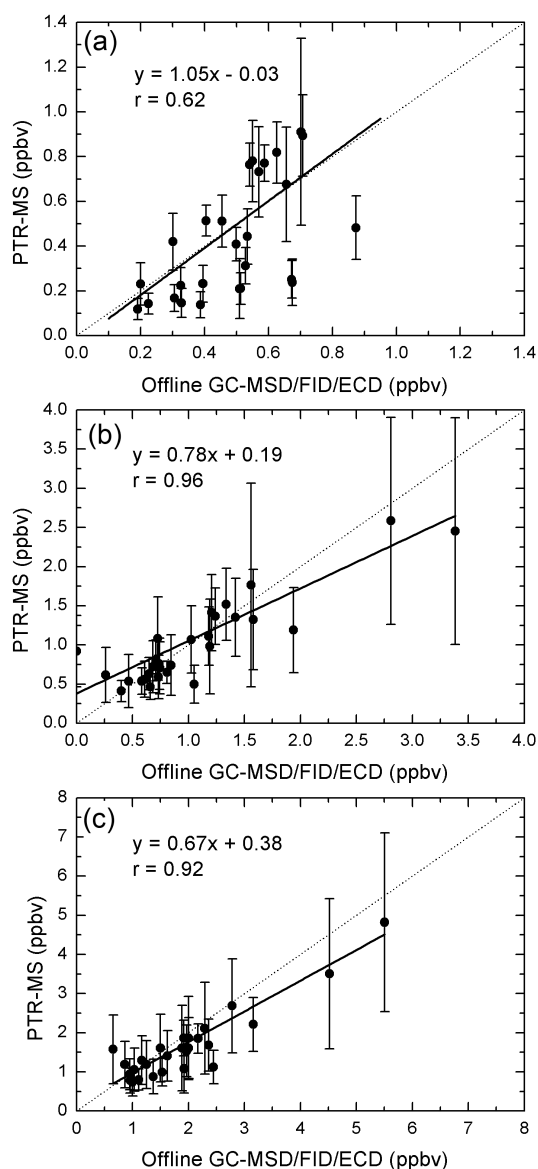
MS/FID were chosen as alternative monitoring methods for acetaldehyde, acetone, and MEK. Relatively higher acetaldehyde levels by PTR-MS were found, while PTR-MS vs. PIT-MS (Warneke et al., 2011a) and PTR-MS vs. online GC-MS (de Gouw et al., 2003) had slopes of 1.25 and 1.56, respectively. Better agreement was obtained between PTR-MS and DNPH-HPLC for acetaldehyde (slope = 1.10, $r = 0.75$) in our study. PTR-MS agreed well with AP-CIMS, online GC-MS, and online GC-MS-FID for acetone, with slopes ranging

from 1.00 to 1.18. In this study, however, the slope is 0.76 (PTR-MS to HPLC) with an offset of 1.88, which could have resulted from other interferences on m/z 59. The slopes of MEK varied in a large ranges (0.85–2.51) in previous studies, but a reasonable correlation between PTR-MS and DNPH-HPLC for MEK (slope $= 0.88$, $r = 0.93$) was found in this study.

Intercomparisons between PTR-MS and alternative methods (both online and offline methods) for benzene, toluene, and C_2-benzenes have been conducted by previous studies in various areas. For benzene, PTR-MS was always reasonably comparable to other online or offline techniques, with slopes ranging from 0.82 to 1.22. In this study, PTR-MS correlated well with offline canister measurements for benzene (slope $= 1.05$), but a higher slope of 1.23 was found between PTR-MS and online GC-FID, which could be due to interferences (e.g., propylbenzene) at m/z 79. Lower toluene levels measured by PTR-MS as compared to offline canister measurements were found in this study, with a slope of 0.78 ($r = 0.96$). Lower toluene levels measured by PTR-MS were also reported for PTR-MS vs. DOAS (Jobson et al., 2010) and PTR-MS vs. online GC-FID (Kato et al., 2004) in an urban area. Similarly, lower C_2-benzenes levels measured by PTR-MS than by offline canister measurements were found with a slope of 0.67 ($r = 0.92$) in this study, which could have resulted from the much longer sampling resolution of offline canister sample. The slopes of C_2-benzenes varied from 0.59 to 3.20 in previous studies with different area types.

4 Conclusions

The effect of ambient RH and T on HCHO measurements by PTR-MS was further investigated in this study. Due to the backward reaction of protonated HCHO with H_2O, the sensitivity of HCHO decreased significantly when ambient RH and/or T varied. Meanwhile, the calibrated reaction rate coefficient of HCHO and H_3O^+ also decreased significantly. The combined effect of RH and T on the HCHO measurement by PTR-MS was explored in this study. A Poly 2-D regression was found to be the best nonlinear surface simulation of $R_{(RH,T)}$, ambient RH and T for HCHO, following the equation $R_{(RH,T)} = 1.63 - 3.81 \times 10^{-3} \cdot RH + 1.92 \times 10^{-2} \times T + 5.10 \times 10^{-5} \cdot RH^2 - 6.41 \times 10^{-4} \cdot T^2 - 3.76 \times 10^{-4} \cdot RH \cdot T$. Through a field sampling study at an urban roadside area at MK AQMS, correction of HCHO concentrations by both ambient RH and T and by absolute humidity in sample air agreed well with each other (slope $= 1.02$, $r = 0.99$).

A field study of OVOCs and VOCs using the PTR-MS was conducted at MK in Hong Kong from May 2013 to August 2014. Good agreement was found between PTR-MS and DNPH-HPLC for formaldehyde (slope $= 1.00$, $r = 0.79$), acetaldehyde (slope $= 1.10$, $r = 0.75$) and MEK (slope $= 0.88$, $r = 0.93$). For acetone, the relatively bad

agreement (slope $= 0.76$, $r = 0.60$) should be the result of the DNPH issue, since there is huge underestimation (35–80 %) for ketones measured by the DNPH-HPLC method when RH > 50 %. Moreover, correction for HCHO concentrations by Poly 2-D regression of ambient RH and T was found to be better than directly correcting by absolute humidity in the sample air. Aromatic hydrocarbons measurements by PTR-MS were intercompared with online GC-FID and offline canister measurements using GC-MSD/FID/ECD. After correcting benzene and C_2-benzenes levels that were measured by the PTR-MS, which could be affected by fragments from ethylbenzene and propylbenzene at m/z 79, good agreements were found between PTR-MS and online GC-FID for toluene (slope $= 1.01$, $r = 0.96$) and C_2-benzenes (slope $= 1.02$, $r = 0.96$), but a higher benzene level was still detected by the PTR-MS when compared with that by online GC-FID (slope $= 1.23$, $r = 0.95$). For the intercomparisons between PTR-MS and off-canister measurements using GC-MSD/FID/ECD, benzene showed good agreement, with a slope of 1.05 ($r = 0.62$); underestimated toluene and C_2-benzenes levels by PTR-MS were obtained with slopes of 0.78 ($r = 0.96$) and 0.67 ($r = 0.92$), respectively. In summary, the PTR-MS instrument can be used in urban roadside areas for OVOC and VOC measurements. But further intercomparisons between PTR-MS and other offline analytical techniques need to be conducted with the higher sampling time resolutions of offline analytical techniques.

5 Data availability

The data shown in this study can be available on request to authors. Please refer to the author list for contact details.

References

Ambrose, J. L., Haase, K., Russo, R. S., Zhou, Y., White, M. L., Frinak, E. K., Jordan, C., Mayne, H. R., Talbot, R., and Sive, B. C.: A comparison of GC-FID and PTR-MS toluene measurements in ambient air under conditions of enhanced monoterpene

loading, Atmos. Meas. Tech., 3, 959–980, doi:10.5194/amt-3-959-2010, 2010.

Atkinson, R. and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chem. Rev., 103, 4605–4638, doi:10.1021/cr0206420, 2003.

Beauchamp, J., Herbig, J., Dunkl, J., Singer, W., and Hansel, A.: On the performance of proton-transfer-reaction mass spectrometry for breath-relevant gas matrices, Meas. Sci. Technol., 24, 125003, doi:10.1088/0957-0233/24/12/125003, 2013.

Blake, D. R., Smith, T. W., Chen, T. Y., Whipple, W. J., and Rowland, F. S.: Effects of biomass burning on summertime nonmethane hydrocarbon concentrations in the Canadian wetlands, J. Geophys. Res.-Atmos., 99, 1699–1719, doi:10.1029/93JD02598, 1994.

Chan, C. Y., Chan, L. Y., Wang, X. M., Liu, Y. M., Lee, S. C., Zou, S. C., Sheng, G. Y., and Fu, J. M.: Volatile organic compounds in roadside microenvironments of metropolitan Hong Kong, Atmos. Environ., 36, 2039–2047, doi:10.1016/S1352-2310(02)00097-3, 2002.

Cheng, Y., Lee, S. C., Huang, Y., Ho, K. F., Ho, S. S. H., Yau, P. S., Louie, P. K. K., and Zhang, R. J.: Diurnal and seasonal trends of carbonyl compounds in roadside, urban, and suburban environment of Hong Kong, Atmos. Environ., 89, 43–51, doi:10.1016/j.atmosenv.2014.02.014, 2014.

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Shirai, T., and Blake, D. R.: Comprehensive laboratory measurements of biomass-burning emissions: 2. First intercomparison of open-path FTIR, PTR-MS, and GC-MS/FID/ECD, J. Geophys. Res.-Atmos., 109, D02311, doi:10.1029/2003JD003874, 2004.

Colman, J. J., Swanson, A. L., Meinardi, S., Sive, B. C., Blake, D. R., and Rowland, F. S.: Description of the Analysis of a Wide Range of Volatile Organic Compounds in Whole Air Samples Collected during PEM-Tropics A and B, Anal. Chem., 73, 3723–3731, doi:10.1021/ac010027g, 2001.

de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26, 223–257, doi:10.1002/mas.20119, 2007.

de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, J. Geophys. Res.-Atmos., 108, 4682, doi:10.1029/2003JD003863, 2003.

de Gouw, J. A., Warneke, C., Stohl, A., Wollny, A. G., Brock, C. A., Cooper, O. R., Holloway, J. S., Trainer, M., Fehsenfeld, F. C., Atlas, E. L., Donnelly, S. G., Stroud, V., and Lueb, A.: Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada, J. Geophys. Res.-Atmos., 111, D10303, doi:10.1029/2005JD006175, 2006.

Eerdekens, G., Ganzeveld, L., Vilà-Guerau de Arellano, J., Klüpfel, T., Sinha, V., Yassaa, N., Williams, J., Harder, H., Kubistin, D., Martinez, M., and Lelieveld, J.: Flux estimates of isoprene, methanol and acetone from airborne PTR-MS measurements over the tropical rainforest during the GABRIEL 2005 campaign, Atmos. Chem. Phys., 9, 4207–4227, doi:10.5194/acp-9-4207-2009, 2009.

Graus, M., Müller, M., and Hansel, A.: High Resolution PTR-TOF: Quantification and Formula Confirmation of VOC in Real Time, J. Am. Soc. Mass Spectr., 21, 1037–1044, doi:10.1016/j.jasms.2010.02.006, 2010.

Guo, H., Lee, S. C., Louie, P. K. K., and Ho, K. F.: Characterization of hydrocarbons, halocarbons and carbonyls in the atmosphere of Hong Kong, Chemosphere, 57, 1363–1372, doi:10.1016/j.chemosphere.2004.07.055, 2004.

Guo, H., So, K. L., Simpson, I. J., Barletta, B., Meinardi, S., and Blake, D. R.: C1–C8 volatile organic compounds in the atmosphere of Hong Kong: Overview of atmospheric processing and source apportionment, Atmos. Environ., 41, 1456–1472, doi:10.1016/j.atmosenv.2006.10.011, 2007.

Hansel, A., Singer, W., Wisthaler, A., Schwarzmann, M., and Lindinger, W.: Energy dependencies of the proton transfer reactions $H_3O + + CH_2O \Leftrightarrow CH_2OH + + H_2O$, Int. J. Mass Spectrom., 167, 697–703, doi:10.1016/S0168-1176(97)00128-6, 1997.

Herrington, J. S. and Hays, M. D.: Concerns regarding 24-h sampling for formaldehyde, acetaldehyde, and acrolein using 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbents, Atmos. Environ., 55, 179–184, doi:10.1016/j.atmosenv.2012.02.088, 2012.

Herrington, J. S., Fan, Z.-H., Lioy, P. J., and Zhang, J.: Low Acetaldehyde Collection Efficiencies for 24-Hour Sampling with 2,4-Dinitrophenylhydrazine (DNPH)-Coated Solid Sorbents, Environ. Sci. Technol., 41, 580–585, doi:10.1021/es061247k, 2007.

Ho, K. E., Lee, S. C., Guo, H., and Tsai, W.: Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong, Sci. Total Environ., 322, 155–166, doi:10.1016/j.scitotenv.2003.10.004, 2004.

Ho, K. F., Lee, S. C., Louie, P. K. K., and Zou, S. C.: Seasonal variation of carbonyl compound concentrations in urban area of Hong Kong, Atmos. Environ., 36, 1259–1265, doi:10.1016/S1352-2310(01)00570-2, 2002.

Ho, K. F., Ho, S. S. H., Lee, S. C., Louie, P. K. K., Cao, J. J., and Deng, W. J.: Volatile Organic Compounds in Roadside Environment of Hong Kong, Aerosol Air Qual. Res., 13, 1331–1347, doi:10.4209/aaqr.2012.10.0278, 2013.

Ho, S. S. H., Chow, J. C., Watson, J. G., Ip, H. S. S., Ho, K. F., Dai, W. T., and Cao, J.: Biases in ketone measurements using DNPH-coated solid sorbent cartridges, Analytical Methods, 6, 967–974, doi:10.1039/C3AY41636D, 2014.

Huang, Y., Ho, S. S. H., Ho, K. F., Lee, S. C., Yu, J. Z., and Louie, P. K. K.: Characteristics and health impacts of VOCs and carbonyls associated with residential cooking activities in Hong Kong, J. Hazard. Mater., 186, 344–351, doi:10.1016/j.jhazmat.2010.11.003, 2011.

Inomata, S., Tanimoto, H., Kameyama, S., Tsunogai, U., Irie, H., Kanaya, Y., and Wang, Z.: Technical Note: Determination of formaldehyde mixing ratios in air with PTR-MS: laboratory experiments and field measurements, Atmos. Chem. Phys., 8, 273–284, doi:10.5194/acp-8-273-2008, 2008.

Jobson, B. T. and McCoskey, J. K.: Sample drying to improve HCHO measurements by PTR-MS instruments: laboratory and field measurements, Atmos. Chem. Phys., 10, 1821–1835, doi:10.5194/acp-10-1821-2010, 2010.

Jobson, B. T., Volkamer, R. A., Velasco, E., Allwine, G., Westberg, H., Lamb, B. K., Alexander, M. L., Berkowitz, C. M., and

Molina, L. T.: Comparison of aromatic hydrocarbon measurements made by PTR-MS, DOAS and GC-FID during the MCMA 2003 Field Experiment, Atmos. Chem. Phys., 10, 1989–2005, doi:10.5194/acp-10-1989-2010, 2010.

Kato, S., Miyakawa, Y., Kaneko, T., and Kajii, Y.: Urban air measurements using PTR-MS in Tokyo area and comparison with GC-FID measurements, Int. J. Mass Spectrom., 235, 103–110, doi:10.1016/j.ijms.2004.03.013, 2004.

Kerns, W. D., Pavkov, K. L., Donofrio, D. J., Gralla, E. J., and Swenberg, J. A.: Carcinogenicity of Formaldehyde in Rats and Mice after Long-Term Inhalation Exposure, Cancer Res., 43, 4382–4392, 1983.

Kuster, W. C., Jobson, B. T., Karl, T., Riemer, D., Apel, E., Goldan, P. D., and Fehsenfeld, F. C.: Intercomparison of Volatile Organic Carbon Measurement Techniques and Data at La Porte during the TexAQS2000 Air Quality Study, Environ. Sci. Technol., 38, 221–228, doi:10.1021/es034710r, 2004.

Lau, A. K. H., Yuan, Z., Yu, J. Z., and Louie, P. K. K.: Source apportionment of ambient volatile organic compounds in Hong Kong, Sci. Total Environ., 408, 4138–4149, doi:10.1016/j.scitotenv.2010.05.025, 2010.

Lee, S. C., Chiu, M. Y., Ho, K. F., Zou, S. C., and Wang, X.: Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong, Chemosphere, 48, 375–382, 2002.

Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., and Pozzer, A.: The contribution of outdoor air pollution sources to premature mortality on a global scale, Nature, 525, 367–371, doi:10.1038/nature15371, 2015.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, Int. J. Mass Spectrom., 173, 191–241, doi:10.1016/S0168-1176(97)00281-4, 1998.

Ling, Z. H., Guo, H., Zheng, J. Y., Louie, P. K. K., Cheng, H. R., Jiang, F., Cheung, K., Wong, L. C., and Feng, X. Q.: Establishing a conceptual model for photochemical ozone pollution in subtropical Hong Kong, Atmos. Environ., 76, 208–220, doi:10.1016/j.atmosenv.2012.09.051, 2013.

Ling, Z. H. and Guo, H.: Contribution of VOC sources to photochemical ozone formation and its control policy implication in Hong Kong, Environ. Sci. Policy, 38, 180–191, doi:10.1016/j.envsci.2013.12.004, 2014.

Louie, P. K. K., Ho, J. W. K., Tsang, R. C. W., Blake, D. R., Lau, A. K. H., Yu, J. Z., Yuan, Z., Wang, X., Shao, M., and Zhong, L.: VOCs and OVOCs distribution and control policy implications in Pearl River Delta region, China, Atmos. Environ., 76, 125–135, doi:10.1016/j.atmosenv.2012.08.058, 2013.

Lyu, X., Guo, H., Simpson, I. J., Meinardi, S., Louie, P. K. K., Ling, Z., Wang, Y., Liu, M., Luk, C. W. Y., Wang, N., and Blake, D. R.: Effectiveness of replacing catalytic converters in LPG-fueled vehicles in Hong Kong, Atmos. Chem. Phys., 16, 6609–6626, doi:10.5194/acp-16-6609-2016, 2016.

Müller, K., Haferkorn, S., Grabmer, W., Wisthaler, A., Hansel, A., Kreuzwieser, J., Cojocariu, C., Rennenberg, H., and Herrmann, H.: Biogenic carbonyl compounds within and above a coniferous forest in Germany, Atmos. Environ., 40, Supplement 1, 81–91, doi:10.1016/j.atmosenv.2005.10.070, 2006.

Ou, J., Guo, H., Zheng, J., Cheung, K., Louie, P. K. K., Ling, Z., and Wang, D.: Concentrations and sources of non-methane hydrocarbons (NMHCs) from 2005 to 2013 in Hong Kong: A multi-year real-time data analysis, Atmos. Environ., 103, 196–206, doi:10.1016/j.atmosenv.2014.12.048, 2015.

Rogers, T. M., Grimsrud, E. P., Herndon, S. C., Jayne, J. T., Kolb, C. E., Allwine, E., Westberg, H., Lamb, B. K., Zavala, M., Molina, L. T., Molina, M. J., and Knighton, W. B.: On-road measurements of volatile organic compounds in the Mexico City metropolitan area using proton transfer reaction mass spectrometry, Int. J. Mass Spectrom., 252, 26–37, doi:10.1016/j.ijms.2006.01.027, 2006.

Sillman, S.: Chapter 12 The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments, in: Developments in Environmental Science, edited by: Jill Austin, P. B. and William, S., Elsevier, 339–385, 2002.

Simpson, I. J., Blake, N. J., Barletta, B., Diskin, G. S., Fuelberg, H. E., Gorham, K., Huey, L. G., Meinardi, S., Rowland, F. S., Vay, S. A., Weinheimer, A. J., Yang, M., and Blake, D. R.: Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C_2–C_{10} volatile organic compounds (VOCs), CO_2, CH_4, CO, NO, NO_2, NO_y, O_3 and SO_2, Atmos. Chem. Phys., 10, 11931–11954, doi:10.5194/acp-10-11931-2010, 2010.

Spanel, P. and Smith, D.: Quantification of trace levels of the potential cancer biomarkers formaldehyde, acetaldehyde and propanol in breath by SIFT-MS, J. Breath Res., 2, 046003, doi:10.1088/1752-7155/2/4/046003, 2008.

Sprung, D., Jost, C., Reiner, T., Hansel, A., and Wisthaler, A.: Acetone and acetonitrile in the tropical Indian Ocean boundary layer and free troposphere: Aircraft-based intercomparison of AP-CIMS and PTR-MS measurements, J. Geophys. Res.-Atmos., 106, 28511–28527, doi:10.1029/2000JD900599, 2001.

USEPA: EPA Method TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), US Environmental Protection Agency, 1999.

Vlasenko, A., Macdonald, A. M., Sjostedt, S. J., and Abbatt, J. P. D.: Formaldehyde measurements by Proton transfer reaction – Mass Spectrometry (PTR-MS): correction for humidity effects, Atmos. Meas. Tech., 3, 1055–1062, doi:10.5194/amt-3-1055-2010, 2010.

von Schneidemesser, E., Monks, P. S., and Plass-Duelmer, C.: Global comparison of VOC and CO observations in urban areas, Atmos. Environ., 44, 5053–5064, doi:10.1016/j.atmosenv.2010.09.010, 2010.

Wang, B., Liu, Y., Shao, M., Lu, S., Wang, M., Yuan, B., Gong, Z., He, L., Zeng, L., Hu, M., and Zhang, Y.: The contributions of biomass burning to primary and secondary organics: A case study in Pearl River Delta (PRD), China, Sci. Total Environ., 569–570, 548–556, doi:10.1016/j.scitotenv.2016.06.153, 2016.

Wang, M., Zeng, L., Lu, S., Shao, M., Liu, X., Yu, X., Chen, W., Yuan, B., Zhang, Q., Hu, M., and Zhang, Z.: Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds, Analytical Methods, 6, 9424–9434, doi:10.1039/C4AY01855A, 2014.

Warneke, C., van der Veen, C., Luxembourg, S., de Gouw, J. A., and Kok, A.: Measurements of benzene and toluene in ambient air using proton-transfer-reaction mass spectrometry: calibration,

humidity dependence, and field intercomparison, Int. J. Mass Spectrom., 207, 167–182, doi:10.1016/S1387-3806(01)00366-9, 2001.

Warneke, C., Roberts, J. M., Veres, P., Gilman, J., Kuster, W. C., Burling, I., Yokelson, R., and de Gouw, J. A.: VOC identification and inter-comparison from laboratory biomass burning using PTR-MS and PIT-MS, Int. J. Mass Spectrom., 303, 6–14, doi:10.1016/j.ijms.2010.12.002, 2011a.

Warneke, C., Veres, P., Holloway, J. S., Stutz, J., Tsai, C., Alvarez, S., Rappenglueck, B., Fehsenfeld, F. C., Graus, M., Gilman, J. B., and de Gouw, J. A.: Airborne formaldehyde measurements using PTR-MS: calibration, humidity dependence, intercomparison and initial results, Atmos. Meas. Tech., 4, 2345–2358, doi:10.5194/amt-4-2345-2011, 2011b.

Watson, J. G., Chow, J. C., and Fujita, E. M.: Review of volatile organic compound source apportionment by chemical mass balance, Atmos. Environ., 35, 1567–1584, doi:10.1016/S1352-2310(00)00461-1, 2001.

Wisthaler, A., Apel, E. C., Bossmeyer, J., Hansel, A., Junkermann, W., Koppmann, R., Meier, R., Müller, K., Solomon, S. J., Steinbrecher, R., Tillmann, R., and Brauers, T.: Technical Note: Intercomparison of formaldehyde measurements at the atmosphere simulation chamber SAPHIR, Atmos. Chem. Phys., 8, 2189–2200, doi:10.5194/acp-8-2189-2008, 2008.

Xue, L., Wang, T., Louie, P. K. K., Luk, C. W. Y., Blake, D. R., and Xu, Z.: Increasing External Effects Negate Local Efforts to Control Ozone Air Pollution: A Case Study of Hong Kong and Implications for Other Chinese Cities, Environ. Sci. Technol., 48, 10769–10775, doi:10.1021/es503278g, 2014.