



# Calibration and intercomparison of acetic acid measurements using proton-transfer-reaction mass spectrometry (PTR-MS)

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**Abstract.** Acetic acid is one of the most abundant organic acids in the ambient atmosphere, with maximum mixing ratios reaching into the tens of parts per billion by volume (ppbv) range. The identities and associated magnitudes of the major sources and sinks for acetic acid are poorly characterized, due in part to the limitations of available measurement techniques. This paper demonstrates that, when properly calibrated, proton-transfer-reaction mass spectrometry (PTR-MS) can be a valuable technique for fast response, accurate quantification of acetic acid in ambient air. Three different PTR-MS configurations were calibrated at low ppbv mixing ratios using permeation tubes, which yielded calibration factors between 7.0 and 10.9 normalized counts per second per ppbv (ncps ppbv<sup>-1</sup>) at a drift tube field strength of 132 Townsend (Td). Detection limits ranged from 0.06 to 0.32 ppbv with dwell times of 5 s. These calibration factors showed negligible humidity dependence. Acetic acid was measured with PTR-MS on Appledore B Island, ME, during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) campaign and validated based on acetic acid measured in parallel using tandem mist chambers coupled with ion chromatography (MC/IC). Mixing ratios ranged from a minimum of  $0.075 \pm 0.004$  ppbv to  $3.555 \pm 0.171$  ppbv, with a median mixing ratio of  $0.530 \pm 0.025$  ppbv. An orthogonal least squares linear regression of paired data yielded a slope

of  $1.14 \pm 0.06$  ( $2\sigma$ ), an intercept of  $0.049 \pm 0.020$  ( $2\sigma$ ) ppbv, and an  $R^2$  of 0.78.

## 1 Introduction

Acetic acid (CH<sub>3</sub>COOH) is among the most dominant organic acids in the troposphere, with maximum mixing ratios in the range of tens of parts per billion (ppbv). Acetic acid influences the acidity of precipitation, cloud water and atmospheric aerosols and thereby modulates pH-dependent chemical processes in the atmosphere (Meng et al., 1995). Primary sources include direct emissions from industrial processes, biomass combustion, vegetation, and soils (Chebbi and Carlier, 1996; Talbot et al., 1999; Kesselmeier, 2001). Acetic acid is also produced in the atmosphere from the oxidation of alkenes by ozone and hydroxyl radical, and through acetylperoxy-hydroperoxy reactions (Niki et al., 1985; Orzechowska and Paulson, 2005; Lee et al., 2006b; Yu et al., 2008; Paulot et al., 2011). The primary atmospheric sinks for acetic acid are dry and wet deposition, with estimated lifetimes ranging from several hours to several days depending on deposition conditions (Chebbi and Carlier, 1996; Grosjean and Grosjean, 1999; Rosado-Reyes and Francisco, 2006). Estimated global emissions of acetic acid are estimated to be between 1217 and 1550 Gmol yr<sup>-1</sup> (von

Kuhlmann et al., 2003; Ito et al., 2007; Paulot et al., 2011), while estimated sinks are estimated to be  $\sim 1426 \text{ Gmol yr}^{-1}$  (Paulot et al., 2011). The temporal and spatial variability in sources and sinks need further constraint, as measurements exceed model predictions in many situations (Paulot et al., 2011).

Proton-transfer-reaction mass spectrometry (PTR-MS) has emerged as a valuable tool for measuring volatile organic compounds (VOCs) in the ambient atmosphere. Requiring only power and a small amount of ultra-pure water for operation, PTR-MS instruments achieve parts-per-trillion by volume (pptv) limits of detection and fast response for a wide range of atmospherically relevant VOCs (Hansel et al., 1995; de Gouw and Warneke, 2006; Blake et al., 2009). The high speed and sensitivity of the PTR-MS make it an appealing tool to measure acetic acid, since its high measurement speed, commercial availability, and online analysis are favorable compared to other techniques that provide lower time resolution and require significant analyst effort. Additionally, PTR-MS allows trace gas mixing ratios to be estimated using proton transfer reaction kinetics, yielding quantitative measurement (albeit with a margin of error because of uncertainties in fragmentation and instrumental losses) of compounds that lack calibration standards (Cappellin et al., 2012). However, the only metrics by which compounds are identified via PTR-MS are the proton affinity of a target compound, which must be greater than that of water ( $> 692 \text{ kJ mol}^{-1}$ ), and the mass-to-charge ratio ( $m/z$ ) of the protonated target compound, which is measured by the mass spectrometer. The majority of PTR-MS instruments currently in use possess quadrupole mass analyzers and are limited to unit mass resolution. This limitation makes it possible for isobaric protonated molecules and ion fragments to convolute the signal at a specific  $m/z$ , leading to inaccuracies in the compound quantification. Therefore, it is important to compare compounds measured by PTR-MS with those from an independent technique to ensure that the signal at a specific  $m/z$  is characteristic of a target compound. For many VOCs, PTR-MS performance has been verified via paired measurements using gas chromatographic (GC) techniques in several different studies (de Gouw et al., 2003; Warneke et al., 2003; Ambrose et al., 2010; Jardine et al., 2010), but there are few comparisons for ambient measurement of acetic acid, and more are needed (de Gouw et al., 2003).

Acetic acid measurements can be subject to signal artifacts due to production and loss from various sampling media. It readily adsorbs to inlets and transfer lines, often resulting in a negative measurement bias. In particular, filter and resin measurements have proven to be problematic with artifacts and non-quantitative trapping (Keene et al., 1989). Although generally quantitative, mist chamber techniques require relatively long sampling times (typically greater than 1 h) and a supply of ultrapure water, which constrains their suitability for continuous measurements over extended time periods (Keene et al., 1989). In contrast, the PTR-MS does not re-

quire large quantities of consumables, and directly samples the air stream, making it a valuable tool for continuous long-term measurements.

The rate constant for the acetic acid reaction with the PTR-MS primary reagent ion ( $\text{H}_3\text{O}^+$ ) is  $3.0 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , with a corresponding proton affinity of  $784 \pm 8 \text{ kJ mol}^{-1}$  (Mackay et al., 1978). Protonated acetic acid ( $\text{CH}_3\text{COOH}$ )  $\text{H}^+$  is measured at  $m/z$  61 in the PTR-MS mass spectrum and can undergo dehydration to produce acylium ions ( $\text{CH}_3\text{CO}^+$  at  $m/z$  43) inside the PTR-MS drift tube. It has been shown that this dehydration pathway is disfavored (endothermic by  $113.7 \text{ kJ mol}^{-1}$ ) at ambient temperatures, but the likelihood increases with temperature, and is also dependent on the field strength of the drift tube (Mackay et al., 1978; Lindinger et al., 1998a). At very high field strengths ( $\geq 200 \text{ Td}$ ,  $1 \text{ Td} = 10^{-17} \text{ V cm}^2$ ), another fragment appears at  $m/z$  15, the methyl cation  $\text{CH}_3^+$  (Lindinger et al., 1998b). Several other conceivable atmospheric compounds can contribute to these mass channels. Compounds that can form a signal at  $m/z$  61 include glycolaldehyde and propanols, while peroxyacetic acid and ethyl acetate form fragments that interfere at  $m/z$  61 (Warneke et al., 1996; Spanel et al., 2003; de Gouw and Warneke, 2006; Rogers et al., 2006; Wyche et al., 2009; Schwarz et al., 2009; Blake et al., 2009). Many compounds may also fragment to give an ion at  $m/z$  43, including fragment ions from acetaldehyde, propanols, butanal, peroxyacetyl nitrates (PANs), and ethyl acetate (Warneke et al., 1996; Steinbacher et al., 2004; de Gouw and Warneke, 2006; Rogers et al., 2006). However, many of these compounds typically are not present at high mixing ratios in the rural troposphere, and are thus not a source of significant interference (de Gouw et al., 2003; Karl et al., 2004; Steinbacher et al., 2004; Steeghs et al., 2004; Karl et al., 2005; Lee et al., 2006b; Holzinger et al., 2007; Maleknia et al., 2007; Yu et al., 2008; Fortner et al., 2009; Wyche et al., 2009; Kim et al., 2010).

Although acetic acid has been measured previously via PTR-MS and related MS techniques (Lindinger et al., 1998b; Holzinger et al., 2000; Williams et al., 2001; Warneke et al., 2004; Karl et al., 2004, 2005; Jobson et al., 2005; Sellegri et al., 2005; de Gouw et al., 2006; Feilberg et al., 2010), few studies report results based on direct instrumental calibration. Lee et al. (2006b) calibrated their instrument by diluting pure acetic acid into a Teflon bag with purified air. Wyche et al. (2009) used a permeation tube to calibrate their chemical ionization reaction time-of-flight mass spectrometer (CIR-TOF-MS). Warneke et al. (1996, 2001) used un-certified permeation tubes to generate gas phase acetic acid to characterize fragmentation and humidity dependence, but did not generate a calibration factor. Recently, Feilberg et al. (2010) used a permeation source to calibrate and explore the humidity dependence of their instrument for measuring emissions from livestock. Additionally, there have been several promising comparisons of acetic acid measurements using PTR-MS and other techniques. de Gouw et al. (2003)

**Table 1.** A summary of acetic acid calibrations reported in the literature and in this study.

Reference	PTR Method	Pressure (mbar)	Temp. (°C)	V Drift (volts)	$E/N$ (Td)	Calibration Method <sup>a</sup>	Calibration Factor (ncps ppbv <sup>-1</sup> ) <sup>b</sup>	Ratio $m/z$ 61/43
Warneke et al. (1996)	PTR-MS (SS)	N/A	N/A	N/A	~ 120	N/A	N/A	5.7
de Gouw et al. (2003)	PTR-MS (SS)	2.4	23	700	~ 120	ID	$8 \pm 0.4$	N/A
Christian et al. (2004)	PTR-MS (SS)	2.0	N/A	600	130	N/A	N/A	2.3
Hartungen et al. (2004)	PTR-MS (SS)	2.0	60	600	138	N/A	N/A	0.9
Lee et al. (2006a)	PTR-MS (HS)	2	N/A	600	120	TB	N/A	N/A
Maleknia et al. (2007)	PTR-MS (HS)	1.8–2.2	60–30	580 <sup>c</sup>	110	HS	N/A	0.04
Wyche et al. (2009)	CIR-TOF-MS	6–9	40	Variable <sup>d</sup>	90	PT	$45.95 \pm 1.38$ (Low $E/N$ )	5.9
					140		$17.42 \pm 0.52$ (High $E/N$ )	7.6
Feilberg et al. (2010)	PTR-MS (HS)	2.1–2.2	60	600	135	PT	N/A	2.3 (0 % RH)– 0.9 (80 % RH)
This work	PTR-MS-1 (SS)	2.0	45	600	132	PT	$7.0 \pm 0.3$	0.9
This work	PTR-MS-1 (SS)	2.0	45	600	132	PT <sup>e</sup>	$6.9 \pm 0.3$	1.05
This work	PTR-MS-2 (HS)	2.0	45	600	132	PT	$8.5 \pm 0.4$	1.5
This work	PTR-MS-1 (HS)	2.0	45	600	132	PT	$10.9 \pm 0.7$	1.9
This work	PTR-MS-1 (HS)	2.0	45	530	116	PT	$14.3 \pm 0.8$	2.9
This work	PTR-MS-1 (HS)	2.0	45	481	106	PT	$17.9 \pm 1.1$	3.7
This work	PTR-MS-1 (HS)	2.0	45	433	95	PT	$23.0 \pm 1.7$	4.5
This work	PTR-MS-1 (HS)	2.0	45	400	88	PT	$30.8 \pm 2.6$	6.0

N/A indicates data not available

<sup>a</sup> ID: Indirect, TB: Teflon Bag, HS: Head Space; PT: Permeation Tube.<sup>b</sup> Signal at  $m/z$  61, normalized to a primary ion signal of  $1 \times 10^6$ .<sup>c</sup> Inferred from reported values.<sup>d</sup>  $E/N$  varied along the length of the drift tube, and the instrument operated in low and high  $E/N$  modes.<sup>e</sup> H<sub>2</sub>O scrubbed from sample.

used an indirect calibration by referencing the PTR-MS signal to mist chamber data. Christian et al. (2004) compared several analytical techniques for measuring biomass burning emissions and found that correcting the signal at  $m/z$  61 for acetic acid fragmentation gave good agreement with open path FTIR (Fourier Transform Infrared Spectroscopy) measurements ( $\text{PTR-MS/FTIR} = 1.17 \pm 0.34$ ). Previously published calibration details, along with the results from this study, are summarized in Table 1.

This work provides the first in-depth discussion on calibrating PTR-MS instruments for atmospheric acetic acid measurements. Moreover, the PTR-MS is compared with a well-established measurement technique to validate its use for acetic acid. Finally, the atmospheric relevance of the acetic acid measurements made with a PTR-MS during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) campaign is examined (Fehsenfeld et al., 2006).

## 2 Experimental

### 2.1 Instrument configuration

Two different PTR-MS instruments (Ionicon Analytik) were employed during the acetic acid calibration study. The first instrument (PTR-MS-1 (SS)) was initially configured as a standard sensitivity model. The second instrument (PTR-MS-2 (HS)) was a high sensitivity model, which features an additional intermediate vacuum stage between the drift

tube and the quadrupole mass spectrometer. PTR-MS-1 (SS) was subsequently upgraded to the high sensitivity configuration (PTR-MS-1 (HS)) using a conversion kit supplied by the manufacturer (de Gouw and Warneke, 2006). The main difference between the standard sensitivity and the high sensitivity configuration is the addition of a second turbo pump, which provides additional pumping capacity in the detection region of the PTR-MS. In addition to the high sensitivity upgrade, PTR-MS-1 (HS) was further modified to reduce the amount of water vapor entering the drift tube from the ion source. By changing the position of vacuum fittings and rotating the ion source 120°, it was possible to replace the original 32-cm-long, 0.62 cm (1/4" inch) outer diameter Teflon tube that links the skimmer region to the turbo pump with a 10-cm-long tube, shortening the flow path to 15 cm from the original 47 cm. As a result, the pumping capacity of the skimmer region was increased, causing more water vapor to exit the ion source through the skimmer instead of through the drift tube. By reducing the amount of water entering the drift tube, the probability of reverse proton transfer reactions to water molecules from ionized compounds was reduced, thereby increasing the response to compounds with a proton affinity close to that of water. This modification was similar to that described elsewhere (Wisthaler et al., 2008; Vlasenko et al., 2010) and was not done to specifically enhance the performance of PTR-MS-1 (HS) for acetic acid measurement.

All instruments were set to an ion source water flow rate of  $11 \text{ cm}^3 \text{ min}^{-1}$  and a discharge current of 8 mA. The drift tube was set to a pressure of 2.0 mbar, a temperature of 45 °C, and

**Table 2.** Average  $\pm$  standard deviation of the primary ion signal for protonated clusters in the primary in PTR-MS configurations used for this study.

Instrument	$E/N$ (Td)	$\text{H}_3\text{O}^+$ ( $m/z$ 19) (Mhz $\pm 1\sigma$ )	$\text{H}_3\text{O}^+(\text{H}_2\text{O})$ ( $m/z$ 37) (hz $\pm 1\sigma$ ) $\times 10^4$	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ ( $m/z$ 55) (hz $\pm 1\sigma$ )
PTR-MS-2 (HS)	132	$5.15 \pm 0.19$	$6.81 \pm 3.12$	$105 \pm 75$
PTR-MS-1 (SS)	132	$3.12 \pm 0.13$	$27.05 \pm 2.16$	$2266 \pm 395$
PTR-MS-1 (SS) Dry	132	$3.61 \pm 0.15$	$2.14 \pm 2.92$	$1306 \pm 396$
PTR-MS-1 (HS)	88	$1.65 \pm 0.11$	$15.96 \pm 9.08$	$55299 \pm 9365$
PTR-MS-1 (HS)	95	$1.36 \pm 0.20$	$5.28 \pm 16.42$	$6632 \pm 3526$
PTR-MS-1 (HS)	106	$1.37 \pm 0.19$	$1.39 \pm 5.87$	$674 \pm 566$
PTR-MS-1 (HS)	116	$1.05 \pm 0.38$	$0.27 \pm 1.22$	$52 \pm 47$
PTR-MS-1 (HS)	132	$1.08 \pm 0.13$	$0.05 \pm 0.10$	$3 \pm 8$

a voltage of 600 V, yielding a corresponding field strength of 132 Td. To ensure that products from the reaction between  $\text{O}_2^+$  and acetic acid did not bias results, the ion source was optimized such that  $\text{O}_2^+$  was less than 1 % of the  $\text{H}_3\text{O}^+$  signal. The primary ion signal ( $\text{H}_3\text{O}^+$ ) in PTR-MS-1 (SS) was  $3 \times 10^6$  hz, in PTR-MS-1 (HS) was  $1\text{--}2 \times 10^6$  Hz, and was  $5 \times 10^6$  Hz in PTR-MS-2 (HS). (The lower ion signal in PTR-MS-1 (HS) is attributed to the smaller amount of water vapor present in the ion source as a result of modification.) The signals for  $\text{H}_3\text{O}^+$  ( $m/z$  19),  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  ( $m/z$  37) and  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$  ( $m/z$  55) for all calibration experiments (Table 2) indicate that each instrument allowed different amounts of water vapor into the drift tube from the ion source, corresponding to differing abundances of protonated clusters. The ratios of each hydrated cluster to  $m/z$  19 are given in Table 2. The ion signals are presented as measured, and no correction was made for transmission losses. The background signals at  $m/z$  61 and  $m/z$  43 were less than 11 normalized counts per second (ncps).

The sensitivity of the PTR-MS to acetic acid is expressed in terms of the calibration factor via

$$\frac{\text{ncps}}{\text{ppbv}} = \frac{m/z 61}{\text{H}_3\text{O}^+ \cdot [\text{Acetic Acid}]} \times 10^6 \quad (1)$$

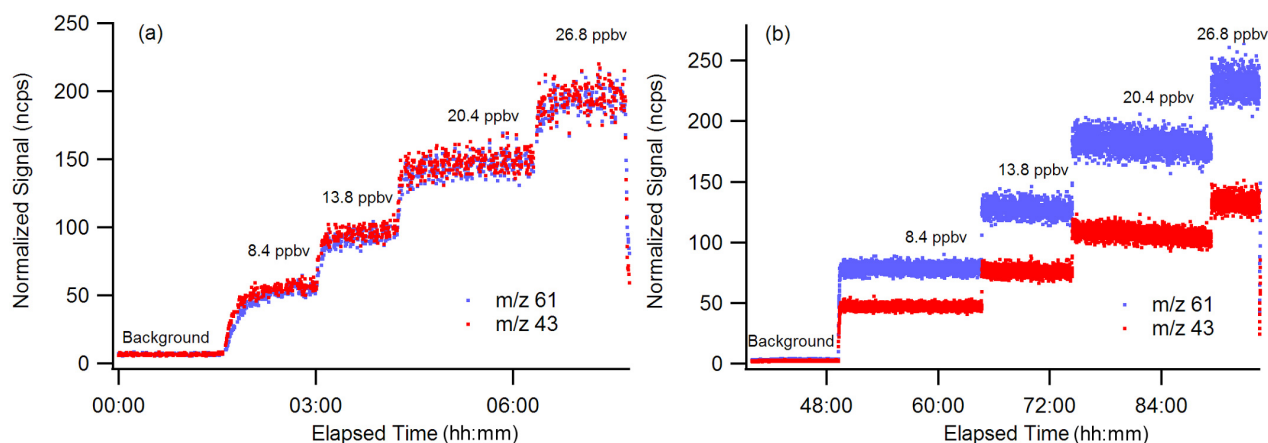
where the calibration factor is defined as the signal (Hz at  $m/z$  61 for every ppbv acetic acid) normalized to the primary ion signal ( $\text{H}_3\text{O}^+$ , Hz at  $m/z$  19), and scaled by  $10^6$  (Warneke et al., 2001).

## 2.2 Permeation system

The instruments were calibrated via dilution and analysis of acetic acid from a permeation source (Talbot et al., 1999). A free-flowing calibration manifold was constructed such that acetic acid was exposed to only inert glass, passivated stainless steel, and Teflon surfaces thereby minimizing hysteresis problems associated with active surfaces and dead volume. The insulated permeation oven was controlled by a thermo-

stat and embedded in a large thermal block to buffer it against variations in room temperature and cycling of the heating elements. Purified air was generated by passing ambient air over Pd-on-alumina (0.5 %) bead-filled catalytic converter (Apel-Riemer Environmental) operating at 425 °C. This purification technique removed hydrocarbons and other reactive impurities from air without altering major constituents including water vapor and  $\text{CO}_2$ . The flow of purified air was then split into two channels, which were controlled by mass flow controllers (MKS Instruments). Both flows were controlled upstream of the permeation oven to avoid exposing the wetted surfaces in the controllers to acetic acid. A constant permeation flow ( $F_{\text{perm}}$ ) of  $100 (\pm 5 \%) \text{ cm}^3 \text{ min}^{-1}$  was directed to the permeation oven through 0.62 cm OD (1/4")/0.47 cm ID Teflon tubing. The second purified air channel was a variable dilution ( $F_{\text{dil}}$ ) flow that ranged between 0 and  $7000 (\pm 5 \%) \text{ cm}^3 \text{ min}^{-1}$ . The dilution flow was mixed with the permeation flow at a T-union, forming a combined flow ( $F_{\text{perm}} + F_{\text{dil}}$ ) that was sampled 61 cm downstream by the PTR-MS. A length of tubing extended beyond the PTR-MS inlet to prevent lab air from mixing into the system. The total length of the transfer lines after the permeation oven was limited to one meter to prevent back pressure from developing in the permeation oven, which would increase the emission rate of the permeation tube. Known mixing ratios of acetic acid were generated by diluting pure acetic acid emitted from a permeation tube (Kin-Tek Inc.) that was gravimetrically certified ( $103 \pm 5 \%) \text{ ng min}^{-1}$  at 30 °C) by the manufacturer. The high dilution flow rates yielded stable acetic acid calibration gas streams at low ppbv levels, within the range of those in ambient air, and much less than ppmv level standards typically generated by other techniques (Veres et al., 2010).

The dilution flow ( $F_{\text{dil}}$ ) was used to control the mixing ratio of acetic acid in the calibration gas. A typical calibration curve is displayed in Fig. 1a. The mixing ratios of acetic acid measured in each curve ( $\pm 1\sigma$ ) were  $8.4 \pm 0.8$ ,  $13.8 \pm 1.4$ ,  $20.4 \pm 2.0$ , and  $26.8 \pm 2.7$  ppbv. As a check for



**Fig. 1.** Calibration curves for acetic acid obtained with the instruments used in this study: (a) PTR-MS-1 (SS) and (b) PTR-MS-2 (HS).

outside contaminants, a mass spectrum collected between  $m/z$  33 and  $m/z$  99 was scanned every 20 measurement cycles.

### 2.3 Acetic acid measurements during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) campaign

From 2 July to 13 August 2004, the PTR-MS-2 (HS) was deployed on Appledore Island, ME, located 11 km off the coast (42.97° N, 70.62° W) as part of the ICARTT campaign (Fehsenfeld et al., 2006). Ambient air was drawn from the top of a 20 m tower through a 30.5-m-long, 9.53 mm ID PFA Teflon tube, with a flow rate of  $\approx 751 \text{ min}^{-1}$ . A membrane pump was used to draw a sub-stream of air from the main inlet line at a flow rate of  $11 \text{ min}^{-1}$ , from which the PTR-MS sampled. The PTR-MS was operated using a drift tube pressure of 2.0 mbar and voltage of 600 V (132 Td), settings identical to those used during the calibration experiments (Sect. 3.1). A total of 25 mass channels corresponding to various VOCs of interest were measured with dwell times between 5–20 s. Every 2.5 h, the PTR-MS control software automatically switched the sample flow through a 13-cm-long, 1.27 cm ID 0.5 % Pd-on-alumina bead catalytic converter at 450 °C for 30 min. The catalytic converter oxidized VOCs in the sample stream to provide a measurement of the instruments background signal (Ambrose et al., 2007). Based on the counting statistics of ambient and background signals, the average uncertainty of the PTR-MS measurements was 9.2 % ( $\pm 1\sigma$ ) using the method described in Hayward et al. (2002).

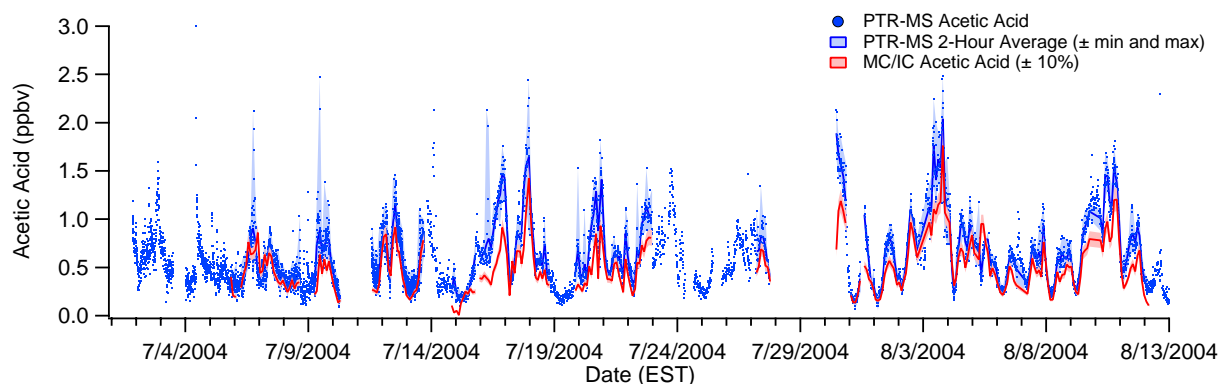
To ascertain the accuracy of the PTR-MS acetic acid measurements, they were compared with co-located acetic acid measurements over 2-h intervals by a tandem mist chamber-ion chromatographic technique (MC/IC) (Keene et al., 2004; Keene et al., 2007). Briefly, for the MC/IC measurements, ambient air was sampled at nominal flow rates of  $201 \text{ min}^{-1}$  through a size fractionating inlet and an inline Teflon filter to

remove super- and sub- $\mu\text{m}$ -diameter particles, respectively, followed by tandem mist chambers containing deionized water. Exposed mist solutions were analyzed on site via ion chromatography. The average detection limit calculated following Keene et al. (1989) was 0.003 ppbv, and the average precision was  $\pm 10\%$  or  $\pm 0.002 \text{ ppbv}$ , whichever corresponded to the higher absolute value (Keene et al., 1989). PTR-MS measurements were averaged over the 2-h sampling interval of the MC/IC (Fig. 2).

## 3 Results and discussion

### 3.1 PTR-MS calibrations at 132 Td

The calibration factors for PTR-MS-1 (SS), PTR-MS-2 (HS), and PTR-MS-1 (HS) at 132 Td ranged from  $7.0 \pm 0.3$  to  $10.9 \pm 0.7 \text{ ncps ppbv}^{-1}$  with the standard sensitivity configuration having the smallest calibration factor and the modified high sensitivity configuration PTR-MS-1 (HS) having the largest (Table 1). At a dwell time of 5 s, these calibration factors correspond to detection limits ( $2\sigma$ ) of 0.06 ppbv for (PTR-MS-2 (HS)), 0.16 ppbv for PTR-MS-1 (SS), and 0.32 ppbv for PTR-MS-1 (HS), assuming no losses in the sampling manifold. The higher detection limit found for PTR-MS-1 in the HS configuration is due to lower primary ion intensity compared to the other configurations tested, resulting in fewer target ions produced and detected. The calibration factor for PTR-MS-1 (SS) is  $\sim 1 \text{ ncps ppbv}^{-1}$  smaller than the value of  $8.0 \pm 0.4 \text{ ncps ppbv}^{-1}$  found for a different standard sensitivity PTR-MS in a previous study (de Gouw et al., 2003). The ratio of  $m/z$  61 to  $m/z$  43 indicates the degree of fragmentation of protonated acetic acid into the acylium ion ( $m/z$  43) (Table 1 and Table 3). The fragmentation was the greatest in PTR-MS-1 (SS), with a  $m/z$  61 to  $m/z$  43 ratio of 0.86 and the least in PTR-MS-1 (HS) with a ratio of 1.9. The total calibration factor, derived using the sum of  $m/z$  61 +  $m/z$  43, was the greatest in



**Fig. 2.** Measurements of acetic acid from the PTR-MS (blue) and MC/IC (red) during ICARTT. For the periods when both techniques were operational, the PTR-MS average mixing ratios over the 2-h MC/IC sampling interval are depicted on the dark blue line with the corresponding individual values as dark blue dots. The range of PTR-MS measurements over each 2-h interval is light blue. The MC/IC average relative uncertainty ( $\pm 10\%$ ) is shown in pink shading.

PTR-MS-1 (HS) with a value of  $15.8 \pm 0.8$  ncps ppbv $^{-1}$ , and the least with PTR-MS-2 (HS) with  $13.4 \pm 0.4$  ncps ppbv $^{-1}$  (PTR-MS-1 (SS) yielded  $14.0 \pm 0.4$  ncps ppbv $^{-1}$ ). This indicates that PTR-MS-2 was not as efficient at delivering product ions to the detector as PTR-MS-1.

The PTR-MS instruments responded quickly to changes in the acetic acid mixing ratio. PTR-MS-2 (HS) exhibited a nearly instantaneous response to mixing ratio changes, which were on the order of a few seconds (Fig. 1). PTR-MS-1 exhibited rise times (time to 90 % of full signal) that varied from 15 min to 48 min ( $0.4\text{--}0.2$  ppbv min $^{-1}$ ) with the faster changes occurring at higher mixing ratios (Fig. 1); fall times from the highest mixing ratio were around 35 min ( $0.7$  ppbv min $^{-1}$ ). The different response times are attributable to the vacuum isolation valves that were installed to protect the instruments during power failures. PTR-MS-2 (HS) used a small diameter (3.75 mm) valve and tubing throughout the inlet system, while PTR-MS-1 had un-swept volume within a 6.35 mm valve and an  $\sim 8$  cm section of tubing that was attached to the 3.75 mm inlet.

### 3.2 Calibration factor dependence on drift tube field strength

PTR-MS-1 (HS) was calibrated over a range of drift tube conditions to explore the relationship between the field strength and the calibration factor for acetic acid. By reducing the field strength, the residence time of  $\text{H}_3\text{O}^+$  in the drift tube is increased, increasing product ion formation. Lower field strengths also decrease the energy of ion-molecule collisions, reducing fragmentation, but allowing the formation of protonated clusters (particularly with water) that do not readily engage in proton transfer reactions with some compounds. This effect can complicate the obtained spectra and introduce numerous challenges to accurate quantification compared to situations where  $\text{H}_3\text{O}^+$  is the

**Table 3.** Cluster and fragment distribution data obtained over a range of  $E/N$  values with PTR-MS-1 (HS).

$E/N$ (Td)	Ratio of ( $m/z$ 61) <sup>a</sup> / ( $m/z$ 43)	Fraction $m/z$ 43 <sup>b</sup>	Fraction $m/z$ 61 <sup>b</sup>	Fraction $m/z$ 79 <sup>b,c</sup>
PTR-MS-1 (HS)				
88	5.96	0.12	0.86	$3.0 \times 10^{-2}$
95	4.48	0.15	0.85	$1.0 \times 10^{-2}$
106	3.66	0.18	0.82	0.00
116	2.89	0.23	0.77	0.00
132	1.94	0.30	0.70	0.00
PTR-MS-1 (SS)				
132	0.86	0.53	0.46	$5.0 \times 10^{-3}$
132 (Dry)	1.05	0.49	0.51	0.00
PTR-MS-2 (HS)				
132	1.47	0.40	0.60	0.00

<sup>a</sup> Fragmentation ratio of protonated acetic acid to the acylium ion.

<sup>b</sup> Fractional strength of each ion in the acetic acid signal at each  $E/N$ .

<sup>c</sup> Presumed  $\text{CH}_3\text{COOH}_2(\text{H}_2\text{O})^+$ .

dominant reagent ion, offsetting the gains made in sensitivity to acetic acid.

During the field strength studies, the drift tube was maintained at 2.0 mbar and 45 °C. At each calibration level, the drift tube was stepped through the following voltages: 400, 433, 481, 530, and 600 V, corresponding to field strengths of 88, 95, 106, 116, and 132 Td.

The average  $\text{H}_3\text{O}^+$  signal was 1.1–1.8 MHz for all field strengths (Table 2). At 132 Td, the ratio of  $m/z$  37 to  $m/z$  19 was  $4.67 \times 10^{-3}$ , and the ratio of  $m/z$  55 to  $m/z$  19 was  $3.0 \times 10^{-6}$ . At the lowest field strength (88 Td), the ratio of  $m/z$  37 to  $m/z$  19 increased to  $9.69 \times 10^{-1}$  and the ratio of  $m/z$  55 to  $m/z$  19 was  $3.34 \times 10^{-2}$  (Table 3). The sensitivity to acetic acid was inversely proportional to field strength, following the trend noted by Wyche et al. (2009). At 132 Td, the calibration factor for  $m/z$  61 was



$10.9 \pm 0.7$  ncps ppbv<sup>-1</sup>, while at a field strength of 88 Td it was  $30.8 \pm 2.6$  ncps ppbv<sup>-1</sup>. The increase in this calibration factor at lower field strengths is due both to the increased reaction time, and the increased importance of proton transfer and ligand switching reactions from protonated water clusters in the drift tube.

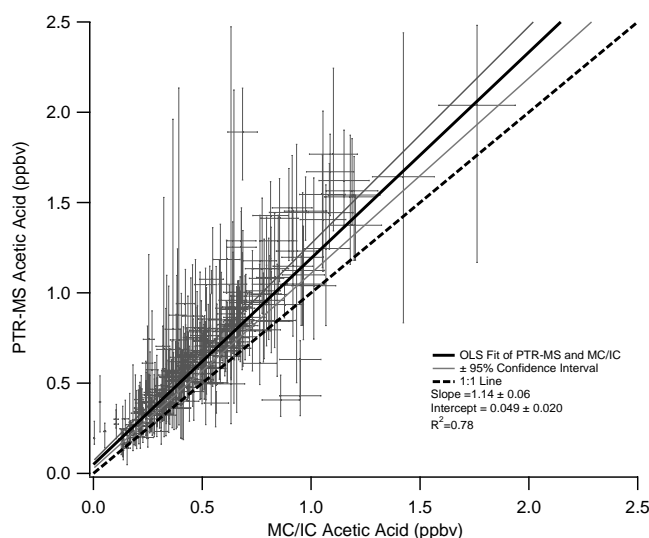
Acetic acid fragmentation increases at higher field strengths and, hence, greater collision energies. The ratio of  $m/z$  61 to  $m/z$  43 was 5.96 at 88 Td and decreased to 1.94 at 132 Td.

### 3.3 Sensitivity dependence on sample air humidity

The available literature regarding the sensitivity dependence on humidity for acetic acid is conflicting. This is important to consider since the humidity of ambient air is variable, and hence could impact the accuracy of measurements if unaccounted for. Warneke et al. (2001) found no relationship between humidity and sensitivity, while, subsequent to our experiments, Feilberg et al. (2010) found a very strong dependence for fragmentation, with the ratio of  $m/z$  61 to  $m/z$  43 ranging from 2.5 (0 % RH) to 0.9 (80 % RH). In our study a separate calibration was done on PTR-MS-1 (SS) using desiccant dried air. The calibration factors for  $m/z$  61 and  $m/z$  43 were  $6.9 \pm 0.3$  ncps ppbv<sup>-1</sup> and  $5.6 \pm 0.3$  ncps ppbv<sup>-1</sup>, respectively. The calibration factor at  $m/z$  61 was within the uncertainty of the calibration factor obtained at ambient humidities, but at  $m/z$  43 it was lower by 1.4 ncps ppbv<sup>-1</sup>. The fragmentation ratio of  $m/z$  61 to  $m/z$  43 was 1.05, greater than that obtained with ambient air (Table 3). The characteristics of reducing the amount of ambient water in the drift tube were decreased fragmentation coupled with somewhat lower ionization efficiency of acetic acid. However, the overall calibration factor did not change significantly from that at ambient humidity, consistent with the result from Warneke et al. (2001).

In contrast, across the different PTR-MS instruments, the amount of acetic acid fragmentation was proportional to the signal at  $m/z$  37 ( $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ ). PTR-MS-1 (HS) had the lowest fraction of  $m/z$  37 and the least amount of fragmentation, while PTR-MS-1 (SS) had the largest fraction of  $m/z$  37 and the most fragmentation (Table 3). As the relative strength of the signal at  $m/z$  37 to  $m/z$  19 is a proxy for the amount of water vapor in the PTR-MS drift tube (Warneke et al., 2001; Tani et al., 2004), this finding shows that fragmentation is also dependent on the amount water vapor in the drift tube, consistent with the findings of Feilberg et al. (2010).

Comparing across the different studies, high levels of water vapor in the drift tube from the ion source make the humidity contributions from ambient air minor, yielding calibration results that are humidity independent. In situations where water vapor from the ion source is reduced, the role of ambient humidity in drift tube water vapor levels will be significant, giving a humidity-dependent instrument response.



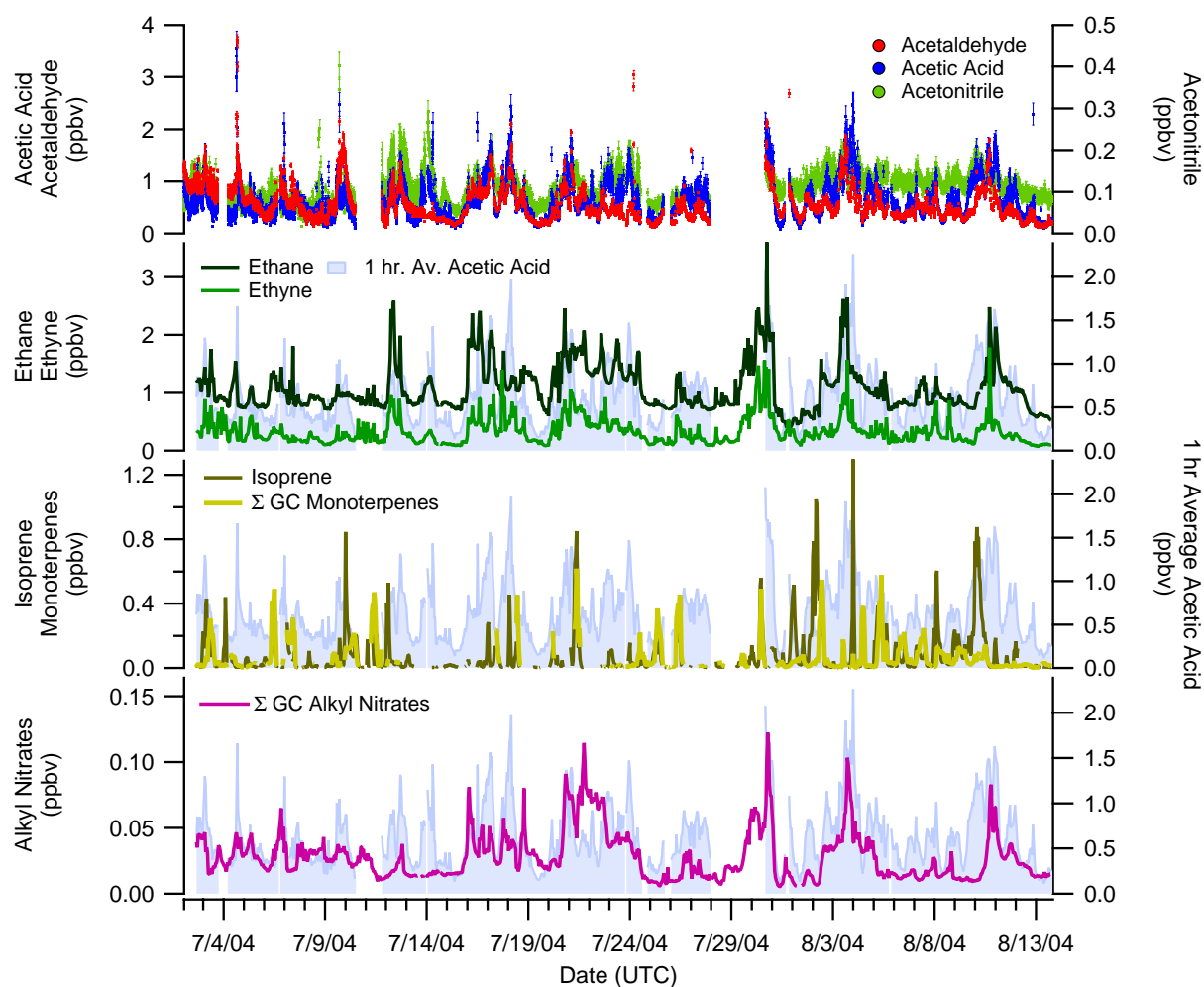
**Fig. 3.** Scatter plot of PTR-MS versus MC/IC measurements of acetic acid on Appledore Island during the ICARTT campaign. The error bars reflect the uncertainty of the individual PTR-MS and MC/IC measurements.

A weak signal at  $m/z$  79 was present at field strengths of 88 Td and 95 Td, but was not detectable at higher field strengths in PTR-MS-1 (HS). A small signal was present in the full mass spectrum of PTR-MS-1 (SS) as well, but not during calibrations using dry air. The signal at  $m/z$  79 is likely to be the hydrated acetic acid cluster  $[\text{CH}_3\text{COOH}_2^+(\text{H}_2\text{O})]$ , formed through a ligand switching reaction with  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ . Hartungen et al. (2004) detected the presence of  $m/z$  79 in their standard sensitivity PTR-MS (comprising 3.7 % of the total acetic acid signal), which was enhanced by the high ambient humidities present in their experiments. It is likely that the hydrated acetic acid clusters undergo collision induced dissociation subsequent to their formation, explaining why the signal at  $m/z$  79 was very small (Mackay et al., 1978; Hartungen et al., 2004).

### 3.4 PTR-MS and MC/IC intercomparison on Appledore Island during ICARTT 2004

The performance of the PTR-MS for measuring ambient acetic acid was evaluated further via direct intercomparison with paired MC/IC measurements (Fig. 2). A weighted orthogonal least squares regression (OLS) (Boggs et al., 1989) of the acetic acid data from the PTR-MS and MC/IC measurements is shown in Fig. 3. The resulting slope of the two datasets ( $N = 271$ ) yielded a slope of  $1.14 \pm 0.06$  ( $2\sigma$ ), an intercept of  $0.049 \pm 0.020$  ppbv ( $2\sigma$ ; statistically significant), and a correlation coefficient ( $R^2$ ) of 0.78.

Agreement between results for the two measurement techniques was probably impacted by two factors involving the performance of the PTR-MS. Unplanned electrical power failures occurred frequently during the campaign. When



**Fig. 4.** The different primary and secondary sources of acetic acid are reflected in relationships with anthropogenic emissions (acetaldehyde (PTR-MS), ethane (GC) and ethyne (GC)), biogenic compounds (isoprene (GC), monoterpenes (sum of  $\alpha$ - and  $\beta$ -pinene, camphene, and limonene; GC), biomass burning (acetonitrile (PTR-MS)), and photochemical production (sum of methyl-, ethyl-, butyl-, propyl-, 2-, and 3-pentyl nitrates (GC)).

power was interrupted, ambient air entered the vacuum system, after which several days were required to fully desorb compounds from instrument surfaces. These outages contributed to the variability in the background signal, causing it to be elevated for periods of up to several days. In addition, at the time of the campaign, the PTR-MS was also relatively new, having only been used a few months, and consequently wetted surfaces within the instrument. Particularly the Teflon spacers in the drift tube and other polymer seals in the instrument may not have been passivated. Both factors contributed to the observed temporal variability of the PTR-MS background signal during the campaign, which are likely to contribute to the non-unity slope of the correlation with the MC/IC measurements. It also is possible that another compound (or set of compounds) with a similar temporal variation to acetic acid contributed a small interference at  $m/z$  61. However, the performance issues introduced by

the frequent power outages make the degree of interference hard to quantify.

Comparing the individual PTR-MS measurements with the 2-h average from the MC/IC (Fig. 2) shows many short timescale events that are resolved by the PTR-MS. There are several events that are fast enough to either be unresolved by the MC/IC or are represented by a single data point. That the PTR-MS was able to capture the full range and temporal variability of acetic acid demonstrates the strength of the technique.

During the ICARTT campaign the PTR-MS made 6626 individual acetic acid measurements. The average ( $\pm 1$  standard deviation) and the median ( $\pm 9.2\%$  measurement uncertainty) mixing ratio of PTR-MS measured acetic acid were  $0.608 \pm 0.342$  ( $1\sigma$ ) ppbv and  $0.530 \pm 0.049$  ppbv, respectively. The mixing ratios ranged from  $0.075 \pm 0.007$  ppbv to  $3.555 \pm 0.327$  ppbv (Fig. 4).



Large-scale atmospheric transport from distinct source regions significantly influences air quality in coastal New England. Air masses transported along the heavily populated mid-Atlantic corridor are highly enriched in pollutants, such as ozone, carbon monoxide, non-methane hydrocarbons, and halocarbons, relative to air masses transported from other regions (Mao and Talbot, 2004a, b; Angevine et al., 2004; Fischer et al., 2006; Chen et al., 2007; Darby et al., 2007; White et al., 2007). Relative temporal variability in acetic acid often correlated with tracers of anthropogenic activities, biomass burning, photochemical processing (Fig. 4), and it was generally elevated when terrestrially sourced air masses passed over Appledore (Haase, 2010). In the dataset for the campaign, acetic acid mixing ratios showed positive correlations with acetaldehyde ( $R^2 = 0.35$ ), ethane ( $R^2 = 0.28$ ), and ethyne ( $R^2 = 0.35$ ), compounds that are associated with mobile sources (Seinfeld and Pandis, 1998; Watson et al., 2001). Acetic acid levels also showed enhancements when acetonitrile ( $R^2 = 0.35$ ), a tracer for biomass burning, was elevated, linking acetic acid this combustion source (de Gouw et al., 2006; Talbot et al., 2011). Hourly average of acetic acid was also elevated when mixing ratios of the alkyl nitrates were correspondingly elevated. Alkyl nitrates are secondary products of hydrocarbon oxidation, and their presence could be taken as an indicator of photochemically produced acetic acid in polluted air masses. Acetic acid did not show correlation with the biogenic isoprene ( $R^2 = 0.02$ ) and monoterpene ( $R^2 = 0.06$ ) compounds. The levels of these compounds were low compared to terrestrial observations owing to photochemical processing before arrival at Appledore Island, so they are not necessarily robust tracers of biogenic emissions of acetic acid. These results have revealed that local levels of acetic acid in New England are controlled by a complex group of sources and processes and are not dominated by a single pathway, clearly warranting further investigation.

#### 4 Conclusions

PTR-MS is a valuable technique for measuring an array of atmospheric VOCs, providing high time resolution, high sensitivity, and online analysis. By using a permeation tube based calibration source and high flow rates of dilution gas in a low back-pressure mixing system, it is possible to calibrate the PTR-MS at low ppbv mixing ratios for acetic acid. Our calibrations and others reported in the literature show that acetic acid fragments to varying degrees in different PTR-MS systems. Fragmentation may be mediated by the amount of water vapor available in the drift tube, as fragmentation increases in instruments that have lower ion source skimmer pumping capacities. The difference in fragmentation ratios between different instruments emphasizes the importance of parameterizing each instrument's performance, as fragmentation of acetic acid is not precisely reproducible from one

system to another. At 132 Td, we obtain calibration factors that vary between 7.0 and 10.9 ncps for this compound.

During the ICARTT campaign, we measured acetic acid on Appledore Island with a PTR-MS and a MC/IC system operating in parallel at the same location. A regression of the PTR-MS averaged over the MC/IC sampling intervals yielded a slope of 1.14, an intercept of 0.049 ppbv, and an  $R^2$  of 0.78. Frequent power outages during the campaign negatively impacted performance of the PTR-MS via associated increases in background variability. However, results suggest minor to negligible interferences by other compounds; the dominant signal is acetic acid. Our results indicate that PTR-MS can reliably quantify acetic acid in coastal New England air, but additional work is recommended to characterize potential chemical interferences in other environments.

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