1 **Comparison of negative-ion proton-transfer with iodide ion**
2 **chemical ionization mass spectrometry for quantification of**
3 **isocyanic acid in ambient air**

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Abstract

Isocyanic acid (HNCO) is a trace gas pollutant of potential importance to human health whose measurement has recently become possible through the development of negative-ion proton-transfer chemical ionization mass spectrometry (NI-PT-CIMS) with acetate reagent ion. In this manuscript, an alternative ionization and detection scheme, in which HNCO is quantified by iodide CIMS (iCIMS) as a cluster ion at m/z 170, is described. The sensitivity was inversely proportional to water vapor concentration but could be made independent of humidity changes in the sampled air by humidifying the ion-molecule reaction (IMR) region of the CIMS. The performance of the two ionization schemes was compared and contrasted using ambient air measurements of HNCO mixing ratios in Calgary, AB, Canada, by NI-PT-CIMS with acetate reagent ion from Dec 16 to 20, 2013, and by the same CIMS operated in iCIMS mode from Feb 3 to 7, 2014. The iCIMS exhibited a greater signal-to-noise ratio than the NI-PT-CIMS, not because of its sensitivity, which was lower (~ 0.083 normalized counts per second (NCPS) per parts-per-trillion by volume (ppt_v) compared to ~ 9.7 NCPS ppt_v^{-1}), but because of a much lower and more stable background (3 ± 4 compared to a range of $\sim 2 \times 10^3$ to $\sim 6 \times 10^3$ NCPS). For the Feb 2014 data set, the HNCO mixing ratios in Calgary air ranged from <12 to 94 ppt_v (median 34 ppt_v), were marginally higher at night than during day, and correlated with nitrogen oxide ($\text{NO}_x = \text{NO} + \text{NO}_2$) mixing ratios and submicron particle volume. The ratios of HNCO to NO_x observed are within the range of emission ratios reported for gasoline-powered motor vehicles.

Highlights

- A new method to quantify HNCO by iodide ion chemical ionization mass spectrometry was developed.
- Iodide was compared to negative-ion proton-transfer chemical ionization mass spectrometry.
- Mixing ratios of HNCO were measured in Calgary, AB, in Dec 2013 and Feb 2014 using both techniques.
- HNCO mixing ratios ranged from <12 to 94 ppt_v (median 34 ppt_v).
- The ratios of HNCO to NO_x and to CO are consistent with gasoline-powered motor vehicle exhaust.

Keywords

isocyanic acid, chemical ionization mass spectrometry, iodide reagent ion, negative-ion proton-transfer, urban pollution

1. Introduction

Isocyanic acid (H-N=C=O) has recently been discovered in ambient air through the invention of a new mass spectrometric measurement technique, negative-ion proton-transfer chemical ionization mass spectrometry (NI-PT-CIMS) with acetate reagent ion (Veres et al., 2008). HNCO is water-soluble at physiological pH and forms carbamates with proteins in vivo; the immune system's inflammatory response to protein carbamylation is believed to cause cataracts, cardiovascular impairment, and chronic diseases such as rheumatoid arthritis (Roberts et al., 2011; Wang et al., 2007). Because of the potential health implications, knowledge of the ambient levels of HNCO and an understanding of its sources and sinks continue to be of interest (Roberts et al., 2014).

Ambient air measurements in Pasadena, CA, Boulder, Erie, and near Fort Collins, CO, and in Toronto, Canada, using NI-PT-CIMS with acetate reagent ion have shown HNCO mixing ratios to be typically on the order of 10s of parts-per-trillion by volume (10^{-12} , pptv), with plume mixing ratios in excess of 1.2 parts-per-billion by volume (10^{-9} , ppbv), and have revealed the existence of both primary and photochemical HNCO sources (Roberts et al., 2011; Roberts et al., 2014; Wentzell et al., 2013). Control studies have confirmed that HNCO is formed as a byproduct during combustion processes. For example, high HNCO concentrations have been observed in tobacco smoke, biomass burning plumes, Diesel and gasoline engine exhaust (Roberts et al., 2011; Roberts et al., 2014; Roberts et al., 2010; Veres et al., 2010; Veres et al., 2011; Wentzell et al., 2013)(Bertram, personal communication and submitted article, 2014). HNCO can also be produced photochemically, for example from the oxidation of amines and amides by the hydroxyl radical (OH) (Borduas et al., 2013; Roberts et al., 2014). Since the rate coefficient for reaction of HNCO with OH and its photolysis frequency are small, HNCO is removed from the atmosphere mainly by dry or wet deposition (Barth et al., 2013; Young et al., 2012).

The ion chemistry used in NI-PT-CIMS is attractive as the acetate reagent ion is a strong gas-phase base which undergoes proton exchange with most inorganic and organic acids that are present in ambient air and enables their measurement (e.g., (Bertram et al., 2011; Roberts et al., 2010; Veres et al., 2010; Veres et al., 2011; Yatavelli et al., 2014)).

However, a challenge is often posed by high background counts that arise mainly from impurities in the reagent gas flow. For example, *Wentzell et al.* were unable to quantify formic acid (HCOOH) at m/z 45 by NI-PT-CIMS because of high background signals, even though they used high-purity N₂ and had coated the inside of their ion source with bicarbonate (Wentzell et al., 2013).

An alternative ionization scheme is to detect acids as anion clusters with either iodide or trifluoromethoxide (CF₃O⁻) reagent ion:

Iodide reagent ion is typically generated by passing a gas stream containing the readily available methyl iodide past a ²¹⁰Po radioactive source (e.g., (Slusher et al., 2004)). Acetate or trifluoromethoxide can be generated in the same manner from acetic anhydride ((C₂H₅C(O))₂O) (Veres et al., 2008) or bis(trifluoromethyl) peroxide (CF₃OOCF₃), respectively; CF₃OOCF₃, however, is not commercially available and requires careful synthesis, storage and handling (Crounse et al., 2006). Several groups have demonstrated that the ion chemistry of reactions R2 and R3 can be used to selectively monitor gas-phase acids of atmospheric interest. For example, iodide CIMS has been used to quantify HCOOH (Le Breton et al., 2012), HCN (Le Breton et al., 2013) and HNO₃ (Le Breton et al., 2014), and CF₃O⁻ reagent ion has been used to quantify HCN (Crounse et al., 2006; Hornbrook et al., 2011).

In addition, iodide CIMS have been used to measure ambient concentrations of molecules other than acids, for example, peroxy-carboxylic nitric anhydrides (PANs) (e.g., (LaFranchi et al., 2009; Mielke et al., 2011; Mielke and Osthoff, 2012; Phillips et al., 2013; Slusher et al., 2004; Zheng et al., 2011)), peroxy-carboxylic acids (Phillips et al., 2013), dinitrogen pentoxide (N_2O_5) (Kercher et al., 2009; Slusher et al., 2004), nitryl chloride (ClNO_2) (Kercher et al., 2009; Mielke et al., 2011; Osthoff et al., 2008; Riedel et al., 2012; Thornton et al., 2010), and molecular chlorine (Cl_2) (Liao et al., 2014; Mielke et al., 2011; Riedel et al., 2012). The trifluoromethoxide anion has also found other uses, for example to measure gas-phase hydroperoxides and biogenic organonitrates such as isoprene hydroxynitrate (Beaver et al., 2012; Crounse et al., 2006; Paulot et al., 2009; St. Clair et al., 2010). As far as we are aware, there has been no report in the literature of either I^- or CF_3O^- reagent ion having been used to quantify HNCO abundances in ambient air.

In this manuscript, measurements of HNCO mixing ratios in Calgary, AB, Canada, by NI-PT-CIMS with acetate reagent ion from December 16th to 20th, 2013, and by the same CIMS but with iodide reagent ion (iCIMS) from February 3rd to 7th, 2014, are presented. The operation of the CIMS with its two ionization schemes, its calibration for HNCO using FTIR, advantages and disadvantages of the two ionization schemes, and the ambient air mixing ratios of HNCO in Calgary are described and discussed.

2. Experimental Section

2.1. Description of chemical ionization mass spectrometer

The CIMS used in this work was purchased from THS instruments (Atlanta, GA) and has been described previously (Mielke et al., 2011; Mielke and Osthoff, 2012). Briefly, the instrument is comprised of three differentially pumped regions that house an ion-molecule reaction chamber (IMR) operated at 22 Torr, a collisional dissociation chamber (CDC) which

is evacuated by a molecular drag pump (Alcatel MDP 3011) to a pressure of 0.5 Torr, an octopole ion guide ($\sim 10^{-3}$ Torr), and a $\frac{3}{4}$ " (1.9 cm) quadrupole mass analyzer ($< 10^{-5}$ Torr) with channeltron detector (Ceramax 7550M). The ion guide and mass analyzer regions are evacuated by a pair of 250 L/s turbo pumps (Varian Turbo-V 81-M).

The CIMS sampled air from a common $\frac{1}{4}$ " (0.635 cm) outer diameter (o.d.) partially heated Teflon inlet manifold (described in section 2.4) at a total flow rate of 7.2 standard-liters per minute (slpm) through a 14 cm long section of $\frac{1}{2}$ " (1.27 cm) o.d. unheated Teflon tubing. This tubing was notched and pressed gently against the front plate of the CIMS which contained a pinhole. The Teflon tubing was cut in such a way as to not generate a tight seal and to allow air escape to the sides, which was pumped to exhaust at a flow rate of 6.0 slpm, set by a 15 slpm capacity mass flow controller connected to a twin head diaphragm pump (KNF Neuberger). Sample air entered the IMR (via the pinhole) at a flow rate of ~ 1.2 slpm.

2.2. Negative-ion proton-transfer chemical of HNCO

In the first part of this study (conducted in Dec 2013), the CIMS was operated in NI-PT mode with acetate reagent ion. Acetic anhydride (99.5%, Sigma-Aldrich) was placed in a 5 mL glass reservoir which was externally heated to 40 °C. Vapors from this reservoir diffused via a 2.5" (5.1 cm) long and 1.0 mm inner diameter (i.d.) glass capillary and a $\frac{1}{4}$ " (0.635 cm) perfluoroalkoxy (PFA) Teflon tee (Entegris Fluid Handling) into a $\frac{1}{4}$ " (0.635 cm) o.d. polyether ether ketone (PEEK) tube continuously flushed with 0.8 standard cubic centimeters per minute (sccm) of N₂ gas (Praxair). This gas stream was diluted further with 500 sccm of N₂ gas and flowed through a ²¹⁰Po radioactive ion source (NRD P-2031) into the IMR. Prior to use, the ion source was twice internally coated with a sodium bicarbonate slurry (Liggio, personal communication, 2013). The pressure in the IMR was controlled (to 22 Torr) using a third N₂ gas flow of 1.3 slpm. All gas flows were controlled using mass flow

controllers (MKS, M100B series). The CDC was operated with a declustering voltage of -23 V. Mass count rates were scaled to 10^6 counts of m/z 59 (acetate). HNCO was quantified using NCO^- anion counts at m/z 42 (Veres et al., 2008).

2.3. Iodide chemical ionization mass spectrometry of HNCO

In the second part of this work (Jan - Mar, 2014), the CIMS was operated with iodide reagent ion, generated by passing 0.8 sccm of 150 ppbv CH_3I in N_2 diluted with a flow of 1.2 slpm of N_2 gas past the sodium bicarbonate coated ^{210}Po ion source. The IMR was humidified with a flow of 750 sccm of N_2 gas (Praxair) which was bubbled through deionized water, to ensure that the responses to ClNO_2 at m/z 208 (Mielke et al., 2011) and to HNCO at m/z 170 (see 2.3.1) were independent of the relative humidity of the sampled air. Mass count rates were normalized to 10^6 counts of the primary reagent ion, m/z 127 (I^-) as described by Mielke et al. (2011). The declustering voltage of the CDC was set to maximize the $\{\text{H}_2\text{O}\cdot\text{I}\}^-$ signal at m/z 145 and $\{\text{HNCO}\cdot\text{I}\}^-$ signal at m/z 170 (to ~ -8.3 V, Figure 1A).

2.3.1. Characterization of water dependence

The water dependence of the response to HNCO at m/z 170 was investigated by varying the IMR humidity while delivering a constant mixing ratio of HNCO (in the range of 11 to 27 ppbv, see section 2.5 for how this mixing ratio was determined). Different humidities were generated using a second 5 slpm MFC delivering dry N_2 in parallel to the flow through the bubbler (which produced a gas stream of 100% relative humidity, RH), while maintaining a constant total flow rate of 750 sccm.

Figure 1B shows the ion count rates at m/z 170 (S_{170} , normalized to 10^6 Hz at m/z 127, concentration-normalized by dividing the ion count rates by their respective HNCO mixing ratios, and given in units of normalized counts per second per ppbv, NCPS ppbv^{-1}) at three

different HNCO mixing ratios plotted against the IMR humidity, measured using the normalized $\{\text{H}_2\text{O}\cdot\text{I}\}^-$ signal at m/z 145 (S_{145}) as a proxy. Data from in-field calibrations (see section 2.5) and the range of m/z 145 ion count rates observed while sampling Calgary air in the winter of 2014 are also shown in Figure 1B.

The HNCO signal decreased with increasing water concentration, which is opposite to what was observed for the PANs (Slusher et al., 2004), Cl_2 , and ClNO_2 (Kercher et al., 2009; Mielke et al., 2011). The observed anticorrelation with water suggests that the $\{\text{HNCO}\cdot\text{I}\}^-$ ion cluster is more reactive towards water vapor than its parent molecule, HNCO, which is long-lived in ambient air (Roberts et al., 2011). To describe the dependence of S_{170} on S_{145} , the parameters of a pseudo-first order exponential decay function were fit to the data:

$$S_{170} = A + B \times \exp(-k \times S_{145}) \quad (1)$$

Here, A and B are empirical constants, and k is a pseudo first-order decay constant which includes the reaction time of the $\{\text{HNCO}\cdot\text{I}\}^-$ cluster with water. Depending on where in the IMR a particular cluster molecule is formed, this reaction time will vary somewhat between cluster molecules; even though equation (1) is therefore only a rough approximation, it nevertheless describes the water dependence remarkably well: The black line in Figure 1B shows the empirical fit, which is in good agreement with the measurements. Hence, HNCO signals can, in principle, be corrected for changes in ambient air water concentration using equation (1); however, this correction was not necessary for the ambient air data in this work because the IMR was sufficiently humidified (yellow shaded area in Figure 1B), such that the HNCO response at m/z 170 was independent of humidity. In this region, the mixing ratio of water vapor was calculated from its saturation water vapor pressure (Goff and Gratch, 1946) and flow dilution ratios to be >6 parts-per-thousand by volume (ppth_v).

2.4. Ambient air measurement location and auxiliary measurements

Ambient air measurements were conducted on the rooftop of the Science B building on the University of Calgary campus. This measurement location has been described previously (Mielke et al., 2011; Odame-Ankrah and Osthoff, 2011). All instruments used in this study (Table 1) were housed in the "Penthouse" laboratory. The gas-phase instruments sampled from a common ~4 m long sample line constructed from ¼" o.d. (0.635 cm) and 3/16" i.d. (0.476 cm) FEP Teflon tubing. The sample line was guided through a partially open window and its tip attached to a 10 feet (3 m) tall tripod (Campbell Scientific CM110). A commercial weather station (Vaisala WXT 520) was mounted on top of the tripod. The outside section (~3 m length) of the gas-phase species sample line was enclosed by a heater (Clayborn Lab) set to a temperature of 75 °C. Because of the high cumulative sample flow rate (10 slpm), the entire section of the sample line inside the laboratory was warm to the touch (i.e., > 30 °C). The inlet was periodically (typically for 10 min once per hour) flooded with scrubbed ambient air generated using a custom-built zero air (ZA) generator.

Nitrogen dioxide (NO₂) was measured using a compact blue diode laser cavity ring-down spectrometer (CRDS) which has been described elsewhere (Taha et al., 2013). Briefly, the instrument uses two 55 cm long optical detection cells: One is used to monitor NO₂ mixing ratios by its optical absorption at 405 nm. The other channel is equipped with an inlet consisting of a ¼" (0.635 cm) o.d. quartz tube. In this study, this channel was heated to 450 °C to dissociate ClNO₂ to NO₂ (Thaler et al., 2011) to calibrate the CIMS (when it was operated with iodide reagent ion) for ClNO₂. The NO₂ CRDS was also used to calibrate the commercial NO/NO_y instrument by simultaneously sampling gas mixtures containing NO delivered from a reference cylinder (Praxair) and up to stoichiometric amounts of O₃ (generated in situ by passing O₂ past a Hg pen ray lamp).

Submicron particle size distributions were monitored using a commercial scanning mobility particle sizer (SMPS), which sampled from its own inlet constructed from conductive tubing supplied by TSI. This sample line was not actively temperature-controlled and differences in relative humidity relative to ambient and associated shifts in size distributions were not characterized. Hence, the data collected by the SMPS were by-and-large qualitative.

2.5. Calibration for isocyanic acid

Gas streams containing dilute concentrations of HNCO were generated in a similar fashion to that described by *Roberts et al.* (2010) and calibrated using Fourier transform infrared spectroscopy (FTIR). Briefly, HNCO was generated by heating its solid trimer, cyanuric acid (98%, Sigma-Aldrich). Because attempts to generate a gas stream containing HNCO from a passive diffusion source as described by *Roberts et al.* (2010) were unsuccessful, a U-tube (i.d.: 1.4 cm; length: 30 cm) constructed from Pyrex glass was used instead, in which a spatula tip of cyanuric acid was placed. This tube was continuously flushed by a small flow (15 sccm) of ultrapure ("zero" grade) air (ZA, Praxair) and resistively heated to between 180 and 190 °C using a Nichrome wire ($R = 13.5 \Omega$) coiled around the arc of the tube, a K-type thermocouple, and a miniature bench top temperature controller (Omega CSI32K) whose output was throttled using a Variac step-down transformer. Upon exiting the U-tube, the gas stream was immediately diluted with a flow (50 sccm) of ZA to prevent polymerization and condensation of HNCO. This flow was delivered (via ¼" (0.635 cm) o.d. FEP Teflon tubing) to the FTIR's gas absorption cell. A single charge of cyanuric acid was used for multiple calibrations over the entire period of this study (~6 months). Some white condensate formed over time within the unheated part of the U-tube neck but this was without further consequence.

The FTIR used to quantify HNCO was a Bruker Tensor 27 equipped with a 6.4 m multipass absorption cell (Gemini Scientific, Venus series) and a deuterated, L-alanine doped triglycine sulfate (DLaTGS) detector (Furgeson et al., 2011; Taha et al., 2013). Absorption cross-sections of HNCO were obtained from the Pacific Northwest National Laboratory (PNNL) database (Sharpe et al., 2004). Sample FTIR spectra of HNCO and PNNL reference spectra of HNCO and CO₂ are shown in Figure 2A. The 2208 to 2273 cm⁻¹ spectral region was used for quantification of HNCO. The source also emitted a small but variable amount of CO₂, likely produced from reaction of HNCO with residual water in the ZA gas stream. Because the IR spectra of CO₂ and HNCO are sufficiently separated, and the contributions of the overlapping ¹³CO₂ band in the 2208 to 2273 cm⁻¹ spectral region was negligibly small, the levels of CO₂ co-emitted by the source could be tolerated.

The gas exiting the FTIR's multipass cell was fed via a ~3 m long ¼" (0.635 cm) o.d. Teflon transfer line to the CIMS inlet. Initial attempts to add the calibration gas directly to the tip of the inlet failed, because the transfer line was not heated and the ambient temperatures were sufficiently low such that the transfer line acted as a cold trap. The calibration gas was therefore connected to the main inlet inside the Penthouse laboratory just behind the room's window.

3. Results

3.1. Comparison of acetate with iodide ion CIMS for HNCO measurements

3.1.1. Figures of merit

Figure 2B shows an example time series of a calibration run with the CIMS operated in iodide ion mode. The FTIR data were shifted by 4 minutes to synchronize the measurements, i.e., to account for the time it takes for HNCO concentration changes measured in the multipass cell to reach the CIMS inlet. The corresponding calibration plot of NCPS at *m/z* 170

against FTIR mixing ratios (using only the FTIR data points shown in red color; the black points were acquired while the CIMS was zeroed or the FTIR signal was unstable) is shown in Figure 2C. The CIMS response was linear ($r > 0.99$) from the lowest concentration that could be quantified with the FTIR (~ 0.5 ppb_v after dilution; ~ 560 ppb_v in the multipass chamber) to up to 25 ppb_v (after dilution), the highest mixing ratio delivered. Two additional calibrations were performed during the ambient measurement period, on Feb 5 and 6, 2014, with slopes of (82 ± 3) and (81 ± 4) NCPS ppb_v⁻¹, respectively, and offsets that were statistically indistinguishable from zero. These response factors are in quantitative agreement with the data shown in Figure 2C.

A combined sensitivity of (83 ± 4) NCPS ppb_v⁻¹ was used to convert the CIMS data at m/z 170 (reagent ion count normalized and background subtracted) to ambient mixing ratios. The background counts at m/z 170 followed Poisson statistics and were generally quite small (average ± 1 standard deviation: (3 ± 4) NCPS for 1 s data, see section 3.1.3). The HNCO detection limits (at a signal-to-noise ratio of 3) for data acquired with an integration time of 1 s (between 7 to 8 s total time resolution) or 40 s (4.7 to 5.3 min time resolution) were 140 or 12 ppt_v, respectively, and sufficed to quantify HNCO in ambient air. The accuracy of the HNCO mixing ratios reported by iCIMS was approximately $\pm 12\%$, limited by the uncertainty of the HNCO IR absorption cross-sections of $\pm 10\%$ (Sharpe et al., 2004) and the precision of the calibrations ($\pm 5\%$).

A calibration plot using CIMS with acetate reagent ion (data not shown) of HNCO at m/z 42 (NCO⁻) against FTIR mixing ratios yielded a sensitivity of (9.66 ± 0.06) NCPS ppt_v⁻¹ ($r^2 = 0.998$) or (9.7 ± 1.0) NCPS ppt_v⁻¹ if the systematic error arising from the uncertainty in the HNCO IR absorption cross-sections is included. Thus, the sensitivity of CIMS operated with iodide reagent ion to HNCO was approximately two orders of magnitude lower than that obtained using acetate. These relative sensitivities are similar for other inorganic acids such as

HONO and HNO₃ (Abida et al., 2011; Le Breton et al., 2013; Le Breton et al., 2014; Le Breton et al., 2012). Detection limits with the CIMS operated with acetate reagent ion varied because the background counts (and hence the uncertainty of the background interpolations) were variable (see section 3.1.3) and were on average 150 ppt_v (range: 50 to 300 ppt_v) for data with 1 s integration time or 30 ppt_v (range: 1 to 100 ppt_v) for data integrated over 40 s, respectively. The (slope) accuracy of the HNCO IR data was the same as for iodide ($\pm 12\%$).

3.1.2. Mass scans

Figures 3A and B show mass scans of ambient air on Dec 17, 2013, 17:30 mountain standard time (shown in red color) and of a background (black), i.e., when the instrument inlet was flooded with zero air, acquired with the CIMS operated in NI-PT mode with acetate reagent ion. The appearance of the small peak at m/z 127 (Figure 3B) is an artifact because the CIMS had been operated with iodide reagent ion for 5 years prior to switching to NI-PT mode. The residual iodide was insufficient to affect the results, as acetate was in considerable excess (>2 orders of magnitude).

All peaks that appear in the ambient air mass scan are also present in the background mass scans at count rates often indistinguishable from the background. The difference in the peak height at m/z 42 is consistent with a HNCO mixing ratio of 79 ppt_v. The large signals are consistent with the general notion that NI-PT-MS is a very sensitive measurement technique (Veres et al., 2008). In the ambient air mass scan, peaks at (amongst others) m/z 26, 35, 37, 42, 45, 46, and 62 were enhanced relative to the background and indicated the presence of cyanic, hydrochloric, isocyanic, formic, nitrous, and nitric acid.

Figure 4 shows mass scans of a blank (shown in black color), of a synthetic HNCO sample (blue), and of ambient air (red) on Feb 5, 2014, 11:30 mountain standard time, acquired with the CIMS operated with iodide reagent ion. Because of the relatively low declustering

voltage, there is little evidence of fragmentation, i.e., the ion count rates at m/z 35, 37, 42, 46, 62 were small (Figure 4A). Further, when 4.6 ppbv HNCO was added (blue trace), the only elevated peak was at m/z 170 (Figure 3B), and there was no indication of the deprotonation product at m/z 42. For the ambient air sample, the ion count rates at m/z 170 were too small to be visible on the scale shown Figure 4; they corresponded to a HNCO mixing ratio of 40 pptv.

Figure 4B shows several additional iodide cluster ions that can also be used for quantification (but were not in this work, except ClNO_2), including m/z 173 (formic acid), m/z 174 (nitrous acid), m/z 187 (acetic acid), m/z 190 (nitric acid) and m/z 208 (nitryl chloride). Some of these peaks (nitrous, nitric, formic, and acetic acid) have an instrumental background, likely arising from impurities in the N_2 gas used and, potentially, from inlet memory effects. The acetic acid peak at m/z 187 was artificially enhanced in these scans because of a memory effect from using acetic anhydride as the reagent ion precursor in the earlier experiments. There was also a small enhancement at m/z 161 in ambient air, assigned to $\{\text{H}_2\text{O}_2\cdot\text{I}\}^-$. The response at m/z 161 to H_2O_2 was verified in an off-line experiment by sampling the head space above a 50% H_2O_2 solution (Sigma-Aldrich). This suggests that I^- forms clusters with H_2O_2 analogous to CF_3O^- (Crounse et al., 2006). The peak at m/z 219 was present in all scans and was an instrumental artifact of unknown origin.

3.1.3. Time series

The time series of reagent ion count rates, those of the analytical ions in both ambient and background mode as well as their difference, and ambient mixing ratios of HNCO over two representative 48 hour monitoring periods are shown in Figures 5 and 6. Figure 5 demonstrates several of the difficulties encountered when acetate reagent ion was used: reagent ion and background analytical ion count rates both exhibited considerable drifts (up to $\pm 70\%$, from $\sim 1.5 \times 10^3$ to $\sim 8.0 \times 10^3$ NCPS at m/z 42). In addition, there were substantial and

often sharp changes in the reagent ion count rates, whose origin is unclear but which added considerably to the noise of the measurement. As a result of these drifts and spikes, the difference between the ambient and background signals (shown in Figure 5B) was variable and, on occasion, negative, leading to poorer HNCO detection limits than might have been anticipated from the method's high sensitivity. In fact, the ambient air data collected on December 15-16 and 19-20 were of such poor quality that they were not included in the analysis presented in section 3.2.

When operated with iodide ion, in contrast, the reagent ion signal at m/z 127 and that of the iodide-water cluster at m/z 145 drifted only slowly and remained steady within the entire measurement period, allowing for a precise normalization of the HNCO signal (Figure 6). The robustness of the signal at m/z 127 also suggests a more stable response of the instrument to ambient air concentration changes than with acetate reagent ion. The lower sensitivity of iCIMS compared to NI-PT-CIMS is apparent from the generally small ion counts (i.e. < 40 NCPS) at m/z 170. Upon averaging to 5 minutes (40 s total integration time), there is a clear difference between ambient and background count rates, and it is also evident that the background count rates are effectively constant. All of the above translate into a more precise and reliable HNCO measurement (Figure 6C) than obtained with acetate reagent ion (Figure 5C).

3.2. HNCO mixing ratios in Calgary

3.2.1. Overview

Figure 7 shows the full time series of the mixing ratios of HNCO, O₃, NO, NO₂, NO_x (calculated by adding NO, measured by CL, and NO₂, measured by CRDS), O_x ("odd oxygen", calculated by adding NO₂ and O₃), and NO_y, and of the SMPS size distribution data collected in Feb 2014. The proximity of the measurement site to nearby NO_x sources and

absence of significant photochemical processing of these emissions is evident from the very high ratio of $\text{NO}_x:\text{NO}_y$, which was close to unity (0.984 on average), and high NO mixing ratios which often titrated O_3 . The integrity of the NO, NO_2 , and O_3 data is confirmed by the time series of O_x which remains constant in these plumes (see, e.g., the orange circled area in Figure 7).

The maximum HNCO mixing ratio observed was 94 ppt_v, with mean and median values of 36 and 34 ppt_v, respectively. For the Dec 2013 data set, the lowest and highest HNCO mixing ratios were 6 and 72 ppt_v (mean and median: 28 and 33 ppt_v), respectively. These abundances are inline with mixing ratios observed at other locations and seasons (e.g., (Roberts et al., 2014; Wentzell et al., 2013)) and are below the level of 0.4 ppb_v suggested by Wentzell and coworkers (2013) (on the basis of Ontario's standard for 24-hour exposure to methyl isocyanate) that may be reason for health concerns. In general, the HNCO data appear as a series of individual spikes, which suggests that HNCO is enhanced in plumes originating from a number of discrete point sources that are distributed over a large area.

3.2.2. Time of day dependence

The time-of-day dependence of the HNCO mixing ratios observed in Dec 2013 and Feb 2014 is shown in Figure 8, along with median, quarterly and 10% and 90% percentile values (calculated over 3 hour bins). In general, there was not a strong time-of-day dependence of HNCO. The February data appear to be slightly elevated at the beginning of the night (max ~ 20:00). A maximum concentration in the early evening was also observed in Toronto by Wentzell and coworkers (2013). At night, mixing heights can be assumed to be lower than during the day; the lower mixing heights serve to amplify concentrations, unless emission sources drop significantly. In both the December and February data sets, a marginal increase in HNCO mixing ratios was observed in the late morning, peaking at ~10:00. The causes for

these trends are unknown. Both the late-morning and the early-evening peaks occur after their respective rush hours, whose emissions peaked between 07:00 and 08:00 and between 16:00 and 18:00, respectively, as judged from the NO_x time series (Figure 7). Levels of NO_x and particles often peak after sunset (e.g., Feb 5 and Feb 6) resulting from a combination of "rush hour" commuter traffic with low mixing heights that are typically found in the nocturnal boundary layer during winter. The rush hour signature is also observed on the mornings of Feb 6 and Feb 7 but was less pronounced than during a previous study at this measurement location (Mielke et al., 2011).

3.2.3. Correlations with auxiliary measurements

Spikes in the time series of the particle counts and NO_x data are also indicative of plumes from point sources, most likely from motor vehicles (see discussion). These plumes often do not coincide with those of HNCO (Figure 7). Figure 9 shows scatter plots of HNCO against submicron particle volume (9A) and NO_x (9B), used here as a tracer of combustion (i.e., of automobile exhaust, see discussion). The coloring of points is consistent between panels and is used to highlight selected plumes of interest (which are also indicated by the colored bars in the time series shown in Figure 7B).

The ratios of HNCO to PM₁ volume (Figure 9A) varied considerably over the course of the measurements, but were relatively constant over shorter periods. For example, on Feb 4, 02:30 to 03:30 local time (dark blue points in Figure 9A), the ratio of HNCO to particles was of similar magnitude (>15) as the range reported by *Roberts et al.* (2014) (superimposed as a gray area in Figure 9A) for a biomass burning plume. Since CRDS NO₂ data were not available prior to Feb 4, 09:00, NO_x was estimated for this period from NO_y and the average observed NO_x:NO_y ratio of 0.984. The ratio of HNCO to NO_x during the Feb 4 plume was $(8\pm1)\times10^{-3}$, the highest observed (dark blue points in Figure 9B).

Part of the data (Feb 5, 16:00 to 23:00 local time, orange points in Figure 9A) was associated with late-afternoon rush hour traffic, with levels of NO_x (orange points in Figure 9B) and PM_{10} remaining high until late evening. The ratio of HNCO to PM_{10} volume during this time period was $(3.0 \pm 0.1) \text{ ppt}_v \mu\text{m}^{-3} \text{ cm}^3$, and the ratio of HNCO to NO_x was $(1.39 \pm 0.06) \times 10^{-3}$ (shown as orange colored trend lines in Figures 9A and 9B). Similar ratios of $(3.7 \pm 0.2) \text{ ppt}_v \mu\text{m}^{-3} \text{ cm}^3$ (HNCO: PM_{10}) and $(1.15 \pm 0.06) \times 10^{-3}$ (HNCO: NO_x) were observed the following evening between 18:30 and 20:15 local time as well (green points in Figures 9A and 9B, fits shown as green trend lines). On the other hand, on Feb 4 during daytime (turquoise points and line in Figure 9A) several plumes containing high PM_{10} volume of up to $250 \mu\text{m}^3 \text{ cm}^{-3}$ (off-scale in Figure 9A) were observed but with virtually no enhancement in HNCO (or NO_x). The existence of such plumes explains the overall lack of correlation ($r = -0.04$) between HNCO and PM_{10} volume for the entire data set.

The ratio of HNCO to NO_x (Figure 9B) averaged over the entire data set and assuming an intercept of zero, i.e., assuming that HNCO only originates from combustion sources, was $(1.49 \pm 0.03) \times 10^{-3}$ ($r^2 = 0.21$). Superimposed in Figure 9B are the ranges of HNCO emission ratios (ER's) for light duty diesel (LDD) vehicle exhaust (Wentzell et al., 2013), shown as a gray area, and of light duty gasoline (LDG) vehicles (Bertram, personal communication and submitted article, 2014), shown in magenta. LDG vehicles exhibit a wide range of ER's (from 1×10^{-4} to 2.3×10^{-2}); these ER's are shown as bins, with darker shades corresponding to more frequently observed values. The ratios of HNCO to NO_x observed in this study are within the range of emission factors for LDG vehicle exhaust.

4. Discussion

4.1. Utility of iCIMS for the quantification of HNCO in ambient air

In this work, two complimentary mass spectrometric methods to quantify HNCO in ambient air were demonstrated, one based on NI-PT-CIMS with acetate reagent ion (Veres et al., 2008) and the other based on iodide ion clustering chemistry (iCIMS). Both techniques were evaluated using the same mass spectrometer by the same operators and with identical inlets and sampling flows, which enabled a fair comparison of the two ionization chemistries.

Most importantly, it is possible to quantify HNCO in ambient air using either method (e.g., Figures 5 and 6). While the NI-PT-CIMS was considerably more sensitive than iCIMS, this advantage was essentially negated by iodide's much greater reagent ion count stability and much lower and more stable background counts. Subtraction of a large background often gave rise to negative values (e.g., Figure 5B); negative values can also be found in other NI-PT-CIMS data sets (e.g., Figure 4 in (Roberts et al., 2014)). Overall, we preferred iCIMS as it was considerably easier to implement and provided more robust, non-negative, and continuous data. However, the experiences presented here may not be the same with instruments with different inlet and IMR configurations, so that each research group should make their own determination which ion chemistry best suits their needs.

By-and-large, the two methods are complimentary: The acetate chemistry can be used to quantify (in parallel to HNCO) a multitude of other inorganic and organic acids in ambient air (e.g., Figure 3 and (Roberts et al., 2010; Veres et al., 2008)). Conversely, iCIMS can be used to quantify (in parallel to HNCO, see Figure 4) iodide ion clusters of HCOOH (Bannan et al., 2014; Le Breton et al., 2012), HCN ((Le Breton et al., 2013), HNO₃ (Le Breton et al., 2014), ClNO₂ (Kercher et al., 2009; Mielke et al., 2011; Osthoff et al., 2008), and Cl₂ (Liao et al., 2014; Mielke et al., 2011; Roberts et al., 2008), but not N₂O₅ (Kercher et al., 2009) as this molecule would dissociate in the heated inlet, and the counts at m/z 62 (NO₃⁻), generated from

reaction of nitrate radical with iodide, are likely compromised by chemical interferences (Wang et al., 2014). Mixing ratios of ClNO₂ were, in fact, quantified in this work, and will be presented in a future manuscript. The inlet temperature used in this study was too low to dissociate a significant amount of PAN and therefore generated only a weak signal at m/z 59 (e.g., Figure 4), even though the count rates at this mass were close to zero (data not shown) when the inlet was flooded with zero air. Because of the potential competition between acetate (generated from PAN dissociation) acid-base chemistry and iodide ion clustering chemistry (Mielke and Osthoff, 2012; Veres et al., 2008), the simultaneous measurement of acids such as HNCO and PAN by iCIMS would be challenging.

The mass scan in Figure 4 shows that measurement of H₂O₂ by iCIMS may be possible, analogous to CF₃O⁻-CIMS (Crounse et al., 2006). Most atmospheric peroxide measurements in use today require extensive sample handling, usually extraction into solution followed by derivatization (e.g., (Snow et al., 2007)), development of a simpler and more direct method would likely be of great interest to the community. Measurement of H₂O₂ by iCIMS will be explored in future work.

4.1.1. Water dependence

An oddity of the detection of HNCO by iCIMS is the inverse dependence of the sensitivity on humidity which can, in practice, easily be tracked using the {H₂O•I}⁻ cluster at m/z 145 (Figure 1B). This inverse relationship was somewhat unexpected as the PANs, N₂O₅, Cl₂ and ClNO₂ all exhibit a positive correlation with water vapor, rationalized by water promoting formation of the iodide ion clusters (e.g., (Kercher et al., 2009; Mielke et al., 2011; Slusher et al., 2004)). Further, *Le Breton* and coworkers did not report any water dependence for HCOOH and HNO₃ (Le Breton et al., 2014; Le Breton et al., 2012) and commented in online discussions accompanying their paper that their instrument's sensitivity to HCN was

independent of iodide-water cluster concentrations (Le Breton et al., 2013). In contrast, *Phillips et al.* reported that their detection sensitivity of peroxyacetic acid (PAA) was inversely proportional to water vapor (Phillips et al., 2013). With CF_3O^- , *Crounse et al.* reported lower signal ion counts at high water vapor mixing ratios for certain analyte molecules, rationalized by exchange reactions, and observed markedly different responses depending on the analyte (Crounse et al., 2006).

The anticorrelation of the HNCO sensitivity with water observed in this work suggests that the $\{\text{HNCO}\cdot\text{I}\}^-$ cluster is reactive towards water, and is removed either by a simple exchange reaction (R4), or by hydrolysis, likely to NH_3 and CO_2 (R5):

For (R5) to occur, the $\{\text{HNCO}\cdot\text{I}\}^-$ cluster would have to be more reactive towards water vapor than HNCO. In solution, hydrolysis of HNCO is catalyzed by bivalent anions (e.g., (Jensen, 1959; Vogels et al., 1970)); in the gas-phase, only the uncatalyzed rate constant is known (Aigner et al., 1995). The most likely hydrolysis products, NH_3 and CO_2 , would not be detected by the iodide ion CIMS. As a result, the mechanistic origin of the inverse dependence of S_{170} on water remains in doubt.

The stability of the HNCO signal at high water concentrations is also an oddity, alas a welcome one as it allowed the measurement to be made independent of ambient RH changes in this study. The independence of S_{170} at high humidity can plausibly be rationalized by one of following explanations: (1) Some cluster molecules that are formed close to the pinhole will have little to no time to react with water, and these would give rise to a water-independent offset. (2) The HNCO iodide ion cluster molecules achieve a steady state with respect to their formation (R2) and their destruction (R4 or R5). (3) The hydrolysis reaction is

not a gas-phase reaction but surface-catalyzed; one would then expect the water dependence to be highly instrument dependent.

Be it as it may, from an analytical viewpoint, the issue of the humidity dependence of the HNCO signal could be neglected in this study because the IMR was sufficiently humidified to make the response independent of the humidity of the sampled air (Figure 1B). However, the issue of the water dependence of the HNCO signal may have to be revisited if iCIMS were to be used to monitor HNCO in humid environments, for example in tropical regions.

4.2. Sources of isocyanic acid in the wintertime Calgary atmosphere

Plumes attributable to individual point sources were not encountered in this work (Figure 7). The only possible exception is the time period of 02:30 to 03:30 on Feb 4, when (possibly) a biomass burning plume was observed (dark blue points in Figure 9). The generally poor correlation shown in Figure 9 suggests that there are multiple, small sources of HNCO in Calgary spread over a wide area. Further, the data imply the absence of large industrial HNCO point sources in the Calgary area. The absence of a mid-afternoon maximum in HNCO concentrations (Figure 8) and the lack of any correlation with ozone (data not shown), as had been reported for the BioCORN campaign (Roberts et al., 2014), suggest that little (if any) photochemical production of HNCO occurred. This is consistent with wintertime measurements in Boulder, CO (Roberts et al., 2014) and can reasonably be expected during winter at a relatively high latitude location such as Calgary. The correlation of HNCO with NO_x mixing ratios (Figure 9B) corroborates that HNCO originates from combustion sources. The most likely sources of HNCO in the study area are therefore primary emissions from anthropogenic combustion, i.e., the automobile fleet, or, possibly, residential heating.

Studies of the emission ratios (ER's) from LDD and LDG vehicle exhaust reported by Wentzell et al. (2013) and the Bertram group (personal communication and submitted article,

2014) have shown that HNCO emissions can vary considerably with type of vehicle and driving mode. Vehicles in Canada fall under federal legislation that duplicates the U.S. EPA's Tier II standard; however, the province of Alberta has to date not implemented an emissions testing program that would remove any high-emitting vehicles from the fleet. In the absence of a monitoring program, emissions from Calgary's automobile fleet are somewhat uncertain and likely exhibit even greater scatter than the literature values shown in Figure 9B.

The slopes of the scatter plot shown in Figure 9B are greater than the range of ER's for LDD (Wentzell et al., 2013) but are in the range of values recently reported LDG vehicle exhaust (Bertram, personal communication and submitted article, 2014). This suggests that LDG vehicles are the dominant HNCO source in Calgary.

According to a 2008 report for the "Calgary Region Airshed Zone" (CRAZ) which includes the City of Calgary (Yang et al., 2012), the automobile fleet is responsible for ~68% of NO_x emissions, followed by the "Upstream Oil and Gas" (UOG) sector, which operates a large number of Diesel generators and whose emissions are estimated at ~18% of the total. Within the automobile sector, 53% of the NO_x emitted within CRAZ is believed to originate from off-road vehicles (ORV), which include construction vehicles that operate on Diesel fuel and generally generate exhaust with high soot content. About 20% of the NO_x originates from heavy duty Diesel (HDD) on-road vehicles (i.e., transport trucks, which also operate on Diesel fuel). A surprisingly small number, (only) 15% of the total NO_x emitted, was attributed to light duty vehicles, most of which are powered by gasoline. The data presented in this manuscript are more consistent with most of the NO_x (and HNCO) originating from LDG vehicle exhaust than the CRAZ emission inventory. However, the CRAZ boundaries extend far beyond the city limits of Calgary and hence the NO_x sources reported may not be representative of Calgary itself. Clearly, a higher-resolution emissions inventory, as well as investigations of the emissions from potential HNCO sources such as ORV and HDD vehicles

and residential home heating (in both the laboratory and in the field) are needed, including studies at temperatures representative of Canadian winters.

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579 **References**

- 580 Abida, O., Mielke, L.H., Osthoff, H.D., 2011. Observation of gas-phase peroxyxynitrous and
581 peroxyxynitric acid during the photolysis of nitrate in acidified frozen solutions. *Chemical*
582 *Physics Letters* 511, 187-192.
- 583 Aigner, M., Zeilinger, M., Hofbauer, H., 1995. Kinetic study of the hydrolysis of isocyanic
584 acid in the gas phase. *Chemical Engineering and Processing* 34, 515-520.
- 585 Bannan, T.J., Bacak, A., Muller, J.B.A., Booth, A.M., Jones, B., Le Breton, M., Leather, K.E.,
586 Ghalaieny, M., Xiao, P., Shallcross, D.E., Percival, C.J., 2014. Importance of direct
587 anthropogenic emissions of formic acid measured by a chemical ionisation mass
588 spectrometer (CIMS) during the Winter ClearfLo Campaign in London, January 2012.
589 *Atmospheric Environment* 83, 301-310.
- 590 Barth, M.C., Cochran, A.K., Fiddler, M.N., Roberts, J.M., Bililign, S., 2013. Numerical
591 modeling of cloud chemistry effects on isocyanic acid (HNCO). *Journal of Geophysical*
592 *Research* 118, 8688-8701.
- 593 Beaver, M.R., Clair, J.M.S., Paulot, F., Spencer, K.M., Crounse, J.D., LaFranchi, B.W., Min,
594 K.E., Pusede, S.E., Wooldridge, P.J., Schade, G.W., Park, C., Cohen, R.C., Wennberg, P.O.,
595 2012. Importance of biogenic precursors to the budget of organic nitrates: observations of
596 multifunctional organic nitrates by CIMS and TD-LIF during BEARPEX 2009.
597 *Atmospheric Chemistry and Physics* 12, 5773-5785.
- 598 Bertram, T.H., Kimmel, J.R., Crisp, T.A., Ryder, O.S., Yatavelli, R.L.N., Thornton, J.A.,
599 Cubison, M.J., Gonin, M., Worsnop, D.R., 2011. A field-deployable, chemical ionization
600 time-of-flight mass spectrometer. *Atmospheric Measurement Techniques* 4, 1471-1479.

601 Borduas, N., Abbatt, J.P.D., Murphy, J.G., 2013. Gas Phase Oxidation of Monoethanolamine
 602 (MEA) with OH Radical and Ozone: Kinetics, Products, and Particles. *Environmental*
 603 *Science & Technology* 47, 6377-6383.

604 Crounse, J.D., McKinney, K.A., Kwan, A.J., Wennberg, P.O., 2006. Measurement of gas-
 605 phase hydroperoxides by chemical ionization mass spectrometry. *Analytical Chemistry* 78,
 606 6726-6732.

607 Furgeson, A., Mielke, L.H., Paul, D., Osthoff, H.D., 2011. A photochemical source of
 608 peroxypropionic and peroxyisobutanoic nitric anhydride. *Atmospheric Environment* 45,
 609 5025-5032.

610 Goff, J.A., Gratch, S., 1946. Low-pressure properties of water from -160 to 212F.
 611 *Transactions of the American Society of Heating and Ventilating Engineers* 52, 95-121.

612 Hornbrook, R.S., Blake, D.R., Diskin, G.S., Fried, A., Fuelberg, H.E., Meinardi, S.,
 613 Mikoviny, T., Richter, D., Sachse, G.W., Vay, S.A., Walega, J., Weibring, P., Weinheimer,
 614 A.J., Wiedinmyer, C., Wisthaler, A., Hills, A., Riemer, D.D., Apel, E.C., 2011.
 615 Observations of nonmethane organic compounds during ARCTAS Part 1: Biomass burning
 616 emissions and plume enhancements. *Atmospheric Chemistry and Physics* 11, 11103-11130.

617 Jensen, M.B., 1959. On the Kinetics of the Decomposition of Cyanic Acid. *Acta Chemica*
 618 *Scandinavica* 13, 659-664.

619 Kercher, J.P., Riedel, T.P., Thornton, J.A., 2009. Chlorine activation by N₂O₅: simultaneous,
 620 in situ detection of ClNO₂ and N₂O₅ by chemical ionization mass spectrometry.
 621 *Atmospheric Measurement Techniques* 2, 193-204.

622 LaFranchi, B.W., Wolfe, G.M., Thornton, J.A., Harrold, S.A., Browne, E.C., Min, K.E.,
 623 Wooldridge, P.J., Gilman, J.B., Kuster, W.C., Goldan, P.D., de Gouw, J.A., McKay, M.,

624 Goldstein, A.H., Ren, X., Mao, J., Cohen, R.C., 2009. Closing the peroxy acetyl nitrate
 625 budget: observations of acyl peroxy nitrates (PAN, PPN, and MPAN) during BEARPEX
 626 2007. *Atmospheric Chemistry and Physics* 9, 7623-7641.

627 Le Breton, M., Bacak, A., Muller, J.B.A., O'Shea, S.J., Xiao, P., Ashfold, M.N.R., Cooke,
 628 M.C., Batt, R., Shallcross, D.E., Oram, D.E., Forster, G., Bauguitte, S.J.B., Percival, C.J.,
 629 2013. Airborne hydrogen cyanide measurements using a chemical ionisation mass
 630 spectrometer for the plume identification of biomass burning forest fires. *Atmospheric*
 631 *Chemistry and Physics* 13, 9217-9232.

632 Le Breton, M., Bacak, A., Muller, J.B.A., Xiao, P., Shallcross, B.M.A., Batt, R., Cooke, M.C.,
 633 Shallcross, D.E., Bauguitte, S.J.B., Percival, C.J., 2014. Simultaneous airborne nitric acid
 634 and formic acid measurements using a chemical ionization mass spectrometer around the
 635 UK: Analysis of primary and secondary production pathways. *Atmospheric Environment*
 636 83, 166-175.

637 Le Breton, M., McGillen, M.R., Muller, J.B.A., Bacak, A., Shallcross, D.E., Xiao, P., Huey,
 638 L.G., Tanner, D., Coe, H., Percival, C.J., 2012. Airborne observations of formic acid using a
 639 chemical ionization mass spectrometer. *Atmospheric Measurement Techniques* 5, 3029-
 640 3039.

641 Liao, J., Huey, L.G., Liu, Z., Tanner, D.J., Cantrell, C.A., Orlando, J.J., Flocke, F.M.,
 642 Shepson, P.B., Weinheimer, A.J., Hall, S.R., Ullmann, K., Beine, H.J., Wang, Y., Ingall,
 643 E.D., Stephens, C.R., Hornbrook, R.S., Apel, E.C., Riemer, D., Fried, A., Mauldin III, R.L.,
 644 Smith, J.N., Staebler, R.M., Neuman, J.A., Nowak, J.B., 2014. High levels of molecular
 645 chlorine in the Arctic atmosphere. *Nature Geoscience* 7, 91-94.

646 Mielke, L.H., Furgeson, A., Osthoff, H.D., 2011. Observation of ClNO₂ in a mid-continental
 647 urban environment. *Environmental Science & Technology* 45, 8889-8896.

648 Mielke, L.H., Osthoff, H.D., 2012. On quantitative measurements of peroxydicarboxylic nitric
 649 anhydride mixing ratios by thermal dissociation chemical ionization mass spectrometry.
 650 International Journal of Mass Spectrometry 310, 1-9.

651 Odame-Ankrah, C.A., Osthoff, H.D., 2011. A compact diode laser cavity ring-down
 652 spectrometer for atmospheric measurements of NO₃ and N₂O₅ with automated zeroing and
 653 calibration. Applied Spectroscopy 65, 1260-1268.

654 Osthoff, H.D., Roberts, J.M., Ravishankara, A.R., Williams, E.J., Lerner, B.M., Sommariva,
 655 R., Bates, T.S., Coffman, D., Quinn, P.K., Stark, H., Burkholder, J.B., Talukdar, R.K.,
 656 Meagher, J., Fehsenfeld, F.C., Brown, S.S., 2008. High levels of nitryl chloride in the
 657 polluted subtropical marine boundary layer. Nature Geoscience 1, 324-328.

658 Paulot, F., Crounse, J.D., Kjaergaard, H.G., Kroll, J.H., Seinfeld, J.H., Wennberg, P.O., 2009.
 659 Isoprene photooxidation: new insights into the production of acids and organic nitrates.
 660 Atmospheric Chemistry and Physics 9, 1479-1501.

661 Phillips, G.J., Pouvesle, N., Thieser, J., Schuster, G., Axinte, R., Fischer, H., Williams, J.,
 662 Lelieveld, J., Crowley, J.N., 2013. Peroxyacetyl nitrate (PAN) and peroxyacetic acid (PAA)
 663 measurements by iodide chemical ionisation mass spectrometry: first analysis of results in
 664 the boreal forest and implications for the measurement of PAN fluxes. Atmospheric
 665 Chemistry and Physics 13, 1129-1139.

666 Riedel, T.P., Bertram, T.H., Crisp, T.A., Williams, E.J., Lerner, B.M., Vlasenko, A., Li, S.-
 667 M., Gilman, J.B., de Gouw, J., Bon, D.M., Wagner, N.L., Brown, S.S., Thornton, J.A.,
 668 2012. Nitryl Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer.
 669 Environmental Science & Technology 46, 10463-10470.

670 Roberts, J.M., Osthoff, H.D., Brown, S.S., Ravishankara, A.R., 2008. N₂O₅ oxidizes chloride
 671 to Cl₂ in acidic atmospheric aerosol. Science 321, 1059.

672 Roberts, J.M., Veres, P.R., Cochran, A.K., Warneke, C., Burling, I.R., Yokelson, R.J., Lerner,
673 B.M., Gilman, J.B., Kuster, W.C., Fall, R., de Gouw, J., 2011. Isocyanic acid in the
674 atmosphere and its possible link to smoke-related health effects. *Proceedings of the National*
675 *Academy of Sciences* 108, 8966-8971.

676 Roberts, J.M., Veres, P.R., VandenBoer, T.C., Warneke, C., Graus, M., Williams, E.J., Lefer,
677 B., Brock, C.A., Bahreini, R., Öztürk, F., Middlebrook, A.M., Wagner, N.L., Dubé, W.P.,
678 de Gouw, J.A., 2014. New insights into atmospheric sources and sinks of isocyanic acid,
679 HNCO, from recent urban and regional observations. *Journal of Geophysical Research*, in
680 press.

681 Roberts, J.M., Veres, P.R., Warneke, C., Neuman, J.A., Washenfelder, R.A., Brown, S.S.,
682 Baasandorj, M., Burkholder, J.B., Burling, I.R., Johnson, T.J., Yokelson, R.J., de Gouw, J.,
683 2010. Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-
684 transfer chemical-ionization mass spectrometry (NI-PT-CIMS): application to biomass
685 burning emissions. *Atmospheric Measurement Techniques* 3, 981-990.

686 Sharpe, S.W., Johnson, T.J., Sams, R.L., Chu, P.M., Rhoderick, G.C., Johnson, P.A., 2004.
687 Gas-phase databases for quantitative infrared spectroscopy. *Applied Spectroscopy* 58, 1452-
688 1461.

689 Slusher, D.L., Huey, L.G., Tanner, D.J., Flocke, F.M., Roberts, J.M., 2004. A thermal
690 dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the
691 simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide. *Journal of*
692 *Geophysical Research* 109, D19315.

693 Snow, J.A., Heikes, B.G., Shen, H., O'Sullivan, D.W., Fried, A., Walega, J., 2007. Hydrogen
694 peroxide, methyl hydroperoxide, and formaldehyde over North America and the North
695 Atlantic. *Journal of Geophysical Research: Atmospheres* 112, D12S07.

696 St. Clair, J.M., McCabe, D.C., Crounse, J.D., Steiner, U., Wennberg, P.O., 2010. Chemical
 697 ionization tandem mass spectrometer for the in situ measurement of methyl hydrogen
 698 peroxide. *Review of Scientific Instruments* 81, 094102.

699 Taha, Y.M., Odame-Ankrah, C.A., Osthoff, H.D., 2013. Real-time vapor detection of
 700 nitroaromatic explosives by catalytic thermal dissociation blue diode laser cavity ring-down
 701 spectroscopy. *Chemical Physics Letters* 582, 15-20.

702 Thaler, R.D., Mielke, L.H., Osthoff, H.D., 2011. Quantification of Nitryl Chloride at Part Per
 703 Trillion Mixing Ratios by Thermal Dissociation Cavity Ring-Down Spectroscopy.
 704 *Analytical Chemistry* 83, 2761-2766.

705 Thornton, J.A., Kercher, J.P., Riedel, T.P., Wagner, N.L., Cozic, J., Holloway, J.S., Dube,
 706 W.P., Wolfe, G.M., Quinn, P.K., Middlebrook, A.M., Alexander, B., Brown, S.S., 2010. A
 707 large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry.
 708 *Nature* 464, 271-274.

709 Veres, P.R., Roberts, J.M., Burling, I.R., Warneke, C., de Gouw, J., Yokelson, R.J., 2010.
 710 Measurements of gas-phase inorganic and organic acids from biomass fires by negative-ion
 711 proton-transfer chemical-ionization mass spectrometry. *Journal of Geophysical Research*
 712 115, D23302.

713 Veres, P.R., Roberts, J.M., Cochran, A.K., Gilman, J.B., Kuster, W.C., Holloway, J.S., Graus,
 714 M., Flynn, J., Lefer, B., Warneke, C., de Gouw, J., 2011. Evidence of rapid production of
 715 organic acids in an urban air mass. *Geophysical Research Letters* 38, L17807.

716 Veres, P.R., Roberts, J.M., Warneke, C., Welsh-Bon, D., Zahniser, M.S., Herndon, S., Fall,
 717 R., de Gouw, J., 2008. Development of negative-ion proton-transfer chemical-ionization
 718 mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the
 719 atmosphere. *International Journal of Mass Spectrometry* 274, 48-55.

720 Vogels, G.D., Uffink, L., van der Drift, C., 1970. Cyanate decomposition catalyzed by certain
 721 bivalent anions. *Recueil des Travaux Chimiques des Pays-Bas* 89, 500-508.

722 Wang, X., Wang, T., Yan, C., Tham, Y.J., Xue, L., Xu, Z., Zha, Q., 2014. Large daytime
 723 signals of N_2O_5 and NO_3 inferred at 62 amu in a TD-CIMS: chemical interference or a real
 724 atmospheric phenomenon? *Atmos. Meas. Tech.* 7, 1-12.

725 Wang, Z., Nicholls, S.J., Rodriguez, E.R., Kumm, O., Horkko, S., Barnard, J., Reynolds,
 726 W.F., Topol, E.J., DiDonato, J.A., Hazen, S.L., 2007. Protein carbamylation links
 727 inflammation, smoking, uremia and atherogenesis. *Nature Medicine* 13, 1176-1184.

728 Wentzell, J.J.B., Liggio, J., Li, S.-M., Vlasenko, A., Staebler, R., Lu, G., Poitras, M.-J., Chan,
 729 T., Brook, J.R., 2013. Measurements of Gas phase Acids in Diesel Exhaust: A Relevant
 730 Source of HNCO? *Environmental Science & Technology* 47, 7663-7671.

731 Yang, F., Vesely, J., Qiu, X., Taylor, N., 2012. All Source Pollutant Emissions Inventory for
 732 the Calgary Region Airshed Zone (CRAZ)
 733 [http://www.craz.ca/assets/fileManager/Reports/CRAZ%20emis2008_Novus_2012-05-](http://www.craz.ca/assets/fileManager/Reports/CRAZ%20emis2008_Novus_2012-05-07_Final%20Report.pdf)
 734 [07_Final%20Report.pdf](http://www.craz.ca/assets/fileManager/Reports/CRAZ%20emis2008_Novus_2012-05-07_Final%20Report.pdf)

735 Yatawelli, R.L.N., Stark, H., Thompson, S.L., Kimmel, J.R., Cubison, M.J., Day, D.A.,
 736 Campuzano-Jost, P., Palm, B.B., Hodzic, A., Thornton, J.A., Jayne, J.T., Worsnop, D.R.,
 737 Jimenez, J.L., 2014. Semicontinuous measurements of gas-particle partitioning of organic
 738 acids in a ponderosa pine forest using a MOVI-HRToF-CIMS. *Atmospheric Chemistry and*
 739 *Physics* 14, 1527-1546.

740 Young, P.J., Emmons, L.K., Roberts, J.M., Lamarque, J.-F., Wiedinmyer, C., Veres, P.,
 741 VandenBoer, T.C., 2012. Isocyanic acid in a global chemistry transport model:
 742 Tropospheric distribution, budget, and identification of regions with potential health
 743 impacts. *Journal of Geophysical Research* 117, D10308.

744 Zheng, W., Flocke, F.M., Tyndall, G.S., Swanson, A., Orlando, J.J., Roberts, J.M., Huey,
745 L.G., Tanner, D.J., 2011. Characterization of a thermal decomposition chemical ionization
746 mass spectrometer for the measurement of peroxy acyl nitrates (PANs) in the atmosphere.
747 Atmospheric Chemistry and Physics 11, 6529-6547.

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751 **Table 1.** List of instruments used in this study for ambient air sampling

Species	Method	Manufacturer + model or reference	Time resolution
HNCO, ClNO ₂	Acetate or iodide ion CIMS	THS instruments	5 - 8 s
O ₃	UV absorption	Thermo 49i	10 s
NO, NO _y	Chemiluminescence	Thermo 42TL	10 s
NO ₂	Compact blue diode laser CRDS	(Taha et al., 2013)	1 s
T, RH, wind speed and direction, precipitation	misc.	Vaisala WXT 520	10 s
PM ₁ size distributions	Scanning mobility particle sizing	TSI 3080L DMA + 3775 CPC	5 min

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Figure captions

Figure 1. Optimizations of iodide ion CIMS operational parameters. (A) Signals at m/z 127 (I^-), m/z 145 ($H_2O \cdot I^-$) and m/z 170 ($HNCO \cdot I^-$) count rates as a function of CDC voltage. The maximum (and optimum) response was at -8 V. (B) Dependence of m/z 170 count rates on humidity, measured using m/z 145 ($H_2O \cdot I^-$) as a proxy, at three HNCO mixing ratios (shown in black, red, and blue colors). The range of humidities encountered while sampling ambient air is indicated by the pale yellow shading. Response factors during in-field calibrations are also shown (as green dots). The black line is a fit of equation (1) to the data with the following parameters: $A = (73.7 \pm 2.6)$ NCPS ppb $_v^{-1}$, $B = (174.1 \pm 2.8)$ NCPS ppb $_v^{-1}$, and $k = (3.07 \pm 0.12) \times 10^{-5}$ NCPS $^{-1}$.

Figure 2. (A) Sample FTIR absorption spectra of 860 ppb $_v$ and 830 ppb $_v$ HNCO (shown in blue and red color). Both spectra contain CO $_2$ that is co-emitted by the HNCO source. The PNNL reference spectra of HNCO and CO $_2$ (Sharpe et al., 2004) are shown in green and black color, respectively. (B) Representative time series of a HNCO calibration run. Red circles indicate FTIR data points used to determine CIMS sensitivity, black circles denote FTIR points when either the source was bypassed, or concentrations were changing too rapidly. (C) Calibration plot derived from the data shown in (2B).

Figure 3. (A, B) Mass scans of ambient air acquired on Dec. 17, 2013, 17:30 local time (red color) and of scrubbed air (black color) with the CIMS operated with acetate reagent ion.

Figure 4. (A, B). Mass scans of a background (black color), an HNCO standard (blue color), and ambient air (red color) acquired on Feb. 5, 2014, 11:30 local time with the CIMS operated with iodide reagent ion.

Figure 5. Selected 48-hour time series of ambient air data collected with the CIMS operated with acetate reagent ion. The pale yellow underlays indicate daytime periods. (A) Reagent ion count rates at m/z 59. (B) Normalized count rates at m/z 42. Data points collected while

sampling ambient air are shown in red color, and those collected while sampling scrubbed air in blue color. (C) HNCO mixing ratios, filtered by removing points below the detection limit.

Figure 6. Selected 48-hour time series of ambient air data collected with the CIMS operated with iodide reagent ion. (A) Reagent ion count rates at m/z 127 and m/z 145. (B) Normalized counts at m/z 170 while sampling ambient (red) or scrubbed air (blue). (C) HNCO mixing ratios. Gaps in the time series are due to random instrument tests and calibration runs.

Figure 7. Time series of ambient air data collected in Calgary. (A) SMPS data. (B) HNCO mixing ratios. (C) Mixing ratios of O_3 , NO, NO_2 , $NO_x (= NO + NO_2)$, $O_x (= O_3 + NO_2)$, and NO_y . The colored bars indicate the time periods highlighted in Figure 9. The orange ellipse indicates a time period during which O_3 was titrated by NO to NO_2 while O_x remained constant (see text).

Figure 8. Time of day dependence of the HNCO data. The trend lines are 3-hour median, 90th, 75th, 25th, and 10th percentiles. The pale yellow underlay shows the daytime period of the Feb 2014 data set.

Figure 9. Scatter plots of the Feb 2014 ambient air data. (A) Plot of HNCO vs. PM_{10} volume. Colored data points correspond to selected time periods of interest (see text). The colored lines show the best linear fits to the colored data, and the black line is the best linear fit to all data. The gray area represents the range of emission ratios from biomass burning plumes reported by Roberts *et al.* (2014). (B) Plot of HNCO vs. NO_x mixing ratios. The gray area is the range of HNCO: NO_x emission ratios reported by Wentzell *et al.* (2013) for light duty diesel (LDD) vehicles. The purple areas are the range of HNCO: NO_x emission ratios measured by the Bertram group (Bertram, personal communication and submitted article, 2014) for light-duty gasoline (LDG) vehicles (see text).