Supporting Information for:

Sources of isocyanic acid (HNCO) indoors: a focus on cigarette smoke

Rachel F. Hems,[†] Chen Wang,[†] Douglas B. Collins,[ǂ] Shouming Zhou,[†] Nadine Borduas-Dedekind, Jeffrey A. Siegel,[‡] Jonathan P.D. Abbatt*[†]

[†]Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada.

[‡]Department of Civil and Mineral Engineering, University of Toronto, 35 Street George Street, Toronto, Ontario M5S 1A4, Canada.

[ǂ]Department of Chemistry, Bucknell University, 1 Dent Drive, Lewisburg, PA 17837, USA.

* Corresponding Author Email: jonathan.abbatt@utoronto.ca

S1. Calibration of HNCO

ToF-CIMS

A source of gas phase isocyanic acid (HNCO) was produced by heating cyanuric acid (98%, Sigma-Aldrich) to 250°C in a stainless-steel flow cell with 200 sccm of N_2 passing over it, which decomposes to 3 molecules of HNCO. This flow was immediately diluted with 1700 sccm of N_2 to minimize polymerization. A second, adjustable dilution of zero air (Air grade zero 0.1; Linde [Canada], Inc.) was added downstream to vary the HNCO concentration. The HNCO flow was delivered to the CIMS inlet and to a bubbler filled with 30 mL of purified water (18.2 MΩ cm) simultaneously for approximately 120 min. The bubbler sample was diluted to 50 mL in a volumetric flask and used for external calibration by ion chromatography on the same day. Assuming that all HNCO was captured as NCO^- in the water bubbler at a constant flow rate, the gas phase concentration of HNCO could be calculated. This assumption was verified by placing a second bubbler in sequence with the first, and confirmed no HNCO breakthrough.

The NCO^- (*m/z* 42.00) signal from the ToF-CIMS was first normalized by the reagent ion signal (acetate, *m/z* 59.01) and then background corrected by subtracting the signal during zero air measurement.

Ion Chromatography

A Dionex Integrion HPIC system (ThermoFisher) was used for calibration of HNCO. A Dionex IonPac (AS19, 4×250 mm) anion analytical column with an AG19 guard column was used to resolve anions of interest. 5 mL samples were injected with a Dionex (AS-DV) autosampler and accumulated on a concentrator (Dionex IonPac TAC-ULP1), then flushed with potassium hydroxide eluent on to the column. A 1 mL/min gradient elution of potassium hydroxide was used, starting at 1 mM, linearly increasing to 20 mM over 12 min, then linearly decreasing again to 1 mM until 15 min to regenerate the initial conditions, with a total run time of 19 min. Calibrations of known isocyanate (NCO^-) concentrations were prepared from serial dilutions of potassium isocyanate (96%, Sigma-Aldrich).

A sensitivity of 0.0226 counts per second / ppb was determined for the ToF-CIMS measurement of HNCO.

Calibration of the Quad-CIMS was carried out in the same way as described above, following the chamber measurements. The sensitivity was determined to be 0.0037 counts per second / ppb.

S2. Details of ToF-CIMS Data Analysis during measurements in the Toronto residence

After processing the raw data in Tofware (Tofwerk, AG, Aerodyne Research Inc. Version 2.5.7) on Igor Pro (WaveMetric Inc. Version 6.37), the high resolution data was exported and all further data analysis was completed in R[1] using some functions from the package "open air".[2] The NCO^- signal (*m/z* 42.00) was normalized to the CH_3COO^- reagent ion signal (*m/z* 59.01) and was then background corrected by linearly interpolating between the hourly zero air measurements. Due to the non-instantaneous nature of the valve switching, data within 20 seconds on either side of a valve change (ie. changing sampling location) was disregarded. The limit of detection was determined, during the measurement period, by calculating 3 times the standard deviation during the zero air (background) measurements.

S3. PTR-MS detection of formamide in chamber experiment

A proton transfer reaction – mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Innsbruck Austria) was used to determine the steady-state OH concentration during select chamber experiments, as described by Wang *et al.*[3] This instrument can detect amines and amides present in the side-stream cigarette smoke. Figure S1 shows the signal at *m/z* 46, consistent with formamide ($[M+H]^+$), during a side-stream cigarette smoke OH oxidation experiment. The *m/z* 46 signal is presented as the ratio to [CO] (in ppb) to account for dilution in the chamber. Elapsed time = 0 indicates the time OH oxidation was initiated, after cigarette smoke had already been introduced into the chamber. The signal for formamide was not significant in the primary cigarette smoke (before 0 minutes), but increases initially with OH oxidation followed by a slow decrease after 50 minutes had elapsed.

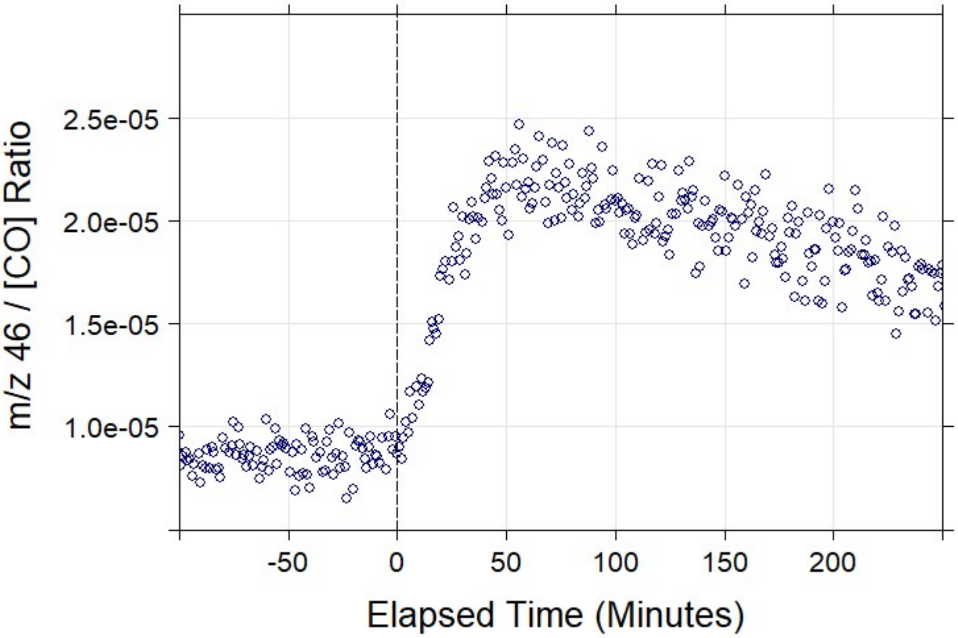

Figure S1. Ratio of signal at *m/z* 46 to [CO], during a representative side-stream cigarette smoke OH oxidation. The vertical line indicates the time at which exposure to OH began.

S4. HNCO Statistical Data – Measurements in the Toronto residence

Table S1. Summary of HNCO measurements in the Toronto residence.

Sampling Location	Minimum [HNCO] (ppb)	Maximum [HNCO] (ppb)	Median [HNCO] (ppb)	Mean [HNCO] (ppb)
Indoor	**< 0.02**	**0.55**	**0.15**	**0.15**
Outdoor	**< 0.02**	**3.3**	**0.08**	**0.10**

S5. Diurnal profiles of HNCO at Toronto Residence

Diurnal plots for HNCO concentrations outdoors and indoors during the study period (compiled from 9 days of measurements) are shown in Figures S2 and S3, respectively. Outdoors, HNCO is highest in the morning (peaking between 8 – 11 am local time), likely corresponding to morning traffic. The median concentration is lower throughout the day (< 100 ppt) and does not show evidence for secondary production in the afternoon when photon flux is highest. Daylight hours during the study period were approximately between 7 am and 5 pm local time. The diurnal profile of HNCO indoors (Figure S3) spans a much narrower range of mixing ratio, with less prominent variation over the day. There is some indication that the HNCO mixing ratio increases in the morning (beginning around 9 am local time) and remains higher throughout the day until approximately 6 pm local time. The difference between the outdoor and indoor diurnal profiles of HNCO demonstrates that there are different sources of HNCO and that the indoor concentration is not merely dependent on outdoor concentration. While there is a large amount of variability in the indoor HNCO mixing ratio, the increased mixing ratio throughout the day could indicate that there is an impact of increased daytime temperature. This observation agrees with the hypothesis that HNCO can partition with surfaces inside the residence, since partitioning behaviour will be influenced by temperature. There is a weak, positive correlation between HNCO and temperature, with an r value of 0.46 and $p < 0.05$.

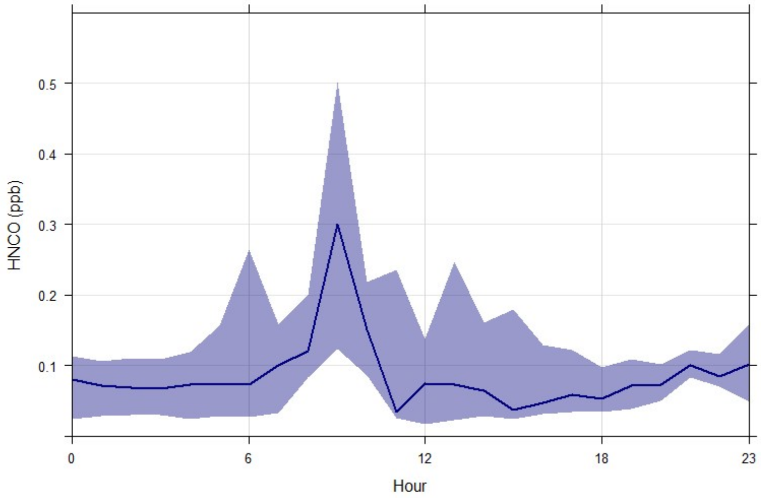

Figure S2. Diurnal plot of HNCO concentration outdoors at the Toronto residence for the duration of the measurement period. The line shows the median concentration, with shading indicating the 25th and 75th percentiles.

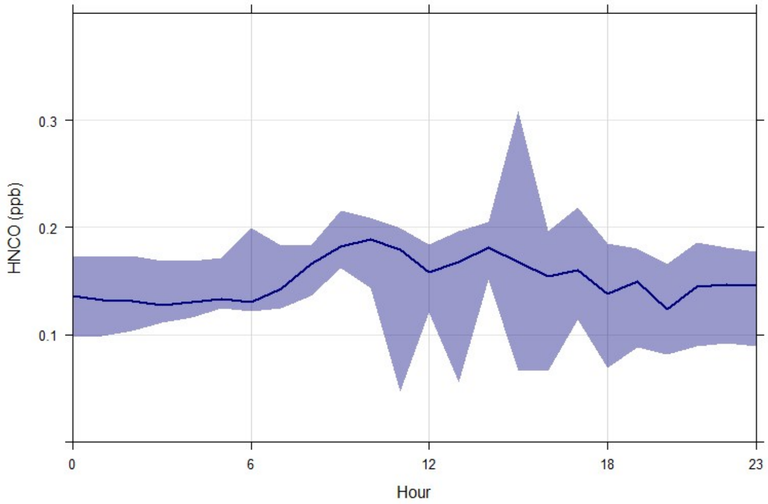

Figure S3. Diurnal plot of HNCO concentration inside the Toronto residence for the duration of the measurement period. The line shows the median concentration, with shading indicating the 25th and 75th percentiles.

S6. Exponential fitting for HNCO and CO loss rate – Measurements in the Toronto Residence

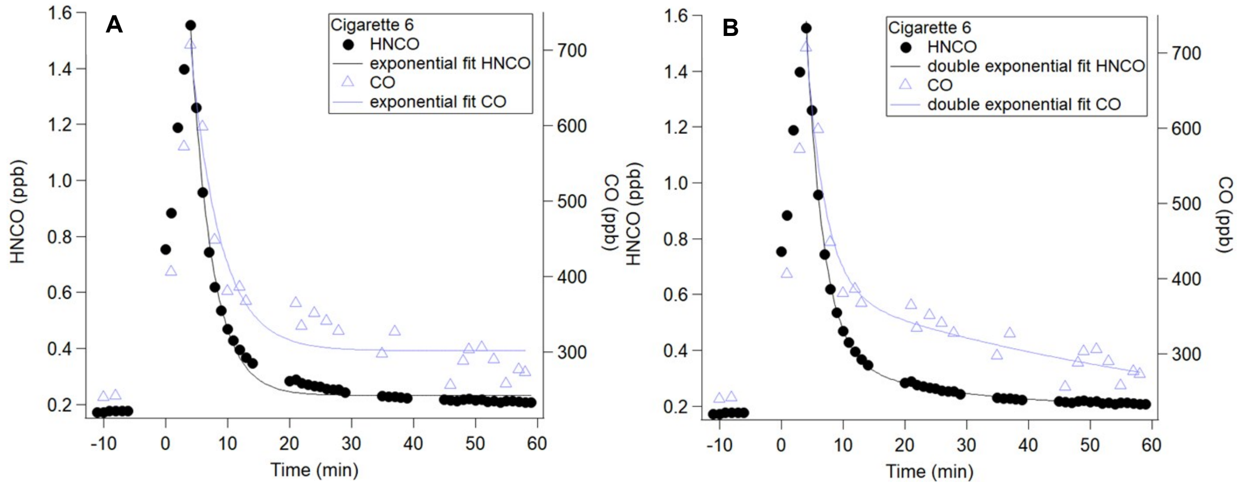

Figure S4. (A) Loss of [HNCO] and [CO] after cigarette is extinguished, fit with a single exponential equation for a representative cigarette experiment in the Toronto residence. (B) The same data as shown in (A) but fit with a double exponential equation.

Lifetime (τ) Determination

Exponential fits were examined only for the four cigarette experiments which had sufficient data immediately after the cigarette was extinguished. The two lifetime (τ) values, which were determined as the time-constant from the exponential fits, are reported below in Figure S5 and summarized in Table S2.

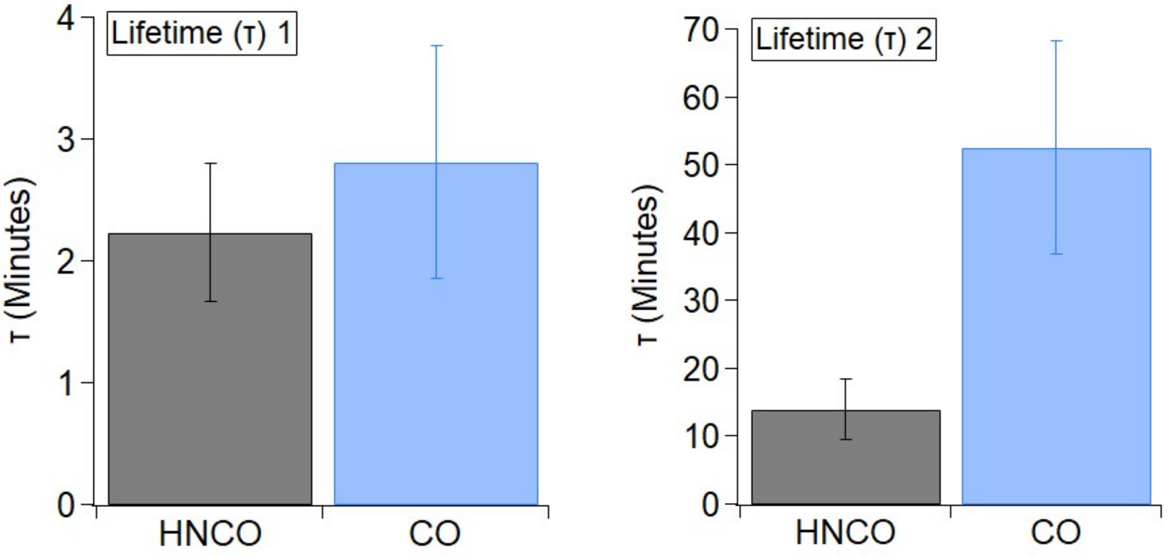

Figure S5. (A) The first lifetime (τ) determined from the exponential fit to the HNCO and CO loss following cigarette extinguishing. (B) The second lifetime (τ) determined from the same exponential fit.

Table S2. Summary of the lifetimes (τ) determined from the double exponential fits to the HNCO and CO loss data in the Toronto residence.

Species	**τ 1 (Minutes)**	**τ 2 (Minutes)**
HNCO	2.2 ± 0.6	14.0 ± 4.4
CO	2.8 ± 0.9	52.5 ± 15.8

References

1 R Core Team, *R: A Language and Environment for Statistical Computing*, R Foundation for Statistical Computing, Vienna, Austria, 2018.

2 D. C. Carslaw and K. Ropkins, *Environ. Model. Softw.*, 2012, **27**–**28**, 52–61.

3 C. Wang, D. B. Collins, R. F. Hems, N. Borduas, M. Antiñolo and J. P. D. Abbatt, *Environ. Sci. Technol.*, 2018, **52**, 4623–4631.