Supplementary Information for:

Validation of a new cavity ring-down spectrometer for measuring tropospheric gaseous hydrogen chloride

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S 1.1 **Ion chromatography analysis**

Aqueous chloride samples collected into an impinger from the HCl PD were analyzed by IC-CD using an ICS-2100 (Thermo Fisher Scientific, Sunnyvale, California, USA) according to the method described by Place et al. (2018). An AS-DV autosampler loaded 1.0 mL of sample onto a concentration column (5 x 23mm, TAC-ULP1, P/N: 061400) and injected into the IC-CD. Anions were analyzed at a flowrate of 1.5 mL min^{-1} using an eluent gradient from 1–60 mM KOH controlled by a Dionex EGC III KOH Potassium Hydroxide Eluent Generator Cartridge (Thermo Fisher Scientific, Sunnyvale, California, USA), and separated on an AS11-HC analytical column thermostated to 30°C, and protected by an IonPac AG11 guard column (4 × 250 mm, P/N: 052960, and 4 x 50 mm, P/N: 052962, respectively). The gradient program started with 1.0 mM KOH held for 7 min followed by a linear increase to 16 mM KOH over the next 9 min. The KOH was held at 16 mM for 4 min then linearly increased to 25 mM from 20 min to 25 min. At 25 min the concentration was linearly increased to 60 mM over a period of 8 min, followed by a stepped decrease to 10 mM KOH and held for 1 min to re-equilibrate the column, yielding a total run time of 33 min. The eluent was suppressed in legacy mode with 124 mA (AERS 500, 4 mm, P/N: 082540) before Cl$^-$ was detected by the CD (DS6 heated conductivity cell, 30 °C).

Annular denuder extracts were analyzed by IC-CD using an ICS-6000 (Thermo Fisher Scientific, Sunnyvale, California, USA). An AS-AP autosampler loaded 250 µL of sample onto a loop and injected into the IC-CD. The sample loop was cut from 0.75mm i.d. polyetheretherketone (PEEK; Thermo Fisher Scientific, Sunnyvale, California, USA, P/N: 052305) tubing, with a length of 56.59 cm. Anions were separated at a flow rate of 1.0 mL min^{-1} using an eluent gradient from 10–60 mM NaOH on an IonPac AS23 analytical column protected by an AG23 guard column (4 × 250 mm, P/N:064149 and 4 × 50 mm, P/N:064147, respectively). Eluent of 100 mM NaOH was prepared from a 9.5 mL aliquot of 50% w/w NaOH diluted to 1800 mL in deionized water, the eluent was purged with N$_2$ for 15 minutes to remove trace CO$_2$. The gradient program held 1.0 mM NaOH for the first 15 min followed by a linear increase to 60 mM NaOH over the next 5 min. The NaOH was held at 60 mM for 5 min, followed by a stepped decrease to 10 mM NaOH and held for 5 min to re-equilibrate the column, yielding a total run time of 30 min. The eluent was dynamically suppressed (ADRS 600, 4 mm, P/N:088666) before Cl$^-$ was detected by conductivity (ICS-6000 CD heated conductivity cell).
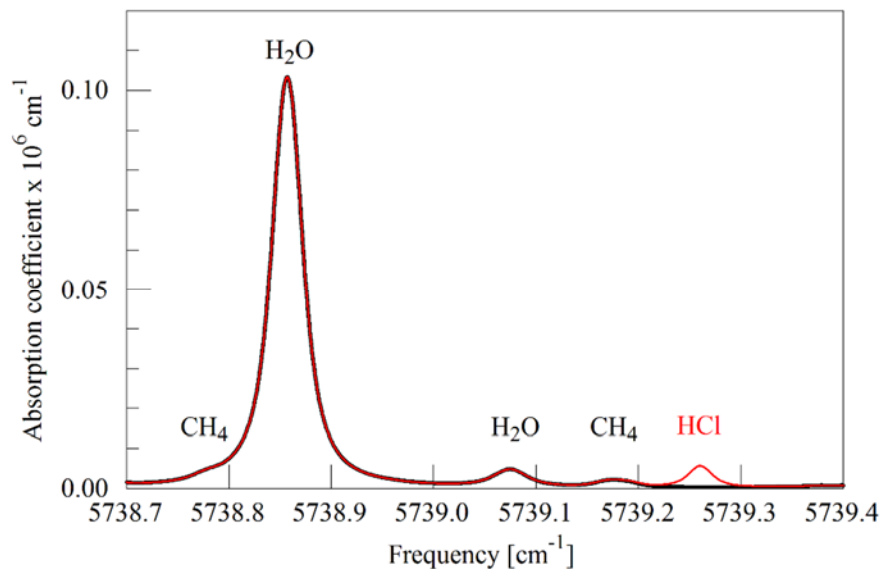
Figure S1. Absorption coefficients modeled from Hitran database for common atmospheric interfering compounds within the relevant wavenumber range of the CRDS laser (Gordon et al., 2017; Kochanov et al., 2019).
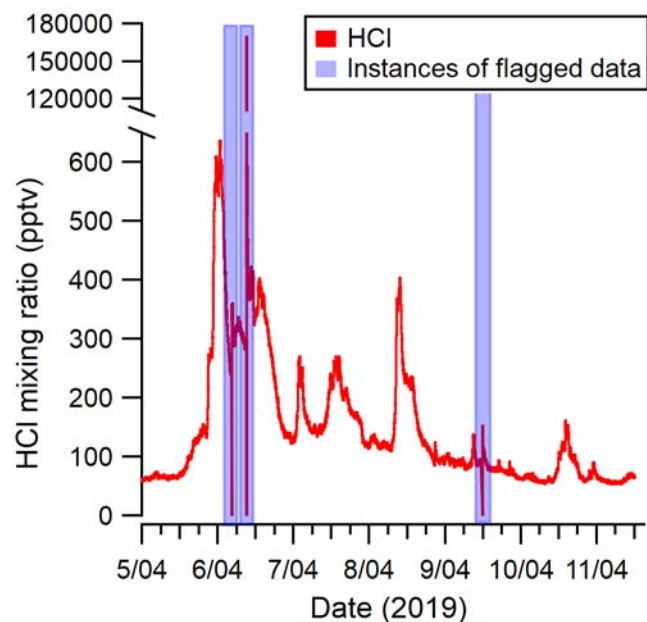

Figure S2. Spectral error for HCl dataset measured in April 2019. Filtered data constituted a 3.5% loss of total data points for the 24-hour averaged CRDS April 6 denuder comparison.
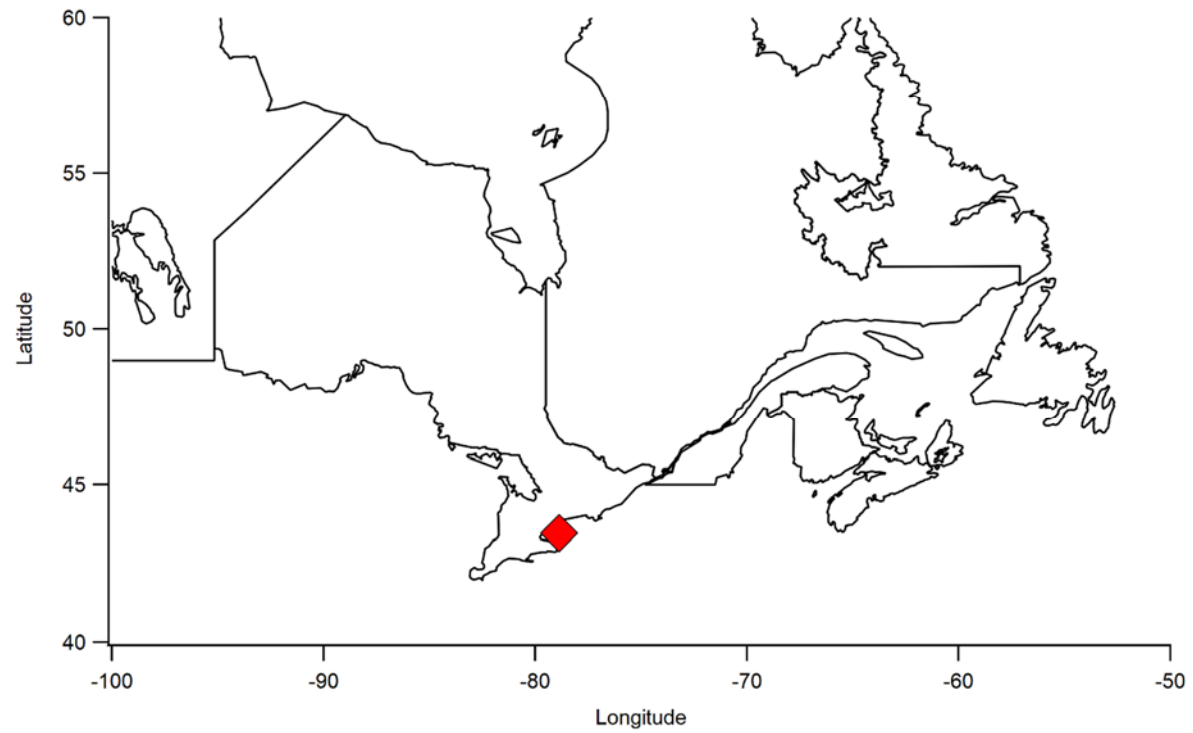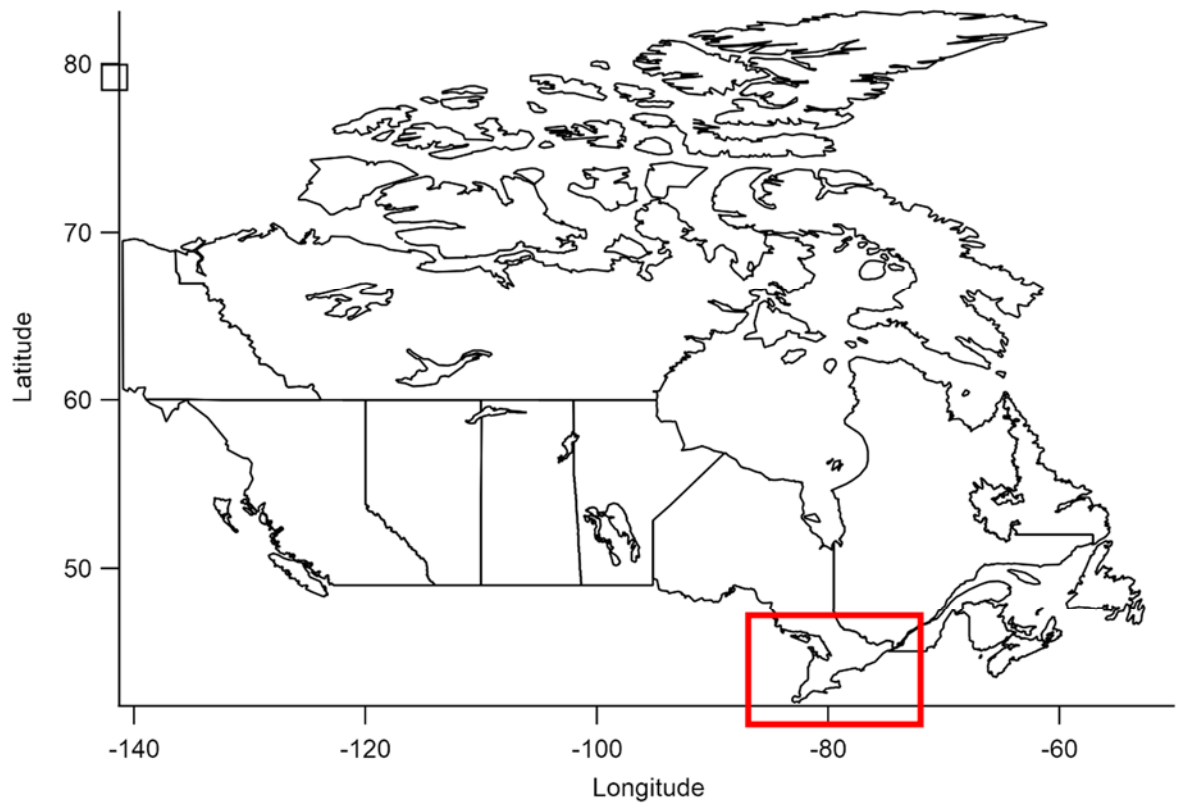
Figure S3. Map of sampling location for ambient measurements.

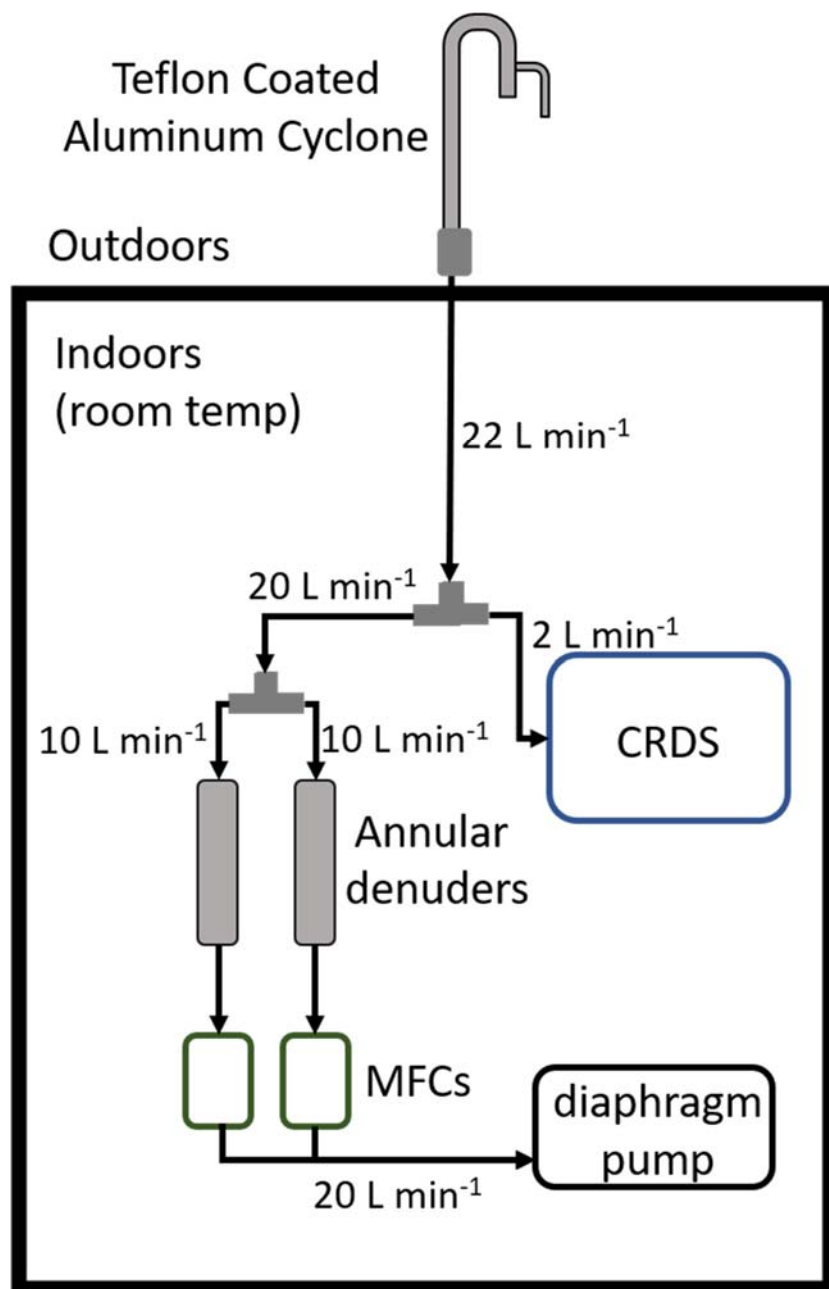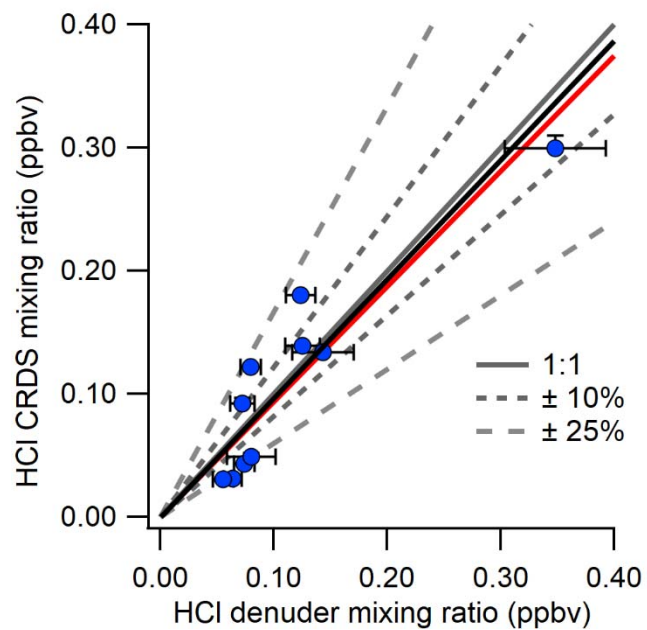**Figure S4.** Ambient intercomparison sampling schematic.

Figure S5. Comparison of HCl measured 4-11 April 2019 using annular denuders and CRDS (averaged to the collection time of denuders. Also shown are a 1:1 correlation line (solid grey), 10 % (short grey dash) and 25 % (long grey dash) deviation from 1:1, orthogonal distance regression (solid black), and the least squares regression (solid red).
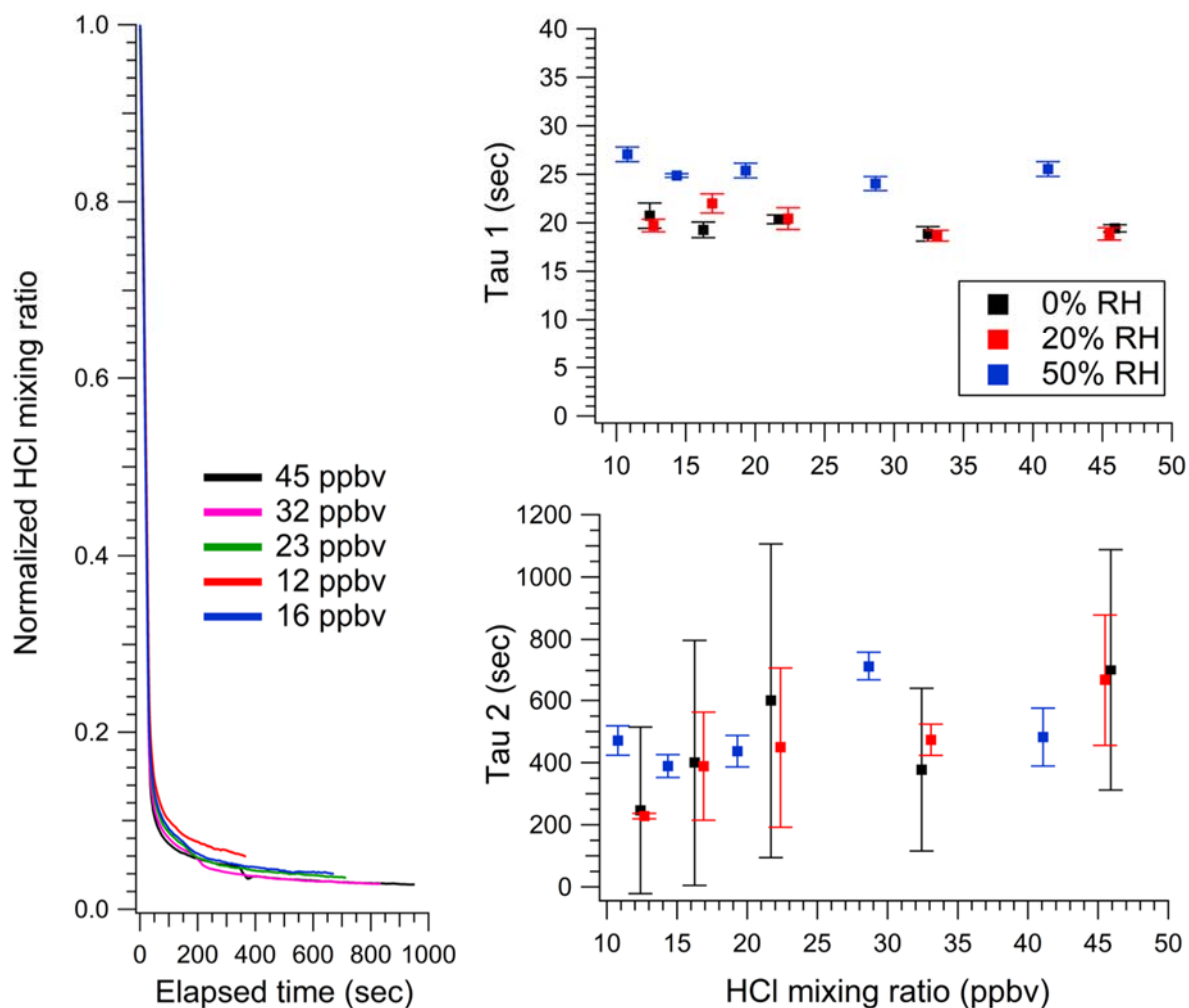
Figure S6. a) Normalized decay curves for 0% RH. b) Tau 1's for increasing humidity. c) Tau 2's for increasing humidity. b) and c) calculated by fitting decays curves to E2.

Table S1. Signal loss decay times for select input HCl mixing ratios, mapping signal loss from zero input.

~Mixing ratio (ppbv)	0% RH		20% RH		50% RH		Residence time (ms)
	$1/e$ (sec)	90% (sec)	$1/e$ (sec)	90% (sec)	$1/e$ (sec)	90% (sec)	
12	26.5	101	30.8	229	38.0	458	21.0
16	24.7	82	31.3	214	34.3	415	28.0
21	26.4	74	30.1	178	33.4	310	37.2
32	24.5	62	28.9	167	29.9	199	55.6
45	25.6	54	28.3	152	31.9	186	78.8

Table S2. Signal loss decay ratios for HCl decay times to residence time.

~Mixing ratio (ppbv)	0% RH		20% RH		50% RH	
	$1/e$	90%	$1/e$	90%	$1/e$	90%
12	0.126	0.481	0.147	1.090	0.181	2.181
16	0.088	0.293	0.112	0.764	0.123	1.482
21	0.071	0.199	0.081	0.478	0.090	0.833
32	0.044	0.112	0.052	0.300	0.054	0.358
45	0.032	0.069	0.036	0.193	0.040	0.236

Table S3. Signal increase upswing times for select input HCl mixing ratios, mapping signal rise from zero input to signal plateau.

~Mixing ratio (ppbv)	0% RH		20% RH		50% RH		Residence time (ms)
	$1 - \frac{1}{e}$ (sec)	90% (sec)	$1 - \frac{1}{e}$ (sec)	90% (sec)	$1 - \frac{1}{e}$ (sec)	90% (sec)	
12	27.2	64	27.2	64	50.8	197	21.0
16	26.4	62	27.9	58	49.3	204	28.0
21	26.3	61	26.8	60	48.5	198	37.2
32	25.7	61	29.3	60	31.8	174	55.6
45	28.2	117	33.3	128	62.9	452	78.8

Table S4. Signal loss upswing ratios for HCl upswing times to residence time.

~Mixing ratio (ppbv)	0% RH		20% RH		50% RH	
	$1 - \frac{1}{e}$ (sec)	90% (sec)	$1 - \frac{1}{e}$ (sec)	90% (sec)	$1 - \frac{1}{e}$ (sec)	90% (sec)
12	0.130	0.305	0.130	0.305	0.242	0.938
16	0.094	0.221	0.100	0.207	0.176	0.729
21	0.071	0.164	0.072	0.161	0.130	0.532
32	0.046	0.110	0.053	0.108	0.057	0.313
45	0.036	0.148	0.042	0.162	0.080	0.574

Table S5. Denuder extraction list.

Extract #	Time and Date	Duration (min)	Mixing ratio (ppbv)
1	21:07 April 4 → 21:00 April 5	1433	0.074
2	9:30 April 5 → 10:06 April 6	1476	N/A*
3	21:00 April 5 → 21:00 April 6	1440	0.347
4	10:06 April 6 → 10:12 April 7	1446	0.123
5	21:00 April 6 → 20:34 April 7	1414	0.125
6	10:12 April 7 → 9:30 April 8	1398	0.143
7	20:34 April 7 → 21:03 April 8	1469	0.079
8	9:30 April 8 → 10:45 April 9	1515	0.072
9	21:03 April 8 → 21:00 April 9	1437	0.080
10	10:45 April 9 → 10:53 April 10	1448	0.064
11	21:00 April 9 → 10:06 April 11	2226	0.055

* Sample lost

Annular denuder codes were recorded for determining and applying systematic error corrections

References

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