High time-resolution measurements of HCl in marine and continental urban areas: Implications for the reactive chlorine budget

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Objectives

Make high time resolution measurements of HCl under different conditions to better understand: 1) the sources and sinks of HCl; and 2) the linkages between HCl and the reactive chlorine cycle.

Introduction

- Atmospheric oxidation is dominated by the OH radical, although Cl atoms can play an important role under certain conditions.

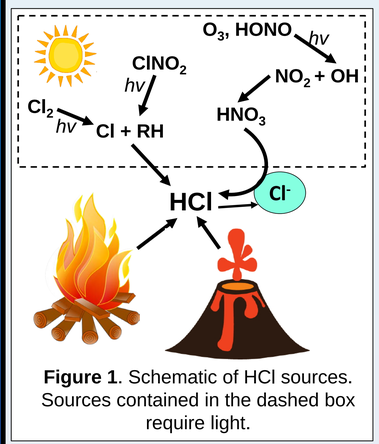

Figure 1. Schematic of HCl sources. Sources contained in the dashed box require light.

- Gas-phase inorganic chlorine (Cl_y) controls the Cl budget.
- HCl dominates Cl_y [1].
- Atmospheric sources and levels of HCl are poorly constrained (Figure 1).
- HCl is a sticky gas and is a challenge to measure with high time resolution.
- Most measurements have been made using time-integrated techniques, such as mist chambers (e.g. [2]).
- Some recent measurements made using chemical ionization mass spectrometry, although issues with calibration and inlet transmission are common (e.g. [1,3]).
- A recently-available cavity-ring down instrument generates reliable measurements of HCl at 0.5 Hz.
- Spectroscopic technique eliminates most calibration issues, while specially designed instrument reduces surface effects.

Continental Winter: Toronto

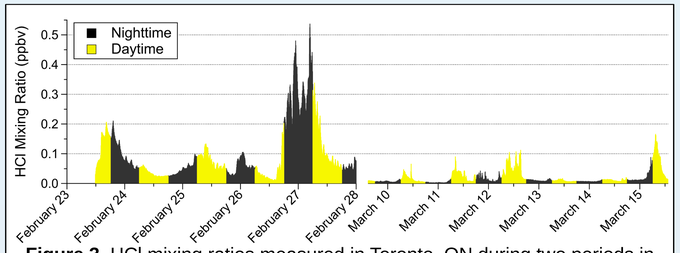

Figure 3. HCl mixing ratios measured in Toronto, ON during two periods in late winter of 2018. Mixing ratios are coloured by measurement time: daytime (yellow), nighttime (black).

- HCl was observed consistently in late winter of 2018 in Toronto (Figure 3).
- Mixing ratios were higher in February than in March (Table 2).
- No diurnal trend observed.
- Elevated HCl occurred during the day and at night.
- Highest HCl observed during the night of February 26/27 (Figure 4).
- HCl sources in the absence of light likely to be direct sources. This is corroborated by high NOx during the same period on February 26/27.
- A snow event occurred on March 11 – 12 where road salt was applied. Since this was the only salting event during the sampling period, we could not conclude this caused the slight elevation of HCl mixing ratios.

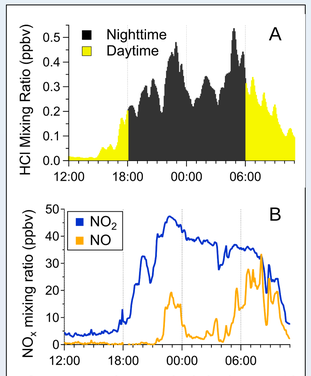

Figure 4. Elevated nighttime HCl in Toronto, ON on the night of February 26/27, 2018: (A) HCl mixing ratios; (B) co-located NO and NO_2 mixing ratios.

Table 2. Measurement statistics for HCl during two periods in Toronto, ON.

Dates	Mean T (°C)	Mean (pptv)	Max (pptv)	Min (pptv)	Median (pptv)
Feb 23 – 28, 2018	4.62	203	541	<4.44	67.3
Mar 9 – 15, 2018	-1.28	61.4	172	<4.44	11.2

Marine Spring: St. John's & Halifax

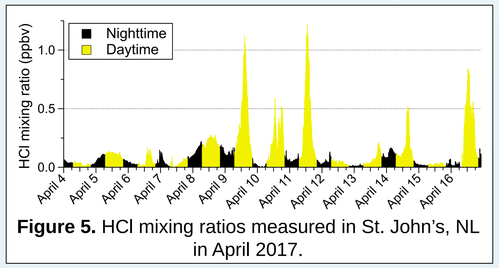

Figure 5. HCl mixing ratios measured in St. John's, NL in April 2017.

- HCl was observed consistently during spring 2017 in St. John's (Figure 5, Table 3).
- Daytime levels were generally higher than nighttime indicating the role of light-mediated processes to HCl in St. John's.
- The sampling period had very little sun. Times of higher irradiance corresponded to fast increases in HCl and the highest observed HCl mixing ratios (Figure 6), suggesting the contribution of photolabile Cl_y species.

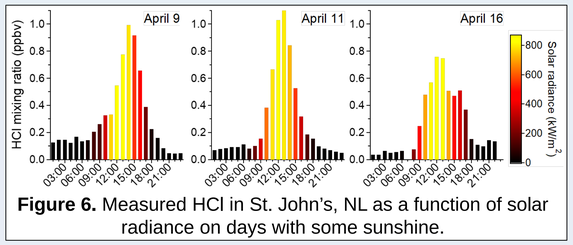

Figure 6. Measured HCl in St. John's, NL as a function of solar radiance on days with some sunshine.

Table 3. Measurement statistics for HCl in St. John's, NL and Halifax, NS.

Dates	Mean T (°C)	Mean (pptv)	Max (pptv)	Min (pptv)	Median (pptv)
Apr 4 – 16, 2017	1.52	110	1210	<15.3	62.0
May 25 – Jun 24, 2019	17.7	114	614	61.7	96.8

- Elevated nighttime HCl events were also occasionally observed. One event on the night of April 6/7 could be attributed to a fire that burned an abandoned building < 1 km from the sampling site (Figure 7).
- HCl was also observed consistently during spring 2018 in Halifax with levels and trends similar to St. John's (Figure 8, Table 3).

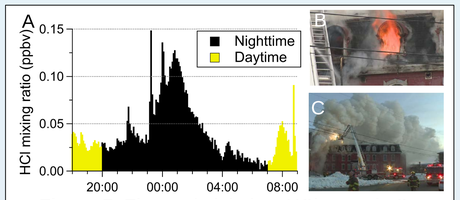

Figure 7. Elevated nighttime HCl event in St. John's, NL on the night of April 6/7, 2017 attributed to a local fire: (A) HCl mixing ratios; (B), (C) photos of local fire event (from Jeremy Eaton/CBC NL).

- HCl in Halifax was measured as part of the Halifax Fog and Air Quality Study (HaliFAQS). Supporting measurements will be used to better understand sources.

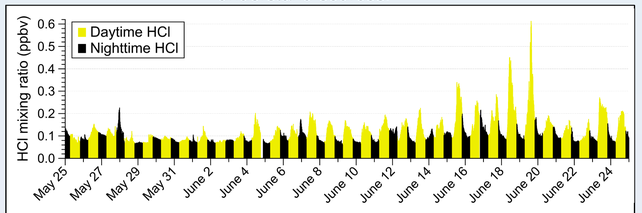

Figure 8. HCl mixing ratios measured in Halifax, NS in spring 2019

Model Comparison

- GEOS-Chem simulations of HCl were run using the method of Wang et al. [4] for the same time periods as measurements were made in St. John's and Toronto.
- Model reproduced general patterns of HCl observations in St. John's, although mixing ratios were consistently under-estimated by a factor of ~4 – 10 (Figures 9, 10).
- Model did not reproduce the HCl patterns observed in Toronto and underestimated mixing ratios by orders of magnitude (Figure 10).
- Model did not include direct sources, which are very poorly constrained for HCl. More work on direct sources is necessary.

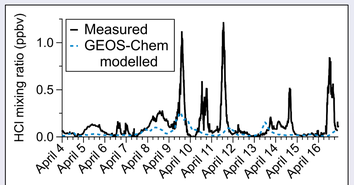

Figure 9. Time series of measured and modelled HCl in St. John's, NL.

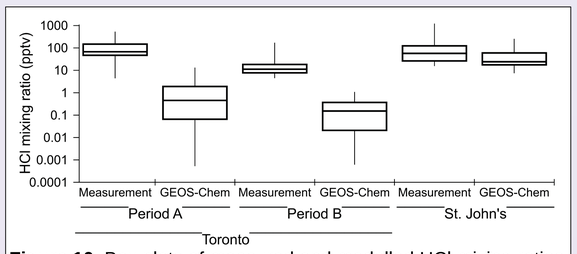

Figure 10. Box plots of measured and modelled HCl mixing ratios for Toronto, ON in 2018 and St. John's, NL in 2017.

Conclusions

- High time resolution measurements of HCl were made in winter and spring in three Canadian cities.
- Levels in winter urban Toronto did not follow a diurnal trend and appeared to be influenced by direct sources.
- Levels in the spring marine boundary layer were higher in the daytime in both St. John's and Halifax. St. John's HCl was strongly influenced by the presence of sunlight, suggesting the importance of photolabile sources.
- Comparison between measured and GEOS-Chem-modelled mixing ratios showed small differences for St. John's and large differences for Toronto.
- More information is needed about direct HCl sources.

Methods

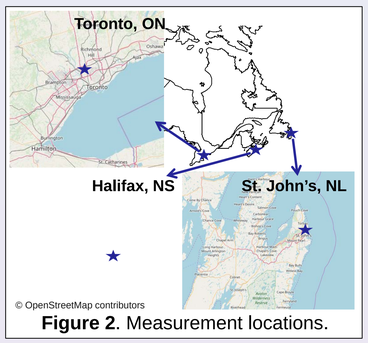

Figure 2. Measurement locations.

- Measurements were made during three campaigns using a Picarro G2108 HCl analyzer.
  - Reports data at 0.5 Hz.
  - Measures absorbance at 5739 cm^{-1}.
  - Cavity at 80 °C and 140 Torr.
  - Effective path length of ~20 km.
  - Contains two interior HEPA filters
- Measurements were made in three Canadian locations: St. John's, Newfoundland and Labrador; Toronto, Ontario; Halifax, Nova Scotia (Figure 2, Table 1).
- Measurements in St. John's were conducted at ground level with a different analyzer of the same model. All supporting measurements were from local sources.
- Measurements in Toronto and Halifax were made with the same analyzer on the roof of a 4- and 5-storey building, respectively. Several co-located measurements were made at each sampling site.
- Limits of detection (LOD) were determined as 3σ of blank measurements.
- For all measurements, ambient air was sampled through a PFA inlet.

Table 1. Details of measurements in St. John's, Toronto, and Halifax; LOD (limit of detection).

Location	Dates	Mean T (°C)	Rainfall (mm)	LOD (pptv, 2 s)	LOD (pptv, 2 min)	Supporting measurements
St. John's, NL	Apr 4 – 16, 2017	1.52	18	15.3	13.9	Local NO_x, O_3, irradiance
Toronto, ON (A)	Feb 23 – 28, 2018	4.62	8.2	4.44	4.05	On-site NO_x, O_3, irradiance
Toronto, ON (B)	Mar 9 – 15, 2018	-1.28	3.4	4.44	4.05	On-site NO_x, O_3, irradiance
Halifax, NS	May 25 – Jun 24, 2019	17.7	86.4	3.24	2.63	On-site NO_x, O_3, irradiance, particle #, composition

References

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Acknowledgements

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