Measurement of Ambient Hydrochloric Acid near Utah's Great Salt Lake

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INTRODUCTON

In addition to the potential of the meteorology and spatial dynamics of Utah's Great Salt Lake (GSL) to modify the behavior of tropospheric ozone (O_3), it has been speculated that atmospheric chlorine, either from the GSL, the adjacent salt flats or nearby industrial sources, may significantly add to the oxidative capacity of the local atmosphere. Atmospheric chlorine is a strong oxidant and known to potentially initiate photochemistry via reactions with various common hydrocarbons. Ravishankara (2009) summarized recently proposed tropospheric mechanisms to process gaseous hydrochloric acid (HCl) into free chlorine atoms and thus contribute to local radical chemistry. Near marine boundary layers typical HCl concentrations are near 200 ppt, while concentrations over continental areas are believed to be significantly lower, with the exception of urban areas which are generally around 1.5-2.0 ppb (Khalil, 1999). Additionally, Kerry et al (2013) found chlorine atoms significantly contribute to local Salt Lake City $PM_{2.5}$ during elevated wintertime episodes with ammonium chloride accounting for 10-15% of the $PM_{2.5}$ mass.

Along with the GSL and adjacent salt flats, other potential sources of atmospheric chlorine or HCl could include a large primary magnesium refinery located on the western shore of the GSL and several local oil refineries located near the southeast corner of the GSL and slightly northwest of Salt Lake City. However, there are little observations of atmospheric chlorides along the Wasatch Front, so it is problematic to assess potential impacts. Stutz et al (2002) measured chlorine oxide (ClO), as well as bromine oxide (BrO), on the southeast shore of the GSL during October 2000 and suggested theoretical atmospheric hydrochloric acid (HCl) concentrations of around two parts per billion (2 ppb). As such, the objective of this study was to perform a spatial survey of local atmospheric HCl concentrations to assess the possible contributions to atmospheric chemistry and identify areas of localized potential emissions.

METHODOLOGIES

In order quantify the concentrations of local atmospheric chlorides, a network of 14 Radiello passive HCl samplers was established around the west, south and east sides of the GSL and into the urban areas along the Wasatch Front, the region dominated, population-wise, by Salt Lake

City. An additional site, located in Cache Valley (Logan, UT) which is topographically separated from the GSL was established to include a location believed to be not as directly impacted by the GSL. The location names and coordinates are shown in Table 1.

Table 1. HCl passive sampler deployment location along Utah's Wasatch Front.

Location	Latitude (°)	Longitude (°)
Logan	41.73077	-111.8364
Brigham City	41.49291	-112.0178
Ogden	41.20693	-111.9751
Syracuse	41.08844	-112.1188
Antelope Island	41.03940	-112.2316
Farmington Bay - Goose Island	40.95733	-111.9307
Farmington Bay - Miller Flats	40.95733	-112.0225
Bountiful	40.90293	-111.8845
Hawthorne (HW)	40.73436	-111.8722
Erda (ED)	40.60056	-112.3558
Badger Island (BI)	40.94212	-112.5620
Saltaire (SA)	40.80598	-112.0498
Beaches (B4) - GSL Marina	40.73347	-112.2119
Lakeside	41.02381	-112.9052
Refineries	40.83651	-111.9141

The Radiello absorber systems consist of a white, hollow diffusive (S/N 120), a supporting plate (S/N 121), a vertical adapter (S/N 122), and a stainless steel net load with silica gel (S/N 169). All components were reusable except the adsorption columns. Three separate four to six day periods from mid-August to mid-September 2015 were monitored (Aug. 18-25, Sept. 3-9, and Sept. 9-13). The diffusion rate to the sample pads was calculated according to an algorithm given by Radiello which was a function of local ambient temperature (Supelco, 2015) and average around 100 mL/min. Over three sample periods, the calculated air volume sampled averaged approximately 825 L for each of the samplers (range: 697 – 920 L). After the specified deployments, the samplers were recovered and stored under dark conditions at 4°C until the compiled collected samples could be processed and analyzed within a 48 hour time period. As specified by the Radiello protocol (Supleco, 2015), the absorbed HCl was measured via elution into 2 ml of de-ionized ($\geq$18.2 MΩ) water and quantified using ion chromatography, following appropriate calibration and QA/QC procedures, at the Environmental Quality Laboratory (EQL) at Utah State University's (USU's) Utah Water Research Laboratory (UWRL).

RESULTS AND DISCUSSIONS

As shown in Figure 1, across the sites, the ambient concentrations ranged from 0.1 ppb to 4.4 ppb, with the highest values consistently observed on the western (Badger Island, Lakeside) or southern boundaries of the GSL. Most of the locations showed ambient HCL concentrations consistently less than 1.0 ppb, including the more removed site at Logan. Across all the sites, the ambient HCl averaged 0.85 ppb, 0.67 ppb, and 1.32 ppb for the first, second and third sampling periods, respectively.

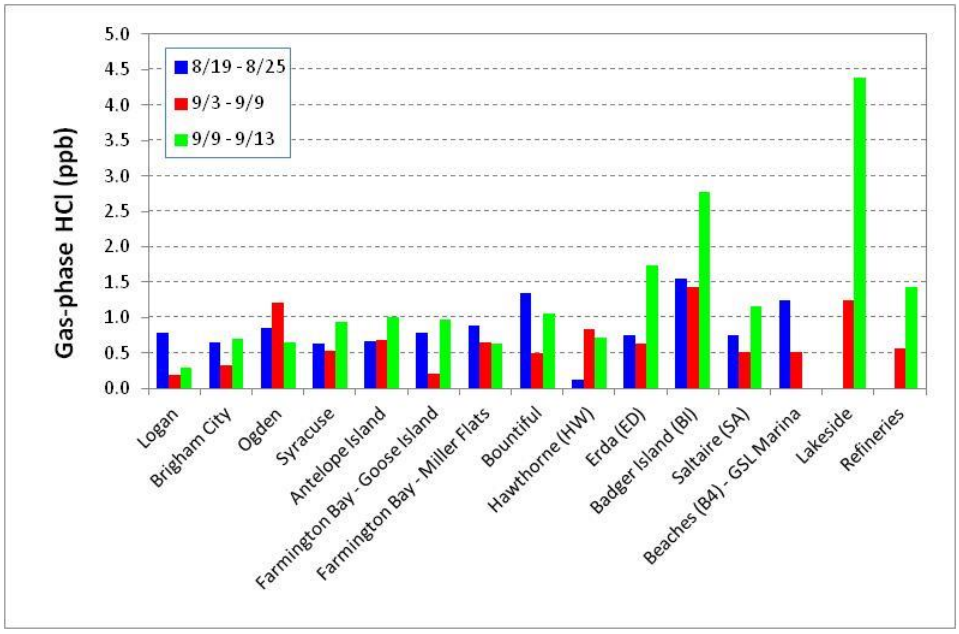
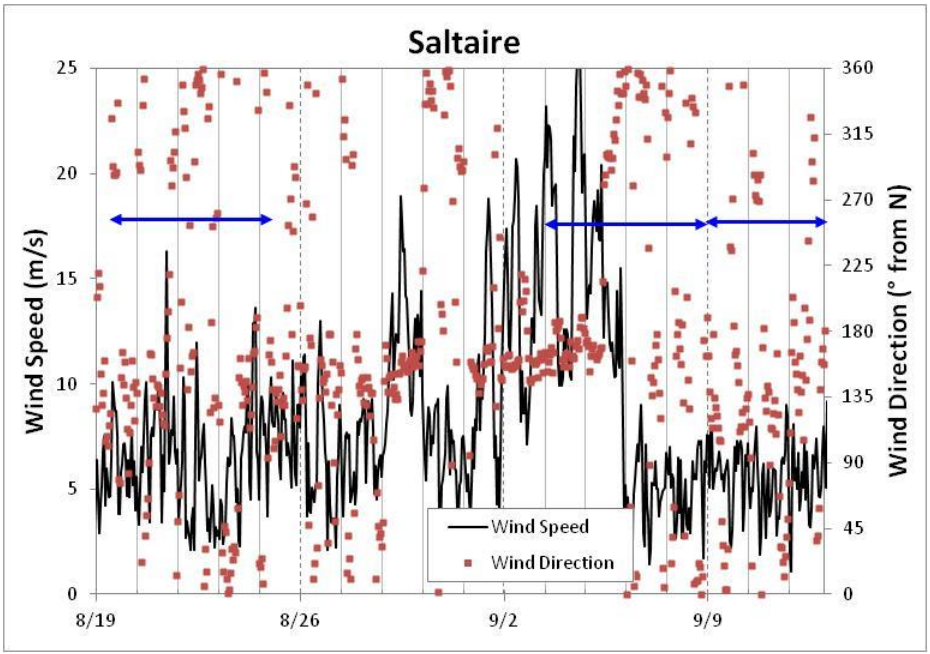


Figure 1. Ambient hydrochloric as measured along Utah's Wasatch Front and adjacent to the Great Salt Lake.

It is of interest to note that the sites located on the western (Lakeside, Badger Island), southern (Erda, Saltaire) and southeastern (refineries) edge of the GSL seemed to show significant increases in HCl concentrations during the final sampling period (Sept. 9-13, 2015). The local meteorology was generally consistent throughout the sample periods with only a trace of precipitation recorded on a very few occasions. The average temperatures for the three sampling periods were similar: 22.9°C, 20.6°C, and 22.1°C, respectively. Similarly, relative humidities averaged 35.9%, 29.0% and 27.9%. Figure 2 shows the wind speed and wind direction data collected at a representative site along the southern shore of the GSL (Saltaire). As can be seen, it was the middle period (Sept. 3-9) that experienced somewhat different meteorological conditions, with higher wind speeds and more consistently southern winds. Anecdotally, large rolling dust clouds were observed along the open shores at the southern end of the GSL.

However, the HCl concentrations observed during this period was not remarkably different from the proceeding period, even seemingly trending lower at several locations from the previous period's concentrations.

Figure 2. Wind speed and direction at Saltaire along the southern shore of the Great Salt Lake. The arrows show the approximate sample periods.



SUMMARY

As can be derived from the Figure 1, the observed ambient HCl concentrations were in the low ppb levels, in line with expected urban levels and those predicted by Stutz et al (2002) based on earlier measurements of ClO. However, it does not appear that the GSL itself, the exposed shoreline and salt flats, nor the local refineries presented dominant sources of the observed HCl. Rather the investigators propose that the area's observed HCl concentrations may strongly be influenced by the magnesium refinery on the lakes western shore line. Figure 3 shows a contour plot of the average HCl concentrations over the three sample periods and a clear west to east gradient can be observed. Additionally, the location of the primary magnesium refinery is shown to be located roughly between the Lakeside and Badger Island sampling locations. Given predominate south winds (Figure 2) it seems reasonable that the Lakeside and Badger Islands would be the most directly impacted from the identified source. In further support, the Utah Division of Air Quality's Toxic Inventory Report for 2009, the last year speciated data were

publically compiled, showed 2.42 million pounds of combined chloride and hydrochloric acid were emitted from the given facility (UDAQ, 2010).

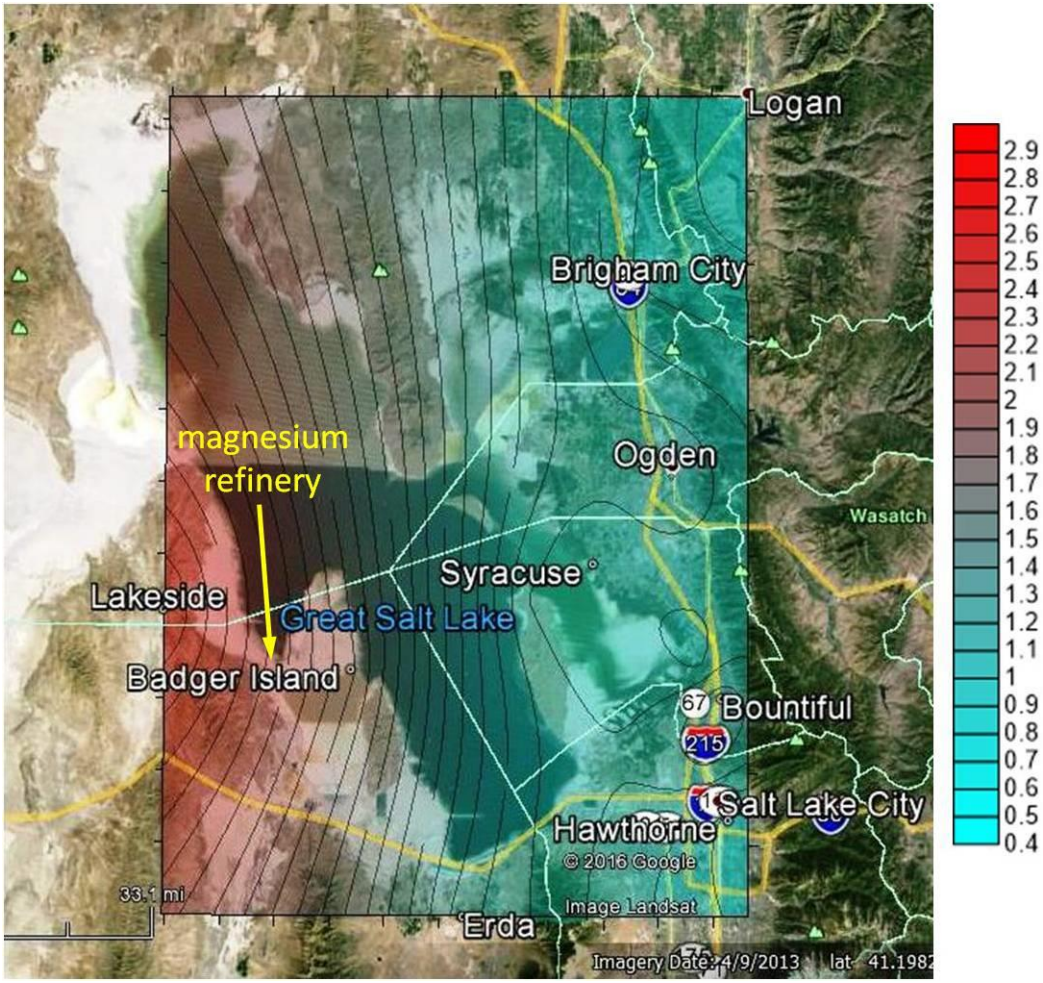


Figure 3. Contour plot of observed average ambient HCl (ppb). For clarity, not all of the individual sample locations are shown.

ACKNOWLWDEMENTS

This work was funded by the Utah State Legislature and the Utah Division of Air Quality (UDAQ). Additional support was provided by USU's Utah Water Research Laboratory. The authors would also like to thank the small army of USU students and UDAQ technicians how helped deploy the samplers to the spatial distant locations in a timely manner.

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APPENDIX – Compiled Data

Tabulated Observed Ambient HCl Concentration along the Wasatch Front and around the Great Salt Lake (Aug.-Sept 2015).

			8/19 - 8/25	9/3 - 9/9	9/9 - 9/13	Average	Std Dev	95% CI
	Latitude	Longitude	HCl	HCl	HCl	HCl	HCl	HCl
Location	(°)	(°)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Logan	41.73077	-111.83644	0.78	0.18	0.29	0.42	0.32	0.36
Brigham City	41.49291	-112.01778	0.65	0.33	0.69	0.56	0.20	0.22
Ogden	41.20693	-111.97512	0.85	1.21	0.66	0.91	0.28	0.32
Syracuse	41.08844	-112.11879	0.64	0.53	0.94	0.70	0.21	0.24
Antelope Island	41.03940	-112.23158	0.66	0.69	1.01	0.79	0.19	0.22
Farmington Bay - Goose Island	40.95733	-111.93072	0.78	0.21	0.98	0.66	0.40	0.45
Farmington Bay - Miller Flats	40.95733	-112.02247	0.89	0.66	0.64	0.73	0.14	0.16
Bountiful	40.90293	-111.88448	1.34	0.50	1.06	0.97	0.43	0.48
Hawthorne (HW)	40.73436	-111.87218	0.13	0.83	0.72	0.56	0.38	0.43
Erda (ED)	40.60056	-112.35583	0.75	0.64	1.74	1.04	0.61	0.68
Badger Island (BI)	40.94212	-112.56197	1.56	1.44	2.78	1.92	0.74	0.84
Saltaire (SA)	40.80598	-112.04981	0.75	0.51	1.16	0.81	0.33	0.37
Beaches (B4) - GSL Marina	40.73347	-112.21188	1.25	0.52		0.88	0.52	0.72
Lakeside	41.02381	-112.90524		1.24	4.39	2.81	2.23	3.09
Refineries	40.83651	-111.91414		0.57	1.42	0.99	0.61	0.84
		Average	**0.85**	**0.67**	**1.32**	**0.98**	**0.51**	**0.63**
max	41.731	-111.836	**1.56**	**1.44**	**4.39**	**2.8**	**2.2**	**3.1**
min	40.601	-112.905	**0.13**	**0.18**	**0.29**	**0.4**	**0.1**	**0.2**

Graphs of Average Observed HCl with 95% Confidence Intervals and Ranges Shown.