

Supporting information for *High gas-phase mixing ratios of formic and acetic acid in the High Arctic*

S1 Calibration data analysis

For each of two calibration experiments, the following data analysis steps were carried out.

1. Perform high resolution peak fits in Tofware v2.5.7 in IGOR Pro
2. Export time series of peak fits from IGOR Pro
3. Import time series to R
4. Perform filtering on the time series to remove points in-between calibration values
 - (i) Calculate the difference between adjacent points in a background peak (C2H3INO-)
 - (ii) Reject all the points where that difference is greater than 0.2
 - (iii) Remove the following 40 points
5. Import flow saved from the Labview flow control program
6. Import relative humidity and temperature saved from the EyeOn temperature probe
7. Normalize FA and AA signals to the sum of I- and I.H2O- (the reagent ions)
8. Subtract the blanks from the signals (the signal at the same mass to charge when none of the target compound is being added to flow)
9. Use the concentration supplied to the LCU to calculate the mixing ratio being supplied by a given volume
10. Use the lm function in R to perform multiple linear regression (regression coefficients shown in Table S1)

When using a multiple linear regression to analyse a calibration experiment, the slopes with respect to each variable are not directly equivalent to the sensitivity to that variable. Instead the effect size of each variable can be considered [Fox and Weisberg(2011)]. The effect sizes of the two calibration variables (humidity and mixing ratio) for each calibration experiment are shown in Fig. S2. The invest function from the investr R package [Greenwell and Kabban(2014)] was then used to apply the calibration function (i.e. perform the inverse estimation), allowing the mixing ratio to be estimated from the measured signal and absolute humidity. The mean of the two calibrated timeseries is presented in the manuscript. The upper and lower range is shown as the shaded area in Fig. SS1. The calibration uncertainty is 15% for FA and 50% for AA. The larger uncertainty in AA can be attributed to the much poorer signal to noise in the AA signal as opposed to the FA signal.

Compound	Absolute humidity slope	Mixing ratio slope	Intercept	R ² (p < 0.001)
FA expt 1	1.4×10^{-1}	2.5×10^{-3}	-3.6×10^3	0.998
FA expt 2	2.9×10^{-1}	2.7×10^{-3}	-6.2×10^3	0.98
AA expt 1	-2.8×10^{-3}	3.1×10^{-5}	6.7×10^{-5}	0.99
AA expt 3	-6.9×10^{-3}	3.8×10^{-5}	1.7×10^{-4}	0.92

Table S1: Multiple regression coefficients for FA and AA.

S2 Mixing height analysis

The mixing height is defined as the height where the potential temperature above the surface is equal to that at the surface. As a measure of stability, the difference between the potential temperature at the surface and at 1 km was calculated. The gradients were in general stronger during the low wind speed regime. The average mixing heights shown in Fig. S5 were used for the analysis.

S3 Precipitation

S3.1 Amount of precipitation

Knowing the funnel diameter (D_f) and measuring the total collected volume of precipitation (V) from the three samplers, the amount of precipitation in mm (P) can be calculated as follows:

$$P = V \left[3\pi \left(\frac{D_f}{2} \right)^2 \right]^{-1} \quad (1)$$

S3.2 Deposition

Deposition is calculated as the amount of precipitation multiplied by the concentration in μmol and expressed as $\mu\text{mol m}^2$.

S3.3 Scavenging

In order to estimate the amount of deposition (Dep) that would result from scavenging the entire column of air, a boundary layer height (BLH) and mixing ration (C) must be assumed. The deposition can then be estimated as follows:

$$Dep = \frac{C n_{air} V_{column}}{N_A P} \quad (2)$$

where N_A is Avogadro's number and the volume of the column (V_{column}) is simply the BLH for a 1 m^2 column.

References

- [Fox and Weisberg(2011)] Fox, J. and Weisberg, S.: An R companion to applied regression, SAGE Publications, Los Angeles, 2nd edn., 2011.
- [Greenwell and Kabban(2014)] Greenwell, B. M. and Kabban, C. M. S.: in-
vestr: An R Package for Inverse Estimation, The R Journal, 6, 90–100, URL
<http://journal.r-project.org/archive/2014-1/greenwell-kabban.pdf>, 2014.

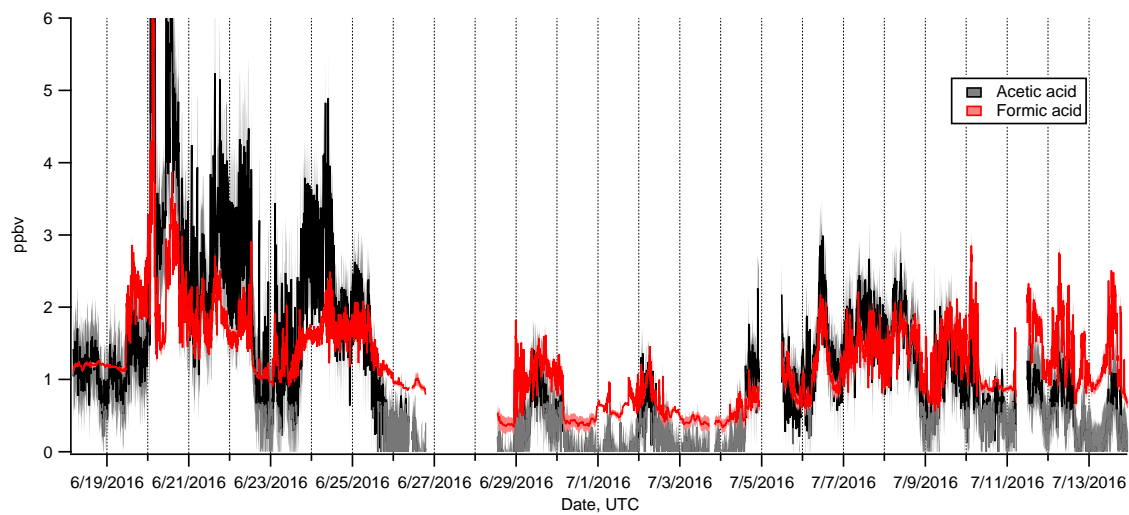


Figure S1: Time series of FA and AA in ppbv (scale truncated at 5 ppbv) with the calibration uncertainty (defined as the spread between the two calibration experiments) shown in the shaded areas. Values of AA below the detection limit are also shown in gray.

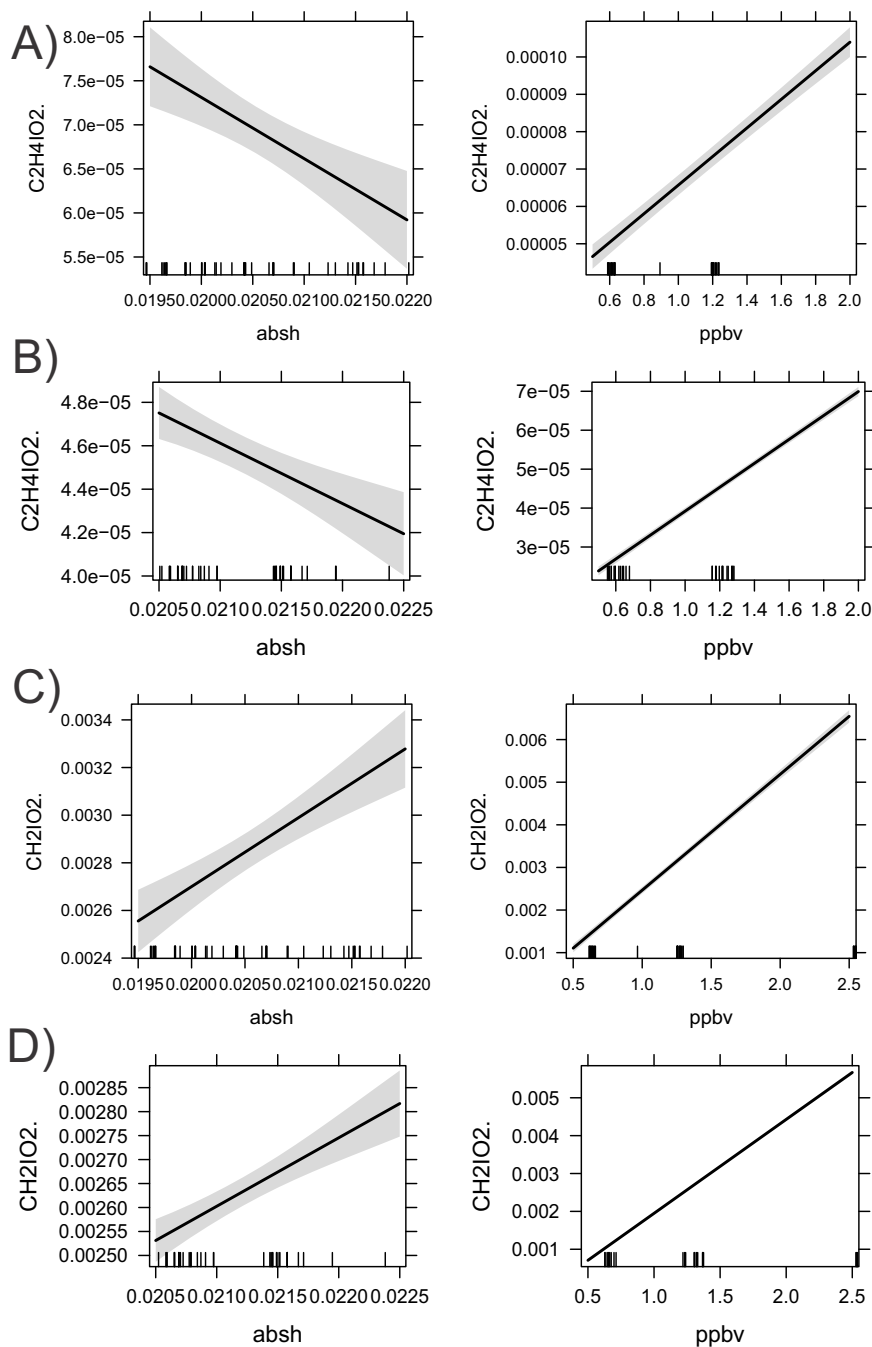


Figure S2: Effect plots showing the relationship between the measured signal and either the mixing ratio or the humidity for each calibration experiment. The tick marks along the x axis indicate the calibration points. The shading shows the 95% confidence interval. A) AA, calibration experiment 1; B) AA, calibration experiment 2; C) FA, calibration experiment 1; D) FA, calibration experiment 2.

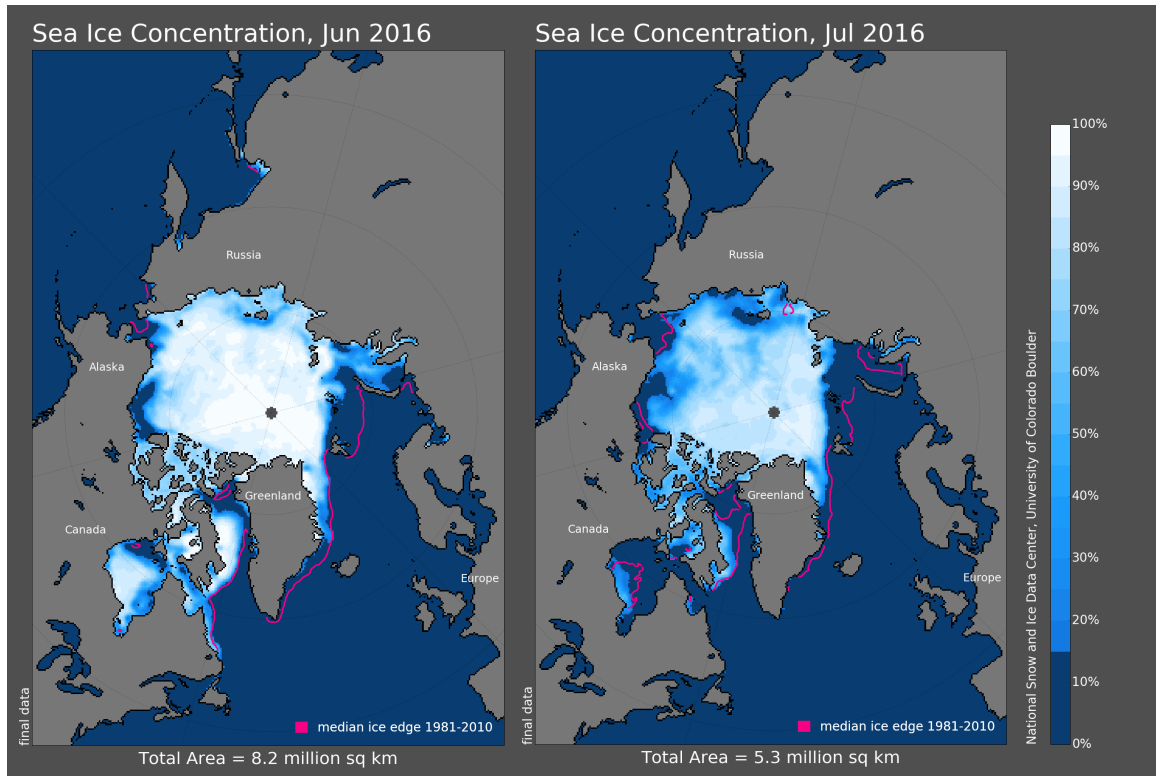


Figure S3: Average sea ice concentration in June and July 2016 showing that Alert was ice-locked. From <https://nsidc.org/data/seaice/index/archives.html>

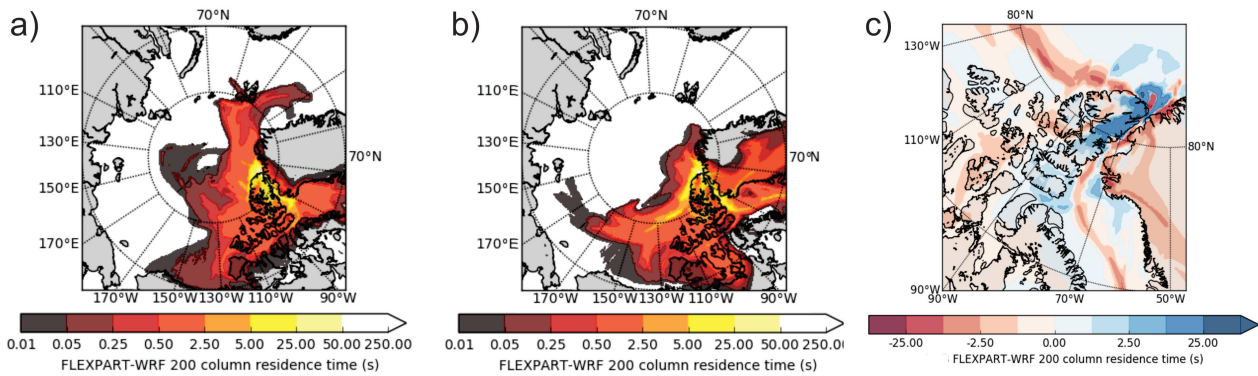


Figure S4: Average potential emission sensitivity during a) low wind speed regime, b) high wind speed regime, and c) the difference between the two.

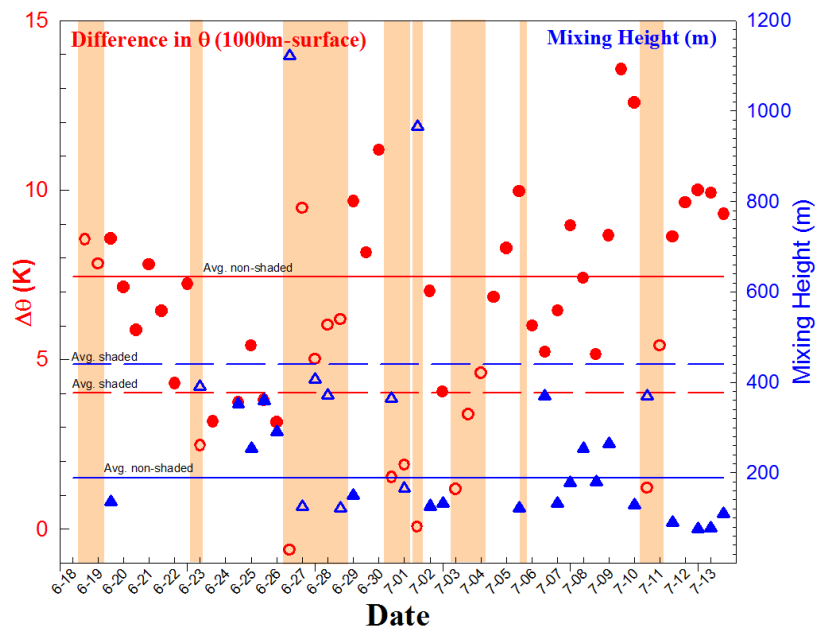


Figure S5: Mixing height and stability information. The difference in potential temperature between 1 km and the surface (a measure of stability) is plotted in red. The mixing height is plotted in blue. Averages for the shaded periods (the high wind speed regime) are shown in solid lines; low wind speed regime averages are shown in dotted lines.



Figure S6: Foam on Ellesmere Island water bodies. Top: A small, shallow meltwater pond on the tundra with foam on the surface, indicating the presence of surfactants within the water. Bottom: Foam at the edge of Kirk Lake.



Figure S7: Image from the All Sky Camera on June 19, 2016 at 21:08:00 showing precipitation.