Sources of organic acids in the summer Arctic marine boundary layer

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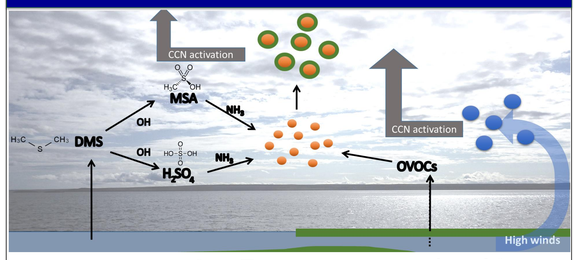
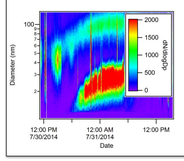
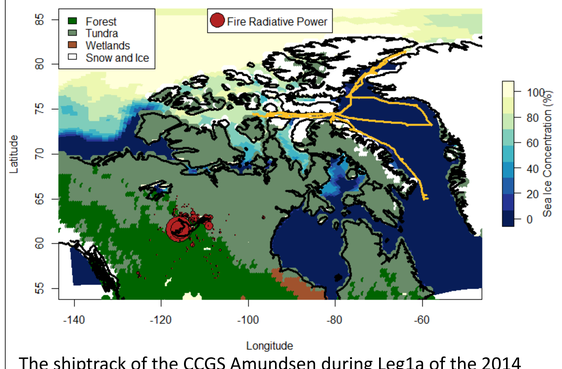
1. Motivation & Objectives





1. **To measure organic acids.**
2. **To explore possible sources of those acids.**
3. To make a link to growth of small particles.

2. The Study Region



The shiptrack of the CCGS Amundsen during Leg1a of the 2014 cruise is shown in yellow.

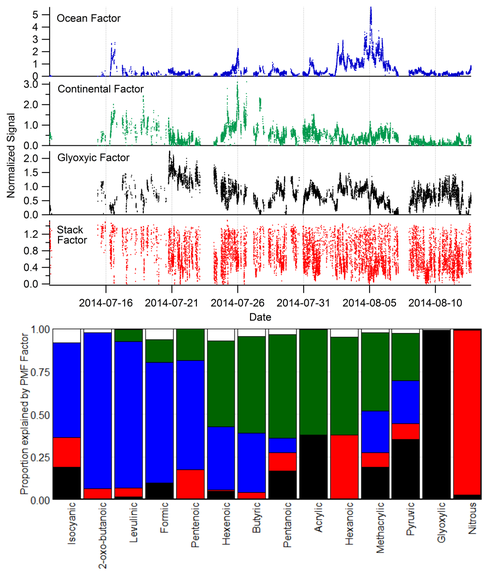
3. Methods

The acetate CIMS was located in a trailer behind the bridge. The sample was pulled through 4 feet of ¼" OD Teflon at a flow rate 10 SLPM. The line was externally heated to 80 C. Background values were obtained using a three stage scrubber, (Pt/Pd catalyst heated to 350 degrees), nylon wool soaked in saturated sodium bicarbonate and activated carbon to remove all species from ambient air. Backgrounds were collected during the last ten minutes of each two hour period. An isotopically labeled internal standard (C-13 propionic acid) served as a constant calibration, allowing for post-calibration in the lab. All of the lab calibrations were carried out with a combination of high pressure cylinders, permeation tubes and standards generated with the Ionicon Liquid Calibration Unit. The data have been screened to remove smokestack influence using a threshold value for HONO (normalized to the reagent ion) of 0.0015.

4. Positive Matrix Factorization

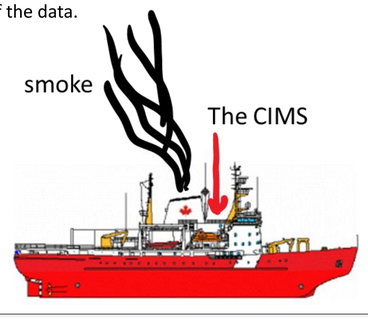
Positive matrix factorization (PMF) was performed on the one-minute time resolution volatile organic compounds (VOCs) measurements to determine their potential sources and formation pathways. The bilinear model was solved using the PMF2 algorithm in robust mode[1] and the final solution was selected using the PMF Evaluation Tool (PET) version 2.06[2]. To prepare a PMF input matrix, a threshold value of 1.5 x 10^{-3} of reagent ion normalized HONO signal was used to eliminate data from the period influenced by ship emissions. The HONO and VOCs measurements were then normalized to their maximal values. In this study, a four-factor solution was selected as the optimum solution based on examination of the PMF quality of fit parameter ($Q/Q_{expected}$) as a function of the number of PMF factors up to ten factors. Increasing the number of factors from four to seven factors only served to further split the factor dominated by saturated monocarboxylic acids, and thus more than five factors were not considered.

PMF Results

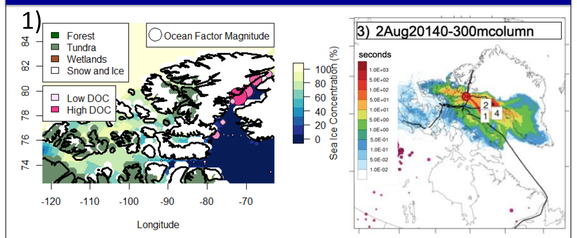


5. Stack Factor

This is a non-ideal sampling location. Fortunately, we were able to satisfactorily screen the data to the extent that PMF could extract a smokestack factor, but we had to remove > 60% of the data.



6. Ocean Factor



Compound 2)	C_g (ppb)	Henry's Law Constant, K_H	Aqueous concentration required (mg/L)
Formic Acid (HCOOH)	1	$5.4x10^3$	600
Isocyanic Acid (HNCO)	0.2	26	0.48
Levulinic Acid	0.01	~10^5	11.5
Butyric Acid	0.05	20	0.27
DOC	-	-	1.1

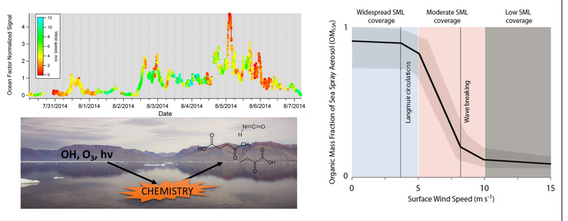
1. We find a good correlation with oceanic dissolved organic carbon
2. Partitioning can't explain the observed concentrations
3. The airmass was locally influenced

$$F = -K_W\left(\frac{C_g}{K_H} - C_l\right) = \frac{hC_g}{t}$$

$$C_l = \frac{hC_g}{K_W t} - \frac{C_g}{K_H}$$

where F is the flux, K_W is the calculated partitioning coefficient[3] under the conditions in question, K_H is the Henry's Law constant of the compound in question, C_g is the gas phase concentration (measured) , C_l is the aqueous concentration, h is the boundary layer height (assumed 100 m), and t is the ventilation time (assumed 1 day).

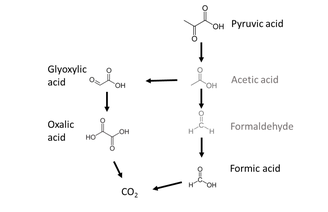
Sea Surface Microlayer Source

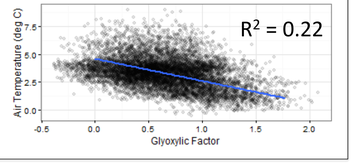


The highest levels of the ocean factor occur at wind speeds < 5 m/s, consistent with a well-developed sea surface microlayer[4]. Laboratory experiments have shown that small carboxylic acids can be generated in the gas phase *via* a surface or photo-enhanced reaction at an air-water interface covered by an organic film[5-7].

7. Glyoxylic Factor

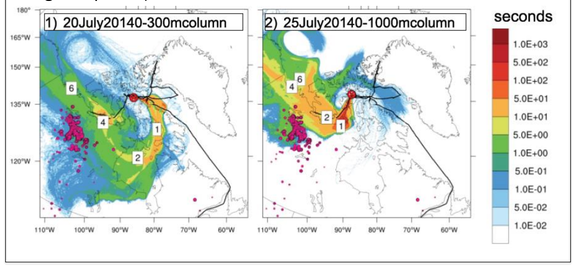
The reaction scheme on the right has been shown to occur in the aqueous phase under cloud-like conditions. We suggest that the glyoxylic acid factor is indicative of cloud processing[8]. It is also negatively correlated to temperature.





8. Continental Factor

The compounds associated with the continental factor have all been observed previously in biomass burning plumes[9]. The potential emission sensitivity plots below show that at times when the continental factor was high, the airmass arriving at the ship originated in the vicinity of wildfires (shown in the magenta points).



9. Conclusions & Future Work

1. Oceanic dissolved organic carbon contributes to measured organic acids in the summer Arctic marine boundary layer, possibly *via* reactions occurring at or in the sea surface microlayer.
2. PMF separates a factor that may be linked to cloud processing.
3. OVOCs from biomass burning and/or continental vegetation are present in the summer Arctic marine boundary layer.

Future Work: Perform PMF on more m/z time series to try to find the link to growth.

10. References

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