FRACTIONATION OF DISSOLVED SOLUTES AND CHROMOPHORIC DISSOLVED ORGANIC MATTER DURING EXPERIMENTAL SEA ICE FORMATION

A Senior Scholars Thesis

by

STEPHANIE DENISE SMITH

Submitted to Honors and Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

May 2012

Major: Marine Biology

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Approved by:

Research Advisor: Rainer Amon
Associate Director, Honors and Undergraduate Research: Duncan MacKenzie

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ABSTRACT

Fractionation of Dissolved Solutes and Chromophoric Dissolved Organic Matter During Experimental Sea Ice Formation. (May 2012)

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In the past decade there has been an overall decrease in Arctic Ocean sea ice cover. Changes to the ice cover have important consequences for organic carbon cycling, especially over the continental shelves. When sea ice is formed, dissolved organic carbon (DOC) and other tracers are fractionated in relation to the initial water. Two separate "freeze-out" experiments were conducted to observe the effects of fractionation during ice formation. In experiment 1, marine and freshwater end members were mixed together in different ratios to create four different salinities. In experiment 2, a brackish water sample was collected. The initial unfrozen water, ice melt, and post-freeze brine water were tested for dissolved organic carbon, total nitrogen (TN), dissolved inorganic carbon (DIC), fluorescence and absorption (optics), water isotopes ($\delta^{18}O$ and δD), and lignin phenols. Results showed a clear fractionation effect for all parameters, where the ice samples contained much less of the dissolved species than the enriched brine samples. This information is important to consider when using these parameters to determine the fate of carbon and the freshwater budget to the Arctic Ocean.

ACKNOWLEDGMENTS

I would like to thank Dr. Rainer Amon for mentoring me for the duration of this research project, as well as providing financial support. Additional thanks to Dr. Patrick Louchouarn, Sally Walker, and Matthew Norwood for training and assistance with lab techniques. Financial support for this research was provided by the National Science Foundation Research Experiences for Undergraduates Program in 2010. Additional support was provided by the Texas A&M Research Scholars program, the Texas Institute of Oceanography Undergraduate Fellowship and the Welch Foundation under Grant BD0046.

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CHAPTER I

INTRODUCTION

The Arctic Ocean is a relatively landlocked ocean with a deep central basin that is surrounded by continental shelves and shallow seas. The Arctic Ocean receives 10% of global freshwater discharge, and terrigenous dissolved organic carbon (DOC) (Opsahl et al., 1999; Cooper et al., 2008). The scale of the freshwater contribution produces strong vertical stratification in the Arctic marine system, separating warmer deeper Atlantic water from the surface where seasonal sea ice is sustained, as a result (Aagaard and Carmack, 1989).

The surface layer of the Arctic Ocean is dominated by sea ice and lower salinity surface water, at relatively cold temperatures of $-2^{o}C$. Below the surface layer, salinity and density rapidly increases, creating a layer called the halocline, which can be found in the upper 300m (Amon, personal communication). The halocline is a layer that isolates the cold and relatively fresh polar surface waters from the warm and salty Atlantic layer, with an average temperature of $1^{o}C$ (Aagaard et al., 1981) (Figure 1).

This thesis follows the style of Marine Chemistry.

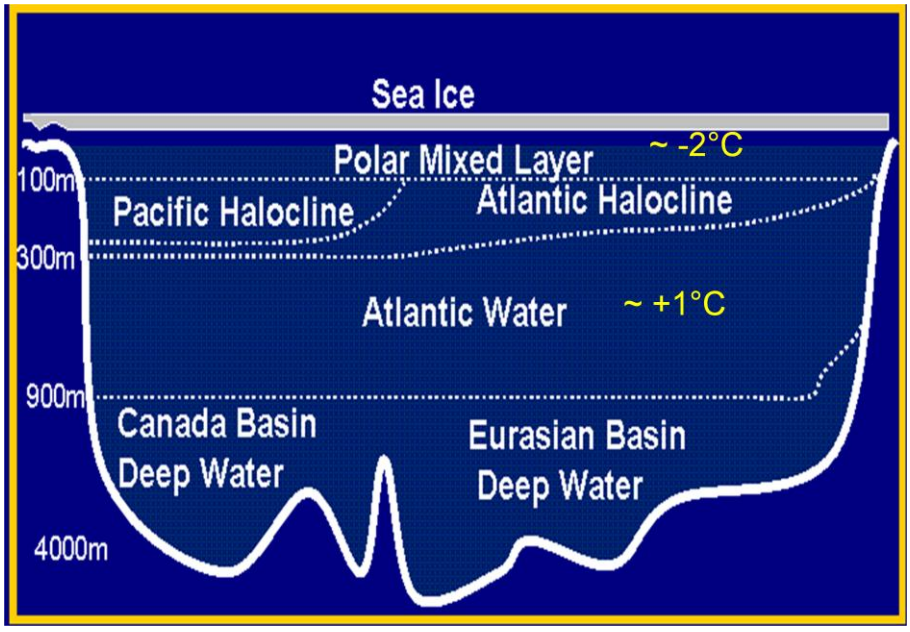

Figure 1. Stratification of the Arctic Ocean. (modified from Jakobsson, A., et al. 2004)

The halocline plays a critical role in the heat budget of the Arctic, but the diverse origins and maintenance of halocline layers are not fully understood, particularly in the Canada basin (Rudels et al., 1996, 2004; Steele and Boyd, 1998; Woodgate et al., 2005). Freshwater flowing from the Arctic to the North Atlantic influences the patterns and intensity of deep water formation, and the global thermohaline circulation. Because freshwater runoff plays an important role in stratification, there is a large interest in the fate and transport of freshwater runoff. Also, climate change in the Arctic could potentially affect the halocline's structure, as well as the global thermohaline circulation (Steele and Boyd, 1998; Martinson and Steele, 1999). Observed environmental changes include: an increase in surface air temperatures, a rapid decline in sea ice cover, as well as a shift in the Arctic freshwater cycle (Schlosser et al., 2002; Richter-Menge et al., 2006; Yamamoto-Kawai et al., 2005, 2008), resulting in a change in river discharge.

There are four individual freshwater sources to the Arctic Ocean including river runoff, sea ice melt, precipitation and low-salinity Pacific inflow. Riverine freshwater can be characterized by a strong concentration of chromophoric dissolved organic matter (CDOM), which can be used as a tracer for water mass modification, and identification of freshwater components (Walker et al. 2009). Fluorescence spectroscopy is used to trace sources of CDOM and if conservative they can be used as a potential tracer of water masses. CDOM is mainly located in the upper 300m and can come from terrigenous sources or from marine sources. Lignin phenols are unique to vascular plants, and are used as a tracer for terrestrial organic matter. (Opsahl and Benner, 1997).

Fluorescence spectroscopy is combined with parallel factor analyses (PARAFAC), a multi-linear regression analysis that's used to distinguish between marine and terrigenous CDOM (Stedmon et al., 2003; Kowalczuk et al., 2005; Stedmon & Markager 2005a,b; Walker et al., 2009). During AOS 2005, an *in situ* fluorometer was used to trace CDOM across the Arctic Ocean. The *in situ* map in Figure 2 shows a strong concentration of fluorescence in the Eurasian basin, which was closely related to the lignin phenol concentrations indicating the predominantly terrestrial origin of CDOM (Amon, personal communication). The Canadian basin shows a low fluorescence signal and a weak relationship between fluorescence and lignin phenols, which would indicate very little river inflow into the Canada Basin surface waters. In contrast, Jones et al., suggest that there was significant river runoff in the upper 50m of the Canadian Basin, based on alkalinity signatures during AOS 2005 (Figure 3). This hypothesis does not

agree with the *in situ* fluorescence in Figure 2. Sea ice formation and DOM rejection on shelves is the most likely process explaining the differing estimates of the riverine contribution to freshwater in the Canada basin surface waters (Amon, personal communication). The goal of this study is to investigate if DOM and other tracers are fractionated during sea ice formation to justify the differences between these two studies which attempt to describe the freshwater distribution within Canada Basin (CB) surface waters.

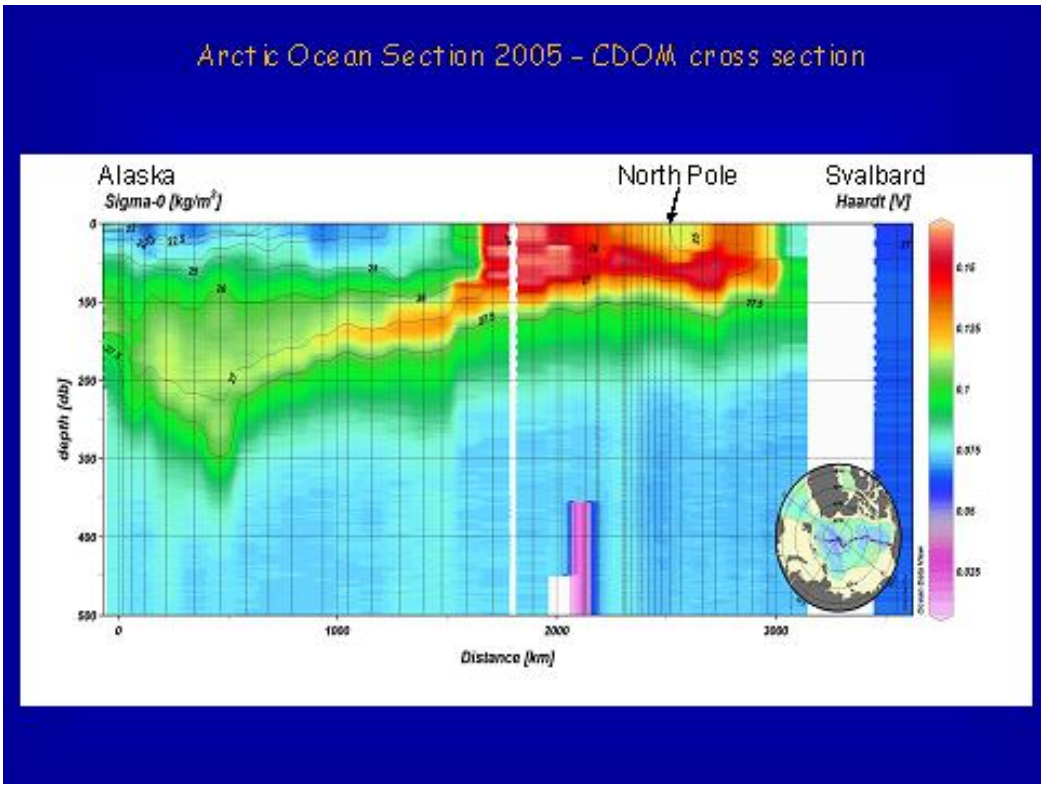

Figure 2. *In situ* fluorescence data collected across the Arctic Ocean during AOS 2005.

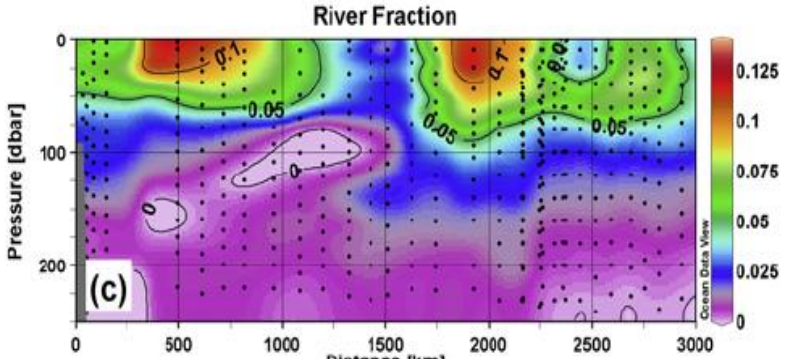

Figure 3. River fraction of fresh water from AOS 2005 based on alkalinity (Jones et al., 2008)

When sea ice is formed, salt and other dissolved matter, like DOC, is rejected from the ice matrix. The density of this post-freezing shelf water is affected by the salinity of the water prior to freezing. In other words, the higher the initial salinity the denser the post winter shelf water (Amon 2004). The density of this water determines how deep it can penetrate the Arctic basin. Results from previous "freeze-out" experiments indicate that the densest brine water had the lowest concentrations of DOC, which demonstrates that the densest shelf water has the greatest potential to penetrate the deep basins of the Arctic Ocean (Amon 2004). While some information is known about the fraction of DOC during ice formation, little is known about the effects on other parameters such as DIC, water isotopes and lignin phenols. Another aspect to consider for this study is the fractionation effect on DIC during sea ice formation. Carbon-dioxide emissions are pushing the waters of the Arctic Ocean towards more acidic conditions. Research carried out in the archipelago of Svalbard has shown in many regions around the north pole seawater is likely to reach corrosive levels for calcium carbonate within 10 years (Lombard et al., 2010). Sea ice formation may affect the concentrations of DIC in the

Arctic, and should be taken into account when determining the rate of ocean acidification.

In this study, two separate freeze-out experiments were conducted to investigate the before and after effects. Measurements were taken from the initial (pre-freeze) mixtures, the (post-freeze) ice melt, and (post-freeze) brine water. A number of analyses were conducted, including the measurements of: dissolved organic carbon (DOC), total nitrogen (TN), dissolved inorganic carbon (DIC), fluorescence and absorption (optics), water isotopes ($\delta 18O$, δD), and lignin phenols.

CHAPTER II

METHODS

Sample collection and mixtures

Two separate experiments were conducted during this study. In experiment 1, ocean water and river water were mixed together to create four solutions of varying salinities. Deep ocean water samples were collected from the deep Gulf of Mexico. River water samples were collected from the Trinity River Island Recreation Center located at 29° 49'N, -94° 44'W. The river water was filtered using a 25 mm sieve. Experiment 1 samples included salinities of: 8, 15, 25, and 32ppt. In experiment 2, a large volume sample was collected from the same location along the Trinity River. At this time the dam was closed which created brackish conditions at the sampling site. The samples collected had a salinity of 12 ppt. From this initial volume, three replicate experiments were conducted to insure reproducibility. The three replicate freezes were conducted over a six month time frame.

Freeze-out experimental design

Before the freeze was conducted, initial water samples were collected for analysis to obtain a before and after comparison. Then, 4 L of each salinity mixture was placed in a polypropylene beaker. The beaker was placed in a styrofoam insulator that was open at the top to facilitate the freezing of water from the surface, and not from the sides of the container (Fig. 4). Parafilm was stretched across the top of the beaker, and a teflon tube

is inserted into the center of the parafilm. The apparatus was then placed in a -20°C freezer. When ~30% of the water was frozen, (approximately 24-30 hours), the beaker was removed from the freezer. The teflon tubing was used to pull out the block of ice, which was then placed in a new pre-cleaned zip lock bag. The bag was sealed in order to prevent gas exchange during the melting process. The brine and ice meltwater were measured for salinity using a refractometer and put into containers specific to each analysis. All glassware and plastic collection devices were either acid washed using 0.2 N HCl, rinsed and/or pre-combusted at 450°C to ensure all containers were organic carbon free.

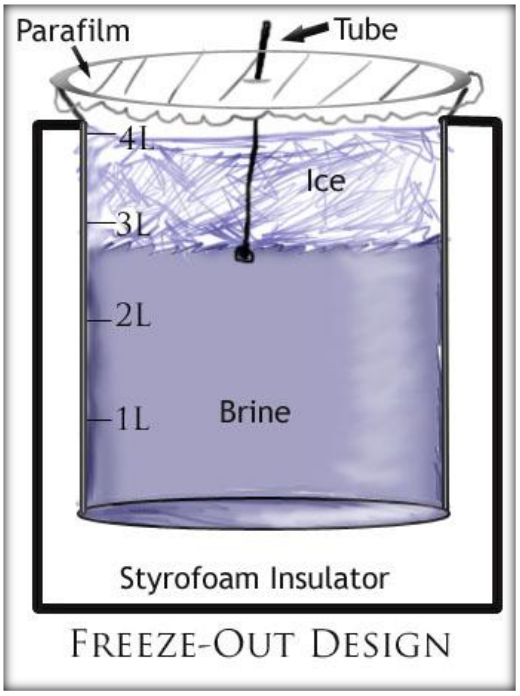

Figure 4. Illustration of the freeze-out apparatus used for the experiments.

Measurements and sample processing

Samples for the optical analyses were kept in 40 mL glass ampules and stored in the freezer. They were brought to room temperature and measured for optical properties. Fluorescence was measured using a Photon Technologies International Fluorometer (Quanta Master-4 SE). The sample was pipetted into a 1 cm quartz cuvette using a pre-combusted glass pipette. Excitation was measured from 240-450 nm, and emission was measured from 300-600 nm. The intensity of fluorescence was measured in Raman Units (R.U., nm-1), and corrected for inner filter effects and Rayleigh and Raman scatter effects. Absorption was measured using a Shimadzu UV-2401PC/2501PC spectrophotometer, from the wavelengths 200-800 nm, collected at 0.5 nm increments. The sample was pipetted into a 5 cm quartz cuvette. Mili-Q water is used as a reference blank for corrections. Absorption coefficients were calculated by the following equation $a(\lambda) = (2.303 * \text{abs/path length of cuvette})$.

The data collected from the fluorometer and photometer was processed using MATLAB. A series of Excitation Emission Matrices (EEMs) was created for each sample. Samples for DOC, TN, and DIC were kept in 25mL glass ampules. DOC and TN samples were stored in the freezer, and the DIC was stored in the refrigerator. The DIC water was filled to the top of the container, to ensure that there was no gas exchange. Concentrations were determined using a TOC Analyzer (Shimadzu TOC-V CSH/CSN). Potassium hydrogen phthalate (DOC), potassium nitrate (TN), and sodium carbonate (IC) standards were used to create daily calibration curves. Deep sea standards supplied

by D. Hansell (University of Miami) are used to assure quality control (Walker et al. 2009). Measured concentrations were normalized to the sample volume in order to calculate a mass balance (not shown). Each yield was near 100% (+/- 5%). Therefore, there was no substantial loss or contamination of the dissolved solutes measured.

Prior to analysis, water isotope samples (exp. 2) were pipetted into 2 mL glass vials, filled to the top to prevent gas exchange, and refrigerated. Samples were analyzed for oxygen and hydrogen stable isotope ratios using a Picarro Cavity Ring Down Spectrometer (Water Isotope Analyzer L2120-i). Three laboratory isotope standards were used to create daily calibration curves throughout the analysis. From this curve, a linear best-fit equation (R^2=0.99) was used to calculate sample concentrations. The laboratory standards have previously been calibrated against international isotope standards for SMOWV (Vienna Standard Mean Ocean Water) and GISP (Greenland Ice Sheet Precipitation) acquired from IAEA.

In experiment 2, the remaining A and B initial and brine samples were acidified to a pH of 2.5 for lignin analyses. The remaining ice samples from the two freeze trials were acidified and mixed together to create one volume large enough for accurate detection of products. The acidified samples were extracted by solid phase extraction (SPE) using C18 cartridges (Varian) at 70mL/min. HPLC grade methanol was initially run through the C18 cartridge, followed by 100mL of acidified Mili-Q water (pH 2.5), sample, and

finally with 1 L of acidified Mili-Q. Following extraction, cartridges were frozen until they were ready to be analyzed.

After thawing the C18 cartridges, samples were eluded using 35mL of HPLC grade methanol at a speed of 70mL/min. The eluded sample was collected into pre-combusted glass vials. The methanol and excess water was evaporated using a LabConco solvent concentrator. The resultant dried paste was dissolved into 2mL of pre-sparged 2N NaOH and sonicated. The sample was then pipetted into pre-loaded steel reaction vessels. The vessels contained 330mg cupric oxide (CuO), 150mg ferrous ammonium sulfate (FAS) and a steel ball bearing. Lignin analyses were performed using the cupric oxidation (CuO) method previously developed (Goni and Hedges, 1992; Louchouarn et al., 2000; 2010).

After oxidation, the reaction products must be extracted. First, 50µl of surrogate standard, trans-cinnamic acid (3-phenyl-2-propenoic acid), was added to each sample to account for losses during each step following the oxidation. Then 1N NaOH was added to the vessel and centrifuged. The collected supernatants were acidified to pH 1 using 6mL of 12N HCl. The extraction was then carried out using 3mL high purity ethyl acetate. This process was repeated three times to maximize recovery of the reaction products. Following this step, the extract was dried with Na_2SO_4 and the solvent was evaporated using a LabConco solvent concentrator. Pyridine (400µl) is used to re-dissolve the extracts, followed by a further dilution with pyridine (50:300µl). A 75µl

aliquot was transferred to a 1.5 mL glass vial to which BSTFA+1% TCMS was added in order to silyate any exchangeable hydrogen present in the sample. The samples were derivatized by heating at 75°C for one hour in a 20-well block heater and then transferred to a 250µl glass auto sampler vial insert. Lignin oxidation products (LOP) and other biomarkers were quantified using a gas chromatography-mass spectrometry (GC/MS) with a Varian Ion Trap 3800/4000 to estimate the fractionation effect on lignin phenols during ice formation.

CHAPTER III

RESULTS

Salinity

In both experiments (Fig. 5, Fig. 6) salinity was lowest in ice samples and highest in brine samples.

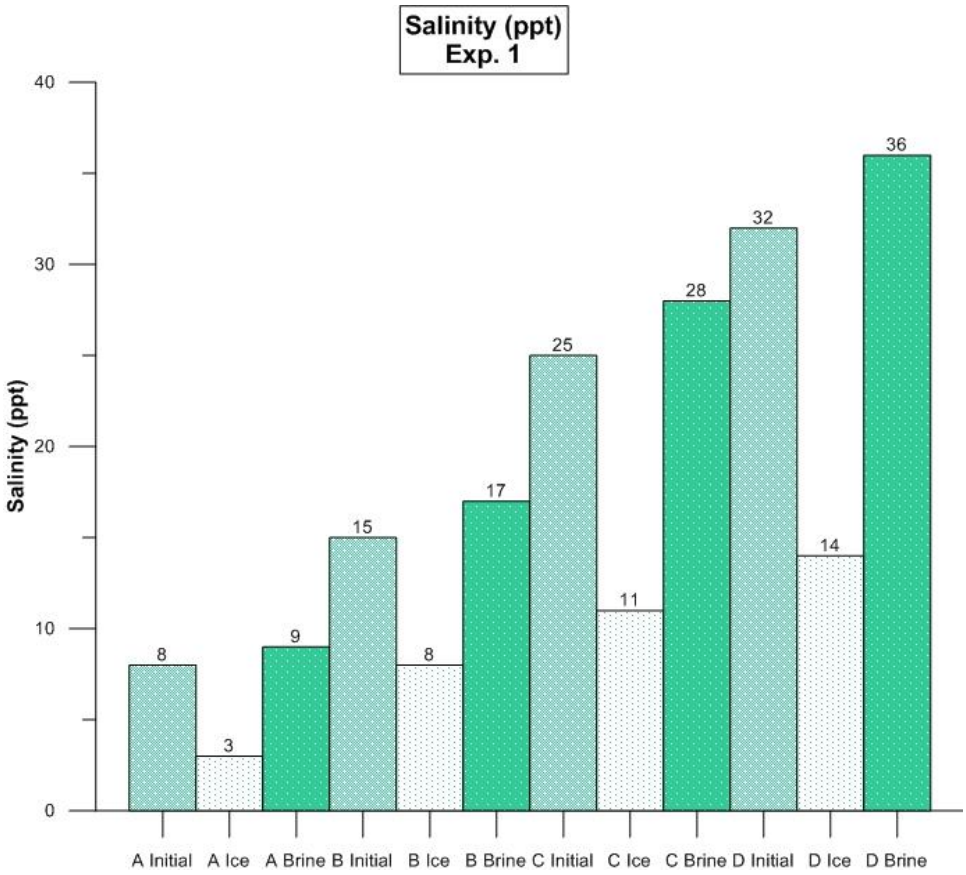

Figure 5. Salinity exp. 1 concentrations (ppt) for each sample type in experiment 1.

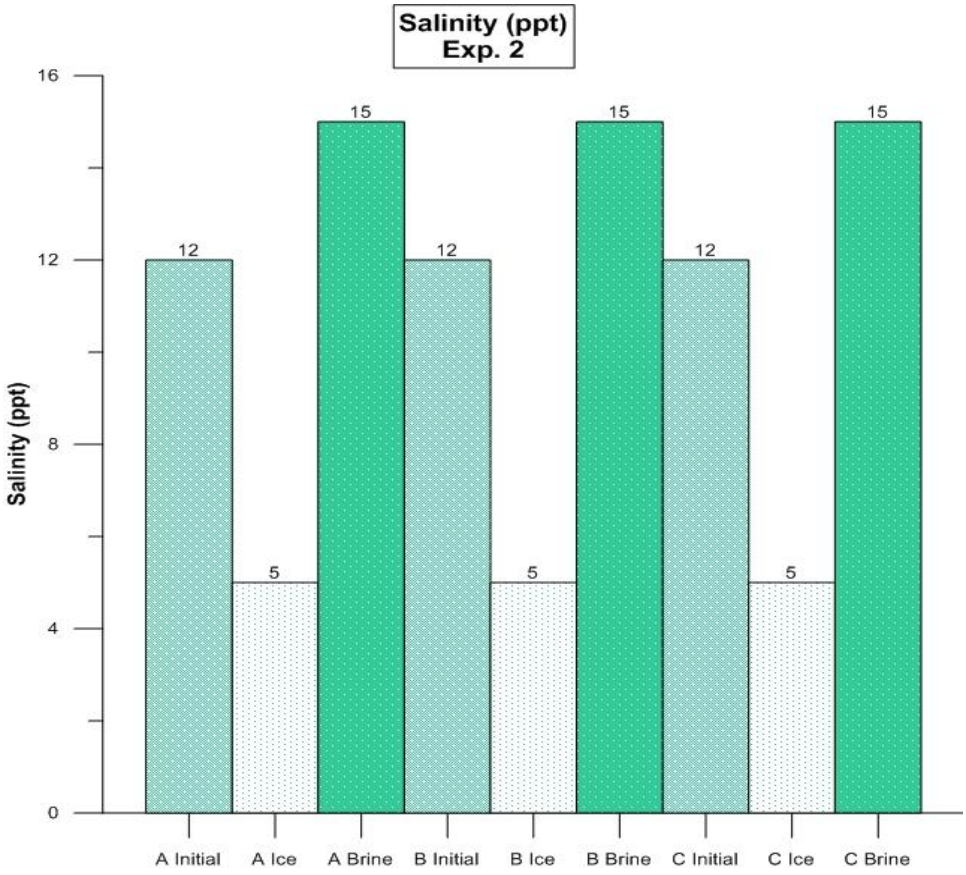

Figure 6. Salinity concentrations (ppt) for the three trials in experiment 2.

Dissolved organic carbon

In experiment 1 (Fig. 7), "A" had the highest concentration of DOC due to the dominance of riverine freshwater in the sample. Compared to the initial water, the ice was depleted in DOC, and the brine was enriched. This same pattern can be seen across the four salinity ranges (Fig. 7), and in experiment 2 (Fig.8).

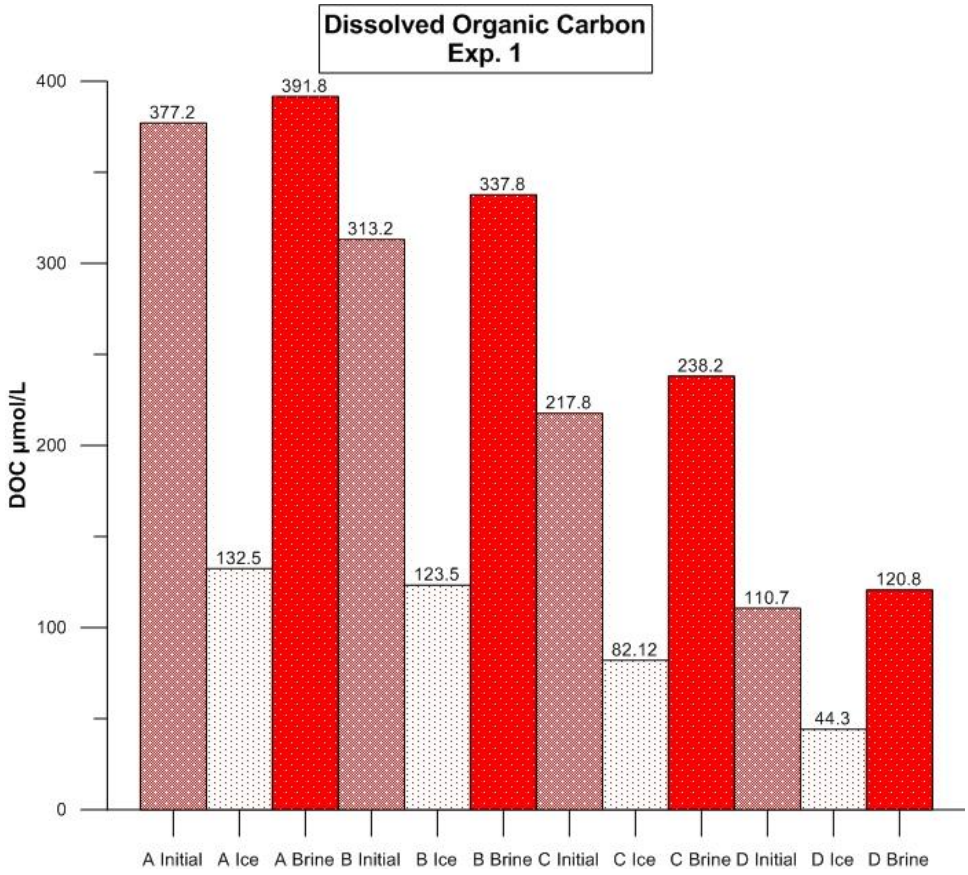

Figure 7. DOC concentrations (µM) for experiment 1.

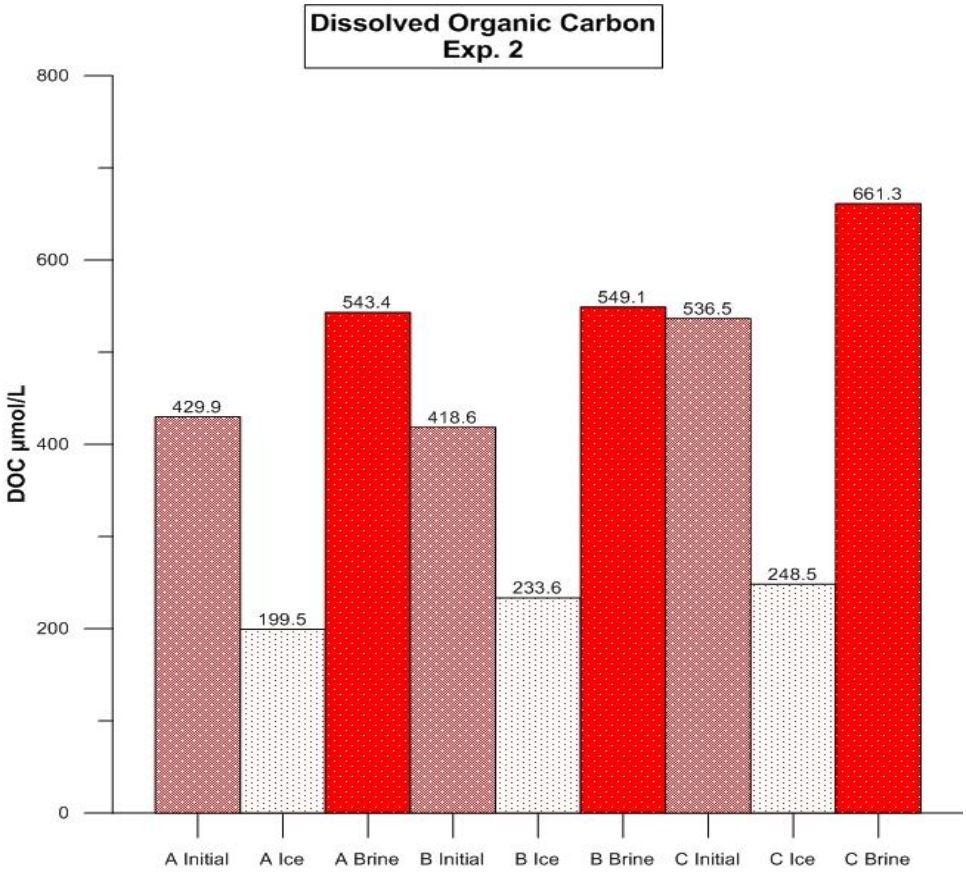

Figure 8. Figure 8. DOC concentrations (µM) for experiment 2.

Total nitrogen

Nitrogen is fractionated in the same way as DOC during ice formation. Figure 9 shows the concentrations for experiment 1. Figure 10 shows the concentrations for experiment 2.

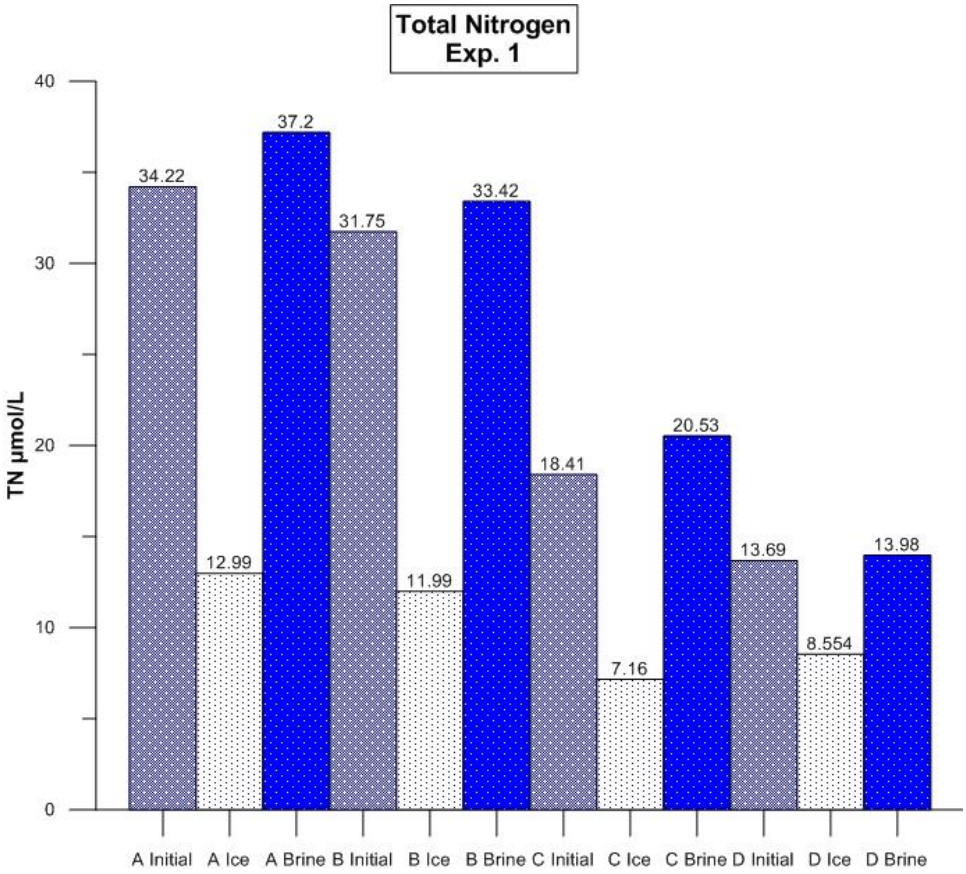

Figure 9. Figure 8. TN concentrations (µM) for experiment 1.

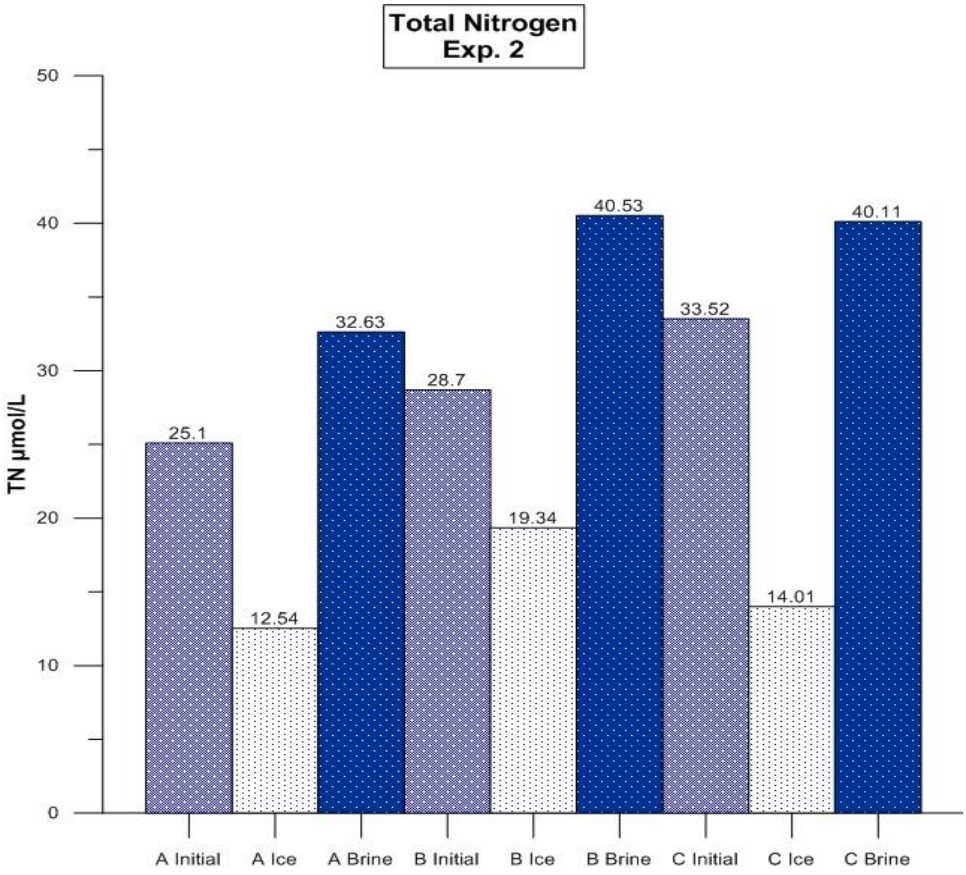

Figure 10. TN concentrations (µM) for experiment 2.

Dissolved inorganic carbon

DIC concentrations were only collected for experiment 1 (Fig. 11) due to time constraints. The same trend is present with the ice having a lower concentration, and the brine having a higher/enriched concentration.

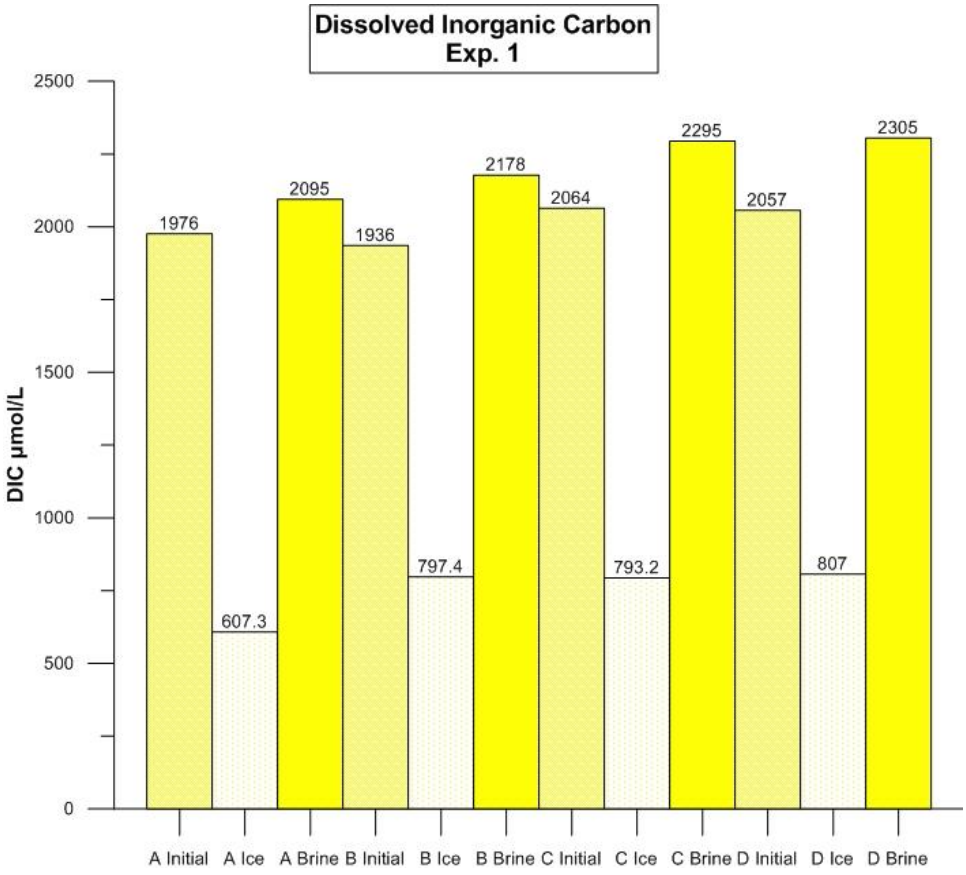

Figure 11. DIC concentrations (µM) for experiment 1.

Water isotopes

Isotopic ratios were measured for experiment 2 samples only. The trend shows that ice melt samples had the most positive values of $\delta^{18}O$ (Fig. 12) and δD (Fig.13). Among the $\delta^{18}O$ samples, there was some notable discrepancy. In particular, sample A Brine was not comparable with brine samples from B and C. Additionally, sample C Initial was not comparable to Initial samples B and C. Possible causes of these discrepancies may be due to the time between freeze-out experiments and the processing of samples. Due to the nature of oxygen isotopes, possible interactions with atmospheric O_2 may be the

cause of the incongruence. Despite the variation of $\delta^{18}O$ samples, there is consistency among ice samples, to which some conclusions can be drawn.

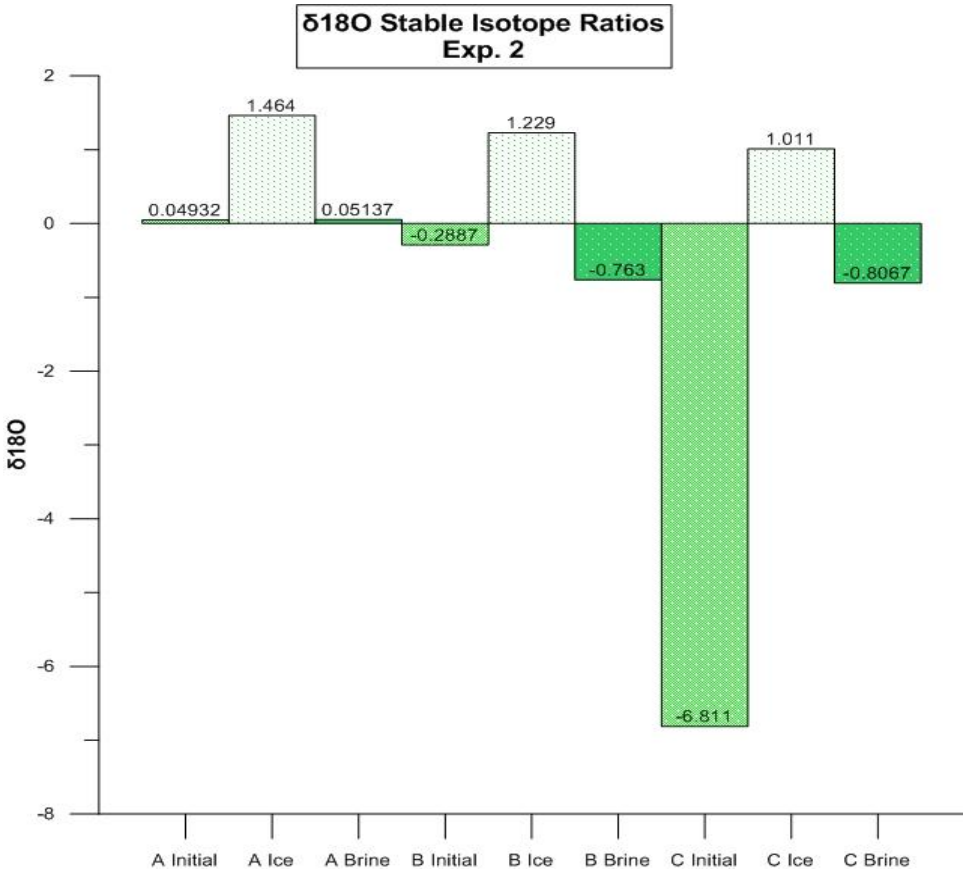

Figure 12. $\delta^{18}O$ isotopic ratios for experiment 2.

Among δD samples (Fig. 13), the measured isotopic ratios were consistent among all three trials. Ice melt samples exhibited a positive δD, and brine samples were more negative than the initial water. A positive δ value means that the sample contains more of the heavy isotope, and a negative δ value means that the sample contains less of the heavy isotope than the standard. The enrichment of heavy isotopes in ice samples may

be due to the loss of lighter isotopes (^{16}O and ^{1}H) to the atmosphere during ice formation.

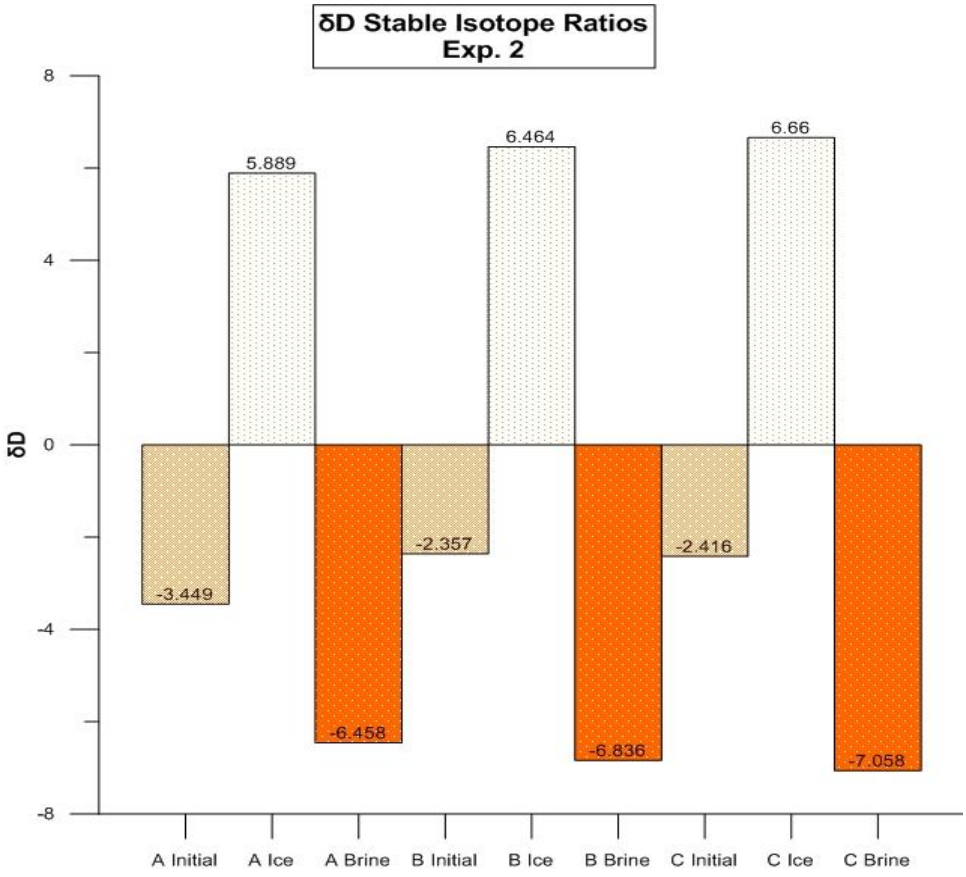

Figure 13. δD isotopic ratios for experiment 2.

Optics

The signal shown in Fig. 14 represents the total fluorescent DOM in Raman units (nm-1). This set of EEMs came from experiment 1A. The EEMs from all other samples are not shown, but they displayed the same relationship. Furthermore, Fig. 15 shows a positive correlation between fluorescence and absorbance for all samples in experiment 2. The discrete locations of fluorescence intensity peaks are used to identify different fluorophores present within the sample. The ice shows a decrease in the fluorescence intensity compared to the initial and brine. The EEMs show another view of how CDOM is being fractionated during ice formation.

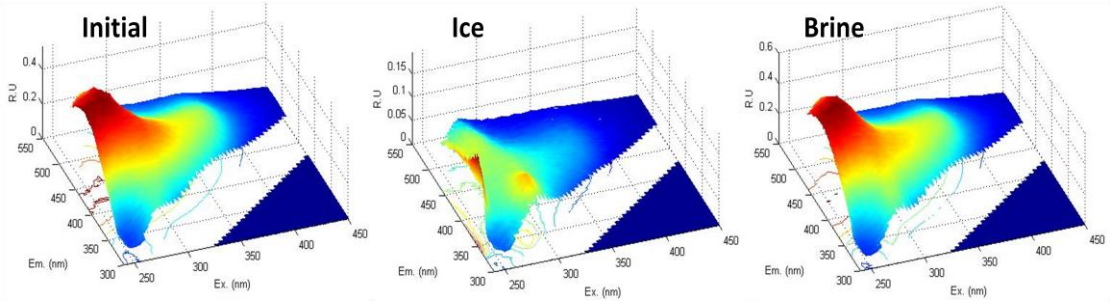

Figure 14. Example EEMs from the "A'' mixture in experiment 1.

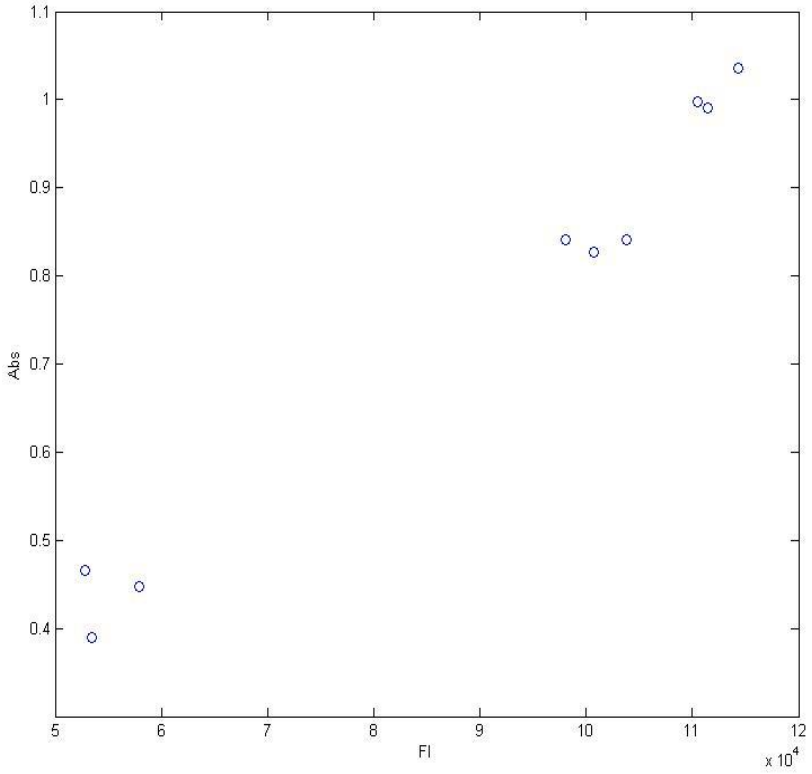

Figure 15. Relationship between fluorescence and absorbance for all samples in exp. 2.

Lignin phenols

Concentrations of total lignin phenols (Sigma6) were calculated by combining the values of all lignin oxidation products (LOP) (Fig.16). Percent yield of lignin (Lambda6) was also calculated by comparing the total lignin concentrations to DOC concentrations (Fig.16). Ice samples had the lowest concentrations of lignin (0.0023mg/L), and brine samples had the highest concentrations. Although the ice contained the lowest concentration of lignin, it had the highest lignin yield (8.5%). Even though a large portion of DOC is rejected from the ice matrix during freezing, a significant amount of the DOC remaining in the ice is made up of lignin phenols.

The relationship of lignin monomers has been used to identify major lignin sources (Hedges and Mann 1979), particularly the ratios of cinnamyl phenols to vanillyl phenols (C/V) and the ratios of syringyl phenols to vanillyl phenols (S/V). It is therefore of interest to see if these ratios are effected by ice formation. In our experiments the S/V and C/V ratios remained relatively stable throughout the samples. However, acid to aldehyde ratios (Vd/Vl and Sd/Sl) are slightly affected by ice formation. Ice samples had lower Ad/Al ratios, meaning that the acidic lignin monomers are more effectively rejected than the aldehyde monomers (Fig.17).

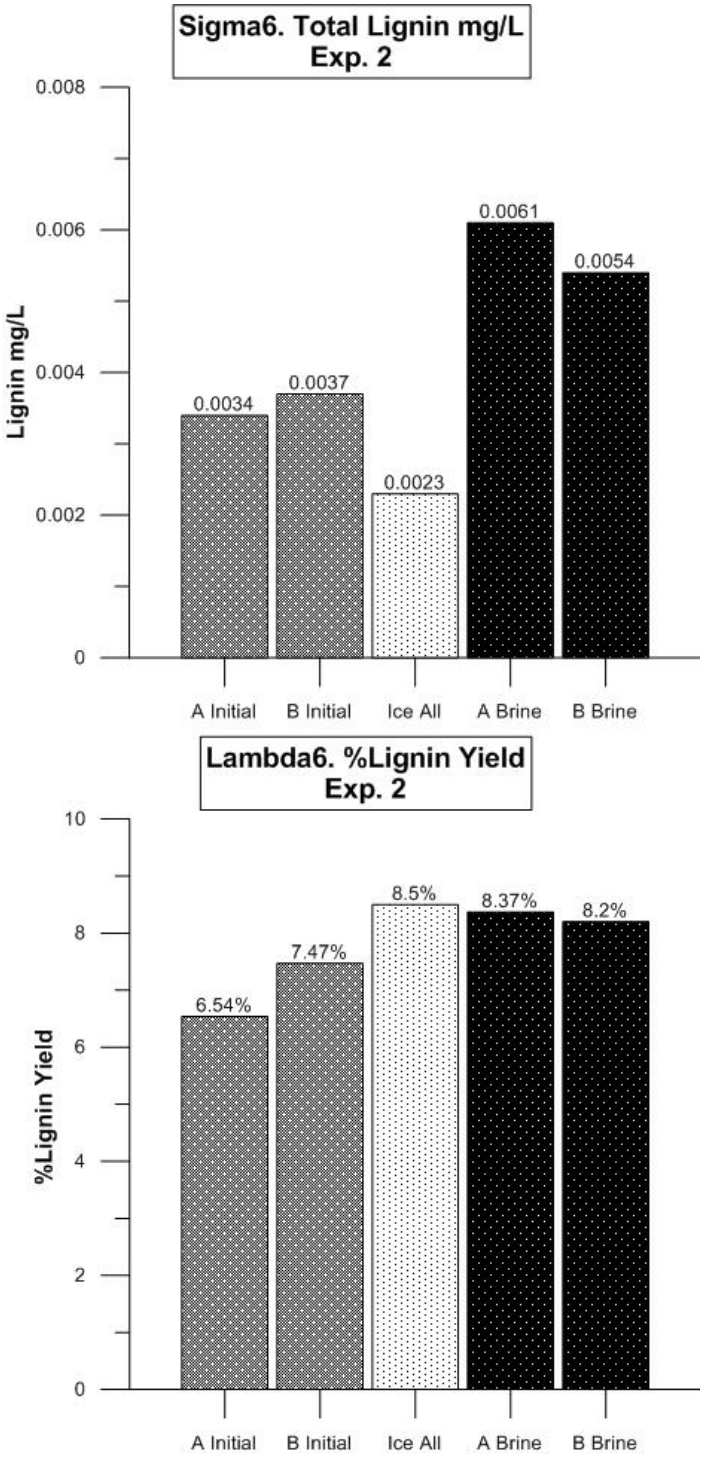

Figure 16. Concentration of total lignin (Sigma6) in mg/L. Percent yield of lignin (Lamda6) compared to DOC concentrations.

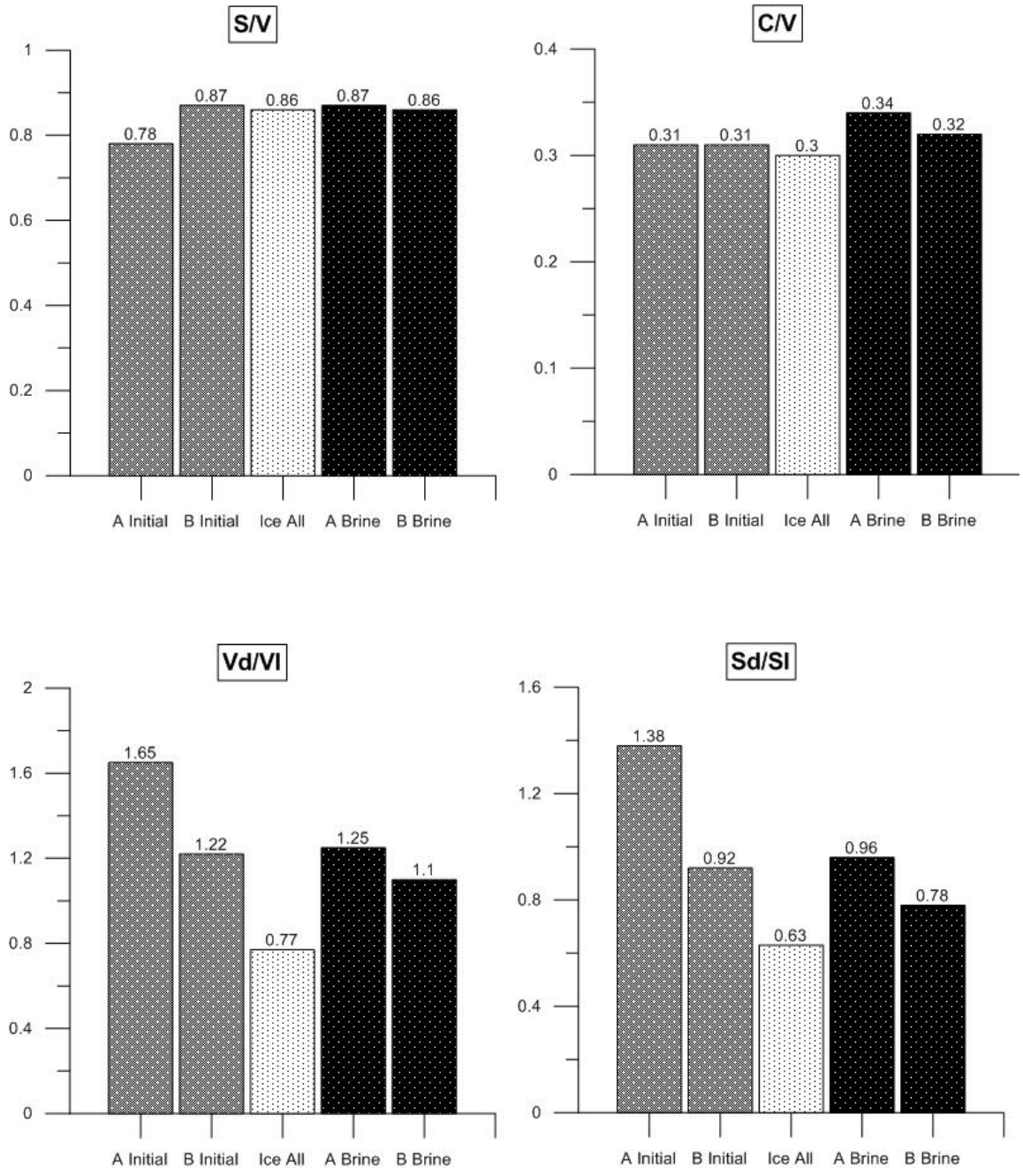

Figure 17. Ratios of different lignin oxidation products for experiment 2.

CHAPTER IV

SUMMARY AND CONCLUSIONS

All of the dissolved solutes investigated in this study were heavily fractionated during freezing. Ice formation has a profound effect on tracers which are used to study physical as well as biological processes such as water mass distribution and mixing, primary production and respiration, respectively. Results from this study should be taken into account when determining the patterns of these processes.

During the AOS2005 cruise, fluorescence and DIC data was collected across the Canadian Basin of the Arctic (Fig.18). Originally, it was thought that the relationship indicated that the fluorescence signal was actually tracing degradation of organic matter. However, after observing the effects of the freeze out experiments, it is possible that this relationship may simply indicate that these two parameters are being driven by the same process: fractionation during sea ice formation.

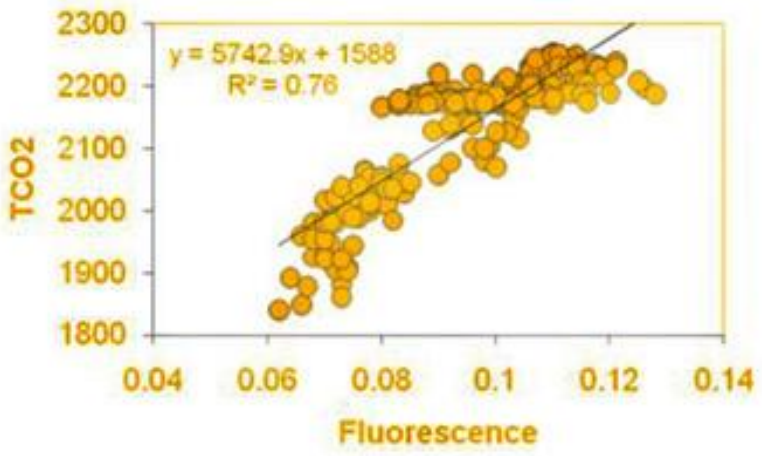

Figure 18. Relationship between total DIC and CDOM fluorescence in the Canadian Basin during the AOS2005 cruise.

Data collected during AOS2005 (Fig. 2) shows that the upper 50m of the Canadian Basin are stripped of CDOM, despite estimates of large river inflow from alkalinity data by Jones et al. The freeze experiments demonstrate how sea ice formation physically removes CDOM from the surface ocean and injects it into deeper layers. The CDOM signal (Fig. 2) is prominent in the deeper layers of the CB. It is possible that the low CDOM concentration in the surface water is due to an increase in sea ice meltwater, as shown by (Yamamoto-Kawai et al., 2008, 2009). Export of ice sheets into the Canadian basin may be diluting the CDOM signal.

The results from the freeze experiments suggest that the Arctic could potentially be drawing down CO_2 from the atmosphere, which could result in an increase of ocean acidification in the Arctic. Yamamato-Kawai et al. (2011) also suggested that extensive melting of sea ice combined with increased atmospheric and surface water temperatures alters the calcium carbonate saturation state. Under-saturation of calcium carbonate is

unfavorable for the growth of calcifying organisms. If this trend continues, it could have many implications for organisms in this ecosystem. Future studies should focus on predicting how the distribution of freshwater components in the Arctic will change in response to future climatic shifts.

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