

SEASONAL AMMONIUM BENTHIC FLUX AND PHOTO-AMMONIFICATION OF
DISSOLVED ORGANIC NITROGEN IN BAFFIN BAY - TEXAS

A Thesis

by

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This thesis meets the standards for scope and quality of
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ABSTRACT

Estuaries and coastal regions are hot spots of global primary production as they account for 30% of the net marine productivity, despite representing only 7% of the total marine surface area. Nutrient patchiness is the second most influential factor (after temperature) in site seasonal variability of net primary production. This guides a consensus that nitrogen (N) loading is a primary factor in eutrophication and hypoxia. Despite this recognized connection between excess N loading and ecosystem decline, the internal N cycling and transformations in coastal areas are still not well characterized. This study quantified the sediment porewater flux of ammonium (NH_4^+) and photo-ammonification from benthic dissolved organic nitrogen (DON) as well as investigated changes in porewater DOM chemical structures of Baffin Bay - Texas during different irradiation time periods using the state of art Orbitrap Fusion Tribrid Mass Spectrometer. Baffin Bay (BB) is a semi-arid inverse estuary ecosystem that has experienced prolonged and intense brown tide blooms (*Aureoumbra lagunensis* species) since the 1990s, and several occurrences of hypoxia conditions that caused seagrass die-off and several occasions of large fish kill over the past decades. Pore water samples were collected from six stations in the bay during six seasons (October 2020, February 2021, June 2021, October 2021, February 2022, and May 2022) for depth profile analysis. The bay showed a large spatial variability of NH_4^+ benthic flux, with BB1 having the lowest average NH_4^+ flux at $56 \pm 27 \mu\text{mol.m}^{-2}.\text{day}^{-1}$ and BB3 had the highest average flux at $347 \pm 211 \mu\text{mol.m}^{-2}.\text{day}^{-1}$. The seasonal NH_4^+ average benthic flux to the entire bay water column was $124 - 244 \mu\text{mol.m}^{-2}.\text{day}^{-1}$ and served as a significant source of inorganic nutrients to support the primary production.

In addition, the photo-ammonification rate of benthic DON (after it entered the water column) ranged from $0.038\text{-}0.361 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$ and served as an additional source of inorganic

nutrients to primary production. Chromophoric dissolved organic matter (CDOM) absorbed sunlight radiation then degraded to lower molecular weight CDOM and released ammonia, deaminated peptides, free amino acids, and organic acids. Peptides and deaminated peptides with chromophoric amino acids such as tryptophan, tyrosine, proline, phenylalanine, and histidine degraded with solar irradiation. It was suggested that rings and conjugated double bonds were responsible for absorbing sunlight radiation and degrading CDOM structures. This study shed light on internal N cycling and transformations in Baffin Bay and the need to consider these processes in any future attempt to remediate and lower the brown tides events in the bay.

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1. INTRODUCTION

Estuaries and coastal regions are hot spots of global primary production as they account for 30% of the net oceanic productivity (Holligan 1992) despite the fact they only represent 7% of total marine surface area (Gattuso et al., 1998). Typical estuaries are semi-enclosed bodies of water where salt water from oceans meets freshwater input from land or terrain and becomes diluted with its salinity range from low saline freshwater to hypersaline seawater. Primary productivity in estuaries and coastal regions is high as a result due to a significant input of inorganic nutrients from different sources (e.g., riverine, groundwater, benthic flux, sewage, and atmospheric deposition). Photoautotrophs such as phytoplankton have the ability to absorb sunlight in oxic condition to synthesize and convert inorganic substances such as ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), Carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), silica (SiO_2) to organic matters. Primary production rate (PPR) in estuaries and coastal area ecosystems could range seasonally and spatially. For example, in the Bristol Channel estuary, UK (a highly turbid estuary), the daily PPR ranged from 18 - 450 $\text{mgC.m}^{-2}.\text{day}^{-1}$ (Joint and Pomroy 1981). In Baffin Bay – TX, the daily PPR ranged from 1-132 $\text{mgC.m}^{-2}.\text{day}^{-1}$ (Blanchard and Montagna 1995). Caffrey et al., (2013) measured an annual PPR from 825 $\text{g C m}^{-2} \text{ year}^{-1}$ in Weeks Bay to 401 $\text{g.C m}^{-2}.\text{year}^{-1}$ for Apalachicola Bay and 377 $\text{g C.m}^{-2}.\text{year}^{-1}$ in Grand Bay in three different estuaries in northern Gulf of Mexico. They found a correlation between the nitrogen loading and annual PPR in these three bays.

Dissolved inorganic nitrogen (DIN) plays an important role in controlling the PPR and the food web in marine system. Nitrogen gas (N_2) from the atmosphere dissolves into seawater at the ocean surface and is taken up and fixed into its bioavailable form, ammonium (NH_4^+), by microorganisms and bacteria. Ammonium is the form of inorganic nitrogen that is most easily

consumed by microorganisms via a process called “assimilation”. When microbes (and other organisms) die, their detritus particulate organic nitrogen (PON) decomposes to dissolved organic nitrogen (DON) in the surrounding seawater. A host of micro-organisms consume PON and DON, converting some of the nitrogen back to ammonium via remineralization (*Figure 1.1*). However, not all DON can undergo complete remineralization and release NH_4^+ in anoxic conditions. Some DON leave behind a peptide skeleton and become refractory for microbes to digest (*Figure 1.1*). In presence of oxygen, ammonium is converted to nitrite (NO_2^-) and to nitrate (NO_3^-) in oxic conditions via “nitrification”. To complete the nitrogen cycle in the ocean, microbes convert nitrate and nitrite back to nitrogen gas through a process called “denitrification”. The reduced form of nitrogen, ammonium (NH_4^+), is easier for most microbes to assimilate than oxidized nitrogen compounds such as nitrate (Francis et al., 2007).

1.1. Ammonium sources to estuaries

Ammonium (NH_4^+) sources contributing to estuaries vary from rivers, groundwater, fixed atmospheric nitrogen, and sediment benthic fluxes (*Figure 1.2*). Nitrogen can enter estuaries as terrestrial runoff from forests, agricultural lands, or urban areas. Nitrogen can also come from atmospheric deposition such as emissions of nitrogen oxides from automobiles and industrial sources, and ammonia emissions from nitrogen fixation. Another source of nitrogen includes sewage treatment plants and industrial facilities (Castro et al., 2003). In addition, sediment benthic flux also contributes nitrogen to estuaries as an internal circulation source (Nixon, 1981; Rizzo, 1990). Release of nutrients from resuspended porewater and sediment particles has been implicated in the stimulation of heterotrophic microplankton in estuarine waters (Wainright, 1987).

Ammonium concentrations in sediment porewaters were reported to be high in anoxic conditions from 1-5 mmol.L^{-1} in the Santa Barbara Basin (Abdulla et al., 2018), and 0.35-3.85

mmol.L⁻¹ in Laguna Madre estuary (Morin et al., 1999). Therefore, its contribution to the water column via benthic flux would need to be considered as a major source.

1.2. Photo-ammonification of benthic dissolved organic nitrogen (DON)

Photo-ammonification is a conversion of dissolved organic nitrogen (DON) to dissolved inorganic nitrogen (DIN) and release of ammonia. DON such as humic substances was believed to make a negligible contribution to eutrophication (Kieber et al., 1989) until it was discovered to be photochemically reactive (Bushaw et al., 1996). Photo-ammonification of DON had been recognized in many studies to be a significant source of bioavailable nitrogen (Morell and Corredor, 2001; Xie et al., 2012), and its essential contribution to biomass production and eutrophication (Rain-Franco et al., 2014; Vahatalo and Jarvinen, 2007). Photo-ammonification was shown to contribute up to 50–178% of the NH₄⁺ needed for phytoplankton in primary production (Rain-Franco et al., 2014). Many studies have been conducted to investigate the relationship between photo-ammonification rate and other ecosystem factors like pH (Zhang and Anastasio, 2003), salinity (Funkey et al., 2015), or temperature (Xie et al., 2012). Mechanism simulation was hypothesized (Davies and Truscott 2001) but the information on reaction pathway was not clarified. There also have been some conflicting results in the photo-ammonification of DON in natural water. Some studies reported the photo-production of NH₄⁺ under natural light (Kitidis et al., 2006) or simulated natural light (Vahatalo and Zepp, 2005; Xie et al., 2012) and some reported no photochemical production of NH₄⁺ (Jorgensen et al., 1998; Mccallister et al., 2005; Wiegner and Seitzinger, 2001), or even photochemical loss of NH₄⁺ (Koopmans and Bronk, 2002; Vahatalo et al., 2003).

Despite all of these studies, no assessment (to the best of our knowledge) of photo-ammonification of benthic DON flux that diffused to the water column has been conducted. Little

is known of benthic DON flux and its transformation in marine waters. Thus, the efflux of DON and ammonia represents a major pathway for organic nitrogen to escape from being preserved in the long geological carbon cycle then stimulate further primary productions resulting in an extended hypoxia event. The benthic DON can be further remineralized to produce NH_4^+ and/or diffused to surface water photic zone where it can be exposed to sunlight and undergo photochemical degradation to produce NH_4^+ , low molecular weight acids and free amino acids, which can support primary production and microbial respirations that possibly support the primary production at the surface water.

1.3. Sampling site - Baffin Bay as a semi-closed aquatic system

Since the early 1990s, the Baffin Bay (BB) ecosystem has experienced prolonged and intense brown tide blooms (*Aureoumbra lagunensis* species) and several occurrences of hypoxia conditions that caused seagrass die-off and several occasions of large fish kill over the past decades (Wetz et al., 2017). Nutrient patchiness is the second most influential factor (after temperature) in site seasonal variability of net primary production (Caffrey, 2004). This guides a consensus that nitrogen (N) loading is a primary factor in eutrophication and hypoxia. Despite this recognized connection between excess N loading and ecosystem decline, the internal N cycling and transformations in coastal areas are still not well characterized. As the freshwater runoff is very low in the bay, this led to speculation that the agricultural runoff is responsible for the nutrient pulses that initiate and sustain the brown tide bloom. However, this speculation overlooks the role of benthic fluxes in delivering dissolved organic nitrogen (DON) and nutrients to the bay. The current estimated dissolved organic matter (DOC) benthic flux from coastal sediments is almost equivalent to the riverine DOC flux to open ocean. Relative to riverine DOM, benthic porewater has a much higher DON. A recent study showed that the depth profile of porewater NH_4^+ strongly

correlated with DON concentration ($R^2 = 0.96$) (Abdulla et al., 2014). Many studies showed NH_4^+ concentrations can buildup up to ~ 7 mM within the first 1-2 meters of the sediment profiles (Abdulla et al., 2014). The fate of DON in sediment porewaters after entering the water column remains mysterious and needs investigating. One of the possible transformations of sediment DON in the water column is photo-oxidation by sun light which leads us to our research, the photo-ammonification of DON in sediment porewaters.

In this research, we quantified the seasonal benthic sediment flux of ammonium (NH_4^+) and photo-ammonification from benthic dissolved organic nitrogen (DON) (*Figure 1.2*) as well as investigated changes in porewater DON chemical structures during different irradiation time periods using the state of art Orbitrap Fusion Tribrid Mass Spectrometer.

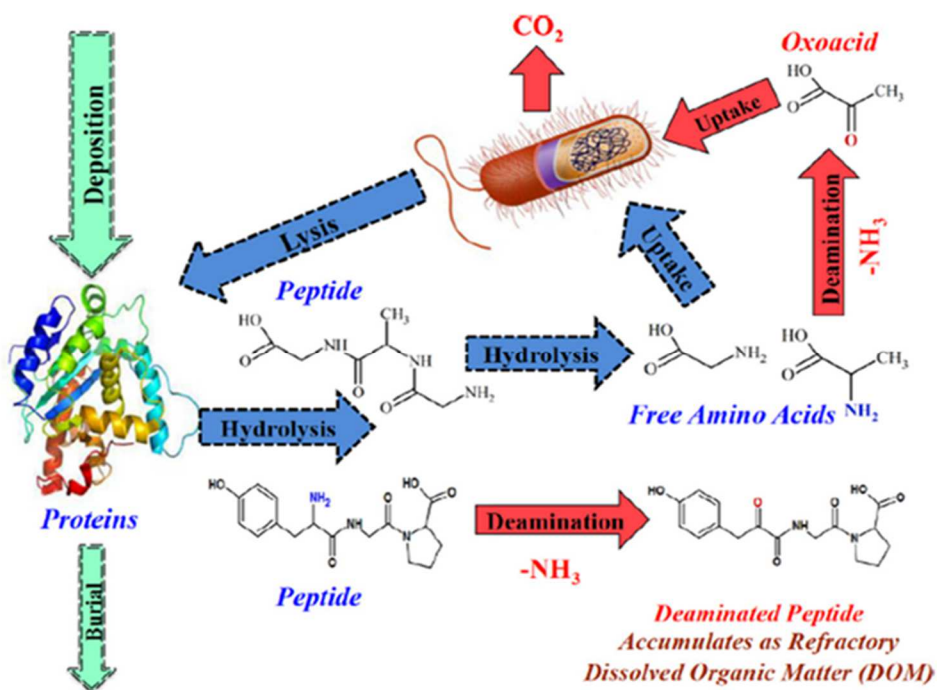


Figure 1.1. Schematic of hypothesized protein hydrolysis and cycling (Abdulla et al 2018).

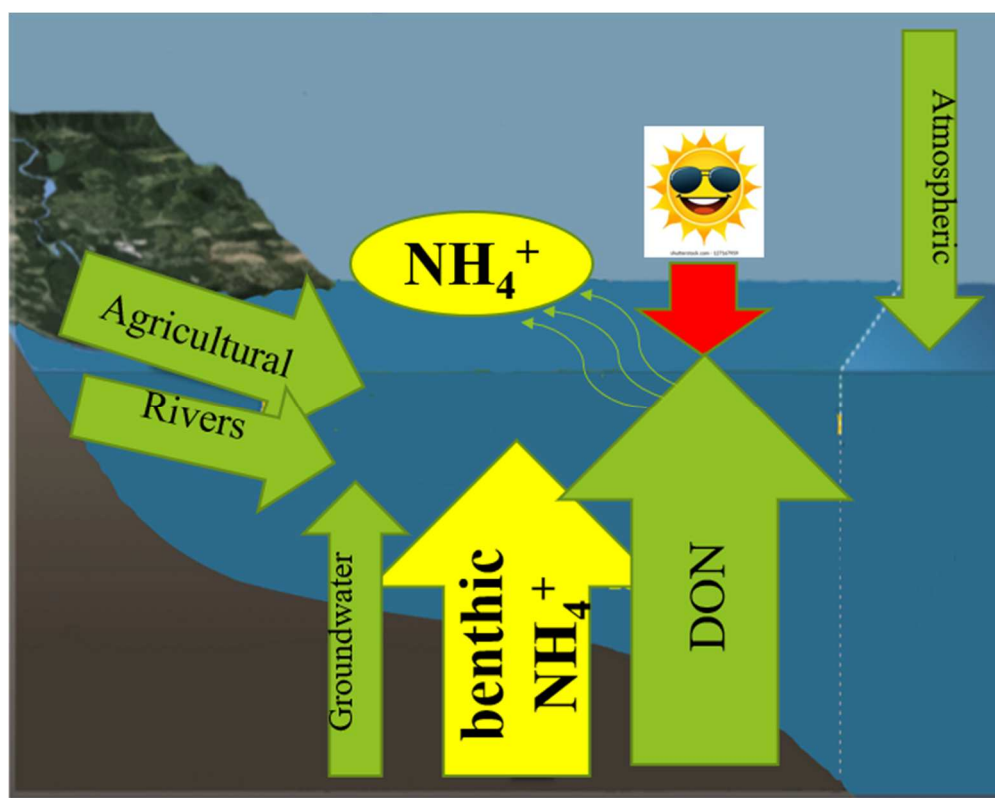


Figure 1.2. Nitrogen sources to the water column.

2. MATERIALS AND METHODS

2.1. Study Sites – Baffin Bay, Texas

Baffin Bay is a shallow (2-3m) subtropical estuary located in a semi-arid region. The bay has three branches: Alazan Bay on the north (BB5), Cayo del Grullo (BB1) and Laguna Salada (BB2) (see Figure2.1). The semi-arid climate along with extensive evaporation rates over precipitation, which is resulted from shallow water and warm climate, can lead to hypersaline conditions in Baffin Bay. Baffin Bay is separated from the Gulf of Mexico by Padre Island leading to limited water exchange with the Gulf of Mexico. The closest freshwater inputs allowing for water exchange between Baffin Bay and Gulf of Mexico are Packery Channel (~41 km north of Baffin Bay), Aransas Pass (~70 km north of Baffin Bay) and Port Mansfield (~80 km south of Baffin Bay). These long distances along with diurnal tidal ranges of only ~2-3 cm results in minimal overall tidal influence (≤ 10 cm on average) and a long mean residence time (> 1 year) in Baffin Bay (Wetz et al., 2017, 2019).

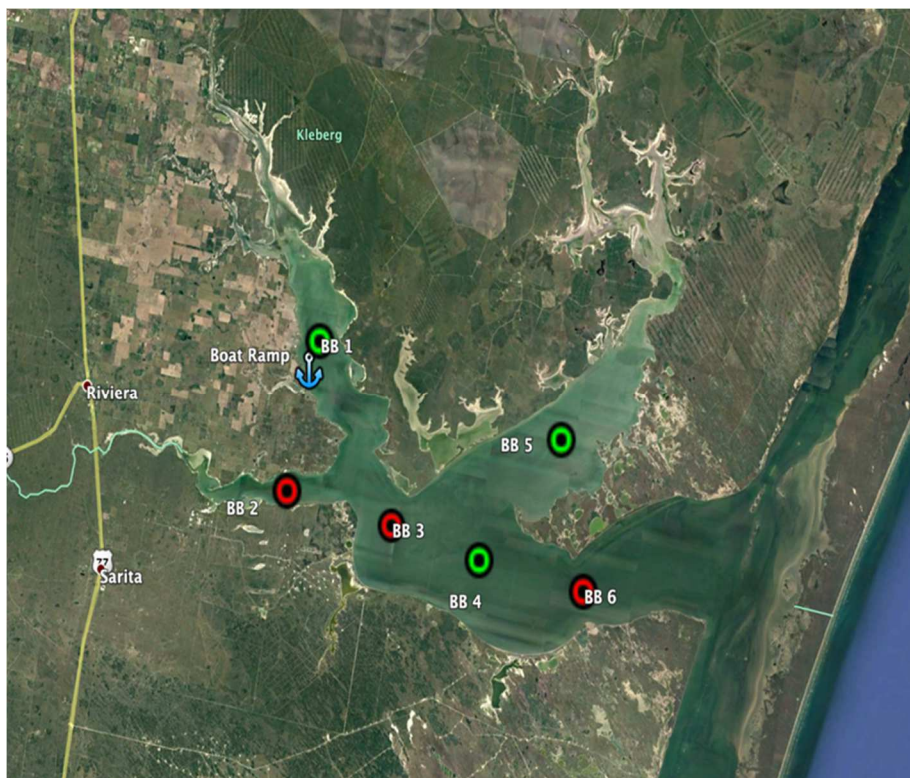


Figure 2.1. Six stations of sampling (Baffin Bay, Riviera, Texas).

2.2. Sample collection

Surface water and porewater samples were collected at Baffin Bay at six different locations (BB1, BB2, BB3, BB4, BB5, BB6) during six different seasons: October 2020 (Oct 31st, 2020), February 2021 (February 4th, 2021), June 2021 (June 12th, 2021), October 2021 (October 6th, 2021), February 2022 (February 8th, 2022), and May 2022 (May 26th, 2022). Before the sample collection, all the glassware was cleaned with tergezime and soaked in 5% HCl for 12 hours followed by cleaning with deionized (DI) and Milli-Q ultrapure grade water, respectively. After cleaning, glassware was oven-dried and combusted at 450°C for 12 hrs. The same cleaning process was applied to the plasticware excluding the combustion. In the field, polycarbonate bottles, cores and the core caps were rinsed several times with bay water before collecting the samples. A total of 72 surface water samples (two 1L bottles per station per season) were collected and stored in

pre-cleaned polycarbonate bottles then filtered through 0.22 μm (cellulose acetate filter, Corning®). Two sediment cores (~35cm, polycarbonate core liner) were collected at each station and were stored in an icebox and transported back to the lab where samples were kept in the refrigerator until further analysis (within 2 days maximum). Field parameters such as salinity were measured using Fisher Scientific Optical Refractometer Cat. No. FS1394627 and pH were measured using Horiba LAQUA twin pH meter Model: S010.

The first core was used for porewater sampling with Rhizone samplers (0.12 μm pore size membrane) at every 2 centimeters depth. The porewaters were subsampled for NH_4^+ , dissolved organic nitrogen (DON), dissolved organic carbon (DOC), NO_3^- concentration and mass spectrometer analysis. The second core was used for solar irradiation experiments and porosity analysis. Sediment was sectioned every 2-cm depth. Subsample sediments were taken for porosity analysis, the remaining sediments were centrifuged at 9,600 rpm for 15 min, filtered, and collected and combined in 500 ml combusted glass bottles. The porewater samples were purged with pure nitrogen gas in a basic environment (add concentrated NaOH to pH ~ 12) to remove almost all the initial ammonium in porewaters prior to the irradiation experiment. Purged porewaters were expected to have less than 5 μM of ammonium. The samples were then acidified to bring back to its origin pH value using concentrated hydrochloric acid.

2.3. Ammonium (NH_4^+) concentration determination

Ammonium (NH_4^+) concentrations were determined using the Ortho-phthaldialdehyde (OPA) method (Holmes et al., 1999) and measurements were conducted with the fluorescence detector in High-Performance Liquid Chromatography (HPLC) Ultimate 3000 model. OPA working solution (WS) is made up of 200mL borate buffer + 1mL sodium sulfite + 10mL OPA as the ratio is Borate : Na_2SO_3 : OPA = 200:1:10. Borate buffer solution: 8g of sodium tetraborate in

200 mL H₂O makes up 200 mL of borate buffer for the WS. Sodium sulfite solution: 0.08g of Na₂SO₃ in 10 mL of H₂O makes up 10 mL of sodium sulfite solution, then take only 1 mL for the WS. OPA fluorescence solution: 0.4g of OPA in 10mL of ethanol makes up 10 mL of OPA fluorescence solution for the WS. The WS will be stored in the dark for at least 1 day prior to reaction with samples. For the determination of ammonium (NH₄⁺) concentration, 0.25 mL of a sample is mixed with 1mL of the WS then incubated in the dark for at least 2 hours prior to the detection by HPLC - fluorescence detector. The NH₄⁺ concentration must be measured between 2-8 hours of incubation time. Ammonium chloride (NH₄Cl) solutions were used as the calibration standard from 0.1 – 400 µM.

2.4. Sediment porosity

Porosity was measured by weighing and then drying 166cm³ saturated sediment core cylinders in an oven at 105° C. After constant weight measurements, sections were weighed for dry mass. Porosity was then derived using the relationship between bulk density and particle density (Avnimelech et al., 2001).

$$\phi = 1 - \frac{\rho_b}{\rho_g} \text{-----} (1)$$

where ϕ is porosity, ρ_b is the bulk density, and ρ_g is the particle density assuming a constant and conventionally agreed upon value of 2.65g/cm³ (Klute, 1986).

2.5. Benthic ammonium flux

The diffusive fluxes of different organophosphate insecticides and herbicides was calculated using Fick's First Law

$$F^i = -\phi D_s^i \frac{dC^i}{dz} \text{-----} (2)$$

where F^i is the diffusive flux of pore water solute i , ϕ is sediment porosity, D_s^i is the whole sediment diffusion coefficient of solute i , and dC^i/dz is the concentration gradient of solute i at sediment

depth. Porosity at various depth interval was calculated using an exponential function that would fit the porosity data from the same sediment cores as described by Komada et al., (2016). D_s^i was calculated from modified Weissberg relation, $D_s^i = D_0^i / \{1 - \ln(\phi^2)\}$ (Boudreau, 1997), where D_0^i is the free seawater diffusion coefficient of ammonium. The following constants were used for ammonia (Schulz 2006): (D_0^i ($\text{m}^2 \text{ s}^{-1}$), $T_{\text{em}}(^{\circ}\text{C})$) = (9.03E-10, 0), (1.1E-9, 5), (1.29E-9, 10), (1.47E-9, 15), (1.66E-9, 20), and (1.85E-9, 25). We assumed steady-state conditions and molecular diffusion is the primary factor controlling ammonium concentrations down the profile.

2.6. Solar Simulator experiments

For this study, a solar simulator (Model: Atlas SUNTEST CPS+) was used to irradiate the sample for a different time interval (up to 72 hrs) and the samples were further analyzed accordingly. with its irradiation wavelength set at 300-400 nm which transfers the following heat fluxes (kJ/m^2): 702 in 3 hours, 2808 in 12 hours, 5616 in 24 hours, and 16848 in 72 hours. Most of all photochemical reactions such as mineralization of dissolved organic carbon at the surface water occur within these wavelengths (Mopper and Kieber 2000; Vähätalo et al 2000; Minor et al., 2007). The solar simulator lamps were kept on for the entire experimental period during the irradiation of the samples.

Five subsamples (60-65mL each) in five quartz flasks and underwent irradiation at 3, 12, 24, 72 hours along with a dark control. A dark control was aluminum wrapped and exposed to irradiation in 72 hours to monitor heat effect. The irradiated waters were then preserved for the following experiments: ammonium concentration, UV-Vis measurement, and structural elucidation by Mass Spectrometry.

2.7. UV-Vis absorption measurement

Chromophoric dissolved organic matter (CDOM) samples were analyzed using a Cary 60 UV-Vis Spectrophotometer (*Agilent*) with the absorption spectra of 200-800 nm, 1 cm wide quartz cuvette, and Milli-Q water as a blank. All the sample spectra were baseline and blank corrected. Instrument absorption of samples was converted to the absorption coefficient, a , using the following equations (Helms et al., 2008):

$$a = 2.303A/l \text{ ----- (3)}$$

- ❖ $a \equiv$ Absorption coefficient (m^{-1})
- ❖ $A \equiv$ Absorbance over a path length
- ❖ $l \equiv$ Path length of cuvette (m)

The equation (3) was derived from the original Beer – Lambert exponential formula:

$$I = I_0.e^{-al}$$

- $I/I_0 = e^{-al}$
- $\log_{10}(I/I_0) = -a.l.\log_{10}(e)$
- $\log_{10}(I_0/I) = A = a.l.\log_{10}(e)$
- $a = \ln(10).A/l = 2.303A/l$

The spectral slope (S) was calculated by fitting absorption data to the following exponential equation (Helms et al., 2008):

$$a_{\lambda} = a_{\lambda_{\text{ref}}} e^{-S(\lambda - \lambda_{\text{ref}})} \text{ ----- (4)}$$

- ❖ $a \equiv$ absorption coefficient (m^{-1})
- ❖ $\lambda \equiv$ wavelength (nm)
- ❖ $\lambda_{\text{ref}} \equiv$ reference wavelength (nm)
- ❖ $S \equiv$ spectral slope (nm^{-1})

$$(4) \rightarrow \ln(a_{\lambda}) = \ln(a_{\lambda_{\text{ref}}}) - S(\lambda - \lambda_{\text{ref}}) \text{ ----- (5)}$$

The spectral function for the 200-800 nm ($S_{200-800}$) interval was determined by plotting the respective values in equation (4). The spectral slope for the interval of 275 – 295 ($S_{275-295 \text{ nm}}$) and 350-400 ($S_{350-400 \text{ nm}}$) was calculated by fitting the best linear regression log-transformed absorption coefficient (a) spectra using equation (5). The ranges, 275–295 nm and 350–400 nm, were chosen because the first derivative of natural-log spectra indicated that the greatest variations in S from a variety of samples (marsh, riverine, estuarine, coastal, and open ocean) occurred within the narrow bands of 275–295 nm and 350–400 nm (Helms et al., 2008). The slope ratio (S_R) was calculated as the ratio of $S_{275-295}$ to $S_{350-400}$. This methodology avoids the use of spectral data near the detection limit of the instruments and focuses on absorbance values that shift significantly during estuarine transit and photochemical alteration of CDOM (Helms, 2008).

2.8. DOM Chemical Characterization & Structural Elucidation by Mass Spectrometry

Samples were prepared for mass spectral analysis using PPL solid phase extraction cartridges (Agilent, Bond Elut PPL, 100 mg resin, 3 mL volume (Dittmar et al., 2008). A lique of 10 mL of filtered porewater samples was acidified using trace metal grade hydrochloric acid (HCl) to pH 2. The samples were extracted using 200 mg, 3mL Bond elute-PPL cartridges. Blank Milli-q water was extracted as a sample. Final DOM extracts were eluted using 6 mL HPLC Optima grade methanol and collected in pre-combusted glass vials. (Dittmar et al 2008; Stucheli et al., 2018). Final SPE-DOM extracts were dried using a Centrivap benchtop concentrator and diluted to 1 mL Milli-q water. The samples were analyzed with both UPLC-OT-FTMS (positive mode) and IC-OT-FTMS (negative mode) according to (Bergmann et al., in preparation).

Liquid Chromatography-Orbitrap Fusion Mass Spectrometer

DOM extracted samples were analyzed for positive mode detection analysis by Vanquish Ultra Pressure Liquid Chromatography – Orbitrap Fusion Tribrid Mass Spectrometer (UPLC-OT-

FT-MS). The analytes were separated on the 1.7 μm ACQUITY UPLC BEH C_{18} reversed-phase column by Waters (130 $\text{\AA}$, 1.7 μm , 2.1 mm $\times$ 150 mm) and guided to a heated electrospray (H-ESI) and the Orbitrap Fusion Tribrid Mass Spectrometer. The injection volume of each sample was 20 μL . The Eluent A, Milli-Q with 0.1 % (v/v) formic acid, and eluent B, acetonitrile with 0.1 % (v/v) formic acid, were mixed with curve 5 to a flow rate of 0.200 mL/min. The total run lasted 31 min with 7 min re-equilibration and the following gradient: 0-2 min hold at 5 % B, ramp to 65 % B for 18 min, then ramp to 100 % B for 1 min and hold at 100 % B for 3 min. The H-ESI setting was 3500V for the positive spray voltage with ion transfer tube temperature at 300 $^{\circ}\text{C}$ and vaporization temperature at 225 $^{\circ}\text{C}$. The three gases on the H-ESI were 35 for sheath gas, 7 for aux gas, and 0 for sweep gas. The OT-FT-MS was set at 500,000 (FWHM at m/z 200) resolution and mass range 80-800 m/z with RF lens at 40%. Two MS^2 were scanned with the Ion Trap following the full scan via two filters, Dynamic Exclusion ($n = 1$ for 30s) and Intensity Threshold (min = 5000, max = $1.0\text{e}20$). Both MS^2 scans were isolated via the Quadrupole with a mass bandpass of 0.7 m/z , but one fragmentation scan was generated using collision-induced dissociation (CID) with assisted energy collision, and the other fragmentation scan was generated with higher-energy collisional dissociation (HCD) with stepped energy collision. Both MS^2 scans had an automatic gain control (AGC) set at $1.0\text{e}4$ and a maximum injection time of 50 msec.

The locking solution was introduced to the sample via a t-shaped connection after the column separation of analytes and before H-ESI. A flow-regulated peristaltic pump assured a continuous but consistent mixing of internal standards with the sample at a flow rate of 0.05 mL/min. The selected standards had masses of 94.0621, 122.0844, 139.1191, and 207.0912 m/z added to the list (max. 8 compounds). This setting instructed the OT-FT-MS to look specifically

for these four compounds, choose the standard with the highest intensity and perform an *on-the-fly* internal calibration for each scan.

Ion Chromatography Orbitrap Fusion Mass Spectrometer

For negative mode analysis, extracted DOM samples were run on Thermo Scientific Dionex ICS-5000⁺ – Orbitrap Fusion Tribrid Mass Spectrometer (IC-OT-FT-MS). The analytes were run in 1-dimension with a Dionex IonPac AS11-HC 4 μm column by Thermo Scientific (2000 Å, 4 μm x 2 mm x 250 mm), a Dionex IonPac AG11-HC 4 μm guard column by Thermo Scientific (13 μm , 2mm x 50 mm), and Dionex AERS 500e Anion Electrolytically Regenerated Suppressor for External Water Mode (2 mm). To enhance the deprotonation of DOM compounds for negative detection, a solution consisting of 1L acetonitrile, 30 mL Milli-Q, and 3 mL ammonium hydroxide was flowing with the sample at 0.2 mL/min to the H-ESI ion source after exiting the conductivity detector via a t-shaped connection. The total analysis run was 20 min with 1 min re-equilibration, 0.4 mL/min flow, 40 μL injection volume, and the following gradient: started with initial 0.1 mM KOH, increased to 4 mM KOH 0.1-5.0 min, ramped to 60 mM KOH 5.0-11.0 min, held at 60 mM KOH from 11.0-16.0 min, and decreased to 1 mM KOH 16.-16.1 min. The temperature in the DC compartment was set at 35.0 °C. The H-ESI was set at 3100V for the negative spray voltage with ion transfer tube temperature at 350 °C and vaporization temperature at 300 °C. The three gases on the H-ESI were 50 for sheath gas, 20 for aux gas, and 2 for sweep gas. The Orbitrap was run at 500,000 (FWHM at m/z 200) resolution and mass range 85-700 m/z with an RF lens at 40 % to focus on low m/z compounds for the full scan analysis. Following the full scan, two MS² were scanned with the Ion Trap via two filters, Dynamic Exclusion ($n = 3$ for 60s) and Intensity Threshold (min = 1000, max = 1.0×10^{20}). Both MS² scans were isolated with the Quadrupole (0.7 m/z), but one fragmentation scan was generated through CID with assisted

energy collision, and the other fragmentation scan was generated through HCD with stepped energy collision. MS² scan with CID had an automatic gain control (AGC) set at 3.0e4 and a maximum injection time of 50 msec, and the MS² scan with HCD had an AGC of 1.0e4 and a maximum injection time of 50 msec.

The locking solution was introduced to the sample via a T-shaped connection after the column separation of analytes and before H-ESI. A flow-regulated peristaltic pump assured a continuous but consistent mixing of internal standards with the sample at a 0.20 mL/min flow rate. The internal calibration was set to "User-defined Lock Mass" and "XCalibur AcquireX enabled for method modification" was tagged. The selected standard had a mass of 184.0711 m/z.

Compound Discoverer software 3.2 (Thermo Fisher) was used to identify the DOM compounds. All chromatography spectra' retention times (RT) were aligned using an adaptive curve with a maximum shift of 0.2 min and 5 ppm mass tolerance. To identify a compound, the following conservative criteria were met: 1) a signal-to-noise (S/N) above 3, 2) a minimum of 5 mass scans per chromatographic peak, 3) a minimum peak intensity of 50,000, and 4) at least one isotope peak ($M + 1$) was detected. We have used the ratio of the $M + 1$ to parent peaks to confirm the number of carbon atoms. We also used the $M + 2$ peak ratios to confirm the presence of the S atom in the compound. *De novo* structural elucidation was performed on the MS² fragments, and these structures were putatively annotated using *in silico* fragmentation prediction software (Mass Frontier). Deaminated peptides and peptides were identified through a combination of the following 5 multi-confidant points: 1) high mass accuracy of OT-FTMS, 2) identification and matching of isotopic patterns (at least $M+1$ isotopes) to confirm ionized charge and the estimated number of carbon atoms, 3) cross-referencing with in-house deaminated peptide database, 4) matching retention times between different samples, 5) structure confirmation through MS²

fragmentation by both CID and HCD techniques and verification using *in silico* fragmentation prediction software with a FiSH score of 70% or higher.

2.9. Peptides and deaminated peptides database

We identified all possible peptides in SBB pore waters by establishing a database applying Python Software that contained all possible small (2–4 amino acid) peptide sequences that could be formed from the 20 primary amino acids. This resulted in a total of 168,400 potential peptides.

To generate a database for deaminated peptides, we performed hypothetical deamination reactions on all of the peptides in our database. We first defined the deamination potential number (DPN), which represents the number of amine groups in every peptide sequence that have the potential to be deaminated. To calculate the DPN of a peptide, we summed the number of NH_2 groups from each amino acid in the peptide and from that subtracted the number of amide bonds. The assigned number of NH_2 group in each specific amino acid was based on previous deamination studies of these amino acids (Nisman, 1954; Zehnder, 1988; Kim and Gadd, 2008; White et al., 2012) and not on the number of nitrogen atoms. After calculating the initial DPN of a peptide, we removed a terminal amino group from the peptide using one of six possible deamination mechanisms: (1) oxidative deamination; (2) reductive deamination; (3) hydrolytic deamination; (4) eliminating deamination; (5) histidine eliminating deamination and (6) desulfurization deamination. After each deamination, a value of one was subtracted from the DPN of the peptide, and deamination was repeated using a combination of these six deamination mechanisms until the DPN of the peptide reached a value of zero. This resulted in a total of 747,368 potential deaminated peptides.

3. RESULTS

3.1. Salinity and precipitation of Baffin Bay during six sampling seasons

The first two seasons, Oct_20 and Feb_21, indicated the hypersaline condition in Baffin Bay with average salinity of 45.1 ± 1.8 and 48.5 ± 1.9 , respectively (*Figure 3.1.1*). According to NOAA (ref. 65), the precipitation in the region was low before sampling dates in Oct_20 (<6 inches) and Feb_21 (<4 inches) (*Figure 3.1.2*). The average salinity dropped significantly to 16 ± 8.3 in Jun_21. There was a heavy precipitation in the region that occurred in May_21 (17.89 inches), which was expected to bring in freshwater and flush the semi-closed water system resulting in a drop in salinity recorded in the next sampling season, Jun_21. After that, the average salinity of the bay gradually increased to 17.9 ± 2.2 , 22.9 ± 1.5 and 33.0 ± 1.0 in Oct_21, Feb_22 and May_22, respectively. The depletion of rainfall during this period (after Jun_21) could be responsible for the increase in salinity of the bay along with high evaporation rate in the region. The average pH of the Baffin Bay surface water ranged from 7.92 to 8.50 with the highest (more alkaline) in Jun_21. The water temperature ranged from 11.93 °C to 29.38 °C, with the highest in Jun_21 (summer) and lowest in Feb_22 (winter). The surface water dissolved oxygen (DO) ranged from 7.11 mg/L to 10.61 mg/L with the highest in Feb_22 and lowest in May_22. *See supplemental materials for other detailed sampling conditions including pH, conductivity, temperatures, and dissolved oxygen.*

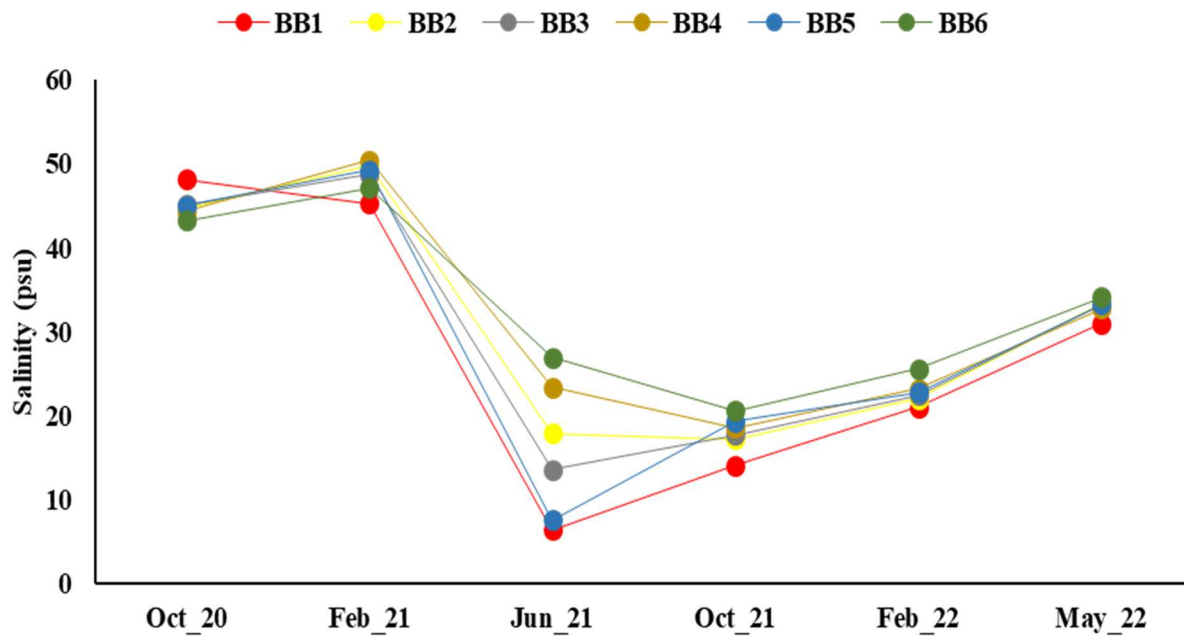


Figure 3.1.1: Salinity of six sampling sites throughout six seasons.

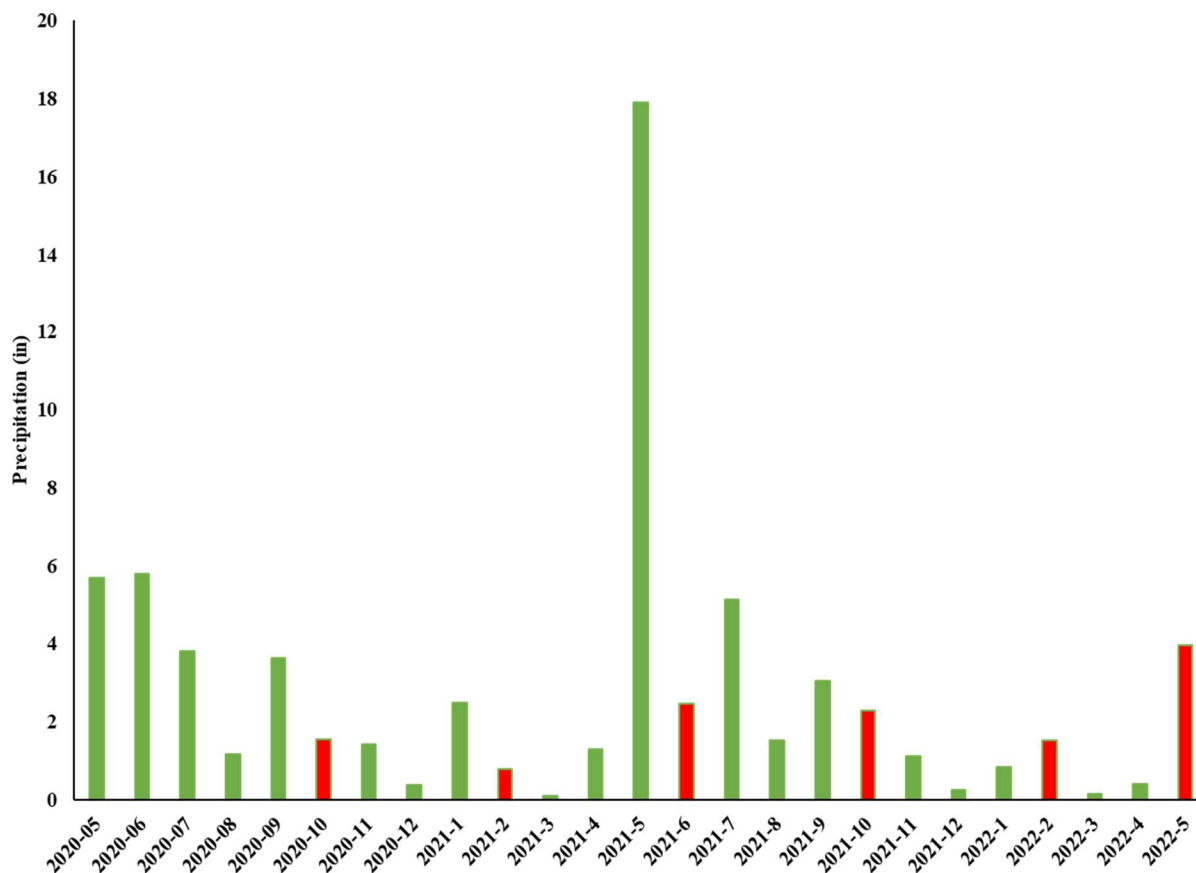


Figure 3.1.2: Precipitation (inches) in Baffin Bay during six sampling seasons (NOAA, Station Kingsville 6.5 SSE, TX US). Precipitation includes rain, melted snow, etc. “Red” columns indicated sampling dates.

3.2. Ammonium (NH_4^+) depth profile

Ammonium concentrations of surface waters ranged from $11 \mu\text{mol-N.L}^{-1}$ to below the detection limit ($0.1 \mu\text{mol-N.L}^{-1}$) in all six stations during six seasons (*Table S6 – Supplemental Materials & Figure 3.2.1*). Oct_20 had the highest average $[\text{NH}_4^+]$ on surface water with $6 \pm 3 \mu\text{mol-N.L}^{-1}$ while May_22 showed that $[\text{NH}_4^+]$ was below the detection limit for all the six stations. Depth profiles of ammonium (NH_4^+) concentrations in porewater were reported for six stations during six seasons (*Table S7 - Supplemental Materials & Figure 3.2.2*). Note that BB1-October 2020 was missing due to the loss of sample core. NH_4^+ concentration ranged from 32 to

2,181 $\mu\text{mol-N.L}^{-1}$. Geographically, the highest average porewater $[\text{NH}_4^+]$ was $935 \pm 637 \mu\text{mol-N.L}^{-1}$ at BB6 (near the Laguna Madre) followed by BB3 (center of the Bay) and BB2 (Laguna Salada) with 861 ± 482 and $618 \pm 342 \mu\text{mol-N.L}^{-1}$, respectively. On the other hand, BB5 reported the lowest average $[\text{NH}_4^+]$ of $381 \pm 128 \mu\text{mol-N.L}^{-1}$. The spatial average $[\text{NH}_4^+]$ showed significant differences between each station with chi-squared = 424, p value = 2×10^{-89} . Seasonally, the highest average porewater $[\text{NH}_4^+]$ was $844 \pm 534 \mu\text{mol-N.L}^{-1}$ in February_2022 followed by February_2021, October_2020 and May_2022 with 684 ± 531 , 660 ± 594 and $634 \pm 169 \mu\text{mol-N.L}^{-1}$, respectively. The lower average $[\text{NH}_4^+]$ was in October_2021 and June_2021 with 482 ± 158 and $434 \pm 249 \mu\text{mol-N.L}^{-1}$, respectively. The seasonal average $[\text{NH}_4^+]$ showed significant differences between each season with chi-squared = 176, p value = 3×10^{-36} .

In general, the NH_4^+ pore water profiles showed an increase along with sediment depth (*Figure 3.2.2*). Ammonium concentrations in six stations were seasonally compared (*Figure 3.2.3*). Significant differences were evaluated using paired t-test on confidence level 95%. BB1 and BB2 reported a slight increase in ammonium concentrations over time (insignificant, $p > 0.05$). The NH_4^+ porewater showed a drastic increase in February 2022 (significant, $p < 0.05$). BB3 was consistent during six seasons (insignificant, $p > 0.05$) except February 2022 with a dramatic increase in NH_4^+ concentrations (significant, $p < 0.05$). BB4 recorded the highest in May 2022 (significant, $p < 0.05$). BB5 and BB6 showed significant changes during the seasons ($p < 0.05$). In both stations, porewater $[\text{NH}_4^+]$ dropped after the rainfall in May_21 then gradually increased back. BB5 peaked in February 2022 and while BB6 lost all its ammonium after the rainfall in May_21 then gradually accumulated it back. Overall, February 2022 reported the highest porewater $[\text{NH}_4^+]$ in Baffin Bay, especially at BB2 and BB3 (significant, $p < 0.05$), while BB6 had the most considerable seasonal variation of porewater NH_4^+ concentration (significant for every

season, $p < 0.05$). At BB6, the first two seasons had a median above $1,800 \mu\text{mol-N.L}^{-1}$. However, the concentration dropped to $67 \mu\text{mol-N.L}^{-1}$ in Jun_21 sampling season. We observed a decrease in water salinity at the BB6 site (from above 40 in the first two seasons to a salinity of 26 in Jun_21) resulted from the heavy rainfall in May_21. The other stations, BB1, BB2, BB4 and BB5 showed no significant changes after rainfall in May_21 ($p > 0.05$).

Comparing the ammonium concentrations between six stations geographically (*Figure 3.2.4*), it showed that BB3 and BB6 peaked in the first two seasons, October 2020 and February 2021 (significant, $p < 0.05$). After the rainfall in May_21, the porewater $[\text{NH}_4^+]$ at BB3 stayed the same ($646 \pm 260 \mu\text{mol-N.L}^{-1}$) (insignificant, $p > 0.05$) while it dropped dramatically to $71 \pm 11 \mu\text{mol-N.L}^{-1}$ at BB6 (significant, $p < 0.05$). BB3 still showed the highest $[\text{NH}_4^+]$ in June 2021, October 2021, and February 2022 until May 2022 (significant, $p < 0.05$) when BB6 and BB4 had higher $[\text{NH}_4^+]$. In six seasons, BB1 and BB5 showed the lowest $[\text{NH}_4^+]$ (significant, $p < 0.05$). In conclusion, porewater $[\text{NH}_4^+]$ varied from seasons to stations and tended to increase with sediment depth.

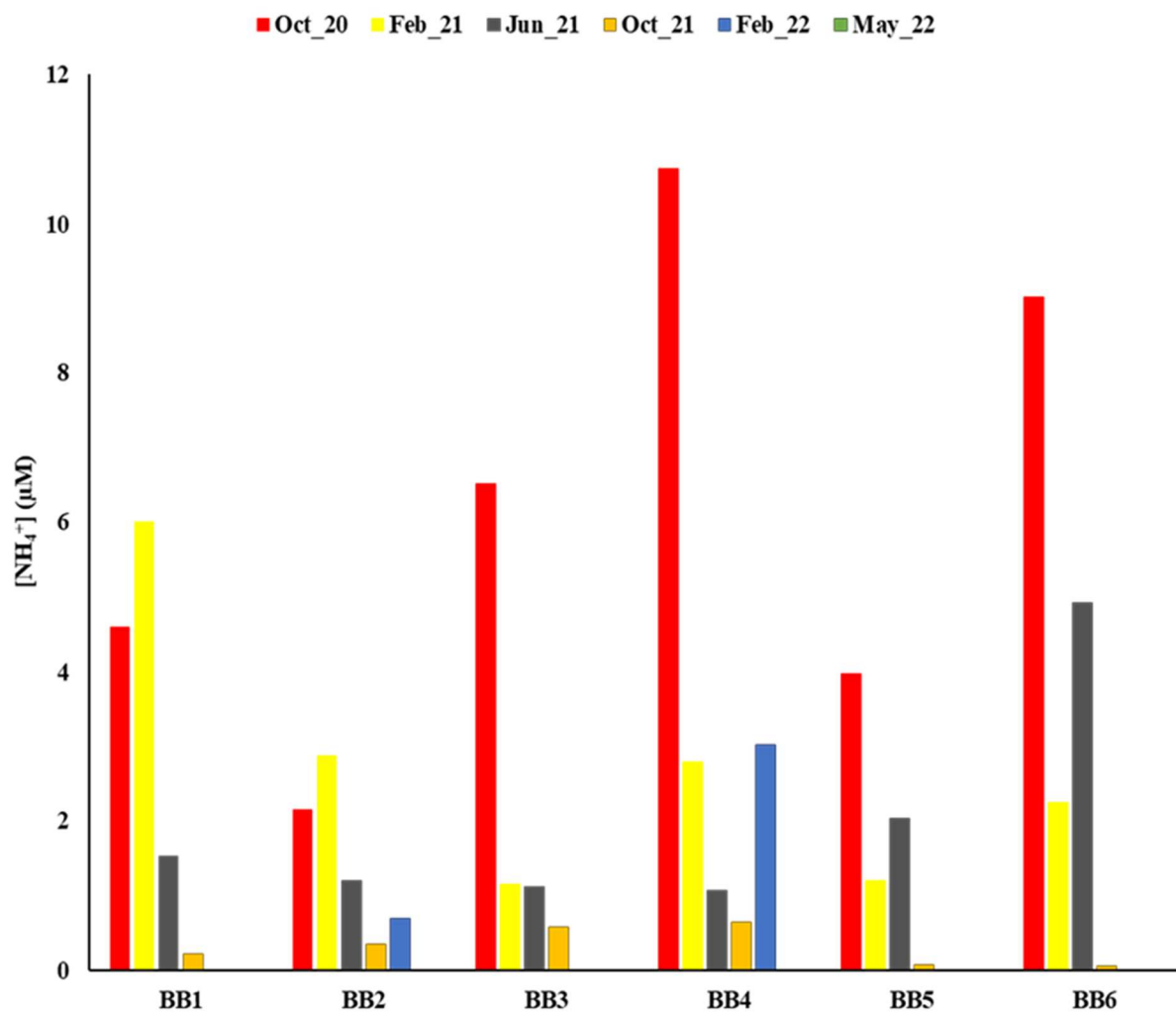


Figure 3.2.1. Ammonium concentration on surface water. February 2022 and May 2022 reported non-detectable concentration (below detection limit).

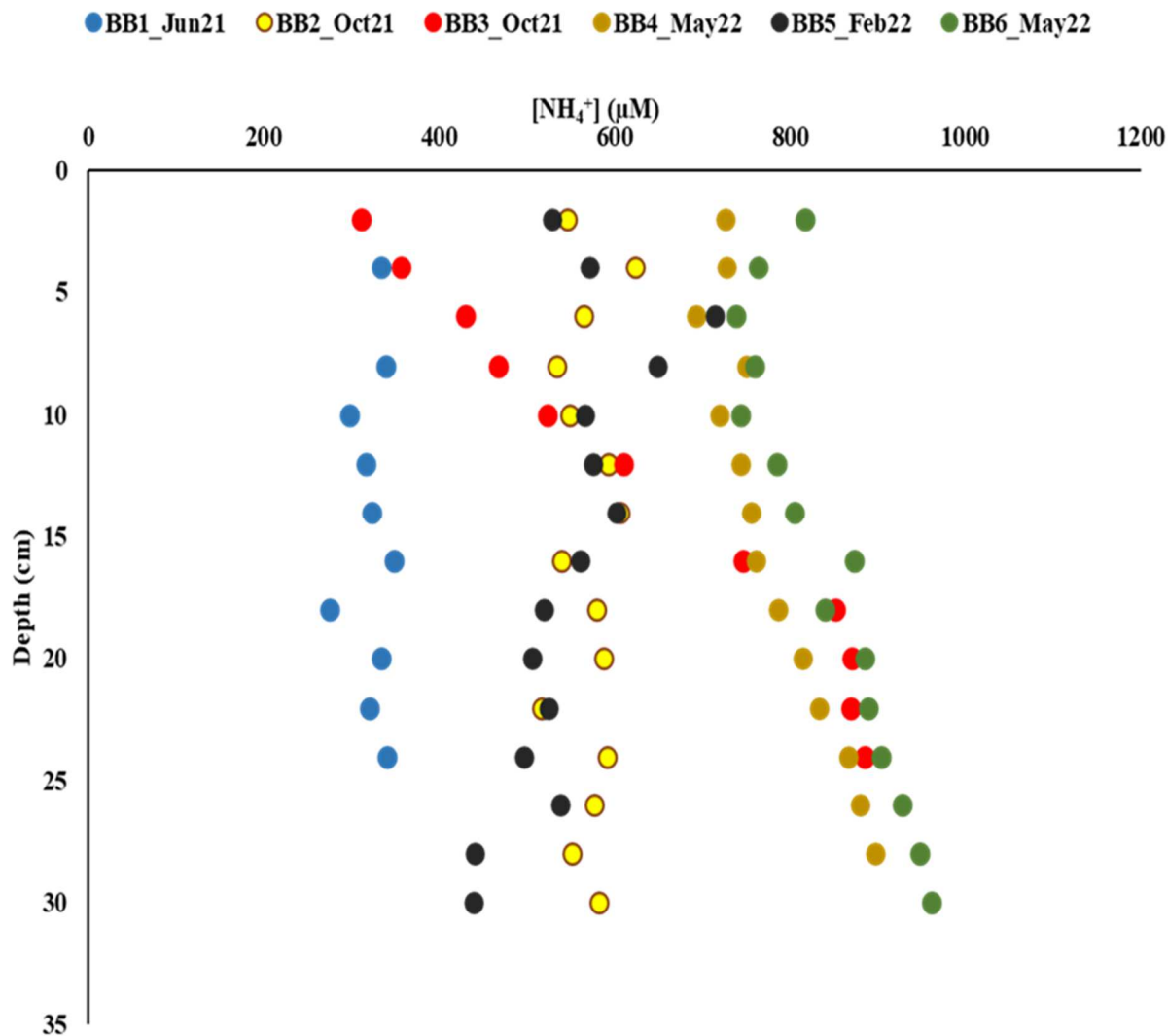


Figure 3.2.2: Ammonium depth profile of pore water. Data points were from BB1_June21, BB2_October21, BB3_October 21, BB4_May22, BB5_February 22, and BB6_May22.

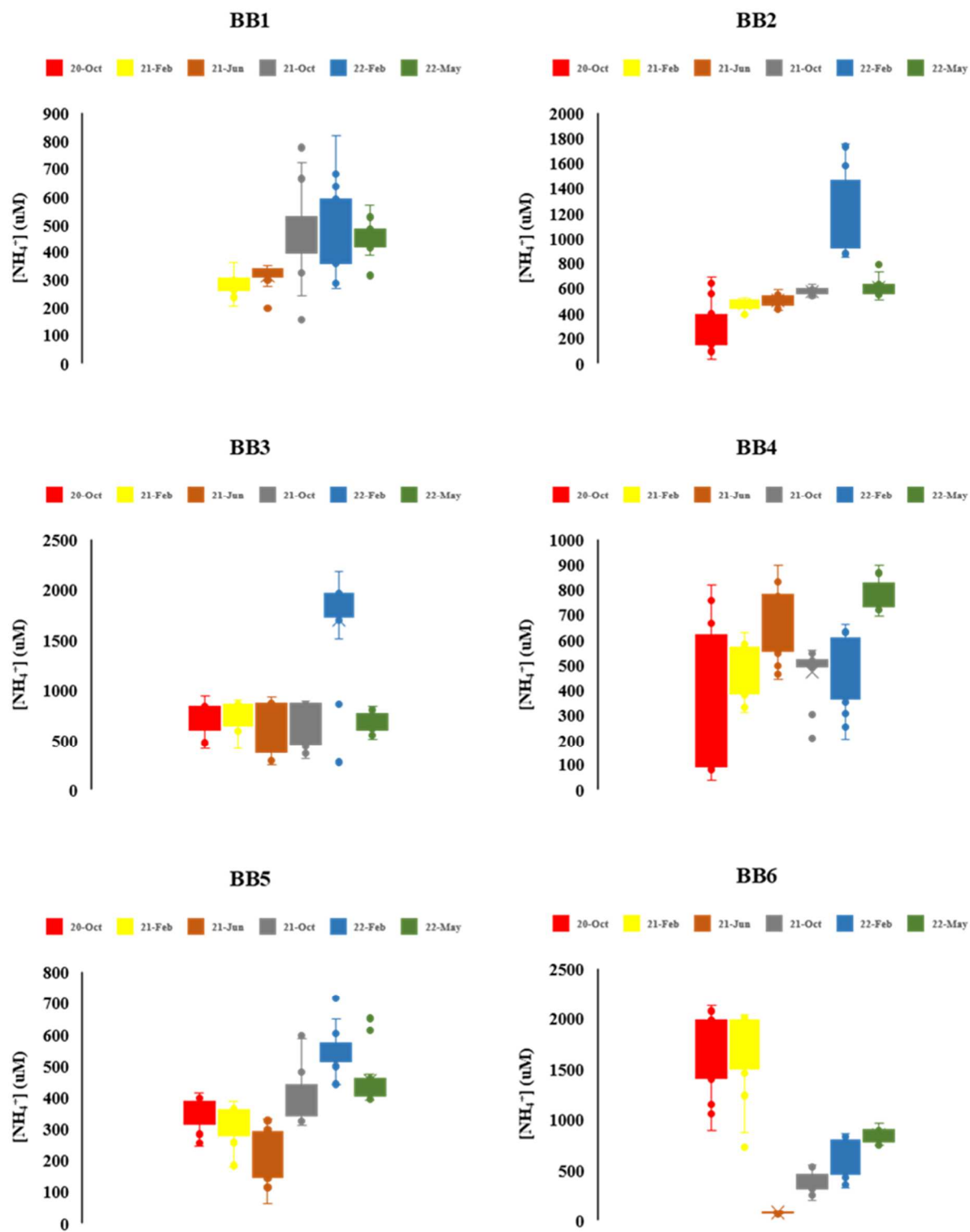


Figure 3.2.3: Seasonal ammonium (NH₄⁺) profile of Baffin Bay porewater in six stations.

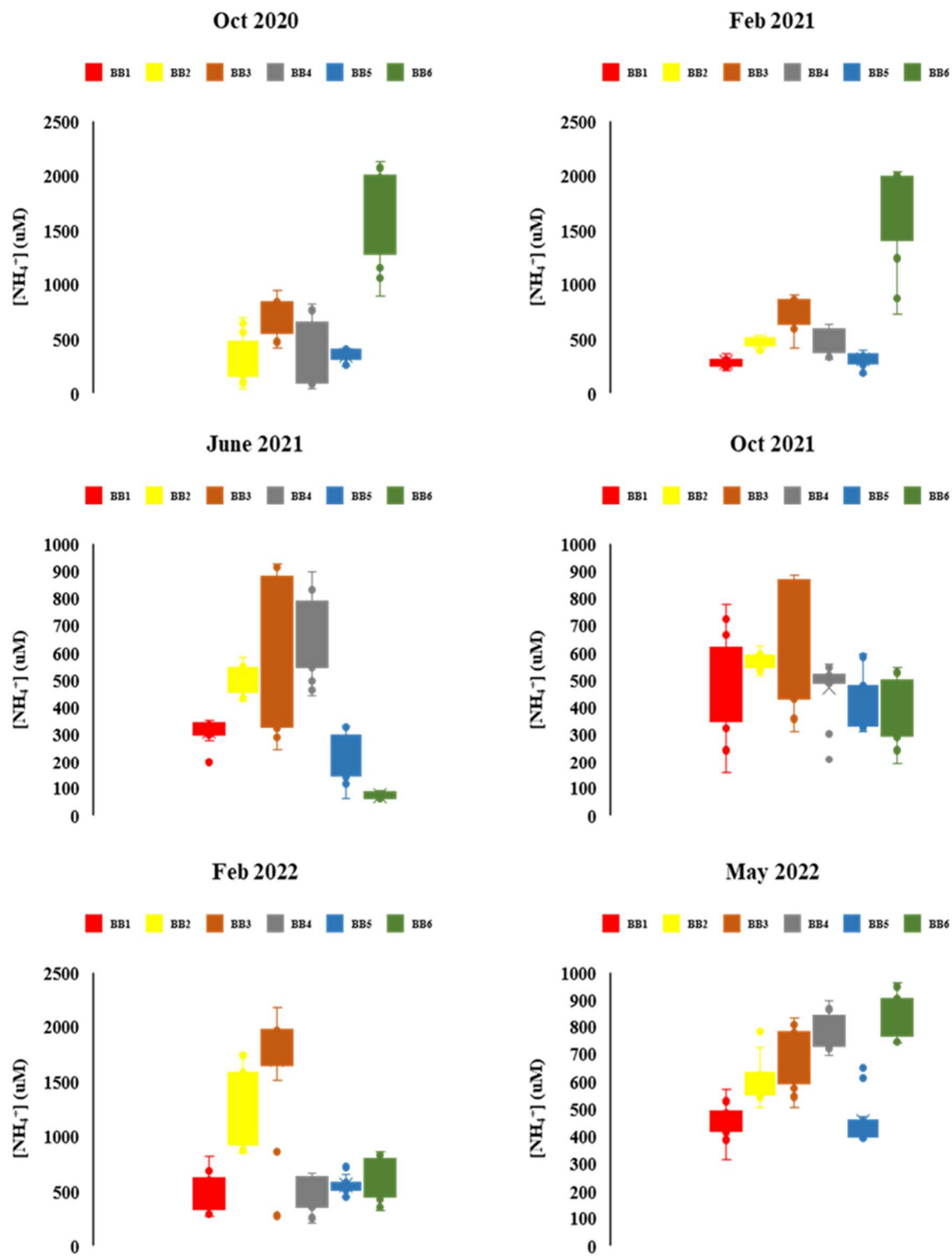


Figure 3.2.4: Geographical ammonium (NH_4^+) profile of Baffin Bay porewater in six stations during six sampling seasons.

3.3. Ammonium benthic flux to the water column

Applying Fick's first law of diffusion, we estimated the ammonium benthic flux to the water column (*Table 3.3*). Spatially, BB1 had the lowest average NH_4^+ flux at $56 \pm 27 \mu\text{mol.m}^{-2}.\text{day}^{-1}$. BB3 porewater diffused with the highest average flux at $347 \pm 211 \mu\text{mol.m}^{-2}.\text{day}^{-1}$, followed by BB6, BB4, BB2, BB5 with fluxes of 215 ± 196 , 191 ± 111 , 108 ± 115 , and $102 \pm 50 \mu\text{mol.m}^{-2}.\text{day}^{-1}$, respectively. The spatial average NH_4^+ fluxes showed significant differences between each station with chi-squared = 325, p value = 4×10^{-68} . Seasonally, May_22 had the lowest average NH_4^+ flux at $124 \pm 79 \mu\text{mol.m}^{-2}.\text{day}^{-1}$. Feb_22 porewater diffused with the highest average flux at $244 \pm 254 \mu\text{mol.m}^{-2}.\text{day}^{-1}$, followed by Jun_21, Feb_21, Oct_20, Oct_21 with fluxes of 187 ± 181 , 187 ± 156 , 161 ± 189 , and $133 \pm 87 \mu\text{mol.m}^{-2}.\text{day}^{-1}$, respectively. The seasonal average NH_4^+ fluxes showed significant differences between each season with chi-squared = 56, p value = 7×10^{-11} . The diffusive flux was a function of sediment porosity (Φ), diffusion coefficient (D_s), and instantaneous change of concentrations over depth (dC/dz). The lowest porosity was at BB1 with an average of 0.35, while BB2 and BB6 were 0.55, BB5 was 0.60, and BB3 and BB4 were 0.70. The sediment diffusion coefficient $D_s^i = D_0^i / \{1 - \ln(\phi^2)\}$ in which the surface water diffusion coefficient D_0^i was known constants at corresponding temperatures. The instantaneous change of concentrations over depth (dC/dz) was the slope of the best fit linear regression between ammonium concentrations from a few data points of top layer sediments and nepheloid layer (x axis) and depth (y axis).

Ammonium fluxes in six stations were seasonally compared (*Figure 3.3.1*). BB1 showed significant differences in ammonium fluxes with the highest flux in Oct_21 at $87 \mu\text{mol.m}^{-2}.\text{day}^{-1}$ and the lowest flux in May_22 at $29 \mu\text{mol.m}^{-2}.\text{day}^{-1}$ (chi-squared = 117, p value = 8×10^{-14}). BB2 and BB3 ammonium flux showed a drastic increase in Feb_22 with 332 and 723 $\mu\text{mol.m}^{-2}.\text{day}^{-1}$,

respectively (chi squared = 610 & 644, significant $p = 1 \times 10^{-129}$ & 7×10^{-137} , respectively). BB4 and BB5 ammonium fluxes showed significant differences during six seasons with chi squared = 325 & 124, significant $p = 4 \times 10^{-68}$ & 3×10^{-25} , respectively. BB6 showed a dramatic decrease in ammonium flux after the rainfall in May_21 then gradually increased back (chi squared = 896, significant $p = 1 \times 10^{-191}$). Overall, Feb_22 reported the highest ammonium fluxes in sediment porewaters of Baffin Bay at BB2 and BB3 and Oct_20 and Feb_21 had the highest fluxes at BB6.

Comparing the ammonium fluxes between six stations geographically (*Figure 3.3.2*), BB3 and BB4 with the highest porosity of 0.7 showed the highest fluxes in Jun_21, Oct_21, Feb_22, and May_22. BB1 with the lowest porosity of 0.35 showed the lowest fluxes in Feb_21, Feb_22, and May_22. BB2 & BB6 and BB5 had similar porosity of 0.6 and 0.55 so its fluxes were significantly dependent on the change of ammonium concentrations over depth. In conclusion, porewater NH_4^+ fluxes were significantly dependent on the sediment porosity and changes in ammonium depth profile.

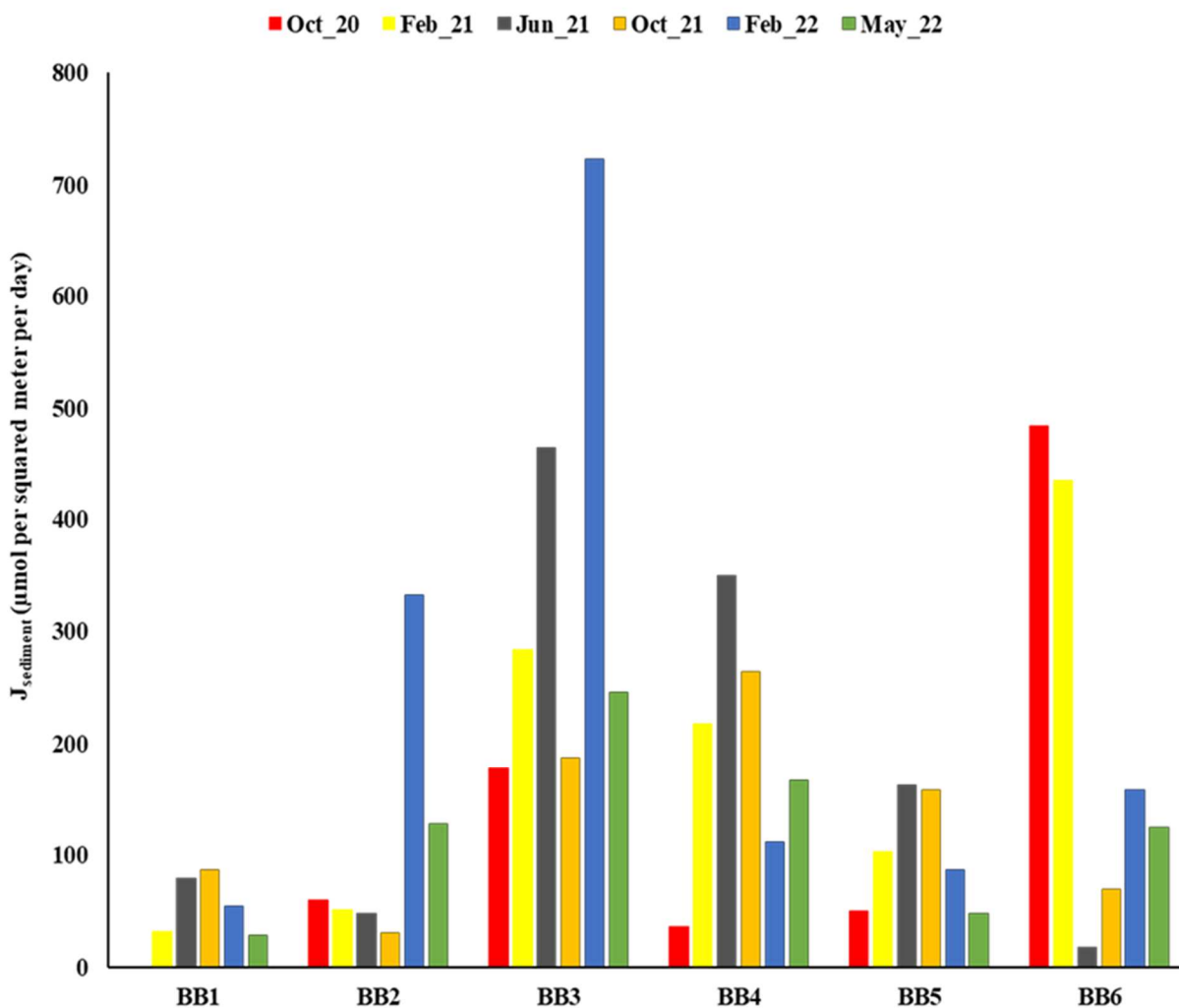


Figure 3.3.1. Benthic ammonium fluxes ($\mu\text{mol.m}^{-2}.\text{day}^{-1}$) of sediment porewater to the water column at six stations during six sampling seasons.

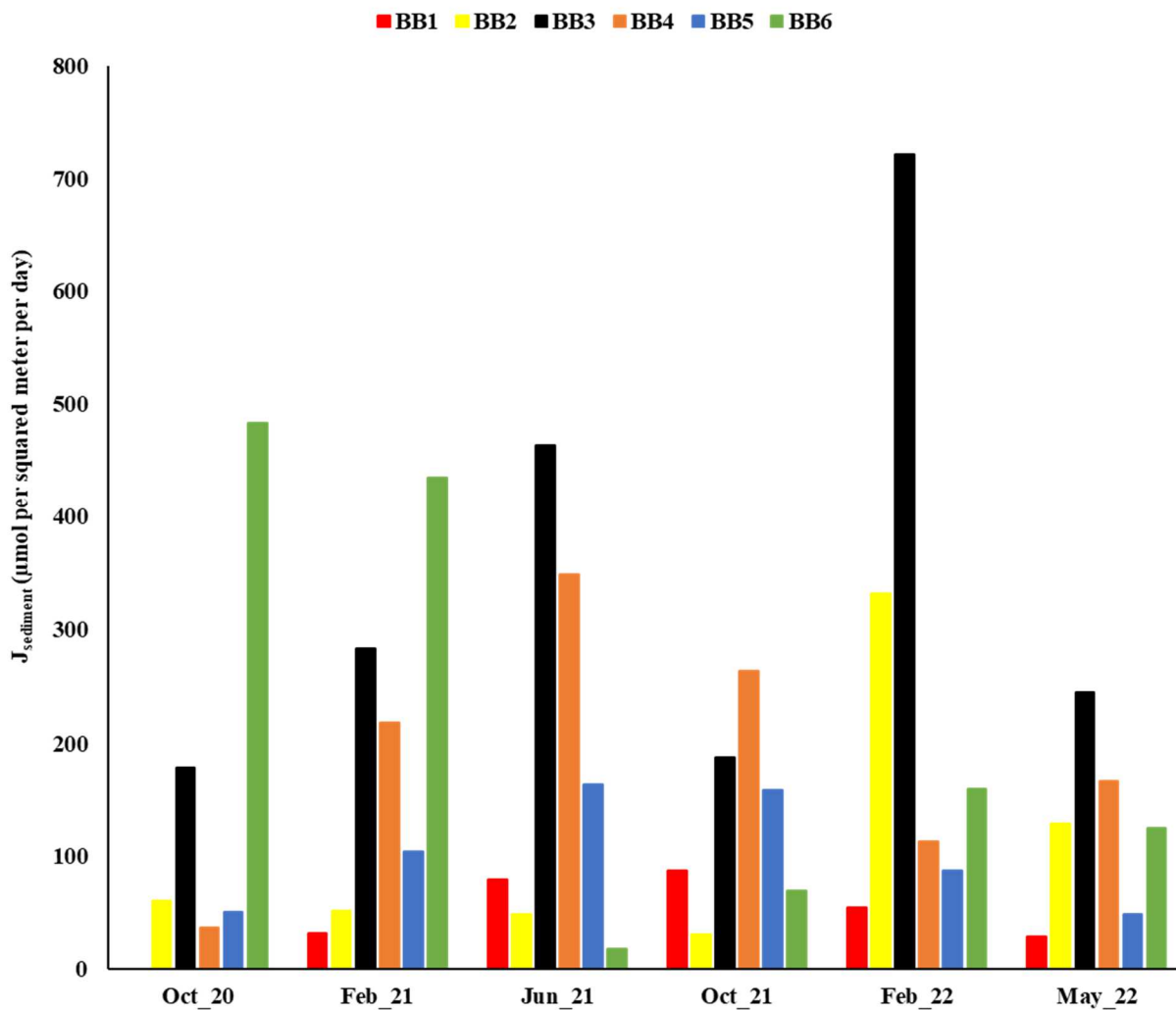


Figure 3.3.2. Benthic ammonium fluxes ($\mu\text{mol.m}^{-2}.\text{day}^{-1}$) of sediment porewater to the water column during six sampling seasons.

Table 3.3. Benthic fluxes ($\mu\text{mol. m}^{-2}.\text{day}^{-1}$) of Baffin Bay in six seasons.

	Oct_20	Feb_21	Jun_21	Oct_21	Feb_22	May_22	Spatial Mean	St. Dev.
BB1		31	79	87	54	29	56	27
BB2	60	51	48	30	332	128	108	115
BB3	177	284	464	188	723	246	347	211
BB4	36	218	349	264	112	166	191	111
BB5	50	103	163	158	87	48	102	50
BB6	484	436	18	69	159	125	215	196
Seasonal Mean	161	187	187	133	244	124		
St. Dev.	189	156	181	87	254	79		

3.4. Ammonium (NH_4^+) photo production

Ammonium concentrations were measured at each irradiation time point: 0 (the initial after ammonia purging), 3, 12, 24, 72 hours along with a dark control. Ammonium concentrations were reported for six stations during five seasons (*Table S8 – Supplemental Materials*). Note that season October 2020 (BB1 only) and June 2021 were missing due to the loss of sample cores. All the irradiation experiments showed an increase in the NH_4^+ concentration with irradiation time (*Figure 3.4*). To estimate the rate of photo-production of ammonium, the slope of the linear regression line between irradiation time (x axis) and ammonium concentration (y axis) was calculated (*Table 3.4*). On average, $[\text{NH}_4^+]$ photo-production rate was the highest at BB1 at $0.19 \pm 0.08 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$ followed by BB2, BB4, BB3, BB6, and BB5 at 0.17 ± 0.09 , 0.17 ± 0.10 , 0.16 ± 0.14 , 0.13 ± 0.04 , $0.11 \pm 0.08 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$, respectively. Seasonally, February 2022 produced the highest average rate of ammonium photo-production at $0.23 \pm 0.08 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$ followed by October 2021, May 2022 at 0.21 ± 0.08 and $0.18 \pm 0.02 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$, respectively. Feb_21 and Oct_20, produced a rate at 0.08 ± 0.04 and $0.05 \pm 0.03 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$, respectively. Note that $[\text{NH}_4^+]$ was the highest at 72-hour and was slightly higher in dark control samples than the initial 0-hour in all the experiments (*Table 8 – Supplemental Materials*). However, $[\text{NH}_4^+]$ in dark control was lower than

the 3-hour irradiation time point which could indicate a slight production due to other factors like thermal changes.

Table 3.4. Ammonium photo-production rates in $\mu\text{mol.L}^{-1}.\text{hr}^{-1}$.

	Oct_20	Feb_21	Oct_21	Feb_22	May_22	Mean	St. Dev.
BB1		0.10	0.27	0.24	0.16	0.19	0.08
BB2	0.03	0.13	0.22	0.25	0.20	0.17	0.09
BB3	0.04	0.04	0.23	0.36	0.15	0.16	0.14
BB4	0.05	0.09	0.31	0.21	0.19	0.17	0.10
BB5	0.03	0.03	0.17	0.11	0.19	0.11	0.08
BB6	0.10	0.12	0.08	0.19	0.16	0.13	0.04
Mean	0.05	0.08	0.21	0.23	0.18		
St. Dev	0.03	0.04	0.08	0.08	0.02		

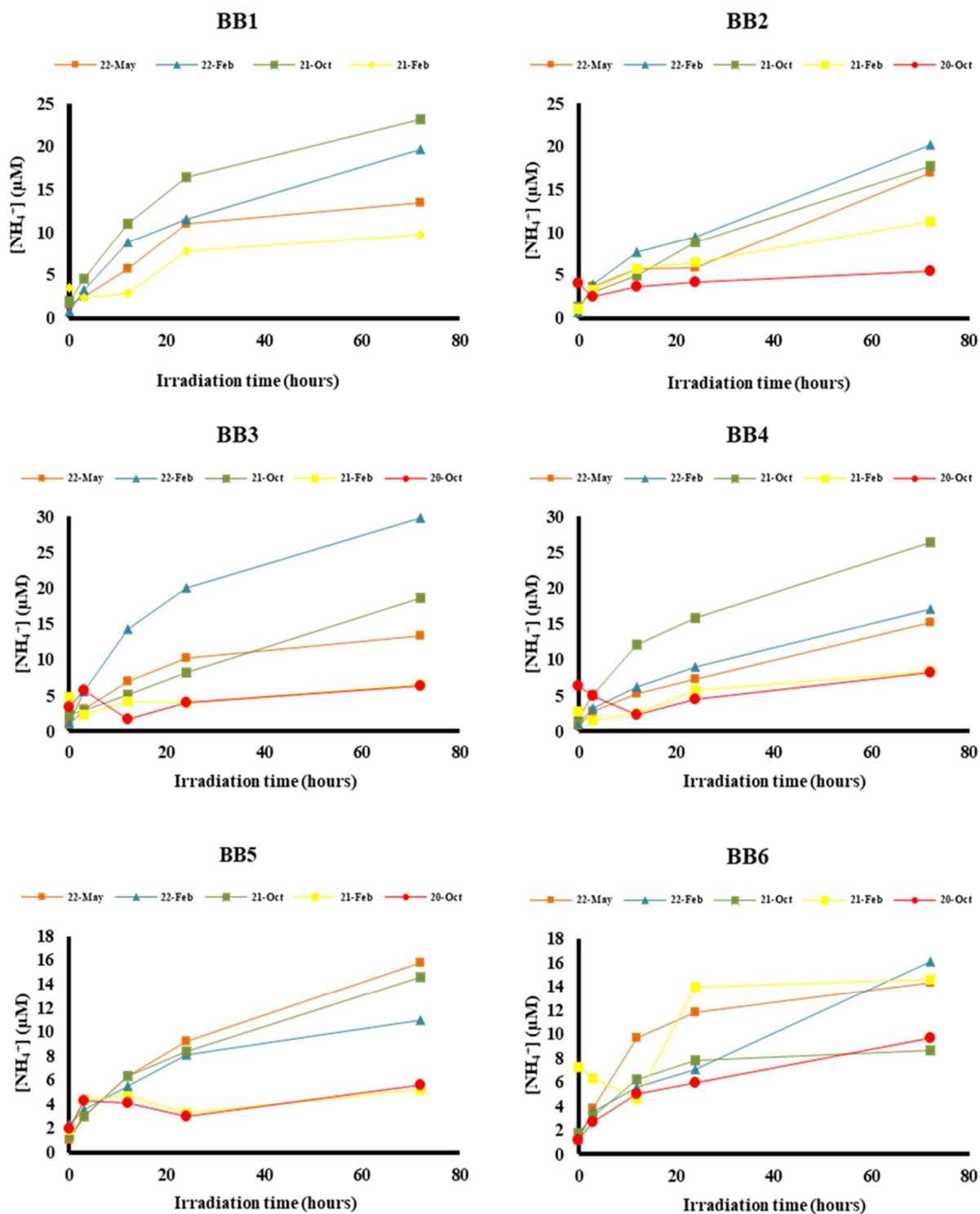


Figure 3.4. Ammonium photo-production at each irradiation increment of six stations during five sampling seasons.

3.5. UV-Vis absorbance measurements

Absorption coefficient spectra were reported for six stations during five seasons (*Figure 3.5.1 and Supplemental Materials*). Absorption coefficients decreased with irradiation time increments at 250-400nm while stayed constantly close to zero at 400-800nm. The absorption was the lowest at 72-hour. Note that the dark control samples showed the same or slightly different absorption as the 0-hour samples. The absorption coefficients were natural-logged (*Figure 3.5.2*) to calculate the spectral slopes, $S_{275-295}$ and $S_{350-400}$. The spectral slopes appeared to be negative, which meant a decrease in absorption along with irradiation increments. Data showed that $S_{275-295}$ became more negative overtime while $S_{350-400}$ became less negative overtime. Slope Ratio (S_R) were calculated by dividing $S_{350-400}$ by $S_{275-295}$ (*Table S9 – Supplemental Materials*). In general, S_R increased along with irradiation time increments and peaked at 72-hour. S_R stayed consistent from 0-hour until 12-hour then abruptly increased at 24-hour and peaked at 72-hour (*Figure 3.5.3*). Note that dark control S_R were the closet to the 0-hour and even the same in some cases.

When we reported the spectral slopes as positive values, slope ratio became $S_R = -(S_{350-400})/-(S_{275-295})$. Hence, S_R and $S_{275-295}$ became positively correlated while S_R and $S_{350-400}$ were negatively correlated. In conclusion, S_R and $S_{275-295}$ increased with irradiation increments while $S_{350-400}$ decreased with irradiation increments.

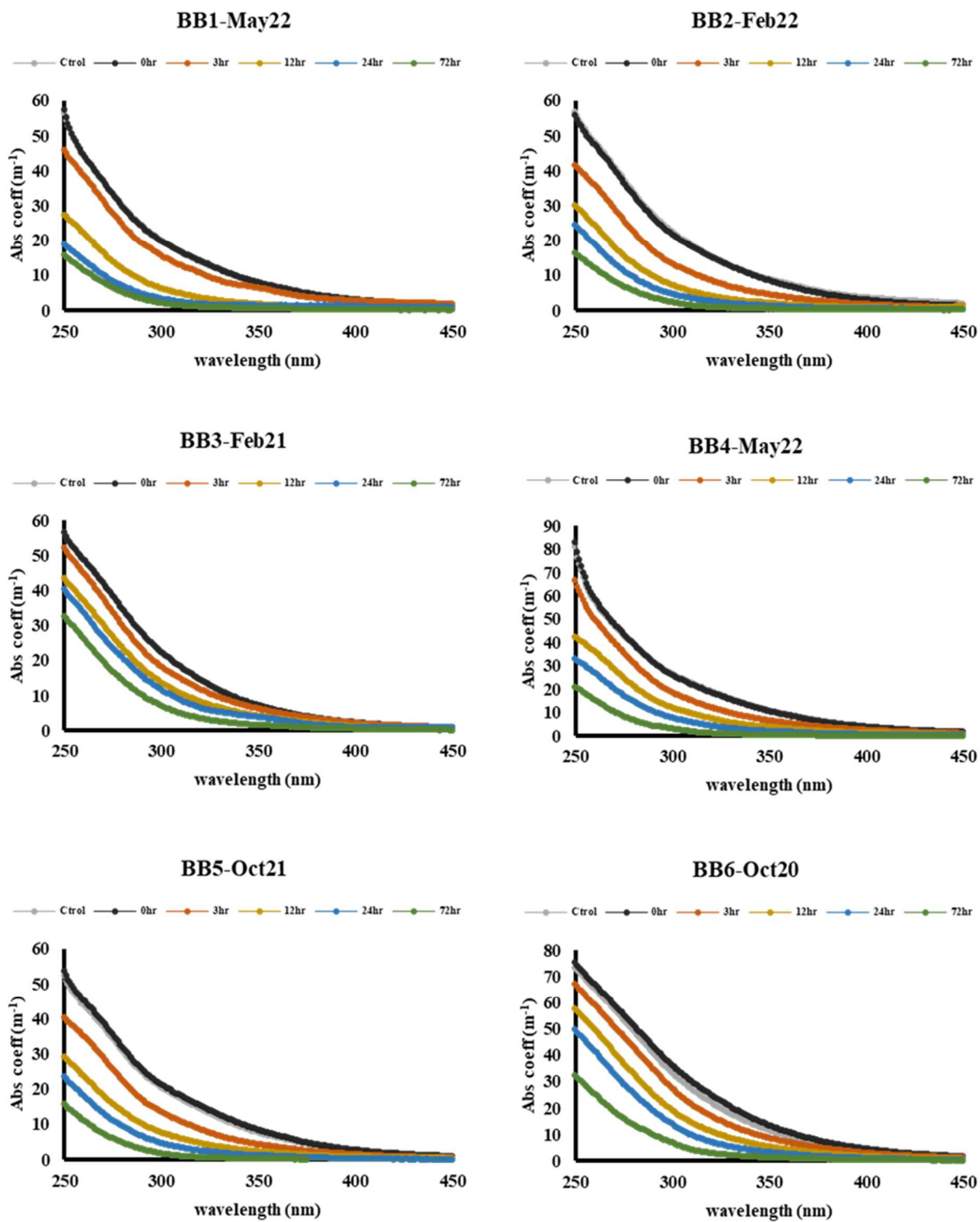


Figure 3.5.1. Absorption coefficient (m^{-1}) spectra of CDOM in porewaters with irradiation time increments.

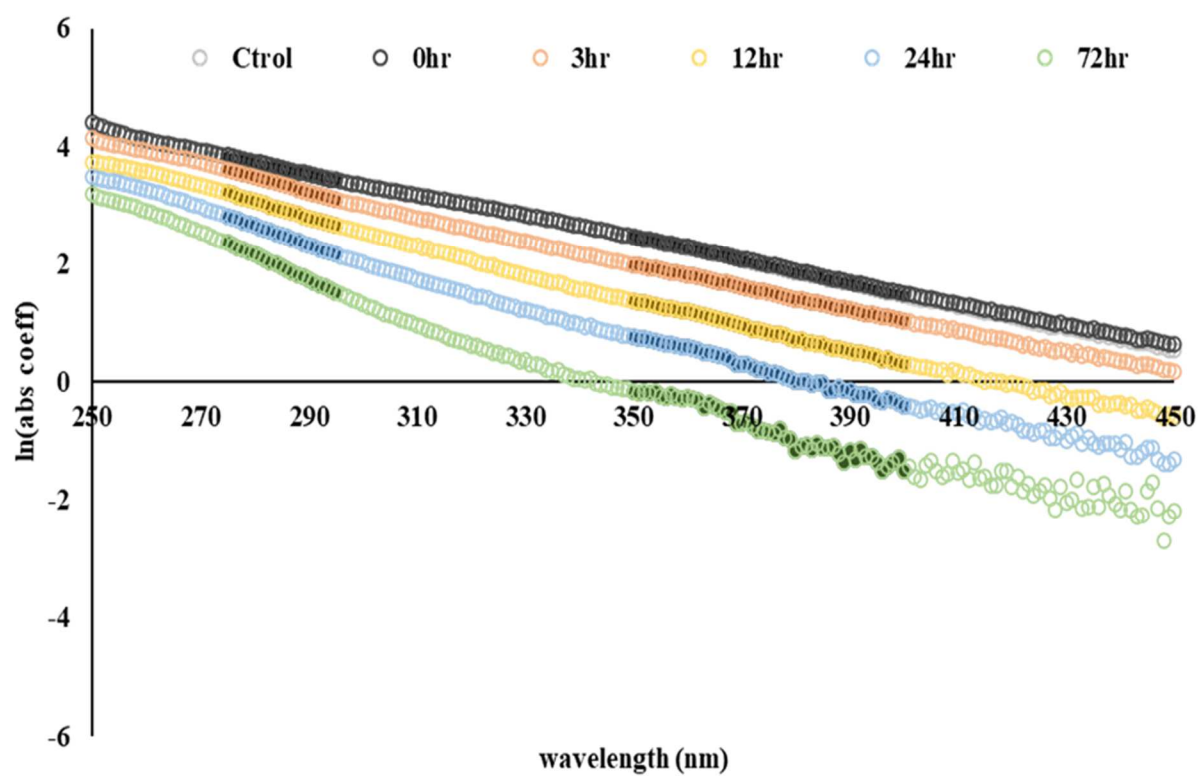


Figure 3.5.2. Natural logarithm of absorption coefficient ($\ln a$) spectra of CDOM in porewaters with irradiation time increments. Shaded areas were Spectral Slope, $S_{275-295}$ and $S_{350-400}$.

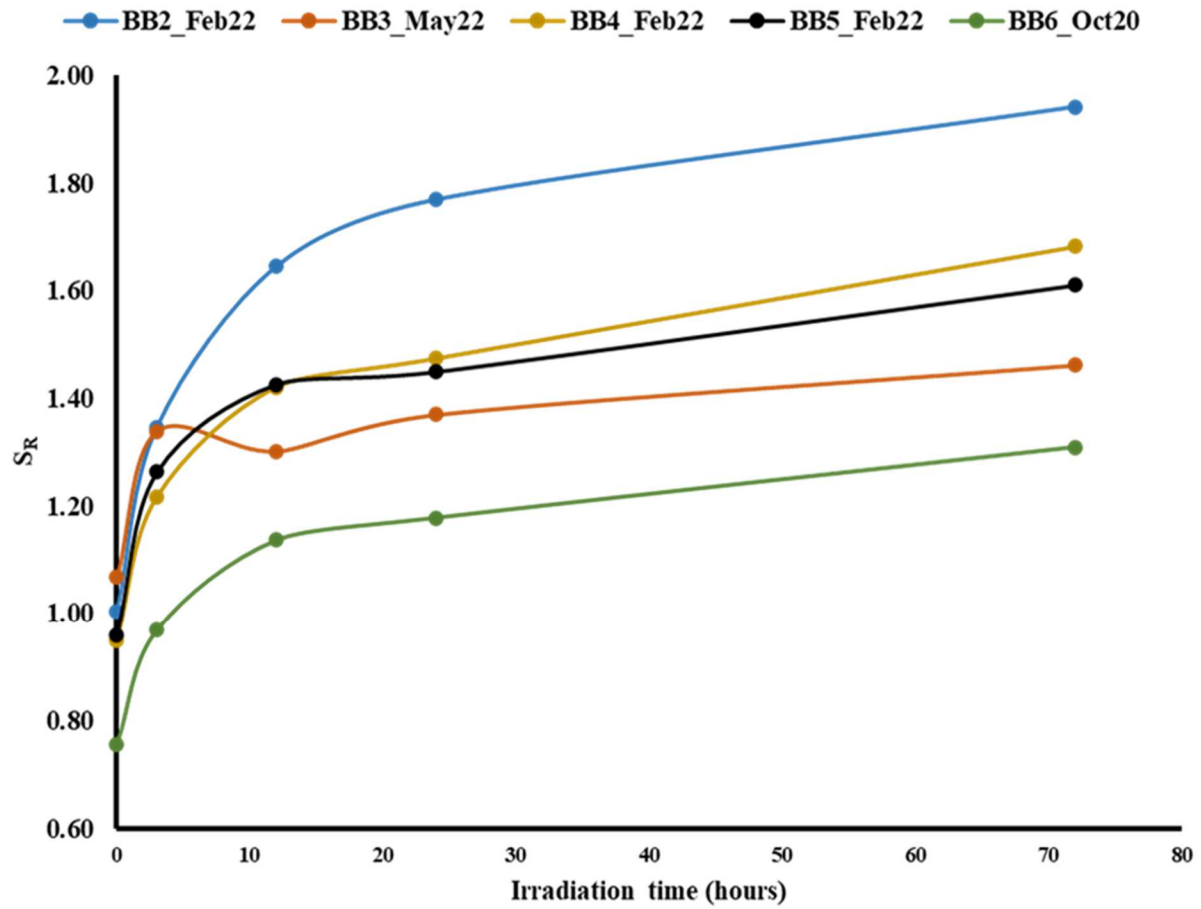


Figure 3.5.3. Slope Ratio (S_R) during irradiation time increments.

3.6. Photochemical & Seasonal changes in DOM Chemical Characterization by Mass

Spectrometry

3.6.1. Molecular composition

We analyzed the mass spectrometry data of the irradiation samples from three seasons: October 2020, February 2021, October 2021. In IC-MS/MS negative mode, 2360 compounds were detected while 2464 were detected in LC-MS/MS positive mode, and the combined total was 4824. In those 4824 compounds, we were able to assign a unique molecular formula to 3815 compounds. Out of 3815 compounds, CHONs were the most dominant with 2044 compounds (54%) followed by CHOs 801 (21%) (*Figure 3.6.1*). With respect to heteroatom composition, nitrogen, phosphorus, and sulfur-containing compounds contributed 70.2%, 7.5 %, and 1.4 % respectively to our DOM pool in irradiated DOM porewater.

3.6.2. Peptides and Deaminated Peptides

After combining both negative and positive detection modes, we structurally elucidated 97 compounds to be peptides and 581 compounds to be deaminated peptides based on our generated databases (678 total). Van Krevelen diagram (*Figure 3.6.2*) showed the distribution of the detected peptides and deaminated peptides by plotting the oxygen/carbon (O/C) ratio versus the hydrogen/carbon ratio (H/C). Peptides had the range of O/C from 0.2-0.64 and H/C from 1.2-2. Deaminated peptides had a range of O/C from 0.2-1 and H/C from 0.93-2. The deaminated peptides appeared to be more oxygenated than the peptides. Both shared the same H/C ratio.

3.6.3. Volcano analysis

Three volcano plots were generated to compare detected compounds between three seasons: Oct_20, Feb_21, and Oct_21 (*Figure 3.6.3a to 3.6.3c*). Compounds were significant to the right-hand region when their “Log2 Fold Change (right side/ left side)” (x axis) were greater

than 1, which meant right-side compounds were more intense at least twice than left-side compounds, and p-values were less than 0.05 (95% confidence level).

Volcano plots indicated 224 significant compounds for Oct_20 vs. 262 significant compounds for Feb_21, 246 significant compounds for Oct_21 vs. 107 significant compounds for Oct_20, and 158 significant compounds for Oct_21 vs. 51 significant compounds for Feb_21. Uniquely, 105 compounds were significant to only Oct_20, 50 compounds were significant to only Feb_21, and 61 compounds were significant to only Oct_21. Out of those 105 significant compounds of Oct_20, 36.5% were classified to be CHO, 36.5% CHON; in 50 significant compounds of Feb_21, 33.3% were classified to be CHO, 30.7% CHON; in 61 significant compounds of Oct_21, 22.4% were classified to be CHO, 51.7% CHON (*Figure 3.6.4*). The 4171 insignificant compounds were present in all three seasons.

Based on our generated database, we were able to structurally elucidate 4 peptides and 10 deaminated peptides that were significant to Oct_20, 2 peptides and 9 deaminated peptides significant to Feb_21, and 2 deaminated peptides (0 peptides) significant to Oct_21. The 595 insignificant peptides and deaminated peptides were present in all three seasons.

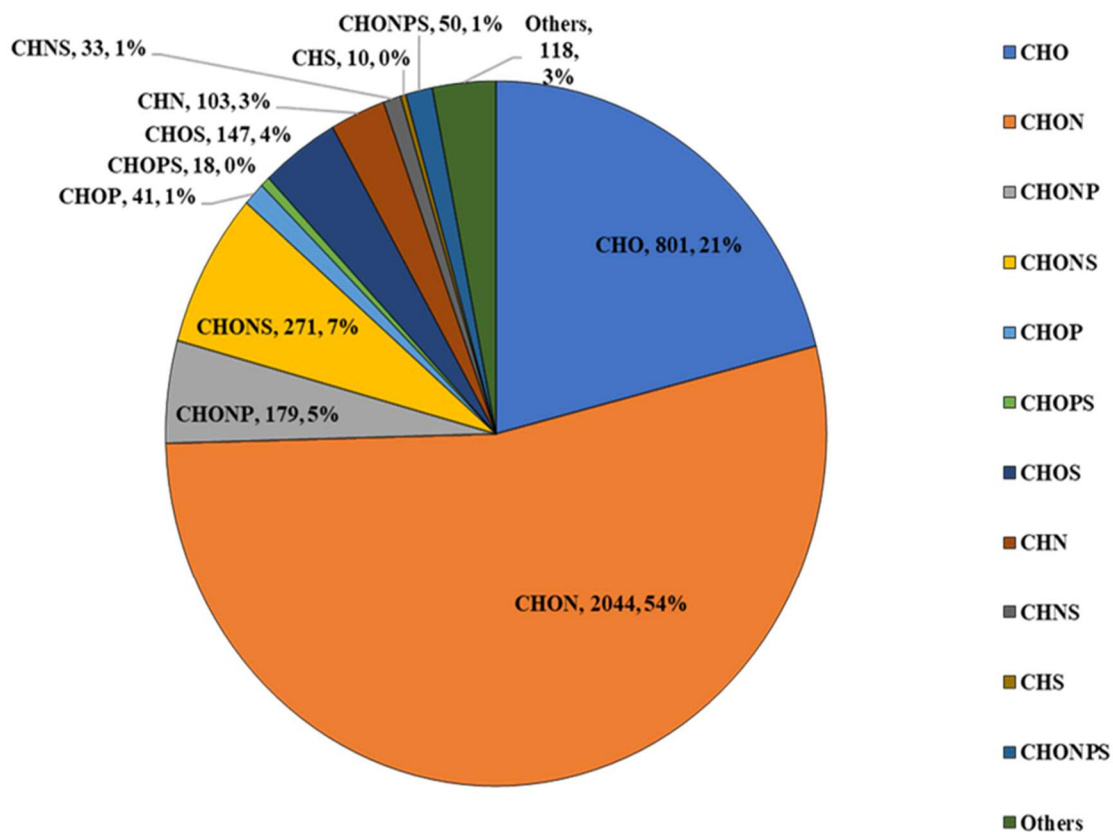


Figure 3.6.1. Classification of 3815 detected compounds with molecular formula assigned.

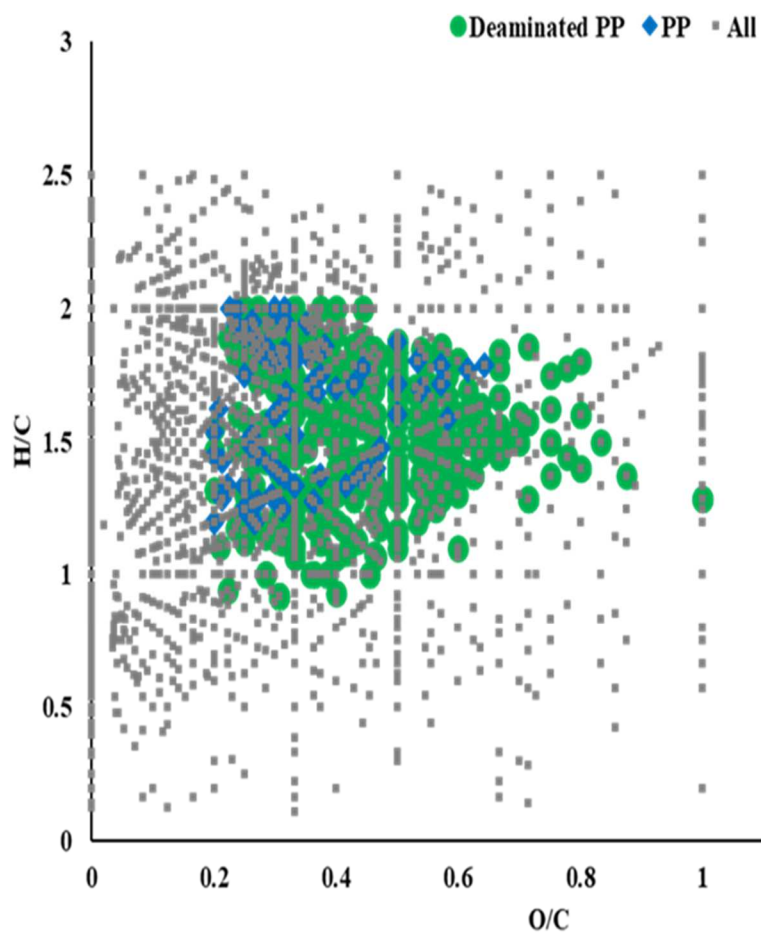


Figure 3.6.2. Van Krevelen diagram of assigned formulas of the pore water DOM. “x” axis represents oxygen/carbon ratio while “y” axis represents hydrogen/carbon ratio. “Grey” dots were all compounds with molecular formulas assigned. “Green” circles were confirmed to be deaminated peptides (581) while “Blue” squares were to be peptides (97).

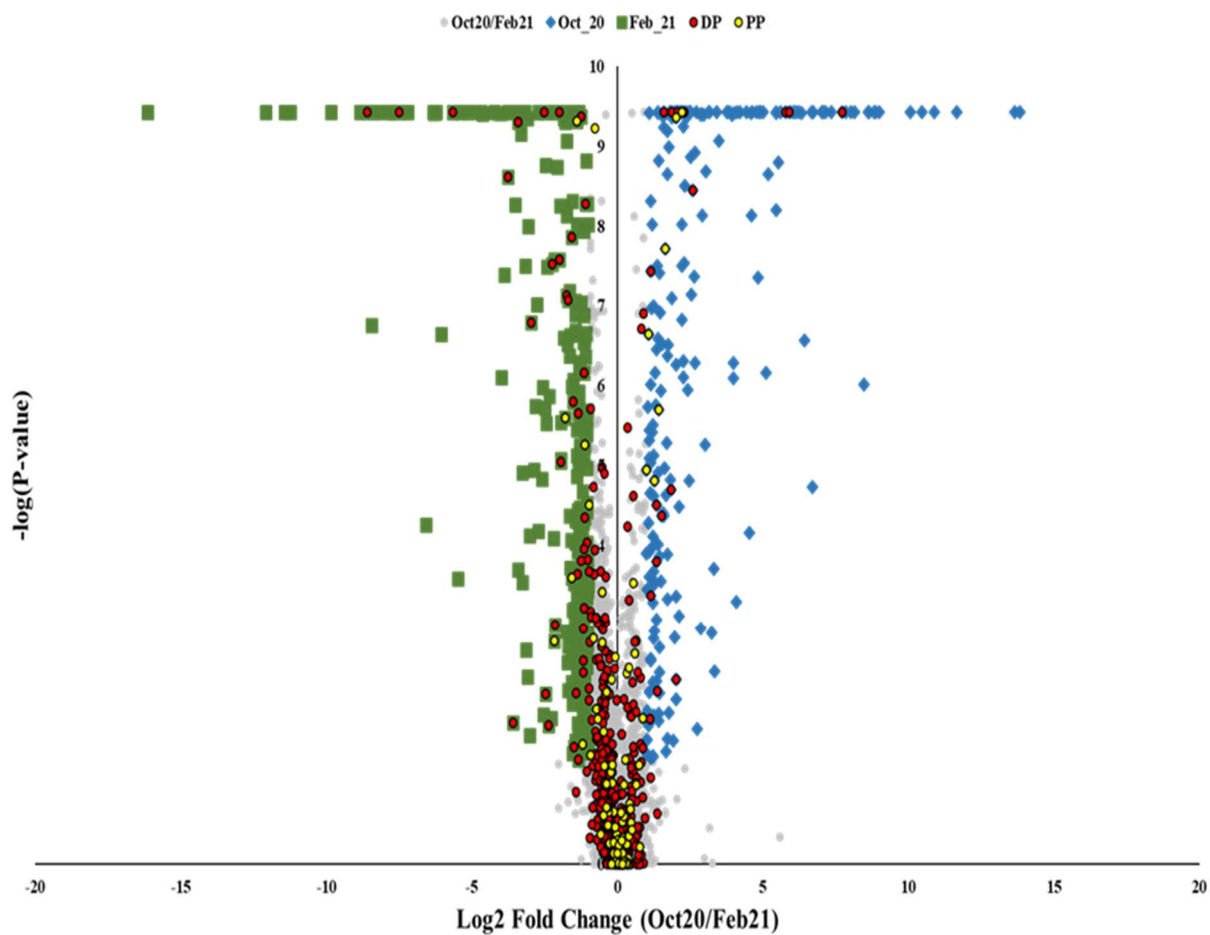


Figure 3.6.3a. Volcano plot of Oct_20 (right half) and Feb_21 (left half) detected compounds. “Blue” squares (224) represent significant compounds for Oct_20 and “Green” squares (262) represent significant compounds for Feb_21. “Grey” circles represent insignificant compounds that appeared equivalently in both seasons. “Yellow” circles are deaminated peptides and “Red” circles are peptides.

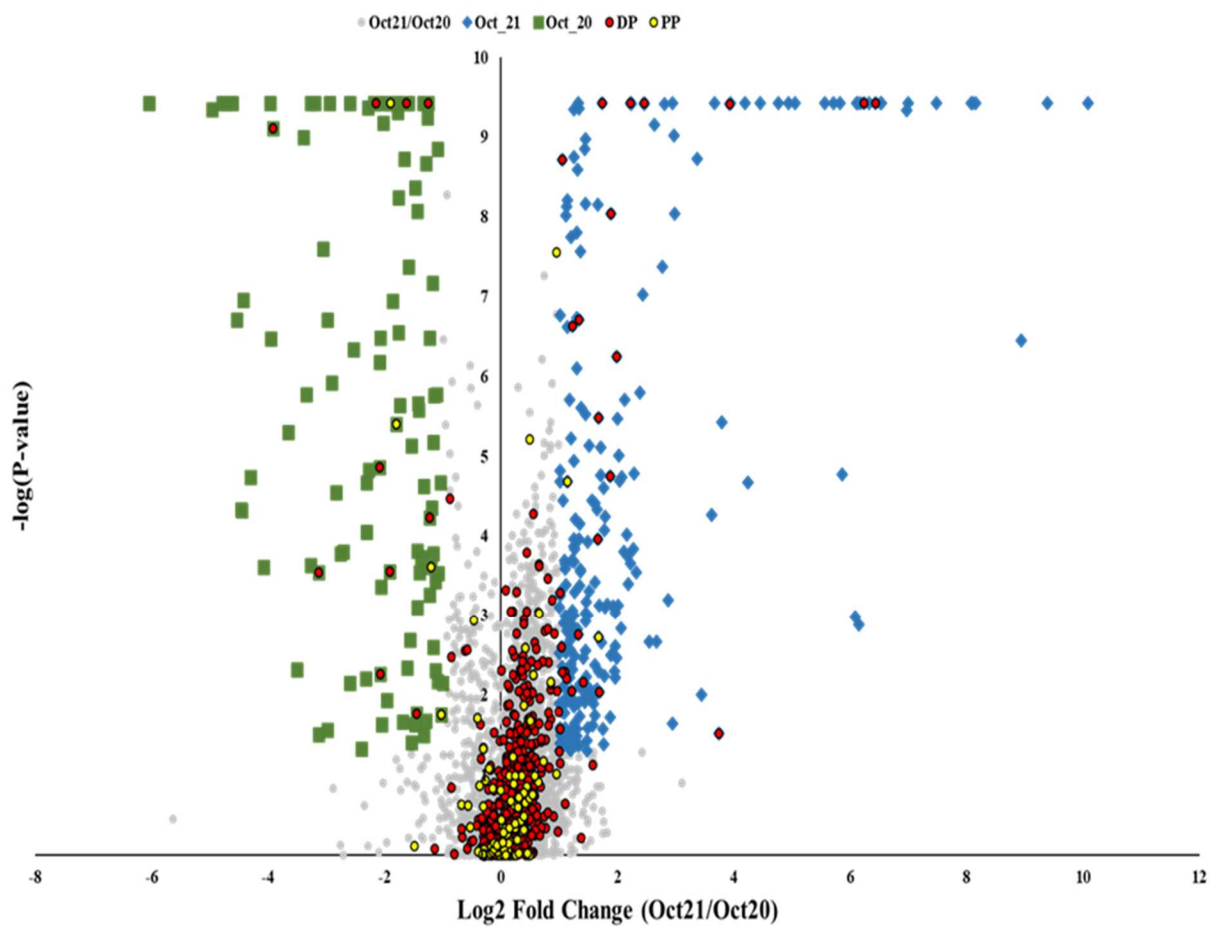


Figure 3.6.3b. Volcano plot of Oct_21 (right half) and Oct_20 (left half) detected compounds. “Blue” squares (246) represent significant compounds for Oct_21 and “Green” squares (107) represent significant compounds for Oct_20. “Grey” circles represent insignificant compounds that appeared equivalently in both seasons. “Yellow” circles are deaminated peptides and “Red” circles are peptides.

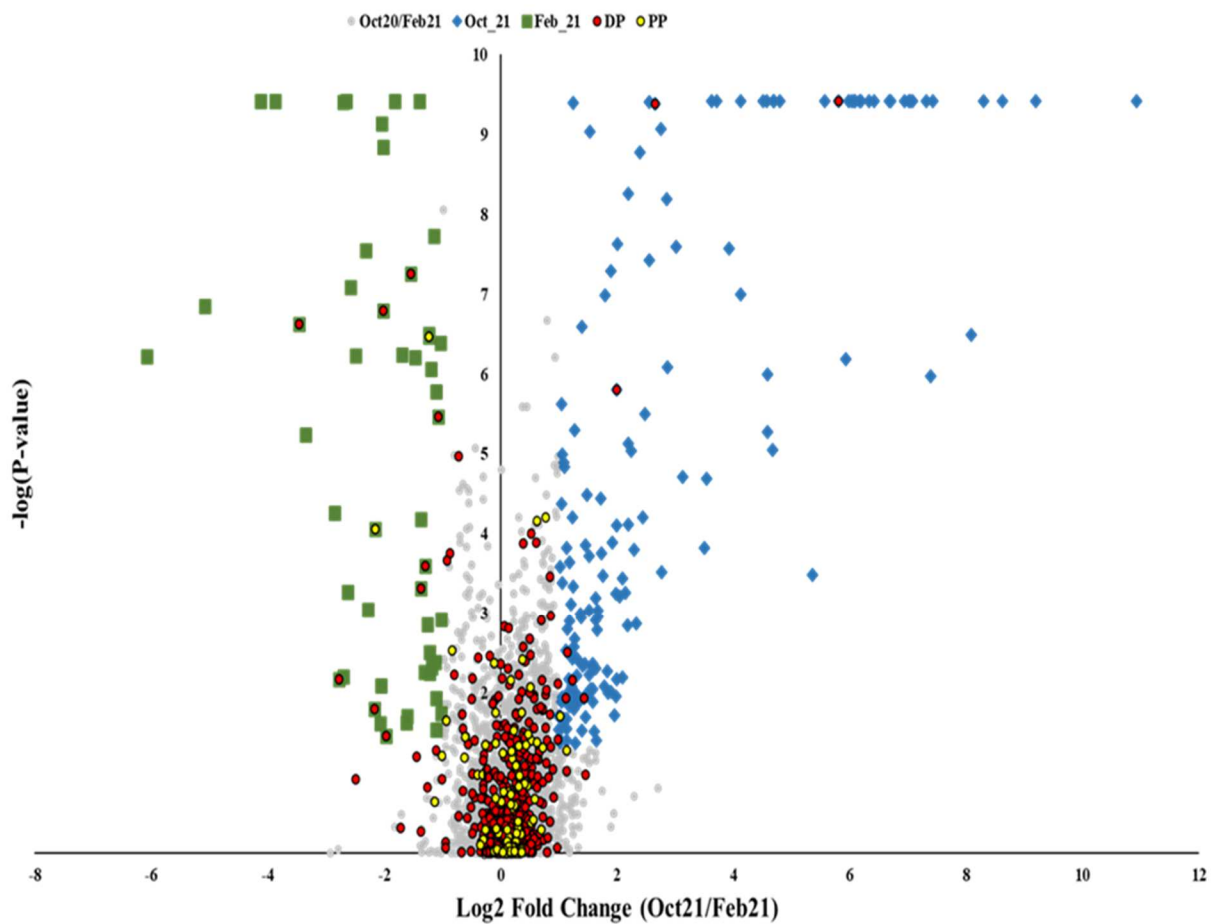


Figure 3.6.3c. Volcano plot of Oct_21 (right half) and Feb_21 (left half) detected compounds. “Blue” squares (158) represent significant compounds for Oct_21 and “Green” squares (51) represent significant compounds for Feb_21. “Grey” circles represent insignificant compounds that appeared equivalently in both seasons. “Yellow” circles are deaminated peptides and “Red” circles are peptides.

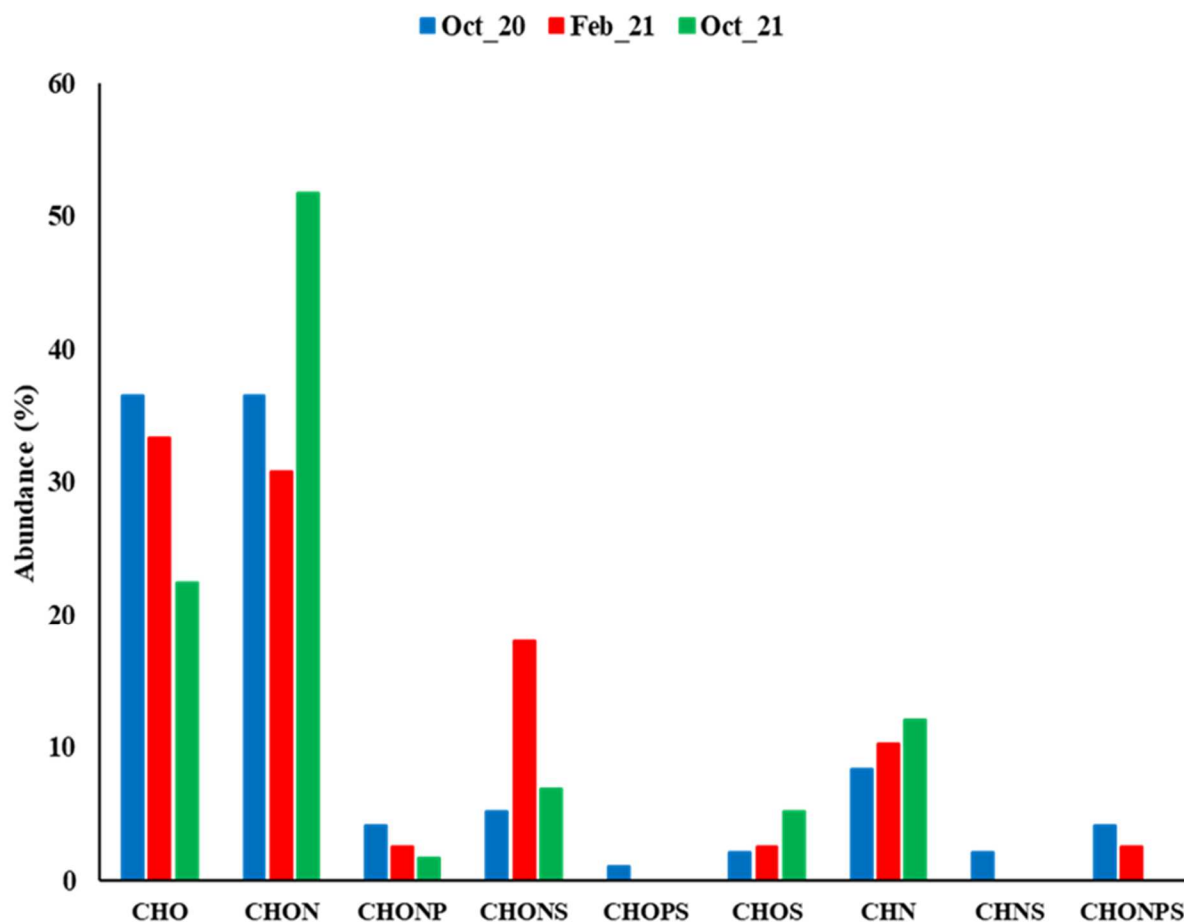


Figure 3.6.4. Classification of significant compounds in each season.

4. DISCUSSION

4.1. Factors controlling the ammonium benthic flux to the water column in Baffin Bay

The diffusive fluxes were significantly dependent on the sediment porosity and changes in the ammonium depth profile. The lowest porosity was at BB1 with an average of 0.35, which resulted in BB1 to have the lowest diffusion rate for porewaters NH_4^+ to the water column. These spatial porosity differences in Baffin Bay are due to the spatial variation of sedimentation type. The type of Baffin Bay's sediment ranged from sandy spits and serpulid reefs, clayey-silt, muddy sand to black mud (*Figure 4.1.1*). BB1 is located on the upper bay that is characterized by sandier facies sediment, which has low porosity. On the other hand, stations BB3 and BB4, which has the highest porosity of 0.7, are in the center of the bay and characterized by black mud sedimentation (Simms et al., 2010; Lopez et al., 2020). Based on sedimentation type, sampling stations were categorized into two groups: 1) Branched stations (BB1, BB2, BB5) where the sediments are coated grains and 2) Center stations (BB3, BB4, BB6) where the sediments are black mud. Center stations have higher porosity than branched stations due to differences in sedimentation type.

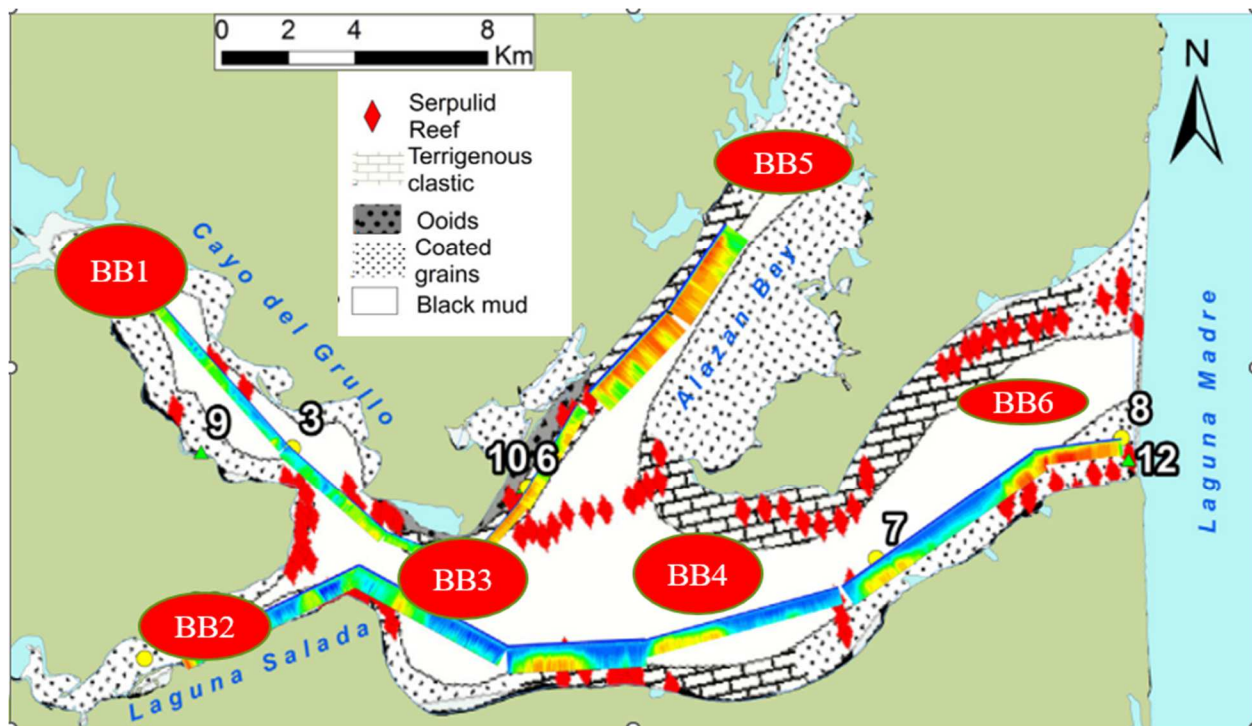


Figure 4.1.1. Sedimentation type of Baffin Bay (Lopez et al., 2020).

The other significant factor responsible for the benthic flux difference between stations was the instantaneous change of concentrations along the depth profile. The steeper the slope and the higher the $[\text{NH}_4^+]$ diffused to the water column, the higher the flux. In branched stations, BB1 and BB5 had low porewater $[\text{NH}_4^+]$ with an average of 411 & 381 $\mu\text{mol.L}^{-1}$, respectively and low $[\text{NH}_4^+]/\text{depth}$ with an average of 29 and 21 $\mu\text{mol.L}^{-1}.\text{cm}^{-1}$, respectively. Therefore, BB5 and BB1 had the lowest fluxes with 102 and 53 $\mu\text{mol.m}^{-2}.\text{day}^{-1}$, respectively. BB2 also had low fluxes of 108 $\mu\text{mol.m}^{-2}.\text{day}^{-1}$ due to low porosity and low $[\text{NH}_4^+]/\text{depth}$ of 31 $\mu\text{mol.L}^{-1}.\text{cm}^{-1}$. In center stations, BB3 had the highest fluxes of 347 $\mu\text{mol.m}^{-2}.\text{day}^{-1}$ due to its highest porosity and high average $[\text{NH}_4^+]/\text{depth}$ of 59 $\mu\text{mol.L}^{-1}.\text{cm}^{-1}$, especially in Feb_22. BB6 had high fluxes of 215 $\mu\text{mol.m}^{-2}.\text{day}^{-1}$ due to its high average $[\text{NH}_4^+]/\text{depth}$ of 57 $\mu\text{mol.L}^{-1}.\text{cm}^{-1}$, even though its porosity was not significantly high (0.55). Similarly, BB4 had higher fluxes of 191 $\mu\text{mol.m}^{-2}.\text{day}^{-1}$ due to its highest porosity of 0.7 even though its average $[\text{NH}_4^+]/\text{depth}$ was only 31 $\mu\text{mol.L}^{-1}.\text{cm}^{-1}$.

Seasonally, BB6 had its fluxes drop dramatically in Jun_21 after the rainfall in May_21 due to the drop in $[\text{NH}_4^+]$ (significant $p < 0.05$) (Figure 3.3.1 & 3.2.3). The dramatic drop in $[\text{NH}_4^+]$ at BB6 in Jun_21 after the heavy rainfall in May_21 was due to freshwaters being brought in to flush the bay ecosystem leading to a decrease in salinity from above 40 to 16 ± 8 and porewater $[\text{NH}_4^+]$. The dramatic drop in porewater $[\text{NH}_4^+]$ was also predicted to have been impacted by an internal force such as submarine groundwater discharge (SGD). On the other hand, it was previously reported at Baffin Bay that there was a decline in chlorophyll abundance (*A. lagunensis*) as salinity decreased after a heavy rainfall in Spring 2015 (Cira & Wetz 2019). We anticipated that a precipitation of rainfall or melted ice would bring in freshwaters and flush away all the residuals in Baffin Bay such as nutrients, phytoplankton or other autotrophs. Lowering the primary production in the bay will lead to lower organic matter sedimentation rates and affect the early diagnosis rate and decrease the ammonia microbial production in the sediment. Also, BB6 was the southernmost and furthest away from the three input branches: Alazan Bay on the north (BB5), Cayo del Grullo (BB1) and Laguna Salada (BB2); therefore, it received the least nutrient inputs and the most freshwaters. In conclusion, the rainfall in May_21 was expected to lower salinity and porewater $[\text{NH}_4^+]$ and remove the algal blooms at BB6.

From a seasonal perspective, Baffin Bay had two-fold changes in the seasonal benthic fluxes. The lowest was $124 \pm 79 \mu\text{mol.m}^{-2}.\text{day}^{-1}$ in May_22 and the highest was $244 \pm 254 \mu\text{mol.m}^{-2}.\text{day}^{-1}$ in Feb_22 (Table 3.3). Feb_22 with the highest average $[\text{NH}_4^+]/\text{depth}$ of $65 \mu\text{mol.L}^{-1}.\text{cm}^{-1}$ accounted for the highest flux and could indicate a large organic matter sedimentation rate from detritus phytoplankton or other photoautotrophs on surface water to the sediment after Oct_21. In a study of algal blooms in Baffin Bay, Cira and Wetz 2019 showed that chlorophyll population (*A. lagunensis*) peaked in the summer months and declined in the winter months. Hence, primary

productivity was predicted to be high from October 2021 to February 2022 and might account for the large biomass accumulation in the sediment.

In 1990, Baffin Bay was reported to have a primary production rate (PPR) at $\sim 1\text{--}132\text{ mg C}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ or $83\text{--}110\text{ }\mu\text{molC}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (Blanchard and Montagna 1995). Assuming the Redfield ratio 106C : 16N, it was converted to $12.5\text{--}16.6\text{ }\mu\text{molN}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. Based on this PPR, the benthic flux of ammonia could supply 992 – 1470 % of the N nutrient needed to sustain this level of PPR. Other studies had reported higher benthic fluxes on other Gulf of Mexico estuaries than our measured fluxes. For example, West Florida estuaries – nearshore Gulf of Mexico NH_4^+ flux was $430\text{--}3360\text{ }\mu\text{molN}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (Dixon et al., 2014), Galveston Bay NH_4^+ flux was $240\text{--}350\text{ }\mu\text{molN}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (Warnken et al., 2000), and Apalachicola Bay – northeastern Gulf of Mexico flux was approaching $3000\text{ }\mu\text{molN}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (Mortazavi et al., 2000). In the other estuarine systems, Great Bay estuary – New Hampshire had NH_4^+ flux at $1400\text{ }\mu\text{molN}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (Percuoco et al., 2015), Curonian lagoon – Lithuania was at $210\text{--}2950\text{ }\mu\text{molN}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (Zulius et al., 2012), and the ammonium flux in Baltic Sea, a semi-enclosed shelf sea, was -40.5 and $1370.1\text{ }\mu\text{molN}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (Lengier et al., 2021). We attributed the lower average benthic flux in Baffin Bay relative to other estuary ecosystems to two factors: 1) The wide spatial sedimentation types in the bay. As some parts were characterized by black mud (center of the bay), in other regions, the sediment had sandy sediment 2) The bay ecosystem was under abnormal conditions during our sampling seasons (results of the heavy rainfall in May_21), as reflected in relatively low salinity values (salinity ranges from 10s- 20s) in most of the seasons than the average salinity of the bay (~ 45) and occasionally reach up to 70 in hypersaline condition (Wetz et al., 2017, 2019). In addition, some studies also showed seasonal changes of the ammonium benthic flux. For example, Dixon et al., 2014 showed a decrease in fluxes from 2007 – 2009 in Tampa Bay, Sarasota Bay, and Sarasota

offshore, but an increase in Charlotte Harbor. The NH_4^+ flux was reported to be low in cold-weather months but high when temperatures rose in the summer (Mortazavi et al., 2000; Warnken et al., 2000; Zilius et al., 2012; Percuoco et al., 2015).

To estimate the N loading from NH_4^+ benthic flux for the entire Baffin Bay, the benthic ammonium fluxes in $\mu\text{mol. m}^{-2}.\text{day}^{-1}$ were multiplied by 60% of the Baffin Bay area for center stations ($0.6 \times 219 \text{ km}^2$) and 40% of the Baffin Bay area for branched stations ($0.4 \times 219 \text{ km}^2$) (Figure 4.1.2). On average, benthic $[\text{NH}_4^+]$ flux was the highest in Feb_22 with $9556 \pm 11219 \text{ mol.day}^{-1}$ followed by Feb_21, Jun_21, Oct_20, and Oct_21 at 7746 ± 7236 , 7480 ± 8276 , 6750 ± 8510 , and $5142 \pm 4009 \text{ mol.day}^{-1}$, respectively. May_22 produced the lowest flux at $4916 \pm 3750 \text{ mol.day}^{-1}$. In comparison with other potential N loading sources to the Baffin Bay, we extrapolated the N loading of atmospheric deposition (in upper Laguna Madre) and the agricultural runoff, urban nonpoint sources to the region measured by Castro et al., (2003) to estimate the N-loading to the entire bay from these two sources. Based on these calculations, the atmospheric deposition delivered $857 \text{ mol-N.day}^{-1}$ from the upper Laguna Madre to the entire Baffin Bay, while the agricultural runoff estimated the N-loading to the entire bay to be $3000 \text{ mol.day}^{-1}$. This indicated that our benthic flux delivered N loading in a 2-3 higher order of magnitude as the atmospheric deposition and agricultural runoff.

Benthic ammonium flux served as a significant source of inorganic nutrients that contributed to the water column along with other nutrient sources to feed photoautotrophs such as phytoplankton. Baffin Bay is a unique closed system of marine ecosystems with little inputs of terrestrial nutrients; therefore, primary production on the surface water is exclusively dependent on ammonium benthic flux and other nonpoint sources (e.g., atmospheric deposition and agricultural runoff). However, ammonium concentrations in surface waters of Baffin Bay are

significantly low ($< 5 \mu\text{M}$) which suggests that the consumption on surface water is highly demanded. Estimating these fluxes is crucial as it serves as another ammonium source to the water column in the bay ecosystem. Phytoplankton and other autotrophs require ammonium and other nutrients in an oxic environment to photosynthesize on the surface water. However, excessive nutrients can also cause eutrophication leading to hypoxia which kills fish and marine animals and is accounted for the experience with harmful brown tide bloom which had been existing and will be lasting for decades in Baffin Bay.

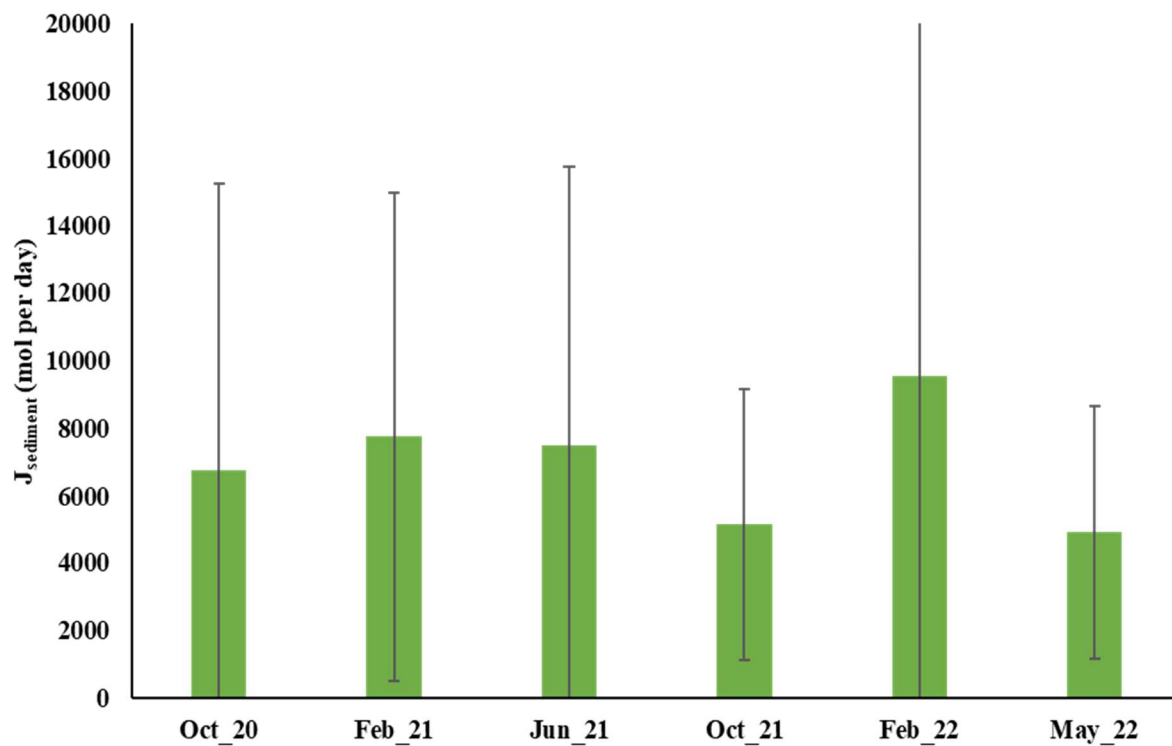


Figure 4.1.2. Average benthic ammonium fluxes (mol per day) of Baffin Bay.

4.2. Photo-ammonification rate from benthic DON

The rate of ammonium photo-production was shown to be positively correlated to the ammonium concentration in porewater. BB5 had the lowest $[\text{NH}_4^+]$ in porewater ($381 \mu\text{mol.L}^{-1}$) and the lowest $[\text{NH}_4^+]$ rate ($0.11 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$). At BB2 and BB3, Feb_22 had the highest $[\text{NH}_4^+]$ in sediment porewater (*Figure 3.2.3*) and the highest $[\text{NH}_4^+]$ rate (*Figure 4.2*). At BB1, the three seasons of Oct_21, Feb_22, and May_22 showed higher porewater $[\text{NH}_4^+]$ as well as $[\text{NH}_4^+]$ photo-production rate than Feb_21. At BB6, the first two seasons Oct_20 and Feb_21 had high porewater $[\text{NH}_4^+]$ but did not have great photo-production rate due to technical and instrumental error at the moment of experiment. During the run of samples in Oct_20 and Feb_21, the solar simulated encountered overheat issue and fuse malfunction which led to the stoppage of the instrument in the middle of the run. Samples in Oct_21, Feb_22, and May_22 were successfully run without any error so data was more trusted. In summary, photo-ammonification rate of Baffin Bay sediment porewater ranged from 0.038 - $0.361 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$. Other studies have shown similar rate; for example, photo-ammonification rate ranged from 0.23 - $0.36 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$ for different river water samples (Bushaw et al., 1996) or much lower rate at $0.015 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$ (river water samples, (Morell & Corredor, 2001), $0.006 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$ for Baltic Sea porewater, (Vahatalo&Zepp, 2005). On the other hand, photo-ammonification rate of surface water in Baffin Bay was reported to range from $0.034 - 0.086 \mu\text{mol.L}^{-1}.\text{hour}^{-1}$ (Shrestha, 2022), or up to $0.032 \mu\text{mol L}^{-1}\text{h}^{-1}$ in the coastal lagoon of Hog Island Bay (Buffam & McGlathery, 2003). We concluded that photo-ammonification of anoxic sediment porewater was 12 - 320 % higher than of oxic surface water in Baffin Bay. Exposure to natural sunlight leading to natural degradation of CDOM in surface water might account for the lower photo-ammonification rate on surface water. Photo-ammonification rates have also been reported to be different with seasonal changes and rainfall

(Yang et al., 2021), or sample type. For example, humic substances (soil samples) had high photo-ammonification rate of $0.34 \mu\text{mol L}^{-1}\text{h}^{-1}$ (Li et al., 2020).

Dissolved organic nitrogen (DON) was expected to degrade and release ammonium. [DON] and $[\text{NH}_4^+]$ were shown to be positively correlated with each other (unpublished data; Abdulla et al., 2018). As $[\text{NH}_4^+]$ was excessive in sediment porewater, DON was expected to be enriched. After DON diffused upwards and entered the water column, it became exposed to UV-Vis electromagnetic radiation in sunlight and started to degrade to release inorganic nutrients that feed autotrophs. Photo-ammonification by UV-Vis radiation along with ammonium benthic flux from sediment enriched the nutrient level in surface water and served as a food web for microbes and phytoplankton or other plants to grow. This significant source of bioavailable N may contribute to brown tide bloom and hypoxia conditions in Baffin Bay.

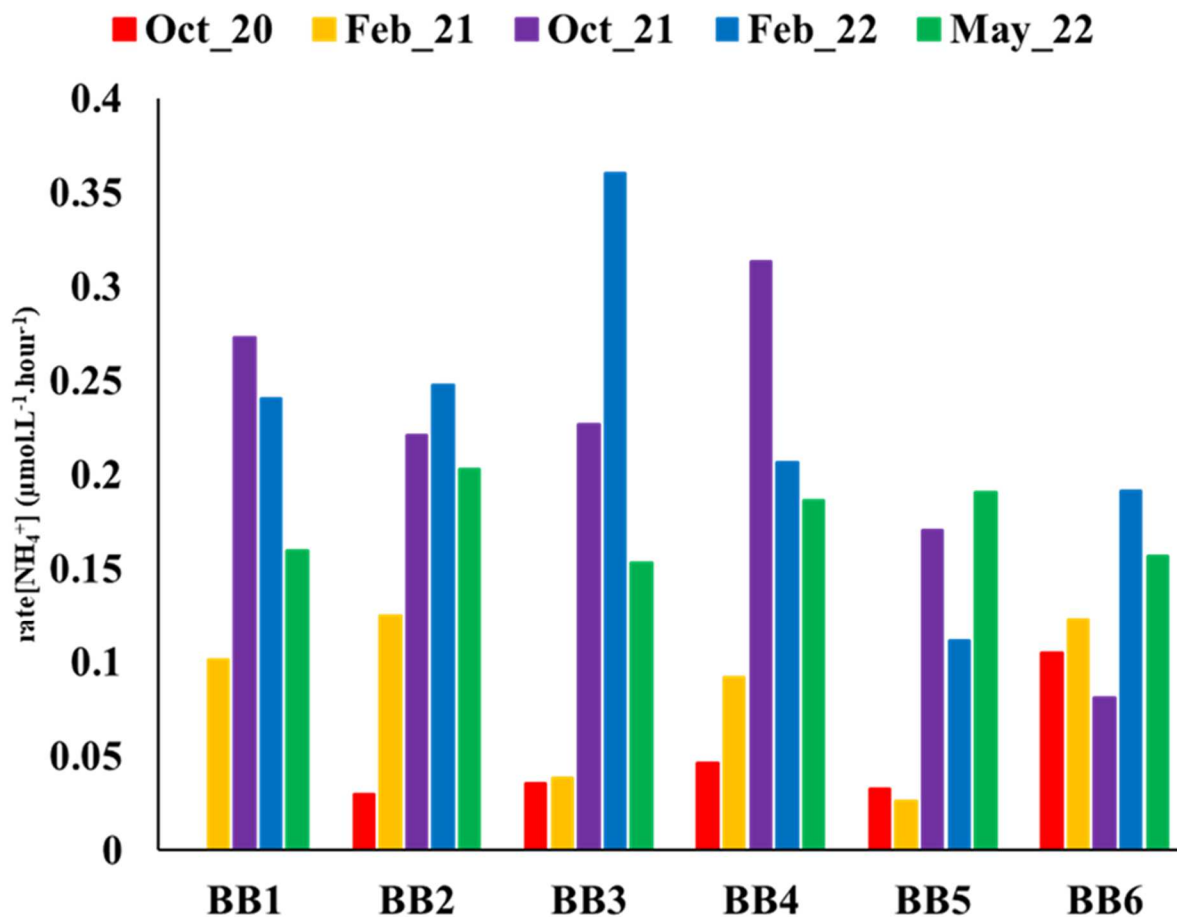


Figure 4.2. Rate of photo-ammonification (mole NH_4^+ per liter per hour) from porewaters at six stations of Baffin Bay during five sampling seasons.

4.3. Photo-degradation of CDOM and photo-ammonification

The chromophoric DOM (CDOM) absorbed visible and UVA and B radiation (300-400nm) from the Xenon lamp. The absorption coefficient at 300 nm (a_{300}) decreasing along irradiation increments indicated a degradation in the chromophoric portion of marine DOM. The absorption of electromagnetic frequency by CDOM degraded its organic structure and led to the photo-transformation of organic matter in the surface water (Del Vecchio and Blough 2002). Previous studies also suggested that photobleaching was a major factor that destroyed chromophores associated with higher molecular weight CDOM causing a breakdown to low

molecular weight CDOM (Moran and Zepp 1997; Helms et al., 2008; Mesfioui et al., 2015). In addition, Helms et al., 2008 also proved that $S_{275-295}$ and S_R were inversely related to the molecular weight of the CDOM. Our calculated data indicated that $S_{275-295}$ and S_R were positively correlated to each other when both increased with irradiation time increments (Pearson slope $p < 0.05$) while $S_{350-400}$ and S_R were negatively correlated to each other when $S_{350-400}$ decreased with irradiation increments ($p < 0.05$). It also showed the negative correlation between a_{300} and S_R (Pearson $R^2 > 0.80$, $p < 0.05$). Degraded CDOM (due to decreasing a_{300}) lowered its molecular weight (due to increasing S_R) and reduced its ability to absorb UV-Vis radiation, and further affected depolymerization and adsorption of DOM while high-molecular-weight DOM exhibited more benefit to bind cadmium than low-molecular-weight DOM (Li et al., 2019). We concluded that the degradation of chromophores associated with high-molecular-weight CDOM during photobleaching transformed a significant portion of the CDOM from the high-molecular-weight pool to the low-molecular-weight pool.

The decreasing a_{300} and increasing $[NH_4^+]$ along with irradiation time showed strong negative correlation between each other (Pearson $R^2 > 0.72$, slope p -value < 0.05). Also, we estimated the correlation between photo-production rate of ammonium and a_{300} at 0-hour in each season of Baffin Bay and found that Oct_20 and Feb_22 showed significant positive correlation (Pearson $R^2 > 0.68$, slope p -value < 0.05). BB3 and BB5 also showed significant positive correlation throughout five seasons (Pearson $R^2 > 0.85$, slope p -value < 0.05). This resulted in the capability of DOM to photo produce ammonium with high absorption coefficient. In conclusion, a strong negative correlation between NH_4^+ photo-production and CDOM a_{300} indicated the photo-degradation of CDOM and the photo-ammonification due to photobleaching.

4.4. Amino acids making up the detected peptides and deaminated peptides

To determine the structural composition of microbial peptides and deaminated peptides, we analyzed the relative abundances of individual amino acids used to build the peptide bond. The microbial proteins' pool indicated high abundances of glycine (~14%), alanine, lysine, proline, serine, glutamine and valine (>7%). On the other hand, glutamic acid, methionine, tryptophan, and arginine contributed with low abundances (*Figure 4.4*). Alanine was also found to be rich in microbial soil with more than 10% relative abundance along with glutamic acid (>10%) while methionine and cysteine typically were the lowest abundance amino acids (Moe, 2013). Tyrosine, glutamine, and asparagine were highly abundant in anoxic sediment porewaters of Santa Barbara Basin while tryptophan, histidine and methionine showed very low abundances (Abdulla, 2018). The amino acid composition of these peptides and deaminated peptides may account for their incomplete hydrolysis to free amino acids and oxoacids, therefore making them refractorily accumulated in sediment.

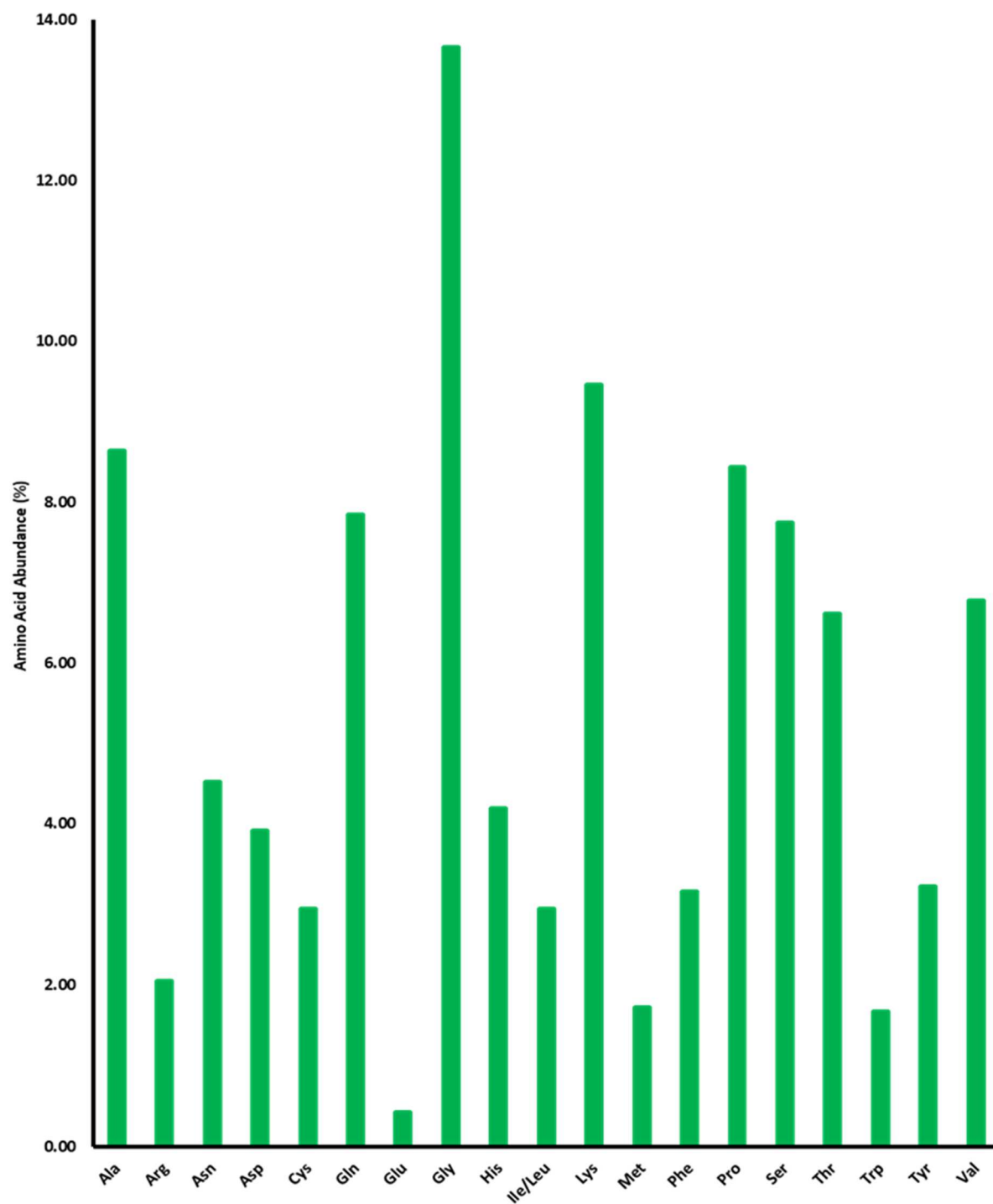


Figure 4.4: Relative abundance of individual amino acids in peptides and deaminated peptides detected in Baffin Bay porewaters.

4.5. Irradiation effects on molecular composition and chemical structures

In 4824 detected compounds, 2500 showed significant changes in concentration (95% confidence level of linear regression slope $\neq 0$) in which 1106 compounds only increased with irradiation time, 1052 only decreased with irradiation time, and 342 showed both increasing and decreasing concentration. In 1394 pre-irradiation compounds, those with decreasing concentrations over irradiation time, CHON made up 50%, followed by CHO, CHONS, and CHONP with 25%, 8%, and 7%, respectively. Nitrogen-containing compounds accounted for 52%, followed by sulfur-containing compounds and phosphorus-containing compounds with 12% and 7%, respectively. In 1448 post-irradiation compounds, those with increasing concentrations over irradiation time, CHON made up 50%, followed by CHO, CHONS, and CHONP with 26%, 8%, and 6%, respectively. Nitrogen-containing compounds accounted for 56%, followed by sulfur-containing compounds and phosphorus-containing compounds with 12% and 7%, respectively. The similar composition did not give us any clue about the role of UV-Vis radiation on these organic matters. Therefore, structural elucidation by mass spectrometry would open a brighter view to these structures.

In 1394 pre-irradiation compounds detected, 164 were confirmed to be peptides or deaminated peptides and 245 peptides or deaminated peptides were confirmed from 1448 post-irradiation compounds. The amino acid components of these peptides and deaminated peptides were examined for composition analysis (*Figure 4.5*). Tryptophan, tyrosine, and cystine-containing peptides/deaminated peptides degraded over irradiation time increments while valine, threonine, and serine-containing compounds concentrated over time. From a structural point of view, the degrading peptides/deaminated peptides contained 81 ring structures and 31 conjugated double-bond structures. From an amino-acid-with-ring-structure point of view, compounds with

proline contributed 38%, histidine 22%, tyrosine 18%, phenylalanine 16%, tryptophan 16%, and cystine 2% (*see Sup. Mat.*). Note that the sum of contribution percentage exceeded 100% due to multiple appearances of an amino acid within one peptide/deaminated peptide structure.

Chromophoric amino acids presented in proteins were tryptophan (Trp), tyrosine (Tyr), phenylalanine (Phe), histidine (His), cysteine (Cys) and cystine according to Davis & Truscott 2001. These chromophoric amino acids absorbed radiation with wavelength > 230 nm while all other major amino acids did not absorb significantly in this region. Peptide bond exhibited a weak absorption at 210-220nm; therefore, chromophoric amino acids were responsible for absorbing UVA-Vis radiation. The photo-oxidation of dissolved organic matter could happen in a direct or indirect way. In conclusion, the molecular composition of CDOM did not account for the photo-transformation of DON hence molecular structures were elucidated to provide a brighter view to these refractory peptides and deaminated peptides. More studies need to be conducted to have a better understanding of the transformation pathways of peptides/ deaminated peptides to free amino acids, organic acids.

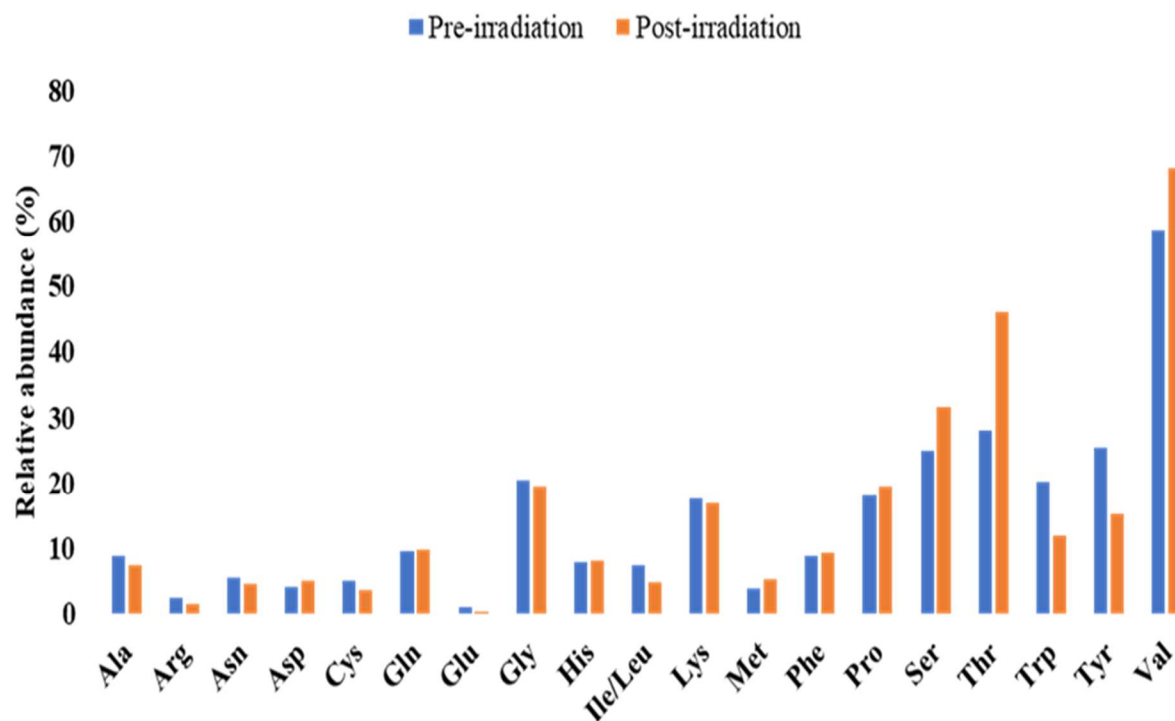


Figure 4.5. Relative abundances of amino acids that made up pre-irradiation and post-irradiation peptides and deaminated peptides.

5. CONCLUSION

The study suggested ammonium benthic fluxes served as a major source of inorganic nutrients that contributed to the Baffin Bay water column along with other nutrient sources to feed photoautotrophs such as phytoplankton. In addition to the benthic flux, photo-ammonification of porewater DON was a significant source of ammonium to the water column when porewater DON exit the sediment to diffuse to the water column and experience the exposure to sunlight radiation. In the water column, chromophoric DOM absorbed sunlight radiation then degraded to lower molecular weight CDOM and released ammonia, deaminated peptides, free amino acids, and organic acids. CDOM with aromatic rings or conjugated double bonds were responsible for absorbing sunlight and shielding biota from harmful UV radiation. Peptides and deaminated peptides with chromophoric amino acids such as tryptophan, tyrosine, proline, phenylalanine, histidine, and cystine degraded along with irradiation time increments. Therefore, more studies need to be conducted to have deeper understanding of the mechanisms that transformed CDOM from high molecular weight to low molecular weight pool. The in-lab solar irradiation study suggested that photo-ammonification of pure porewaters served as a significant source of ammonium and CDOM were responsible for the photo-transformation of DON in pore waters. In the next chapter of the study, surface water samples would be structurally elucidated to compare the effect of sunlight radiation with simulated solar radiation and quantify the portion of porewater CDOM that was photo-reactive in surface water.

Baffin Bay showed significant differences in spatial and seasonal benthic fluxes of ammonia to surface water. This was possibly due to the spatial sedimentation type and seasonal change in rainfall precipitations and primary production rates. This study highlights the role of the internal circulation of nutrients as a significant source to the bay, which needs to be taken into

account when an attempt to provide a plan for any remediation and reduce the occurrence of brown tides and other harmful algal blooms events in the bay.

6. FUTURE STUDIES

Surface water analysis - Future work will structurally elucidate the surface water DOM samples to compare the effect of sunlight radiation with simulated solar radiation and quantify the portion of porewater CDOM that is photo-reactive in surface water.

Isotopic analysis - The reduced form of nitrogen, ammonium (NH_4^+), is easier for most microbes to assimilate than oxidized nitrogen compounds such as nitrate. However, relatively few microbes can reduce nitrogen (i.e. converting nitrogen gas to ammonium). Irradiation of peptides and deaminated peptides was proven to be one of the potential sources for ammonium production in the coastal region in addition to microbial remineralization; hence, its pathways must be tracked to provide a full understanding of the nitrogen cycle in the open ocean using the following equation:

$$\delta^{15}\text{N}_{\text{NH}_4^+} (\text{sea water}) = f(\text{raw pore water}) * \delta^{15}\text{N}_{\text{NH}_4^+} (\text{raw pore water}) \\ + f(\text{nitrogen-purged \& irradiated pore water}) * \delta^{15}\text{N}_{\text{NH}_4^+} (\text{nitrogen-purged \& irradiated pore water})$$

We anticipated to track and label which ammonia in sea water coming from sediment pore water, river water and from photo-ammonification in euphotic zone.

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