Controls of Dissolved Organic Matter Distribution and Fate in the Ocean

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CONTROLS ON DISSOLVED ORGANIC MATTER DISTRIBUTION AND FATE IN THE OCEAN

By

Robert T. Letscher

A DISSERTATION

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of the University of Miami
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CONTROLS ON DISSOLVED ORGANIC MATTER DISTRIBUTION AND FATE IN
THE OCEAN

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Marine dissolved organic matter (DOM) is quantitatively important for the biogeochemical cycling of carbon and nitrogen. It exerts its influence through the ocean’s biological pump, with the fate of dissolved organic nitrogen (DON) and carbon (DOC) impacting the ocean’s fertility and its capacity for storing carbon on climate-relevant timescales, respectively. This dissertation identifies and quantifies important mechanisms and timescales for DOM degradation in the marine environment by combining observations from ship-based studies, assessments of ocean circulation, and incubation experiments to interrogate the relevant processes.

The fate of terrigenous DOC (tDOC), delivered to the ocean by rivers, was investigated during its transit across the broad Siberian continental shelves. Observations of DOC coupled with tracers of freshwater ($\delta^{18}O$) and shelf water ($^{228}$Ra/$^{226}$Ra) identified an aged riverine component present in the Transpolar Drift over the central Arctic basins. Residency on the shelf reduced the DOC content relative to conservative mixing with marine water, indicating significant removal of tDOC during river-to-ocean transport. The $^{228}$Ra/$^{226}$Ra age tracer was used to constrain the timescale of tDOC removal, finding
a removal rate several times higher than previously reported in the western Arctic Beaufort gyre (holding more highly aged shelf water). These findings highlight the enhanced lability of fresh tDOC upon delivery to the Arctic Ocean. tDOC mineralization is important in that it mitigates the strength of the surface Arctic Ocean atmospheric CO$_2$ sink; a sink that will be further reduced with an increase in labile tDOC flux and mineralization due to Arctic warming and permafrost thaw. Extending the analysis to include terrigenous DON (tDON), evidence for significant tDON mineralization was found as well, however riverine delivery of both inorganic and organic nitrogen had only a minor (<15%) impact on Arctic shelf export production.

The global distribution of DON in the surface ocean in conjunction with DON mineralization incubation experiments were employed to understand the fate of DON and its role as a source of nitrogen supporting export production in oligotrophic systems. Inputs of nitrate to the euphotic zone at equatorial and eastern boundary upwelling centers fuel net production (accumulation) of DON that resists rapid remineralization. This material was found to be recalcitrant to degradation by surface microbial communities; instead microbial DON mineralization is a slow process (months) that occurs once surface DON is exposed to microbial communities found in the upper mesopelagic zone. DON transported towards the oligotrophic ocean by surface currents is vertically mixed to depths within the deep euphotic zone (~50 to 100 m) at the eastern edges of the subtropical gyres. These results suggest the primary fate of surface DON to be removal via vertical mixing and subsequent mineralization below the mixed layer, implying a limited role for direct DON support of gyre export production from the
surface layer. DON may contribute to export production at the eastern edges of the subtropical gyres, but after its mineralization within the deep euphotic zone.
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Chapter 1. Introduction

1.1 Perspective

The past two decades have seen a surge in interest in the field of marine dissolved organic matter (DOM) biogeochemistry. The seminal paper by Sugimura and Suzuki [1988] showing a large and dynamic pool of dissolved organic carbon (DOC) in the oceans generated a stir in the oceanographic community, causing researchers to reevaluate the role of DOM in the cycling of carbon (C), nitrogen (N), and phosphorus (P) in the sea. DOC comprises the second largest pool of reactive carbon in the ocean (~662 Pg C) and is an important sink for autotrophically fixed carbon as well as a substrate for microbial heterotrophs [Hansell, 2002]. After more than two decades of research, DOC is recognized as an integral part of the marine carbon cycle and the functioning of the “biological pump”, which stores carbon in the deep ocean over climate-relevant timescales [Hansell et al., 2009]. Despite this progress, fundamental questions remain regarding the mechanisms by which DOM exerts its influence on the biogeochemical cycles of C, N and P.

One ongoing avenue of DOM research involves determining the fate of land-derived (terrigenous) DOM (tDOM) upon delivery to the marine environment. Terrigenous organic material enters the ocean at a rate of ~0.25 Pg C yr$^{-1}$ via rivers, which represents the largest transfer of reduced carbon from the continents to the ocean [Cauwet, 2002]. Dissolved lignins, a class of compounds produced solely by land-based vascular plants, have been used in myriad studies as an unambiguous tracer of tDOM in marine systems [Dittmar and Kattner, 2003; and references therein]. Results from these
studies have shown tDOM to act conservatively across estuaries and coastal environments, suggestive of a long-lived material, yet low lignin content in the open ocean suggests a sink for tDOM in the ocean [Opsahl and Benner, 1997]. Hansell et al. [2004] provided the first evidence for active removal of tDOM from the Arctic water column, finding a sink for tDOM within the surface waters circulating within the Beaufort gyre of the western Arctic Ocean, which they attributed to microbial remineralization. This study and others [reviewed in Bianchi, 2011] have shifted the tDOM paradigm from one of a long-lived recalcitrant material to a dynamic pool of carbon and nutrients that influences the marine carbon cycle, spurring a reassessment of the role of tDOM in ocean biogeochemical cycles.

Concurrent with the surge in interest for DOM studies has been a series of rapid developments in the marine N cycle [Capone et al., 2008] owing to the development of new molecular and geochemical analytical tools as well as the recognition of new metabolic pathways such as annamox. However, with increasing knowledge has come new questions and renewed uncertainties, thus stimulating controversy. Geochemical estimates of the marine nitrogen budget show the sources and sinks of nitrogen to be in approximate balance [Gruber and Sarmiento, 2002; Gruber, 2004] while biological rate estimates suggest the marine nitrogen cycle is out of balance with sinks outweighing sources [Codispoti et al., 2001; Codispoti, 2007]. This controversy has guided marine N biogeochemistry research towards a better quantification of all source and sink terms of the marine N budget.

The convergence of marine DOM and N cycling research has yielded questions about the function of dissolved organic nitrogen (DON) within the marine nitrogen cycle
and its role in ocean fertility. Interest in marine DON has focused on its role as both a pool of reduced nitrogen supporting autotrophic primary production and as a substrate for the heterotrophic “microbial loop”. Recent studies in the Atlantic Ocean have attempted to quantify the importance of allochthonous (external to the system) inputs to surface waters of semilabile DON resulting from new production at the gyre margins, and its potential as a source of N for export production after advection to the interior of gyres [Mahaffey et al., 2004; Roussenov et al., 2006; Charria et al., 2008; Torres-Valdés et al., 2009]. However, these studies have been limited by a lack of knowledge regarding the bioavailability of the transported DON to utilization by surface ocean microbial communities. Biologically accessible chemical moieties such as urea, amino acids, and nucleic acids have been identified within the bulk DON pool, however their concentrations are typically very low, leaving the chemical composition of the majority of the DON pool a “black box” [Benner, 2002; Bronk et al., 2007]. The lack of knowledge about the chemical nature of the marine DON pool has limited our understanding of the processes that control its open ocean distribution, sources and sinks.

Although DOM has become a common element of many biogeochemical studies, research regarding the marine DON pool has lagged behind that of DOC [Bronk, 2002]. Marine DON research has also been hindered by the analytical methods available to measure the bulk DON pool. Current methods use either high-temperature combustion (HTC) or a form of chemical oxidation (UV, persulfate) to convert the total nitrogen (TN) in a sample to inorganic NOx (HTC) or nitrate (UV, persulfate). The DON pool is then calculated as the difference between the TN measured in a sample following oxidation and the inorganic-N forms measured prior to digestion. For deeper ocean
waters where nitrate makes up a large fraction of the total nitrogen, the calculation of DON concentration results from the subtraction of two large numbers, and is inherently associated with large errors [Hansell, 1993]. To date, no method has been developed to remove inorganic-N prior to DON concentration analysis as can be done for analyses of DOC. Despite the limitations of the available analytical tools to study marine DON, it has emerged as an important actor in the biogeochemical cycling of N in the ocean, warranting further study.

1.2 Objective

This dissertation aims to further our understanding of the dynamics of DOC and DON by constraining the processes that control its distribution, sources, and sinks within the marine environment. I concentrate on processes that remove (remineralize) DOC and DON in the ocean and their consequent effects on the marine biogeochemical cycles of C and N. My focus is on determining the fate of terrigenous DOC and DON (tDOC, tDON) upon delivery to the Arctic Ocean, as well as an assessment of the fate of DON within oligotrophic marine systems. With regards to the fate of tDOM, I address the following questions: (1) Is the tDOC and tDON that is delivered to the Arctic Ocean by rivers remineralized within the marine environment or does it resist degradation? (2) If tDOM is degraded, what are the mechanisms, quantity, and timescale for its removal? and (3) What are the impacts of tDOC and tDON mineralization on the Arctic Ocean C and N cycles? With regard to marine DON dynamics in oligotrophic systems I ask: (1) What is the global distribution of DON in the surface ocean and what processes control its spatial gradients? (2) Upon identification of a sink for surface ocean DON, I ask what are the
biological and physical controls influencing that sink?, and (3) Is allochthonous DON supply an important source of new N sustaining export production within the ocean’s oligotrophic subtropical gyres?

The approach used to address these questions includes (1) measurements of DOC and DON concentration, as well as other biogeochemical parameters, (2) assessments of ocean circulation from observed and modeled tracer distributions, and (3) incubation experiments designed to interrogate the relevant processes controlling the fate of DOC and DON in marine surface waters. Data for the tDOM study within the Arctic Ocean include those from the Western Arctic Shelf-Basin Interactions (SBI) project conducted in summer 2002, Polarstern expedition ARKXXXIII/3 in summer 2008, and the RUSsian-American Long-term Census of the Arctic 2009 (RUSALCA). The study of the fate of surface ocean (marine) DON uses data from the U.S. Global Ocean Carbon and Repeat Hydrography program (http://cdiac.ornl.gov/oceans/RepeatSections/), operating within the global CLImate VARiability and Predictibility (CLIVAR) Programme, coupled with an investigation of potential sinks for surface ocean DON using laboratory incubation experiments of marine DOM and microbial communities. This work assesses of the fate of DOC and DON in the marine environment, and focuses on identifying and quantifying the mechanisms, timescales, and biogeochemical impact of its removal.

1.3 Background

1.3.1 DOM fractions

At 662 ± 32 Pg C [Hansell et al., 2009], DOC represents the second largest pool of exchangeable C in the ocean behind that of the dissolved inorganic carbon (DIC) pool
(~38,000 Pg C) [Hansell, 2002]. Traditionally, the DOC pool has been separated into 3 or more fractions characterized by their lability, or the rate at which they are removed by biological and/or physical processes [Hansell et al., 2012]. The refractory fraction comprises the vast majority of DOC in the ocean (~640 Pg C) [Hansell et al., 2012], with turnover times on the order of centuries to millennia, thus representing a long-term reservoir for C in the ocean. At the opposite end of the reactivity spectrum is labile DOC, which turns over on timescales of minutes to days and is the dominant source of carbon sustaining microbial growth and respiration in the ocean [Carlson, 2002]. It is estimated that ~50% of global net primary production (NPP) cycles through the DOM pool [Ducklow and Carlson, 1992], however due to its rapid exchange between autotrophs-DOM-heterotrophs-CO₂, this large flux does not result in the accumulation of carbon in the DOC pool. Between the labile and refractory fractions lie the semilabile and semi-refractory fractions, which together comprise ~20 Pg C and have turnover times on the order of months-to-years and years-to-decades, respectively [Hansell et al., 2012]. Much work has sought to understand the dynamics of labile and semilabile DOM pools [Carlson, 2002] with only recent examination of the longer-lived fractions [Hansell et al., 2012]. The ultimate source of all of these DOM fractions is organic matter generated by autotrophs, with additional production mechanisms for the longer-lived fractions an ongoing matter a matter of ongoing debate, including produced de novo [McCarthy et al., 2004] or via heterotrophic processes in the microbial carbon pump “MCP” [Jiao et al., 2010].
The studies of tDOM and DON that comprise this dissertation examine dynamics of these pools on timescales on the order of a few years, and thus pertain to the semilabile DOM fraction.

1.3.2 Terrigenous DOM

Organic carbon fixed on land by vascular plants differs in chemical composition from that fixed by algal producers in marine environments. This difference in chemical composition has long been viewed as imparting recalcitrance to tDOM upon its delivery to the ocean, where marine microbial communities lack the metabolic capabilities to degrade tDOM [Hedges and Keil, 1995]. Contrary to this view, studies of dissolved lignin (a terrestrial biomarker) in open ocean environments concluded that a marine sink for tDOM must exist [Hedges et al., 1997; Opsahl and Benner, 1997] and many recent studies have attempted to elucidate tDOM removal processes [Hansell et al., 2004; Cooper et al., 2005; Holmes et al., 2008]. Many of these studies have been concentrated in the Arctic Ocean where large terrestrial inputs of DOM relative to those from marine sources provide a unique environment in which to study the fate of tDOM in marine systems.

The storage and cycling of carbon at high-latitudes has become an important component of global climate change science. High-latitude soils and peatlands store \(~50\%\) of global soil organic carbon [Dixon et al., 1994] with growing concern that continued warming of the Arctic region could mobilize a portion of this organic carbon (OC) to the Arctic marine environment, thus providing a positive feedback to warming if the OC is mineralized to \(\text{CO}_2\) [Freeman et al., 2001; 2004; Frey and Smith, 2005]. Thus, determining the fate of Arctic tDOM upon delivery to the Arctic Ocean (mineralization
vs. preservation) is important for discerning its role in climate feedbacks. The tDOC and tDON studies within this dissertation advance this question by extending assessment of tDOM dynamics to waters overlying the broad continental shelves of the Eurasian Arctic.

1.3.3 DON

Inputs of DON to the ocean can come from both terrestrial and marine sources. Terrestrial delivery of DON is important in coastal and nearshore regions with significant inputs via rivers [Seitzinger and Harrison, 2008] and to a lesser degree, from atmospheric deposition [Cornell et al., 1995]. Anthropogenic factors such as usage of fertilizers and livestock feed, industrial nitrogen fixation, and release of sewage have increased the flux of DON from terrestrial systems to the marine environment in recent times; however, marine sources still account for ~80% of global DON production [Harrison et al., 2005].

Phytoplankton are the largest contributor to marine DON. DON release from phytoplankton can result from active exudation or passive diffusion across the cell membrane [Bronk et al., 2007]. Nitrogen-fixing autotrophs are thought to be significant sources of DON, releasing up to 50% of recently fixed-N as DON [Glibert and Bronk, 1994]. Other sources of DON include “sloppy feeding” [Carlson, 2002], bactivory by microzooplankton on both phytoplankton and bacteria [Nagata, 2000], or by viral infection and subsequent cell lysis [Suttle, 1994]. Bacteria are generally DON consumers, however they can also release various forms of DON, including urea [Solomon et al., 2010]. Zooplankton also contribute to DON via excretion [Le Borgne and Rodier, 1997; Steinberg et al., 2002] and dissolution from fecal pellets [Jumars et al., 1989; Steinberg et al., 2002].
Three main sinks have been identified for DON: utilization by heterotrophic bacteria, utilization by photoautotrophs, and abiotic photochemical mineralization. Utilization of DON by bacteria is believed to be the dominant loss term, however there has been a renewed focus on the potential for DON to serve as a source of N for photoautotrophs in the open ocean [Mahaffey et al., 2004; Roussenov et al., 2006; Charria et al., 2008; Torres-Valdés et al., 2009], and especially harmful algal bloom (HAB) species in coastal environments [Bronk et al., 2007]. Phytoplankton can grow exclusively on certain types of DON in culture, especially urea and select amino acids [Dzurica et al., 1989; Palenik and Henson, 1997; Berman and Chava, 1999; John and Flynn, 1999] and possess cell surface enzymes (amine oxidases) that allow them to cleave N-containing amine groups from larger DON molecules for assimilation [Palenik and Morel, 1990a; 1990b; 1991; Mulholland et al., 1998].

Absorption of UV-light by DON molecules can release ammonium (photo-ammonification) for subsequent uptake by autotrophs, along with release of smaller DON moieties such as dissolved free amino acids (DFAA) and dissolved combined amino acids (DCAA) that are generally utilized by bacteria [Bronk, 2002]. Most studies documenting this process have examined the release of ammonium from UV-absorbing humic material [e.g. Bushaw et al., 1996], however proteins do not absorb light within the solar spectrum and a number of studies have shown the bioavailability of DON to decrease following irradiation [Keil and Kirchman, 1994; Naganuma et al., 1996; Tranvik and Kokalj, 1998; Reitner et al., 2002]. Photo-ammonification rates in the open ocean are not well constrained with only one report from unpublished data, ranging from 1-10 nM h⁻¹ [Bronk, 2002]. It is unknown over what temporal and spatial scales this rate
applies or the extent to which photo-ammonification of marine DON is important in the open ocean environment.

Heterotrophic bacteria are the main consumers of DON in freshwater and marine systems, being able to utilize smaller DON molecules such as dissolved free aminio acids (DFAA) via direct uptake [Antia et al., 1991] or by release of extracellular enzymes (peptidases) to harvest N from larger molecules [Rosso and Azam, 1987; Hoppe, 1983; 1991; Hoppe et al., 2002]. Up to 50% of bacterial N-demand is satisfied by utilization of DFAA and dissolved combined amino acids (DCAA) [Coffin, 1989; Keil and Kirchman, 1991; Kirchman, 2000; Middelboe et al., 1995]. In addition to direct assimilation of DON, bacteria remineralize DON to produce dissolved inorganic N species (NH₄⁺, NO₃⁻, NO₂⁻). It is estimated that 12-72% of DON is bioavailable to bacteria across a broad range of temporal and spatial scales [Bronk, 2002].

Much of what is known about DON dynamics to date has focused on the production, release, and uptake of specific DON species (e.g. urea, DFAA, etc.) within cultures and bioassays in the laboratory or from freshwater and coastal environments. The lack of chemical characterization of the majority of the bulk oceanic DON pool [Aluwihare and Meador, 2008] has hindered insight into the dynamics and transformations of this potentially important reservoir in the marine nitrogen cycle. Despite these difficulties, the surface ocean DON concentration data included here represent the first global picture of bulk DON distributions in the oceans including an examination of the processes influencing its sources and sinks.
Chapter 2. Fate of terrigenous dissolved organic carbon within the Eurasian Arctic Ocean

2.1 Background

The Arctic Ocean represents 1% of the world ocean volume, yet receives ~ 10% of the global freshwater discharge from rivers [Dittmar and Kattner, 2003], a process that is intensifying under warming global temperatures [Peterson et al., 2002]. Arctic rivers drain a catchment of $15.5 \times 10^6$ km$^2$, carrying with them large amounts of terrigenous dissolved organic carbon (tDOC) to the Arctic basin, estimated at 25 to 36 Tg C yr$^{-1}$ [Raymond et al., 2007]. The fate of tDOC within the Arctic Ocean is of importance for understanding the regional carbon cycle and budgets, with extrapolation to the role of tDOC in the global carbon cycle. Earlier Arctic studies addressing this issue suggested a largely refractory tDOC pool based on apparently conservative mixing behavior of tDOC across the Eurasian continental shelf in late summer [Cauwet and Sidorov, 1996; Kattner et al., 1999; Köhler et al., 2003; Amon and Meon, 2004], coupled with only small losses of tDOC observed in extended laboratory incubations [Köhler et al., 2003; Amon, 2004]. However, with recent field campaigns capturing the historically undersampled Arctic spring freshet, new evidence has emerged for a more dynamic tDOC pool in terms of composition [Neff et al., 2006; Spencer et al., 2008], biolability [Holmes et al., 2008], and age [Raymond et al., 2007]. Hansell et al., [2004] and Cooper et al., [2005] observed significant removal of tDOC within the Beaufort gyre of the western Arctic Ocean, based on interpretations of the DOC-salinity relationship and regional ocean circulation. These new insights warrant a reexamination of the fate of tDOC delivered to the Arctic Ocean.
River waters delivered to the Arctic Ocean first encounter shallow shelf seas overlying the continental shelves. Here the dynamics of dissolved organic carbon (DOC) in near surface waters are complex owing to transport, production, consumption, and sea ice processes [Amon, 2004; Mathis et al., 2005]. The fate of tDOC is in part controlled by its residence time over the shelf, which is in turn dependent on the rate of exchange of shelf water with the ocean interior. The western Arctic (i.e., the Canada Basin and adjacent shelf seas), with relatively narrow continental shelves, is dominated by the anticyclonic circulation of the Beaufort gyre, allowing for long-term retention of surface waters. There, the slow decay of tDOC in surface waters was observed over the decade long timescale of circulation as determined by use of a dissolved Ra-age model [Hansell et al., 2004]. The eastern Arctic (i.e., the Eurasian Basins and adjacent continental shelf seas), in contrast, is dominated by the inflow of Atlantic water over the shelf seas, which is then exported as the return flow of the Transpolar Drift (TPD) towards Fram Strait following a multiyear residence overlying broad shelves [Schlosser et al., 1994; Ekwurzel et al., 2001; Karcher and Oberhuber, 2002]. While tDOC removal in the west largely occurs offshore over the deep basin where surface waters are retained during circulation within the Beaufort gyre, the expansive shelf area present in the eastern Arctic, and the variable residence of water in that system, may provide the environment necessary for removal of tDOC prior to its export from the basin, as has been observed in other shelf environments [Moran et al., 1999; Raymond and Bauer, 2000; Hopkinson et al., 2002].

Having previously examined the fate of tDOC delivered to the western Arctic [Hansell et al., 2004; Cooper et al., 2005], our primary goal here is to identify the fate of tDOC delivered to the eastern Arctic system. We investigated the surface layer
distribution of DOC over a large extent of the summertime Arctic Ocean, including the
shelf break and ocean interior from the Beaufort gyre west to the Laptev Sea. Included
are measurements of salinity and stable oxygen isotope ratios, the latter useful for tracing
the sources of freshwater, whether meteoric or from sea-ice melt (SIM), within surface
waters (e.g. [Ostlund and Hut, 1984; Bauch et al., 1995; Macdonald et al., 1995]). The
distribution and transport pathways of freshwater are important for interpreting the DOC
pool in the context of regional hydrography [Cooper et al., 2005; Mathis et al., 2005]. In
addition, dissolved radium isotopes are employed here to trace the extent and rate of
exchange between shelf waters and the ocean interior, as applied previously in the Arctic
[Rutgers van der Loeff et al., 1995; 2003; Kadko and Muench, 2005]. Combining the
DOC distribution with knowledge of water mass origins and transport gained from the
isotopic tracers, we determine the rate of removal of tDOC from the surface waters of the
eastern Arctic.

2.2 Regional hydrography
Our focus is on the eastern Arctic system, defined here as the region from 0°–
180°E. The region from 180°W–0° defines the western Arctic. Runoff from the major
Siberian watersheds empty into the shelf seas, whereupon surface flow is generally along
shelf to the east (Fig. 2.1). Runoff from the Ob and Yenisey rivers enters the Kara Sea,
passing through the Vilkitsky Strait into the Laptev Sea, where it mixes with runoff from
the Lena River [Guay et al., 2001]. The direction of surface flow and the geographic
position for detachment of the fluvial discharge from the shelf to enter the Transpolar
Drift is influenced by the prevailing atmospheric conditions [Ekwurzel et al., 2001;
Schlosser et al., 2002], represented by the sign of the Arctic Oscillation (AO) [Anderson et al., 2004].

Fig. 2.1. Map showing station locations (red dots) in reference to generalized surface circulation and major river mouths (black arrows) of the Arctic Ocean. The large scale cyclonic circulation of the Eastern Arctic (0°–180°E) is dominated by the Transpolar Drift (TPD; originating at the shelf break of the Makarov Basin), contrasting the anticyclonic circulation of the Beaufort Gyre (BG) in the Western Arctic (180°W–0°). Shelf seas and deep basins are marked as follows: EB = Eurasian Basins, MB = Makarov Basin, CB = Canada Basin, KS = Kara Sea, LS = Laptev Sea, ESS = East Siberian Sea, CS = Chukchi Sea, CB/MR = Chukchi Borderland/Mendeleyev Ridge, and BS = Beaufort Sea. The solid white line approximates the minimum sea-ice extent during September 2008.
During negative phases of the AO, a stronger Beaufort high over the Arctic weakens the subpolar westerlies, shifting the axis of the TPD west towards the Eurasian Basins. Surface flow in the Laptev Sea follows a northerly route with the river runoff discharge crossing the Laptev shelf for export to the deep basin near the Lomonosov Ridge [Anderson et al., 2004]. During the positive phase of the AO, a weaker Beaufort high intensifies the subpolar westerlies, shifting the axis of the TPD towards the Canada Basin. River runoff entering the Kara and Laptev seas flows strongly to the east, passing through the Sannikov and Dmitry Laptev straits before entering the East Siberian Sea, to mix with runoff from the Kolyma River [Dmitrenko et al., 2005; 2008]. Once there, the fluvial waters cross the continental shelf, passing offshore with the river discharge entering the interior Arctic near the Mendeleyev Ridge [Guay et al., 2001; Anderson et al., 2004].

2.3 Methods

2.3.1 Field sampling

Dissolved isotopic tracer and biogeochemical samples were collected aboard the German icebreaker FS Polarstern during cruise ARKXXXIII/3 (Aug. 12 to Oct. 17, 2008). The cruise circumnavigated the Arctic with extensive occupation of the western Chukchi/East Siberian Sea shelf break and adjacent Mendeleyev Ridge region (Fig. 2.1). In addition, a transect crossing the Canada, Makarov, and Eurasian basins at ~ 80°N was occupied, including the source waters of the Transpolar Drift in the Makarov Basin (Fig. 2.1). Sea-ice-free conditions were generally present south of 80°N in the study region with heavy ice conditions present to the north (white line, Fig. 2.1). Sampling of
the Polar Surface Layer (PSL) was carried out through the ship's hull-mounted seawater intake line at a depth of ~ 10 meters. A total of 179 underway samples were collected for the analysis of DOC, with a subset (66) concomitantly collected for analysis of isotopic tracers $^{228}\text{Ra}/^{226}\text{Ra}$ and $\delta^{18}\text{O}$. Salinity was measured by conductivity using the ship's salinometer mounted at the seawater intake.

2.3.2 DOC

Samples were filtered for the removal of particulate organic carbon (POC) using precombusted Whatman GF/F filters (nominal pore size, 0.7 µm) held in acid-cleaned polycarbonate filter holders. Filter holders were connected inline with the clean seawater line using acid-cleaned, DOC-free silicon tubing. Samples were collected into preconditioned and acid-cleaned 60 mL HDPE bottles and immediately frozen upright at $-20^\circ\text{C}$. New filters were loaded prior to each sample collection to ensure no contamination from previous filtrations.

Analyses of DOC were performed by high temperature combustion at our onshore laboratory using two Shimadzu TOC-V systems [Dickson et al., 2007]. Standardization was achieved using potassium hydrogen phthalate (KHP). Deep seawater and low carbon reference waters as provided by the Hansell CRM Program were measured every sixth analysis to assess the day-to-day and instrument-to-instrument variability. The precision of the DOC measurement was 2–3 µM or a CV of 3%–5%.

2.3.3 Isotopic tracers

Approximately 200-L samples for the detection of radium isotopes, $^{228}\text{Ra}$ and $^{226}\text{Ra}$, were collected in 300-L plastic tanks using the ship seawater intake. The tanks were slowly drained (~ 300 mL min$^{-1}$) using electric motors, passing the seawater
through plastic cartridges containing Mn-coated acrylic fibers. Radium adsorbs to these fibers efficiently and without fractionation [Moore et al., 1985]. Following filtration, the fibers were sealed and stored in plastic Petri dishes for subsequent analysis on land. The activities of $^{228}$Ra and $^{226}$Ra were measured from the activities of the radium daughters upon ingrowth using gamma ray spectrometry with a high purity germanium detector [Michel et al., 1981].

Samples for stable oxygen isotope measurements ($\delta^{18}$O) were collected unfiltered into 10-mL glass vials and immediately capped and sealed. Analyses were performed by mass spectrometry at the Stable Isotope Laboratory at the Rosenstiel School of Marine and Atmospheric Science, Miami, Florida, using a modified method of Epstein and Mayda [1953] detailed elsewhere [Swart, 2000]. Counts were calibrated using Vienna Standard Mean Ocean Water (VSMOW) and expressed using the conventional $\delta^{18}$O ‰ notation. Samples were analyzed in duplicate, with a precision of ± 0.08‰.

2.3.4 Calculating river and ice melt fractions in the polar surface layer

$\delta^{18}$O and salinity data were used to calculate the fractions of marine water, river water and sea-ice melt (SIM) present in the PSL (e.g., [Cooper et al., 2005; Mathis et al., 2007]). Each end member was assigned characteristic $\delta^{18}$O and salinity values and the fractions of each in a given sample were computed by solving a system of three equations. Oxygen isotope values of end members ($\delta^{18}$O) were assigned as follows: marine water $\delta^{18}$O = +0.3‰ [Bauch et al., 1995], SIM $\delta^{18}$O = −1.9‰ [Eicken et al., 2002], western Arctic river water $\delta^{18}$O = −19.6‰, and eastern Arctic river water $\delta^{18}$O = −18.6‰. Riverine end members were assigned using the flow weighted $\delta^{18}$O values from Cooper et al. [2008] for the Mackenzie and Yukon Rivers (western Arctic
river water) and the Ob, Yenisey, Lena, and Kolyma Rivers (eastern Arctic river water). Eastern hemisphere stations (i.e., west of 180°E) were assigned the eastern Arctic river water end member value while western hemisphere stations (i.e., east of 180°E) were assigned the western Arctic river water end member. Salinity (S) values were assigned as follows: eastern Arctic marine (Atlantic) water \( S = 34.9 \), western Arctic marine (Pacific/Anadyr) water \( S = 33 \) [Coachman et al., 1975], SIM \( S = 4.5 \) [Mathis et al., 2007], and both western and eastern Arctic river water \( S = 0 \). Eastern and western Arctic marine end member salinities were assigned following the same hemisphere divisions as \( \delta^{18}O \) and reflect the Atlantic influence in the eastern Arctic and Pacific influence of the western Arctic. Fractions were calculated by simultaneous solutions to the equations below:

\[
S = (S' \times SW) + (0 \times RW) + (4.5 \times SIM) \tag{1}
\]

\[
\delta^{18}O = (+0.3\%o \times SW) + (\delta^{18}O' \times RW) + (-1.9\%o \times SIM) \tag{2}
\]

\[
1 = SW + RW + SIM \tag{3}
\]

where \( S = \) salinity of sample, \( S' = S \) for western (33) or eastern (34.9) Arctic marine water, \( \delta^{18}O = \) oxygen isotope composition of sample, \( \delta^{18}O' = \delta^{18}O \) for western (−19.6‰) or eastern (−18.6‰) Arctic river water, and SW, RW, and SIM are fractions of marine water, river water, and SIM, respectively.

2.4 Results

2.4.1 Salinity and DOC
The surface distributions of salinity and DOC are shown in Fig. 2.2a and 2.2b, respectively. Salinity in the PSL was generally low (< 33) due to the presence of freshwater from both river runoff and SIM. A salinity front was observed just east of 180°E (Fig. 2.2a), separating the fresher (< 29) western Arctic waters from the saltier (> 29) eastern Arctic waters. An exception was where the cruise track crossed an ice-free region centered at ~160°E over the Makarov Basin (indicated by an arrow, Fig. 2.2a), characterized by reduced salinity (< 29) relative to surrounding waters.

Surface DOC concentrations over the deep basins were generally lower in the western Arctic (60–65 µM) than in the eastern Arctic (60–120 µM) (Fig. 2.2b). In the western Arctic, DOC concentrations were highest (> 100 µM) at the few stations located near the mouth of the Mackenzie River, with much lower concentrations found offshore.

Fig. 2.2. Surface distribution of (a) salinity, (b) DOC (µM C), (c) δ¹⁸O (%), and (d) ²²⁸Ra/²²⁶Ra activity ratio. The black arrow denotes relatively fresh, shelf-water dominated stations in the Makarov Basin described in the text.
over the Beaufort gyre. The highest DOC concentrations in the eastern Arctic (> 100 µM) coincided with low salinity water located over the Makarov Basin (indicated by an arrow, Fig. 2.2b) and the adjacent Eurasian Basin, suggesting a stronger influence of river runoff there. Elsewhere, over the Chukchi Borderland/Mendeleyev Ridge region, DOC concentrations were reduced at both the western and eastern Arctic stations (due to mixing with SIM; evidence given below).

2.4.2 Isotopic tracers

Surface distributions of δ¹⁸O and ²²⁸Ra/²²⁶Ra activity ratios are shown in Fig. 2.2c and 2.2d, respectively. Values of δ¹⁸O were depleted across the study region due to the presence of freshwater from both rivers and sea-ice melt, both of which have depleted δ¹⁸O signatures (Fig. 2.2c). The most depleted values (< −4.0‰) in the east coincided with the low salinity region in the Makarov Basin (indicated by an arrow, Fig. 2.2c). Elsewhere in the eastern Arctic, δ¹⁸O values typically ranged between −2.5‰ and −1.5‰. The western Arctic stations showed slightly depleted values relative to the eastern Arctic, with typical values between −3.0‰ and −2.0‰, reflecting freshwater storage in the upper Canada Basin [Aagaard and Carmack, 1989].

The ²²⁸Ra/²²⁶Ra activity ratios, with lower values indicating greater time since a water mass left the shelf, showed marked differences between the two systems owing to the contrasting circulation patterns (Fig. 2.2d). In the western Arctic, where the anticyclonic gyre circulation allows for significant decay of ²²⁸Ra during the recirculation of surface waters (Kadko and Muench, 2005), activity ratios were reduced and nearly constant, averaging 0.45 ± 0.06, n = 13 (Fig. 2.2d). In the eastern Arctic, where circulation is dominated by shelf transport and cross basin transport via the Transpolar
Drift, activity ratios were more varied, ranging from 0.4 to > 2.0. The highest ratios were observed offshore over the Makarov and Eurasian basins, corresponding with the low salinity, high DOC water (indicated by arrow, Fig. 2.2d). Ratios were reduced over the outer East Siberian shelf and Mendeleyev Ridge region (1.0–1.5), possibly due to mixing with western Arctic waters near the salinity front or, perhaps, due to simple aging.

Fig. 2.3. Surface distribution of calculated freshwater fractions. (a) River water. (b) Sea-ice melt water. Dotted black circle denotes stations overlying the Makarov and Eurasian basins (110–180°E) used for DOC-salinity regressions described in text.

2.4.3 Distributions of river and ice melt fractions in the polar surface layer

The fractional distributions of river water (RW) and SIM are shown in Fig. 2.3a
and 2.3b, respectively. River water is ubiquitous in the PSL with fractions reaching 20% in the western Arctic and 25% in the low salinity region over the Makarov Basin. The distribution of SIM shows a larger influence in the western Arctic, reaching 12% in the Beaufort Sea. Contributions of freshwater due to SIM were small in the eastern Arctic, with ~ 5% at stations located at the shelf break of the East Siberian/Chukchi Sea, decreasing to negligible amounts at stations located over the Eurasian Basins. These distributions of SIM likely reflect the dominant flow systems: SIM is retained in the gyre circulation of the Beaufort gyre while in the east it is removed from the regions of formation with sea ice flow off the shelf and across the shelf break.

2.5 Discussion

2.5.1 Geographic distribution of river discharge in the eastern Arctic

Taken together, the distributions of both RW and SIM in the eastern Arctic indicate a large riverine influence in the PSL overlying the deep basins (dotted outline, Fig. 2.3). The low salinity region over the Makarov Basin near ~160°E coincides with the highest DOC concentration (129 µM), lowest δ¹⁸O value (−4.42‰), highest $^{228}$Ra/$^{226}$Ra activity ratio (2.24), and largest RW fraction (25%) measured. The results agree with the findings of Jones et al. [2008], who reported a large influence of fluvial water over the central Makarov Basin during the 2005 Arctic Ocean Section. In addition, the elevated surface DOC concentrations measured over the Makarov and Eurasian basins are consistent with previous measurements in the same region [Wheeler et al., 1997; Bussmann and Kattner, 2000; Amon and Benner, 2003]. Working with a simple parameterization of tDOC concentrations in river runoff to the Arctic Ocean within an
ocean general circulation model, Manizza et al. [2009] predicted the highest concentrations of riverine DOC to be in the nearshore Siberian seas (Kara, Laptev, East Siberian), with the river discharge crossing and detaching from the shelf at ~150–180°E, coincident with the low salinity region observed over the Makarov Basin in this study.

The geographical position of the Eurasian river discharge detachment from the shelf is known to be variable [Guay et al., 2001; Schlosser et al., 2002] and dependent on the prevailing summertime atmospheric wind conditions, represented by the sign of the Arctic Oscillation [Anderson et al., 2004; Dmitrenko et al., 2005]. AO was negative during the summer of 2008, following a three-year period of predominantly positive phase [CPC, 2009]. The data presented here provide evidence that the 80°N transect in this study crossed the Eurasian River runoff discharge during the summer of 2008 as it joined the Transpolar Drift. The location of the river discharge sampled in 2008 midway between the Mendeleyev and Lomonosov Ridges in the Makarov Basin (~150–170°E) may be explained by a shift in the axis of the Transpolar Drift from near the Mendeleyev Ridge during the positive AO phase [Anderson et al., 2004] toward the Lomonosov Ridge in summer 2008.

2.5.2 Non-conservative behavior of tDOC

DOC-salinity plots have been commonly used to discern the controls exerted by Arctic hydrography on DOC distributions [Cauwet and Sidorov, 1996; Kattner et al., 1999; Bussmann and Kattner, 2000; Köhler et al., 2003; Hansell et al., 2004; Cooper et al., 2005; Mathis et al., 2005]. It has been assumed in these analyses that sea ice formation and melt leave impermanent imprints on the DOC-salinity relationship such that careful use of data allows its interpretation. If the DOC-enriched brine formed during
sea ice formation [Giannelli et al., 2001] is dense enough to penetrate the pycnocline, a physical mechanism for tDOC removal from the PSL exists, thereby permanently affecting the DOC-salinity relationship in surface waters. There are few analyses on the export of DOC to the subpycnocline with brine formation. Amon [2004] reported that low-salinity, tDOC-rich shelf water in the Kara Sea does not become dense enough, following sea ice formation to penetrate the pycnocline. Schauer [1997] reached a similar conclusion for the Laptev Sea, whereby the resulting increase in shelf water salinity post-sea-ice formation in winter was insufficient to mix with the underlying halocline waters. These results suggest that DOC and salinity concentrations in the PSL may be impacted by ice formation on the short term, but not necessarily over the full annual scale. The extent to which sea ice formation and brine export affect the DOC-salinity relationship over the multi-year residence of Eurasian shelf waters [Ekwurzel et al., 2001; Karcher and Oberhuber, 2002] needs to be ascertained, since small changes could accumulate to a larger impact over several freeze/thaw cycles. However, for the purposes of this study and employing judicial use of the data (favoring waters less impacted by SIM and for which SIM corrections can be made) we assume these processes to have modest impacts.

A plot of DOC versus salinity (Fig. 2.4) reveals mixing between three end members present in the PSL during the summer of 2008: low salinity/DOC-enriched riverine water, high salinity/intermediate DOC marine water, and low salinity/DOC-poor SIM. The presence of SIM during the summer months has been shown to dilute salinity and DOC concentrations in the PSL [Mathis et al., 2005]. This dilution of the DOC signal is apparent during the time of our study, as evidenced by the low DOC concentrations at low salinities (Fig. 2.4), thereby complicating analyses of mixing between marine and
river waters. The reduced DOC concentrations observed over the Beaufort gyre of the western Arctic (Fig. 2.4, crosses) also reflect “aged” river water [Hansell et al., 2004], whose tDOC has degraded over its decade long recirculation. Those data fitting the mixing line between the riverine and marine end members (Fig. 2.4, open circles) coincided with river water influenced stations overlying the Makarov and Eurasian basins with negligible influence from SIM, and are used for the subsequent DOC-salinity regressions below (Fig. 2.3a and 2.3b, indicated by a dotted outline). These data are the focus of the following analysis.

Fig. 2.4. Plot of DOC (µM C) versus salinity showing apparent mixing lines between three end members present in the PSL during summer 2008. Stations from the Beaufort gyre (crosses) contain “aged” river water [Hansell et al., 2004] whose DOC concentrations have degraded over the decade long recirculation of surface waters and have been diluted due to summer-time sea ice melt. Stations over the Makarov and Eurasian basins (west of 180°E) show mixing between river and marine end members with negligible contributions from sea ice melt (open circles). Stations located in the Chukchi Borderland–Mendeleyev Ridge region exhibit intermediate influence of all three end members (gray diamonds). See Fig. 2.1 for regional reference.
If tDOC in eastern Arctic River water behaved conservatively across the estuarine salinity gradient, its mixing with marine water would be approximated by the dotted line in Fig. 2.5a. The net loss of DOC across the salinity gradient would follow the curved dashed line. However, in this study only salinities > 25 are sampled in the PSL, where the loss curve fits a straight line. The regression of this line can be used to infer the DOC concentration of the river water fraction from the zero-salinity intercept, as has been done previously for the western Arctic [Hansell et al., 2004; Cooper et al., 2005]. Plots of DOC concentration versus salinity, SIM-corrected salinity, and RW fraction for the Makarov and Eurasian basins are shown in Fig. 2.5b and 2.5c. The regression of DOC concentrations versus measured salinity indicates an apparent river water tDOC concentration (± SE) of 331 ± 7 µM C, while DOC versus SIM-corrected salinity and RW fraction returned apparent river water DOC values of 309 and 308 ± 7 µM C, respectively. Here we take the average zero-salinity (100% river water) DOC value from the three regressions, 315 ± 7 µM C, as representative of the tDOC concentration in the eastern Arctic river fraction located over the basins.

The apparent tDOC concentration in the eastern Arctic River water fraction reported here is reduced relative to the DOC concentrations in Eurasian rivers [Cooper et al., 2008], suggesting that significant removal of tDOC occurs over the Siberian Arctic shelves. In order to quantify tDOC removal there, tDOC concentrations in the rivers that drain into the eastern Arctic basins need to be established. Cooper et al. [2008] provide annual flow weighted estimates of concentrations for DOC and other tracers in six major Arctic rivers. Of those six rivers, Ob, Yenisey, Lena, and Kolyma empty into the eastern Arctic basin, to eventually join the Transpolar Drift.
Fig. 2.5. Theoretical and observed correlations of DOC and salinity. (a) Theoretical mixing lines for DOC between eastern Arctic river and marine waters: conservative (dotted line); non-conservative with net loss of DOC (curved dashed line); and the zero salinity intercept (solid, arrowed line) based on correlations observed at high salinities (in the box). (b) Observed correlation between DOC (µM) and salinity (\(\text{DOC} = -7.60 \times \text{salinity} + 331; R^2 = 0.84; n = 32; \text{solid line}\)) for stations from the Makarov and Eurasian Basins outlined in Fig. 3. (c) Plot of DOC (µM) versus river water fraction (\(\text{DOC} = 239.49 \times \text{RW} + 69; R^2 = 0.80; n = 16; \text{solid line}\)). Theoretical conservative mixing (dotted lines in (b) and (c)) is shown for reference.
The annual flow weighted DOC concentration taken for these four rivers yields a mean eastern Arctic river water tDOC concentration (± SE) of 724 ± 55 µM C (799 ± 24 µM C if only the Lena and Kolyma rivers are considered, as they are the major rivers local to the East Siberian Shelf). Although there are many small rivers that drain into the eastern Arctic, these are assumed here to not have a significant impact on our river runoff end member estimate. Stable oxygen isotope data from this study fell along a mixing line between the flow weighted eastern Arctic river water (δ¹⁸O = −18.6‰, S = O) and marine water (δ¹⁸O = 0.3‰, S = 34.9) (not shown), providing evidence that the mean character of Ob, Yenisey, Lena, and Kolyma provide a reasonable estimate for the cumulative eastern Arctic river runoff end member. The difference in DOC concentrations measured in the eastern Arctic rivers and the apparent DOC concentration in the river water fraction inferred from the regressions observed offshore implies tDOC loss of 409 ± 55 µM C from the freshwater river component over the eastern Arctic shelf system.

2.5.3 tDOC removal rate estimates

River water entering the eastern Arctic has a multiyear residence overlying the continental shelf [Schlosser et al., 1994; Ekwurzel et al., 2001; Karcher and Oberhuber, 2002] before being transported into the interior Arctic Ocean to join the Transpolar Drift [Guay et al., 2001; Anderson et al., 2004]. The dissolved ²²⁸Ra/²²⁶Ra activity ratio of seawater is a useful tracer of the timescale of shelf to deep basin interaction because it provides information on the time since a parcel of water was last in contact with the continental shelf [Rutgers van der Loeff et al., 1995]. Here we combine the timescale for shelf-to-basin exchange at the East Siberian Sea shelf break–Makarov/Eurasian basins, as gauged using measurements of ²²⁸Ra/²²⁶Ra, with the available estimates of shelf residence
time in the Eurasian Arctic to arrive at an estimate for the timescale of tDOC removal in the eastern Arctic system.

The residence time of river water on the Eurasian shelves has been estimated previously using a variety of techniques. Early estimates for the Kara Sea were 2.5 years [Hanzlick and Aagaard, 1980] and 3.5 years [Pavlov et al., 1993] based on the mass balance of water. [Schlosser et al., 1994; Ekwurzel et al., 2001] estimated residence times of 3.5 ± 2 years and 2–5 years, respectively, for the Eurasian shelves using a He/3 H technique. A recent modeling study by Karcher and Oberhuber [2002] places the residence time on the shelf at 2–3 years, with a total residence time of 4.1–6.5 years for river runoff in the eastern Arctic before exiting at Fram Strait. Based on these estimates we assign a Eurasian shelf residence time for the river runoff fraction of 3.5 ± 1.5 years. Assuming that the removal of tDOC occurs predominately during the residence time of river water on the Eurasian shelves, we can calculate the tDOC removal rate. If the 724 ± 55 µM C of tDOC entering the eastern Arctic is reduced to 315 ± 7 µM C on the timescale of 3.5 ± 1.5 years, a first order tDOC decay constant, $\lambda = 0.24 \pm 0.07 \text{ yr}^{-1}$, is calculated for the region. The loss of 409 ± 55 µM C occurred almost entirely over the shelves such that > 50% of tDOC entering the Eurasian shelf seas is removed from the water column before transit to the Arctic Ocean interior.

The measurements of DOC assessed here were made over the deep basin, and we assumed above that removal of tDOC occurred over the shelves and that subsequent transfer of tDOC-enriched shelf water to the basin site was essentially instantaneous. To test this assumption, we collected measurements of dissolved $^{228}\text{Ra}/^{226}\text{Ra}$ from the PSL to estimate the timescale of shelf-to-basin exchange of shelf water. Measurements of
$^{228}\text{Ra}/^{226}\text{Ra}$ in surface waters have been used previously in the Arctic Ocean to infer rates of shelf-basin exchange [Rutgers van der Loeff et al., 1995; 2003; Kadko and Muench, 2005; Kadko and Aagaard, 2009] and to study tDOC removal in the western Arctic [Hansell et al., 2004]. Rapid mixing between high $^{228}\text{Ra}/^{226}\text{Ra}$, low salinity shelf water and low $^{228}\text{Ra}/^{226}\text{Ra}$, high salinity marine water results in conservative linear mixing trends, thus defining the “zero-age” trend for a region. Lower than expected $^{228}\text{Ra}/^{226}\text{Ra}$ values based on the zero-age trend for a given salinity indicate “aging” of that water parcel relative to when it left the shelf. High $^{228}\text{Ra}/^{226}\text{Ra}$ ratios have been reported in surface waters in the eastern Arctic [Rutgers van der Loeff et al., 1995; 2003], indicating rapid transport (< 3 years; uncertainty of $^{228}\text{Ra}/^{226}\text{Ra}$ measurement [Rutgers van der Loeff et al., 1995]) of waters overlying the Eurasian shelves into the central Arctic Ocean. In contrast, low $^{228}\text{Ra}/^{226}\text{Ra}$ ratios found in the western Arctic (i.e., at Ice Station T3 [Kaufman et al., 1973]) and at the Chukchi shelf break [Kadko and Muench, 2005] indicate “aging” of those waters during recirculation within the Beaufort gyre. The $^{228}\text{Ra}/^{226}\text{Ra}$ ratios from this study are plotted by region against SIM-corrected salinity in Fig. 2.6. Data from the western Arctic largely fell along the line indicating “aged” water over the Beaufort gyre [Kadko and Muench, 2005] while data from the Makarov and Eurasian basins (open circles, Fig. 2.6) fit a linear mixing trend (line Siberian–Makarov, Fig. 2.6), suggesting rapid exchange of Eurasian shelf waters at the shelf break with the ocean interior. Rapid mixing of Eurasian shelf waters with PSL waters over the Makarov and Eurasian Basins precludes significant aging of surface waters during the transit from the shelf break to the offshore sampling location at ~ 80°N, within the uncertainty of the $^{228}\text{Ra}/^{226}\text{Ra}$ dating technique of < 3 years [Rutgers van der Loeff et al.,]
1995]; thus, the removal of tDOC occurs almost entirely over the expansive shelf area in the eastern Arctic system.

Fig. 2.6. Plot of $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio versus sea ice melt corrected salinity showing data collected in the western Arctic, i.e., Beaufort gyre and Beaufort Sea (crosses), Chukchi Borderland/Mendeleyev Ridge region (gray diamonds), and Makarov and Eurasian Basins of the eastern Arctic (open circles) (see Fig. 2.1 for reference). Stations in the western Arctic largely fall along the “aged” line for recirculated waters in the Beaufort gyre [*Kadko and Muench*, 2005] (dashed line). Stations overlying the Makarov and Eurasian Basins fit a conservative mixing line (line Siberian-Makarov) suggesting rapid (<3 years) mixing of Siberian shelf water with central Arctic Ocean water. Chukchi Borderland/Mendeleyev Ridge stations lie geographically between the Beaufort gyre-dominated western Arctic and shelf-dominated eastern Arctic and likely represent mixing of waters between the two systems.
2.5.4 Lability and multi-compartment fractions of Arctic tDOC

Recent analyses point to a significant sink of tDOC over the continental shelves of the eastern Arctic, supporting the view that Arctic tDOC is initially labile. *Cooper et al.* [2005] suggested that ~30% of tDOC initially entering the Eurasian Arctic is removed on the shelves. Field studies capturing the traditionally undersampled spring thaw period of greatest river flow have highlighted a more dynamic tDOC pool in the Arctic than previously believed. Studies by *Neff et al.*, [2006] and *Raymond et al.*, [2007] have shown that the tDOC transported during the spring flood, when up to 60% of annual tDOC discharge occurs, is young in radiocarbon age, most likely comprising recently fixed carbon present in surface leaf litter and soils. Of this tDOC transported in spring, ~50% is 1–5 years in age and ~35% aged 6–20 years [*Raymond et al.*, 2007]. *Holmes et al.* [2008] found that 20%–40% of the tDOC delivered during the spring freshet in Alaskan rivers is labile on the timescale of months, while DOC present during lower flow summer periods was more resistant to degradation. Similarly, *van Dongen et al.* [2008] estimated 20% of terrestrially-derived TOC (POC + DOC) delivered to the sub-Arctic Kalix River estuary was degraded over the timescale of days. As lability (or reactivity) negatively correlates with age [*Raymond and Bauer*, 2000], each DOC age cohort should exhibit a unique removal constant, with the youngest material being removed most rapidly upon export to the coastal system.

These findings of age fractionated tDOC pools in Arctic rivers [*Neff et al.*, 2006; *Raymond et al.*, 2007] indicate that the Arctic tDOC pool is made up of multiple fractions characterized by their lability, as is characteristic of both soil organic matter on land [*Six and Jastrow*, 2006; *Denef et al.*, 2009] and marine DOC in the world oceans [*Kirchman*}
The most labile tDOC fraction delivered after spring freshet [Holmes et al., 2008] is likely rapidly removed nearshore by microbial remineralization processes as has been observed in other estuarine environments [Moran et al., 1999; Raymond and Bauer, 2000; Hopkinson et al., 2002; Hernes and Benner, 2003], with the less labile fractions removed over longer timescales offshore. These multiple tDOC fractions or compartments, coupled with the contrasting shelf area and freshwater circulation between the eastern and western Arctic systems, influence the calculated tDOC removal rates for each region. The first order tDOC decay constant, \( \lambda \), obtained here for the eastern Arctic (0.24 \pm 0.07 yr\(^{-1}\)) is 2.5 times higher than that reported for the western Arctic (0.097 \pm 0.004 yr\(^{-1}\)) [Hansell et al., 2004] or 4 times that rate (0.06 yr\(^{-1}\)) as revised by Cooper et al. [2005]. This difference is most likely due to an observational bias arising from the timescale of observation between the two systems. River runoff delivered to the eastern Arctic has 2–5 years of shelf residence time before passing offshore to join the Transpolar Drift. The decay constant calculated here for the eastern Arctic (0.24 \pm 0.07 yr\(^{-1}\)) captures the rapid removal of the young, relatively labile Arctic tDOC pool that occurs on the continental shelves. By contrast, tDOC delivered in river runoff to the western Arctic transits relatively narrow continental shelves, quickly passing offshore to mix with older waters that have recirculated within the Beaufort gyre for a decade [Hansell et al., 2004]. This rapid mixing of the labile tDOC fraction into the older waters of the Beaufort gyre containing less labile tDOC biases the calculated decay constant towards slower rates. The most refractory tDOC is likely removed over longer timescales in the halocline and deep waters, though at an undetermined rate. The timescales of tDOC removal processes are illustrated in Fig. 2.7.
Fig. 2.7. Schematic for the timescale of the removal of Arctic tDOC illustrating multi-compartment fractions along with the inferred first order decay rate constants. Relatively labile tDOC is rapidly removed over the Eurasian shelves in less than 5 years time at a rate of $\lambda = 0.24$ yr$^{-1}$ found in this study. tDOC delivered to the western Arctic is mixed with older Beaufort gyre waters and removed over decades, yielding an integrated rate of $\lambda = 0.06$–0.097 yr$^{-1}$ [Cooper et al., 2005; Hansell et al., 2004]. More refractory tDOC is removed over longer timescales in the halocline and deep waters at an undetermined rate. The distinct labilities of Arctic tDOC suggest its removal can best be described by a multi-compartment model as compared to a reactivity continuum model (dashed line).

2.5.5 Relevance to the cycling of carbon in the surface Arctic Ocean

The mineralization of tDOC over the shelves impacts air-sea exchange of CO$_2$ in the system, and these impacts should vary as land-to-ocean transfer of water and organic matter changes with a changing climate at these high latitudes. Hansell et al. [2004] found approximate mass balance for carbon, where the decrease in tDOC was matched by
an increase of dissolved inorganic carbon (DIC) in the PSL, suggesting that microbial degradation and photo-oxidation predominate as tDOC removal mechanisms. Consistent with this, Anderson et al. [2009] attributed an excess of DIC over the East Siberian and Laptev shelves to the microbial remineralization of terrigenous organic matter. The remineralization of terrigenous organic matter and accompanying increase in DIC of shelf waters likely counters enhancement of the Arctic Ocean CO₂ sink resulting from reduced sea ice extent [Bates et al. 2006]. As the amount of river discharge continues to increase [Peterson et al., 2002], along with increasing DOC export due to climatic warming and permafrost thawing [Spencer et al., 2009], the remineralization of terrigenous organic matter over the Arctic shelves should reduce the Arctic Ocean's ability to absorb atmospheric carbon dioxide.

Using the flow-weighted DOC concentrations and annual fluvial discharges from Cooper et al. [2008], total annual delivery of DOC into the Arctic Basin from the six largest Arctic rivers is ~ 17.6 Tg C yr⁻¹. Of this, 2.8 Tg C yr⁻¹ is delivered to the western Arctic (via the Mackenzie and Yukon Rivers) and the remaining 14.8 Tg C yr⁻¹ empties into the eastern Arctic (via the Ob, Yenisey, Lena, and Kolyma Rivers). If western Arctic tDOC decays at the rate representative of that system (0.06–0.097 yr⁻¹) over a residence time estimated at 11 to 15 years [Bauch et al., 1995] or 12 to 14 years [Karcher and Oberhuber, 2002], then the initial 2.8 Tg C will be reduced to 0.7–1.5 Tg C by the time it exits the Arctic. A similar calculation using the decay rate found here (0.24 yr⁻¹) for the eastern Arctic follows that the 14.8 Tg C entering the eastern Arctic will be reduced to 3.1–5.7 Tg C over 4 to 6.5 years of residence time of river water in the Eurasian Arctic [Karcher and Oberhuber, 2002]. This estimate provides an upper limit for tDOC decay in
the eastern Arctic because the decay rate (0.24 yr\(^{-1}\)) only applies to waters overlying the shelf with slower rates offshore. Therefore, the 17.6 Tg C of tDOC that enter the Arctic Basin annually via the six largest rivers will be reduced to 3.1–5.7 Tg C (15–41% of input) by the time it reaches Fram Strait. If this analysis of the six largest rivers can be extrapolated to include all river runoff to the Arctic Basin, then the total tDOC input of 25 Tg C yr\(^{-1}\) [Raymond et al., 2007] will be reduced to 5.3–10.3 Tg C before subsequent export to the North Atlantic. By comparison, the analysis of lignin content, a biomarker for terrestrially derived carbon, indicated that 12%–40% of Arctic tDOC is exported via the East Greenland Current at Fram Strait [Opsahl et al., 1999] or 20%–50% as estimated using DOM fluorescence [Amon et al., 2003].

2.6 Summary

In this study we observed the removal of a significant fraction of tDOC delivered to the eastern Arctic system. This removal occurred largely over the Eurasian shelf seas such that the source waters of the Transpolar Drift contain < 50% of eastern Arctic tDOC concentrations originally added to the system. The tDOC decay constant calculated here, \(\lambda = 0.24 \pm 0.07\) yr\(^{-1}\), reflects the rapid removal of a relatively labile Arctic tDOC pool over a multi-annual (2–5 years) Eurasian shelf residence time. This tDOC decay constant agrees well with that found for the western East Siberian Arctic shelf of \(\lambda = 0.3\) yr\(^{-1}\) [Alling et al., 2010]. These results reinforce the idea of a dynamic tDOC pool in the Arctic, consisting of biolabile components supporting the microbial loop in the Arctic Ocean. Remineralization of terrigenous organic matter over the shelves mitigates the air–sea disequilibrium of CO\(_2\), with implications for the net air-to-sea flux of atmospheric
CO$_2$ over the Arctic Ocean that warrants further investigation. The decay constants for 
tDOC found in this and earlier studies for the Arctic Ocean can be incorporated into 
regional biogeochemical models to represent the dynamic tDOC pool within the Arctic 
carbon cycle. Further studies in the more temperate regions of the globe are needed to 
accurately include tDOC dynamics in global biogeochemical models.
Chapter 3. Dissolved organic nitrogen dynamics in the Arctic Ocean

3.1 Background

Dissolved organic nitrogen (DON) is an important source of reactive nitrogen in the surface ocean, and the dominant pool of fixed N when inorganic nutrients are depleted. Marine DON ultimately results from primary production in the surface ocean, subsequently providing N as substrate for heterotrophic growth [Azam and Hodson, 1977; Azam and Cho, 1987] via direct uptake of smaller molecules and extracellular hydrolysis of the bulk pool. In addition, moieties such as urea and amino acids are directly bioavailable for autotrophic growth [Bronk et al., 2007]. However, to date, analytical uncertainties in the measurement of marine DON [Sharp, 2002; Sharp et al., 2002] have made it difficult to adequately resolve spatio-temporal gradients within the open ocean from which DON dynamics can be inferred.

The Arctic Ocean provides a unique system in which to study the dynamics of DON. Inflow shelves [e.g., Barents and Chukchi Seas; Carmack and Wassmann, 2006] are highly influenced by Atlantic and Pacific Ocean inflow of nutrient-rich waters and can be highly productive seasonally (during sea-ice retreat) [Hansell et al., 1993; Sakshaug, 2004; Bates et al., 2005], while there are large inputs of terrigenous organic material from the many rivers that drain into the interior shelves (e.g., Siberian shelves and Beaufort Sea shelf) [Carmack and Wassmann, 2006; Raymond et al., 2007; Seitzinger and Harrison, 2008; Holmes et al., 2011]. As Arctic permafrost thaws due to a warming climate, river export of DON is expected to increase by another half in western Siberia by year 2100 [Frey et al., 2007], with similar increases expected for Alaskan
rivers [Frey and McClelland, 2009]. Terrigenous material comprises a significant fraction (20-30%) of the surface DON pool in the Siberian shelf seas [Kattner et al., 1999; Dittmar, 2004], but this terrigenous DON (tDON) was reported to be largely refractory and resistant to degradation based on near conservative mixing gradients [Dittmar et al., 2001]. However, recent studies show that terrigenous material exported via river runoff to the Arctic Ocean is partially labile and that there is a significant sink for the terrigenous dissolved organic carbon (tDOC) pool within the Arctic marine environment [Hansell et al., 2004; Cooper et al., 2005; Holmes et al., 2008; van Dongen et al., 2008, Alling et al., 2010;Letscher et al., 2011].

Terrestrially derived DON that survives degradation can be exported from the Arctic shelves to the Polar Surface Layer (PSL), the relatively fresh upper 30 meters of a vertically stratified water column formed from inputs of river runoff and sea-ice melt in the Arctic basins (e.g., Canada and Eurasian Basins). Elevated concentrations of DON ([DON]) reported for Arctic rivers (8-65 µM N) [Cauwet and Sidorov, 1996; Gordeev et al., 1996; Lara et al., 1998; Lobbes et al., 2000; Dittmar and Kattner, 2003; Köhler et al., 2003; Guo and Macdonald, 2006; Holmes et al., 2011], compared with lower concentrations of ~3-8 µM N found in Arctic marine waters [Davis and Benner, 2005; Mathis et al., 2009], provide sufficiently resolved spatio-temporal gradients required to overcome the analytical limitations of DON measurement, thereby allowing elucidation of geochemical transformations and processes that influence the Arctic DON pool.

In addition to fluvial inputs, marine waters entering the Arctic Ocean via the North Atlantic in the east and Bering Strait in the west carry large loads of nitrate (~4-25 µM N) [Hansell et al., 1993; Olsen et al., 2003], in turn supporting high rates of
phytoplankton production in the Barents [Sakshaug, 2004] and Chukchi Seas [Springer and McRoy, 1993; Hill and Cota, 2005; Walsh et al., 2005; Bates et al., 2005], respectively. The annual generation of large amounts of organic matter in these highly productive shelf ecosystems [Walsh, 1995; Macdonald et al., 2010] suggest the likelihood of observing significant marine DON production.

In this study, we combine observations of [DON], nitrogenous nutrients, and tracers of freshwater taken within the summer-season PSL of the Arctic Ocean during the last decade. Surface distributions of [DON] from four cruises determine those shelf processes important for controlling DON dynamics. In addition, analyses of dissolved nitrogen species from the six largest Arctic rivers are presented and the fate of tDON in the marine environment investigated.

3.2 Regional hydrography

3.2.1 Eastern Arctic

The eastern Arctic system (here defined as waters north of the Arctic Circle in the eastern hemisphere 0-180°E) receives marine water with a mean salinity of ~34.9 from the Atlantic Ocean (Fig. 3.1). Surface flow is generally cyclonic; to the east over the Barents Sea shelf, passing into the Kara Sea [Stein and Macdonald, 2004] and subsequent transport into the Laptev and East Siberian Seas. Inflowing Atlantic Ocean waters are initially high in nitrate (up to 12 µM) [Olsen et al., 2003], however these nutrients are largely removed over the Barents Sea shelf leaving the interior Siberian shelves nutrient impoverished. Kara Sea surface waters are also modified by river runoff from the Ob and Yenisey Rivers, which together deliver ~1030 km³ of fresh water each year [Cooper et
These waters continue eastward, passing into the Laptev Sea, where they receive another ~560 km$^3$ yr$^{-1}$ from the Lena River [Cooper et al., 2008]. The direction of flow within the Laptev and East Siberian Sea shelves is strongly influenced by the prevailing summertime winds that in turn are controlled by the phase of the Arctic Oscillation (AO) [Ekwurzel et al., 2001; Guay et al., 2001; Anderson et al., 2004]. During a negative AO phase, weakened subpolar westerlies due to a stronger Beaufort High allow for a northerly flow in the Laptev Sea, with shelf discharge joining the Transpolar Drift (TPD) near the Lomonosov Ridge. In contrast, a positive AO phase is characterized by a weaker Beaufort High, which intensifies the subpolar westerlies, driving a strong easterly flow from the Kara and Laptev Seas into the East Siberian Sea. There, the fluvial component mixes with runoff from the Kolyma River [114 km$^3$ yr$^{-1}$; Cooper et al., 2008] before detachment from the shelf to join the TPD near the Mendeleyev Ridge. This circulation in the eastern Arctic system allows for a 2-5 years residence for river runoff over the Eurasian shelves [Schlosser et al., 1994; Ekwurzel et al., 2001; Karcher and Oberhuber, 2002] before export to the interior Arctic Ocean. The combined input of Atlantic Ocean waters across the Barents Sea and freshwater from Siberian rivers is approximately balanced by shelf-basin transport into the Eurasian Basin and eventual export out of the Arctic with the Transpolar Drift through Fram Strait.
Fig 3.1. Station locations for cruises ARKXXXIII/3 (black dots), SBI (red dots), and RUSALCA (purple dots) in reference to general surface circulation (black arrows) and rivers of the Arctic Ocean. The eastern Arctic system (0º-180ºE) is characterized by cyclonic circulation over the Eurasian shelf seas with return flow in the Transpolar Drift (TPD) towards Fram Strait. The anticyclonic circulation of the Beaufort Gyre (BG) dominates the western Arctic system (180ºW-0º). Geographic features are marked as follows: Atl = Atlantic Ocean, FS = Fram Strait, BarS = Barents Sea, KS = Kara Sea, EB = Eurasian Basin, LS = Laptev Sea, LR = Lomonosov Ridge, MR = Mendeleyev Ridge, MB = Makarov Basin, ESS = East Siberian Sea, CS = Chukchi Sea, BS = Bering Strait, BerS = Bering Sea, BfS = Beaufort Sea, CA = Canadian Archipelago, and CB = Canada Basin.
3.2.2 Western Arctic

The western Arctic system (here defined as those waters in the western hemisphere 0-180°W, north of Bering and Fram Straits) receives Pacific Ocean water with a mean salinity of ~33 via Bering Strait [Coachman et al., 1975]. These waters contain elevated levels of nitrate (up to 25 µM), which support high seasonal levels of phytoplankton primary production in the Chukchi Sea during sea-ice retreat [Sambrotto et al., 1984; Hansell et al., 1993; Mathis et al., 2009]. In addition, the Bering Strait inflow is influenced by the Yukon River [Woodgate and Aagaard, 2005], delivering 214 km³ yr⁻¹ of freshwater to the eastern Bering Sea shelf [Cooper et al., 2008]. Waters overlying the Chukchi Sea shelf flow north and east, with a portion entering the anticyclonic circulation of the Beaufort Gyre over the Canada Basin. The PSL of the Beaufort Gyre is further modified by input from the Mackenzie River [322 km³ yr⁻¹; Cooper et al., 2008]. At 12-15 years, the residence time for the fluvial component in the PSL is much longer in the western than the eastern Arctic due to retention within the Beaufort Gyre circulation [Kadko and Muench, 2005]. Western Arctic waters are largely exported to the North Atlantic through the Canadian Archipelago.

3.3 Methods

3.3.1 Field collected data sets

Observations of dissolved nitrogen species [TDN] (total dissolved nitrogen), [NO₃⁻ + NO₂⁻], [NH₄⁺], stable oxygen isotopes, and salinity within the PSL were collected from numerous CTD/hydrocast stations on four cruises in the Arctic over the last decade (Fig. 3.1). During the western Shelf-Basin Interactions (SBI) project
[Grebmeier and Harvey, 2005], samples were collected in spring (May 5 – June 15, 2002; ~80-100% sea-ice cover) and summer (July 16 – Aug 26, 2002; ~0-20% sea-ice cover) cruises with hydrocast stations located in the outer shelf region of the Chukchi Sea shelf and in deep waters of the adjacent Beaufort Gyre. The timing of the two cruises allows direct comparison of biogeochemical conditions during sea-ice cover and subsequent sea-ice retreat in the same year. Cruise ARKXXIII/3 occupied stations over the deep Arctic basins from August 12 to October 17, 2008 and spanned waters of the western and eastern Arctic systems from the Canada Basin west to the Eurasian Basin. The RUSALCA 2009 cruise occupied the southern and western Chukchi Sea as well as the adjacent East Siberian Sea during September 1 to September 30, 2009. Data reported here were collected at depths <10 m, well within the ~30 m deep PSL.

The marine data reported here are also compared to nitrogen species in the six largest Arctic rivers sampled during the 2003-2006 PARTNERS (Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments), with annual flow-weighted mean values calculated for [DON], [NO$_3^-$ + NO$_2^-$], and [NH$_4^+$] following the approach of Cooper et al. [2008], using discharge data collected by the Russian Federal Service of Hydrometeorology and Environment Monitoring (Ob, Yenisey, Lena, Kolyma), the USGS (Yukon), and the Water Survey of Canada (Mackenzie). Concentration and discharge data were taken from http://arcticgreatrivers.org/.

3.3.2 Nitrogen species

**Sampling** – Samples were filtered for the removal of particulate organic matter (POM) using precombusted Whatman GF/F filters (nominal pore size, 0.7 µm) held in acid-cleaned polycarbonate filter holders. Filter holders were connected inline with the
seawater source (clean seawater intake during ARKXXIII/3 and CTD-Niskin bottle during RUSALCA-09 and SBI) using acid-cleaned, DOC-free silicon tubing. Seawater was collected into preconditioned 60 mL HDPE bottles and immediately frozen upright at -20ºC. New filters were loaded prior to each sample filtration.

**TDN** -- Analyses of total dissolved nitrogen were performed by high temperature combustion using a Shimadzu Total Nitrogen analyzer coupled to a Shimadzu TOC-VCSH system [Dickson et al., 2007]. The oxidation product nitric oxide (NO) is quantified by reaction with ozone and detection of the resulting chemiluminescence. Standardization for TDN was achieved using potassium nitrate. Deep seawater and low carbon reference waters as provided by the Hansell CRM Program [Hansell, 2005] were measured every sixth analysis to assess the day-to-day and instrument-to-instrument variability. The precision for TDN analyses is ~0.5 µM or a CV of 5-10%.

**NO$_3^-$ + NO$_2^-$** -- For cruises ARKXXIII/3 and RUSALCA-09, the sum of [NO$_3^-$ + NO$_2^-$] in filtered (0.7 µm) samples was measured by reduction to NO using a solution containing heated, acidic V(III), followed by chemiluminescent detection of NO [Braman and Hendrix, 1989]. Standardization was achieved using potassium nitrate. The limit of detection is 0.05 µM with a precision of ± 0.1 µM. Nitrate + nitrite from the SBI 2002 cruises were taken from the SBI data archive at http://www.eol.ucar.edu/projects/sbi/.

**NH$_4^+$** -- For the RUSALCA-09 cruise, ammonium was measured on frozen-archived samples using a fluorescence technique with orthophthalldialdehyde (OPA) [Holmes et al., 1999]. Filtered (0.7 µm) samples are allowed to react for 2 hours at room temperature with an OPA-containing solution, with subsequent measurement of fluorescence at an excitation/emission of 350nm/410-600nm. Standardization was
achieved using ammonium chloride. The limit of detection was 0.025 µM with a precision of ± 0.01 µM. For the SBI 2002 cruises, ammonium values, measured by the Berthelot reaction \[ \text{Patton and Crouch, 1977} \], were retrieved from the SBI data archive. No measurements of ammonium were made for cruise ARKXXIII/3, however surface \([\text{NH}_4^+]\) at deep ocean stations during SBI 2002 were observed to be relatively low (<0.025 µM).

\( \text{DON} - [\text{DON}] \) was calculated by subtracting the sum of dissolved inorganic nitrogen \( ([\text{DIN}] = [\text{NO}_3^- + \text{NO}_2^-] + [\text{NH}_4^+]) \) from the measured \( [\text{TDN}] \); \( [\text{DON}] = [\text{TDN}] - [\text{DIN}] \). Ammonium was not measured during ARKXXIII/3, but the very low ammonium values in the off-shelf PSL (see Results) add only a small error to the DON estimate. Propagation of error yields a precision on DON determinations of ± 0.5 µM.

3.3.3 Stable oxygen isotopes and salinity

\( \delta^{18}O \) -- For cruise ARKXXIII/3, samples for stable oxygen isotope measurements \( (\delta^{18}O) \) were collected unfiltered into 10 mL glass vials and immediately capped and sealed. Analyses were performed by mass spectrometry at the Stable Isotope Laboratory at RSMAS, University of Miami, using a modified method of \textit{Epstein and Mayda} [1953] detailed elsewhere \[ \text{Swart, 2000} \]. Counts were calibrated using Vienna Standard Mean Ocean Water (VSMOW) and expressed using the conventional \( \delta^{18}O \)‰ notation. Samples were analyzed in duplicate with a precision of ±0.08‰. Oxygen isotope data for the SBI 2002 cruises were taken from the SBI data archive; precision was reported to be ±0.04‰. Oxygen isotopes were not measured during cruise RUSALCA-09.
Salinity – Salinity was measured by conductivity using the ship’s salinometer mounted at the seawater intake (cruise ARKXXXIII/3, RUSALCA-09) or a Guildline Autosal 8400A salinometer (SBI 2002 cruises).

3.3.4 Calculations of river and sea-ice melt fractions in the polar surface layer

Oxygen isotope and salinity data were used to calculate the fractions of river water (RW), sea-ice melt (SIM), and marine water (SW) present in samples collected from the PSL [e.g. Cooper et al., 2005; Bates, 2006; Mathis et al., 2007; Letscher et al., 2011]. Each end-member was assigned a characteristic \( \delta^{18}\)O and salinity based on values reported in the literature. The water source fractions (RW, SIM, and SW) were calculated from the mass balance solutions to these equations:

\[
\delta^{18}\text{O} = (\text{RW} \delta^{18}\text{O} \times \text{RW}) + (\text{SIM} \delta^{18}\text{O} \times \text{SIM}) + (\text{SW} \delta^{18}\text{O} \times \text{SW})
\]

\[
S = (\text{RW} S \times \text{RW}) + (\text{SIM} S \times \text{SIM}) + (\text{SW} S \times \text{SW})
\]

\[
1 = \text{RW} + \text{SIM} + \text{SW}
\]

Stations were separated by hemisphere, with those from the eastern hemisphere (west of 180°E) assigned eastern Arctic end-member values and those from the western hemisphere (east of 180°E) assigned western Arctic end-members. Eastern Arctic end-member values were: RW \( \delta^{18}\text{O} = -18.6\%\), RW S = 0; SIM \( \delta^{18}\text{O} = -1.9\%\) [Eicken et al., 2002], SIM S = 4.5 [Mathis et al., 2007]; Atlantic SW \( \delta^{18}\text{O} = +0.3\%\) [Bauch et al., 1995], Atlantic S = 34.9. Western Arctic end-members were assigned: RW \( \delta^{18}\text{O} = -19.6\%\), RW S = 0; SIM \( \delta^{18}\text{O} = -1.9\%\), SIM S = 4.5; and Pacific SW \( \delta^{18}\text{O} = +0.3\%\), Pacific S = 33 [Coachman et al., 1975]. Riverine end-members were assigned using the
flow weighted δ¹⁸O values from Cooper et al. [2008] for the Mackenzie and Yukon Rivers (western Arctic RW) and the Ob, Yenisey, Lena, and Kolyma Rivers (eastern Arctic RW).

3.4 Results

3.4.1 Delivery of nitrogen species by Arctic rivers

The six major Arctic rivers exhibit the largest fluxes of dissolved nitrogen (DON, NO₃⁻, NH₄⁺) in the early summer months following the spring freshet. This seasonality is shown for the Lena River in Fig. 3.2. Typically, the month of June coincides with both the highest seasonal concentration of each nitrogen species and the highest river volume flow. Fluxes of DON and NH₄⁺ during the winter months (November to April) are two orders of magnitude lower than the summer peak while NO₃⁻ has a generally lower but more varied wintertime flux. These six Arctic rivers deliver each year a total of 32 Gmol N as DON, 13 Gmol N as NO₃⁻, and ~3 Gmol N as NH₄⁺ [Holmes et al., 2011].

Annual flow weighted mean concentrations in the rivers ranged from 8.1–17.7 µM for DON, 3.1–9.5 µM for NO₃⁻, 0.5–6.9 µM for NH₄⁺, and 13.4–33.1 µM for TDN (Table 3.1). A mean end-member [DON] in eastern Arctic rivers was calculated by weighting [DON] in the Ob, Yenisey, Lena, and Kolyma Rivers to their respective volume flows, yielding a value of 15.4 ± 0.8 µM for the eastern Arctic system. A similar calculation using data from the Yukon and Mackenzie Rivers yields a western Arctic river end-member DON concentration of 10.5 ± 0.6 µM.
Fig. 3.2. Lena River average monthly flux in mol s$^{-1}$ of TDN (triangles), DON (circles), NO$_3^-$ (open squares), and NH$_4^+$ (crosses) during 2003-2006 from the PARTNERS dataset (http://arcticgreatrivers.org/).

Table 3.1. Annual flow weighted mean concentrations (µM) ± SE of nitrogen species in six major Arctic rivers.

<table>
<thead>
<tr>
<th>River</th>
<th>DON</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>TDN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ob</td>
<td>17.2 ± 1.1</td>
<td>9.0 ± 0.9</td>
<td>6.9 ± 2.4</td>
<td>33.1 ± 2.2</td>
</tr>
<tr>
<td>Yenisey</td>
<td>13.1 ± 0.8</td>
<td>4.0 ± 0.9</td>
<td>0.5 ± 0.2</td>
<td>17.7 ± 0.5</td>
</tr>
<tr>
<td>Lena</td>
<td>17.7 ± 0.8</td>
<td>3.1 ± 0.8</td>
<td>1.3 ± 0.1</td>
<td>22.1 ± 0.9</td>
</tr>
<tr>
<td>Kolyma</td>
<td>8.3 ± 0.5</td>
<td>4.5 ± 0.5</td>
<td>0.6 ± 0.1</td>
<td>13.4 ± 0.3</td>
</tr>
<tr>
<td>Mackenzie</td>
<td>8.1 ± 0.3</td>
<td>6.9 ± 0.5</td>
<td>0.6 ± 0.1</td>
<td>15.6 ± 0.5</td>
</tr>
<tr>
<td>Yukon</td>
<td>13.9 ± 1.0</td>
<td>9.5 ± 0.7</td>
<td>2.1 ± 0.3</td>
<td>25.5 ± 0.9</td>
</tr>
</tbody>
</table>
3.4.2 Summertime salinity distributions, river runoff and sea-ice melt contributions to the Arctic Ocean PSL

Salinity – Salinities at Bering Strait and in the southern Chukchi Sea were ~31-32 (Fig. 3.3a), reduced from the characteristic salinity of 33 for Pacific Ocean inflow waters due primarily to the presence of river runoff. Farther downstream at the outer Chukchi Sea shelf, salinities were reduced further to ~26-28 by both sea-ice melt and river water. Low salinities (~22-24) were also found in the waters of the Beaufort Gyre.

Salinities were generally higher in the eastern Arctic, with a salinity front observed over the outer shelf just east of 180°E separating the higher salinity (~29-30) eastern Arctic from the lower salinity (~27) western Arctic. Salinities over the Eurasian Basin (Fig. 3.3a) were ~34-35, characteristic of the Atlantic inflow waters. Elsewhere in the eastern Arctic, isolated regions of low salinity were observed over the Makarov Basin and the eastern sector of the East Siberian Sea, decreasing to values of 26-27.

RW – River water, with its contribution having been determined using oxygen isotopes, was ubiquitous within the summertime PSL, with contributions ranging from 5-25% (Fig. 3.3b). Highest river water contributions (~20-25%) were observed in the eastern Arctic coinciding with the regions of reduced salinity over the Makarov Basin and East Siberian Sea. Contributions were more varied over both the Eurasian Basin and the outer Siberian shelf, ranging from 6-12%. Highest fractions in the western Arctic were found within the southern Beaufort Gyre, reaching 18-19%. Lower river water contributions were found on the Chukchi Sea shelf, decreasing from ~15% on the northern outer shelf to ~5% in the southern Chukchi Sea.
Fig. 3.3. Surface distribution of (a) salinity, (b) fraction of river water (RW), and (c) fraction of sea-ice melt (SIM).
SIM – A composite map of sea-ice melt fractions from data collected in the summers of 2002 and 2008 is shown in Fig. 3.3c. The stations were located in open (ice-free) water, post sea-ice retreat, with the exception of all stations north of 80°N in the eastern Arctic, which were located in pack ice. In general, contributions from sea-ice melt were higher in the western Arctic compared to the eastern Arctic, ranging from 10-18% over the Beaufort Gyre to 4-9% over the outer Siberian shelf. Highest sea-ice melt fractions (>30%) were observed off the north coast of Alaska; these stations had been sampled ~2 weeks after sea-ice breakup and retreat. Sea-ice melt contributions were negligible over the deep basins of the eastern Arctic owing to the continued presence of sea-ice at these stations throughout the summer season.

3.4.3 Dissolved nitrogen in the Arctic Ocean PSL

DON – The summertime distribution of [DON] within the Arctic Ocean PSL is shown in Fig. 3.4a. Highest concentrations (6-8 µM) were observed in the southern Chukchi Sea, immediately north of Bering Strait. Concentrations elsewhere in the western Arctic were lower, generally ~5 µM over the outer shelves decreasing to <4 µM within the Beaufort Gyre. In the eastern Arctic, [DON] of ~5 µM were observed over the outer East Siberian shelf and within the Eurasian Basin. Higher concentrations (6-7 µM) were found in the Makarov Basin and the eastern sector of the East Siberian Sea. [DON] in the surface Arctic Ocean are lower than reported by Wheeler et al. [1997], perhaps reflecting interannual variability or differences in analytical techniques. There were contrasting relationships between [DON] and salinity (Fig. 3.3a, 3.4a) between the two Arctic systems. In the eastern Arctic, the highest [DON] correlated with the low salinity waters of the Makarov Basin and East Siberian Sea. By contrast, lower salinity water
within the Beaufort Gyre had the lowest [DON], while the highest [DON] in the western Arctic were found in the high salinity Pacific water of the southern Chukchi Sea.

Fig. 3.4. Surface distribution of (a) DON (µM), (b) NO$_3^-$ + NO$_2^-$ (µM), and (c) NH$_4^+$ (µM).
\(NO_3^-\) -- Nitrate concentrations within the PSL were generally low (<0.5 \(\mu M\)) (Fig. 3.4b), while values reached 15 \(\mu M\) in the Pacific waters present in Bering Strait. In addition, nitrate reached 2-3 \(\mu M\) over the Eurasian Basin.

\(NH_4^+\) -- Ammonium concentrations within the PSL were low (<0.05 \(\mu M\)) over the outer East Siberian and Chukchi Sea shelves (Fig. 3.4c), indicative of tight temporal coupling between \(NH_4^+\) production and consumption processes. Concentrations increased to 0.5–2 \(\mu M\) in the southern Chukchi Sea shelf where elevated [\(NH_4^+\)] has been observed previously [Codispoti et al., 2005].

### 3.5 Discussion

Property-salinity plots have been used extensively in the Arctic to discern hydrographic controls on chemical distributions, as for example, evaluation of the dissolved organic carbon (DOC) pool [Kattner et al., 1999; Köhler et al., 2003; Hansell et al., 2004; Cooper et al., 2005; Mathis et al., 2005; Letscher et al., 2011]. Here we employ DON-salinity plots along with estimates of river water fractions present in the Arctic PSL to investigate the behavior of DON across shelf-to-basin mixing gradients.

#### 3.5.1 Non-conservative behavior of tDON over the eastern Arctic shelves

A plot of [DON] versus salinity for stations occupying the eastern Arctic is shown in Fig. 3.5. Mixing between two end-members is evident: DON-enriched river water at low salinities and lower DON marine water at high salinity. Regression analysis reveals an apparent [DON] within the river water fraction of 9.1 ± 1.0 \(\mu M\) N, taken from the y-intercept (salinity = 0) in Fig. 3.5. This apparent river end-member [DON] can be compared to estimates of the [DON] in the Siberian rivers draining to the region from
analysis of the PARTNERS data. The calculated annual mean flow weighted [DON] within the four Siberian rivers (Ob, Yenisey, Lena, and Kolyma) is $15.4 \pm 0.8 \mu M N$. The [DON] found within the river water fraction from the regression observed over the Makarov and Eurasian Basins is low relative to that measured in the regional riverine sources, indicating a net loss of $6.3 \pm 1.3 \mu M tDON$ over the Siberian Arctic shelves. If the annual flow weighted [DON] for the more local eastern Siberian Lena and Kolyma Rivers is employed instead ($16.4 \pm 0.8 \mu M N$), the net loss of tDON is $7.3 \pm 1.3 \mu M$.

Coupling of shelf residence times for the river water fraction with the apparent loss of DON provides a first-order decay constant for tDON, as described previously for the Arctic tDOC pool in this region [Alling et al., 2010; Letscher et al., 2011]. Eastern Arctic river water has a multi-year residence on the Eurasian shelves before transport offshore to join the TPD [Schlosser et al., 1994; Guay et al., 2001; Anderson et al., 2004]. Using a He/3H technique, Schlosser et al. [1994] and Ekwurzel et al. [2001] estimated the Eurasian river water shelf residence at $3.5 \pm 1.5$ years and 2-5 years, respectively. System modeling by Karcher and Oberhuber [2002] found a similar result of 2-3 years. In addition, measurements of $^{228}$Ra ($t_{1/2} = 5.7$ yr), a tracer of shelf water provenance, did not show significant decay across the shelf break into the TPD [Letscher et al., 2011]. Here we assign an eastern Arctic river water shelf residence time of $3.5 \pm 1.5$ years. Using this residence time with the estimates of tDON loss within the river water fraction yields a first-order decay constant, $\lambda = 0.15 \pm 0.07 \text{ yr}^{-1}$ if all four Siberian Arctic rivers are considered or a slightly higher value, $\lambda = 0.17 \pm 0.07 \text{ yr}^{-1}$ if only the Lena and Kolyma are selected as contributing riverine waters to the observation region (Table 3.2).
Fig. 3.5. DON-salinity plots for the late summer season eastern Arctic system. Fraction of RW is represented by the color data points. Stations lacking δ^{18}O data, for which estimates of RW cannot be made, are shown with black data points. Calculated regression for the eastern Arctic [dashed line]: DON = -0.154 x salinity + 9.1; R^2 = 0.18, n = 98; standard error of intercept = ± 1.0 µM.

These decay constants are sensitive to the choice of river end-member [DON] and residence times and assume an equal lability of tDON from each Arctic river. Moreover, a gradient in tDON lability likely exists in conjunction with that found for the organic carbon pool, with older more degraded material in the western Siberian rivers (Ob and
Yenisey) than the eastern Siberian rivers (Lena, Indigirka, and Kolyma) [Gustafsson et al., 2011]. Our analysis indicates that 25-55% of Siberian Arctic river tDON is removed during transit of the Eurasian shelves over a 2-5 year timescale.

3.5.2 Non-conservative behavior of tDON within the Beaufort Gyre of the western Arctic

Data from spring and summer cruises within the SBI 2002 field season allow comparison of the DON distribution between pre- and post-bloom conditions in the NE Chukchi Sea and Beaufort Gyre. The DON-salinity plot for the SBI 2002 spring (May-early June) cruise is shown in Fig. 3.6a. Higher river water fractions were present at lower salinities, yet [DON] at lower salinity was not enriched relative to the marine end-member concentrations; this relationship is contrary to the observations from the eastern Arctic (Fig. 3.5). Here, the [DON] within the river and marine end-members appear to be similar (mean of the data in Fig. 3.6a is 4.0 ± 0.7 µM N).

The similarity between river water [DON] and marine [DON] is eliminated during the summer months (Fig. 3.6b), as evidenced by an increase in [DON] at the higher salinities of the marine end-member. However, [DON] at low salinities during the summer remains relatively unchanged from its spring value (3.8 ± 0.5 µM N at salinities <28). These samples with high river water fractions and ~3.8 µM DON (the lower salinities within Fig. 3.6b) correspond to stations within the Beaufort Gyre (see Fig. 3.4b for reference), which has been shown to retain western Arctic river water for several years [Macdonald et al., 2002; Kadko and Muench, 2005]. Hansell et al. [2004] used measurements of dissolved radium isotopes to estimate the residence time of western Arctic river water within the PSL of the Beaufort Gyre, arriving at a mean age of 13 ± 1 years.
Fig. 3.6. DON-salinity plots for the (a) spring season western Arctic system (SBI 2002 data only), and (b) summer season western Arctic system. Fraction of RW is represented by the color data points. Stations lacking δ¹⁸O data, for which estimates of RW cannot be made, are shown with black data points.
As noted above, the absence of a DON concentration gradient with salinity during spring, and the continued low values at low salinity during summer, suggests that the river and marine fractions during spring have essentially equal concentrations of DON. Aged Beaufort Gyre river water with a mean [DON] of 3.8 ± 0.5 µM can be compared with [DON] of the western Arctic rivers. The mean annual flow weighted [DON] within the Yukon and Mackenzie Rivers (using the PARTNERS data) yielded a value of 10.5 ± 0.6 µM N. Thus a net tDON loss of 6.7 ± 0.8 µM over a 13 ± 1 years timescale is indicated from the river water fraction of the Beaufort Gyre PSL, yielding a first-order decay constant, λ = 0.08 ± 0.01 yr\(^{-1}\) (Table 3.2). This concentration change represents a 55-70% removal of tDON during the decadal timescale of Beaufort Gyre circulation.

Table 3.2. Terrigenous DON removal and calculated first-order decay constants (λ) for tDON within the eastern and western Arctic systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Arctic Rivers</th>
<th>[DON](^a) river (µM ± SE)</th>
<th>[DON](^b) aged RW (µM ± SE)</th>
<th>[DON] lost(^c) (µM ± SE)</th>
<th>RW res. time (yr)</th>
<th>λ (yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastern</td>
<td>Ob+Yenisey+ Lena+Kolyma</td>
<td>15.4 ± 0.8</td>
<td>9.1 ± 1.0</td>
<td>6.3 ± 1.3</td>
<td>3.5 ± 2 yr(^d)</td>
<td>0.15 ± 0.07 yr(^{-1})</td>
</tr>
<tr>
<td>Eastern</td>
<td>Lena+Kolyma Mackenzie+</td>
<td>16.4 ± 0.8</td>
<td>9.1 ± 1.0</td>
<td>7.3 ± 1.3</td>
<td>3.5 ± 2 yr(^d)</td>
<td>0.17 ± 0.07 yr(^{-1})</td>
</tr>
<tr>
<td>Western</td>
<td>Yukon</td>
<td>10.5 ± 0.6</td>
<td>3.8 ± 0.5</td>
<td>6.7 ± 0.8</td>
<td>13 ± 1 yr(^e)</td>
<td>0.08 ± 0.01 yr(^{-1})</td>
</tr>
</tbody>
</table>

\(^a\)Initial river DON concentration (µM ± SE)

\(^b\)Aged river DON concentration (µM ± SE)

\(^c\)Difference between initial and aged river DON concentrations (µM ± SE)

\(^d\)Residence time for river water on the Eurasian shelves (eastern Arctic) was estimated from He/\(^3\)H ages [Schlosser et al., 1994; Ekwurzel et al., 2001].

\(^e\)River water residence within the Beaufort Gyre (western Arctic) was estimated using a \(^228\)Ra/\(^226\)Ra aging technique [Hansell et al., 2004].
3.5.3 Net production of marine DON over the Chukchi shelf

Nutrient-enriched Pacific waters entering the western Arctic at Bering Strait support summertime net community production (NCP) rates on the Chukchi Sea shelf of up to ~300 g C m$^{-2}$ yr$^{-1}$ [Bates et al., 2005; Mathis et al., 2009]. Inspection of the spring and summer DON distributions within this region allows assessment of the fraction of this production that is released as DON. Spring (pre-bloom) [DON] within surface waters located over the Chukchi Sea shelf have a mean value of 4.0 ± 0.7 µM N (Fig. 3.6a). Concomitant [NO$_3^-$] within the end of winter surface waters are correlated with salinity (Fig. 3.7a), ranging from ~14 µM NO$_3^-$ at salinity = 33 in the southern Chukchi Sea near Bering Strait to near zero within the Beaufort Gyre PSL at salinity = 30-31. This surface layer nitrate is almost completely utilized in the summer season (Fig. 3.7b; Fig. 3.3b), fueling NCP over the Chukchi shelf. A portion of this NCP is released as DON, represented by the increase in summer season [DON] at salinities >29 (Fig. 3.7b). Net production of marine DON over the Chukchi shelf ranged from ~0 – 8.0 µM, with an average over the SBI region of 1.6 ± 1.0 µM. This estimate is ~40% lower than the ~2.8 µM seasonal increase observed for total (terrigenous + marine) DON in the SE Beaufort Sea [Simpson et al., 2008]. Taking summertime [NO$_3^-$] to be essentially zero, the ratio of the slopes in Fig. 3.7b (0.377:4.584) for marine DON (red line; showing DON accumulation between spring and summer) and winter ice-melt-corrected nitrate (dashed black line; which is a measure of NO$_3^-$ utilized) indicates that 8 ± 1% of seasonal nitrate drawdown is converted to marine DON in the Chukchi Sea region. The contribution of urea to the observed seasonal increase in marine DON was low at 2-4% (urea data from
the SBI program). As expected, net production of marine DON is not observed over the Beaufort Gyre where PSL [NO$_3^-$] is low year-round.
Fig. 3.7. (a) The end-of-winter (pre-bloom) NO$_3^-$-salinity correlation (NO$_3^-$ = 4.584 x salinity – 138.9; n = 111, R$^2$ = 0.86), redrawn in (b) as the solid black line. (b) Observed correlations between DON and salinity (filled circles) and NO$_3^-$ and salinity (open circles) during summer over the Chukchi Sea shelf. Observations of variables against the salinity field will vary due to sea-ice melt between the winter and summer observations, and hence need to be considered. The impact of sea-ice melt on the winter NO$_3^-$-salinity correlation would be to dilute the salinity by a mean of 7% (from Fig. 3.3c), as indicated by the dashed line, which shifts the correlation to the left on the x-axis (indicated by arrow in (b)). The difference between the summertime observed NO$_3^-$ (essentially zero) and the dashed line indicates NO$_3^-$ consumed between winter and summer as a function of salinity. Near complete nitrate utilization during the bloom results in net production of DON at elevated salinity (red line, DON = 0.377 x salinity – 5.6; n = 126 at salinity >29, R$^2$ = 0.10). The ratio of the slopes of summer DON and sea ice melt-shifted winter nitrate indicates that net DON production is 8 ± 1% of nitrate drawdown. The RW fraction did not change appreciably between late winter and summer and so is not considered in this calculation.
3.5.4 Impact of fluvial inputs of dissolved N on Arctic ecosystem productivity

The riverine input of nitrate and ammonium, along with decay of tDON by remineralization to DIN, represents a source of allochthonous nitrogen to the Arctic shelf seas, thus supporting export production. Here we combine the fluxes of nitrate, ammonium, and DON from the six largest Arctic rivers reported by Holmes et al. [2011] with estimates of export production for the Arctic shelf seas to assess the impact of riverine delivery of bioavailable dissolved nitrogen on ecosystem productivity. The first-order decay constants determined for the Arctic tDON pool from this study are used to estimate the amount of DIN released from the decay of tDON over the residence time of the fluvial waters within each region. Table 3.3 lists the sum of nitrogen inputs to each Arctic region by the respective river(s) of influence. Estimates of export production are taken from Macdonald et al. [2010] with the exception of the eastern East Siberian Sea taken from Anderson et al. [2011]. Values were converted from carbon to nitrogen units using a C:N molar ratio of 6.6. Fluvial inputs of dissolved nitrogen have the largest impact over the Siberian shelf seas (Kara, Laptev, and western East Siberian Seas), where they support ~7-14% of export production, with about half of terrigenous N inputs deriving from tDON decay. River N inputs had less of an impact in regions influenced by high-nutrient Pacific water, with ~2-8% of export production supported by fluvial N over the eastern East Siberian Sea, Beaufort Sea, and the Canada Basin.
Table 3.3. Fluvial inputs of nitrogen species and impact on ecosystem productivity.

<table>
<thead>
<tr>
<th>Arctic Region</th>
<th>Export Prod.(^a) Gmol N yr(^{-1})</th>
<th>River</th>
<th>DIN from tDON(^c) Gmol N yr(^{-1})</th>
<th>% Export Prod. from remin. tDON</th>
<th>ΣN input(^d,e) Gmol N yr(^{-1})</th>
<th>% Export Prod. from ΣN River input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kara Sea</td>
<td>116</td>
<td>Ob+Yenisey</td>
<td>2.3 ± 0.9</td>
<td>1-3%</td>
<td>12.1 ± 0.9</td>
<td>10-11%</td>
</tr>
<tr>
<td>E. Siberian Sea</td>
<td>74</td>
<td>Lena</td>
<td>5.6 ± 2.3</td>
<td>4-11%</td>
<td>7.9 ± 2.3</td>
<td>7-14%</td>
</tr>
<tr>
<td>Laptev+west</td>
<td>76(^b)</td>
<td>Kolyma</td>
<td>2.1 ± 1.0</td>
<td>1-4%</td>
<td>2.6 ± 1.0</td>
<td>2-5%</td>
</tr>
<tr>
<td>Beaufort Sea</td>
<td>27</td>
<td>Mackenzie</td>
<td>0.2 ± 0.1</td>
<td>~1%</td>
<td>2.1 ± 0.1</td>
<td>7-8%</td>
</tr>
<tr>
<td>Canada Basin</td>
<td>56</td>
<td>Mackenzie</td>
<td>3.6 ± 0.1</td>
<td>6-7%</td>
<td>3.6 ± 0.1</td>
<td>6-7%</td>
</tr>
</tbody>
</table>

\(^a\)Export production estimates are from Macdonald et al. [2011].

\(^b\)Rate for East Siberian Sea taken from Anderson et al. [2011].

\(^c\)DIN released by tDON decay using calculated eastern and western Arctic decay constants, \(\lambda\), and river water residence times.

\(^d\)\(\Sigma N = (NO_3^-) + (NH_4^+) + (\text{DIN released from tDON})\).

\(^e\)Uncertainties in the sum of nitrogen inputs reflect the propagated uncertainties in annual dissolved nitrogen delivery, tDON decay rate, and river water residence time.

### 3.5.5 Uncertainties

First, upon delivery of fluvial N to the shelf, biological conversion of riverine DIN to DON increases the [DON] within the river end member, thereby altering apparent tDON removal estimates. Thus the removal of tDON observed within the river water fraction represents the net of tDON decay and DON production from riverine DIN. Therefore, the tDON removal rates calculated here from the net DON loss within the river water fraction are possible underestimates of the true removal rate for the tDON delivered to the rivers from the watersheds. If we assume that ~8% of riverine DIN is converted to DON, then an additional 0.6 μM and 0.7 μM DON is added to the river water fraction in the eastern and western Arctic systems, respectively. If the DON originating from riverine DIN is fully conserved, the tDON removal rate constants must
be adjusted upward ~6% to λ values of 0.16 – 0.18 ± 0.08 for the eastern Arctic while the value for the western Arctic, 0.08 ± 0.01, is essentially unchanged.

Second, in the calculation of the removal rate constants, the removal of tDON is assumed to be a slow process occurring at a constant rate over the timescale of river water residence time in Arctic surface waters. However, if tDON removal is rapid upon delivery to Arctic shelves and then slows with aging, the removal rate constants calculated here are lower limits.

Third, dilution by sea ice melt freshwater in summer with an unknown [DON] could potentially alter the observed DON-salinity relationship, affecting interpretation of river water and marine end members. Sea ice melt has a [DON] = 4.5 ± 1.0 µM N (n = 45), measured in sea ice cores collected from the SBI program in the NE Chukchi Sea. It appears that sea ice forms with a [DON] not significantly different from the [DON] found in surface marine water. Upon sea ice melt in summer, the addition of freshwater containing DON to the PSL only acts to lower the salinity, while leaving the observed [DON] essentially unchanged, e.g. a ~15% addition of sea ice melt freshwater reduces the salinity of the western Arctic PSL by >4, while adding ~0.1 µM DON. This small effect is within the DON analytical error and does not significantly alter identification of end members.

Lastly, we assumed that the majority of tDON removal is in the surface layer, and that this material is kept there in support of export production. However, Dittmar [2004] observed evidence for tDON present in the deep Arctic Ocean, which he hypothesized was the result of entrainment of tDON within dense water formation on the Siberian shelves and subsequent advective transport to the deep ocean. This suggested sink of
tDON will not affect the calculation of the removal rate constant, but failure to account for it results in overestimation of the mineralization sink (i.e., the mass of mineralized products available to support export production). Anderson et al. [1999] used CFC-12 and CCl₄ distributions to estimate the renewal rate of Arctic Ocean deep waters (>200m) by the shelf water entrainment and advective transport process. The renewal rate for the Eurasian basin is ~2.5% per year, which when multiplied by the 2-5 year shelf water residence, yields a loss of 5-13% of shelf water with its enriched tDON content to the deep Arctic ocean. The renewal rate and shelf water residence time for the western Arctic is much lower, with an estimated loss of tDON via dense water export of <1%.

3.6 Summary

We presented the surface distribution of the dissolved organic nitrogen pool within the summertime Arctic Ocean. The distribution of DON in the Arctic PSL is controlled by competing processes: riverine input with subsequent decay of terrigenous DON over the shelves and net production of marine DON over the Chukchi Sea shelf. The six largest Arctic rivers deliver ~30 Gmol N yr⁻¹ as DON to the Arctic basin, of which 30-50% and 55-70% is removed during river water transport over the Eurasian shelves and within the Beaufort Gyre, respectively. When coupled with PSL residence times for the Eurasian shelves and Beaufort Gyre, these tDON losses yield first-order decay constants, \( \lambda \), of 0.15 ± 0.07 yr⁻¹ and 0.08 ± 0.01 yr⁻¹ for the eastern and western Arctic systems, respectively. Fluvial inputs of nitrate, ammonium, and the apparent shelf-remineralized tDON were found to have modest impact on Arctic ecosystem productivity, supporting ~2-14% of export production. In contrast, inputs of dissolved
nitrogen nutrients with Pacific Ocean waters entering the Chukchi Sea support net
production of marine DON following the seasonal bloom, averaging $1.6 \pm 1.0 \, \mu M \, N$, 
with a range of $\sim 0 - 8.0 \, \mu M \, N$ for the Chukchi Sea. We estimate that $8 \pm 1\%$ of the 
seasonal nitrate drawdown in the mixed layer is converted to DON in this region. We find 
contrasting behaviors in terrigenous and marine DON in the cycling of nitrogen in the 
Arctic Ocean.
Chapter 4. Distribution and fate of dissolved organic nitrogen in the global surface ocean

4.1 Background

Over much of the surface global ocean (upper 200 m), most of the standing stock of fixed nitrogen (N) is in the form of dissolved organic nitrogen (DON) [Bronk, 2002; Aluwihare and Meador, 2008]. Accumulation of N within this pool results from a decoupling of DON production and consumption processes primarily carried out by autotrophic plankton and heterotrophic bacterioplankton, respectively. This relatively biologically recalcitrant material can accumulate via its direct production [McCarthy et al., 2004] or diagenetic alteration of the molecular structure [Amon and Benner, 1996]. However, if a portion of the euphotic zone (<100 m) bulk DON pool eventually becomes ‘bioavailable’ to the resident microbial community, then the remineralized N can represent a potential source of new N to support primary and export production in oligotrophic systems.

Prior efforts to quantify the sustenance of upper ocean productivity by DON have focused on the Atlantic Ocean where the greatest density of DON observations exist and a clear east-to-west gradient in DON concentration ([DON]) has been observed (>5 µmol kg⁻¹ in the east to ~4.5 µmol kg⁻¹ in the west) [Mahaffey et al., 2004; Roussenov et al., 2006; Charria et al., 2008; Torres-Valdés et al., 2009]. These studies have considered the allochthonous input of semilabile DON (lifetime of months to years), produced at the productive gyre margins, to the subtropical gyre interior and its potential role as an organic nutrient for enhancing export production there. In order for allochthonous DON to be a quantitatively important source of new N, a substantial fraction of the advected
DON must become ‘bioavailable’ to the photoautotrophic community within the euphotic zone. Mechanisms that make DON bioavailable to photoautotrophs include direct assimilation [Bronk et al., 2007], extracellular hydrolysis [Palenik and Morel, 1991], heterotrophic remineralization to inorganic N with subsequent uptake [Bronk, 2002], or photo-oxidation to NH$_4^+$ [Bushaw et al., 1996]. Considering these euphotic zone sinks for DON, the annual advective flux of DON to the North Atlantic subtropical gyre ranges from ~0.01 – 0.08 mol N m$^{-2}$ yr$^{-1}$ [Mahaffey et al., 2004; Roussenov et al., 2006; Charria et al., 2008; Torres-Valdés et al., 2009], similar in magnitude to rates of advective supply of inorganic nutrients [i.e. nitrate (NO$_3^-$)] [Williams and Follows, 1998] and N$_2$-fixation [Gruber and Sarmiento, 1997; Hansell et al., 2004]. If these rates are accurate, the process supplies a significant amount of the N needed to explain geochemical estimates of export production in that system [Jenkins and Wallace, 1992].

An alternative fate for surface ocean DON is vertical transport (by mixing) to depth (>100 m), with subsequent mineralization by mesopelagic heterotrophic bacterioplankton. Abell et al. [2000] reported that DON remineralization along subsurface isopycnals, initially ventilated by subduction, explained ~20% of oxygen demand in the upper mesopelagic (100 to 300 m). In a study of the biological controls on dissolved organic carbon (DOC) utilization at the Bermuda Atlantic Time-series Study (BATS) site, Carlson et al. [2004] found that the surface accumulated, semilabile DOC pool was recalcitrant to the surface bacterioplankton community but available to the bacterioplankton community within the upper mesopelagic zone (~250 m depth). Other studies at the BATS site have found euphotic zone DON to be recalcitrant to microbial
utilization throughout the year [Hansell and Carlson, 2001; Knapp et al., 2005], suggesting that DON mineralization is largely restricted to the mesopelagic zone.

The upper layer (<200 m) of the eastern sectors of subtropical gyres is highly modified by vertical mixing en route to the gyre interior, being sites of subtropical mode water formation [Siedler et al., 1987; Hautala and Roemmich, 1998]. The physical dynamics of gyre circulation (including vertical mixing) coupled with preferential utilization of DON by subsurface bacterioplankton serves as an additional mechanism for establishing the observed east-west gradients in [DON]. To the extent that this alternative model is valid, the allochthonous DON supply would not directly contribute to export production from the euphotic zone. Thus, quantifying the importance of these DON loss pathways is relevant for understanding sources of new N supporting export production in oligotrophic gyres.

In this study we present the global surface ocean distribution of [DON] and characterize the spatial gradients. Three mechanisms are proposed to describe the DON distribution and its sinks: 1) Net DON production in highly productive upwelling systems, 2) net DON removal via mineralization in support of export production from the surface euphotic zone and 3) DON mineralization upon vertical mixing of the water column. Here we employ seawater incubation experiments to test the relative importance of mechanisms 2 vs. 3. Insights from these experiments are combined with an assessment of the physical dynamics of subtropical gyre circulation aided by use of a statistical model of the wind-driven Ekman layer derived from drifting buoy observations to determine the primary driver of the observed upper ocean DON gradients. We conclude
with an assessment of the role of allochthonous DON supply in the biogeochemistry of oligotrophic ocean gyres.

4.2 Methods

4.2.1 Field collected data sets

We employed observations of DON and other hydrographic variables collected on numerous oceanographic cruises as part of the US Global Ocean Carbon and Repeat Hydrography program [http://ushydro.ucsd.edu/]. Observations of DOC and DON were made on full water column CTD casts at ~60 nautical mile resolution. Sample analyses were performed by the Hansell and Carlson labs at the University of Miami and University of California, Santa Barbara, respectively. Data were downloaded from CDIAC [http://cdiac.ornl.gov/oceans/RepeatSections/]. Additional observations of DON were from World Ocean Circulation Experiment (WOCE) lines I08N in 1995, A05 in 1998, US Joint Global Ocean Flux Study (JGOFS) Arabian Sea Process Cruise #2 in 1995, and the NOAA North American Carbon Program (NACP) west coast cruise from 2010.

4.2.2 Incubation experiments

Incubation experiments were carried out over the course of several months in the laboratory using field-collected seawater from the Florida Straits at 27° N 79.5° W on March 10, 2011 (hereafter Exp0311) and 27° N 79.9° W on December 7, 2011 (hereafter Exp1211). The surface waters at this location are stratified year-round and annual mean sea surface chlorophyll a concentrations are low (< 0.1 mg m⁻³) [http://disc.sci.gsfc.nasa.gov/giovanni/] with the deep chlorophyll maximum (DCM)
found at ~80 to 90 m, providing an oligotrophic environment analogous to the adjacent North Atlantic subtropical gyre. The experimental objective was to quantify the remineralization potential of the surface DON pool given exposure to distinct bacterioplankton communities (surface vs. upper mesopelagic). Mixing conditions paired filtered (0.2 µm) surface (10 m) seawater with whole water (unfiltered) inocula from either of 10 m or 180 m depth (Exp0311); or 10 m and 130 m depth (Exp1211) in order to test the availability of surface DON to removal by surface vs. upper mesopelagic bacterioplankton communities. The dilution culture technique closely follows that used by Carlson et al., [2004], which allows the bacterioplankton to be released from grazer pressure, stimulating bacterial growth and substrate utilization.

Seawater was collected from Niskin bottles attached to a CTD rosette and stored in acid-cleaned 10-liter polycarbonate carboys in the dark at in situ temperatures until incubation initiation on shore (within 12 hours). Eight liters of 10 m seawater were gravity filtered through an acid-cleaned Acropak 1000 Supor membrane 0.8/0.2-µm cartridge filter into incubation carboys. The 0.2-µm filtrate was inoculated with 2 L of whole water (hereafter inoculum), which contained the resident microbial communities found within either the euphotic or upper mesopelagic zones. For Exp0311, two 10-L carboys received the 10 m surface water inoculum (hereafter, surface-surface) and 2 carboys received an inoculum from 180 m depth (hereafter, surface-meso). During Exp1211, 3 carboys received a 10 m surface water inoculum (surface-surface) while 3 carboys received an inoculum from 130 m depth (surface-meso). The sampling depth of the mesopelagic bacterioplankton community water targeted the top of the nitracline, where [NO$_3^-$] $\approx$ 1 µmol kg$^{-1}$ (hereafter referred to as the nitracline) [Cullen and Eppley,
and where organic N remineralization is known to occur [Ward et al., 1989]. The incubation carboys were well mixed and stored in the dark at room temperature (21°C), slightly above the in situ temperature for each inoculum (Exp0311 = 19.5°C; Exp1211 = 17°C). Subsamples of incubation water were collected at >10 time points over the course of 90 days (Exp0311) or 180 days (Exp1211) to monitor for changes in the concentration of DON as well as the products of DON remineralization, i.e. ammonium (NH$_4^+$) and NO$_3^-$.

4.2.3 Sample collection and analysis

*Sampling* – Samples from the oceanographic cruises were filtered for the removal of particulate organic matter (POM) using precombusted Whatman GF/F filters (nominal pore size 0.7 µm) held in acid-cleaned polycarbonate filter holders. Filter holders were connected inline with the CTD-Niskin bottle using acid-cleaned silicon tubing. Seawater was collected into acid-cleaned and preconditioned (with seawater) 60 mL HDPE bottles and immediately frozen upright at -20°C. Inocula for the incubation experiments were collected unfiltered to minimize contamination and to include the resident bacterioplankton population.

*DOC and TDN concentration* – DOC and total dissolved nitrogen (TDN) were analyzed by high temperature combustion (HTC) using a Shimadzu TOC-V$_{CSH}$ system coupled with a Shimadzu Total N analyzer [Dickson et al., 2007]. The N oxidation product nitric oxide (NO) is quantified by reaction with ozone and detection of the resulting chemiluminescence. Standardization was achieved using potassium nitrate for TDN and potassium hydrogen phthalate for DOC. Deep seawater and low carbon (C) reference waters as provided by the Hansell CRM Program [Hansell, 2005] were
measured every sixth analysis to assess the day-to-day and instrument-to-instrument variability. The precision for TDN analyses is \( \sim 0.5 \, \mu\text{mol kg}^{-1} \) or a CV of 5-10%. The precision for DOC analyses is \( \sim 1 \, \mu\text{mol kg}^{-1} \) or a CV of 2-3%. TDN measurements for WOCE lines A05 + I08N and US JGOFS Arabian Sea Process Cruise #2 were performed by the UV-oxidation method [Walsh, 1989]. Measurements of TDN along WOCE line P18 made using the UV-method [Hansell and Waterhouse, 1997] were typically \( \sim 10\% \) higher than those from the more recent CLIVAR occupation of the line made using the HTC method (both cruises were analyzed by Hansell laboratory).

\( NO_3^- + NO_2^- \) concentration – Nutrient analyses for the cruise transects were carried out at sea by standard colorimetric methods; these data were taken from the CDIAC and JGOFS [http://www1.whoi.edu/] websites. For samples collected during the incubations, water was collected in duplicate at each time point and stored frozen at \(-20\degree\text{C}\) until subsequent analysis. The sum of \([NO_3^- + \text{nitrite (NO}_2^-)]\), hereafter \([NO_3^-]\), was measured by reduction to NO using a solution containing heated, acidic V (III), followed by chemiluminescent detection of NO [Braman and Hendrix, 1989]. Standardization was achieved using potassium nitrate. Samples were analyzed in a configuration yielding a limit of detection of 0.03 \( \mu\text{mol kg}^{-1} \) with a precision of \( \pm 0.025 \, \mu\text{mol kg}^{-1} \) when \([NO_3^-]\) \(< 0.1 \, \mu\text{mol kg}^{-1} \) or a limit of detection of 0.1 \( \mu\text{mol kg}^{-1} \) with a precision of \( \pm 0.05 \, \mu\text{mol kg}^{-1} \) when \([NO_3^-]\) \(> 0.1 \, \mu\text{mol kg}^{-1} \).

\( NH_4^+ \) concentration – The concentration of \( NH_4^+ \) in incubation samples was performed on duplicate samples collected at each time point and measured daily using a fluorescence technique with orthophthalaldialdehyde (OPA) [Holmes et al., 1999]. Samples reacted for 2 hours at room temperature with an OPA-containing solution, with
subsequent measurement of fluorescence at an excitation/emission of 350nm/410-600nm (Turner Designs Model 7200-000). Standardization was achieved using ammonium chloride. The limit of detection was 0.025 µmol kg\(^{-1}\) with a precision of ± 0.01 µmol kg\(^{-1}\).

**DON concentration** – The concentration of DON ([DON]) was calculated by subtracting the sum of dissolved inorganic nitrogen ([DIN] = [NO\(_3^-\) + NO\(_2^-\)] + [NH\(_4^+\)]) from the measured [TDN]; [DON] = [TDN] – [DIN]. Propagation of error yields a precision on [DON] measurements of ± 0.5 µmol kg\(^{-1}\) or a CV of ~10%. Measurements of [NH\(_4^+\)] were not performed on the global surface ocean [DON] dataset, as open ocean [NH\(_4^+\)] are typically <0.1 µmol kg\(^{-1}\) [Lipschultz, 2001].

**Bacterioplankton cell C** – Samples for the enumeration of cell abundance were collected at each time point of the incubation experiments and fixed with particle-free 25% glutaraldehyde (Exp0311) or 10% formalin (Exp1211) to a final concentration of 1.0% and stored at 4°C until preparation. Cells were filtered onto Lrgalan black-stained 0.2-µm polycarbonate filters; samples were stained with 4′-6′-diamidino-2-phenylidole (DAPI) [Porter and Feig, 1980] and enumerated with a Nikon Eclipse E400 epifluorescence microscope (1000x). The slope of the regression of cell abundance from the initial time point until the end of the log-phase growth was used to assess whether cell production was significant (\(p<0.05\)). Bacterioplankton cell C was calculated from cell abundance using a C conversion factor typical for oceanic bacterial assemblages of 12.4 fg C cell\(^{-1}\) [Fukuda et al., 1998].

4.2.4 Statistical model of simulated upper ocean tracer advection

In order to assess the timescale of upwelled waters to reach the central gyres, we employed a statistical model of upper ocean tracer advection for waters circulating in the
wind-driven Ekman layer (upper 50 m). The simulation is based upon probability distribution functions derived from the trajectories of over 15,000 satellite-tracked drifting buoys of the Global Drifter Program drogued at 15 meters [Niiler, 2001]. For each simulation, a tracer is released at a point and integrated forward at \( \frac{1}{2}^\circ \) resolution for 730 days at 5-day time steps following the description in Maximenko et al., [2012] and Lumpkin et al., [2012]. The initial release locations were chosen to be the surface waters located at the most equatorward extent of each of the four largest eastern boundary upwelling systems (EBUS), i.e. the NW African, Benguela, Peru, and western North American upwelling systems.

### 4.3 Results

#### 4.3.1 Surface Ocean DON distributions

The surface ocean (10 m) distribution of [DON] is presented in Fig. 1. Values ranged from 2 to 7 \( \mu \text{mol kg}^{-1} \) (with a mean for all observations of 4.4 ± 0.5 \( \mu \text{mol kg}^{-1} \)); however, 75% of all observations fell within the narrow range of 3.8 to 4.8 \( \mu \text{mol kg}^{-1} \) (indicated by the green colors in Fig. 1). Regions exhibiting [DON] \( \geq 5 \mu \text{mol kg}^{-1} \) were commonly adjacent to or immediately downstream from eastern boundary and equatorial upwelling zones (as well as the monsoon-driven upwelling system of the Arabian Sea), indicating a source of DON within these systems. Lower [DON] poleward and westward of these upwelling systems are assumed to reflect a sink for DON within the ocean’s subtropical gyres. Concentrations of DON were highly variable within the Southern Ocean due, at least in part, to the large analytical uncertainty in samples containing elevated [NO\(_3\)] [Hansell, 1993]. In general, calculation of [DON] resulted in a CV
>25% at [NO$_3^-$] >6 µmol kg$^{-1}$. Where surface [NO$_3^-$] was <1 µmol kg$^{-1}$, [DON] at 10 m plotted against the depth of the top of the nitracline demonstrates an inverse relationship (Fig. 2b).

Fig. 4.1. Distribution of [DON] (µmol kg$^{-1}$; colored dots) at 10 m in the global ocean. Isolines indicate annual mean surface ocean (10 m) [NO$_3^-$] (µmol kg$^{-1}$), using gridded data of the World Ocean Atlas, 2005 [http://www.nodc.noaa.gov/]. Atlantic Ocean lines: A13.5 = ~0º E, A16 = ~25º W, A20 = ~52º W, A22 = 66º W, A05 = 24.5º N; Pacific Ocean lines: P18 = ~103º W, P16 = ~150º W, NOAA NACP west coast = ~120º W, P02 = ~30º N; Indian Ocean lines: I08S-I09N = ~95º E, I08N = ~80º E, I06S = ~30º E, SR03 = ~145º E, I05 = ~34º S, JGOFS Arabian Sea Process Cruise #2 = ~15ºN 65º E. Plotting done with Ocean Data View [Schlitzer, 2012].

The y-axis intercept approaches 4.8 µmol kg$^{-1}$ and corresponds to locations with very shallow nitraclines, while [DON] is ~4.3 µmol kg$^{-1}$ where the nitracline is deepest over the subtropical gyres. A plot of the stock of DON in the upper 50 m versus the depth of the top of the nitracline (Fig. 2a) exhibits a similar gradient from ~230 mmol N m$^{-2}$ at locations with shallow nitraclines, decreasing to ~200 mmol N m$^{-2}$ at locations with deep nitraclines over the subtropical gyres.
Fig. 4.2. Surface ocean (10 m) [DON] (a) (µmol kg\(^{-1}\); open circles) and upper 50 m DON stock (b) (mmol N m\(^{-2}\); top panel, open squares) plotted versus depth (m) of the top of the nitracline (defined as depth where [NO\(_3^-\)] = 1 µmol kg\(^{-1}\)), at all locations where surface [NO\(_3^-\)] <1 µmol kg\(^{-1}\). Solid black line is model II reduced major axis regression for the bottom panel [DON = (-0.003 x nitracline depth) + 4.8; \(r^2 = 0.07\); n = 516] and the top panel [DON stock = (-0.156 x nitracline depth) + 233; \(r^2 = 0.10\); n = 405].

4.3.2 Incubation experiments

4.3.2.1 Exp0311

*Surface-surface* – Results for the surface-surface incubations from Exp0311 are shown in Fig. 4.3 (red). Both [DOC] and bacterioplankton cell C were monitored to assure 1) no measurable DOM contamination in our experimental setup and 2) active bacterioplankton growth during the incubations. There was no evidence of contamination by extraneous organic matter; initial [DOC] within the surface-surface incubation carboys was consistent with mass balance calculations of the [DOC] resulting from the mixing of surface whole water ([DOC] = 77.7 µmol kg\(^{-1}\)) and surface 0.2-µm filtered water ([DOC]
Bacterioplankton growth was observed, reaching stationary phase after 4-7 days and resulting in a ~ten-fold accumulation of cell carbon (Fig. 4.3b). Bacterioplankton growth was supported by consumption of DOC (Fig. 4.3a), which averaged (average of replicate incubations, ± 1 S.D.) $\Delta$DOC = 10.4 ± 0.7 µmol kg$^{-1}$ over the 90-day incubation. [TDN] averaged (± 1 S.D.) 4.4 ± 0.3 µmol kg$^{-1}$ and remained constant within analytical uncertainty throughout the incubation (Fig. 4.3c), indicating conservation of mass for N within the incubation water. Changes in [DON] were not observed within the ~0.5 µmol kg$^{-1}$ analytical uncertainty, with the time-course concentration averaging 4.3 ± 0.5 µmol kg$^{-1}$ (Fig. 4.3d). This large uncertainty precludes detection of small changes within the DON pool by measurements of [DON] alone. However, by measuring the products of DON remineralization, NH$_4^+$ and NO$_3^-$, which have orders of magnitude lower analytical uncertainty, rates of net DON remineralization can be derived. [NH$_4^+$] increased to a maximum of ~0.1 µmol kg$^{-1}$ after two weeks, then cycled between ~0.04 – 0.10 µmol kg$^{-1}$ over the remainder of the incubation (Fig. 4.3e). [NO$_3^-$] was low (≤0.06 µmol kg$^{-1}$) and near constant throughout the incubation with no significant increase (ANOVA, $p>$0.10) (Fig. 4.3f). The production of NH$_4^+$ indicates that a net of ~0.10 µmol kg$^{-1}$ DON had been mineralized over the course of the incubation.

**Surface-meso** – Figure 4.3 shows results from the Exp0311 surface-meso incubations (in blue). Initial [DOC] within the incubation carboys confirmed the absence of measurable contamination and was as expected from mass balance calculations of the predicted [DOC] resulting from mixing 8 L of surface 0.2-µm filtered water ([DOC] = 71.3 µmol kg$^{-1}$) and 2 L of mesopelagic water (180 m) ([DOC] = 58.3 µmol kg$^{-1}$). Bacterioplankton cell C (Fig. 4.3b) and DOC consumption (Fig. 4.3a) were similar in
pattern and magnitude to the surface-surface incubation, with a ~ten-fold accumulation of cell C and net DOC consumption of $8.5 \pm 2.2 \, \mu\text{mol kg}^{-1}$ after 90 days. Measurements of [TDN] averaged ($\pm$ 1 S.D.) $5.4 \pm 0.3 \, \mu\text{mol kg}^{-1}$ and remained constant (Fig. 4.3c). No changes in [DON] were observed within the analytical uncertainty, which averaged $4.0 \pm 0.5 \, \mu\text{mol kg}^{-1}$ (Fig. 4.3d). Similar to the results from the surface-surface incubation, $[\text{NH}_4^+]$ increased to $\sim 0.10 \, \mu\text{mol kg}^{-1}$ after two weeks (Fig. 4.3e), however this $\text{NH}_4^+$ was slowly nitrified to $\text{NO}_3^-$ over the course of one month, as indicated by the decrease in $[\text{NH}_4^+]$ in Fig. 4.3e and an accumulation in $[\text{NO}_3^-]$ of $0.30 \pm 0.05 \, \mu\text{mol kg}^{-1}$ (ANOVA, $p<0.0001$) over the course of the experiment (Fig. 4.3f).

Figure 4.3. Property time-series for Exp0311. (a) DOC ($\mu\text{mol kg}^{-1}$), (b) bacterioplankton cell carbon ($\mu\text{mol kg}^{-1}$), (c) total dissolved nitrogen (TDN, $\mu\text{mol kg}^{-1}$), (d) DON ($\mu\text{mol kg}^{-1}$), (e) $\text{NH}_4^+$ ($\mu\text{mol kg}^{-1}$), and (f) $\text{NO}_3^-$ ($\mu\text{mol kg}^{-1}$). Red colors are surface-surface incubations; open and filled circles represent replicate experiments. Blue colors are surface-meso incubations; open and filled triangles represent replicate experiments. Error bars equal $\pm$ 1 S.D.; error bars are omitted from (b) for clarity, SD equals $\pm$ 0.02 $\mu\text{mol C kg}^{-1}$.
The net accumulation of \([\text{NO}_3^-]\) indicated \(0.30 \pm 0.05 \text{ µmol kg}^{-1}\) DON had been consumed by 90 days.

4.3.2.2 Exp1211

**Surface-surface** – Results for the surface-surface incubations from Exp1211 are shown in Fig. 4.4 (red). Initial [DOC] confirmed the absence of contamination during experimental setup (Niskin [DOC] = 75.2 \text{ µmol kg}^{-1}). [DOC] was consumed over two months, averaging \(\Delta \text{DOC} = 5.8 \pm 0.7 \text{ µmol kg}^{-1}\) (Fig. 4.4a). Bacterioplankton cell C increased ~five-fold within the first two weeks of incubation and was variable over the remainder of the experiment (Fig. 4.4b). [TDN] was constant within analytical uncertainty over the course of the experiment, \(4.9 \pm 0.5 \text{ µmol kg}^{-1}\), indicating conservation of N mass (Fig. 4.4c). [DON] averaged (± 1 S.D.) \(4.6 \pm 0.5 \text{ µmol kg}^{-1}\) with no observable change within uncertainty over the 180-day incubation (Fig. 4.4d). \([\text{NH}_4^+]\) increased after day 30 to ~0.10 \text{ µmol kg}^{-1} (Fig. 4.4e), which was then nitrified to \(\text{NO}_3^-\), as indicated by the [\(\text{NO}_3^-\)] increase in Fig. 4.4f. The production of \(\text{NH}_4^+\) and net accumulation of \(\text{NO}_3^-\) indicated \(0.14 \pm 0.05 \text{ µmol kg}^{-1}\) (ANOVA, \(p<0.007\)) of net DON consumption after 180 days.

**Surface-meso** – Exp1211 surface-meso incubation results are shown in Fig. 4.4 (blue). Initial incubation [DOC] was as expected from mass balance calculations of the mixing of 8 L of 0.2-µm filtered surface water ([DOC] = 74.3 \text{ µmol kg}^{-1}) with 2 L of mesopelagic water from 130 m depth (Niskin [DOC] = 57.4 \text{ µmol kg}^{-1}) confirming the absence of contamination (Fig. 4.4a). A small net consumption of DOC was observed after ~two weeks, averaging (average of replicate incubations) \(\Delta \text{DOC} = 1.4 \pm 0.5 \text{ µmol kg}^{-1}\) (Fig. 4.4a). Bacterioplankton cell C (Fig. 4.4b) was similar in pattern and magnitude
to the Exp 1211 surface-surface incubations (red colors). [TDN] averaged (± 1 S.D.) 7.5 ± 0.5 µmol kg\(^{-1}\) and was constant with time (Fig. 4.4c). No changes were observed within analytical uncertainty for [DON], which averaged (± 1 S.D.) 4.6 ± 0.5 µmol kg\(^{-1}\) (Fig. 4.4d). [NH\(_4^+\)] remained below the detection limit throughout the incubation (Fig. 4.4e). Net accumulation of [NO\(_3^-\)] was observed (Fig. 4.4f), averaging (± 1 S.D.) 0.38 ± 0.10 µmol kg\(^{-1}\) (ANOVA, \(p<0.0001\)), indicating net consumption of DON over 180 days.

![Fig. 4.4. Property time-series for Exp1211. (a) DOC (µmol kg\(^{-1}\)), (b) bacterioplankton cell carbon (µmol kg\(^{-1}\)), (c) total dissolved nitrogen (TDN, µmol kg\(^{-1}\)), (d) DON (µmol kg\(^{-1}\)), (e) NH\(_4^+\) (µmol kg\(^{-1}\)), and (f) NO\(_3^-\) (µmol kg\(^{-1}\)). Red colors are surface-surface incubations; open and filled circles and stars represent replicate experiments. Blue colors are surface-meso incubations; open and filled triangles and bowties represent replicate experiments. Error bars equal ± 1 S.D.; error bars are omitted from (b) for clarity, S.D. equals ± 0.02 µmol C kg\(^{-1}\).]

4.3.3 Statistical model of simulated ocean tracer advection

*Atlantic* -- The probability density of simulated tracer concentration, in units of log10 (initial concentration), up to one year is shown for the North and South Atlantic Oceans...
in Fig. 4.5a and 4.5b, respectively. The penetration of waters exiting the EBUS towards the gyre centers is a slow process owing to the sluggish surface currents of the eastern limbs of the gyre circulations. After 90 to 180 days, the timescale of our incubation experiments, the core of these waters were located near 20 to 30º W in the North Atlantic.

Fig. 4.5. Concentration of simulated tracer after 30, 90, 180, and 365 days since release in the North Atlantic at 21º N 18º W (a) and in the South Atlantic at 18º S 11º E using the statistical model based on surface ocean drifter observations. Color scale is the log10 of concentration where initial concentration is 1.
South Atlantic upwelled waters reach ~5° E and 5° W after 90 and 180 days, respectively. Upwelled waters are still within ~1000 km of the coast after six months, only reaching the basin centers after ~1 year.

Fig. 4.6. Concentration of simulated tracer after 30, 90, 180, and 365 days since release in the North Pacific at 34° N 121° W (a) and in the South Pacific at 6° S 82° W (b). Color scale is the log10 of concentration where initial concentration is 1.

Pacific -- The slow transport towards the subtropical gyres characteristic of the Atlantic Ocean is similar for upwelled waters in the Pacific Ocean. Surface waters leaving the Peru upwelling system travel to ~90 and 100° W after 90 and 180 days, respectively, and reach ~110° W after 1 year (Fig. 4.6b). Upwelled waters leaving the California current system penetrated even less into the North Pacific gyre, remaining
~500 km from the coast after 90 to 180 days near 120º W, reaching ~130º W after 1 year (Fig. 4.6a).

4.4 Discussion

4.4.1 DON removal mechanisms

The surface ocean distribution of [DON] characterized by enrichment near upwelling regions (Figs. 4.1, 4.2) and depletion of this signal poleward and westward across the subtropical gyres (Fig. 4.1) implies a sink for DON in the subtropical gyres on the order of ~0.5 µmol kg⁻¹ or ~30 mmol N m⁻² from the upper 50 m of the water column (Fig. 2). Figure 4.7 describes potential mechanisms for this DON removal.

In Fig. 4.7a (Mechanism I), DON produced within upwelling zones along the equator or eastern boundary resists immediate utilization and is transported by the surface ocean circulation towards the subtropical gyres. En route, DON is removed by direct assimilation of DON and/or its remineralization products and supports export production. After sinking out of the euphotic zone, the particulate organic nitrogen is remineralized and accumulates as NO₃⁻ in the upper mesopelagic zone. Mechanism I is analogous to that proposed by Torres-Valdés et al. [2009], and is distinct from the presumed flux of N through the DON pool that supports regenerated production in oligotrophic systems [Bronk et al., 2007; Knapp et al., 2011].

In Mechanism II (Fig. 4.7b), DON removal occurs upon vertical mixing of the upper water column. In this case, DON is largely recalcitrant to utilization by the surface microbial community; instead it is preferentially consumed after being vertically mixed or entrained into the upper mesopelagic water column. This model describes a fate for
surface accumulated DON similar to that found for the seasonally accumulated surface ocean DOC pool at the BATS site [Carlson et al., 2004]. Under this mechanism, the lateral input of DON does not have an immediate impact on export production within the subtropical gyres, though it will have an indirect impact to the extent that the NO$_3^-$ produced upon DON remineralization is returned to the surface layer with subsequent mixing events.

![Diagram of mechanisms](image-url)
Fig. 4.7. Proposed mechanisms for DON removal from the surface ocean. (a) Mechanism I: Removal via surface consumption of DON and export as sinking particulate N. Oligotrophic gyre export production is directly supported by allochthonous DON input in this model. (b) Mechanism II: Removal of DON upon vertical mixing of the water column to the upper mesopelagic zone where the resident microbial community contains the necessary metabolic capacity to remineralize DON. Gyre export production is not directly supported by allochthonous DON in this model. (c) Mechanism III: Removal via a two-step vertical mixing and sinking particle process. DON is removed from the surface layer via vertical mixing to the deep euphotic zone where heterotrophic microbes mineralize DON, regenerating inorganic N for autotrophic production in the deep euphotic zone. This source of new N results in net formation of sinking particles, which remove N from the base of the euphotic zone to the mesopelagic where it is remineralized. This two-step process results in indirect allochthonous DON support of subtropical gyre export production.

4.4.2 Insights from incubation experiments

The incubation experiments were designed to examine the lability of surface accumulated DON when exposed to the extant surface microbial assemblages versus mesopelagic microbial assemblages. The surface-surface incubations tested Mechanism I by evaluating the bioavailability of surface ocean DON to the microbes found there. The
surface-meso incubations investigated Mechanism II, testing for microbial utilization of surface ocean DON under conditions simulating vertical mixing.

During the surface-surface incubations, accumulation of NO$_3^-$ and/or NH$_4^+$ indicated that the maximum quantity of DON mineralized was $\sim$0.1 $\mu$mol kg$^{-1}$. The source of this inorganic N could have been either microbial intracellular N or remineralized DON, since these two pools were not differentiated in our analysis. If, for the purposes of this study, we assume that all of the NH$_4^+$ produced was by remineralization of DON, then <3% of the surface bulk DON pool was bioavailable to the extant surface ocean microbial community over a period of 3-6 months. Under natural environmental conditions and natural light fields, both phytoplankton and heterotrophic bacteria would compete for this NH$_4^+$ [Kirchman, 1994], initially supporting regenerated production [Dugdale and Goering, 1967]. Assuming steady state for N in the euphotic zone, this N would eventually be exported. The relative recalcitrance of surface ocean DON to microbial utilization within the euphotic zone suggests a limited role for Mechanism I for DON removal within the oligotrophic gyres.

The results of the surface-meso incubations more strongly support a role for Mechanism II in the removal of surface ocean DON from oligotrophic gyres. During Exp0311, the accumulation of 0.30 ± 0.05 μmol kg$^{-1}$ inorganic N throughout the three-month experiment is three times the net remineralization in the surface-surface incubation. During the Exp1211 surface-meso incubations (Fig. 4.4e), the accumulation of 0.38 ± 0.10 μmol kg$^{-1}$ inorganic N after 180 days (Fig. 4.4f) also indicated a three-fold greater net DON remineralization than observed in the Exp1211 surface-surface incubations. Our simulated mixing experiments indicate that DON consumption in the
upper mesopelagic is a slow process, occurring on the timescale of months at a rate of ~1 μmol N kg⁻¹ yr⁻¹, about three-fold faster than the rate in the surface layer. This upper mesopelagic rate is consistent with both the rate and magnitude of surface ocean DON loss at BATS [Hansell and Carlson, 2001; Knapp et al., 2005], as well as the Sargasso Sea and North Pacific Gyre [Knapp et al., 2011].

4.4.3 Export of DON-enriched waters at the gyre margins

Mechanism II requires that two conditions be met: 1) accumulated surface ocean DON is mixed to the upper mesopelagic, and 2) it is remineralized there on relatively rapid time scales. The second condition has been demonstrated above, so the first condition must now be tested. Do DON-enriched waters of the EBUS actually mix to subeuphotic zone depths?

We first consider the time scale for transport of surface waters from the upwelling region into the gyre center. If transfer is rapid (i.e. on the order of weeks), then DON-enriched waters may escape subduction at the sites of subtropical mode water formation at the eastern gyre margins, thus being retained in the upper 50 m within the central subtropical gyres. By contrast, if transfer is slow, DON-enriched waters may persist at the gyre margins long enough to be mixed vertically prior to significant horizontal penetration into the gyre center.

The relatively slow transport of upwelled waters towards the gyre centers observed in both the North and South Atlantic (Fig. 4.5) indicates that the DON-enriched surface waters of EBUS are mixed vertically during wintertime convective mixing prior to transport into the gyre center. If we assume upwelled waters leaving the NW African and Benguela EBUS begin transit towards the gyre in the summer months [Chavez and
Messié, 2009], six months later (in mid-winter) the core of these waters reach ~30° W in the North Atlantic (Fig. 4.5a) and ~5° W in the South Atlantic (Fig. 4.5b), respectively.

During winter mixing, surface water density reaches maximum values, and DON will be subducted to the corresponding isopycnal surface. For the northeast subtropical Atlantic, wintertime (January-March) convective mixing reaches a maximum surface density of σ 24.0 to 26.0 (Fig. 4.8a), thus redistributing the DON-enriched surface waters into this density range. In the summer months (July-September), the water column is capped by a lighter density layer of σ 23.0 to 25.0 (Fig. 4.8b), causing the subducted, DON-enriched waters to penetrate the gyre along the σ 25.0 to 26.0 density horizon. Similar seasonal mixing dynamics in the South Atlantic result in the DON-enriched waters leaving the Benguela upwelling system to be subducted within essentially the same density horizon of σ 25.0 to 26.0 (Fig. 4.8a, 4.8b).

The exported DON leaves the euphotic zone and enters the upper mesopelagic to the extent that this isopycnal layer does so. The σ 25.0 to 26.0 surface reaches a maximum depth of ~100 m in the eastern basins in winter (Fig. 4.8c, 4.8d). This relatively shallow mixing retains DON-enriched waters within the euphotic zone (typical euphotic zone depths are ~100 to 130 m in the eastern sectors of the gyres where subduction occurs [http://disc.sci.gsfc.nasa.gov/giovanni/]). In fact, the farther west the surface waters reach before the onset of vertical mixing, the lighter the density surface these waters would subduct to (Fig. 4.8a, 4.8b) and thus the DON-enriched water would be retained at shallower depths (i.e. ~50 to 100 m). These physical dynamics preclude subducted DON from escaping the euphotic zone within the eastern sectors of the subtropical gyre.
Fig. 4.8. Mean geographic distribution of surface outcrops of isopycnal surfaces in the Atlantic for (a) January-March and (b) July-September. Depths of the $\sigma_{26.0}$ isopycnal surface for (c) January-March and (d) July-September. Black dashed boxes indicate the regions of transit for waters from the eastern boundary upwelling systems towards the gyre centers within 6 months of upwelling (determined from drifter observations in Fig. 4.5). Plots created using data from the World Ocean Atlas, 2005 [http://www.nodc.noaa.gov/].
Fig 4.9. Mean geographic distribution of surface outcrops of isopycnal surfaces in the Pacific for (a) January-March and (b) July-September. Depths of the $\sigma_{25.0}$ isopycnal for (c) January-March and (d) July-September. Black dashed boxes indicate the regions of transit for waters from the eastern boundary upwelling system towards the gyre centers within 6 months of upwelling (determined from drifter observations in Fig. 4.6). Plots created using data from the World Ocean Atlas, 2005 [http://www.nodc.noaa.gov/].

Surface waters that subduct in the eastern subtropical Pacific Ocean reach a maximum density of $\sigma_{25.0}$ in both the North and South Pacific (Figs. 9a and 9b, respectively). These waters are capped in the summer months by the surface layer with a density of $\sigma_{\sim 24.0}$ (Fig. 4.9a, 4.9b). Again assuming that upwelled waters begin their transit towards the gyre during the summer months [Chavez and Messié, 2009], six months later (mid-winter) the core of these waters reach $\sim 120^\circ$ W in the North Pacific (Fig. 4.6a) and $\sim 90^\circ$ W in the South Pacific (Fig. 4.6b). In these regions, subducted water
in the \( \sigma 24.0 \) to 25.0 layer penetrates to a maximum depth of \( \sim 100 \text{ m} \) with wintertime mixing (Fig. 4.9c, 4.9d). Shallow vertical mixing prevents DON from penetrating below the euphotic zone in the eastern Pacific basins, similar to the physical constraints in the Atlantic.

It appears that the first condition required for Mechanism II is not observed; DON-enriched waters of the EBUS do not actually mix to subeuphotic zone depths.

4.4.4 The fate of DON within ocean subtropical gyres and related uncertainties

It appears that subduction of surface water enriched in DON in the eastern sector of each ocean basin, and its presumed removal at depth, contributes to the observed [DON] zonal gradient at the surface (as described by Mechanism II; Fig. 4.7b), but that export of DON is relatively shallow (i.e. to the deep euphotic zone). The relative recalcitrance of DON to surface microbial communities and its three-fold greater bioavailability to mesopelagic microbes (Figs. 4.3, 4.4) is consistent with Mechanism II. These findings limit the role for allochthonous DON in directly support export production across ocean subtropical gyres (as required in Mechanism I; Fig. 4.7a). However, vertical mixing in the eastern basins appears to be restricted to depths shallower than 100 m, thus retaining the DON-enriched waters within the euphotic zone.

If subsequent mineralization of the subducted DON primarily occurs within the deep euphotic zone (\( \sim 50 \) to 100 m), any additional export production supported by remineralized DON must occur via a two-step process (Mechanism III; Fig. 4.7c). In this model, DON is exported to the deep euphotic zone with winter mixing, where it is rapidly mineralized. This mechanism requires that a microbial assemblage capable of remineralizing DON at rates similar to the microbes we tested in the upper mesopelagic
(~130 to 180 m) is active at the base of the euphotic zone. While some vertical overlap in microbial assemblages occurs in the upper ~500 m, vertically stratified bacterial communities are typically partitioned according to physical and chemical gradients [Morris et al., 2005; Carlson et al., 2009; Treusch et al., 2009]. For example, the microbial community within the DCM (~120 m depth) at the BATS site was distinct from that in the upper mesopelagic (200 to 300 m) [Treusch et al., 2009]; thus it is unclear whether DCM microbial communities harbor similar capabilities for mineralization of surface accumulated DON. In support of Mechanism III, Knapp et al. [2011] observed a statistically significant decrease in [DON] of ~0.5 µM below the mixed layer, i.e. within the DCM (~60 to 100 m) of the Sargasso Sea, with a further ~0.5 µM [DON] decrease in the upper mesopelagic (100-200 m) zone.

These results suggest that the primary fate of surface DON is removal via vertical mixing and subsequent mineralization below the mixed layer. DON may contribute to export production near the eastern edges of the subtropical gyres via an indirect two-step process (Mechanism III), however investigation of the DON mineralization potential of DCM microbial communities is required to validate the model.

One further uncertainty is that the primary DON removal mechanism considered here, remineralization by heterotrophic bacterioplankton, may not be the only process removing DON in surface ocean waters. While photo-mineralization of DON to inorganic species such as NH$_4^+$ and NO$_2^-$ occurs with exposure to UV-light in near surface waters [Bushaw et al., 1996; Kieber et al., 1999; Vähätalo and Zepp, 2005; Stedmon et al., 2007], these studies have focused on dissolved humics and terrigenous DOM within coastal regions. The photo-oxidation of marine-produced organic matter is not well
constrained in the open ocean. Phytoplankton are also capable of utilizing low molecular weight DON moieties such as urea [Bronk et al., 2007], providing a third potential sink for surface accumulated DON. However, much of the DON found in open ocean surface waters occurs as larger, complex organic molecules with amide functional groups [McCarthy et al., 1997; Aluwihare et al., 2005], which are thought to be largely unavailable to photoautotrophs, instead requiring extracellular breakdown by microbes to release N [Berges and Mulholland, 2008]. Thus, alternative surface ocean sinks for DON not tested in our incubation experiments are considered unlikely to contribute significantly to DON removal in the euphotic zone.

4.5 Summary

We presented the global surface ocean DON distribution and observed a global mean concentration of 4.4 ± 0.5 µmol kg⁻¹ within the upper 50 meters. Elevated [DON] (≥5 µmol kg⁻¹) was found in waters adjacent to and downstream from the major upwelling zones. Zonal gradients in surface ocean [DON] indicate a sink of this material within the gyres, on the order of ~0.5 µmol kg⁻¹ (~30 mmol N m⁻²) from the upper 50 m, and we explored two possible mechanisms for this DON loss: removal by autotrophic utilization with export of sinking particulate N from the euphotic zone (Mechanism I) or by vertical mixing to below the mixed layer with subsequent consumption (Mechanism II). Incubation experiments designed to test the biological capacity for surface ocean DON removal found DON to be mostly recalcitrant to utilization by surface ocean microbes; instead DON remineralization occurred with exposure to the heterotrophic
microbial community from the upper mesopelagic zone at a rate of ~1 \( \mu \text{mol N kg}^{-1} \text{yr}^{-1} \).

These results suggest a limited role for DON removal via Mechanism I.

The estimated time scale for transport of DON-enriched waters from the upwelling zones to the interior of the subtropical gyres was found to be long (months to years), allowing the excess DON to persist at the gyre margins long enough to be subducted upon wintertime convection, thus supporting Mechanism II. However, the depth of subduction was shallow (<100 m), so DON and its products would be retained within the deep euphotic zone. If relatively fast remineralization of DON occurs there, this new N could support phytoplankton growth and particle export from the DCM, described as a two-step process (Mechanism III).

We conclude that the primary fate for surface DON is removal via vertical mixing to and subsequent mineralization below the mixed layer. The precise depth at which the DON is mineralized (i.e. within or below the deep euphotic zone) determines the potential importance for DON to support export production in the subtropical gyres (i.e. Mechanism II vs. III). If the euphotic zone is sufficiently deep, Mechanism III may operate in the eastern sectors of the major ocean basins, thus providing indirect support of export production after mineralization of DON to \( \text{NO}_3^- \) within the deep euphotic zone.

We found little support for a direct role for allochthonous DON to sustain export production from the mixed layer in the interior of oligotrophic gyres (Mechanism I). Future work should explicitly test Mechanism III by investigating the DON mineralization potential of DCM microbial assemblages. Additionally, quantification of the photo-oxidation DON sink in the open ocean is necessary.
Chapter 5. Conclusions

5.1 Fate of terrigenous dissolved organic matter in the marine environment

In support of the evolving paradigm surrounding the fate of terrigenous DOM in the marine environment, I found evidence for the removal of both tDOC and tDON upon delivery to the Arctic Ocean. Having previously documented the removal of tDOC from waters circulating the Polar Surface Layer (PSL) of the Beaufort gyre in the western Arctic Ocean [Hansell et al., 2004], I investigated the fate of tDOC and tDON delivered to the broad continental shelf environment characteristic of the eastern Eurasian Arctic Ocean. My analysis revealed that ~55% of tDOC and ~40% of tDON delivered to the Eurasian shelves is removed during the 2-5 year transit of riverine waters along the shelves before export to the Transpolar Drift (TPD) of the Arctic Ocean. Extending the analysis of tDOM removal to the western Arctic Ocean, I found that ~65% of tDON was removed over the 12-14 year residence time of PSL waters in the Beaufort gyre. Hansell et al. [2004] previously determined the removal of tDOC within the Beaufort gyre to be ~75% of the western Arctic river inputs.

Coupling the quantity of tDOM removal with the timescale over which that removal occurs allowed the calculation of first-order removal rate constants (λ) for tDOC and tDON in both the Eurasian shelf and Beaufort gyre domains. Both tDOC and tDON were removed at a faster rate over the Eurasian shelves (λ tDOC = 0.24 yr\(^{-1}\); λ tDON = 0.17 yr\(^{-1}\)) than within the Beaufort gyre (λ tDOC = 0.10 yr\(^{-1}\); λ tDON = 0.08 yr\(^{-1}\)), highlighting the initially greater lability of tDOM to removal upon delivery to the Arctic marine environment. The majority of tDOM removal occurs within the shallower shelf
environment, removing >50% of river inputs. Export to and residence within the Arctic Ocean further removed a smaller quantity (~15-20%) of tDOM material.

Based on the calculated removal rate constants, tDOC is relatively more labile to degradation than tDON in the Arctic Ocean. This observation for the tDOM pool is contrary to that for marine-produced DOM in which the C:N ratio has been shown to increase with diagenetic processing and removal [Benner, 2002]. Freshly produced tDOM is enriched in C (C:N = ~50) relative to marine DOM (C:N = ~15) due to the large carbohydrate-based structural material found in land-plants and the loss of this material with tDOM removal may account for the enhanced lability of tDOC relative to tDON in the Arctic.

The mechanism by which tDOM is removed from the PSL appears to be microbial mineralization to DIC and inorganic nutrients. Hansell et al. [2004] found approximate mass balance for tDOC loss with salinity-normalized DIC increase in the PSL of the Beaufort gyre, implicating microbial remineralization as the dominant tDOC removal process. If export of tDOC out of the PSL via physical mixing were an important sink process, the Arctic halocline waters would be enriched with tDOC and its remineralization product, DIC, which Hansell et al. [2004] did not observe. A similar mass balance approach for tDON loss and nitrate accumulation is difficult to observe due to nitrate being a limiting nutrient for phytoplankton growth in the Arctic PSL and thus any regenerated N from tDON decay would be efficiently utilized by microbes. However, evidence for physical mixing removal of tDON from the PSL was not observed in halocline waters given the datasets in hand. A third potential sink for tDOM in the Arctic Ocean is its photochemical oxidation upon exposure to UV light, however this sink
appears to be of minor importance. Tank et al. [2012] estimated the photo-
ammonification sink of tDON in the Arctic to remove ~5% of initial river inputs over the
shelf residence.

5.2 Impacts of river inputs of tDOM on the biogeochemical cycles of carbon and
nitrogen in the Arctic Ocean

Mineralization of tDOC within the Arctic PSL affects the Arctic Ocean’s ability
to take up and store atmospheric CO$_2$. Currently, the PSL waters of the Arctic Ocean are
undersaturated with respect to atmospheric pCO$_2$ [Bates, 2006; Bates et al., 2006;
Jutterström and Anderson, 2010]. This undersaturation is maintained by the strong
biological productivity and drawdown of DIC over the productive inflow shelves of the
Arctic (Barents, Chukchi) combined with seasonal sea ice cover which acts as a physical
barrier to air-sea pCO$_2$ equilibration [Bates et al., 2006]. Contrary to the high rates of
productivity characteristic of the inflow shelves, the interior Siberian shelves of the
Arctic (Kara, Laptev, East Siberian) experience low rates of primary production and a
large influx of river material [Carmack and Wassmann, 2006; Anderson et al., 2010].
Mineralization of this material to CO$_2$ results in elevating the pCO$_2$ of the PSL, thereby
decreasing the gradient between air-to-sea ΔpCO$_2$ and can even push the system to
oversaturation with respect to pCO$_2$ [Anderson et al., 2011]. Thus the mineralization of
tDOC within the PSL of the Arctic shelves and open ocean acts to mitigate the strength of
the Arctic Ocean CO$_2$ sink. Given the increasing freshwater discharge [Peterson et al.,
2002] and projected tDOM flux [Spencer et al., 2009] with permafrost thaw in the Arctic
region as the climate continues to warm, this process will further reduce the Arctic Ocean
CO$_2$ sink in the future.
As mentioned above, the interior Arctic shelves (Kara, Laptev, East Siberian) experience low nutrient supply and primary productivity as well as large inputs from the voluminous Ob, Yenisey, Lena, and Kolyma Rivers [Carmack and Wassmann, 2006]. The annual flux data from the recent PARTNERS program (http://arcticgreatrivers.org/) made it possible to assess the importance of fluvial delivery of nutrients and organic matter on Arctic shelf productivity. I estimated the sum of nitrogen inputs [$\text{NO}_3^- + \text{NH}_4^+ + (\text{N released by tDON decay})$] from the six largest Arctic rivers (Ob, Yenisey, Lena, Kolyma, Mackenzie, and Yukon) to each of the Arctic shelf seas. Comparison of the N inputs to literature estimates of export production for each Arctic shelf sea allowed an estimate of the importance for fluvial inputs of nutrients on Arctic shelf sea productivity. Despite the large influence of river runoff to the shelf environments, these inputs were found to have only a minor importance (< 15%) on shelf productivity. This result is somewhat expected for the inflow shelves (Barents, Chukchi, Bering), which receive large fluxes of nutrients with waters, transported from the adjacent Atlantic and Pacific Oceans. However, the interior shelves sustain levels of productivity much higher than can be supported by river inputs alone, highlighting a potentially larger role for horizontal and vertical advection of nutrients in supporting the export flux in these regions.

The enhanced productivity due to river inputs of N results in DIC drawdown over the Arctic shelf seas, thus counteracting the pCO$_2$ increase within the PSL caused by tDOC mineralization. At current estimates of river N delivery, this process could offset ~13% of eastern Arctic or ~11% of western Arctic DIC accumulation due to tDOC mineralization.
5.3 On the role of dissolved organic nitrogen in open ocean nutrient cycles

The study detailed in Chapter 4, “Distribution and fate of dissolved organic nitrogen in the global surface ocean”, was motivated by recent reports in the literature of the importance for allochthonous supply of organic nutrients (both DON and DOP) to surface waters of the ocean’s subtropical gyres in sustaining export production [Mahaffey et al., 2004; Roussenov et al., 2006; Charria et al., 2008; Torres-Valdés et al., 2009]. These authors observed east-to-west zonal gradients in both [DON] and [DOP] in the Atlantic Ocean and interpreted the surface ocean loss of organic nutrients to be due to utilization by the extant microbial communities, thus supporting export production from the surface ocean. I set out to test this hypothesis utilizing the >55,000 observations of DON from the open ocean found in the US Global Ocean Carbon and Repeat Hydrography program dataset.

Upon examination of the global surface (<50 m) distribution of [DON], I found the east-west zonal gradient observed previously for the Atlantic to be a common feature of all the major ocean basins, including the presence of meridional gradients moving poleward from the equator. The magnitude of these gradients is on the order of 0.5 µmol kg\(^{-1}\) from the upper 50 m or ~0.025 mol N m\(^{-2}\). I interpret these gradients as arising from net production of a DON pool within the productive upwelling regions that resists rapid microbial utilization to be carried by the surface circulation towards the subtropical gyre centers. The zonal and meridional gradients observed in surface [DON] imply a loss from the surface ocean, for which I investigated the biological and physical controls on this surface ocean sink. I proposed the DON sink to occur via two mechanisms with opposing importance for DON to directly support export production from the surface ocean: DON
removal via incorporation into sinking particles (Mechanism I; Fig. 4.7a) and DON removal upon vertical mixing to the mesopelagic (Mechanism II; Fig. 4.7b).

Seawater incubation experiments carried out to investigate the bioavailability of surface ocean DON to extant microbial assemblages from both the surface and mesopelagic ocean found surface ocean DON to be recalcitrant to microbial degradation while at the surface (euphotic zone). Only when surface ocean DON was exposed to microbes from the mesopelagic was net remineralization of that DON to nitrate observed. Investigation of the dynamics of surface ocean circulation and vertical mixing in the eastern sectors of the subtropical gyres found that as upwelled waters containing elevated DON circulate towards the gyre center, they are vertically mixed to the subsurface (~50-100 m). The coupling of the biological and physical controls on the surface ocean [DON] found from this study leads me to reject Mechanism I as being responsible for the surface ocean DON sink, implying a limited role for direct DON support of gyre export production from the surface layer. Instead the primary fate of surface DON is removal via vertical mixing and subsequent mineralization in the subsurface.

The vertical location of subsurface DON remineralization determines the potential importance for DON to support export production. The incubation experiments tested the DON remineralization potential of upper mesopelagic microbial assemblages as in Mechanism II; Fig. 4.7b. However, the vertical mixing for the DON-enriched waters leaving the upwelling zones was found to only penetrate to the shallow subsurface (~50-100 m; Fig. 4.8, 4.9), which retains these waters in the deep euphotic zone. If the microbial assemblages found at these depths are capable of remineralizing DON to nitrate, similar to that ability found for the mesopelagic microbes (Section 4.3), a two-
step mechanism (Mechanism III; Fig. 4.7c) would provide a source of new N to support export production from the base of the euphotic zone in the subtropical gyres. I propose that this third mechanism may operate in the eastern sectors of the major ocean basins where shallow ventilation removes surface DON to the deep euphotic zone. However, the incubation experiments presented here did not specifically test the DON remineralization potential of deep euphotic zone microbial assemblages which should be included in future work to confirm or reject this supposed mechanism, owing to its potential importance regarding an indirect mechanism for DON support of gyre export production.

5.4 Dissolved organic matter fractions in the cycling of carbon and nitrogen

As mentioned in the “Background” (Section 1.3), the pool of dissolved organic matter found in the ocean is characterized as being made up of multiple long-lived fractions, each with varying quantities and timescales for removal. The work presented here is consistent with that view and provides estimates of the quantities, rates and mechanisms for removal of a few of these DOC and DON fractions. Terrigenous DOM delivered to the marine environment is comprised of at least two degradable fractions, with about half found to be rapidly removed within a few years over the continental shelf and another smaller fraction (~20%) removed over a decadal timescale in the open ocean. The semilabile fraction of DON produced within ocean upwelling systems was found to contain ~0.5 µmol kg\(^{-1}\) or 10% of the bulk pool, which is subsequently removed by remineralization in the subsurface after vertical mixing. DON was found to accumulate at a rate of ~8% of net community production for the highly productive Chukchi Sea region of the Arctic Ocean. This similarity in DON fraction that is seasonally produced and
consumed suggests that for systems dominated by marine microbial DON sources and sinks, the semilabile DON fraction is ~10% of the bulk pool.
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