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Dissolved and particulate phosphorus distributions and elemental stoichiometry throughout the Chukchi Sea

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ABSTRACT

As a major gateway from the Pacific to the open Arctic Ocean, biogeochemical transformations of nutrients in the Chukchi Sea are important for understanding the Arctic ecosystem as a whole. This study examines the biogeochemical cycling of the macronutrient phosphorus (P) relative to carbon (C) and nitrogen (N) in the eastern Chukchi Sea during the ICESCAPE mission. Sea ice and water column dissolved and particulate P samples were collected during summer expeditions in 2010 (n=543) and 2011 (n=553). Nearly all forms of P were higher in Pacific Winter Waters (PWW), indicating the potential importance of PWW to Chukchi Sea nutrient pools. Annual means of P concentrations in all its forms in the offshore waters throughout the Chukchi Sea were also consistently higher ($TP_{2010}=1.56\pm0.61$ μM, $TP_{2011}=1.67\pm0.68$ μM) relative to waters inshore and within the Alaska Coastal Current (ACC), suggesting coastal inputs were relatively minor during our sampling. Rather, biological modification of P pools dominated, with 30–40% of the total dissolved P pool (TDP) and nearly 50% of the total particulate P pool (TPP) comprised of organic P. Nutrient analyses of first year sea ice suggest that sea ice melt contains highly variable P concentrations that span an order of magnitude depending on particulate matter content. As such, sea ice melt may contribute significant nutrients to summer waters on a transient basis. Low N:P ratios (<2) within the mixed layer are consistent with summertime N limitation of biological production and demonstrate that the Chukchi Sea is a major source of excess P to other regions of the Arctic Ocean. Deeper water column dissolved N:P ratios of 7–9.1, while lower than the canonical Redfield ratio, are consistent with particulate N:P ratios of a diatom-dominated biological community. Combined, results suggest that the eastern Chukchi Sea plays an important role in the composition and magnitude of P that ultimately reaches other Arctic Ocean waters.

1. Introduction

The Arctic Ocean is undergoing significant changes in its physical and biogeochemical environment due to rising water temperatures, melting sea ice, and increases in riverine discharge (Arnell, 2005, Serreze et al., 2007; Stroeve et al., 2012; Post et al., 2013). The 2007–2010 average September sea ice extent declined by 40% compared to measurements taken 20–30 years earlier, with sea ice distributions reaching record lows in 2012 (Stroeve et al., 2012). Furthermore, models suggest that the entire Arctic will become seasonally ice free as early as 2040 (Holland et al., 2006; Wang and Overland, 2009). Indeed, some Arctic seas have already begun to experience ice-free seasons, including the Chukchi Sea (Stroeve et al., 2012).

As nutrient-rich Pacific waters make their way further into the Arctic Ocean through the Chukchi Sea via the Bering Strait, they are impacted by a variety of processes, including coastal inputs, sediment resuspension, redox reactions (e.g., denitrification), variable ice cover, and primary production (Frey et al., 2014). Similar to the rest of the Arctic Ocean, the Chukchi Sea has experienced an increase in satellite derived net primary production of almost 50% over the past 12 years, among the highest increases in primary production throughout the region (Arrigo and van Dijken, 2015). This dramatic increase is likely due to greater light penetration as a result of declining sea ice and an enhanced number of melt ponds (Arrigo and van Dijken, 2011, 2015, Lowry et al., 2015; Grebmeier, 2012; Petrenko et al., 2013). It is important to note that the increase in water column primary productivity does not consider possible alterations in sea ice primary production, which contributes significantly to primary production within the central Arctic Ocean (Gosselin et al., 1997); nor does this estimate take into account the

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changes in primary productivity occurring beneath sea ice, such as the massive under ice bloom observed in 2011 (Arrigo et al., 2012). It is hypothesized that up to 70% of the resulting carbon fixed in the southeast Chukchi from water column primary production may settle to the sea floor where it can be utilized by benthic fauna (Cooney and Coyle, 1982; Walsh et al., 1989; McTigue et al., 2015).

During the summer months, waters make their way through the eastern Chukchi Sea in one of two major water masses: the Alaskan Coastal Waters or the Chukchi Summer Waters (von Appen and Pickart 2012; Brugler et al., 2014); the latter is also referred to as Bering Sea Water (Gong and Pickart, 2015), Summer Bering Sea Water (Steele et al., 2004), and Eastern Chukchi Summer Water (Shimada et al., 2001). The Alaskan Coastal Waters are pumped through the Chukchi Sea by the Alaskan Coastal Current (ACC) and remain trapped within 50 km of the coast (Schumacher and Reed, 1986). However, the Chukchi Summer Waters (CSW) move through the Chukchi Sea in a variety of pathways. As they make their way through the Chukchi Sea, these new summer waters mingle and aid in the transportation of remaining Pacific Winter Water (PWW). The PWW is hypothesized to form during sea ice formation, increasing water density and concentrating nutrients (Lowry et al., 2015). Both summer waters and remnant winter waters traverse the Chukchi Sea via four main routes: Long Strait, Herald Valley, Central Channel, and Barrow Canyon. Barrow Canyon has the fastest flowing output with rates up to 1 Sv during the summer months, and is the major exit pathway assessed in this study (Münchow et al., 1999; Weingartner et al., 2005). As waters exit Barrow Canyon, they are focused into the Beaufort Shelf Jet, a narrow shelf break jet, as they make their way into the Beaufort Sea (Pickart, 2004; Nikolopoulos et al., 2009).

Phosphorus (P) is an essential macronutrient that influences biological production and plankton community structure in a variety of marine systems (Karl, 2014). Within the ocean, P occurs in both organic and inorganic forms and is actively partitioned between dissolved and particulate phases via a suite of biologically and chemically mediated reactions. While many previous studies have focused mainly on inorganic P, as it is the most readily available form (e.g., Benitez-Nelson, 2000, Paytan and McLaughlin, 2007), numerous studies now recognize that organisms also utilize organic P compounds even when inorganic P concentrations are relatively high (>0.2 μM) (e.g., Mortazavil et al., 2000; Dyhrman et al., 2006; Sylvan et al., 2006; Huang and Zhang, 2010; Karl, 2014). Therefore, understanding the distribution and concentrations of all P forms is critical for examining nutrient dynamics. Nevertheless, relatively little is known regarding the distribution of P within marine dissolved and particulate matter in the Arctic Ocean, particularly in the Chukchi Sea.

In this study, we analyzed multiple water column and sea ice core samples for dissolved and particulate P that were collected throughout the eastern Chukchi Sea during the summers of 2010 and 2011 as part of NASA's Impact of Climate Change on the Ecosystems and Chemistry of the Arctic Pacific Environment (ICESCAPE) mission. In order to fully understand the processes influencing P biogeochemistry, total phosphorus (TP) was further broken down into total dissolved P (TDP) and total particulate P (TPP). These pools were then chemically separated into inorganic and organic phases: particulate inorganic P (PIP), particulate organic P (POP), soluble reactive P (SRP), and dissolved organic P (DOP). The goal of this study was to improve our understanding of the source, composition, and distribution of dissolved and particulate P within this climate impacted ecosystem.

2. Materials and methods

2.1. Study site and sample collection

As part of the ICESCAPE field mission, the Chukchi Sea was sampled during two summer cruises, 15 June–22 July, 2010 and 25 June–29 July, 2011, aboard the USCGC *Healy* (WAGB-20) (Fig. 1). During the 2010 cruise, water column ($n=135$) and ice ($n=10$) stations were sampled from the Bering Strait northward to Barrow Canyon. Dissolved and/or particulate P were sampled from 121 of these stations with a total of 543 samples analyzed in 2010. Due to decreased ice cover, the 2011 cruise extended from the Bering Strait northward to the southern Beaufort Sea; 173 stations were sampled, including nine ice stations. Dissolved and particulate data were analyzed in 553 samples from 104 stations. All ice stations were comprised of only first year ice.

Both cruises sampled multiple water masses. The ACC was identified by high temperatures (≥ 3 °C) and salinities ≥ 30, while the CSW were characterized by lower temperatures (-1 to 2 °C), and similar salinities (Brugler et al., 2014). Atlantic deep waters were characterized by low temperatures (<-1.26 °C) and high salinities (>33.64) (Brugler et al., 2014). Lastly, some stations were able to capture remaining PWW. These waters were characterized by temperatures lower than -1.6 °C and salinities higher than 31.5, consistent with other work from the ICESCAPE mission (Brown et al., 2015, Gong and Pickart, 2015, Lowry et al., 2015, Mills et al., 2015).

Water column data were obtained by deploying a conductivity, temperature, and depth sensor (CTD) on a rosette system equipped with twelve 30 L Niskin bottles. The CTD/rosette system also included a photosynthetically available radiation (PAR) sensor and fluorometer. Water samples were collected at standard depths (roughly 2, 10, 25, 50, 100, 200, 500, 1000, and 2000 m depending on water depth) and analyzed for chlorophyll *a* and dissolved inorganic nutrients (i.e., nitrate silicate, and phosphate), as described in Brown et al. (2015) and Mills et al. (2015) (all nutrient data available at seabass.gsfc.nasa.gov).

Ice core data were collected using a custom built CRREL ice coring system with a diameter of 10 cm. Cores used for nutrient analysis during the 2010 cruise ($n=21$) were melted in a known amount of filtered surface seawater (usually 2 L per 10 cm section), with salinity measurements recorded pre and post melt. As such, dissolved nutrient data are not available from ice cores sampled for particulate nutrients in 2010. Samples were then filtered for particulate P analysis onto a 1 N HCl washed and 500 °C combusted, 25 mm GF/F (~ 0.7 μm) and frozen until analysis. In 2011, the ice cores used for nutrient measurements were melted without dilution. Particulate and dissolved nutrient analyses were conducted on the resulting melt water. During the 2010 cruise, ice cores were both visibly sediment laden and sediment free, while in 2011, all ice core samples were visibly sediment free.

2.2. Ship board analyses

Continuous profiles of chlorophyll *a* fluorescence were collected at each station using a Wetlabs fluorometer. Additional samples for chlorophyll *a* analysis were filtered onto a 25 mm GF/F (~ 0.7 μm), placed in 5 mL of 90% acetone and extracted in the dark at 3 °C for 24 h. Chlorophyll *a* concentrations were then measured fluorometrically using a Turner fluorometer 10-AU (Holm-Hansen et al., 1965). A chlorophyll *a* standard (Sigma-Aldrich #C5753) was used to calibrate fluorescence-based chlorophyll *a* measurements in remaining samples (Holmes et al., 2000).

Total inorganic nutrients (unfiltered) were analyzed on a segmented continuous flow auto analyzer within a few hours of