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An ammonium enrichment event in the surface ocean: Wind forcing and potential ramifications

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ABSTRACT

Ammonium is a nutrient frequently preferred by microorganisms that photosynthesizes at the base of the marine food web and removes atmospheric carbon dioxide via carbon fixation. Because their photosynthesis is concentrated in the ocean's thin euphotic zone, its nutrient concentrations are critical to oceanic carbon fixation. Identification of replacement processes for euphotic-zone ammonium thus becomes important. These processes were investigated in a two-experiment, Lagrangian field study that produced results consistent with an apparent inverse effect of wind forcing on upper-ocean ammonium concentrations. At low wind speeds (especially ≤4 ms^{-1}), continuous seawater sampling, supported by sulfur-hexafluoride (SF6) water-mass tracing and meteorological measurements, detected 1.1–4.4-km-wide boluses of surface seawater exhibiting ammonium enrichments that were 5 - to-10-fold above background. In the first experiment, ammonium maxima comprising the enrichment event disappeared at higher wind speeds. In the second experiment, which had consistently higher wind speeds, an ammonium event composed of such maxima was never found. The apparent correlation between elevated ammonium concentrations and low wind stress could therefore be viewed as potentially important for understanding ammonium cycling and carbon fixation in the ocean.

1. Introduction

Processes affecting the nutrient regime within the ocean's euphotic zone are fundamental to upper-ocean carbon cycling (Eppley and Peterson, 1979). Even though photosynthetic carbon fixation in the euphotic zone is a major factor maintaining much of it in a nutrient-depleted (i.e., oligotrophic) condition, between one-third and one-half of the global-ocean export production occurs in oligotrophic regions (Sarmiento and Gruber, 2006). Therefore research continues on nutrient enrichments within oligotrophic euphotic zones. How often do enrichments occur? When and under what conditions do they occur, and how long do they last? Answers to these and other major questions about euphotic zone nutrients are often difficult to obtain due to the complexity of the zones and the problems involved in studying them.

Dissolved forms of nitrogen, phosphorus, and silicon are commonly considered to be principal plant nutrients in the sea because they provide the primary chemical elements required by organisms that can become limiting—see Pilson (2013) and references therein. Which of these nutrients are more likely to be limiting is an ongoing question, but the major inorganic forms of nitrogen—nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+)—appear more likely to be limiting at the spatial and temporal scales associated with metabolic processes (Sarmiento and Gruber, 2006). Ammonium is often a preferred nitrogen source for phytoplankton (McCarthy et al., 1977; Dortch, 1990). Our

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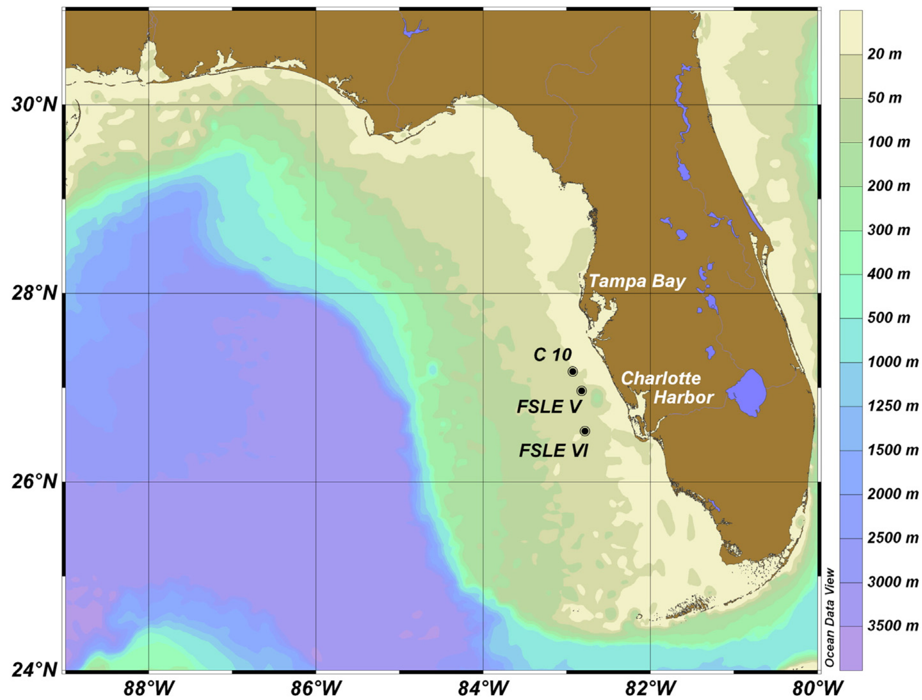

Fig. 1. Locations of SF_6 injection sites for the FSLE V and FSLE VI Lagrangian experiments in the eastern Gulf of Mexico in April, 2001 and November, 2002, respectively. The SF_6-labeled surface seawater tended to drift southward during the experiments, in accord with the general circulation patterns (Weisberg et al., 2009). The location of a nearby current-meter mooring with meteorological instrumentation (C10) is also shown; it is part of the West Florida Shelf mooring array maintained by the University of South Florida COMPS program (http://comps.marine.usf.edu/). The color-coded variable quantified on the right-hand side of the figure is water depth.

investigation focused on these three nitrogenous nutrients, and on ammonium in particular.

The euphotic zone selected for this nutrient-enrichment study was the West Florida Continental Shelf (WFS). Our data on surface [NO_3^-], [NO_2^-], and [NH_4^+] from six previous WFS cruises nearly always showed low values: mostly <80 nM (e.g., see Fig. 8 of Masserini and Fanning (2000)). Interestingly, the vertical NH_4^+ concentration pattern in the upper 150 m at the Bermuda Atlantic Time-series Study (BATS) site shows essentially the same range of values as on the WFS (see Fig. 3 of Lipschultz (2001)). Zero-to-80 nM appears to indicate un-enriched WFS water (Section 3.1).

The goals of our research were 1) to characterize nitrate, nitrite, and ammonium enrichments in the low-nutrient WFS euphotic zone in terms of location, magnitude, duration, and associated environmental parameters and 2) to investigate the role that physical processes might play in the formation and/or destruction of these enrichments.

2. Methods and experimental design

Field research on nitrate, nitrite, and ammonium in oligotrophic waters requires specially adapted techniques. First, the low, nanomolar concentrations of the three nutrients in WFS waters require analytical methods with greater sensitivities than conventional ones (e.g., Grasshoff, 1976; Gordon et al., 1993). Second, determining the physical details of near-surface seawater boluses containing nutrient enrichments requires that sampling be conducted on horizontal spatial scales well below the kilometer range. Third, evaluation of the changes in nanomolar-scale nutrient enrichments requires surveys of near-surface waters over longer time spans. Fourth, knowledge of the kinetics of in situ reactions between nutrients and biota is needed in order to estimate the lifetimes of those enrichments.

Several special experimental protocols and methods were utilized. The Masserini and Fanning (2000) high-sensitivity fluorometric system, designed for euphotic zones with detection limits ≤10 nM, provided nitrate, nitrite, and ammonium concentrations in the upper two meters of the WFS water column at known positions on the order of 300 m apart during surface surveys. Sulfur hexafluoride (SF_6) tracer (Wanninkhof et al., 1997) provided the ability to track nutrients within a seawater patch in time and space. Measured nutrient consumption and production rates (Mulholland et al., 2006; Bronk et al., 2014) provided in situ reaction rates for use in evaluating enrichment durations. Finally, meteorological data were used to assess the impact that weather-related processes might have on euphotic-zone nutrients.

Two Lagrangian field experiments were conducted in the WFS euphotic zone (Fig. 1). This zone is similar to the oligotrophic central gyres of the ocean basins in that WFS nutrients are scarce and often limit phytoplankton growth (Vargo et al., 2008). Phytoplankton communities in oligotrophic regions are generally believed to persist through the use of recycled nutrients (e.g., Eppley et al., 1973; Kiefer and Atkinson, 1984). The two experiments—FSLE V and FSLE VI of the series of Florida Shelf Lagrangian Experiments started by Wanninkhof et al. (1997)—were conducted during the drier, cooler season of the year when northwesterly weather fronts pass through the area (see Sections 3.2, 3.3, and 4.2.1).

Each experiment began with an initial survey southward from C10 (Fig. 1) until a nutrient peak or enrichment was encountered in a patch of SF_6-free seawater. At that point SF_6 was injected (Wanninkhof et al., 1997) into the patch as a label or tracer in order to guarantee that nutrient surveys maintained contact with the patch as it drifted and mixed with the surrounding seawater. Spatial and temporal variations in surface nutrient concentrations were then followed from the *R/V F.G. Walton Smith* in a zigzag pattern of survey transects at three knots (5.6 km h^{-1}) across the patch into the surrounding seawater and back. During each transect, regular measurements were made of [SF_6] and of [NH_4^+], [NO_3^-], and [NO_2^-] according to the procedures of Wanninkhof et al. (1997) and Masserini and Fanning (2000), respectively. These measurements were conducted on sub-samples of a stream of seawater drawn from the upper 2 m through a port in the ship's hull into its scientific seawater system. Also, two-to-four times per day, vertical distributions of nutrients, SF_6, temperature, salinity,