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Determination of nanomolar levels of nutrients in seawater

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ABSTRACT

Nutrients (phosphate, nitrate, nitrite, ammonium and silicate) exert strong controls on oceanic primary productivity. In oligotrophic areas, which cover approximately 40% of the world's oceans, nutrient concentrations can drop to nanomolar levels or lower due to biological uptake, so highly sensitive methods and technologies are urgently needed for nutrient measurements in such areas. In this work, we review procedures for phosphate and nitrite/nitrate analyses published since the review of Patey et al. [32], and procedures for analysis of ammonium and silicate at nanomolar levels. Our review includes aspects of measurement protocols that bear strongly on the quality of analyses of trace nutrients, including contamination of reagents, sample storage, and preparation of nutrient-free seawater. This review excludes methods that have limits of detection greater than 1 μM, and methods that are not specific to seawater.
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1. Introduction

1.1. Trace nutrients in the ocean

Essential macronutrients in aqueous systems include phosphate, nitrate, nitrite, ammonium and silicate. In fresh waters and coastal seawater, excess nutrient inputs lead to eutrophication and degradation of the aquatic system. In contrast, oligotrophic areas in the open ocean are often subject to N/P/Si limitation due to vertical stratification and drawdown from primary production. The importance of N and P and their cycles in the ocean has been comprehensively reviewed [1–6]. While nitrate and phosphate are required nutrients for all phytoplankton, silicate constitutes an additional requirement for siliceous phytoplankton, such as diatoms, which occasionally dominate inorganic carbon sequestration in the upper ocean. Over areas of the tropical and subtropical ocean, silicate in the euphotic zone can be seasonally or chronically depleted to <0.1–0.6 μM. At these levels, silicate can limit diatom productivity and, thereby, the export of carbon from the surface ocean [7,8].

Typical vertical profiles for five nutrients are shown in **Fig. 1** [9]. Normally, in well-lit surface waters, biological uptake reduces nutrients to low-nM levels; while remineralization of sinking particulate matter causes nutrient concentrations (e.g., nitrate and phosphate) to increase to μM levels with depth.

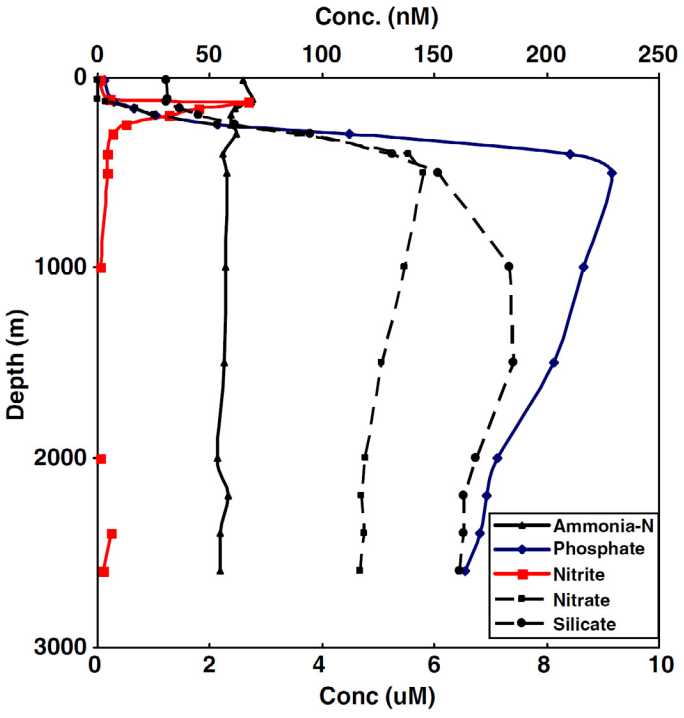

Fig. 1. Depth profile of ammonium, phosphate, nitrite, nitrate and silicate in the eastern Mediterranean [9], with permission from Elsevier.

1.2. Previous reviews of methods for nutrient analysis

Due to the importance of nutrients in marine systems, measurements of nutrient concentrations are among the most commonly performed analyses in oceanographic research. Previous comprehensive reviews of nutrient analyses include: journal publications between 2003 and 2013, including the works of Miró et al. [10], Gray et al. [11] and Worsfold et al. [12]; book chapters on seawater analysis [13–15]; and, the GO-SHIP guideline [16].

Reviews specific to one or two nutrients include the works of: Moorcroft et al. [17] for nitrite and nitrate analysis; Molins-Legua et al. [18] and Gray et al. [19] for ammonium analysis; and, Estela and Cerdà [20], Motomizu and Li [21], Villalba et al. [22] and Berchmans et al. [23] for phosphate analysis.

1.3. Techniques for trace-nutrient analysis

Over much of the world's surface oceans, nutrient concentrations often fall below the limit of detection (LOD) of conventional analytical techniques. Because nutrients play a controlling role in primary productivity and carbon sequestration, it is highly desirable to develop sensitive methods to address this measurement challenge. Applications vary widely and include determinations of the nutrient conditions that control diazotroph distributions [24–26], investigations of plankton-community structure relative to ambient nutrient concentrations [27,28], examination of complex microbial relationships [29], and assessments of the effects of climate change on marine populations [30] and freshwater and estuarine populations [31].

In 2008, Patey et al. [32] ritically reviewed methods for determination of nitrite/nitrate and phosphate in seawater at nanomolar concentrations based on publications before early 2007. Our present article provides an update on techniques for nitrite/nitrate and phosphate analysis, and a review of ammonium and silicate techniques. Measurements of the latter two nutrients (especially ammonium) have proved challenging for both analytical and marine chemists.

Several approaches can be used to lower LODs for nutrient analyses [32]:

- optimization of chemistries – for nutrient analyses, improvement opportunities are very limited because nutrient-analysis chemistries have been investigated comprehensively;
- preconcentration of analytes or analyte-derivatives using liquid-liquid extraction or, more recently, solid-phase extraction (SPE) techniques;
- amplification of the detected spectrophotometric signal (i.e., absorbance) by increasing the path-length of the absorption cell;

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