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Computation of nitrate concentrations in coastal waters using an in situ ultraviolet spectrophotometer: Behavior of different computation methods in a case study a steep salinity gradient in the southern North Sea

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HIGHLIGHTS

- Direct determination of nitrate in seawater via UV-spectrophotometry.
- First successful use in a steep salinity and CDOM gradient.
- Comparison of three methods all of which perform good to excellent.

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ABSTRACT

Absorption spectra of seawater can be used to estimate the concentration of nitrate based on the UV absorption characteristic of nitrate. However the results of that estimation show an increased uncertainty compared to wet chemical methods. This is caused by the close proximity and the magnitude of the bromide peak (as the main component of seawater salt) close to the nitrate signal in the UV. Current data processing methods are optimized to give good results under constant conditions in terms of temperature, salinity, and CDOM concentration. However, in coastal regions all three parameters are highly variable.

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Wadden sea
Data processing

In this work three methods to determine nitrate concentration from the seawater UV spectrum are compared: (A) via the subtraction of the seawater spectrum and CDOM absorbance from the total absorbance of the sample and then fitting the nitrate absorption to the remaining absorbance, (B) the subtraction of the seawater spectrum and fitting the spectral signature of nitrate and CDOM as suggested by Sakamoto et al. (2009) and (C) the direct determination via the fitting of the spectral signature of all components to the sample spectrum. The results of all three methods correlate ($R > 0.99$) very well with each other as well as to the results of the wet chemical analysis.

An extensive dataset of a transect from the Southern North Sea into the Weser estuary (RV HEINCKE transect 345), which covers a broad salinity range as well as a broad range of nitrate concentrations, is used to exemplary show the potential and the limitations of all three methods under these conditions.

1. Introduction

As an essential nutrient the determination of nitrate concentration is one of the standard procedures during marine ecological and biogeochemical observations. Wet chemical analysis of nitrate is well described in standard literature (Grasshoff et al., 1999) but facing several problems related to sample preservation and contamination (MacDonald and McLaughlin, 1982; Dore et al., 1996). Furthermore, laboratory analysis are very time-consuming. Automated online systems based on wet chemical analysis are capable of analyzing a higher throughput of samples without any sample preservation and almost without any manual interaction. Therefore contamination problems are reduced to a minimum but these systems are still not fast, reliable, and sensitive enough for continuous use on monitoring stations or voluntary observing ships (VOS) (Adornato et al., 2010).

Besides wet chemical analysis, nitrate concentration can also be determined directly via its ultraviolet (UV) absorption spectrum. Field applications of commercially available in-situ spectrophotometers show that results are sufficiently stable under most conditions (Johnson et al., 2013). Though, results of field experiments in highly dynamic coastal regions with strong gradients in salinity, turbidity, and CDOM are not sufficiently accurate using only built-in postprocessing routines (Zielinski et al., 2007; Carroll et al., 2007).

Sakamoto et al. (2009) compared three different postprocessing methods for the computation of nitrate from UV absorption spectrum of seawater. While bromide absorption strongly depends on sample temperature these three methods differ in the way how bromide interference is compensated. In the first method Sakamoto et al. (2009) omitted a temperature compensation and used the same bromide absorption spectrum for all samples. In the second approach a correction of bromide absorption with sample temperature was done, using this processed spectrum as input for the further fitting process. Within the third approach Sakamoto et al. (2009) subtracted a temperature corrected theoretical salinity spectrum calculated on the basis of a reference spectra of seawater and continuously measured CTD data. These experiments were very successful, but they tested their methods only with samples of similar salinities (32.4–34.7 psu) within a comparable limited range of nitrate concentrations of up to 42 μmol L^{-1}. In the experiment described here, samples with salinities between 11 and 32 psu and nitrate concentrations between the detection limit to more than 150 μmol L^{-1} were observed. The CDOM ($a_{440\ nm}$) concentrations of these samples ranged from 0.02 to 0.7 m^{-1}. Samples were measured online on board of R/V Heincke using a flow-through cuvette. The observed area in the German Bight is characterized as a highly turbid area of the Southern North Sea with mayor river inputs and tidal influence. Within this paper three methods to determine nitrate