Deep-Sea Research II 86-87 (2013) 10–18

Contents lists available at SciVerse ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Nitrate *in situ* measurements in the northern Japan Sea

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ARTICLE INFO

Available online 6 August 2012

Keywords:
Northern Japan Sea
Nutrients in sea water
Dissolved oxygen
Vertical profiles
Step-like structure
Mesoscale intrusions
Upwelling
ISUS measurements

ABSTRACT

The results of nitrate *in situ* measurements by the In Situ Ultraviolet Spectrophotometer (ISUS MBARI) in the northern part of the Japan Sea are reported. The observations were implemented in three cruises of R/V *Akademik M.A. Lavrentyev* during 2009–2010 including SoJaBio expedition. The instrument was attached to CTD/water sampling system and thus allowed to measure high resolution vertical profiles of nitrate concentration as well as profiles of water temperature, salinity, dissolved oxygen and chlorophyll-a content down to 1000 m depth. The ISUS data were calibrated using results of chemical analysis of nitrate content in water samples taken at standard depths. Comparison of discrete samples and vertical profiles showed a good correlation of $R=0.93$ for 240 pairs of data. On a background of general increasing of nitrate concentration with depth the ISUS profiles showed at many stations an existence of local nitrate extremes which form inversions or step-like structure of the profiles. They had a typical vertical scale from a few tens to hundred meters and were observed in various layers below seasonal pycnocline (40–50 m) and down to 1000 m. These anomalies coincide well with the anomalies in dissolved oxygen, temperature and salinity profiles and thus could be explained by mesoscale advections of low nutrient/high oxygen water associated with mixing processes in the shelf/slope area as well as at the frontal zone and mesoscale eddies. High nutrient/low oxygen intrusions were also detected at depth 40–60 m and were associated with high salinity subsurface water transported from the southern part of the sea. However, a process of organic matter remineralization just below pycnocline could be also responsible for increasing nitrate concentration there as well for the formation of local maximum or step-like structure in the subsurface layer (40–150 m) observed at many stations located close to the shelf area. Anomalies of larger vertical extent (up to 200–300 m) were associated with mesoscale anticyclonic eddies which carry water of lower nutrient and higher oxygen content. All these peculiarities are important for understanding the biodiversity features observed during the SoJaBio expedition.

1. Introduction

The Japan Sea (Fig. 1), also known as the East Sea in Korea, is a large semi-enclosed oceanic basin located in subtropical and subpolar areas with monsoon climate and relatively limited exchange with surrounding basins because of narrow and shallow straits (e.g. Ichiye, 1984; Preller and Hogan, 1998).

The northern and southern parts of the sea are hydrographically distinct in the upper water column with the southern portion being more tropical/oligotrophic and the northern portion being more boreal/eutrophic. The two regions are separated by a persistent marked front (the Subpolar or Subarctic Front) which is extended from west to the east across the basin. The hydrographic characteristics of the southern portion of the sea are determined by the inflow of subtropical mode water through the Tsushima/Korea Strait (150 m deep) (Ichiye, 1984; Hase et al., 1999).

The northern portion of the Japan Sea is characterized by a cyclonic gyre with colder fresher temperate/boreal water originated in the northern part of the sea and transported southwestward along the Russian Coast by Primorye (Liman) Current and further south by North Korean Cold Current. It flows along the coast of Korea and collides with the East Korea Warm Current at approximately 37.5–38°N. Both currents then turn to the east from their confluence point at the Subarctic Front (Huh and Shim, 1987). The front hence is the juxtaposition of cold, fresh northern subarctic water and warmer, saltier subtropical water and thus influencing on distribution of marine biota (Ashjian et al. 2005).

The area of the Sea of Japan Biodiversity Study (SoJaBio) expedition was located at the northern part of the Japan Sea over the deep Japan Basin and the continental slope of Primorye area, Russia (Fig. 1).

The most recent and detailed classification of water masses of the sea including their physical and chemical properties is provided

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http://dx.doi.org/10.1016/j.dsr2.2012.08.005

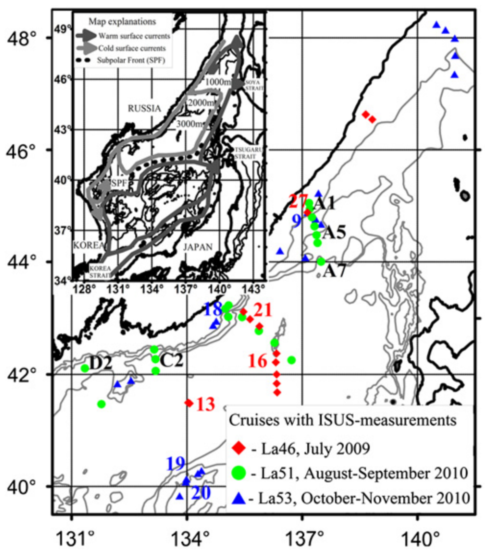

Fig. 1. The Japan Sea (inset) and locations of ISUS-measurements in the cruises of R/V "Akademik M.A. Lavrentyev" in July 3–20, 2009 (La-46, diamonds); August 11–September 5, 2010 (La-51, circles, SoJaBio expedition) and October 27–November 14, 2010 (La-53, triangles).

in Talley et al. (2006). In general there are two surface water masses (the colder northern water and warmer southern water), high salinity subsurface water in the southern part of the sea originated from Tsushima Warm Current, intermediate low salinity water subducted from the north at the subarctic front zone, intermediate high salinity water formed by deep convection in the northern part of the sea, deep and bottom waters. Two intermediate waters are distributed over the most part of the sea. Distribution of nitrate is maximum in the northern area and minimum at the southern part at the surface layer and vice versa at the subsurface and intermediate depth. There is also more detailed classification of water masses for the northwestern part of the sea including shelf zone (Zuenko and Yurasov, 1995; Zuenko, 1997). However, there is not much detailed information of the local distribution of nitrate.

The goal of this paper is to analyze more detailed distribution of nitrate in the northern part of the sea with particular emphasis on their vertical distribution based on high resolution *in situ* measurements by special compact spectrophotometer MBARI ISUS V3 (Operation Manual for MBARI-ISUS V3, 2009) attached to the CTD system. The observations were partially done during the SoJaBio expedition in summer of 2010 as well as in two more cruises during 2009–2010. In this paper, we analyze the experience of using ISUS and its calibration procedures.

The information on nitrate is important in order to obtain a vertical profile data of nitrate uptake/release which provides effective constraints on nitrate budget estimate. Biological uptake of nitrate varies according to the vertical gradients of environmental parameters and the vertical structure of biological communities (Kanda, 2008). Recent studies concerned with the NO_3 measurements of dissolved oxygen concentration in an attempt to resolve the problem of understanding of nutrient supply mechanisms including nitrogen fixation, diffusive transport and vertical entrainment. We believe it to be insufficient to supply the required nutrients for photosynthesis (Johnson et al., 2010). Hence we also consider the nitrate vertical profiles and the oxygen profiles. The information on nitrate in the Japan Sea is also important with regard to the denitrification process found here under the conditions of high oxygen (Tishchenko et al., 2007). We also analyzed water mass properties which are important for understanding biological community life in the region of SoJaBio interest.

2. Data and methods

In this paper we discuss the results of nitrate *in situ* measurements obtained during three cruises of R/V "Akademik M.A. Lavrentyev" in the northern part of JS: La-46 (July 3–20, 2009), La-51 (August 11–September 5, 2010, SoJaBio Project) and La-53 (October 27–November 14, 2010). The measurements locations are shown in Fig. 1.

The data during the first and the second cruises (La-46 and La-51) were collected in the warm period of the year while during the third one (La-53) there was a beginning of a cold season. This allows us to consider peculiarities of nitrate distribution during different seasonal conditions in the region.

During the first (La-46) and the third (La-53) cruises data of chemical analysis of nitrate from water samples taken by Niskin bottles were available. This allowed us to compare the ISUS nitrate profiles with the results of laboratory analysis for discrete depths and to obtain a calibration equation for measurements of ISUS.

As in most parts of the world ocean concentration of nitrate in the Japan Sea is minimal at the surface mixed layer and increases with depth. The concentration of nitrate measured in the Japan Sea at 1000 m is around 24–26 μmol/kg (Talley et al., 2004). The data obtained from Niskin bottles in cruises La-46 (warm season) and La-53 (cold season) are shown in Fig. 2 separately for two depths ranges. Generally they have a good agreement with the data published in the Atlas of Japan (East) Sea hydrographic properties based on basin wide extensive hydrographic survey implemented in summer 1999 (Talley et al., 2004).

The subject of our study is to analyze the detailed structure of the vertical profiles of nitrate obtained by *in situ* measurements. Simultaneous *in situ* measurements of temperature, salinity, dissolved oxygen and chlorophyll-a concentration were also involved in the analysis. The oxygen was measured by SBE 43 oxygen sensor attached to SBE-911 CTD unit. This is a Clark polarographic membrane type sensor which allows 2% initial accuracy of saturation and 2% stability per 1000 h (911plus CTD System Operating and Repair Manual (2009)). To measure chlorophyll-a concentration we used Seapoint Chlorophyll Fluorometer (Seapoint Sensors, Inc., Seapoint Chlorophyll Fluorometer User Manual, 2009) with minimal detectable level of 0.02 μg/l (seapoint units at the figures are correspondent to mg/l concentration) attached to the CTD. The measurement range for fluorometer is 0–15 mg/l.

The MBARI ISUS (Monterey Bay Aquarium Research Institute (MBARI) In Situ Ultraviolet Spectrophotometer (ISUS)) is the compact spectrophotometer which allows one to make *in situ* observation within the water environment (sea or river waters). It uses an ultraviolet absorption spectroscopy to measure *in situ* dissolved chemical species. The sensor is a chemical-free, solid-state instrument that offers real-time and continuous measurements of dissolved compounds of interest to oceanographers and limnologists, e.g., nitrate, nitrite, bisulfide, bromide, iodide, thiosulfate, and organic material which can absorb ultraviolet (UV) light (Johnson et al., 2006).

The MBARI-ISUS V3 unit accuracy has been declared as ± 2 μM or 10% of the obtained value, whichever is larger. The precision of measurement has been announced as ± 0.5 μM (Operation Manual for MBARI-ISUS V3, 2009). The ISUS unit was set to "CONTINUOUS" operational mode with the "SEAWATER" dark correction method and fitting range 200–300 nm.

The *in situ* measurements by the ISUS are based on illuminating a sample of seawater with UV light onto a UV spectrometer with a further calculation of the absorption spectra. The calibration process of the system creates a library of absorption spectra for the main absorbing species in this region of the spectrum.