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Baseline

Hydrochemistry and nutrient distribution in southern deep-water basin of the Caspian Sea

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ABSTRACT

In this work, the results of hydrochemical studies aboard the R/V Iran Behshahr in southern Caspian Sea in late-winter 2014 were presented. Salinity, temperature, dissolved oxygen, pH, total dissolved inorganic carbon, total alkalinity, nitrate, phosphate and silicate concentrations in water column of Neka-Amir Kabir oil platform section in the southern Caspian Sea were measured to study the status of hydrochemistry of this area. Results showed that the hypoxia continues to intensify in the deep-water basin of the South Caspian Sea. Near-zero concentration of dissolved oxygen and accumulation of phosphate, silicate and total dissolved inorganic carbon in near-bottom layers in the study area showed that vertical winter mixing of water column did not reach the near-bottom layers at the time of this survey. Nitrate showed its maximum concentration at the intermediate maximum depth of 300 m.

The Caspian Sea is the largest inland water body on earth with a surface area of about 380,000 km^2 and approximate volume of 78,000 km^3 (Nasrollahzadeh et al. 2008). About 130 rivers with various sizes flow into the sea with an annual freshwater inflow of about 300 km^3. The main input is the Volga River in Russia (85% of the total volume of inflow), while all rivers from Iran contribute only 4–5% of the annual inflow (CEP 2002). The outflow in the Caspian Sea is mainly by evaporation at the sea surface. The sea level in the Caspian Sea displays a clear seasonal cycle, generally reaching its lowest seasonal value in winter and increasing during May–July, following the spring floods (Birol Kara et al. 2010). Thus, it is mainly a function of evaporation–precipitation and these local effects can be important in predicting the upper ocean variables (Rodionov 1994).

The chemical properties of seawaters directly control the condition and functioning of the biotic part of marine ecosystems. In particular, the concentrations of dissolved oxygen and nutrients control the existence of marine biota. The first hydrochemical studies of Caspian Sea waters were performed at the beginning of the twentieth century (Andrey G. Kostianoy 2005). It was stated that the Caspian Sea, especially its northern shallow-water part, significantly differs from other regions of the World Oceans in terms of salt composition and high nutrient content; the latter defines the equally high biological productivity of the waters of the sea (Andrey G. Kostianoy 2005). In the mid-1950s, a regular program for onboard hydrochemical observations over a network of standard cross sections in the north, middle and South Caspian Sea was initiated under the supervision of the State Oceanographic Institute, Hydrometeorological Service of the USSR (Andrey G. Kostianoy 2005). Several published reports, papers and books resulted from the program, (Ambrosimov et al. 2011; Ambrosimov et al. 2012; Andrey G. Kostianoy 2005; Brezgunov 2015; Dukhova et al. 2015; Lein et al. 2010; Lukashin et al. 2010; Sapozhnikov et al., 2006; Sapozhnikov et al., 2010; Sapozhnikov et al. 2012; Sapozhnikov et al. 2007; Sapozhnikov et al. 2008a; Sapozhnikov et al. 2011; Vinogradova et al. 2011) showed that in deep basins, Caspian Sea has experienced two types of hydrochemical regimes in different periods in the last 100-years. Based on the results (to 2013), during last decade, the hydrochemical regime of the Caspian Sea has approached to the condition observed in the 1920s–1930s.

In this work the results of hydrochemical studies in late-winter 2014, within the research project of "Master Plan for Combating and Collecting Caspian Oil Pollutants" of Khazar Exploration and Production Company (KEPCO), in southern Caspian Sea were presented. Salinity, temperature, dissolved oxygen, pH, total dissolved inorganic carbon (C_T), total alkalinity (A_T), nitrate, phosphate and silicate concentrations in water column of a 250-km transect in southern Caspian Sea (Fig. 1) were measured to determine the current status of hydrochemistry of this area.

Aboard the R/V *Iran Behshahr*, sampling was performed at 5 stations in a section at the south of Caspian Sea from Neka (Mazandaran province, Iran) to the Amir Kabir oil platform in March 2014 (Fig. 1). Table 1 shows the depth and position of the sampling stations.

Seawater temperature, salinity, pH and dissolved oxygen (DO) were

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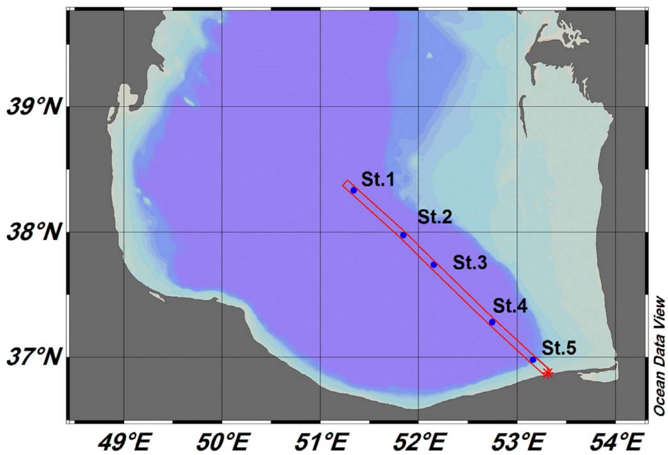

Fig. 1. The position of the sampling stations in the southern Caspian Sea. R/V *Iran Behshahr* (March 2014).

Table 1
Sampling stations characteristics.

Station	Longitude	Latitude	Depth (m)
1	51.33532	38.33388	730
2	51.84138	37.97582	630
3	52.15143	37.74068	550
4	52.74463	37.2811	480
5	53.16163	36.97993	100

measured onboard by a portable multimeter (HACH, model HQ40d) and CTD probe (Idronaut, Ocean Seven 316). Water samples for determination of dissolved inorganic nutrients (nitrite, nitrate, phosphate and silicate), total alkalinity (A_T) and total dissolved inorganic carbon (C_T) were taken with Rosette water sampler (Hydro-Bios) equipped with twelve 2.5-liter bottles to collect discrete water samples. Samples were taken from the standard horizons and in the horizons that were chosen according to the presence of specific features on the temperature-salinity curves.

Water samples for determining dissolved inorganic nutrient were filtered by syringe filters (0.45 μm, cellulose acetate), collected in 100 mL high density polyethylene bottles and quickly frozen till analysis (Klaus Grasshoff and Ehrhardt, 1999). Water samples for determining A_T and C_T were collected in 500 mL glass bottles and poisoned by 200 μL saturated mercury(II) chloride ($HgCl_2$) solution to stop the biological activities (Andrew Gilmore Dickson and Christian, 2007). Samples were stored in refrigerator at 4 °C until laboratory analysis.

Dissolved inorganic nutrients were determined using spectrophotometric techniques (ROPME 1999) with a UV–Vis spectrophotometer (Analytikjena, specord 210). A_T was determined by Gran potentiometric titration technique using an automatic digital 715 Dosimat titrator (Hydro-bios). An ANATOC series II (SGE Analytical Science) was applied to measure C_T based on acidification of a fixed volume of sample followed by IR determination of released CO_2 in a closed loop. Ocean Data View program was used to analyze the data and plot the figures (Schlitzer, R., Ocean Data View, http://odv.awi.de, 2012).

Temperature was decreased from about 12 °C at the surface to the minimum value of 6.04 °C at the near-bottom layer in station 1 (Fig. 2a). Salinity was at the range of 12.34 to 12.55 which the minimum was occurred at horizon level of 100 m near the Iranian coast of southern basin of the Caspian Sea (Fig. 2b). Data of temperature and salinity showed significant thermohaline stratification in the South Caspian Sea at the time of this study (March 2014).

Dissolved oxygen was found to be at the range of 0.08–13.16 mg/L. Fig. 3a shows the distribution of DO in water column of the studied section. Almost in all stations, the concentration of DO was reduced to about 3.4 mg L^{-1} (30% saturation) at horizon level of 300 m and reached to 0.08 mg L^{-1} at near bottom water in the station 1. Results showed that the hypoxia continues to intensify in the deep-water basin of the South Caspian Sea. Since 1960s, hypoxia in the Caspian Sea first recorded in the mid-2000s (Dukhova et al. 2015). pH of water in the section was recorded to be at the range of 7.86–8.62 (Fig. 3b). The average amount of pH at surface water was 8.60 and reached below 8.0 at horizon level of 300 m. At sea surface, primary production activities (photosynthesis) followed by CO_2 consumption is the main reason for higher pH, while, in the bottom waters of the basin, degradation activities followed by production of CO_2 results in lower values of pH.

Phosphate (Fig. 3c), total dissolved inorganic carbon (C_T) (Fig. 3e) and silicate were accumulated in the bottom waters of the basin as a result of organics mineralization and dissolution of SiO_2 particulates. The concentration of phosphate was found to be at the range of near zero (below detection limit) at the surface to about 2.31 μM at the bottom water of the station 2. Average C_T of the surface water in the studied section was 3500 μmol kg^{-1} and increased to about 3900 μmol kg^{-1} at the bottom water of station 4. Dissolved inorganic Si was found to be at the range of 2.11 to 3.6 μM at the surface to 82.4 μM at the bottom layer in station 2. The extent of accumulation of phosphate, silicate and C_T in bottom waters of the southern basin of the Caspian Sea is characterized by the role of the biochemical

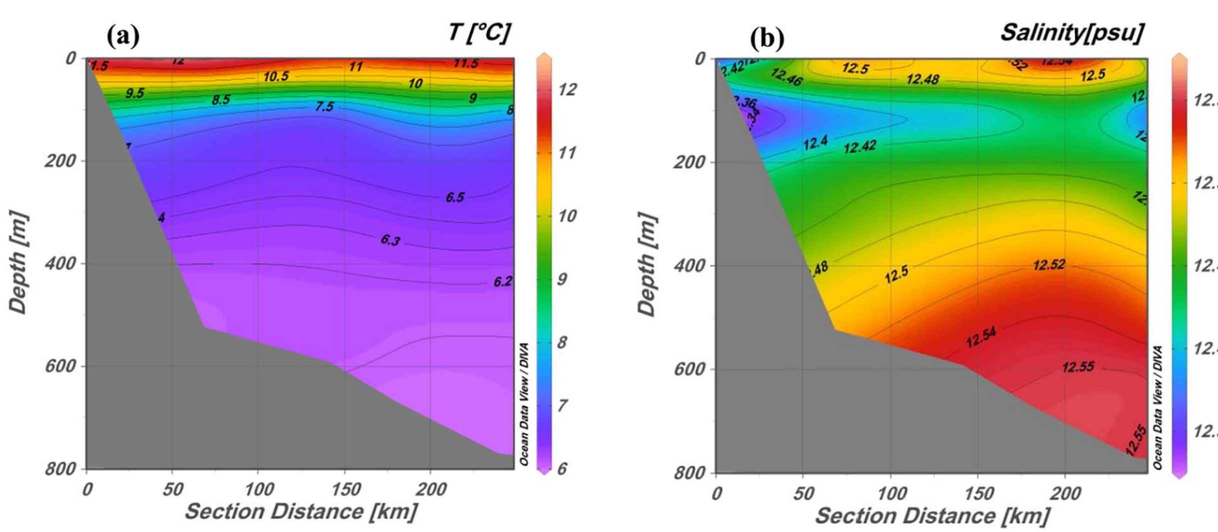

Fig. 2. Temperature (a) and salinity (b) over the Neka-Amir Kabir oil platform section in South Caspian Sea (March 2014).