

# Variability of Dissolved Oxygen and Active Reaction in Deep Water of the Southern Caspian Sea, Near the Iranian Coast

Siamak Jamshidi<sup>1,2\*</sup>, Noordin Bin Abu Bakar<sup>1</sup>

<sup>1</sup>Department of Geophysics, School of Physics, Universiti Sains Malaysia,  
11800 USM, Penang, Malaysia

<sup>2</sup>Department of Physical Oceanography, Iranian National Center for Oceanography,  
P.O. Box 14155-4781, Tehran, Iran

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## Abstract

Nowadays, great values of urban sewage and industrial pollutants discharge into the Caspian Sea and threaten its marine environment. This study evaluates characteristics and variability of dissolved oxygen and active reaction (pH, is a parameter for measuring of the acidity or basicity of a solution or seawater) in deep waters of the southern Caspian Sea near the Iranian coast during March to November 2008. The vertical distribution of active reaction showed a general reducing trend with depths that reached 8.2 at depth of 350 m in midsummer. Moreover, observations in November showed active reaction value of 8.3 at 450 m depth. In comparison, amounts of active reaction (pH) in mid-summer (August) were less than that in other seasons. Dissolved oxygen concentrations ranged between 2.0-7.5 mg·L<sup>-1</sup> at the surface layers. Below 100 m, a rapid drop in values of dissolved oxygen was observed and measured about 1.2 mg·L<sup>-1</sup> at 450 m in mid-summer and mid-autumn, while 2.0 mg·L<sup>-1</sup> was recorded below 300 m in late winter. The seasonal variations of dissolved oxygen and active reaction (pH) were considerable, especially in intermediate and deepwater layers. According to levels of dissolved oxygen concentrations and active reaction (pH) values in deepwater of the Caspian Sea, increased observations and serious efforts for decreasing entry of pollutants into the marine environment are necessary.

**Keywords:** Caspian Sea, seasonal variations, dissolved oxygen, active reaction (pH)

## Introduction

### The Caspian Sea

The Caspian Sea, with a volume of about 78,000 km<sup>3</sup> and surface area of 400,000 km<sup>2</sup>, is unique in its size and characteristics. As the largest inland body of water in the world, the sea, located in a large continental depression about 27 m below ocean level (with the length of coastline

about 7500 km at this level). The sea is characterized by rich hydrocarbon (oil and gas) and biological resources [1-5]. It extends from south to north with a length of 1,030 km from 36° to 48°N and with a average width of 435 km from west to east between 48° and 54°E [6-8]. Geographically, the Caspian is shared between Kazakhstan, Iran, Turkmenistan, Russia, and Azerbaijan [9]. The Caspian is divided into three parts: south, middle, and north basin, with maximum depths of 1,025 m, 788 m, and 20 m, respectively, and average water depth about 210 m. The Iranian coastline is about 900 km in the southern Caspian,

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\*e-mail: si.jamshidi@gmail.com

where the coastal area is limited with Elburz Mountains toward south [1, 8-10]. Based on Caspian Sea surface monitoring, the northern basin shows higher diversity and productivity relative to the middle and southern parts of the sea [11].

Due to the isolation of the Caspian from the open seas, its natural structure is under the effect of external factors such as discharge of rivers and atmospheric processes. The hydrological structure and circulation of Caspian seawater is defined by these factors [12]. About 130 rivers with various outflow volumes enter the sea. The main sources of freshwater inputs to the Caspian Sea are the Volga (with total volume about 80-85% of inflow), and the Ural, Emba, and Terek rivers in the north [13, 14]. In the southern part, the total volume inflow of Iranian rivers to the sea is about 4-5%, with the Sepidrood River being the major contributor [8, 15].

### Seawater Temperature and Salinity

The southern coastal area of the Caspian has warm summers and mild winters (warm and humid subtropical climate) [13, 16]. The maximum and minimum air temperatures are in August and January, respectively. In winter, the air temperature ranges between 8-12°C and in summer the mean monthly air temperature over the entire sea equals 24-26°C [8]. According to the results of a study, water temperature in the southern Caspian ranges between 9-26°C during a period of winter to summer. In addition, seasonal sharp thermocline forms between 20 m and 40 m depths. Seasonal variations of the salinity values are less than 0.4 PSU, and mean annual salinity increases with depth at a rate of 0.1-0.3 PSU from the sea surface to the bottom [7]. In the south, the mean annual wind speed is 3-4 m sec<sup>-1</sup>, and the recurrence rate of weak winds here reaches 90%. Also in the south, the number of days with storms (wind speed greater than 15 m sec<sup>-1</sup>) is not more than 20-30 per year [8].

In other research, surface water temperature in this part was presented about 10°C in winter and 27-28°C in summer [1]. Moreover, based on International Atomic Energy Agency (IAEA) measurements near the Iranian coast in September 1995, surface water temperature was about 27.5°C with a salinity of 12.24 PSU [17]. Based on measurements taken in the south in August 2001, sea surface temperature was about 28°C [18].

The salinity of the Caspian Sea is variable with an average of about 13 ppt [19] and about 12.28 g·kg<sup>-1</sup> [20]. In addition, the average values of salinity in the southern basin were reported between 12.8-13.5 ppt (i.e. about one-third open seawaters) by Dumont (1998) [1]. Volga and Ural Rivers and surface evaporation control fluctuation of sea water level. The former causes sea level increases while the latter causes sea level decreases. Values of the salinity in the northern part of the Caspian are strongly influenced by freshwater discharge of the Volga and Ural Rivers. The southern and northern parts are predominated by brackish water with variation in salinity between 13 to 10 ppt [21]. According to recent field measurements in the southern coastal waters of the Caspian, the surface water temperature and salinity were in the ranges 9.9-28.6°C and 10.85-13.18 ppt (years 1996-7) and 9.2- 28.8°C and 10.23-13.19 ppt (year 2005) [22]. With regard to the results of other research on variations of temperature and salinity in coastal waters of Babolsar Port in the eastern part of southern coasts of the Caspian (Fig. 1), surface water temperature was in the range of 8-12°C in winter and 26-28°C in summer. The average salinity at the surface waters was observed around 11.9±1.2 ppt [23].

### Dissolved Oxygen and Active Reaction (pH)

Since the beginning of the 20<sup>th</sup> century, the large river discharge into the Caspian Sea was characterized by reduced concentrations of dissolved oxygen and increased

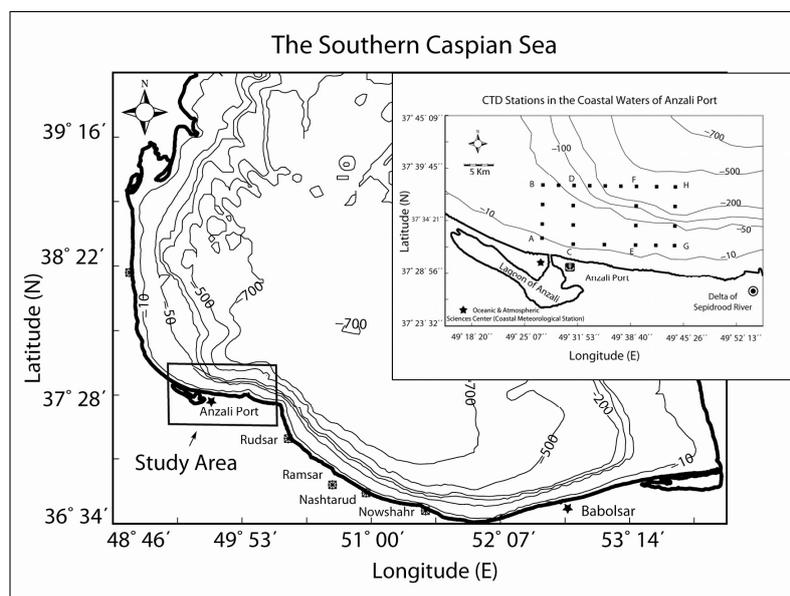


Fig. 1. Study area and locations of stations in the south Caspian Sea.

nutrient contents. Enhancement in the nutrient supply (due to increase of rivers inflow) and reduction of winter severity are the most important factors for unfavorable ventilation of deep waters of the southern Caspian. Amounts of dissolved oxygen in the Caspian's deep waters are unsuitable for most aquatic organisms [24]. Dissolved oxygen levels of below  $3 \text{ mg}\cdot\text{L}^{-1}$  are stressful to most marine biota. Oxygen concentrations of at least  $5\text{-}6 \text{ mg}\cdot\text{L}^{-1}$  are usually required for growth [25, 26]. In the southern basin, dissolved oxygen content decreases with depth. Moreover, the percentage of saturation reaches 50% at a level of 200 m and less than 10% at 600 m depth [16].

Nowadays the marine environment of the Caspian Sea (especially the south basin) is one of the most heavily polluted water bodies in the world. Its environment is under high stress because of extensive exploitation and discharge of large magnitudes of human waste [3, 27]. The main sources of Caspian Sea pollutants consist of industrial and agricultural wastewaters, municipal domestic sewage waters, heavy metals, oil and petroleum products, nutrients such as phosphate and nitrate, pesticides, and detergents [3, 4, 27]. Pollution is a significant threat to the biodiversity of the Caspian. It should be noted that the main flow of pollution comes from rivers to the Caspian Sea [28]. Furthermore, Iranian lagoons and coastal regions have also been anthropogenically polluted [29].

On the other hand, pH values in the Caspian are significantly greater than in the waters of other regions of the world. The principal reason for the enhanced pH values lies in the great contribution of the riverine waters characterized by a high content of anions of weak acids, primarily carbonic acid, to the formation of the hydrochemical regime of the Caspian Sea [24].

Therefore, the investigation of seawater properties (such as dissolved oxygen and active reaction) is an important requirement for water quality studies, ecological characteristics, and level of safety of the marine environment in the Caspian [30, 31]. Under these conditions, it is necessary to increase the number of ecological and environmental studies of the structure and dynamics of Caspian waters [4].

Field measurements and analysis of chemical and physical characteristics of seawater represent the interest for oceanography and marine research. According to the importance of oxygen content and active reaction (pH) in seawater of the Caspian, we attempted to investigate the distributions of dissolved oxygen and active reaction (pH) in the southern coastal waters of the Caspian in the current study. To the best of our knowledge, there have been no studies in literature that give careful information on seasonal variations of dissolved oxygen and active reaction (pH) in the deep waters of the southern Caspian. This research, at this temporal and spatial scale, is a new work in the Iranian coastal waters of the Caspian Sea. The main objective of this study is to examine the seasonal variations of dissolved oxygen and active reaction (pH) in seawater in the western part of the southern boundary of the Caspian Sea.

## Methods

### Study Area

Field measurements were done in the southern coastal waters of the Caspian Sea near the Iranian coasts between  $\text{N}37^{\circ} 29'$  and  $\text{N}37^{\circ} 36'$  latitude and between  $\text{E}49^{\circ} 25'$  and  $\text{E}49^{\circ} 44'$  longitude. The study area covers a rectangular area of coastal waters with a length of 25 km and width of 15 km adjacent to the port and lagoon of Anzali. Fig. 1 illustrates an overview of the study area and locations of measuring stations for field survey. Mean temperature in Anzali Lagoon was about  $16^{\circ}\text{C}$ , which varies from  $4.5^{\circ}\text{C}$  in February to  $27.5^{\circ}\text{C}$  in August [32]. In the eastern part, the continental shelf has a width of 8 km and a maximum depth of about 50 m. The water depth from the west to the east increases to about 500 m. In a northward direction, the water depth from the coast gently increases to about 50 m near the shelf break and after that reaches to 200 m depth at 12 km [31].

### Experimental Details and Field Observations

Observations in the study area were carried out in 2008 at 23 stations along four survey lines perpendicular to the coastline and two transects parallel to the coast. The distance between stations reached an average of 2 km along transects. Measurements in the winter were limited to stations A, B, E, and F in a rectangular area in 15 stations. In the following field surveys (the next seasons) the number of stations and transects was extended for profiling in deeper stations in the eastern part of the study area. The maximum depth of sampling stations during the field measurements in March was 365 m, and in the next seasons was around 470 m. In order to collect data, a portable Ocean Seven 316 probe developed by IDRONAUT was used. Data gathering was performed with a profiler in free falling mode in every second with time interval one meter per second. In analysis, for computation of depth using hydrostatic pressure, the equations presented by Emery and Thomson (2001) [33] were used with regard to density of the Caspian seawater. Dissolved oxygen and active reaction (pH) measurements were made using an oxygen sensor and pH probe meter with accuracy of  $0.1 \text{ mg}\cdot\text{L}^{-1}$ , 1% saturation, and 0.01 pH.

## Results

### Seasonal Variations of Active Reaction (pH)

Seasonal variability of active reaction (pH) in the study area along transects were presented in Figs. 2-5. Vertical distributions of active reaction (pH) over the continental shelf zone in front of the mouth of Anzali Lagoon (transect AB) during 2008 were shown in Figs. 2a-2d. Here in late winter (March), changes of active reaction (pH) were detected between 8.9 and 9 at the surface, which decreased with depth. The amount of active reaction (pH) ranged

around 8.8 below 10 m depth until near bottom (at 25 m depth). At this time, variations of active reaction (pH) from the surface to the bottom were relatively uniform. According to our recorded data in April, vertical and horizontal gradients of active reaction (pH) were considerable above 10 m depth. At the sea surface, values changed from 8.0 to 8.7 and reached 8.6 near the bottom. Observed values in spring (April) were relatively less than measured values of active reaction (pH) in late winter (March). In mid-summer, active reaction (pH) ranged around 8.2 at the surface near the mouth of the lagoon and reached 8.4-8.5 in the water column. In November, values in the middle of the transect were great and changed the normal regime of active reaction in the area. In this time, the amount of pH ranged around 8.7 near the beginning of the transect. Over the continental shelf zone, distributions of pH at the sea surface were under the effect of lagoon outflow. Comparison of the surface and bottom layers showed higher variations in pH values in the former.

In the eastern part of the coastal waters and far from the mouth of the lagoon (along survey line EF), vertical structure of active reaction showed values of 8.8 over the continental shelf in March, when the values reached 8.7 toward

the deeper stations. Outside the shelf, active reaction from 8.8 at surface layer was reduced to 8.7 at 100 m depth. Distribution of pH in vertical direction showed a decrease with depth and at 170 m depth was around 8.6. In deep water and at 270 m depth, the pH values measured were close to 8.5 (Fig. 3a). At this time, below this level at 350-365 m depth active reaction ranged around 8.4. Similarly, values of pH reduced with depth along transect BF, and reached 8.7 around 100 m depth (intermediate layer), in March. Above 100 m depth, active reaction (pH) varied uniformly (mainly about 8.8) over the continental shelf zone and outside the shelf (onshore and offshore stations).

In contrast, in early spring (April) active reaction (pH) was measured at 8.7 over the continental shelf region and at the end of section it reached 8.6 at the surface (Fig. 3b). At this time of measurement, values were around 8.8 over the shelf break. Below a depth of 50 m active reaction decreased from 8.7 at 100 m level and below 320 m observed around 8.4 (Fig. 3b). In April, the contour of pH (8.7) was parallel to sea water level and horizontal gradient of active reaction was slight (Fig. 4a). At this transect, the trend of decrease of the active reaction (pH) was regular and at 350 m depth, it reached 8.4 in early spring.

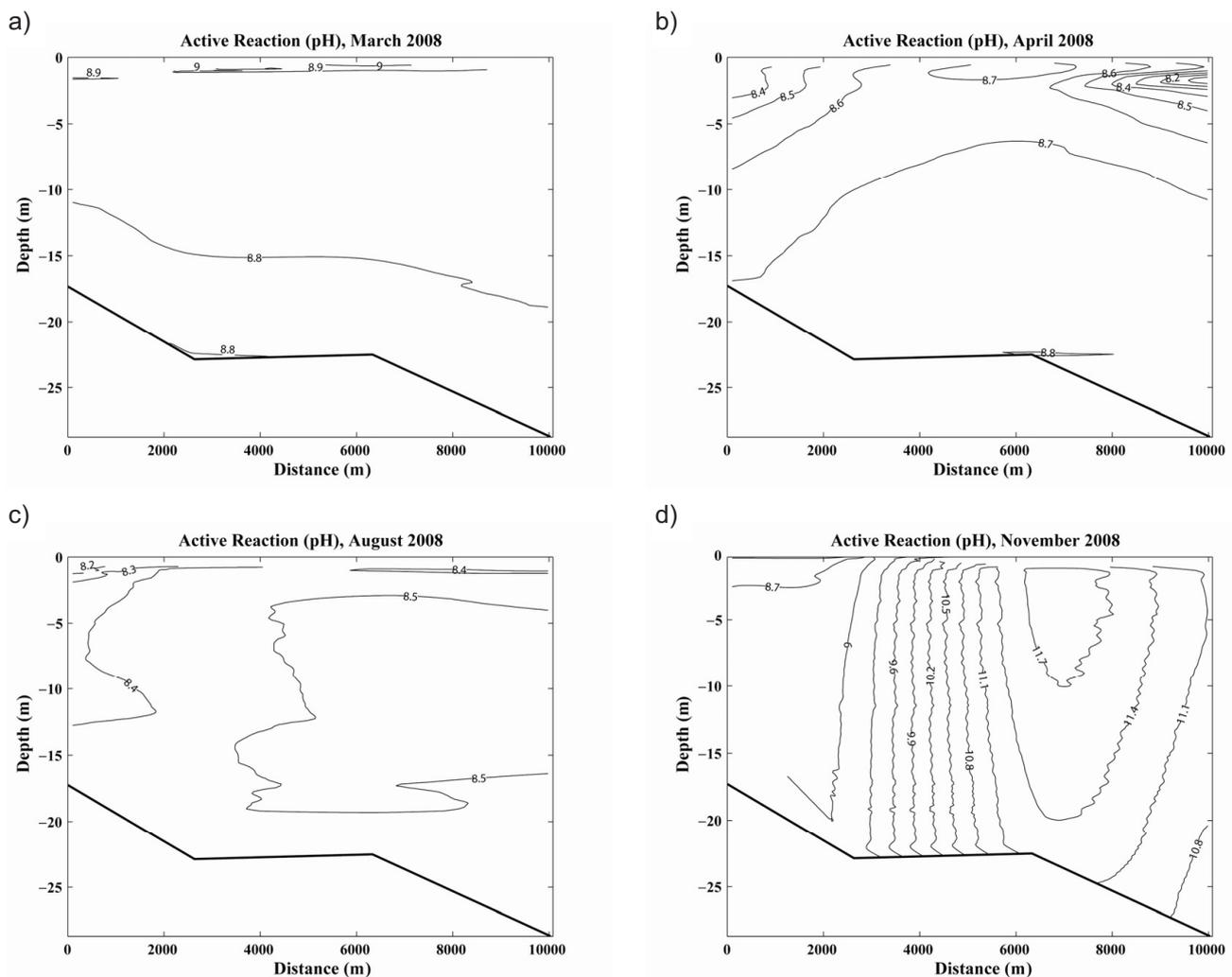


Fig. 2. Seasonal variations in vertical distribution of active reaction (pH) along transect AB over the continental shelf.

Below 450 m depth the amount of pH with a vertical gradient of 0.5 recorded about 8.3 (Figs. 4a and 5b). In April, over the continental shelf (and along transect BH) amounts of 8.7-8.8 were detected. Outside the shelf, horizontal difference was considerable above 100 m depth (in transect BH, Fig. 5b).

In midsummer over the continental shelf along transect EF, pH varied from 8.1 to 8.5 from the coast toward the shelf break (Fig. 3c). In offshore stations at the end of the transect, active reaction was around 8.4 at surface and increased to 8.5 at 50 m depth. Below this level, pH values of about 8.3 were observed at 220 m depth. In this time, in section GH active reaction ranged between 8.3-8.4 at the surface mixed layer over the continental shelf zone and outside the shelf. Here, the amount gradually decreased and reached 8.2 at a depth of 350 m (Fig. 4b). In comparison, the vertical structure of active reaction showed that values of pH along transect GH in August (midsummer) was less than that in April.

As shown in Fig. 5c, in August pH values at the surface along transect BH were recorded around 8.4, which were enhanced to 8.5 over the continental shelf and in deepwater stations. In this section, pH decrease from 8.5-8.6 around

50 m depth to 8.2 at 350 m depth. In comparison, it is assumed that in this transect amounts of active reaction in August were less than that in April.

Values of active reaction (pH) in mid autumn (November) were higher than in the other seasons in the region. It is assumed that at the time of measurements in November, port activities such as discharge of the sediment of stilling basin of port into this sea disturbed the natural structure of active reaction in the region. Thus, contours with high values of pH were observed in a distance of 8 km from the beginning of transects AB, EF, and GH. Along transect EF, amounts of pH were mainly around 9.0 in the shallow waters stations and increased to 9.9 over the shelf. Outside the shelf, active reaction (pH) measured about 10.2 at surface decreased to 9.0 in deepwater (Fig. 3d).

Active reaction (pH) was recorded from 8.6 to 8.8 over the shallow waters area at the beginning of transect GH in November. In contrast, outside the shelf and over the slope, values substantially increased to around 9.2, especially at the surface layers. Generally, at this time values of pH reduced with depth in this transect and ranged around 8.6 at 400 m depth (Fig. 4c). In this season, amounts of active reaction along transect BH from west to east were reduced

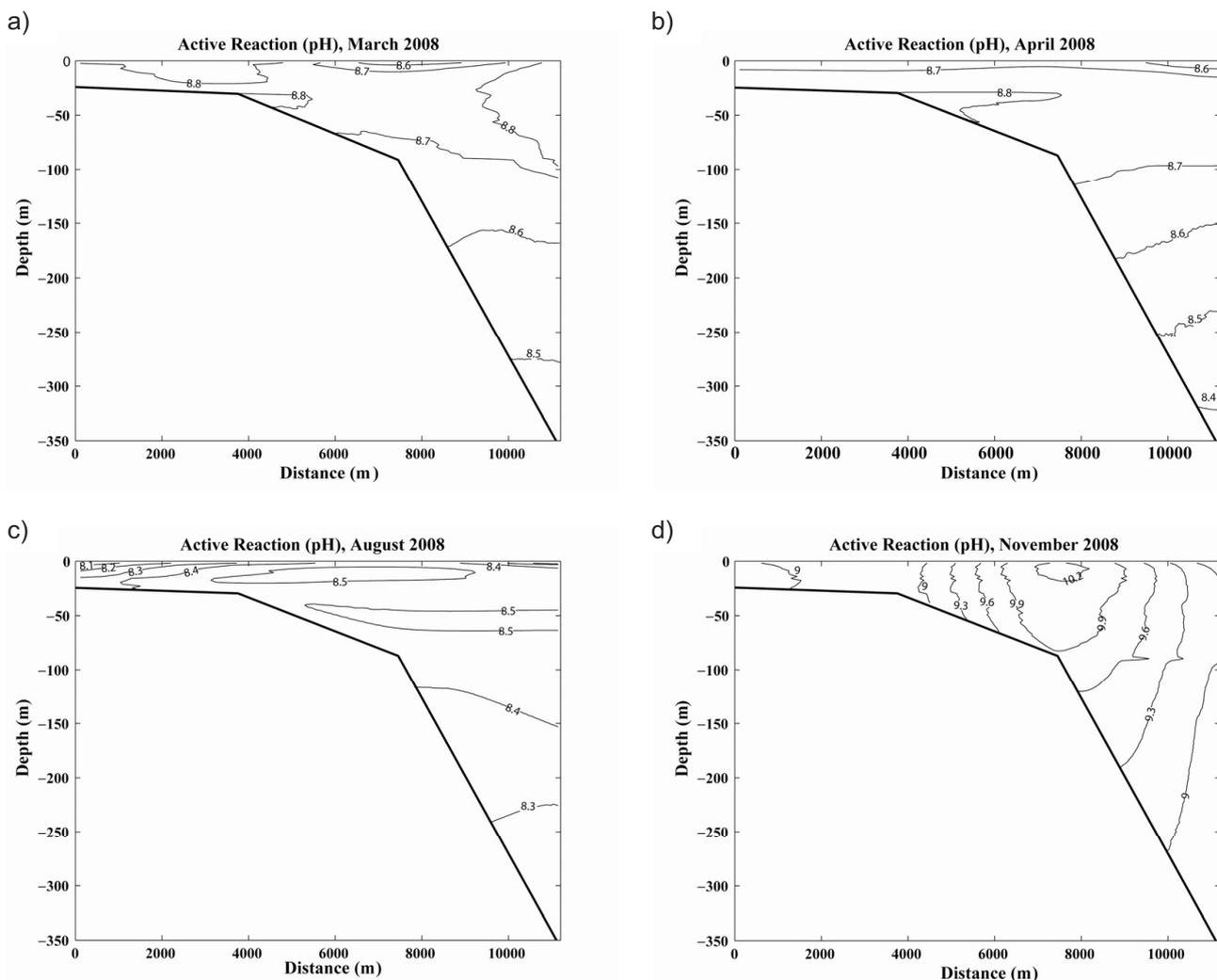


Fig. 3. Seasonal variations in vertical distribution of active reaction (pH) along transect EF.

(Fig. 5d). Over the shallower area pH varied between 10.8-8.7. This decreasing trend continued from the west over the western continental shelf toward deepwater area in the east. High values contours of active reaction in the middle of the

section was observed over the slope. At the deep area of the transect (eastern part), pH gradually found the natural regime and reached to 8.7 around 300 m depth (Fig. 5d).

### Seasonal Variations of Dissolved Oxygen

Seasonal variations of dissolved oxygen (concentration and percentage saturate) in the investigated region are indicated in Figs. 6-8. Due to the location of transect AB, being close to the mouth of Anzali Lagoon, the structure of seawater properties in this area was under the effect of lagoon outflow. In March, thermal stratification in the water column was weak in the sea. Water temperature at the sea surface was recorded around 10°C over the continental shelf. Vertical profiles of temperature in the study area in various seasons were indicated in Fig. 9. At this time of the year, over the continental shelf (transect AB, Figs. 6a and 6b) dissolved oxygen concentrations ranged between 4 and 4.5 mg·L<sup>-1</sup> (40-44% sat.). According to Figs. 6c and 6d, amounts of dissolved oxygen in seawater were found in a range of 2-2.5 mg·L<sup>-1</sup> (28-36% sat.) in August.

In comparison, concentrations of dissolved oxygen in seawater over the continental shelf zone in autumn (Figs. 6e and 6f) was more than that in August and March. The maximum record of dissolved oxygen in fall season (November) was at the sea surface around 7.0 mg·L<sup>-1</sup> (78-82% sat), which reduced to 4 mg·L<sup>-1</sup> (46% sat) at 15 m depth. Here, vertical variations of dissolved oxygen concentration in November were more than that March and August, especially in the upper 5 m depth. In March, the vertical structure of dissolved oxygen showed that its concentration over the continental shelf (4-4.75 mg·L<sup>-1</sup> with 42-46% sat.) across transect EF was less than similar depth outside the shelf (Figs. 7a and 7b). Outside the shelf, values of dissolved oxygen changed from 5-5.25 mg·L<sup>-1</sup> (46-48% sat.) at the sea surface to about 2 mg·L<sup>-1</sup> (18% sat.) near the bottom (350 m depth) (Figs. 7a and 7b). In midsummer (August), distribution of dissolved oxygen showed a range of 4-5.75 mg·L<sup>-1</sup> (54-80% sat.). In this time, variations of dissolved oxygen in shallow waters (in this transect) were observed to be more than that in late winter (March). Outside the shelf, in offshore stations concentrations of dissolved oxygen were about 4.75 mg·L<sup>-1</sup> (with 64% sat.) and reached 5.5-6 mg·L<sup>-1</sup> (50-54% sat.) below 50 m depth. Below this level, dissolved oxygen gradually reduced with depth and reached 1.5 mg·L<sup>-1</sup> (14% sat.) near the seabed at 350 m depth. In deeper layers (below 300 m depth), dissolved oxygen concentrations in August (mid summer) were less than its values in March (in winter). In November, concentrations of dissolved oxygen over the continental shelf and outside the shelf ranged from 4.0 to 4.5 mg·L<sup>-1</sup> (48-54% sat.), in surface mixed layer. Below the surface mixed layer and across the thermocline dissolved oxygen measured around 5.25 mg·L<sup>-1</sup> (50-54% sat.). In deep waters, dissolved oxygen concentrations decreased from 5 mg·L<sup>-1</sup> at 100 m depth to 2.25 mg·L<sup>-1</sup> at seabed (350 m depth) (Figs. 7e and 7f).

As shown in Figs. 8a and 8b, dissolved oxygen over the continental shelf was mainly changed 4.25-4.5 mg·L<sup>-1</sup>

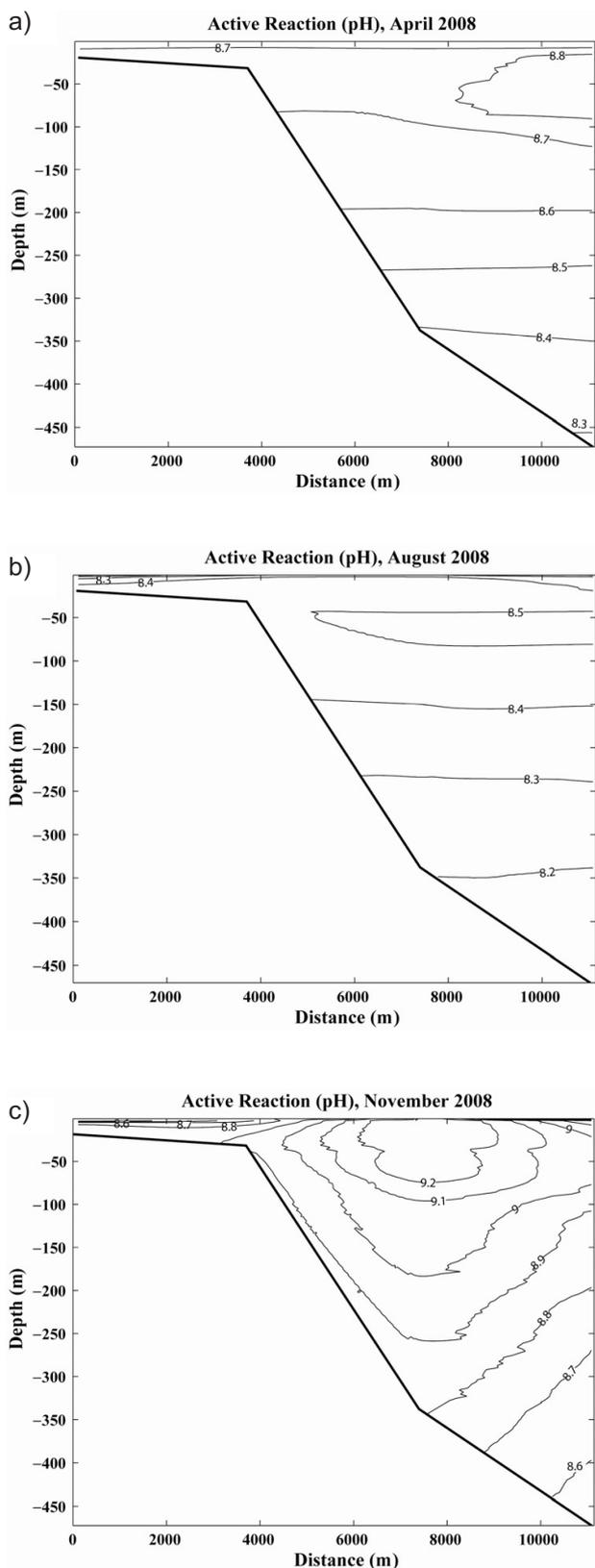


Fig. 4. Seasonal variations in vertical distribution of active reaction (pH) along transect GH.

(with 42-44% sat.), while it was detected between 4.75-5.25 mg·L<sup>-1</sup> (44-48% sat) outside the shelf in upper layers, in March. Below 100 m depth (intermediate layer), concentrations reduce with depth to 3 mg·L<sup>-1</sup> at 200 m depth and 2 mg·L<sup>-1</sup> near to the bottom at 350 m depth. In mid-summer (August), values of dissolved oxygen in onshore stations were found to be between 2.5 and 3.0 mg·L<sup>-1</sup> (33-39% sat.) in surface layer (above 50 m depth). However, in offshore stations (deep-waters), concentrations of dissolved oxygen increased in similar depth in this time and reached 5.5 mg·L<sup>-1</sup> (75% sat.). Here, maximum dissolved oxygen concentrations were observed around 7.25-7.5 mg·L<sup>-1</sup> (66% sat.). Decreasing procedure of dissolved oxygen concentrations were started from below thermocline to the bottom at 470 m depth, which were measured at about 1.25 mg·L<sup>-1</sup> (12% sat.). Measurements of dissolved oxygen along transect AB were less than the values over the continental shelf area in transect EF in August. In midautumn (November), in surface mixed layer mainly dissolved oxygen values varied in a range of 3.25-4.5 mg·L<sup>-1</sup> (36-50% sat.), while outside the shelf this value was around 4.5 mg·L<sup>-1</sup>. Far from the shallow water stations, concentrations changed from 5.0 to 5.5 mg·L<sup>-1</sup> (48-54% sat.) across the thermocline.

In November, concentrations of dissolved oxygen at a depth of 470 m (1.25 mg·L<sup>-1</sup> (12% sat.)) did not show major changes in comparison to midsummer (Figs. 8e and 8f). Seasonal distributions of dissolved oxygen showed that the recorded values in midsummer (August) were more than those in late winter (March) and mid autumn (November). Below the thermocline, the dissolved oxygen concentrations decreased with depth (also with temperature). Amounts of dissolved oxygen in intermediate and deepwater layers (below the thermocline) in midsummer and midautumn displayed significant reductions in concentrations compared to late winter. In winter, the surface layers comprising around 50 m depth were quasihomogenous, and concentrations of dissolved oxygen were observed to be between 4.25-5.25 mg·L<sup>-1</sup> in this layer. In the southern coastal waters of the Caspian, formation and destruction of seasonal thermocline (and pycnocline in position of thermocline) occurs during early spring to late autumn. Thus, it is expected that during this time the pycnocline prevent the ventilation of the deeper layers. Thus, as a result the concentrations in the near bottom layers are reduced. The lowest values of dissolved oxygen concentrations were recorded below 100 m level (intermediate and deepwater layers).

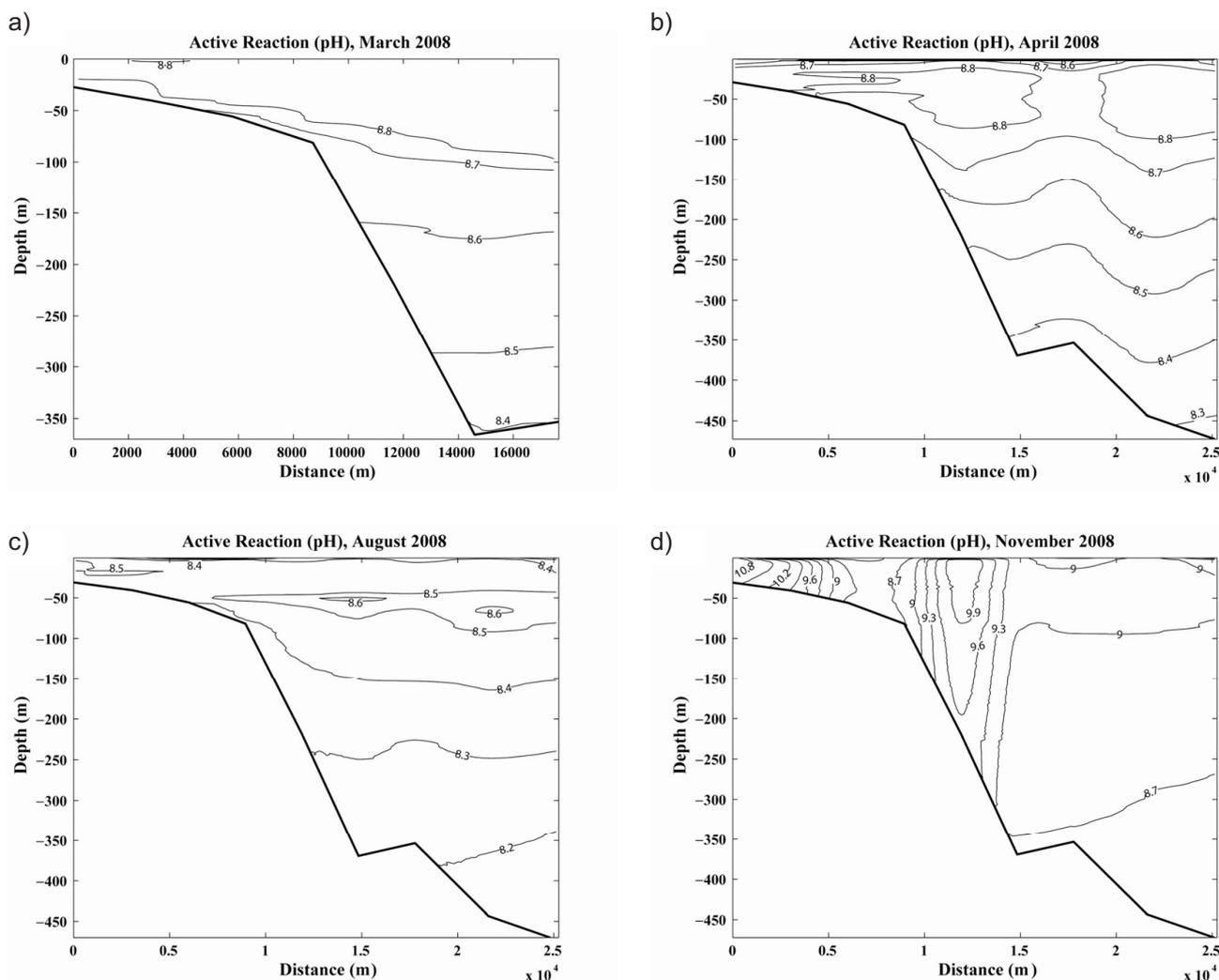


Fig. 5. Seasonal variations in vertical distribution of active reaction (pH) along transect BH (in plot (a) transect BF).

Here, seasonal variations of dissolved oxygen concentrations were minor. In winter, due to mixing in the water column (especially in upper 100 m depth), dissolved oxygen content was uniform, relative to midsummer and midautumn.

### Discussion

In this research, seasonal variability in vertical structures of active reaction (pH) and dissolved oxygen was evaluated. Based on results of previous measurements [24],

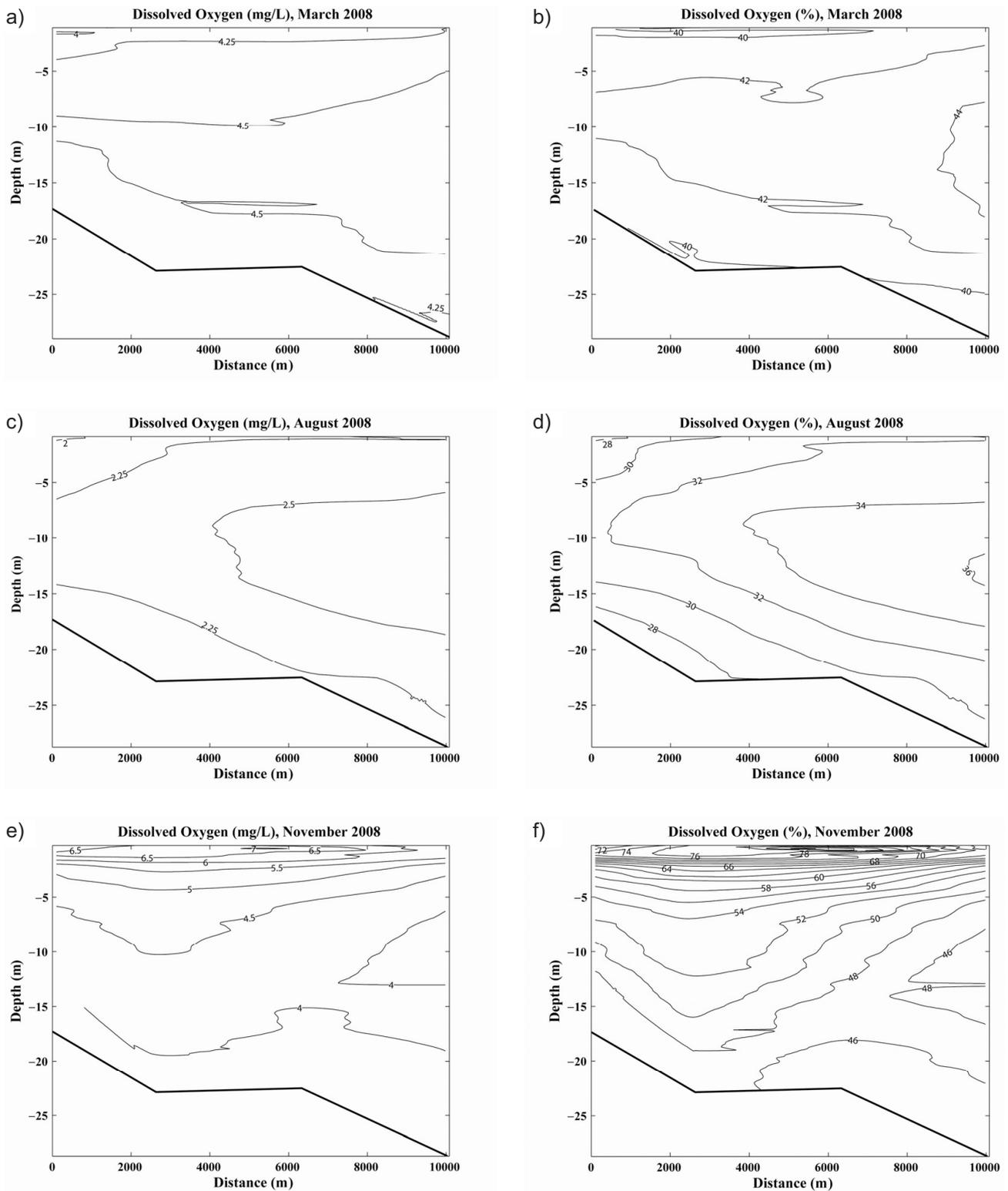


Fig. 6. Seasonal variations in the vertical structure of dissolved oxygen concentrations along transect AB over the continental shelf.

climatic fields of the active reaction (pH) in surface layer in winter were about 8.55 and in summer were more than 8.45 near the study area (Anzali port) in current research. In addition, climatic fields of active reaction (pH) at intermediate layer (100 m level) were about 8.35 and more than 8.275 in aforementioned seasons, respectively [24].

Climate data fields represent essential tools for climate, biogeographical, and agricultural research to run models and to provide observational data for the verification of global climate models. Climate data fields are generated through interpolation of observations taken at meteorological stations [34].

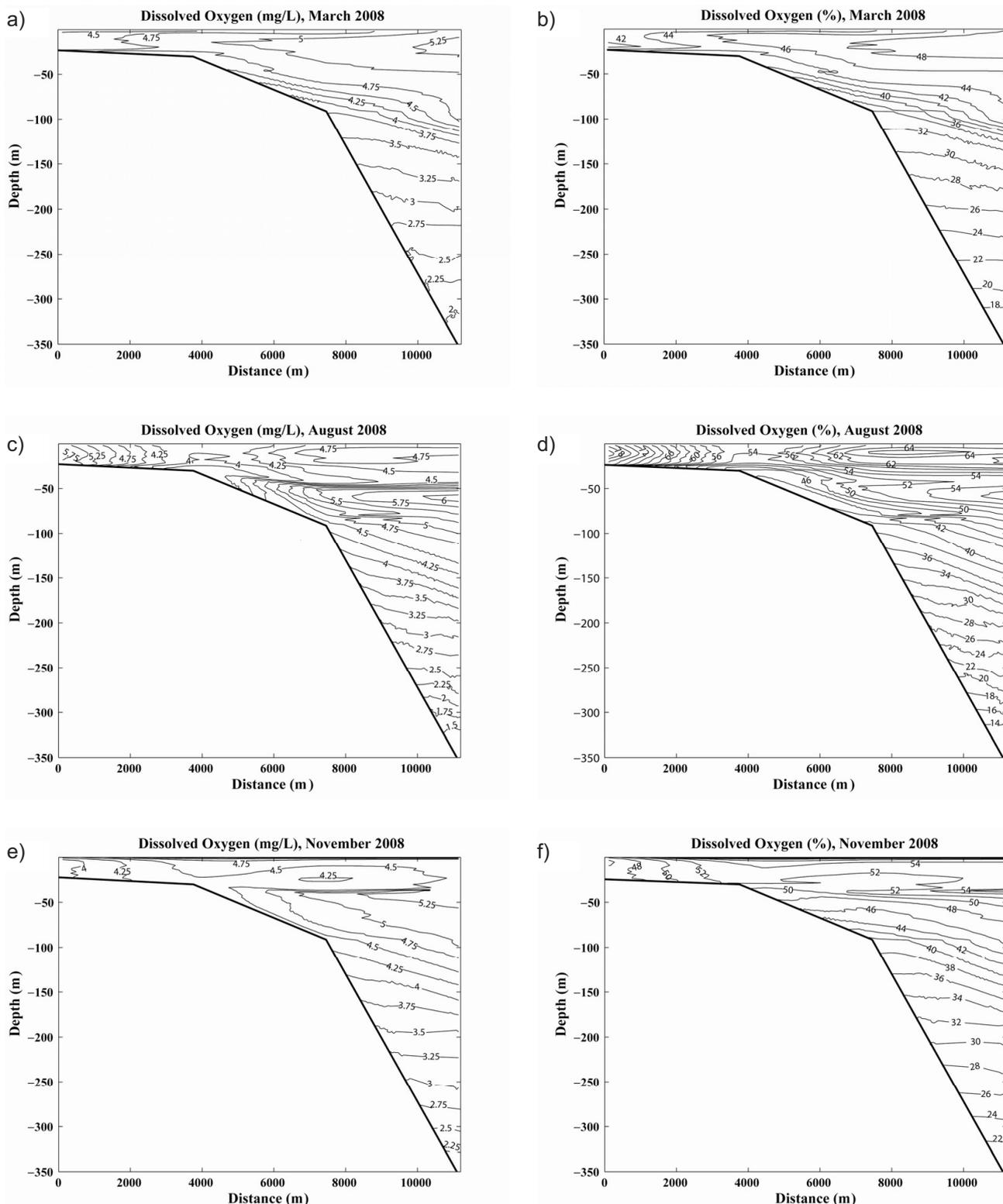


Fig. 7. Seasonal variations in vertical structure of dissolved oxygen concentrations along transect EF.

Bruevich in 1937 for the first time showed that the values of active reaction (pH) in the Caspian Sea were more than waters of the world [35]. The most important reason for the high values of active reaction (pH) was reported in riverine discharge into the Caspian [24]. Based on the results of measurements in current study, in the intermediate layer (at a level of 100 m), amounts of active reaction

(pH) in late winter (March) were similar to values of active reaction (pH) in early spring (April). The decreasing trend of values in aforementioned seasons continued with depth. In deep layers and below 275 m depth, values of 8.5 were observed. In midsummer (August), amounts of active reaction (pH) in the intermediate and deepwater layers (until 470 m) were less than that in late winter and early spring.

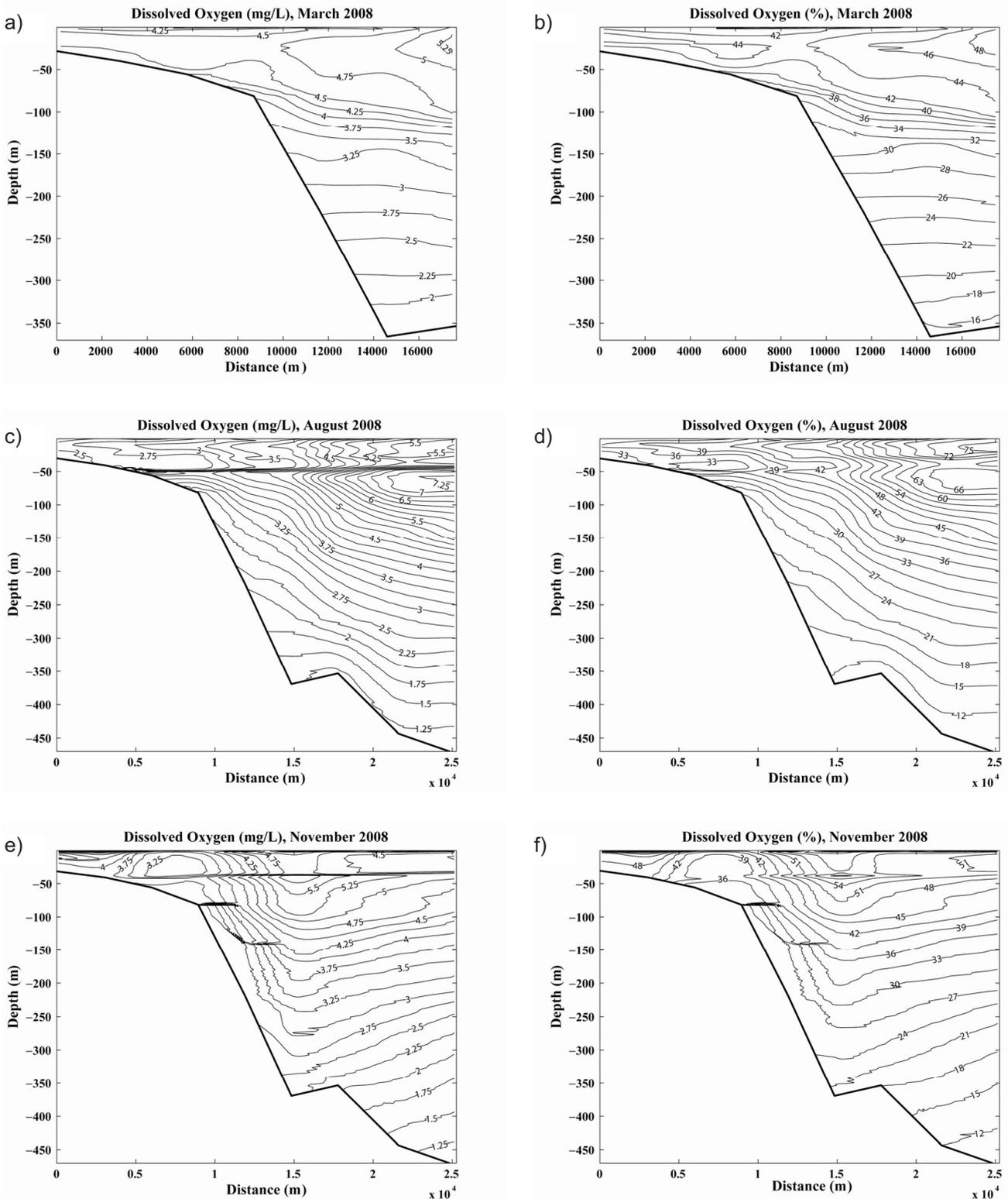


Fig. 8. Seasonal variations in vertical structure of dissolved oxygen concentration along transect BH (in plot (a and b) transect BF).

In contrast, background values of summertime pH in seawater were lower than those in winter and spring. This is clearly confirmed by results of [24] in the southern basin of the Caspian. In the northern Caspian values of pH are under the effect of river discharge, while in the southward direc-

tion increase of active reaction (pH) is caused by the effect of temperature enhancement [24]. An analysis of vertical structure of active reaction (pH) in deep water stations in November showed amounts of pH in mid autumn were more than that in other seasons both in intermediate and deep layers. Based on analysis of the data in the study area, local factors and port activities changed the natural structure of active reaction (pH). Lagoon and rivers discharge can be noted as important sources for entry by urban and industrial wastes and other pollutants into the coastal waters, and change the natural regime of chemical properties, including active reaction (pH) and environmental parameters of the seawater. It also should be remembered that intensive production processes also affect the structure of active reaction (pH) in the Caspian Sea [24].

Lagoons and coastal regions in the southern boundary of the Caspian have been steadily polluted with anthropogenic sources (fertilizer and pesticides used in agriculture and increased nutrient load of river flows due to deforestation of woodland) since the early 1980s. Thus, simultaneous rises in nutrients contributed to increases in chlorophyll-a values [29, 36]. Due to locating the investigated area near the Anzali Lagoon, the chlorophyll-a concentrations in the area were considerable, especially in summer and autumn (Fig. 9). Along transect AB and close to the mouth, chlorophyll-a structure in summer (August) showed higher concentrations than spring (April) and fall (November) values (Fig. 9). The maximum concentrations of chlorophyll-a in the upper five meters of less saline outflow water can be seen in Fig. 9b. High values of chlorophyll-a concentrations (phytoplankton increase as a response to nutrient enrichment) in this area in comparison with a decrease in the dissolved oxygen values indicate the significant effect of lagoon discharge on seawater properties. It is assumed that nutrient pollution proceeding from the lagoon discharges increase phytoplankton blooms, with the subsequent sinking and degradation in the bottom, it produces oxygen declines that influence active reaction (pH) values (see Figs. 2, 6, and 9) near the mouth of the lagoon (sampling stations along transect AB). As a result, the lagoon discharge is one of the most important reasons for the change in active reaction (pH) and dissolved oxygen regime in the study in front of the lagoon mouth.

The maximum dissolved oxygen concentrations for the entire water column from the surface to bottom (less than  $7.5 \text{ mg}\cdot\text{L}^{-1}$ ) were observed in midsummer (Table 1). The regime of dissolved oxygen in shallow waters (over the continental shelf) differed from that through intermediate and deepwater layers. The dissolved oxygen concentrations decreased with depth in the investigated area. This reducing trend was confirmed by the results of previous measurements in the southern Caspian Sea [16]. Amounts of dissolved oxygen concentrations of below  $3 \text{ mg}\cdot\text{L}^{-1}$  are stressful and unfavorable to most marine ecosystems [25, 26]. According to recorded data and shown in the vertical structure of dissolved oxygen along transects EF and BH (Figs. 7 and 8), the concentrations below a depth of 200 m are undesirable for fish and other marine organisms. Discharge of pollutants consists of urban, industrial, and

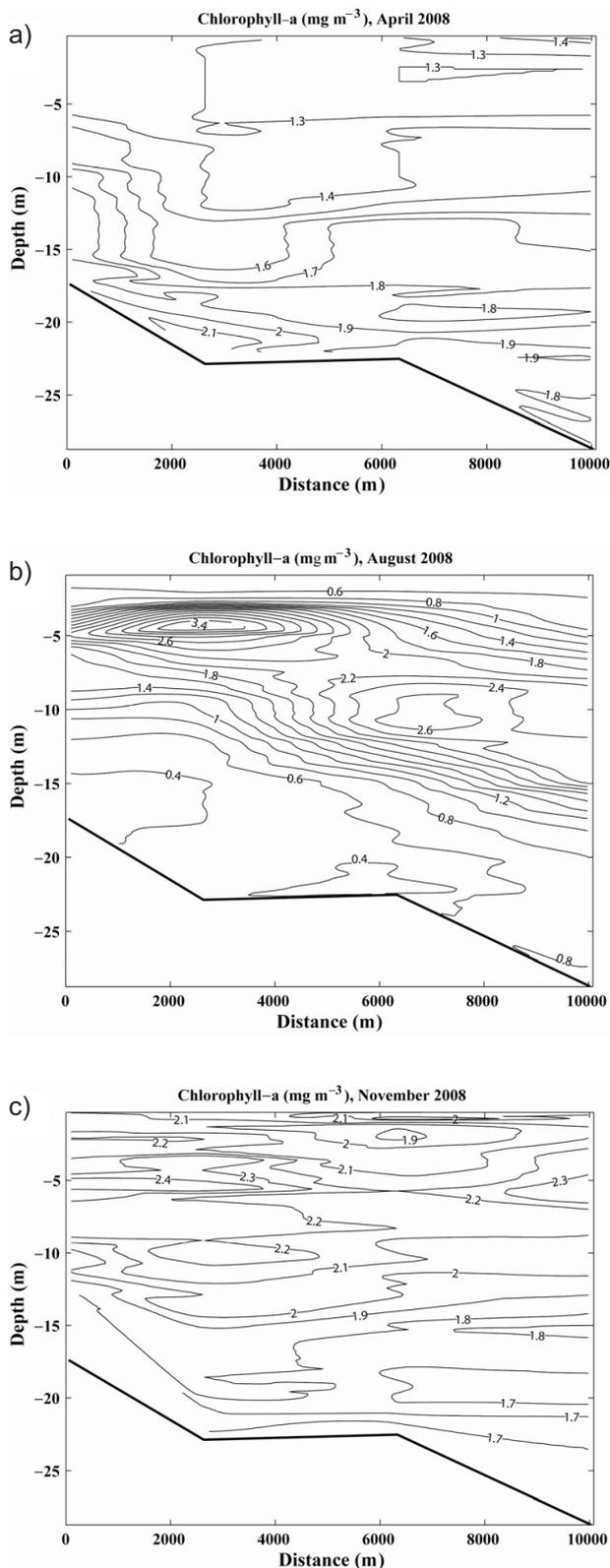


Fig. 9. Seasonal variations in vertical distribution of chlorophyll-a along transect AB.

Table 1. Statistical summary of active reaction (pH) and dissolved oxygen (DO), collected in the southern coastal waters of the Caspian Sea during measurements, 2008.

Variables	Time	Minimum	Maximum	Average	Average (Surface)	Average (100 m Depth)	Average (350 m Depth)
pH	March	8.279	9.134	8.695	8.829	8.727	8.422
	April	6.983	8.912	8.644	8.368	8.733	8.411
	August	7.41	8.617	8.373	8.303	8.456	8.211
	November	8.095	12.54	9.123	9.179	9.117	8.658
DO	March	1.62	5.33	3.475	4.258	4.396	1.81
	August	1.04	7.3	3.609	3.957	5.121	1.656
	November	1.04	7.26	3.679	5.231	4.545	2.05

agricultural wastewaters, municipal domestic sewage, pesticides, detergents, and nutrients into the Caspian Sea, decreasing the dissolved oxygen concentrations and threatening its marine environment. Moreover, these materials decreasing the biodiversity and natural biological resources in the sea. Increased amounts of phytoplankton in water bodies in reaction to the enhancement of nutrient supply can have severely damaging effects on marine organisms. It is possible that low values of dissolved oxygen concentration in deeper parts and strong stratification in water column with the happening of algal bloom phenomena present dangerous results for Caspian ecosystems. Zaker [29] expected this phenomenon in previous studies in the southern Caspian Sea. Therefore, cooperation and commitment of the surrounding countries to reduce entry of the pollutants to the sea is vitally important. At present, the Caspian requires progressive studies and certain measures to improve water quality and enhance levels of safety of the marine environment.

According to the vertical structures of the dissolved oxygen and active reaction (pH), thermal stratification and thermocline layer affect the distribution of oxygen concen-

trations and active reaction (pH) values. This result was reported in previous field measurements in the southern coastal waters of the Caspian Sea [29]. In the southern Caspian Sea, the formation of seasonal thermocline normally started in spring and was in maximum development in midsummer [37, 38]. The vertical structure of temperature in southern Caspian waters is characterized by a seasonal thermocline above 50 m depth in summer, with a vertical gradient of around 15°C. Formation of the seasonal thermocline layer starts with warming the seawater in spring and shows the strongest condition in August. Destruction of the seasonal thermocline occurred with the general cooling of the sea surface water and deepening of the mixed layer during late autumn to winter [12, 38]. Vertical profiles of seawater temperature in the study area in various seasons can be seen in Fig. 10. During the measurements, sea surface temperatures were in the ranges 9–10°C in March, 17–18°C in April, 27–29°C in August, and 19–20°C in November. Water temperature decreased with depth and was measured in the range of 6.37°C (365 m depth) in March and at 470 m depth was around 6.14°C in April, 6.12°C in August, and 6.22°C in November. Based on vertical structures of active reaction (pH) and dissolved oxygen, and vertical profiles of seawater temperature during the measurements, it is seen that dissolved oxygen concentration and active reaction (pH) were gradually decreased with temperature (with increase in depth).

## Conclusions

The seasonal variations in vertical distribution of seawater properties consisting of dissolved oxygen and active reaction (pH) in southern deep waters of the Caspian Sea off Anzali Port throughout 2008, were presented and discussed. The dissolved oxygen and active reaction (pH) are two important factors for evaluating the level of safety of marine environments. The results of the study represent preliminary information on vertical structure and variability of seawater characteristics in the region during the year. The characteristics of Caspian deep waters were different compared to its shallow areas.

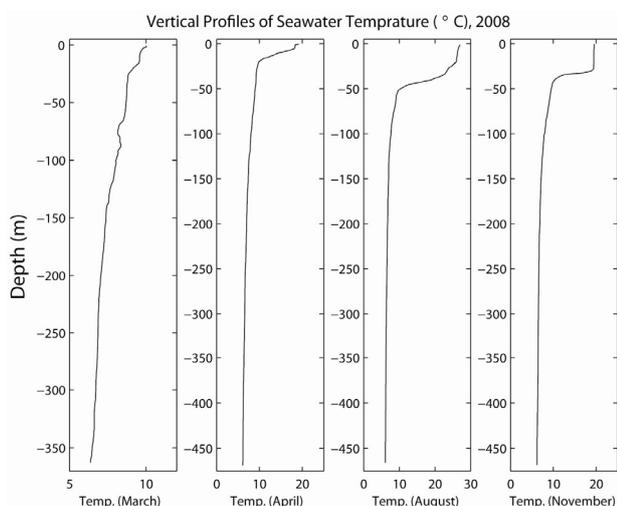


Fig. 10. Seasonal variations of seawater temperature (°C) in the study area, 2008.

The formation and destruction of seasonal thermocline affect the distribution of dissolved oxygen in the water column. Moreover, seasonal variations of the dissolved oxygen from sea surface to bottom were correlated to seasonal changes in vertical structure of water temperature. Concentrations of dissolved oxygen at surface layers ranged between 2.0-7.5 mg·L<sup>-1</sup> during measurements. In midsummer, dissolved oxygen concentrations below the thermocline were about 7.5 mg·L<sup>-1</sup> at a depth of 50 m in off-shore stations. It is possible that there was enough light to allow phytoplankton bloom development.

Discharge of large amounts of industrial, agricultural, and urban wastes threaten Caspian Sea ecosystems. As a result of the elevated pollutants and nutrient loading to the Caspian Sea, the average of dissolved oxygen concentrations in the deeper layers of the Caspian was reduced.

The active reaction (pH) values in water column reduced with depth throughout the year. Amounts of pH in late winter (with maximum value of 9.0) and early spring (with maximum value of 8.8) were more than that in midsummer (with maximum value of 8.6). During the measurements in autumn, external factors changed the natural structure of pH in the region. Although far from the main source of changing pH over deepwater stations, the maximum value of pH at the surface was 9.0. Characteristics of Anzali Lagoon water was one of the important factors for causing changes in the active reaction (pH) and dissolved oxygen regimes in the seawater over the continental shelf near the mouth of the lagoon in the investigated area. In addition, outflow of local rivers (as sources for entrance to urban and industrial wastes) and port activities change seawater properties in the study area. The results indicated the need for serious efforts to reduce entry of pollutants into the Caspian Sea environment.

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