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Impact of Physical Properties on Distribution of Active Reaction in the Coastal and Offshore Areas of the Southern Caspian Basin

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ABSTRACT

Assessing the impact of physical properties on active reaction changes in the coastal and offshore area is one the most important aspect of marine environment of the Caspian Sea. Therefore, updated techniques and modern instruments have been used in order to evaluating the coastal and offshore area conditions. In the current research, collected data with spatial and temporal variety have been evaluated for investigation on seawater characteristics in the shallow and intermediate layers over the southern Caspian Sea. Some phenomena such as mixing, turbulence, water column stability and stratification are the effective elements on variability of physical and natural structures of the sea. Active reaction and dissolved oxygen as two properties of seawater are very important items for coastal engineering, piping in seabed, breakwaters and port constructions. Thus, in the current study, the above mentioned parameters were assessed over the southern shelf of the Caspian Sea. Vertical and horizontal variations of chemical characteristics such as active reaction of seawater were observed in several stations between coastal and offshore stations across surface, intermediate and deep layers. Results of the field operations showed that the normal values of pH in the study almost varied around 7.9-8 while during some seasons increased ore decreased more than 0.5 units due to human activates.

1. Introduction

The Caspian Sea, located between Europe and Asia continents, is the biggest semi-closed water body in the world. It is introduced by exclusive conditions, contains rich hydrocarbon mines, natural resources [1-4]. During the last decades, the large riverine water discharge containing various urban and industrial pollutants into the Caspian basins was characterized by reduced concentrations of oxygen, changing of active reaction and increased nutrient contents. Generally, enhancement in nutrient amounts due to increase in rivers inflow contents and reduce in severity of winter are main factors for insufficient ventilation of intermediate and deeper layers of the southern basin of the sea. On the other hand due to same reason the levels of active reaction through the water column show high variability in different time and seasons. Therefore, range of active reaction and dissolved oxygen in the seawater of southern basin is going to be inappropriate to the most marine organisms [5]. At the present time the marine environment of the Caspian Sea, especially south coastal and offshore area, is one of the deeply polluted water bodies in the region. The coastal and marine environment along the onshore and offshore areas of the southern border of the Caspian Sea is under stress because of extensive exploitation and discharge of great magnitudes of human wastes [2,6]. The main sources for pollutants entrance to the southern coastal area of the sea are consisted of industrial, agricultural and municipal wastewaters (pesticides and detergents), urban sewage waters, desalination industry project, heavy metals, petroleum products, and nutrients [2,3,6]. The above mentioned pollution is main threat to the environment, biodiversity and population of fish and animals of the sea. It is important to consider that the main flow of pollution approaches via coastal drainage and rivers to the sea [7]. Furthermore, the southern bay, coastal areas and offshore regions also have been contaminated by the anthropogenic sources [8]. In addition to the above mentioned factors, due to the special condition and chemical characteristics of the Caspian Sea water, active reaction value is significantly greater than in the waters of other regions in the World seas and oceans. The major reason for the high values of active reaction associated to the great contribution of the riverine waters characterized by a high content of anions of weak acids, carbonic acid and pattern of distribution of hydro chemical aspects of the Caspian [5]. According to the physical and chemical conditions of the Caspian Sea, the investigation on seawater properties (such as active reaction…) is one of the most important necessities for safety level of marine environment and ecological characteristics in the southern boundary of the sea [9-10]. Under these conditions, it is vital and necessary to consider the increasingly physical and dynamical aspects of oceanography through the ecological and environmental studies of the sea water [4]. On the other side, field measurements and observations, data gathering and analysis of chemical and physical characteristics represent the interest for oceanography, ocean engineering and marine researches. According to the importance of properties of seawater of the Caspian Sea in the offshore and onshore regions, it is attempted to investigate the distributions of mentioned factors in the southern coastal waters and offshore sampling stations. Based on the fast variability of natural condition of seawater characteristics, and lack of sufficient accurate data and analysis in the literature that give careful information on monthly variations, the current study was programmed and performed. Aim of the research, is evaluation of temporal and spatial variability of active reaction in the Iranian coastal waters and offshore along the Caspian.

2. Methods

2.1Field Operation and Site

Field measurements have been made over the middle part of the southern continental shelf of the Caspian Sea. According to the geomorphologic characteristics, topography, and width of the shelf study area and sampling stations have been selected. The length of the Caspian Sea is about 1030 km between 36ºN and 48ºN and its width is around 200-400 km between 48ºE and 54ºE [11-13]. It is divided into three parts with maximum depths of 1025 m, 788 m and 20 m, respectively and average depth of 210 m [1,13-14]. Surface monitoring in the Caspian Sea showed that the northern part of the sea had largest diversity and productivity [15]. The main sources of freshwater inputs to the Caspian Sea are the Volga, Ural, Emba and Terek Rivers in the north part [16-17]. In the southern part, the total volume inflow of Iranian rivers to the sea is about 4-5%, which Sepidrood River with most contribution is distinguished [13,18]. Due to the isolation of the Caspian Sea from the open seas, its natural structure is under effect of external factors such as discharge of rivers and atmospheric processes. The hydrological structure and circulation of the Caspian Sea water are defined by these factors [19]. The southern coastal area of the Caspian Sea has warm summers and mild winters (warm and humid subtropical climate) [16,20]. Mean temperature in the southern coast of the Caspian Sea was reported about 16ºC, which varies from 4.5ºC in February to 27.5ºC in August [21]. For measuring seawater properties a portable CTD probe (Ocean Seven 316) developed by IDRONAUT was used. The probe was set in Timed Data Acquisition mode with one-second time intervals. Data collection was performed with profiler in free falling mode into the seawater column down to seabed with a time interval of one meter per second. The accuracy of pressure, temperature and conductivity sensors of Ocean Seven 316 probe was 0.05 full-scale, 0.003 ºC and 0.005 mS cm^{-1}, respectively. Dissolved oxygen and active reaction measurements were made using the oxygen sensor and pH meter of probe with the accuracy of 0.1 mg L^{-1}, 1% saturation and 0.01 pH. Dissolved oxygen levels of below 3 mg L^{-1} are stressful to most marine biota. Its levels of at least 5-6 mg L^{-1} are usually required for growth. In the southern basin dissolved oxygen content decreases with depth. Moreover, percentage of saturation reaches to 50% at level of 200 m and less than 10% at 600 m depth [20].

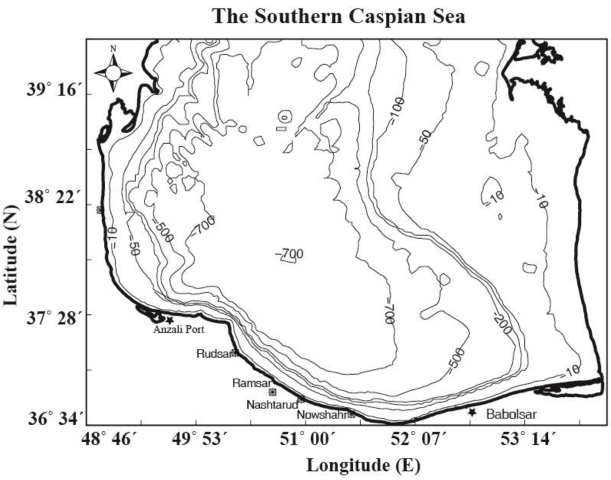

Figure 1. Study area located in the southern baundary of the Caspian Sea

2.1Computation and Modifications

During the sampling, the sensed parameters by CTD probe were calibrated by UNESCO formulas [22-23]. Due to the difference between the compositions of the Caspian Sea from the world ocean waters, some correction coefficients needed to be used. Some of the experimental, empirical and chemical equations were used for calculation of salinity and density of the Caspian Sea water. Millero and Chetirkin, (1980) carried out density laboratory measurements using some samples collected in the near shore surface waters of the southern part [24]. In the current research, the coefficients that were presented by Peeters et al., (2000) on IAEA data (1996) for calibration the salinity and density values is used [25-26].

$$S_{Caspian} = 1.1017 S_{CTD} \quad (1)$$

$$\rho_{Solution}(T,S,p) = \rho_{Sea}(T,0,p) + f(T,p)(\rho_{Sea}(T,S,p) - \rho_{Sea}(T,0,p)) \quad (2)$$

where,

- $\rho_{Sea}(T,S,P)$ is the density of water from UNESCO formulas using in situ temperature, pressure and salinity and $f(T,p)$ is the correction factor [22-23].
- $\rho_{Sea}(T,0,P)$ is the density of the water from UNESCO formulas using in situ temperature and pressure, S = 0 .

In computations presented by Peeters *et al.*, (2000) [25] for the ionic composition of the Caspian Sea and for S = 12.3, T = 25°C and P = 0 was given by f = 1.0834.

International UNESCO Algorithm using in situ temperature, pressure and salinity, calculated from the following equation [22-23]:

$$\rho(T,S,p) = \frac{\rho(T,S,0)}{1 - \frac{p}{K(T,S,p)}} \quad (3)$$

Where, T is temperature, S is salinity and p is pressure, and K(T,S,p) is the secant Bulk Modulus can be calculated as follows:

$$K(T,S,p) = K(T,S,0) + Ap + Bp^2 \quad (4)$$

$$K(T,S,0) = K_W + (54.6746 - 0.603459T + 1.09987\times10^{-2}T^2 - 6.1670\times10^{-5}T^3)S + (7.944\times10^{-2} + 1.6483\times10^{-2}T - 5.3009\times10^{-4}T^2)S^{\frac{3}{2}} \quad (5)$$

$$A = A_W + (2.2838\times10^{-3} - 1.0981\times10^{-5}T - 1.6078\times10^{-6}T^2)S + 1.91075\times10^{-4}S^{\frac{3}{2}} \quad (6)$$

$$B = B_W + (-9.9348\times10^{-7} + 2.0816\times10^{-8}T + 9.1697\times10^{-10}T^2)S \quad (7)$$

Where K_W, A_W and B_W are the water terms as follows:

$$K_W = 19652.21 + 148.4206T - 2.327105T^2 + 1.360477\times10^{-2}T^3 - 5.155288\times10^{-5}T^4 \quad (8)$$

$$A_W = 3.239908 + 1.43713\times10^{-3}T + 1.16092\times10^{-4}T^2 - 5.77905\times10^{-7}T^3 \quad (9)$$

$$B_W = 8.50935\times10^{-5} - 6.12293\times10^{-6}\times10^{-8}T^2 \quad (10)$$

Where, $\rho(T,S,0)$ is density of sweater at p=0 calculated from the following equations:

$$\rho(T,S,0) = \rho_W = (8.244493\times10^{-1} - 4.899\times10^{-3}T + 7.6438\times10^{-5}T^2 - 8.2467\times10^{-7}T^3 + 5.3875\times10^{-9}T^4)S + (-5.72466\times10^{-3} + 1.0227\times10^{-4}T - 1.6546\times10^{-6}T^2)S^{\frac{3}{2}} + 4.8314\times10^{-4}S^2 \quad (11)$$

$$\rho_W = 999.842594 + 6.793952\times10^{-2}T - 9.095290\times10^{-3}T^2 + 1.001685\times10^{-4}T^3 - 1.120083\times10^{-5}T^4 + 6.536332\times10^{-9}T^5 \quad (12)$$

In above mentioned equations, T temperature, S salinity, p pressure. For more information see (UNESCO 1981a, 1981b) [22-23]. Density is generally written in terms of Greek lowercase letter sigma-t as follows [27]:

$$\sigma_t = \rho(T,S,p) - 1000 \quad (13)$$

For computation of water column stability the following equations were used. Which N is named Brant-Vaisala Buoyancy Frequency.

$$E = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial z}\right) - \frac{g}{c^2} \quad (14)$$

$$N = (gE)^{\frac{1}{2}} \quad (15)$$

3. Results and Discussion

3.1 Physical structure

The surface water temperature over the continental shelf reached a maximum of 29°C in summer and then, in accordance to the reduction of air temperature due to climate changes in the region, it decreased gradually to 20 °C at the beginning of autumn (October) and 11.5 °C in the middle of winter. With increasing temperature of surface waters in consequence of enhancement of the air temperature in early spring, vertical gradient of temperature in the water column is increased. Therefore, the thermal stratification of the water column is established through the water column in the spring season. In May, three layers in the water column over the continental shelf including a thin mixed surface layer, thermocline, and deeper water are formed. It is assumed that thermal stratification developed in the summer season and became stable in midsummer (August) [28]. A strong seasonal thermocline with a thickness of about 30 m is located between depths of 20 and 50 m. The 27.5°C temperature above the thermocline decreases to 10.5°C below it. In the mixed surface layer, the temperature ranges between 28.5°C at the water surface to 27.5°C above the thermocline in a depth of20 m. Below the thermocline, the temperature decreases gradually to 8.5 °C at 80 m depth and 7 °C at 160 m depth. In the beginning of autumn (October), the thickness of the thermocline reduced to 15 m and thermocline was located between 45 m and 60 m depths. Below thermocline, deep water is located with 2 degree vertical temperature gradient. The water body on the shelf is mainly located in the surface mixed layer and only a limited area below 60 m depth over the shelf break includes the thermocline layer. A comparison between vertical temperature structures in summer and autumn indicate that, the top level of thermocline has fallen from 20 m depth to 40 m depth over and outside of the shelf. In autumn, the thickness of the thermocline has decreased substantially in comparison to that in summer (as it is shown in the contour plot of the vertical structure of temperature in transect). In comparison between physical structure between summer (August) and autumn (October), the temperature and thickness of the surface mixed layer in October decreased about 9 ºC and 20 m respectively, indicating the deepening of the surface mixed layer due to seasonal climate changes. Over the continental shelf, the upper layer of the surface water was completely mixed with a temperature of 20-19.5ºC with no horizontal gradient across the continental shelf.

3.2 Stability and Layering of Water Column

Based on the collected data and comparison with other previous studies, thermal stratification of seawater column showed three layers in the water column, in offshore stations, consisting of surface mixed layer, thermocline, and deep water. A sharp seasonal thermocline was visible between 20-50 m depths with around 15 degree which temperature decreasing across it [28]. Below the thermocline layer, water temperature varied between 11ºC and 7ºC around 150 m depth. The highest surface water temperature was observed in summer (around 29ºC) while the lowest surface water temperature was recorded in winter season (around 9ºC). The most variations of seawater parameters were observed through the mixed layer and thermocline. Below the layer of 100 m depth, monthly variations of the seawater characteristics were slight. By comparing vertical profiles, the correlation between variations of temperature and density was clearly seen. Seasonal stratification patterns and variations of thermohaline at the deepest sampling station far from the coasts were clearly observed. The sharpest thermocline was observed in the summer season, it moved down to around 40 m during autumn and after that disappeared in winter [28. The higher seasonal variations of water salinity were detected from the surface to 50 m depth in the spring–autumn periods. Based on the collected data in June showed that the water salinity changes continue from sea surface to lower than 150 m depth. It is assumed that seasonal changes of pycnocline followed the pattern of seasonal variations of thermocline. Forming the pycnocline started from spring season together thermocline in the study area. Pycnocline was in a strong situation in summer located in position of thermocline and deepened to 40 m in autumn. Vertical structures of temperature and density in the times of measurements in June and August were approximately similar. Vertical profile of water temperature in deepest station illustrated that the water temperature in water column in upper layer was approximately uniform. The natural regime of structures of seawater parameters in the Caspian Sea is under effect of external factors such as riverine runoff and atmospheric activity. Study on the mentioned factors shows that they define a rapid and significant variability in the hydrological structure and circulation of the waters of the Caspian Sea relative to the other open seas. Therefore, comprehensive monitoring of the natural environmental conditions of the Caspian Sea and changes in its main parameters is necessary [5].

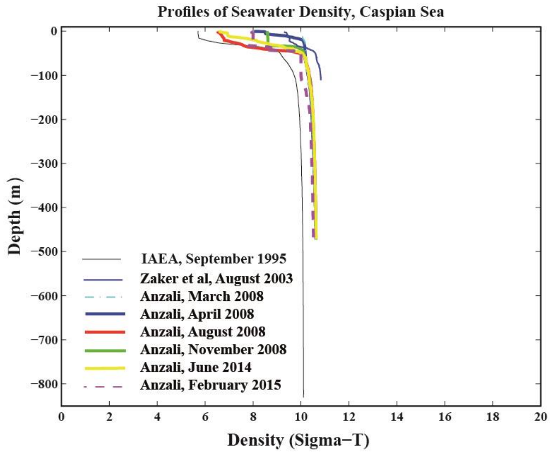

Figure 2. A sample of vertical structure of water density

Structure of the physical properties of the Caspian Sea water is corresponded to the various factors such as atmospheric effects and freshwater discharge in different times. So, it is expected that the vertical structure and stratification of the Caspian Sea water column is different. Vertical structure of temperature in the time of measurements in March and February (winter) shows rapid changes from surface to near bottom layer. The cause of this phenomenon is lower vertical gradient of temperature in water column relative to the other vertical profiles in other seasons. In winter difference in temperature between surface layer and near bottom layer is low. In the other hand, there is no strong thermal stratification in water column and the changes of temperature are rapid. This point is important that, due to increase in speed and severity of wind over the region in winter, kinetic energy and turbulence in water column increase. Thus water column is mixed with rapid temperature profile. Based on the results, the maximum values of stability frequency can be seen in upper layer including surface mixed layer and thermocline (pycnocline) [28]. Oscillation of data in the time of measurements in June was considerable. Maximum value of frequency was observed at the boundary of upper layers in February. Frequency of stability in deep layer was very slight in February. Variations of stability frequency in deep layer in June were more than its variations in February [28].

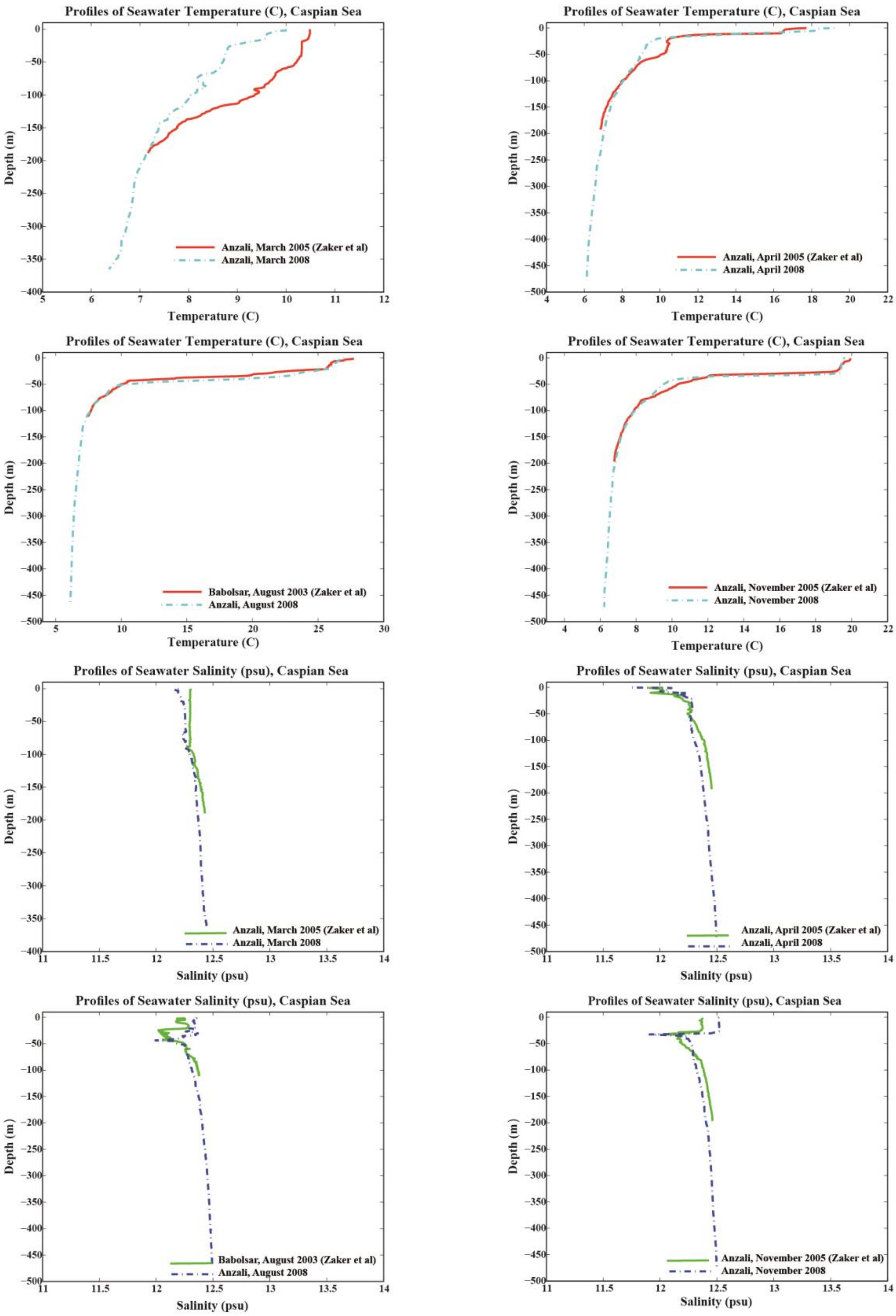

Figure 3. Comparison of physical properties of the Caspian seawater in varoius field operations

3.3. Active Reaction and Oxygen

Variability of seawater properties such as active reaction (pH) and oxygen and saturated values are very important from view point of oceanography. Therefore, it is tried to evaluate the mentioned factors changes in the study area over the continental shelf zone in front of Nowshahr.

Based on some of the previous researches, natural changes in structure of hydrodynamics and hydro physic (thermohaline) in seawater can affects the multi-annual trend of variations in the active reaction amounts. Some parameters such as temperature and turbulence of seawater layers have important role on its vertical structure changeability in the south Caspian Sea.

Variability of pH along a transect perpendicular to the coast line in the study area from March 2014 to February 2015 were evaluated. In late winter (March), changes of active reaction were detected between 8.2 and 8.6 at the upper layer, which decreased with depth. Amount of active reaction ranged around 8.2 below 30 m depth until depth of 60 m. collected data showed that the value of pH at depth of 110 m was measured around 8. At this time, variations of active reaction from the surface to the bottom were not uniform. Regarding to recorded data in April, vertical and horizontal gradients of active reaction was considerable above 70 m depth. At the sea surface, values changed from 8.2 to 8.4 and reached to 8 near 140 m depth. pH values decreases with increase depth over the southern shelf. Observed values from upper layer in April were relatively less than measured values of pH in late winter (March). In May 2014, vertical structure of active reaction along the survey line showed values of 8.2 to 8.3 over the continental shelf, which the values reached to more than 8.4 amounts toward the deeper stations. Outside the shelf active reaction from 8.2 at surface layer reduced to 8.4 at 90 m depth. Distribution of pH in vertical direction showed a decrease with depth. During measurement in June, values of pH changed between 8.6 and 8.8 along transect, and reached to 8.7 around 120 m depth across intermediate layer. Above 100 m depth, active reaction was uniformly varied (mainly about 8.8) outside the shelf break (off shore stations). In mid-summer (August), collected data by the probe showed that the active reaction ranged around 8.1 across the surface mixed layer and thermocline. Below thermocline, values decrease with depth and reached to 8 at depth of 80m in water column. In September, values at the beginning and middle of transect were around 8.1 over the continental shelf and there was no considerable changes during surface mixed layer. In the time of observation, amount of pH ranged around 8.2 at the end of transect. Over the continental shelf zone, distributions of pH at the sea surface were under effect of mixing. With a comparison, it can be seen that active reaction variations at the surface layers were more than near bottom layers (7.8 at depth of 140 m). It is assumed that, the rivers outflow was one of the most important reasons for changing pH regime in shallow waters stations. Values of active reaction across surface mixed layer in autumn (October) were uniform with a value of 8.1. In deeper layers below surface mixed layer pH of sea water was detected about 8. At the time of measurements, below depth of 50 m depth active reaction decreased with depth and reached 7.9 at depth of 100 m. It is assumed that in the time of measurements in January, human activities such as leakage of waters and other materials from the ships in anchorage area of Nowshahr Port or operation of transfer and discharge the sediments of harbor basin into this area disturbed the natural structure of active reaction in the region. Thus, contours with high values of pH were observed in a distance of 11 km from the beginning of transect. Along transect, amounts of pH were mainly around 10.0 in shallow waters stations and increased to 8.4 over the shelf. Outside the shelf, active reaction measured about 9.3 at surface decreased to 8.7 in deep-water. In mid-winter (February) active reaction was measured 7.8-7.9 over the continental shelf region and out of shelf. At this time of measurements, values were around 8 over the shelf break. Below depth of 50 m active reaction decreased from 7.9 at 70 m level to value of 7.8 below 100 m depth. In February, contour of pH was parallel to sea water level and horizontal gradient of active reaction was very slight.

Based on the Russian research projects in the Caspian Sea, climatic fields of the active reaction in surface layer in winter were about 8.55 and in summer were more than 8.45 near the current study area. In addition, their results of the climatic fields at intermediate layer (100 m level) were about 8.35 and more than 8.275 in aforementioned seasons, respectively. Bruevich for the first time in year of 1937 showed that the levels of pH in the Caspian Sea are further than that in the waters of the World open seas and ocean [29]. The major important reason of the high values of pH was reported in riverine discharge in the north and south parts of the Sea [5]. In the intermediate layer, values of pH were similar to active reaction amounts in late winter (March) and early spring (April). Decrease trend of values in aforementioned seasons continued with depth. In midsummer, amounts of active reaction in the intermediate and deep water layers were less than that in late winter and early spring. In contrast, background values of summertime pH of seawater were lower than winter and spring. This is clearly confirmed by results of [5] in the southern basin of the Caspian Sea. In north of the Caspian Sea values of pH is under effect of rivers discharge while in southward direction increase of pH is caused by the effect of temperature enhance [30]. An analysis on vertical structure of pH in deep water stations in November showed that amounts of pH in mid-autumn was more than that in other seasons both in intermediate and deep layers [30]. By the comparison of the results analysis on data, local issues and human activities varies the natural configuration of active reaction distribution. The rivers discharge, port activities and exchange water between bay and lagoon with the coastal waters can be presented as important sources for entrance the urban and industrial wastes. Therefore the mentioned pollutants inflow to the coastal waters and far from the coast can changes the natural regime of chemical properties including active reaction and environmental parameters of the seawater. It noted to remember that intensive production processes also effect on the pattern of active reaction [5].

Several oceanographic studies based on field measurements have been were carried out in the region [31-33]. The mentioned works were focused either on changes of seawater properties at the surface or were done at a short duration in of the southern coastal waters of the Caspian Sea. Considering the fast variability of the natural pattern of seawater properties and hydrodynamics of the Caspian, enhanced inflow of pollutants and development of gas and oil industries, comprehensive oceanographic and environmental studies for evaluate the Caspian Sea situation is required [13,6,19].

Analysis of physical properties data showed that the structure of seawater properties in onshore areas and offshore stations was not exactly similar. Over the continental shelf, seawaters were mainly located through the surface mixed and thermocline layers in all seasons. By comparing on the vertical structure of physical characteristics over the continental shelf during various months, it seems that the effect of local and coastal characteristics in shallow waters stations were dominant.

Changes of the salinity near the bottom were less than surface layers. Thermohaline structure in this area was under the effect of air sea interaction factors such as rain and wind. Density variations at the sea surface, was correlated with salinity due to entry of less saline waters in the continental shelf while in lower layers temperature was the effective factor in monthly variations of the density. The forming of the stratification, mixed surface layer developed during March and April. Vertical gradient of salinity during spring was higher than in winter. Results of the comparison between winter time and summer measurements of seawater indicated that the water was both colder and denser in winter than in summer. Salinity in surface mixed layer was observed to be higher than salinity across the thermocline, which could be due to evaporation intensity effect. The average salinity in the surface mixed layer and thermocline was higher than in winter and spring.

An investigation on vertical structure of the salinity showed that its values increased with depth throughout the whole seasons. Seasonal changes of the salinity were limited above the 100 m depth. The density of seawater in offshore area is determined by temperature field (70-80%) as well as the effects of outflow of the freshwater defined by salinity [19].

In the southern coastal waters of the Caspian Sea formation and destruction of seasonal thermocline (and pycnocline in position of thermocline) occurs during the period of early spring to late autumn [28]. Thus, it is expected that during this time the pycnocline prevent the ventilation of the deeper layers [28]. Thus, as a result the concentrations in the near bottom layers reduce. The lowest values of dissolved oxygen concentrations were recorded below 100 m level. Variations of dissolved oxygen concentrations in various times of measurements were minor. In winter due to mixing in water column especially in upper 100 m depth, dissolved oxygen content was uniform, relative to August and November. The maximum vertical gradient of dissolved oxygen concentrations for the entire water column from the sea surface to bottom (12.5 mgL^{-1}) were observed in June. The regime of dissolved oxygen in shallow waters (over the continental shelf) differed from that through intermediate layer. The dissolved oxygen concentrations decreased with depth in the investigated area. This reducing trend is confirmed by the results of previous measurements in the Caspian Sea [20].

Regarding to the previous data collection; distribution of dissolved oxygen along deep water transect in the first month of summer showed a range of variation between 2.5 and 1.5 mgL^{-1}. In the offshore area, concentrations of dissolved oxygen were about 8.5 mg L^{-1} and reached 12.5 mgL^{-1}, below 50 m depth. Below this level, dissolved oxygen gradually reduced with depth and reached 9.5 mgL^{-1} at level of 100 m. In deeper layers (below 100 m depth), dissolved oxygen concentrations in July reached values of 3.5 mgL^{-1} [5,34]. Outside the shelf, values of dissolved oxygen changed between10.5 mgL^{-1} at the sea surface and about 10 mgL^{-1} at 100 m depth. The concentrations of oxygen in lower layers reached to 8.5 mg L^{-1} at 150 m depth. In General, concentrations of dissolved oxygen decreased with depth in offshore area in June and February [34]. As a result of analysis on observed data, saturated oxygen in deep water transects the concentrations in deeper layer and intermediate is insufficient for fish and other marine organisms [5,4].

Based on the results of some of the previous studies in the southern boundary of the Caspian Sea such as Zaker et al., 2007, Zaker 2007, Nezlin 2005 and Nasrollahzadeh et al., 2008, discharge of pollutants consists of urban, industrial and agricultural wastewaters, municipal domestic sewage, pesticides, detergents, and nutrients into the Caspian Sea, treat its marine environment. These materials decrease 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 the marine organisms. It is possible that low values of dissolved oxygen concentration in deeper parts and strong stratification in water column together happening of algal bloom phenomena present dangerous results for Caspian ecosystems. Zaker (2007) expected this phenomenon in previous studies in southern Caspian Sea.

Generally, values of pH in deep water zone in the study area reduced with depth. In a previous research, climatic fields of the active reaction in surface layer in winter about 8.55 and in summer were more than 8.45 near the current study area. In addition, their results of the climatic fields at intermediate layer were about 8.35 and more than 8.275 in aforementioned seasons, respectively. Bruevich in 1937 for the first time showed that the values of active reaction in Caspian Sea were more than waters of World Ocean. The most important reason of the high values of active reaction was reported in riverine discharge into the Caspian Sea [5]. In intermediate layer values of pH were similar to active reaction amounts in winter (February). Decrease trend of values in aforementioned time continued with depth. In June, amounts of active reaction in the intermediate and deep water layers were more than that in February. In north of the Caspian Sea values of pH is under effect of rivers discharge while in southward direction increase of pH is caused by effect of temperature enhance [5]. Based on analysis additional information of research project performed by Roohi et al., 2008 and Tuzhilkin et al., 2005, local factors and human activities changed the natural structure of active reaction. At the last decades, increasing in the entrance of urban and industrial wastes into the coastal zone changed natural regime and normal mode of chemical properties. It is important that intensive production processes also effect on the structure of pH in the Caspian Sea [5]. Therefore, cooperation and commitment of the all countries to reduction entrance of the pollutants to the sea has high level of importance. So, the Caspian Sea requires to progressive plans and certain measures for improve the water quality and decrease levels of pollution in the marine environment.

5. Conclusions

The impact of physical properties on active reaction changes in the coastal and offshore area was analyzed. The values of active reaction and oxygen are two important chemical factors for quality control of seawater and evaluating the safety level of coastal and open sea areas. The output of the current research gives a preliminary view and basic information on vertical configuration of variability of seawater characteristics in the southern region during the year. By the comparison and analysis the collected data, it can be seen that the characteristics of the Caspian offshore area were different in comparison to the coastal waters. The inter-annual variability of formation and destruction of the thermocline and physical structure of water column affect the distribution of can change active reaction and oxygen in seawater. Moreover, for get a good knowledge of monthly and seasonal variations in levels of active reaction and saturated oxygen understanding and study of physical structure of water temperature is needed as well as current pattern.

To achieve a clean marine and coastal environment and ecosystem, one of the most fundamental actions is to prevent the entrance of urban and village water waste in the rivers and coastal waters. The release of large amounts of industrial, agricultural and urban wastes threats the marine ecosystems in the onshore and offshore region. Also, transferring sediment by the dredger ships from harbor to the offshore area changes the natural pattern of active reaction in water column. If the conditions continue, with elevation of pollutants and nutrient contents in seawater, average of dissolved oxygen concentrations in the deeper layers of the Caspian Sea was reduced. Its consequence is the forming of death area in deeper parts of the water column. Finally, the results indicated the need of serious efforts for reducing entrance of urban and industrial wastes and pollutants into the coastal and offshore areas.

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