Variations in Nitrate and Phosphate Contents of Waters in the Southwest Caspian Sea

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Abstract
Science and technological developments provide new opportunities to exploit aquatic resource. Hence, it is important to understand biotic and abiotic conditions of aquatic ecosystems. Objective of this Paper is to report findings of the study of nitrate and phosphate contents of water and effects of other physical-chemical parameters in the southwest regions of the Caspian Sea in the spring and summer of 2008. It focuses on the evaluation of nitrate and phosphate concentrations and compares the variations of these parameters with those of previous surveys. Forty-eight Water samples were collected from 18 stations along 6 transects: Astara, Lisar, Anzali, Kiashahr, Chamkhaleh and Chaboksar. Water samples were collected below 10 m depths in western parts of the southern coasts of the Caspian Sea. Temperature, pH and salinity of water were measured and recorded in situ. No significant differences were detected between concentrations of nitrate, phosphate and other parameters studied in the water column at different depths and stations in the six transects. Comparison of results obtained from the present study with those of previous surveys indicated that increasing trends in concentrations of nitrate and phosphate are probably caused by discharge of untreated domestic sewage and the discharge of pesticides from agricultural activities into rivers.

Keywords: Caspian Sea, Nitrate, Phosphate, Temperature, Salinity

1. Introduction

The Caspian Sea is divided into three sections as follows: Northern, Middle and Southern. The Southern Caspian Sea has the largest volume of water (approximately, 64% of the total volume, with 35% of the total area of the sea). The southern Caspian is the deepest part of the sea with the maximum depth reaching 1025 m. The average depth of the southern Caspian Sea is 300 m (Kasimov, 1987).

Phosphorus is considered as a chemical material on which the life of flora and fauna is dependent, because it plays a crucial role in the structure of DNA and RNA, ATP, amino acids and enzymes including phosphatase, which controls the life of an organism (Ahern et al., 2007). Phosphorous content varies in various water bodies; for example, it is found at higher concentrations close to the river mouth due to the destructive effects of water waves on the river bank; however, in natural waters which are less polluted, phosphorus concentration varies from 0.1 to 1000 μg L⁻¹. In closed water bodies, the concentration increases given the type and degree of pollutants (Mann, 2000).

In aquatic environments, dissolved inorganic phosphate is biologically available as orthophosphate...
Phytoplankton primary production in fresh water systems are usually controlled by phosphorus availability, whereas in marine environments elemental nitrogen (N) is more commonly the limiting nutrient (McCarthy and Carpenter, 1983). According to a research carried out by Kasimov (1987) on the distribution of nitrate and phosphorus in the Iranian coasts of the Caspian Sea in various seasons, the western coast contains the maximum levels of total nitrogen and nitrate and their concentrations fluctuates depending on seasonal variations. Nitrate and phosphate concentrations showed seasonal variations and the highest concentrations for these nutrients in the south Caspian Sea basins were reported in the western coast (Kasimov, 1987).

Nitrate and phosphate levels are of crucial importance and any changes in their concentrations may entail changes in phytoplankton population and consequently long term effects in the food chain. Chemical fertilizers and pesticides are widely used along the southern Caspian Sea coast due to agricultural intensification. Nitrates and phosphates are the main components of most chemical fertilizers used in Iran. Entry of pollutants to the Caspian Sea in recent years has affected the water quality and this trend may naturally lead to phytoplankton growth and there by mortality of marine resources (CEP, 2002). Increased nutrient loads have augmented the proliferation and increased distribution of harmful algal blooms in estuaries and coastal waters across the world (Anderson et al., 2002). Given the circumstances, this study attempts to investigate the variations in nitrate and phosphate concentrations in the south-west area of the Caspian Sea.

2. Materials and Methods

2.1. Sampling

Six transects vertical to the Caspian Sea coastline were selected (Fig.1) in the area located between the cities of Astara and Chaboksar (Table 1).
Table 1- Geographical location of transects of sampling stations in the southwest Caspian Sea in 2008.

<table>
<thead>
<tr>
<th>Transects</th>
<th>Location</th>
<th>Latitude(N)</th>
<th>Longitude (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Astara</td>
<td></td>
<td>38° 25' 32&quot;</td>
<td>48° 54' 45&quot;</td>
</tr>
<tr>
<td>2 Lisar</td>
<td></td>
<td>37° 59' 47&quot;</td>
<td>49° 00' 16&quot;</td>
</tr>
<tr>
<td>3 Anzali</td>
<td></td>
<td>37° 52' 23&quot;</td>
<td>49° 35' 16&quot;</td>
</tr>
<tr>
<td>4 Chamkhaleh</td>
<td></td>
<td>37° 29' 07&quot;</td>
<td>49° 59' 31&quot;</td>
</tr>
<tr>
<td>5 Kiashahr</td>
<td></td>
<td>37° 13' 07&quot;</td>
<td>50° 18' 17&quot;</td>
</tr>
<tr>
<td>6 Chaboksar</td>
<td></td>
<td>37° 00' 29&quot;</td>
<td>50° 33' 47&quot;</td>
</tr>
</tbody>
</table>

Three sampling stations were identified in each transect. Water samples were collected in triplicate (surface, 5, and 10 m below surface) using a Niskin sampler. Sampling was carried out on a monthly basis during the spring and summer of 2008. Transects were Astara, Lisar, Anzali, Kiashahr, Chamkhaleh and Chaboksar. The collected samples were filtered in the field (Whatman filter paper, 0.45 micron), the samples were kept in a cool place over ice and transported to laboratories for analysis (APHA, 1989).

Table 2: Physical and chemical parameters in the southern Caspian Sea, Iranian coast during 2008

<table>
<thead>
<tr>
<th>Transects</th>
<th>Nitrate (mg L⁻¹)</th>
<th>Phosphate (mg L⁻¹)</th>
<th>pH</th>
<th>Salinity</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10m</td>
<td>5m</td>
<td>surface</td>
<td>water</td>
<td>10m</td>
</tr>
<tr>
<td>Astara</td>
<td>0.17</td>
<td>0.16</td>
<td>0.15</td>
<td>0.069</td>
<td>0.068</td>
</tr>
<tr>
<td>Lisar</td>
<td>0.41</td>
<td>0.34</td>
<td>0.30</td>
<td>0.072</td>
<td>0.076</td>
</tr>
<tr>
<td>Anzali</td>
<td>0.26</td>
<td>0.16</td>
<td>0.16</td>
<td>0.032</td>
<td>0.045</td>
</tr>
<tr>
<td>Chaboksar</td>
<td>0.19</td>
<td>0.12</td>
<td>0.03</td>
<td>0.009</td>
<td>0.003</td>
</tr>
<tr>
<td>Astara</td>
<td>0.42</td>
<td>0.26</td>
<td>0.06</td>
<td>0.093</td>
<td>0.093</td>
</tr>
<tr>
<td>Lisar</td>
<td>0.21</td>
<td>0.33</td>
<td>0.32</td>
<td>0.06</td>
<td>0.09</td>
</tr>
<tr>
<td>Anzali</td>
<td>0.42</td>
<td>0.26</td>
<td>0.06</td>
<td>0.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The highest concentration of phosphate (0.61 mg L⁻¹) was detected in the surface waters of the Chaboksar station in summer, while the lowest concentration (0.028 mg L⁻¹) was reported in the water sample collected from 5 m depths of Kiashahr station, in spring (Table 2). The distribution of inorganic phosphate during spring and summer was higher in the surface layers as compared to the other layers (Fig. 2). However, no significant differences (P>0.05) were detected in the phosphate concentrations in the various water depths studied.

2.2. Sample Analyses

The concentration of phosphate was analyzed by the ascorbic acid method as outlined in APHA (1989) and nitrate by the sulfanilamide method described in MENVIOQ (1992). The concentrations of nitrate and phosphate in the samples were determined using spectrophotometer (HACH DR-2500) and reported in terms of mg L⁻¹. Other parameters including water salinity rate (ATAGO s/mill-E) and pH (pH Tester 30) were also measured using portable kits. Data obtained were analyzed by One-Way ANOVA and SPSS software. Statistical summary of environmental and biological parameters collected from waters in the southern Caspian Sea-Iranian coast during 2008 is shown in Table 2.

Fig. 2: Mean variations in phosphate concentrations at depths less than 10 m in the southwest Caspian Sea during the spring and summer of 2008 (bars show standard error).
Nitrate concentrations in the south Caspian Sea fluctuated between 0.14 and 0.66 mg L\(^{-1}\) in spring and between 0.3 and 0.87 mg L\(^{-1}\) in summer (Fig. 3). No significant differences were reported in nitrate concentrations in the various water depths studied in the study area (P>0.05).

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Fig. 3: Mean variations in nitrate concentrations at depths less than 10 m in the southwest Caspian Sea during the spring and summer of 2008 (bars show standard error).
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Other parameters in water were determined in situ using portable instruments. Water salinity fluctuated between 7.1 and 12 ppt in the study area (Table 2). Highest salinity was recorded at 10 m depths in Chaboksar in spring, while the lowest salinity was reported in surface water samples collected from the Chaboksar station in summer (Fig. 4). Results indicated that except for the surface waters in Anzali and Kiashahr which are influenced by the rivers flowing into them, salinity was high in the other water depths in all the stations studied (Fig. 4).

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Fig. 4: Mean variations in salinity at depths less than 10 m in the southwest Caspian Sea during the spring and summer of 2008 (bars show standard error).
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The maximum temperature recorded was 31.8 °C in summer in the surface waters of Anzali, while the minimum water temperature during the study was recorded as 21.2 °C in spring at 10m depths in Chamkhale (Fig. 5).

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Fig. 5: Mean variations in temperature at depths less than 10 m in the southwest Caspian Sea during the spring and summer of 2008 (bars show standard error).
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Mean water temperature during spring and summer of 2002 in depths of 0-10 meters are reported as 21.2 and 31.8 °C, respectively (Table 2). The highest pH (8.7) was recorded in the surface waters of Anzali in summer, while the lowest pH (8.1) was recorded at 5 m depths in Chaboksar, in March (Fig. 6).

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Fig. 6: Mean variations in pH at depths less than 10 m in the southwest Caspian Sea during the spring and summer of 2008 (bars show standard error).
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No significant differences (P>0.05) were detected in the concentrations of nitrate and phosphate and other parameters studied in the different depths in the six transects.
Major parts of the southern coasts of the Caspian Sea are less than 10 meters in depth. The shallow regions are of prime significance due to the ecological conditions prevailing, higher productivity, as well as higher life span of fish fingerlings and for tourist attractions in summer. Marine waters possess almost all kinds of chemical materials some of which are of great significance for marine resources. For example, nitrate and phosphate which are highly essential for the synthesis of organic matter, play a key role in their life and growth (Laloei, 2004).

The findings of this study revealed that the highest phosphate concentration (0.44 mg L\(^{-1}\)) in the south-west part of the sea was recorded in Chaboksar in spring, which was probably due to the effects of northern cold waters of the Volga River and the entry of the Sepidrud River, but the highest phosphate concentrations in summer time were recorded in Anzali, Chamkhale and Chaboksar. Phosphate and nitrate concentrations in Astara were reported to be the lowest as compared to the other areas (Table 2). Previous studies indicated that the highest rate of nutrient transferred annually through the Sepidrud River is 1840 tons per year and 171 tons per year through the Challus River. The lowest nutrient loading rate was recorded in the far west region of the Caspian Sea (CEP, 2002).

The study conducted by Kasimov in 1987 on the phosphorous variations in the Caspian Sea suggested that its distribution in the southern Caspian Sea was more heterogeneous or amorphous than the other areas and its highest transfer rate was recorded in the west coast. Meanwhile, its volume varied depending on seasonal variations (Kasimov, 1987).

Nitrate concentrations follow similar trends. Phytoplanktons first consume inorganic nitrogen when they are in the early stages of growth. Then, they convert organic nitrogen in various water layers into inorganic nitrogen for consumption. The present study showed that nitrogen levels in the south-west coast lines in spring were characterised by fluctuations from 0.16 to 0.66 mg L\(^{-1}\). With the beginning of summer inorganic nitrogen levels increase significantly compared to that of spring which may be due to the increase in agricultural activities.

Variations in salinity levels showed minor increases form the surface to greater depths in the study area. Kideys et al. (2001) stated that such variations (0.1 – 0.2 ppt) from the surface to the depths in the Caspian Sea are insignificant. On the other hand, with regard to the geographical location and prevailing climatic conditions of the Caspian Sea, water vapour in the region increases and reaches saturation (CEP, 2002). This results in a decrease in evaporation thereby, increasing salinity during summer to a maximum level of 9.1 ppt in the Lisar region, due to the influence of fresh water flowing into this region through the navigational canals at the estuary.

The temperature regime in the Caspian Sea is one of the main factors for the circulation of water in this sea. No significant differences (\(P>0.05\)) were detected in the vertical variations in water temperature in the sampling stations in the six transects. This is because the water depth at the stations studied was less than 10 m and thermal stratification had not set in these depths. Statistical comparison of data pertinent to pH revealed that the lowest values belonged to the pelagic waters of the first station in each transects. This may be attributed to the effects of the remains of marine organisms and organic matter which are deposited close to the coastal region (Duxbury et al., 2000).

pH in the Caspian Sea has seasonal and spatial variations. In summer, the increase in phytoplankton production results in the absorption of \((\text{CO}_2)\) and a chain reaction that take the free Hydrogen ion from the sea water, reduce the acidity and increase pH (Hajizadeh and Eghtesadi, 2008). In this study, the maximum value for pH was observed 8.7 at the water surface in summer. Nasrollahzadeh et al. (2008) reported that the maximum pH value for the Caspian Sea was 8.6 in summer.

Comparison of data collected in this study and those related to 2002 in the southwestern zone of the sea (CEP, 2002) indicated an increasing trend in nitrate and
phosphate concentrations. On the basis of CEP reports nitrate concentrations ranged between 0.03-0.41 mg L\(^{-1}\) and that of phosphate ranged between 0.03 and 0.15 mg L\(^{-1}\). In the present, study a significant increase was recorded compared to that of 2002, which can be attributed to the discharge of household wastes as well as discharge of fertilizers and pesticides into the rivers during agricultural activities.

Leonov et al. (2000) reported that the Sepidrud River is the main source of pollution that enters the Caspian Sea on the Iranian coastline. Dumont (1998) stated that the main part of nutrients in the Caspian Sea was supplied through Volga River, but their levels in the Caspian Sea were generally low. Phosphorus as well as nitrate levels during spring and summer are low in the South Caspian Sea. It was in 1970 that agricultural and domestic waste materials led to an increase in nutrient levels (Dumont, 1998). According to investigations carried out by Shiganova et al. (2001) in the Black Sea increase in water temperature in summer resulted in an increase in the biomass of ctenophores. Increase in feeding intensity of ctenophore ultimately led to a decrease in the population of zooplanktons and an increase in that of phytoplanktons. Krupatkina (1991) attributed nutrient accumulation (phosphorous, nitrogen and sometimes silica) to intensive pollution and unfavorable conditions of life including pH, temperature, salinity and even wind during the favorable seasons such as spring and summer in particular, which has changed into a problem in the Caspian Sea region.

Entry of nutrients through agricultural, industrial and urban waste discharge results in phytoplankton bloom under normal circumstances. Algal blooms were reported between Anzali and Nowshahr in September 2005 due to an imbalance in nitrate and phosphate levels. Meanwhile in 2006, algal blooms caused a change in water colour in the coasts of Anzali. The occurrence of this bloom is associated to flooding from the Anzali lagoon and entry of nutrients into the sea (CEP, 2006). Phytoplankton bloom is highly significant as it is an indication of an environmental alert for the Caspian Sea. Therefore, identifying the causes of such developments and their impacts on the marine resources are of great significance.

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