PHOSPHORUS FRACTIONS AND ITS POTENTIAL RELEASE IN THE SEDIMENTS OF KOYCEGIZ LAKE, TURKEY

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Abstract
This study was conducted to find out the seasonal and spatial patterns of the phosphorus in the littoral sediment and its potential release into the Koycegiz Lake, south west Turkey, between November 2011 and March 2012 at two months intervals. The scanning electron microscopy was used for elemental compositions of the sediment. The amounts and forms of phosphorus (P) in surface sediments of Koycegiz Lake were examined using a not sequential chemical extraction procedure. Four fractions of sedimentary P, including organic bound phosphorus fraction (Org≈P), calcium bound phosphorus fraction (Ca≈P), iron+aluminium bound phosphorus fraction (Fe+Al≈P) and carbonate bound phosphorus fraction (CO₃≈P) were separately quantified. The results indicated that the contents of different phosphorus fractions in the sediments varied greatly. The proportion of phosphorus fractions was estimated as Org≈P (90.20 %), this fraction was followed by Ca≈P) (9.06 %), Fe+Al≈P (0.47 %) and CO₃≈P (0.27 %) in this study. The level of phosphorus release from the sediment to the lake is calculated as low. The sediment phosphorus release fluctuated between -6.647–75.883 µg/m².d⁻¹ and the total phosphorus (TP) concentrations of the sediment samples were changed between 980.39 µg/gDW (Dry Weight) - 1990.81 µg/gDW. The results show that it can be evaluation as eutrophic for Koycegiz Lake.

Keywords: phosphorus fractions; phosphorus release; sediments; Koycegiz Lake

INTRODUCTION
Various pollutants may be adsorbed to the sediments accumulated on the bottom of the rivers or lakes. These sediments may accumulate over long periods and can act as new pollutant sources to the overlying water after the water quality has improved (Lijklema et al., 1993). As a major nutrient for aquatic ecology, phosphorus (P) is often accepted as the most critical limiting nutrient for primary lake productivity (Dorich et al., 1985), and its excess supply can lead to eutrophication (Bostrom and Pettersson,
Phosphorus has a strong association with particulate matter (Gerritse, 1993; Stumm and Morgan, 1996). In water systems, both inorganic and organic forms commonly occur; however, both tend to be insoluble, while any component that exhibits greater solubility generally becomes adsorbed to the sediment matrix (Fabric and Bell, 1993). Physical and chemical characterizations of sediments are important for evaluating the P exchange processes between sediments and overlying waters (Gonsiorezyk et al., 1998). P can be released into the overlying water under certain environmental conditions (Bostrom and Pettersson, 1982; Furumai et al., 1989; Wentzel et al., 1989), which may lead to continuing water eutrophication. The role of the P in lake sediment in promoting lake eutrophication can be more efficiently evaluated on the basis of the contents of different P fractions, instead of total P content (Kaiserli et al., 2002). The information of the different chemical P fractions in lake sediments is useful in understanding whether the sediment acts as an adsorber or source of phosphorus (Tiyapongpattana et al., 2004). Solubility of phosphate in the interstitial water of sediment is significantly controlled by its chemical composition and the interactions with other minerals or amorphous materials (Maine et al., 1992). The association of phosphate with iron, aluminum, and calcium, and the adsorptive properties of carbonates and clays are of special interest (Bostrom and Petter, 1982; Jensen et al., 1992).

P remobilization from the sediments is probably controlled by its speciation, and it is important to know which part of the stock can be mobilized. According to Hielte and Lijklema (1980), the extracted P fractions in lake sediments may be characterized as the loosely adsorbed P (NH4Cl-P), metal oxide bound P (mainly of iron and aluminum, NaOH-P) and calcium bound P (HCl-P). Given that iron and aluminum have major roles in retaining inorganic fractions, mobility also depends on redox potential. For instance, anoxic microzones perhaps generated through sulfate reduction to sulfide, causing ferrous ion formation at the sediment-water interface, reduce Fe (III) and hence retention capacity by returning Fe (II) and associated phosphorus to solution (Bostrom, 1988). The mobilizations of NaOH-P fractions are the most important mechanism of P release under high pH values and anaerobic conditions (Kaiserli et al., 2002).

The objective of the present study was to estimate the amount and forms of P in the sediments of Koycegiz Lake, using a not sequential extraction procedure, to evaluate their possible contributions to the P-loadings of the Koycegiz Lake systems.
1 MATERIALS AND METHODS

1.1 Study area

The Koycegiz Lake is located in the south-west of Turkey within the boundaries of Mugla. It lies within 36 ° 54' N and 28 ° 38' E longitude coordinates. Koycegiz Lake is a tectonic lake and it has 5400 hectare area (Fig. 1).

The most sensitive regions of Turkey for environmental problems are those known as having important touristic potentials. Touristic investments done in a lot of cities, districts and towns on the shorelines of Mediterranean and Aegean Regions lose their traditional qualities increasingly due to population growth and structuring and these regions are left to the hands of tourism called as an “uncertain” area by the influence of economical motives without having any cultural and social preparation. Thus, Mugla shoreline is the region which is the most effected and mostly changed by them. In this way, the basin is the first sample in Turkey as a planned tourism progress directed by the State which is examined due to damages to natural environment and ecological values. In this context, the region is included into the “Private Environment Protection Area (PEPA) set by a decree law dated as 13th November 1989 and numbered as 383 (Ozdemir, 1998).

![Fig. 1 The map of study area](image)

1.2 Sampling and pretreatment

Water and sediment samples were collected from three stations with an average water depth of 70 cm between November 2011 and March 2012 at two months intervals in the Koycegiz Lake (Figure 2). Sediment samples
were collected using plastic pipe, 50 mm in diameter and 15 cm length. Sediment samples were taken to the laboratory in liquid nitrogen tank, and separated three sections (surface, medium, and bottom); each section is 5 cm, by steel band. These samples were air dried, homogenized, passed thorough 0.5 mm sieve and stored. Porewater of the sediment samples were obtained from the sediment with using centrifugal technique. The overlying water samples were collected 10 cm above the sediment and filtered by gauze immediately.

1.3 Analysis and phosphorus fractions

**Total phosphorus (TP) and Total iron (TFe)**

5 g of dried the sediment samples was digested by microwave incinerator (Berghof MWS+3) with HNO₃ (4 ml), H₂SO₄ (4 ml) and HF (2 ml). The solution was transferred, diluted and filtered through a 0.45-µm GF/C filter membrane. TP concentrations in the solution each sample were analyzed by using the ascorbic acid method (Anonymous, 2005). TFe concentrations in the solution each sample were measured by (Inductively Coupled Plasma - Atomic Emission Spectrometry) ICP-AES (PerkinElmer Inc.-Optima 2000 DV).

All reagents were of analytical reagent grade. Deionized water was used throughout the study. All the plastics and glass wares were washed in nitric acid for 15 min. and rinsed with deionized water before use. Instrument calibration. Standard solutions were prepared from commercially available materials. High purity argon was used as inert gas.

![Fig. 2 The map of stations.](image-url)
**Total filterable orthophosphate (TFO)**

The water samples and the porewater of the sediment samples were filtered through a 0.45-µm GF/C filter membrane. TFO concentrations in the water samples and the porewater of the sediment samples were analyzed by using the ascorbic acid method (Anonymous, 2005).

**Water content of sediment (%)**

Sediment samples were dried at 110 °C for 16 hours. Then, water content calculated as the difference between before and after weighing (Shrestha and Lin, 1996).

**Phosphorus fractions**

The method (Hieltjest and Lijklema, 1980) was used to analyze P fractions in the sediment at the beginning and end of the experiment. The phosphorus fractions in this method are organic bound phosphorus fraction (Organic=P), calcium bound phosphorus fraction (Ca=P), carbonate bound phosphorus fraction (CO3=P) and iron+aluminium bound phosphorus fraction (Fe+Al=P). The contents of the P fractions were determined using the not sequential extraction scheme suggested by Fig. 3. The difference between TP and IP ((Ca=P) + (Fe+Al=P) + (CO3=P)) is the Organic=P. For each fraction, three replicates were performed and all the data were expressed as the average.

![Fig. 3 Phosphorus fraction method](image-url)
Phosphorus release

Phosphorus release from sediment to lake water, which is used in the calculation formula (1) molecular diffusion (Shaw and Prepas, 1990).

\[
\text{Flux} = \varphi \cdot D \cdot Q^2 \cdot \frac{dc}{dx} \cdot 86400
\]

Flux = TFO mg/m².d⁻¹

The symbols are:

- \( \varphi \) = water concen of sediment (%)
- \( D \) = molecular diffusion coefficient (1.24 \( \times \) 10⁻⁹ m².s⁻¹)
- \( Q^2 \) = Tortusite (\( \varphi^{-0.8} \))
- \( \frac{dc}{dx} \) = across the sediment-water interface (mg·m⁻⁴)
- 86400 = factor to convert second to day.

Sediment characteristics

The elemental compositions of the sediments were determined with scanning electron microscope JSM-7600 F FEG equipped.

2 RESULTS AND DISCUSSION

2.1 Characterization of sediment

Sediment characteristics

The general features and the chemical component contents of the sediments are presented in Fig. 4-7. The elemental composition of sediment samples calculated from EDX spectra was summarized in Fig. 5-7; each value represents an average of three spectra taken at different spots of the sample.

Fig. 4 SEM images of the sediments
Fig. 5 SEM-EDS analyzes of the sediment at first station

Fig. 6 SEM-EDS analyzes of the sediment at second station

Fig. 7 SEM-EDS analyzes of the sediment at third station
2.2 Total phosphorus (TP)

Sediments in aquatic systems can be classified according to their levels of total phosphorus. The level of the total phosphorus of sediment (TP) was found 325-771 mg/gDW for eutrophic lakes (Carignan, 1985). In this study; the total phosphorus (TP) concentrations of the sediment samples were changed between 980.39 µg/gDW and 1990.81 µg/gDW. These values show that it can be evaluation as eutrophic for Koycegiz Lake. The amount of TP in the sediments of the Koycegiz Lake is compared with other sediment of the lakes in Table 1. The amount of TP in the surface sediments of Koycegiz Lake is similar to that of Lake Erken and Lake Koronia, It was reported that these lakes are mesotrophic lakes (Rydin, 2000; House and Denison, 2002; Kim et al., 2004; Fytianos and Kotzakioti, 2005; Jin et al., 2006; Sun et al., 2008).

<table>
<thead>
<tr>
<th>Sediment source</th>
<th>TP (mg/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Erken, Sweden</td>
<td>1814</td>
<td>Rydin, 2000</td>
</tr>
<tr>
<td>Thames, UK</td>
<td>53–20119</td>
<td>House and Denison, 2002</td>
</tr>
<tr>
<td>Han River, Korea</td>
<td>580–1450</td>
<td>Kim et al., 2004</td>
</tr>
<tr>
<td>Lake Koronia, Greece</td>
<td>1305</td>
<td>Fytianos and Kotzakioti, 2005</td>
</tr>
<tr>
<td>Taihu Lake, China</td>
<td>420–3408</td>
<td>Jin et al., 2006</td>
</tr>
<tr>
<td>Haihe River, China</td>
<td>968–2017</td>
<td>Sun et al., 2008</td>
</tr>
<tr>
<td>Koycegiz Lake, Turkey</td>
<td>980-1990</td>
<td>The present study</td>
</tr>
</tbody>
</table>

2.3 Total iron (TFe)

Hydrated oxides of iron and aluminum provide most effective surfaces for adsorbing phosphates and a form of ion exchange with hydroxyl ions is the likely mechanism. The humic-iron complexes are generally regarded as more efficient than organic matrix in adsorbing phosphate (Enell and Lofgren, 1988). The release of phosphorus from sediment was investigated in shallow and eutrophic Lake Blankensee by Ramm and Scheps (1997). They reported that If TFe/TP ratio is greater than 21 in the sediment, phosphorus release is blocked from TFe in the sediment. In this study; TFe/TP ratio fluctuated as 23 in the sediment. The total iron (TFe) concentrations of the sediment samples were changed between 17800 µg/gDW and 31202 µg/gDW. This situation show that the iron+aluminium...
bound phosphorus fraction (Fe+Al≈P) may be effective because of the high content of iron.

2.4 Total filterable orthophosphate (TFO)

The amount of particulate phosphorus is very high in sediments. Although particulate phosphorus is generally not mobile, it can be solubilized into porewater of the sediments. Phosphorus may be transport from porewater into lake water by diffusion, groundwater, mixing and bioturbation (Sondergaard et al., 2001). In this study; the total filterable orthophosphate (TFO) concentrations of the porewater of the sediment samples were changed between 15.17 mg/m³ and 272.98 mg/m³. The other hand, the water content of the sediment samples were changed between 9.34 % – 39.28 %.

The total filterable orthophosphate TFO concentrations of water samples were changed between 1.52 mg/m³ and 50.05 mg/m³. The concentrations of TFO in the porewater of the sediments are more high that the concentrations of TFO in the water of the Koycegiz Lake. This result shows that phosphorus may not be transport from porewater of the sediment to Koycegiz Lake.

2.6 Phosphorus fraction composition

Determination of phosphorus fraction in the sediment is very important for the release of phosphorus from sediment to water. The amounts of different average P fractions are shown in Fig 8. The concentrations of P fractions in all the sediment are order. The concentrations of organic fractions phosphorus in all sediment samples are higher than IP (Ca≈P + Fe+Al≈P + CO₃≈P). IP fractions in all the stations are also order. The concentrations of Ca≈P in all the stations are high than other IP fractions. The other hand, sediment P fractions were measured in surface (0–5 cm), medium (5-10 cm) and bottom sediment (10-15 cm) in the three stations. In each station, P fractions from surface, medium and bottom sediment are similar. There are not various for the concentrations of P fractions in surface, medium and bottom sediment samples (Fig. 8)

The organic fractions phosphorus (Org≈P) is exceeding fraction during mineralization of sediment into the water (Goedkoop and Pettersson, 2000). Org≈P) and the iron+aluminium bound phosphorus fraction (Fe+Al≈P) are the most effective phosphorus fractions for phosphorus release from sediments (Sondergaard et al., 2001). The Org≈P concentrations of the sediment samples were changed between 860.29
µg/gDW and 1902.90 µg/gDW (Fig. 8). The more proportion of phosphorus fractions in hindering phosphorus release into the lake was estimated as Org≈P (90.20 %).

Fig. 8 The distribution of average phosphorus fractions (µg/gDW)

Ca≈P (HCl-P) represents the P fraction sensitive to low pH and was assumed to mainly consist of apatite P (natural and detritus) including P bound to carbonates and traces of hydrolysable organic P. This P fraction was deemed as a relatively stable fraction of IP in the sediments (Kaiserli et al., 2002). The high HCl-P content was attributed to the calcareous terrain of the recharge area. High portions of calcium mineral P were also observed in lakes having varying trophic status. In these lakes, HCl-P and residual-P, fractions were dominant, together comprising 35–90% of the TP, with calcareous sediments close to the upper end of the range (Penn et al., 1995). Ca≈P was not the main IP fraction, and its sediments was not calcareous. In this study; the calcium bound phosphorus fraction (Ca≈P) concentrations of the sediment samples were changed between 67.90 µg/gDW and 180.72 µg/gDW. Ca≈P contents in sediments were the second highest among (9.06 %) the four P fractions (Fig. 8). It was reported that in heavily polluted lakes, the rank order of Fe+Al≈P (NaOH-P) > HCl-P was found (Lijklema et al., 1993), while it was the opposite order of HCl-P > NaOH-P in mesotrophic lakes (Kaiserli et al., 2002). The rank order of P fraction suggests that Koycegiz Lake can be mesotrophic. This situation is not consistent with the TP results.

Fe+Al≈P (NaOH-P) is exchangeable including P bound to metal oxides, mainly of Al and Fe (Kaiserli et al., 2002). Fe+Al≈P was once used for the estimation of available P in the sediments and was an indicator of algal available P (Zhou et al., 2001). This fraction can be released for the
growth of phytoplankton when anoxic conditions prevail at the sediment–water interface (Ting and Appan, 1996). In this study; the iron+aluminium bound phosphorus fraction (Fe+Al=P) concentrations of the sediment samples were changed between 1.21 µg/gDW – 38.22 µg/gDW. Fe+Al=P contents in sediments were the second lowest among (0.47 %) the four P fractions (Fig. 8).

CO3=P (NH4Cl-P) represents the loosely sorbed P in the sediments, and this fraction may include dissolved P in the pore water (Kaiserli et al., 2002). The P was released from CaCO3-associated P or leached P from decaying cells of bacterial biomass in deposited phytodetrital aggregates (Pettersson, 2001), and this P fraction is also a seasonally variable pool of P compounds (Rydin, 2000). In this study; the carbonate bound phosphorus fraction concentrations of the sediment samples were changed between 0.91 µg/gDW and 16.68 µg/gDW. CO3=P contents in the sediments were the lowest among (0.27 %) the four P fractions (Fig. 8). These results indicated that CO3=P content was not strongly positively related with TP. The previous study reports that CO3=P contribution to TP was between 1 and 25% in the sediments, and also was found to contribute more in the sediments of calcareous lakes than that in other lakes because of the high degree of CaCO3 over saturation.

2.7 Phosphorus release

One of the most important factors affecting the P concentration of lake ecosystem is the P release from the sediments into the overlying water. However, the amounts of P released from the sediments were not coincident with the amounts of TP the amounts of P released was strongly in positive correlations with CO3=P (NH4Cl-P) NH4Cl-P (Sun et al., 2008). The soluble IP in water is low and Ca-P is relatively stable and difficult to release in physical and chemical processes (Ruban and Demare, 1998). The CO3=P (NH4Cl-P) and Fe+Al=P (NaOH-P) may be easily released from the sediments, and it was main contributors of the release P source in the sediments and of the sources for the overlying water. The P released from the sediments in Koycegiz Lake was estimated from the calculation formula (1) molecular diffusion. Sediment phosphorus release fluctuated between -6.647 - 41.577 µg/m².day (Fig. 9). The level of the release P was very low (14 mg/m².day). This situation is consistent with the CO3=P (NH4Cl-P) results. The level of the release oligotrophic lakes is 2.2 mg/m².day and the level of the release eutrophic lake is 14 mg/m².day (Nürnberg et al, 1986).
3 CONCLUSIONS

This study evaluated sediment characteristics, P fractions forms of Koycegiz Lake in Turkey.

1. The total phosphorus (TP) concentrations of the sediment samples were changed between 980.39 µg/gDW and 1990.81 µg/gDW. These values show that it can be evaluated as eutrophic for Koycegiz Lake.

2. Organic fractions phosphorus was the main P fraction in the sediments of Koycegiz Lake. The concentrations of organic fractions phosphorus in all sediment samples are more high than IP (Ca≈P + Fe+Al≈P + CO₃≈P). The concentrations of Ca≈P in all the stations are high than other IP fractions. The rank order of P fraction suggests that Koycegiz Lake can be mesotrophic. This situation is not consistent with the TP results.

3. P fractions from surface, medium and bottom sediment are similar. There are not various for the concentrations of P fractions in surface, medium and bottom sediment samples.

4. The P released from the sediments in Koycegiz Lake was estimated from the calculation formula (1) molecular diffusion. Sediment phosphorus release fluctuated between -6.647 - 41.577 µg/m².day.

5. The concentrations of TFO in the porewater of the sediments are more high that the concentrations of TFO in the water of the
Koycegiz Lake. This result shows that phosphorus may not be transport from porewater of the sediment to Koycegiz Lake.

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REFERENCES


