

A sequential extraction to determine the distribution of phosphorus in the seawater and marine surface sediment

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ABSTRACT

The distribution of phosphorus species among environmental compartments (e.g., between water and sediment), significantly affects the bioavailability of these species to organisms. The eastern Mediterranean Sea is one of the most extreme oligotrophic oceanic regions on earth in terms of nutrient concentrations and primary productivity. The paper presents the results of inorganic and organic forms in surface sediment and seawater from NE Mediterranean Sea (Burclar Bay, Erdemli, South Anatolia of Turkey) in May 2007. Speciation of phosphorus in seawater and surface sediment using inductively coupled plasma-atomic emission spectrometer (ICP-AES) has been reported here. The method is based on sequential extractions of the seawater and sediment each releasing four forms of inorganic phosphorus: loosely sorbed phosphorus, phosphorus bound to aluminium (P-Al), phosphorus bound to iron (P-Fe) and phosphorus bound to calcium (P-Ca).

The most abundant form of inorganic phosphorus in the seawater and surface sediment is calcium-bound phosphorus. Relative abundances of the remaining phosphorus forms in sediment follow the order: P-Al > P-Fe > loosely bound-P and in seawater follow the order P-Fe > P-Al > loosely bound-P.

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1. Introduction

Phosphorus cycle in aquatic environment is a topic of scientific importance in several decades [1]. Its main forms in natural waters are ortho-, meta-, pyro-, and polyphosphates and various phosphorus-containing organic compounds. An increase in the phosphorus concentration in water reservoirs due to various effluents produces an uncontrolled amount of vegetative biomass, which in its turn leads to the reorganization of the aquatic life and to the prevailing of putrefactive processes. Therefore, the determination of phosphorus as both dissolved and suspended compounds in ground, surface, and sewage waters is an essential part of water quality control [2]. As a major nutrient for aquatic ecology, phosphorus has been recognized as the most critical nutrient limiting marine productivity. One of the most important factors determining the phosphorus concentration of the sea overlying water was the phosphorus release from the sediments. Such release may have a significant impact on water quality and may result in continuing eutrophication. The sediment plays an important role in the overall nutrient dynamics of marine science. Phosphorus availability is regarded as the most important factor for determining the

water quality of sea. However, not all of the phosphorus fractions can be released from the sediments and render to eutrophication. Thus, to assess the risk of eutrophication in aquatic systems, it is necessary to know not only the total phosphorus content in the sediments but also the contents of different phosphorus fractions. Chemical sequential extractions have been widely used in order to describe the many different forms in which phosphorus occurs in the sediment [3–15].

Phosphates [P(V)], the most abundant form of phosphorus in the environment, are readily available for assimilation, and for this reason, they have traditionally been used as fertilizers. In addition, phosphate and other phosphorus compounds are widely employed as detergents and food additives, among other uses. There is various phosphorus containing fertilizers and pesticides used in agriculture. Extensive input of phosphorus by over fertilization, by industrial and domestic wastewater pollution result in over abundance in aquatic media. Consequently, monitoring of phosphorus content in natural and wastewaters is essential to control and avoid eutrophication of the aquatic environment. Its current abundance in the Earth's crust is approximately 0.12%; however, almost all of the phosphorus on Earth is found in the form of minerals including apatites (chloro and fluoro), vivianite, wavellite, and phosphorites. Apatite {Ca₅(PO₄)₃[F, OH or Cl]}, the largest reservoir of phosphate on Earth, is relatively insoluble in water. Most of the phosphorus released into the current natural environment

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is present in particulate form and is not biologically available, limiting primary production. For these reasons, it is postulated that, on the primitive Earth, phosphate would also have been limited; restricting the synthesis of biologically essential compounds [3]. The sorption of phosphate on sediments has a major influence on transport, degradation, and ultimate fate of phosphorus in marine ecosystems. Phosphorus is found in nature in various forms including: (1) mineral forms; (2) organic forms such as phospholipids, nucleic acids, proteins, polysaccharides, nucleotide cofactors, and as phosphonates; (3) dissolved inorganic forms such as pentavalent, trivalent or univalent dissolved species; (4) gaseous forms in the III oxidation state; and (5) particulate or colloidal forms. Several procedures for phosphorus extraction in sediments have been proposed in order to suit studies of different sediment mineral phases [3–7,15]. Exponential increase in aquaculture production in the Mediterranean Sea over the past two decades has caused various environmental problems, which are less pronounced in the water column, but quite severe at the sediment in the vicinity of the cages, such as organic matter, nitrogen and phosphorus accumulation, bacterial activity enhancement, benthic assemblages modification and seagrass degradation [13]. The bioavailability and environmental fate of P in aquatic and terrestrial environments are not only related to its concentration in solution, but also to its distribution over the different species present in solution, e.g., free orthophosphate (mainly $\text{H}_2\text{PO}_4^{2-}$, denoted further as PO_4^{3-}), organic P esters (P–O–C bonds) and colloidal complexes. Understanding the dynamics of P in the natural environment builds on a sound fractionation scheme of the different aqueous P species [16].

The aim of this study is to investigate the distribution of phosphorus bioavailability (total phosphorus, organic and inorganic phosphorus) in the seawater and surface sediment from Burclar Bay located west of Mersin city at NE Mediterranean Sea (Erdemli; South Anatolia of Turkey). Speciation of inorganic phosphorus was carried out using a method based on sequential extractions of the sediment each releasing of four forms of inorganic phosphorus: loosely sorbed phosphorus, phosphorus bound to aluminium (P–Al), phosphorus bound to calcium (P–Ca) and phosphorus bound to iron (P–Fe).



Fig. 1. Sampling stations.

2. Experimental

Seawater and surface sediment samples were collected on a daily basis from onboard NE Mediterranean Sea during May 2007. Sampling station was selected in the present study: Latitude $36^{\circ}50'N$; Longitude $34^{\circ}19'E$ (Burclar Bay, Erdemli, Mersin, Turkey). Fig. 1 shows the locations of stations in Mediterranean Sea. The depth at the study site ranges from 1.0 m to 3.0 m. The top 5 cm of the surface sediment samples collected with a stainless steel grab sampler were placed in acid-washed nylon bags and closed tightly and then properly cooled in refrigerator ($4^{\circ}C$) until they were transported to the laboratory where they were stored at $-20^{\circ}C$ until further treatment [17].

Seawater samples were collected from Burclar Bay (17 km west of Erdemli), in clean glass bottles, filtered and kept in the cold storage till the analysis [1,18,19].

Reagents used were Merck suprapur when available or analytical grade and used without further purification. Deionized-distilled water was used throughout and was directly obtained from a Milli-Q system (Millipore, USA). A stock standard solution of orthophosphate (100 mg PL^{-1}) was prepared from KH_2PO_4 (Merck). Working solutions were prepared by stepwise dilution of the stock phosphorus solution. The solutions, which are 1.0 M NH_4F , 1.0 M NH_4Cl , 0.5 M NH_4F , 0.1 M NaOH , 1 M H_2SO_4 were used as extractants.

Phosphorus forms analyses were performed with an Optima model 2100 DV inductively coupled plasma-atomic emission spectrometer (ICP-AES) and its operating conditions are listed in Table 1. The selection of instrumental parameters and optical wavelength were based on obtaining good sensitivity, reasonable detection limits, and eliminating interferences [20,21]. Spectral wavelength selection for phosphorus analysis by ICP-AES is very important; lines chosen should have minimum interference and maximum detection. 213.617 nm has been chosen as spectral wavelength for phosphorus analyses [22].

Certified reference standard sediment, SRM 2702 from the national institute of standards and technology (NIST) was used to the analytical and instrument accuracy of the methods. The sediment sample is dissolved in mixture of perchloric and sulfuric acids (1:1). Following filtration total phosphorus is determined using ICP-AES (Fig. 2). A quantitative method is described for the speciation of phosphorus in seawater and marine surface sediment [23].

Determination of total inorganic phosphorus was carried out using a method shown in Fig. 3. Satisfactory reproducibility for total phosphorus in seawater and sediment was obtained in replicate samples (the relative standard deviation for 10 samples was less than 3%). In this study the phosphorus fractions were focused on the inorganic phosphorus fraction. The contents of different phosphorus fractions were determined using the sequential extraction scheme of seawater and surface sediment (Fig. 4). The extracts were centrifuged and the supernatants were filtered through $0.45\ \mu\text{m}$ GF/C filter membrane. The soluble phosphorus in each sample was determined. This extraction procedure divided inorganic phosphorus fractions in the sediment into loosely sorbed phosphorus

Table 1
Instrumental details and operating conditions for ICP-AES.

| View | Axial view |
|--|------------------------------------|
| Optical system | Echelle |
| Power (W) | 1450 |
| Plasma gas flow (L min^{-1}) | 15 |
| Auxiliary gas flow (L min^{-1}) | 0.2 |
| Detector | Liquid state detector |
| Sample flow rate (mL min^{-1}) | 1.5 |
| Nebulizer nebulizing chamber | Cyclonic |
| Nebulizer | Concentric glass (Meinhard) type A |

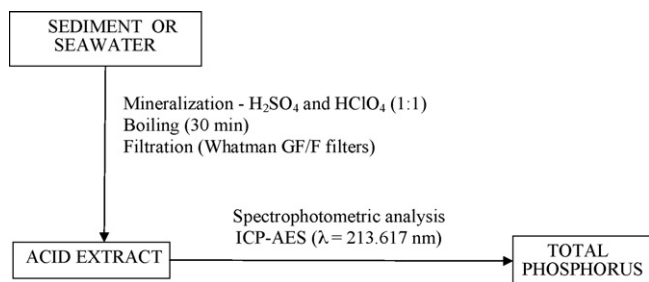


Fig. 2. Method for total phosphorus determination in marine surface sediment and seawater.

($\text{NH}_4\text{Cl-P}$), phosphorus bound to aluminium ($\text{NH}_4\text{F-P}$), phosphorus bound to iron (NaOH-P) and phosphorus bound calcium ($\text{H}_2\text{SO}_4\text{-P}$). The reliability and comparability of data for any of these fractions will depend on the operational protocols used and the accuracy of the method [12,24].

3. Results and discussion

The paper presents the results of phosphorus forms in seawater and marine surface sediment of NE Mediterranean Sea (Burclar Bay, Erdemli, Mersin, South Anatolia of Turkey). Surface sediments collected from NE Mediterranean Sea were mainly sands. Phosphorus content of sediment is also affected by the degree of mineralization. It can be assumed that in those samples collected in May, most of the organic matter originated from fall blooms of the previous year, and that by the time samples were collected, the phosphorus was mineralized to a large extent. An oxidized microlayer at the sediment-water interface partially inhibits sediment phosphorus release under well-mixed conditions in spring and autumn [1,14]. Total phosphorus from $206.24 \mu\text{g P g}^{-1}$ to $210.18 \mu\text{g P g}^{-1}$ dw (with a mean value of $208.21 \mu\text{g P g}^{-1}$ dw) and $1.616\text{--}1.826 \mu\text{g P g}^{-1}$ dw (with a mean value of $1.721 \mu\text{g P g}^{-1}$ dw) for surface sediment and seawater of Burclar Bay was found respectively.

The inorganic phosphorus was higher than organic phosphorus for the studied area and its content ranged from $202.32 \mu\text{g g}^{-1}$ to $205.38 \mu\text{g g}^{-1}$ (mean 203.85) and from $1.608 \mu\text{g g}^{-1}$ to $1.828 \mu\text{g g}^{-1}$ (mean 1.718) for sediment and seawater respectively (Tables 2 and 4). Organic phosphorus was determined as the difference between total phosphorus and total inorganic

phosphorus. The range and mean concentration of the organic phosphorus were $2.85\text{--}5.87$ (4.36) $\mu\text{g g}^{-1}$ for surface sediment and $0.002\text{--}0.004$ (0.003) $\mu\text{g g}^{-1}$ for seawater. Preservation of phosphorus in sediments depends on several factors including the nature of phosphorus compounds supplied to the sediment/water interface, sedimentation rate, bioturbation, or irrigation by bottom current, bottom-water oxygen content, diagenetic processes (i.e., formation of authigenic phosphorus-bearing mineral such as carbonate fluorapatite). Because these parameters vary in different sedimentary environments, burial flux of phosphorus may vary depending on the type of depositional environment [6,11]. The surprisingly large amount of phosphorus release from deep sediments during summer–autumn poses the problem of how much of it has been stored in sediment for along time and how much of it is derived by recent sedimentation and early diagenesis.

In other words, the problem is to quantify the net sedimentation (NS) for phosphorus in terms of the gross sedimentation (GS) and the releasing rate (RR).

Bearing in mind the basic equation:

$$\text{NS} = \text{GS} - \text{RR}$$

Two extreme hypotheses can be considered:

1. most of the released phosphorus comes from the sediments where it has been stored in the past;
2. most of the released phosphorus comes from recently sedimented material after a short diagenesis [25].

As a major nutrient for aquatic ecology, phosphorus has been recognized as the most critical nutrient limiting marine productivity. One of the most important factors determining the phosphorus concentration of the sea overlying water was the phosphorus release from the sediments. Such release may have a significant impact on water quality and may result in continuing eutrophication. However, not all of the phosphorus fractions can be released from the sediments and render to marine eutrophication. Thus, to assess the risk of eutrophication in aquatic systems, it is necessary to know not only the total phosphorus content in the sediments but also the contents of different phosphorus fractions. It is now widely accepted that the accessibility of the various elements for biota uptake depends strongly on their specific chemical forms and binding sites. A commonly used technique for identification

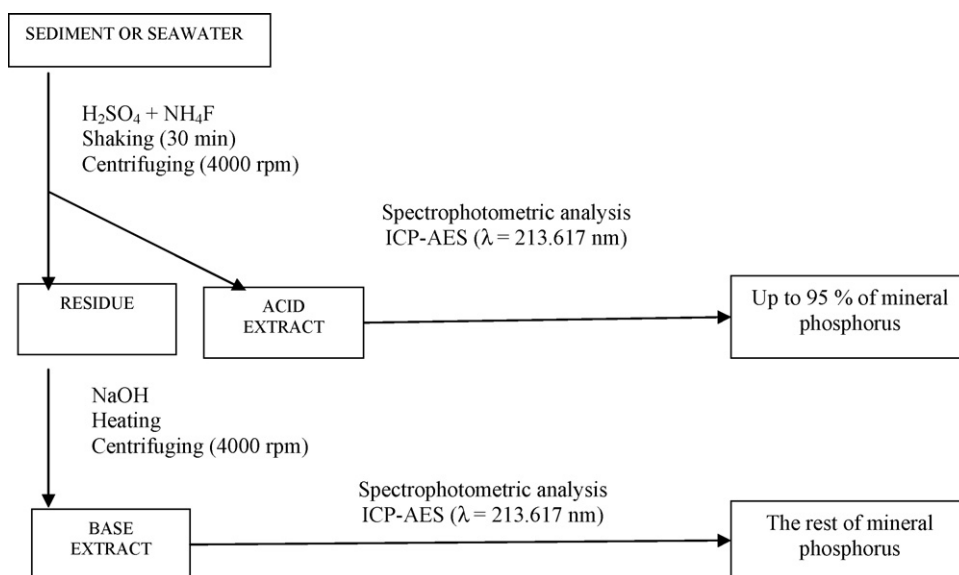


Fig. 3. Method for total inorganic phosphorus determination in sediment and seawater.

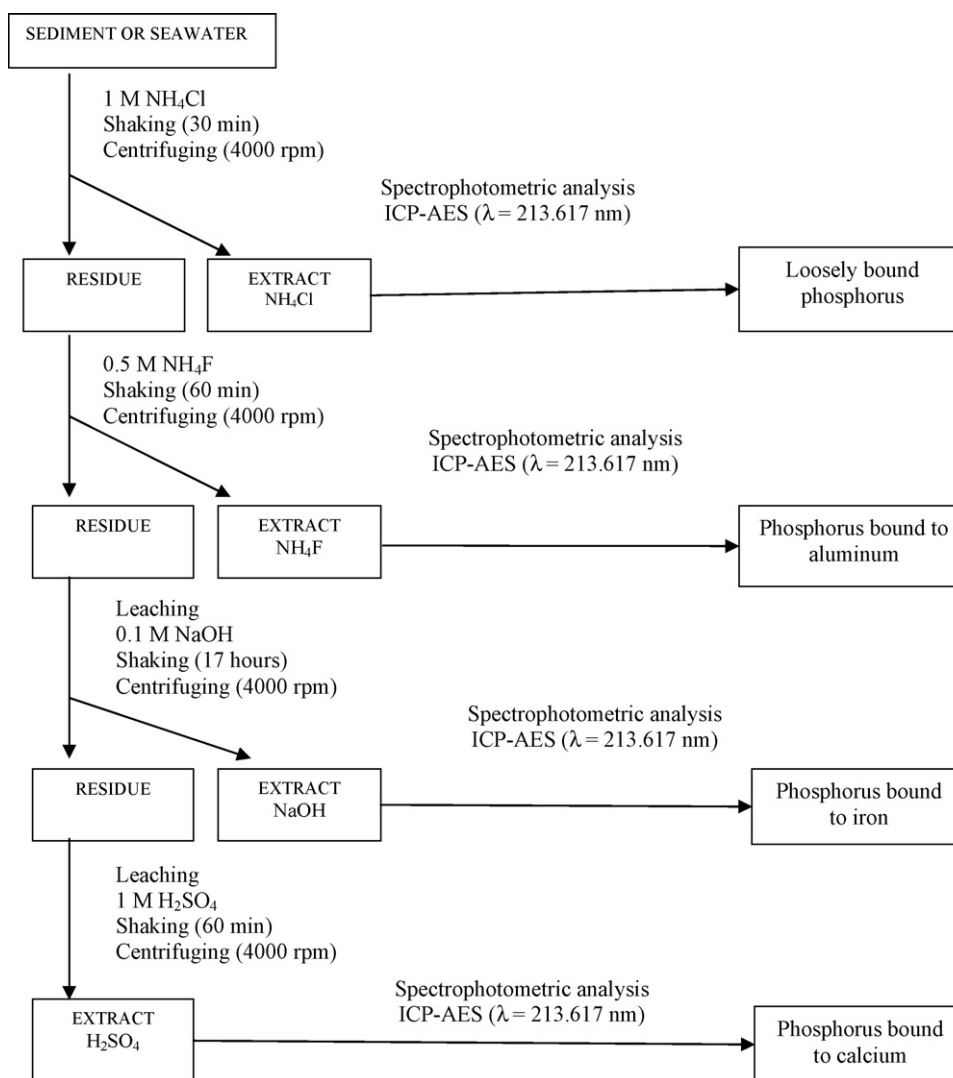


Fig. 4. Method for inorganic phosphorus forms determination in sediment and seawater.

of the phase associations of elements in solid phases is based on the application of sequential extractions [23]. Chemical (sequential extraction) fractionation techniques were applied here (Figs. 2–4). A number of fractions were collected for each reagent for determination using ICP-AES. The results are compared with seawater and its marine sediment (Tables 2–5). The concentrations are in good agreement with the reference values. The summation of phosphorus contents of all phases were compared with the certified values and with the values obtained from total digestion. Total inorganic phosphorus in the seawater and its sediment consisted only of the four forms of inorganic phosphorus examined in this work. No other forms of inorganic phosphorus were investigated in the samples, and organic phosphorus was present in very small amounts.

Table 2

Values of total phosphorus, mineral phosphorus, and organic phosphorus for sediment core (May 2007, Burclar Bay, NE Mediterranean).

| $\mu\text{g P g}^{-1}$ | Total P | Mineral P | Organic P |
|------------------------|---------|-----------|-----------|
| Minimum | 206.24 | 202.32 | 2.85 |
| Maximum | 210.18 | 205.38 | 5.87 |
| Mean | 208.21 | 203.85 | 4.36 |
| RSD | 0.37 | 0.54 | 0.02 |
| Mean (%) | 100 | 97.91 | 2.09 |

Table 3

Average values of mineral phosphorus speciation for marine surface sediment (in brackets are the relative standard deviation values).

| | $\mu\text{g P g}^{-1}$ | % |
|-----------------|------------------------|--------|
| P-mineral | 201.23 ± 2.13 | 100.00 |
| P-Ca | 161.61 ± 1.02 | 80.31 |
| P-Al | 16.89 ± 0.49 | 8.39 |
| P-Fe | 9.56 ± 0.27 | 4.75 |
| Loosely bound-P | 9.29 ± 0.32 | 4.62 |

The most abundant form of inorganic phosphorus in the Burclar Bay both seawater and surface sediment is calcium-bound phosphorus (H_2SO_4 -extracted phosphorus). Results presented phosphorus bound calcium as the major phosphorus form both

Table 4

Values of total phosphorus, mineral phosphorus, and organic phosphorus for seawater (May 2007, Burclar Bay, NE Mediterranean).

| $\mu\text{g P g}^{-1}$ | Total P | Mineral P | Organic P |
|------------------------|---------|-----------|-----------|
| Minimum | 1.616 | 1.612 | 0.002 |
| Maximum | 1.826 | 1.824 | 0.004 |
| Mean | 1.721 | 1.718 | 0.003 |
| RSD | 0.042 | 0.017 | 0.001 |
| Mean (%) | 100 | 99.83 | 0.17 |

Table 5

Average values of mineral phosphorus speciation for seawater (in brackets are the relative standard deviation values).

| | $\mu\text{g P g}^{-1}$ | % |
|-----------------|------------------------|--------|
| P-mineral | 1.92 ± 0.012 | 100.00 |
| P-Ca | 1.05 ± 0.025 | 54.69 |
| P-Fe | 0.53 ± 0.009 | 27.60 |
| P-I | 0.11 ± 0.003 | 5.73 |
| Loosely bound-P | 0.02 ± 0.001 | 1.04 |

seawater and sediment, related mainly with the oversaturation of calcite and co-precipitation of phosphate. The co-precipitation kinetics of phosphorus and calcite may be described in terms of simultaneous precipitation of calcite and adsorption of inorganic phosphorus onto its surface. [6]. Relative abundances of the remaining phosphorus forms follow the order: Fe-P > Al-P > loosely bound-P in seawater and Al-P > Fe-P > loosely bound-P in surface sediment (Table 3, Table 5).

Phosphorus gets into the marine from diffuse sources (particularly agriculture) and point sources (treated and untreated sewage effluents originating from households and industry) showing important differences [6]. An increase in the total phosphorus content at the sediment has been related to a progressive eutrophication. The importance of the effect of sediment on water column depends on the chemical form of phosphorus in which this element is combined. For this reason, the study of phosphorus speciation is particularly interesting [7,26].

The eastern Mediterranean Sea is one of the most extreme oligotrophic oceanic regions on earth in terms of nutrient concentrations and primary productivity. Phosphorus is incorporated into sediments in both inorganic and organic forms including physically adsorbed onto mineral surfaces, biologically assimilated in cells and in detritus coming from the sediment organisms. The speciation of total phosphorus in different forms is necessary for the understanding of phosphate exchange mechanisms by sediments, its potential removed from the water column and the availability of phosphorus for primary producers. In appearance, chemical co-precipitation of phosphate, biological and hydrological processes control the phosphorus concentration in the surface sediment more than external factors such as the lithology of drainage area and sewage inputs [6]. The information on the different chemical forms of phosphorus in aquatic sediment is useful in understanding whether that sediment acts as an adsorber or source of phosphorus [27].

The Mediterranean Sea, compared to Atlantic regions, has higher temperatures, microtidal regimes, lower nutrient content, lower primary production a biotic component containing a larger proportion of endemic species and a more varied coastal morphology [8]. Exponential increase in aquaculture production in the Mediterranean Sea over the past two decades has caused various environmental problems, which are less pronounced in the water column, but quite severe at the sediment in the vicinity of the cages, such as organic matter, nitrogen and phosphorus accumulation, bacterial activity enhancement, benthic assemblages modification and seagrass degradation [13].

This study provides an initial assessment of phosphorus concentration and phosphorus speciation through a range of sampling site within special Mediterranean seaside that covers contrasting topography, geology, soils and human impacts. In the most eutrophic systems, a strongly negative retention occurred in May suggesting that the on set of the increasing biological activity in spring triggered the release of some of the phosphorus retained during winter. In early summer retention was found to be less negative owing to the occurrence of a clear water phase following late-spring development of a high zooplankton biomass and its grazing on phytoplankton. When entering the sediment, phosphorus becomes a part of the numerous chemically and biologically

mediated processes and is ultimately either permanently deposited in the sediment or released by various mechanisms and returned in dissolved form to the water column via the interstitial water [14,28,29]. It should be emphasized, however, that surface sediments can be very different and highly variable regarding chemical composition. Parameters such as dry weight, organic content and content of iron, aluminum, manganese, calcium, clay and other elements with the capacity to bind and release phosphorus may all influence sediment-water interactions. The interstitial water of the sediment, which normally contains less than 1% of the sediment's total phosphorus pool, is important for the phosphorus transport between sediment and water as interstitial phosphate constitutes the direct link to the water phase above and the solid-liquid phase boundary between water and sediment. An upward transport of phosphorus is created via a diffusion-mediated concentration gradient, normally appearing just below the sediment surface [14,30–34].

4. Conclusions

The eastern Mediterranean Sea is one of the most extreme oligotrophic oceanic regions on earth in terms of nutrient concentrations and primary productivity.

The phosphorus released from marine surface sediment and seawater mainly originating from inorganic phosphorus fraction, so this study the phosphorus fractions were focused on the inorganic phosphorus fraction. The contents of different phosphorus fractions were determined using the sequential extraction scheme of surface sediment and seawater.

The paper presents the results of phosphorus forms (total phosphorus, organic and inorganic phosphorus) in the surface sediment and seawater from Burclar Bay located west of Mersin city at NE Mediterranean Sea (Erdemli; South Anatolia of Turkey). Total phosphorus concentration in the seawater is on average $1.721 \mu\text{g P g}^{-1}$ and in the surface sediment $208.21 \mu\text{g P g}^{-1}$ DW at Burclar Bay, NE Mediterranean Sea in May 2007. ICP-AES method was applied to determine the phosphorus forms.

The inorganic phosphorus concentrations were higher than organic phosphorus for the studied area and their mean % contents were 97.91% and 99.83% for surface sediment and seawater, respectively. The mean concentrations of the organic phosphorus were $4.36 \mu\text{g g}^{-1}$ for surface sediment and $0.003 \mu\text{g g}^{-1}$ for sea water.

The most abundant form of inorganic phosphorus in surface sediment and seawater is calcium-bound phosphorus (80.31% sediment and 54.69% seawater). Relative abundances of the remaining phosphorus forms in sediment follow the order: P-Al (8.39%) > P-Fe (4.75%) > loosely bound-P (4.62%) and in seawater follow the order P-Fe (27.60%) > P-Al (5.73%) > loosely bound-P (1.04%).

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