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A case study on trace metals in surface sediments and dissolved inorganic nutrients in surface water of Ölüdeniz Lagoon-Mediterranean, Turkey

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ABSTRACT

Hydro-chemical parameters (salinity, temperature, pH, dissolved oxygen, nitrate, silicate and phosphate) in seawater and major trace metals (Al, Fe, Mn, Cr, V, Zn, Pb, Cu) in sediments were evaluated for the assessment of quality of seawater and sediments in very small lagoon in Mediterranean, Ölüdeniz. Enrichment factors for metals in sediment were in the range of 1.62–8.09, comparable to crustal rock composition. For metals, comparison with literature data revealed relatively low metal concentrations for Ölüdeniz sediments. Correlation analyses on the sediment metal data showed strong correlation in between Cr, Fe and Zn. Surface water salinity slightly decreases within the lagoon, indicating that limited fresh waters inflow to the lagoon. In October, the lagoon waters contained very low phosphate concentrations but measurable values of nitrate and silicate, yielding high NO_3^-/PO_4^{3-} ratios (90). Very low Chlorophyll-*a* (biomass indicator) concentrations measured in the lagoon suggest the phosphorus limitation of primary productivity.

1. Introduction

The assessment of impacts of man-related activities on the marine environments, especially on enclosed systems such as Ölüdeniz Lagoon, can be achieved by measuring various chemical markers including nutrients, organic compounds and toxic heavy metals in water column, biota and sediments (Alley, 2000; Simeonov et al., 2000). Recent measurement programs like MEDPOL, have been adopted for coastal waters of the Mediterranean countries aiming to study levels and potential sources of pollutants as well as long-term trends in the marine ecosystems.

Lagoons having limited water exchanges with near-shore zones are economically and ecologically important sites (Vazquez et al., 1999). In principle, coastal Lagoons act as a sink for land-based inorganic sediments and various chemical pollutants. In recent years, considerable attention has been given to the assessment of marine pollution, which can be monitored by chemical analyses of sediment, biota and seawater samples. For example, heavy metals introduced into the coastal waters, including Lagoon ecosystems are known to be highly phytotoxic and influence the production rate and diversity of planktonic species (Sunda, 1989; Simeonov et al., 2000). Therefore, they are widely used as markers for monitoring and identifying the possible sources of pollutions in the coastal environments. Sediment analysis is a sound tool for the assessment of marine pollution as settled particles on the seafloor with different chemical constituents reflects long-term changes in the marine ecosystems. In addition, concentrations of heavy metals in the sediments are much higher than overlying water, permitting us to determine the interested metals accurately in sediment phase (Libes, 1992).

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In coastal lagoons, metals can enter surface waters principally through atmospheric deposition, industrial effluent discharges and streams. Wastewater discharges from various locations are the major sources of organic and inorganic pollutants (including heavy metals and nutrients) in the coastal water ecosystems. Nutrient discharges act as a pressure on algal production, resulting in drastic eutrophication in the coastal waters when physical mixing processes are not sufficient for the dilution of nutrient-enriched wastewaters in the receiving waters. Therefore, measurements of nutrients, heavy metals and biomass in the same environment would lead us to assess both the levels and types of pollution in the coastal marine ecosystems including lagoons (Kjerfve, 1994).

The Ölüdeniz Lagoon, located in the intersection of the South Aegean and West Mediterranean coast of the Turkey (Fig. 1), is vulnerable to several pollution sources due to large number of tourists, unplanned beach houses and uncontrolled population increase. Although Turkish Government assigned the region as the natural heritage area, there has not been any scientific research to characterise main sources and current levels of pollution within the lagoon due to tourism and community activities.

The present study aims to assess the present status of the lagoon ecosystem, basing on nutrient data in seawater and metals in sediments, which will also be a base for understanding long-term changes in this environment. For this goal hydrological parameters (salinity, temperature, pH, dissolved oxygen [DO], nitrate, silicate and phosphate) in the Lagoon seawater and concentration of major and trace metals (Al, Fe, Mn, Cr, V, Zn, Pb, Cu) in lagoon surface sediments were studied. Enrichment factor analysis was applied to sediment results for understanding possible sources of chemical pollutants in the studied site.

2. Materials and methods

2.1. *Study area and sample collection*

Oludeniz is one of the unique lagoons in the world, with a maximum depth of 14 m (Fig. 1). The width and length of the lagoon is ~650 and 1300 m, respectively and the water circulation is provided by a narrow and shallow opening (~60 m wide and maximum depth, 7 m). Geochemical properties of the Ölüdeniz region show that lagoon has a cretaceous housement and the adjacent coast contains high amount of calcium carbonate rocks.

Fig. 1 shows the locations of stations selected for seawater and sediments. Seawater samplings for chemical (pH, DO, nutrients and chlorophyll-*a* [chl-*a*]) and hydrographic (salinity, temperature) measurements were carried out in October 1999 at a total number of 11 stations (5 sampling points inside, the others outside the lagoon). Sediment samples for heavy metals were collected in February 2002 from 7 locations (S1–7) only inside the lagoon (Fig. 1). The top 3 cm of the surface sediment samples collected with a stainless steel grab sampler were placed in acid-washed nylon bags and closed tightly. Then, they were dried in an oven at 100 °C. The research vessel of Middle East Technical University, R/V BILIM, was used to collect samples from the outside of the

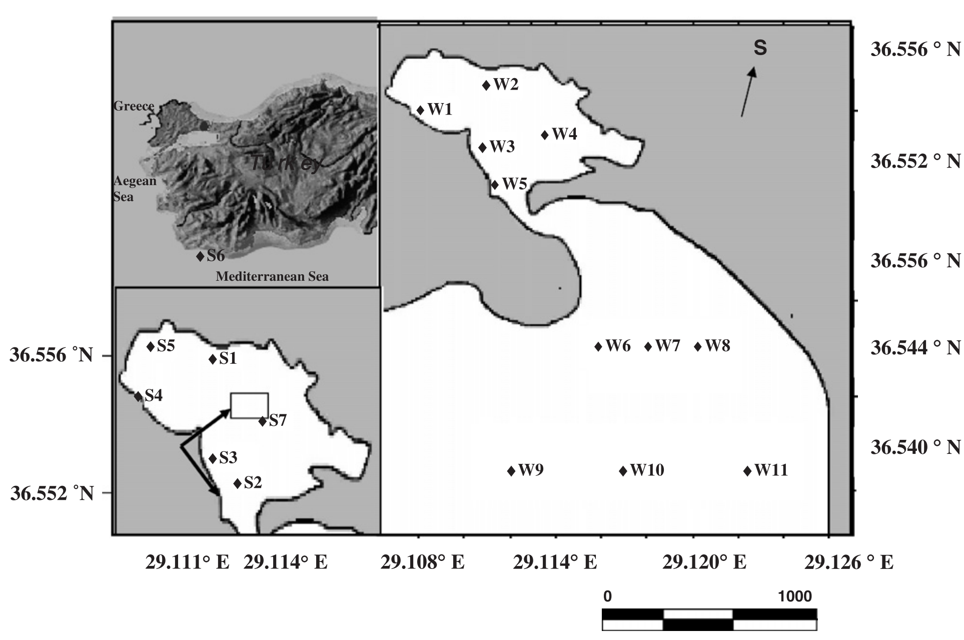

Fig. 1 – Map showing the location of Ölüdeniz Lagoon in NE Mediterranean (left upper). Seawater sampling stations (W1–11) carried out in October 1999 inside and outside of Oludeniz Lagoon (right) and sediment sampling points (S1–7) in February 2000 inside of Oludeniz Lagoon (left down).

lagoon. Water sampling within the lagoon were carried out at selected depths (0.5, 5, 10, 25 m) by a small boat and using special Niskin bottles.

2.2. Sample dissolution

Summary of the sample treatment, analytical techniques and methods followed in this study were as follows: seawater samples for nutrient analysis were just kept cool or frozen until processing. Quantitative measurements of nitrate+nitrite (referred to as nitrate in the text), reactive phosphate and silicate were carried out by colorimetric techniques, using a three channel Technicon AII model auto-analyzer (Hansen and Grasshoff, 1983; Yılmaz and Tuğrul, 1998). chl-*a* containing organic particles in seawater samples were retained on GF/F filters and extracted into acetone. Then Chl-*a* measurements were performed by using a Hitachi F-3000 model spectrofluorometer. DO concentrations of seawater samples were determined by the conventional Winkler titration method having a sensitivity of nearly 3.0 μM after the fixation of oxygen in seawater with oxygen-free chemicals. Salinity and temperature of the seawater were measured in situ using a Sea-Bird Model 19 CTD probe.

Sediments were dried in STUART scientific (252 D) oven at 100 °C and grinded. Digestion of sediment and standard reference material (SRM) samples were carried out as follows: approximately, 0.3 g of the grinded sediment was digested in a microwave oven after the addition of 0.5 ml HF (38–40%) and 4 ml HNO_3 (65%) acid mixture (Sastre et al., 2002). Ethos 900 Milestone Microwave Digestion System was used for the digestion of the sediment and SRMs. The digested samples were diluted to 25 ml with deionized water and stored in acid-washed polyethylene bottles until analysis.

2.3. Analytical methods

Measurements of Al, Fe, Mn, Cr, V, Z and Cu in sediment samples were performed with inductively coupled plasma atomic emission spectrometer (ICP-AES)—Leeman—Direct Reading Echelle. Lead in sediment samples was measured with graphite furnace atomic absorption spectrometer (GF-AAS)—Perkin Elmer 1100 B Model, with HGA 700 Electrothermal Atomizer.

Aqueous standard stock solutions of 100 mg/l (Leeman Labs) and 1000 mg/l (Aldridge Company) were used for the quantification of metals in sediments.

Detection limits (μg/l) of the instruments for the selected metals were as follows: Zn (1.8), Cu (5.4), Mn (1.4), Fe (6.2), V (7.5), Al (45), Cr (7.1) and Pb (0.58).

2.4. Quality assurance

The accuracy of ICP-AES and GF-AAS techniques throughout this work was tested continuously by the SRMs (GSP-2 and STM-1) digested in the acid mixture used for the sediment samples. The measured and certified values for the concentrations of elements in GSP-II and STM-I are given in Table 1. Precision of measurements was better than 5% for both instruments.

Table 1 – Accuracy of the methods

Element	Certified value	Experimental value	% Error
Al (%)	7.88 ± 0.11	8.19	4
Fe (%)	3.43 ± 0.11	3.54	3
Mn (%)[a]	0.17 ± 0.01	0.16	5
Cr (ppm)	20 ± 6.0	23	13
V (ppm)	52 ± 4.0	53	1
Zn (ppm)	120 ± 10.0	125	4
Pb (ppm)	42 ± 3.0	45	7
Cu (ppm)	43 ± 4.0	44	3

[a] STM-I used for Mn, and GSP-II for the other elements.

3. Results

3.1. Principal hydro-chemical properties of Ölüdeniz Lagoon

Salinity and temperature data obtained in October 1999 indicate that the surface water temperature in the lagoon was about 25 °C (Fig. 2a and b) and a seasonal thermocline was formed at about 8 m depth from the surface. Lower salinity values measured in the lagoon surface waters indicate that limited fresh water flow into the lagoon during the dry summer–autumn period slightly reduced the surface salinity of nearshore waters flowing into the lagoon via surface circulations. In other words, the freshwater flux into the Lagoon still exceeds the water loss via evaporation during the dry season. In the central part of the lagoon, where the total depth exceeds 14 m, the hydro-chemical properties of the subhalocline waters were almost similar to the open sea observations, indicating that the ventilation rates have been strong enough to keep the bottom water well oxygenated.

Concentrations of dissolved inorganic nutrients measured in surface waters within and outside of the lagoon exhibit considerable spatial variations in October 1999 (Fig. 3, Table 2). The nitrate and silicate values increase from the open sea to inside the lagoon, due to markedly high nitrate and silicate concentrations but very low phosphate content of unpolluted fresh waters like Lamas stream flowing to NE Mediterranean (Doğan-Sağlamtimur and Tuğrul, 2004). The nutrient data from the Lamas in dry season show that unpolluted fresh waters are rich in nitrate and silicate but very poor in phosphate, yielding very high N/P ratios but nitrate/silicate ratios of nearly 1. The streams in Ölüdeniz region also look like Lamas stream which is short and have low flow rate. Thus phosphate input from freshwater sources is very limited and concentrations were as low as 0.02–0.03 μM within the Lagoon, rising slightly to levels of 0.04–0.06 μM in the nearshore surface waters of the open sea.

Rain water in the NE Mediterranean coastal region contains high nitrate but low phosphate concentrations yielding very high N/P ratios (Markaki et al., 2003), similar to the clean stream waters. It appears that unpolluted fresh and coastal seawater ecosystems such as Ölüdeniz Lagoon on NE Mediterranean coast are fed by nitrate-rich fresh water during

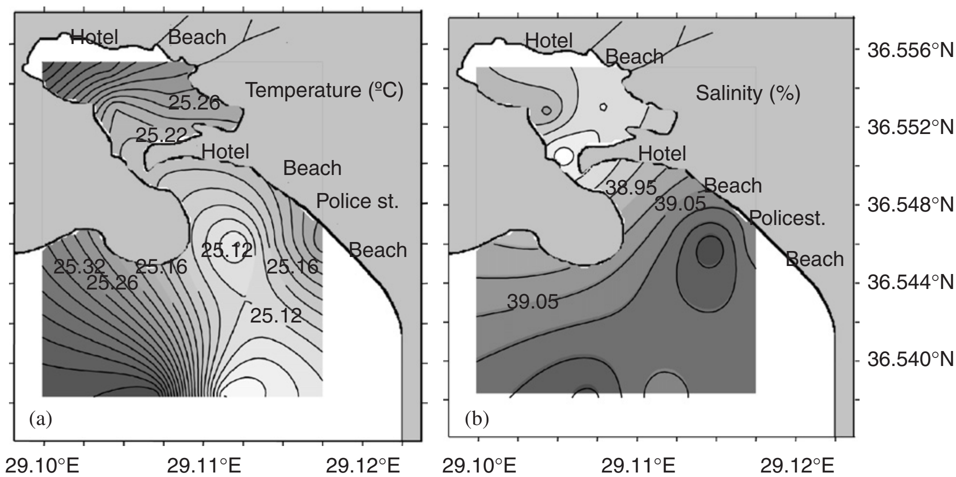

Fig. 2 – (a) Spatial variations of temperature (°C) and (b) salinity in surface waters around the Ölüdeniz Lagoon in October 1999.

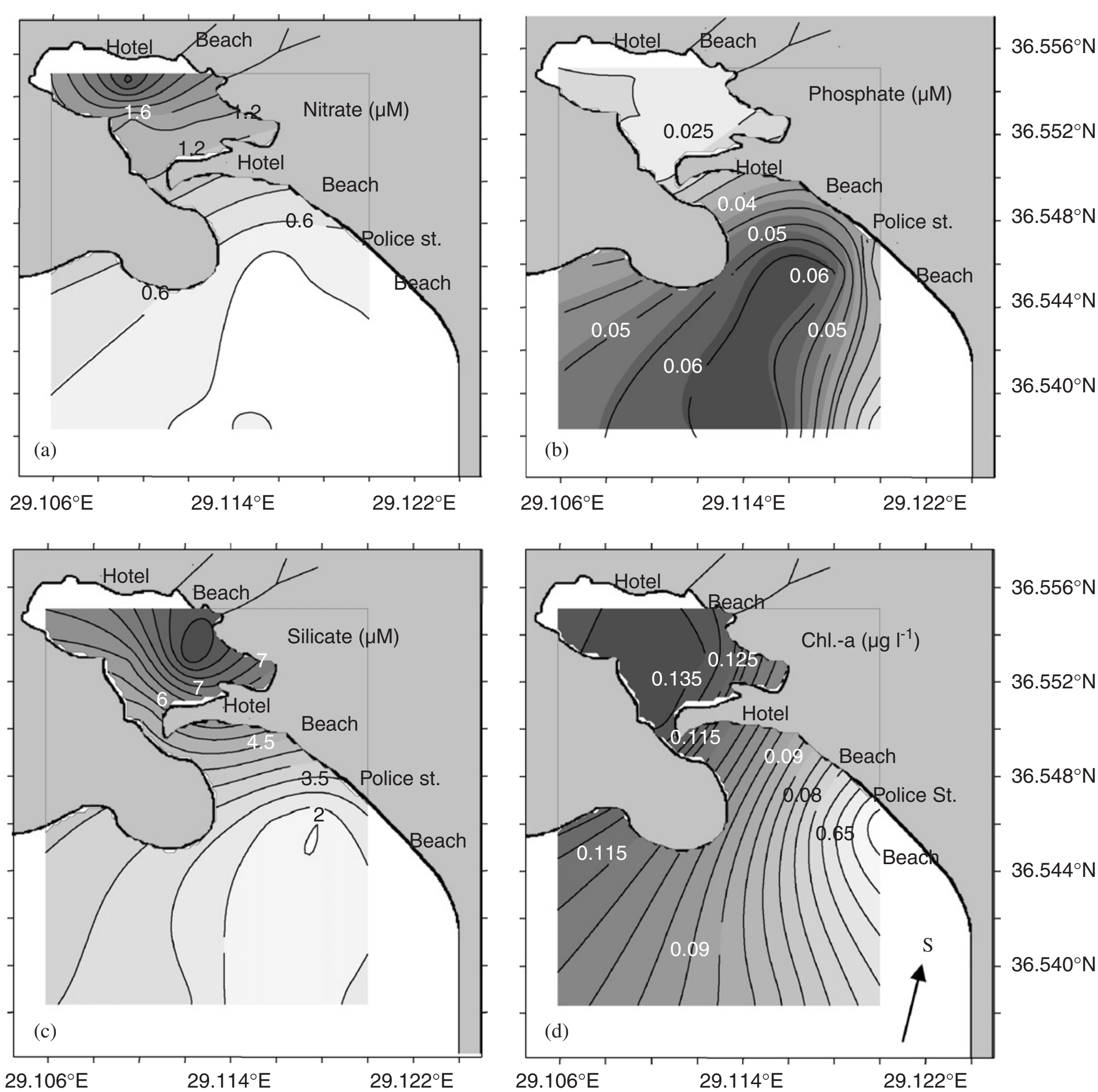

Fig. 3 – Distributions of nutrients (nitrate, phosphate and silicate) and chlorophyll-*a* concentrations inside and outside of the Oludeniz Lagoon (values are the mean of 0–10 m depths).

Table 2 – Hydrochemical parameters in surface water of Ölüdeniz Lagoon

Sampling points	Salinity	T (°C)	pH	DO (μM)	NO_3^- (μM)	PO_4^{3-} (μM)	N/P	SiO_2 (μM)	Chlorophyll-*a* (μg/L)
Inside									
W1	38.9	25.5	8.22	215	2.56	0.03	85.33	7.46	0.0551
W2	38.9	25.4	8.31	221	3.73	0.03	124.3	9.75	0.0637
W3	39.0	25.2	8.29	217	1.99	0.03	66.33	7.45	0.0541
W4	38.8	25.3	8.30	227	2.02	0.02	101.0	14.3	0.0670
W5	38.7	25.2	8.30	213	1.44	0.02	72.00	5.35	0.0614
Outside									
W6	39.1	25.1	8.35	216	0.45	0.05	9.00	2.42	0.0459
W7	39.2	25.2	8.29	216	0.76	0.06	12.67	1.30	0.0730
W8	39.1	25.3	8.39	215	0.65	0.02	32.50	2.79	0.0597
W9	39.2	25.5	8.38	212	0.64	0.06	10.67	3.69	0.0604
W10	39.1	25.0	8.35	238	0.51	0.02	25.50	1.68	0.0631
W11	39.1	25.1	8.35	215	0.44	0.02	22.00	2.99	0.0665

Table 3 – Comparison of our nutrient data with literature (units in μM)

Parameter	Our data		Küçüksezgin and Pazı (2006)	Yılmaz and Tuğrul (1998)
	Inside lagoon	Outside lagoon	NE Mediterranean	NE Mediterranean
PO_4^{3-}	0.026±0.006	0.038±0.002	0.02±0.0007	0.02±0.01
NO_3^-	2.35±0.87	0.58±0.12	0.16±0.007	0.21±0.23
SiO_2	8.86±3.42	2.48±0.88	1.27±0.04	1.77±0.40
N/P	89.80±23.5	18.72±9.41	10±0.1	10.5

both dry and wet periods of the year. In other words, primary productivity within the Lagoon is primarily limited by biologically available phosphate in ambient waters. Therefore, the lagoon ecosystem is expected to be very sensitive phosphorus-rich wastewater discharges of various origins, as suggested for the entire NE Mediterranean Sea (Markaki et al., 2003).

A close relationship observed between the spatial variations of salinity and nutrients in the surface waters of the lagoon indicates that the nitrate and silicate increases towards the coastline principally originated from freshwater discharges. The nitrate concentrations of surface waters ranged between 1.44 and 3.73 μM within the lagoon, dropping to 0.44–0.76 μM levels outside the lagoon. The *t*-test results indicate a statistically significant difference between the means of the inside and outside concentrations. The silicate concentrations, as high as 5.35–14.3 μM inside the lagoon, declined to 1.30–3.69 μM outside the lagoon. The molar ratio of N/P in the surface water was as high as 60–120 within the lagoon, much exceeding those (9–52) calculated for the near-shore surface waters outside the lagoon. Such large N/P ratios strongly suggest that primary production in the lagoon is mainly limited with the reactive phosphate as proposed for the open eastern Mediterranean waters (Krom et al., 1991, 1992; Yılmaz and Tuğrul, 1998). The deep water of the NE Mediterranean is well known to be relatively poor in orthophosphate, yielding an N/P ratio of about 25, greater than in the deep waters of the oceans (Takahashi et al., 1985). It should also be noted that the N/P ratios given in this report are most probably underestimated because the eastern Mediterranean and thus the lagoon surface waters are very poor in phosphate (between 0.02 and 0.06 μM) and cannot be determined accurately by the conventional automated method (detection limit:0.015 μM). Moreover, phosphate values measured by this method are very likely to include weak acid-labile fractions of dissolved organic phosphate and polyphosphate compounds present in the phosphate-poor Mediterranean surface waters as emphasized by Thomson-Bulldi and Karl (1998). In Table 3, our data is compared with literature in the same study area which supports the above argument.

Subsurface waters of the central lagoon contained very low and almost vertically homogeneous nutrients but saturated levels of DO concentrations as encountered at similar depths of near-shore waters outside the lagoon in October 1999. The regional similarities in the subsurface layer chemistry, together with lower surface salinity values within the lagoon, strongly suggest relatively fast exchanges of the lagoon waters with the open sea and thus relatively short residence time of saline waters within the lagoon.

In October 1999, the representative of dry season in the region, the concentrations of chl-*a* (biomass indicator), displaying insignificant local variations as depicted in Table 2, were very similar to the near-shore water values of 0.37 μg/l. The measurements of very low chl-*a* in the lagoon water having measurable nitrate and silicate concentrations but very low phosphate, suggest P-limited algal production as proposed for the oligotrophic eastern Mediterranean Sea.

3.2. *Metal concentrations in sediment samples*

Average concentrations, standard deviations and ranges of all the measured metals in the lagoon surface sediments are depicted in Table 4. The highest values were recorded for Al, Fe, and Mn, which originate in a large extent from the earth crust. Other metals, Ni, Cu, Cr, V and Pb, which were measured in the lagoon sediments, originate both from natural the anthropogenic sources. The relative abundances of these metals in the lagoon were as follows: Al > Fe > Mn > Cr > V > Zn > Pb > Cu.

Correlation analyses performed on the metal data in the lagoon sediments indicate strong correlations between Al and Cr, Cu, Fe, Mn, V and Zn at 95% confidence level (Table 5), which indicate a similarity in their geochemical source, i.e., weathering of crustal rocks in the drainage area of the Lagoon. Chromium is significantly correlated with iron and zinc ($r = 0.91, 0.94$) while copper is strongly correlated with V, Mn and Fe ($r = 0.71-0.92$) in the lagoon sediments. Therefore, the variation of these metal concentrations shows the same trend from one sampling point to another one. Iron has also a strong correlation with Zn, Mn and V ($r = 0.88 - 0.91$) whereas Mn exhibits a significant correlation with V ($r = 0.96$) and this strongly suggests important associations between the oxide-oxyhydroxides of Fe–Mn and other elements (Ergin et al., 1996).

Table 4 – Basic statistics of the measured concentrations of metals in sediments

Elements	Mean	Minimum	Maximum	s
Al (%)	0.35	0.19	0.75	0.20
Fe (%)	0.34	0.18	0.67	0.16
Mn (ppm)	132	80	209	43
Cr (ppm)	34	21	56	12
V (ppm)	18	12	25	4
Zn (ppm)	15	10	24	5
Pb (ppm)	7	5	10	2
Cu (ppm)	7	5	9	1

Table 5 – Correlation matrix analysis for trace metals in sediments

	Al	Cr	Cu	Fe	Mn	Pb	V	Zn
Al	—	0.93	0.86	0.96	0.92	0.31	0.87	0.82
Cr	0.93	—	0.71	0.91	0.75	0.43	0.70	0.94
Cu	0.86	0.71	—	0.92	0.89	0.43	0.97	0.71
Fe	0.96	0.91	0.92	—	0.90	0.44	0.91	0.88
Mn	0.92	0.75	0.89	0.90	—	0.10	0.96	0.62
Pb	0.31	0.43	0.43	0.44	0.10	—	0.26	0.62
V	0.87	0.70	0.97	0.91	0.96	0.26	—	0.62
Zn	0.82	0.94	0.71	0.88	0.62	0.62	0.62	—

Enrichment factor (EF) given in Eq. (1) was also performed on the metal concentrations of the lagoon sediments. This EF formula is a double normalization of a given element to a marker element in the sample and in the earth crust.

$$(EF_X)_{sample} = \frac{R_{sample}}{R_{crustalaverage}} = \frac{(X/Y)_{sample}}{(X/Y)_{crustalaverage}}. \quad (1)$$

Generally Al is selected as a normalizing parameter because it is a lithophilic element mostly originating from the soil. The ideal case is to use local soil composition in the denominator of the formula (1), but usually local soil composition is not known for the study areas and that is why Mason's (1966) crustal abundances were used in this study.

Ranges and median values of enrichment factors calculated for each metal in the sediments are shown in Fig. 4. Elements in this figure are arranged according to the increasing median enrichment factors, which indicate the increasing contribution of anthropogenic source to the metal content of the lagoon sediments. An EF value of 1 indicates that the given element has principally originated from lithogenic source. However, in order to distinguish anthropogenic inputs from natural sources for a given element, EF estimates should be at least 10 or greater. The EF values calculated for Fe, Pb, Mn, V, Cu, Zn and Cr elements are relatively small (1.62, 1.63, 3.50, 3.66, 3.81, 5.28–8.09, respectively), indicating very limited input from man-made sources. In other words, these elements have not been enriched in the lagoon sediments with respect to their crustal averages. A relatively high EF value of about 8.1 calculated for Cr in the sediment does not indicate a selective man-made source for Cr but selectively Cr-enriched crustal rocks in the drainage area of the Lagoon as recently experienced in surface sediments of the Gulf of

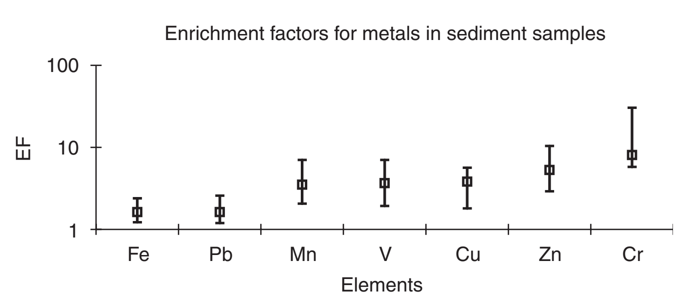

Fig. 4 – Enrichment factors calculated for heavy metals in the Lagoon surface sediments.

Table 6 – Comparison of metal concentrations obtained in the Lagoon sediments with those found in the other seas and some average rocks

References	Fe (%)	Al (%)	Mn (ppm)	Cu (ppm)	Cr (ppm)	Zn (ppm)	V (ppm)	Pb (ppm)
(1) This study	0.34	0.35	134	7	35	16	18	7
(2) Iskenderun Gulf	0.42	4.4	606	23	250	74	Nd	26
(3) Mersin Bay	5.3	7.5	1103	42	551	107	Na	Nd
(4) Eastern Aegean Shelf	0.5–5.7	Nd	103–2625	3–77	9–312	19–62	Na	Nd
(5) Marmara Sea Shelf	1.7–5.1	Nd	307–2059	4–14	89–186	50–169	Na	31–306
(6) Golden Horn Estuary	2.6–3.8	Nd	333–565	333–3900	242–485	450–8750	Na	124–702
(7) Southern Black Sea Shelf	0.2–4.9	Nd	112–1064	15–82	13–224	24–138	Na	12–66
(8) Basic	3.2–5.9	Nd	285–2159	40–84	124–683	121–318	Nd	2–110
(9) Ultrabasic Rocks	5.0–7.6	0.4–16	700–2600	46–62	500–7000	Na	Nd	Na
(10) Average Shale	4.70	8.0	850	50	100	90	Nd	20
(11) Average Sandstone	0.98	2.5	50	5	35	16	Nd	7
(12)Average Limestone	0.38	0.4	1100	4	11	20	Nd	9
(13) Crustal Average	5.0	8.1	950	55	100	70	Nd	13

(1) This study; (2) Ergin et al. (1996); (3) Shaw and Bush (1978); (4) Ergin et al. (1993); (5) Bodur and Ergin (1994); (6) Ergin et al. (1991); (7) Yücesoy and Ergin (1992); (8.9) Analysis of rocks surrounding the Gulf of İskenderun Aslaner (1973); (10,11,12) Kiratli and Ergin (1996) (13) Mason and Moore (1982); Na = not available, Nd = not detected.

Iskenderun situated in the NE Mediterranean Sea (Ergin et al., 1996).

4. Discussion

According to the findings of the study of Ergin et al. (1996), cretaceous ophiolitic succession (i.e., basic and ultrabasic rocks) represented by the various basic (mainly gabbro, amphibolite, diabase and basalt) and ultrabasic (mainly dunite, harzburgite, and serpentinite) rock comprises a potentially important source of some heavy metals like Cr, besides regional comparisons shows similar Mg, Cr, Ni and Co enrichment in the surface sediments in other parts of the Mediterranean, Aegean and Black Seas, as a result of the seaward dispersal of detrital minerals from nearby ultrabasic rocks.

Rose et al. (1979) and Mason and Moore (1982) have also stated that Mg, Cr and Ni are commonly known to be guide elements of most ultrabasic-basic rocks or their ferromagnesian minerals such as olivine, pyroxene, chromite. Therefore, weathering of average rocks could serve as a primary source for relatively high EF value for Cr in lagoon sediments.

Metal concentrations obtained in sediments from different marine environments are compiled in Table 6. Comparison of data set reveals that Ölüdeniz Lagoon sediments possess relatively low metal concentrations but comparable with the average compositions of crustal rocks and average sandstone. The results presented here show that the elemental distribution in marine sediments can be used as guidance in finding the source rocks.

5. Conclusions

The lower salinity values observed in the lagoon surface waters even in dry autumn period indicates that freshwater inflow to the lagoon compensates the water loss by evaporation. Moreover, the freshwater input appears to increase the concentrations of nitrate, and silicate in lagoon surface waters of the NE Mediterranean origin but have very limited effect on the phosphorus pool of the lagoon water. In other words, the lagoon and the eastern Mediterranean surface waters receive limited inputs of phosphate from various sources, with high N/P ratios as experienced in the eastern Mediterranean (Krom et al., 1992; Yılmaz and Tuğrul, 1998), unpolluted river waters (Doğan-Sağlamtimur and Tuğrul, 2004) and rain waters of the region (Markaki et al., 2003). The present data set indicate oligotrophy in the lagoon during the dry season. It should be emphasized that the phosphate-poor lagoon ecosystem with the present volume and water exchanges with the open sea is very sensitive to chemical discharges of both natural and anthropogenic origins.

Metal concentrations (Al, Fe, Cr, V, Mn, Cu, Cr and Pb) of the lagoon surface sediments are relatively low as compared to the measurements from other seas (Table 6). In addition, relatively small EF values (<10) indicate insignificant metal enrichment in the lagoon sediments, originating principally from weathering of crustal rocks surrounding the lagoon.

Acknowledgments

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