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RESEARCH PAPER

Environmental assessment of heavy metal and organic matter contamination, related to anthropogenic production in Ildır Bay, Eastern Aegean Sea, Türkiye

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Abstract

Ildır Bay, a semi-enclosed bay in the Eastern part of the Aegean Sea, is important in many areas such as fishing, aquaculture and also tourism. Due to these activities, the ecosystem of the bay has been significantly affected anthropogenically. It is not known which activity affects how much the ecosystem. However, the rapid development in the field of aquaculture is remarkable. The main purpose of this study is to describe the organic carbon and heavy metal distribution in sediments of the bay and the changes in the ecological level especially those caused by domestic and aquaculture effluent.

Sediment samples were collected by Gramp Sampler in 2007 at surface and subsurface levels from nine stations in Ildır Bay and one in Gerence Bay. Organic carbon and selected heavy metals were analyzed. Results of analyses showed that the concentrations of some transitional metals (Mn, Ni, Zn, Hg, Cr) and Pb in the sub-surface layers were less compared with surface layers. Significant differences between surface and sub-surface sediments were observed regarding contamination with organic carbon. Differences were also observed all over the bay, ranging from 1.29 to 27.69 mg/g. In addition, metal/organic matter association decreased in comparison with the lower surface layers. Principal Component Analysis supports that a negative trend began in the marine sediment criteria in Ildır Bay.

Introduction

Within the marine ecosystem, marine sediments play a major role as a fundamental and sensitive indicator to monitor the enrichment of contaminants (Larsen and

Jensen 1989). The degree of contamination of organic carbon (OC) and heavy metals from lithogenic or any pollution sources has been indicated and component analysis has been applied by Aksu et al. 1998; Rubio et al.

2001; Simeonov et al. 2001, Santos et al.2005; El Nemr et al. 2006; Pekey 2006; Zhang et al. 2007; Bhuiyan, et al. 2015; Pazı 2011. The distribution of sedimentary organic matter in the marine environment depends on the nutrient content and bio-chemical processes, in the layer of the marine area that receives sunlight, throughout the water column and in the sediments (Tribovillard et al. 1994; Ransom et al., 1998; Duan, 2000). Several studies have discussed cause-effect relationships on organic matter impoverishment or enrichment in the marine environment (Keil and Cowie, 1999; Holmer, 1999, Hedges et al., 1999; Duan 2000, Vetö et al. 2000, Harnett and Devol, 2003, Arnarson and Keil, 2007; Magni et al. 2008; Adalioglu and Caliskan, 2020).

The complexity of marine sediments is the result of several simultaneous factors. These include biological factors, such as the specific role of heavy metals in the physiology of algae, photosynthesis, detrital processes and aerobic or anaerobic respiration; hydrodynamic factors, such as climate, vertical and horizontal circulation, grain-size, geo-chemical factors and formation of inorganic and organic wastes from anthropogenic pollution (Lazzari et al. 2004, Morillo et al. 2004; El Nemr et al. 2006). These studies investigated whether there is a series of factors acting on organic matter content in sediment ecology. Investigation of OC changes is crucial for determining marine pollution caused by domestic and aquaculture effluent, which leads to a change in the nutrient chain of living things.

Although it may seem like an advantage to have many data, it can sometimes be challenging in the decision stages. Principal Component Analysis or PCA is used to reveal the relationship between variable parameters. Ildır Bay is important for tourism as well as for aquaculture production. Contaminated sediment from aquaculture and tourism can have a negative impact on the ecological basin, the people of the gulf and indirectly on human health. Researchers emphasized that aquaculture activities increased rapidly after 2006 and drew attention to the anthropogenic effects in Ildır Bay (Türk Çulha and Karaduman 2020; Basaran et al., 2006). This study was carried out in 2007 and will be an important reference for the rate of change of recently measured data. When this study is examined chronologically, it includes sediment data belonging to the period when the capacity of aquaculture industries began to increase rapidly. It is an important reference for analyzing historical variation in coastal areas, which displayed the first changes in sediment structure.

Materials and Methods

Study Area:

The study was conducted at Ildır Bay, located on (38°18’28’’–38°26′41 N, 26°21′48 E–26°23′46 E) the Eastern coast of the Aegean Sea (Figure 1). The bay covers approximately 40 km of coastline and an area of 134 000 km^2. While the permanent population of the town of Ildır is approximately 34 000, it is estimated that during the summer season (between May and October which is the peak season) the population reaches approximately 500 000 (Kocasoy et al. 2008). The bay is important for tourism and also important for aquaculture production. Contaminated sediment from aquaculture production and tourism may have a negative effect on the ecological basin, on the community of the bay and indirectly on human health.

Sampling and Analytical Techniques:

Sediment samples were collected from 9 stations in Ildır Bay and one sample was collected from the middle part of the station in Gerence Bay (Figure 1) by using a Van Veen Grab Sampler. Two samples were collected from each station. Surface sediment samples at the water interface were taken by carefully scraping and these samples were referred as "surface sediments". A sample was collected from 25 cm below as a second sample and refered to as "sub-surface sediments". Sub-samples were taken for grain size analysis, for heavy metal analysis and for OC analysis. They were dried at 40˚C immediately.

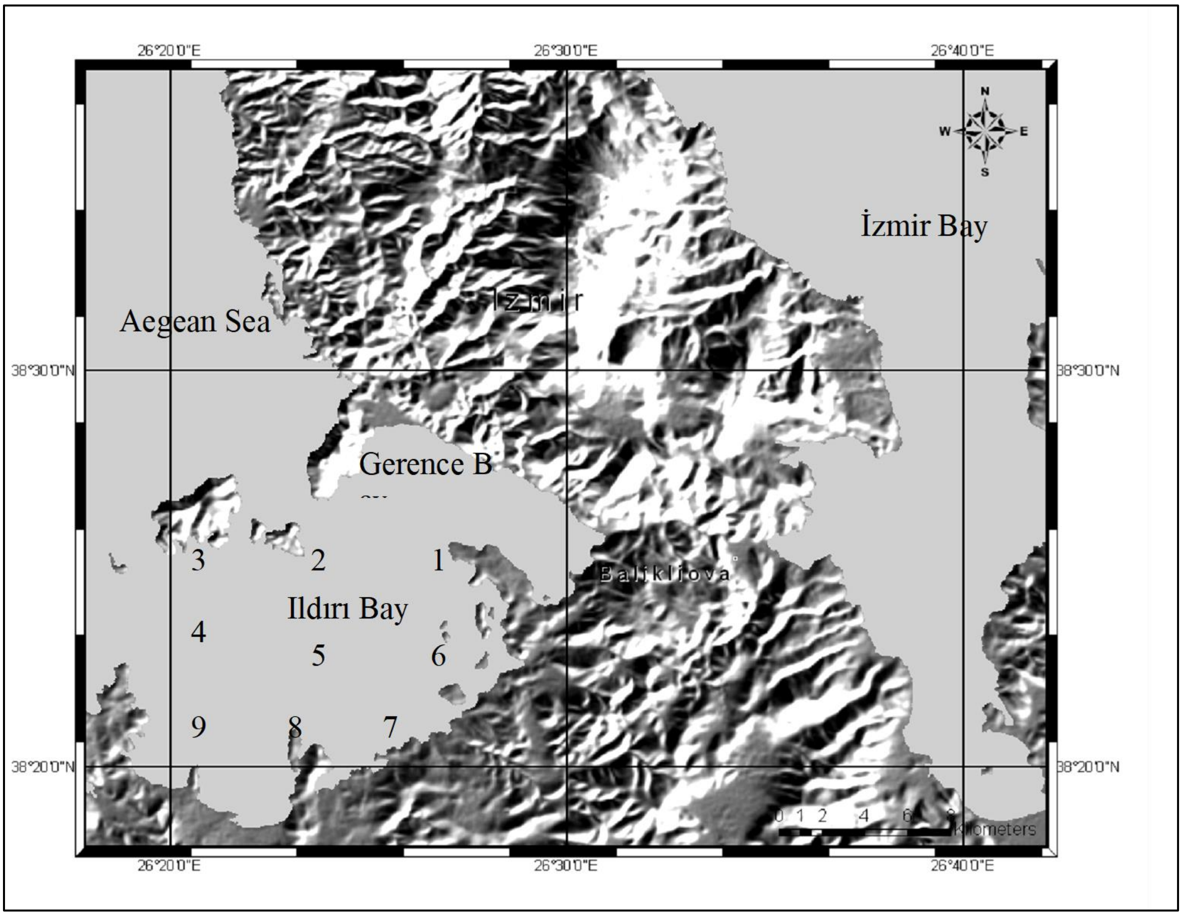

Figure 1. Locations of stations at Ildır Bay

Grain Size Analysis:

Each dried sample was shaken in a shaker with a standard set of sieves for 20 minutes. The collected sieves fractions were weighed. After using a standard sieving technique, hydrometer techniques were also used for the analysis of grain size (Hakanson and Jansson 1983). The textural triangle was plotted to estimate soil classification of the bay according to the proportions of silt, clay and sand.

Heavy Metal Analysis:

Homogenized samples reduced to fine powder (about 60gr) were shipped to the Acme Lab for analysis.

Digested samples were analysed by inductively coupled plasma- mass spectrometer (ICP-MS) analysis (ACME Analytical Labs, Vancouver, BC, Canada), which was used to analyze for concentrations of Fe, Mn, Ni, Cu, Pb, Hg, Cr, Al and As.

In order to determine the enrichment factor, sub-surface data was used as preaquaculture industrial (pi).The enrichment factor was calculated to evaluate the levels of heavy metal pollution. Each metal concentration (C_x) was divided by normalizing element concentration then divided by its pre-aquaculture industrial reference value (eq. 2). Because it is a conservative element, Al was selected as the normalizing element

(Balkis and Cağatay 2001; Odabası et al. 2002; Van der Weijden 2002; Cobelo-Garcia and Prego 2003).

$EF=(C_x/C_{Al})_{surface}/(C_x/C_{Al})_{pi}$ eq1

For the assessment of contamination of sediment, the "degree of contamination" factor was developed and tested by Hakanson (1980) and Kwon and Lee (1998).

$Cf^i = C_e/C_{pi}$ eq2

where C_e is the concentration of the surface element and C_{pi} is the reference value for the pre aquaculture industry element. The meaning of C*f in terms of* Sediment quality according to the sediment quality directive of Sediment quality guidelines (SQG) by USEPA, Perin et al. (1997), if Cf < 1, Quality level "Low contamination factor", if Cf is between 1-3, "Moderate contamination factor", if Cf is between 3-6, "Considerable contamination factor", Cf > 6 is defined as "High contamination factor".

The "degree of contamination", Cd is referred to as the sum of selected contamination factors of various heavy metals for a given base (eq 4)

$Cd = \sum_{i=0}^{n} Cf\mathrm{i}$ eq3

Assessment degrees of contamination depend on Cd. If Cd is lower than the number of selected elements (n) the sediment can be described as having a low degree of contamination; if Cd is between n and 2n, there is a moderate degree of contamination; if Cd is between 2n and 4n, there is aconsiderable degree; and if Cd is bigger than 4n, there is a very high degree of contamination.

Carbon Analysis:

The surface and sub-surface sediments were immediately placed in a polyethylene bag and then stored at low temperature until arrival at the laboratory. Whole samples were dried in an oven at 40 °C. To achieve a constant weight, samples were homogenized. Organic carbon and nitrogen were analysed by using a Carlo Erba 1108 elemental analyser with a combustion method to convert the sample elements to CO_2, H_2O, and N_2 gases.

Sediment samples weighing approximately 10 g were kept in a precleaned porcelain jar. 0.20-0.40 g of these samples were placed directly in a tin capsule. Total carbon and total nitrogen were determined by using a Carlo Erba, EA-1108 model CHN analyser (Quality Assurance Pilot Study Selected Methods, 1996). The other part of the samples was treated with 10ml of 2N HCl in order to remove inorganic matter. Then, samples were dried at approximately 40-50 °C. Each sample was carefully placed in a tin capsule, and then OC and ON contents of the samples were determined quantitiavely using a CHN analyser. Inorganic carbon (IC) can be calculated directly by determining the difference between total carbon (TC) content and organic carbon (OC) content, as in eq 5.

TC=OC+IC eq4

The samples of organic matter supply in the sediment layers varies depending on the samples characteristic structure of the region (Aure and Dahl, 1994). for comparison, normalized organic carbon would be a more accurate approach. Normalised Total Organic carbon (TOCN) values are normalised OC following EPA standards for classification based on environmental quality criteria. Normalization was performed to correct artefacts in samples based on grain size of each sample and samples with large average grain sizes. (Molvær et al., 1997;).

TOCN=OC+18(1-F), eq5

where TOCN is normalised OC, and F is silt/clay fracion (%) (less than 0.063 mm).

Statistical Analysis:

In addition to basic statistical anayses (such as minumum maximum and average) Principal Component Analysis (PCA) was also performed. In order to perform PCA analysisOrganic Matters and 10 metal elements data were selected. Sampling adequacy criteria were controled by PCA compliance test. In the analysis made by examining all the data, the unrelated or irrelevant main components were removed and the relationship graphs were drawn as surface and subsurface. The aim was to reduce the coefficients of unimportant variables and to make the results more meaningful. In the PCA Analysis, the eigenvalue of both components was greater than 1. When it is greater than 1, the result of principal component analysis is considered as significant (Garizi et al., 2011).

Results

Grain Size:

The geographic distribution of sand, silt and clay in Ildır Bay surface and sub-surface sediments is shown in Figure 2. Silty sands and sandy-silts occur in all regions of the bay. Northern stations 1,2,3 and 10 were silty (60-90 %), while stations 4,5,6,7,8 and 9 were sandy (70- 80 %). These distributions are similar in both surface and sub-surface sediments.

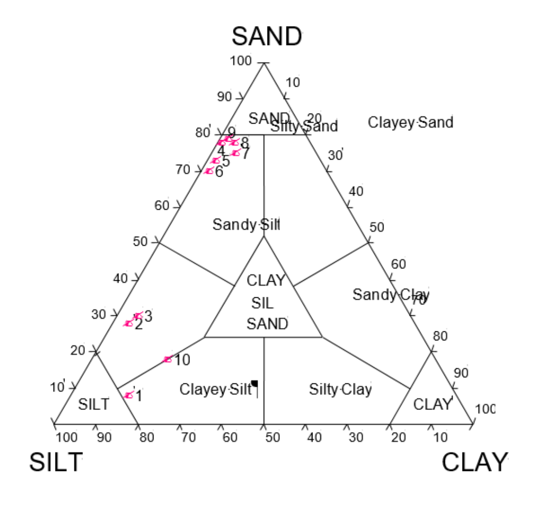

Figure 2. Geographic distribution of sand, silt and clay in Ildır Bay

Heavy Metal Content:

Heavy metals, such as Fe, Mn, Ni, Cu, Zn, Pb, Hg, Cr, Al and As were analysed in both surface and sub-surface sediments. Heavy metal concentrations at the surface varied from 1.514% to 8.166% for Fe, 289.823–1,073 mg/kg for Mn, 27.605–65.145 mg/kg for Ni, 10.552–22.587 mg/kg for Cu, 1.131-2.753 % for Al, 33.498–66.262 mg/kg for Zn, 17.696–73.868 mg/kg for Pb, 77.359–517.965 mg/kg for Hg, 40.424–107.793 mg/kg for Cr, 8.71-21.05 mg/kg for As.

Sub-surface sediment concentrations varied from 1.342 % to 7.926% Fe, 242.388–1,010.9 mg/kg for Mn, 34.419–47.461 mg/kg for Ni, 9.564–17.94 mg/kg for Cu, 1.134-2.658 % for Al, 30.198–88.752 mg/kg for Zn, 14.666–76.459 mg/kg for Pb, 74.030–493.593 mg/kg for Hg, 34.96–101.092 mg/kg for Cr, 6.71- 19.5 mg/kg for As.

Sta_4 had higher heavy metal concentrations than the other stations (Table 1). Among the elements the highest concentrations of Fe, Mn Zn, Hg Cr, Al, Pb and As were found. However, Cu and Ni were observed lower in Sta-4 station than others.

Ef in the sediments of Ildır Bay were calculated as between 1-1.2. Only Gerence and station 9 are between 1.4 and 1.9. (Figure 3). The Cf values for the sediment samples and classification from Ildır Bay is generally low according to the Hakanson (1980) classification. However, the metal contaminations in the sediment of only two stations studied (sta_1 and sta_9) show that very slight increases were observed in the heavy metal between surface and sub-surface sediments. Cf value indicates that station 9 was slightly contaminated with Cu, Ni, Zn and Mn and that station 1 was slightly contaminated with Cu and As. It is known that the exchange of metal in areas where biological activity is intensive is slower than in areas where industrial activities are intensive. Metal enrichment and contamination factors indicate that there is no significant difference in heavy metal concentration and grain size between the surface sediment and the sub-surface sediment, but a slight increase is observed. This area is not yet under the influence of human-induced activities. For this reason, we do not observe sharp differences in sediment classification.

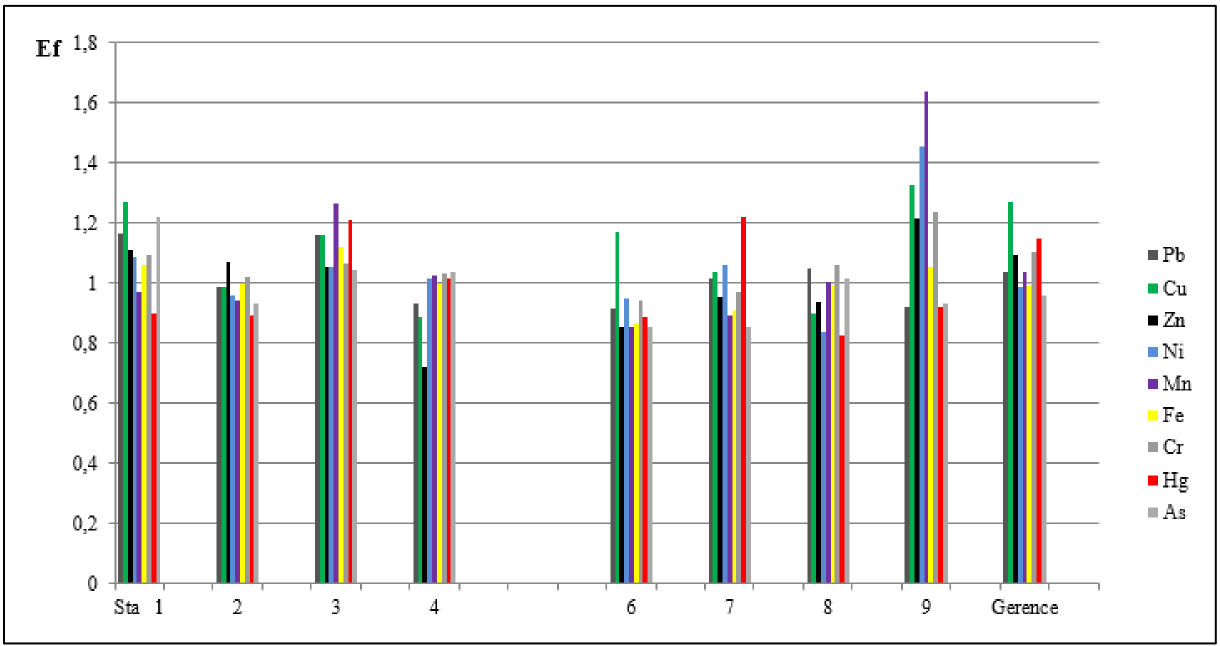

Figure 3. Enrichment Factor EF in stations

Table 1. Comparative table of the maximum concentration of heavy metals, between sta-4 and otherstations.

	Fe%	**Mn** mg/kg	**Zn** mg/kg	**Hg** mg/kg	**Cr** mg/kg	**Al%**	**Cu** mg/kg	**Pb** mg/kg	**Ni** mg/kg	**As** mg/kg
In text Sta-4 Max. conc	8.17	1073.26	88.75	517.97	107.79	2. 75	17.94	76,46	49,93	210.45
Max conc of other stations	4.36	955.77	70.42	75.42	97.48	2.032	22.58	51.79	65.14	60.75

Organic Matter:

Sedimentary carbon concentrations are shown in Table 2. TC concentration in surface sediments ranged from 20.11 to 34.98 while TC concentration in sub-surface sediments ranged from 1.30 to 21.18. OC concentrations of the bay ranged from 1.29 to 27.69 mg. C g^{-1}. Analyses showed that the range of TC concentrations in surface and sub-surface sediments along the south-west (sta-8 and sta-9) coastline of the bay was relatively high due to the effect of anthropogenic wastes over a long period of time. At the eastern part of the bay at sta-1, TC in surface sediments was generally higher than in sub-surface sediments, the station being near the tuna farms, where there are 50 m diameter polyethylene cages with a 400t/year capacity.

Table 2. Statistical analysis of sedimentary nitrogen and carbon at surface and sub surface

Sediment type		TN (mg/g)	TC (mg/g)	ON (mg/g)	OC (mg/g)	Normalised OC (mg/g)
Surface	Standard dev.	0.06	5.47	0.04	8.76	8.85
	Average	0.08	27.53	0.05	13.98	25.94
	Min.	0.03	20.11	0.01	1.69	13.62
	Max.	0.23	34.98	0.14	27.70	41.44
Sub-surface	Standard dev.	0.05	8.14	0.02	4.39	8.80
	Average	0.09	20.23	0.04	7.74	18.49
	Min	0.03	7.34	0.01	1.30	5.47
	Max	0.15	31.99	0.06	15.58	33.58

OC concentrations in surface sediments were generally higher than those from sub-surface sediments (Table 3). Sta-5 had the highest values for OC (41.45 mg g^{-1}) for surface sediments. The surface concentrations of OC were greater than the sub-surface concentrations except for sta-8 and sta-9. The ratio between surface and sub-surface sediments was highest at sta-1. Sediments are classified in Table 3 as excellent , good, intermediate, poor and very poor, based on the SFT criteria (Molvær et al., 1997).

Table 3. Classification for Ildır Bay sediment environmental quality, by using normalised TOCN contents based on (SFT criteria) (Molvær et al., 1997) and contamination rate between surface and sub-surface.

Ist		Normalised OC (mg/g)	Cr_OC	Classification*
sta_1	surface	29.18	5.34	intermediate
	sub-surface	5.47		excellent
sta_2	surface	26.13	1.60	good
	sub-surface	16.31		excellent
sta_3	surface	13.62	2.07	excellent
	sub-surface	6.59		excellent
sta_4	surface	15.83	1.02	excellent
	sub-surface	15.51		excellent
sta_5	surface	41.44	1.23	very poor
	sub-surface	33.58		intermediate
sta_6	surface	35.62	1.82	poor
	sub-surface	19.52		excellent
sta_7	surface	26.98	1.15	good
	sub-surface	23.53		good
sta_8	surface	23.15	0.98	good
	sub-surface	23.56		good
sta_9	surface	21.54	0.96	good
	sub-surface	22.39		good
sta_Gerence	surface	32.22	1.01	intermediate
	sub-surface	31.98		intermediate

***** Normalized Oc content <20 mg/g environmental quality classification is determined as "excellent", 20-27 "good", 27-34 "moderate", 34-41 "poor", and >41 "very poor"

Comparison between the coastal zone stations and the offshore stations shows that the coastal zone stations have higher OC concentrations than the other stations. However, Figure 4 shows that normalised TOCN concentration changes were observed between surface and sub-surface sediments, and the classification changes were determined at sta-6. Comparison between the degree of TOCN contamination shows that the enrichment is dominant at stations 1, 6, 2, 5 respectively.

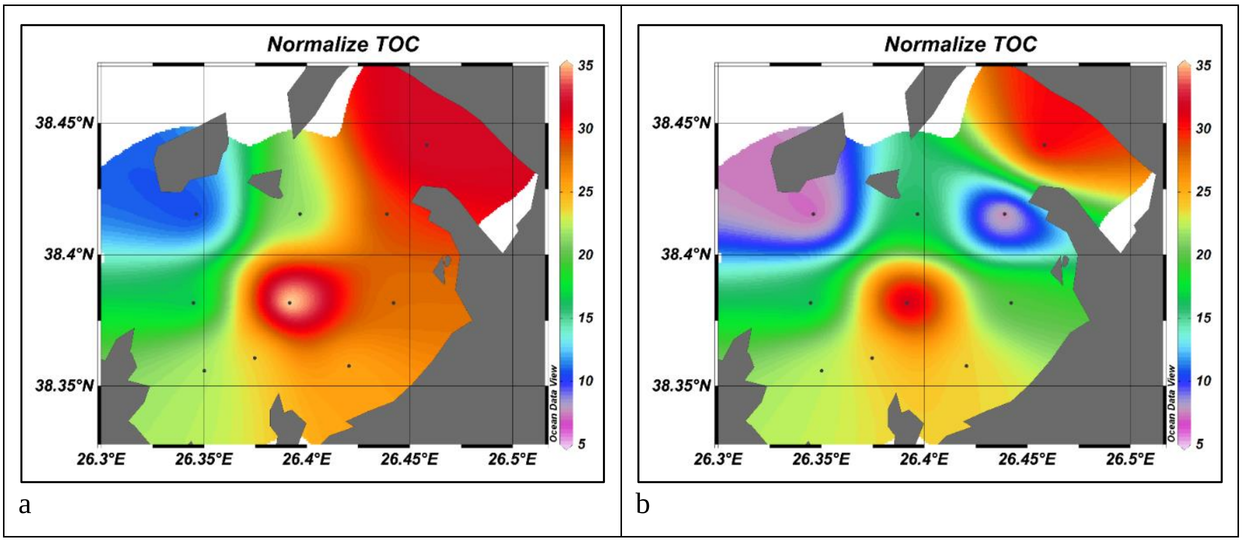

Figure 4. Normalized OC (mg/g) in surface sediments(a) and sub-surface sediments(b)

The factor analysis performed produced a linear combination of heavy metal and organic and inorganic nutrient all data for Ildır Bay, which is responsible for identifying the variables that characterize the overall assessment of the observation (Table 4). The values shown in bold in the table indicate that the correlation is at an acceptable level. The results showed that a strong correlation was observed between heavy metals. Of these elements, Pb, Mn, Zn, Fe and Ca show a remarkable dependence. Also, the increase in Pb, Cu and Mn at station 9 is much higher than at other stations. (Figure 3).

No significant relationship was observed with OC. Similarly, when two different sediments were handled as separate groups in factor analysis, Data matrices are divided into surface and subsurface normalized OC+ON. Especially Cu and Zn values were different from each other (Table 5). Descriptive statistical data also given at Table 6. More associations were observed in the underground area. The results show that the PCA performed with the raw data without normalization also showed that the relationship OC, ON and Cu on the surface was negative (Figure 5).In other words, these data changes draw attention regardless of elemental change.

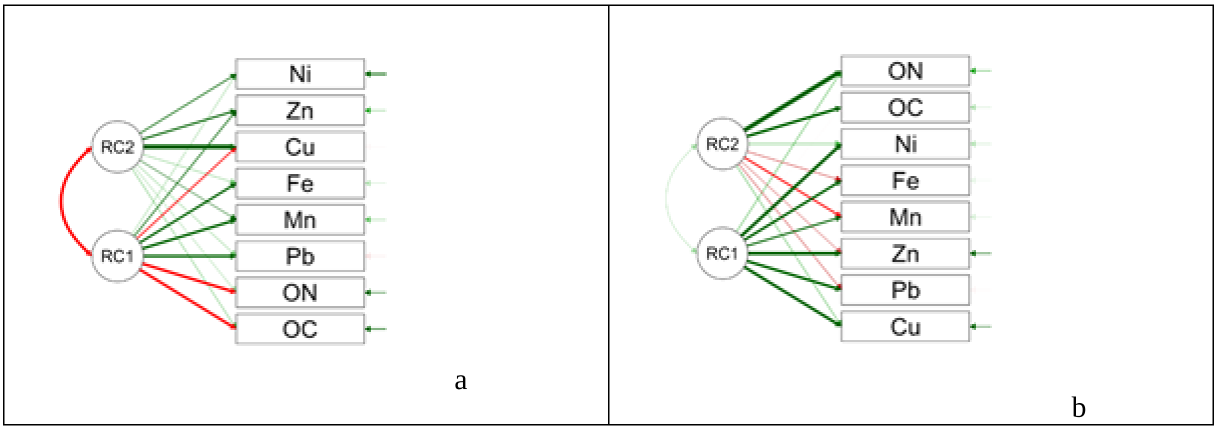

Figure 5. Principal Component Analysis diagram of surface(a) and subsurface (b) with relationship between the data of some metal elements and organic nitrogen and organic carbon. The color of the arrows indicates the direction of the factor (red is negative direction, green is positive direction) and the thickness indicates the load of the factor. The amount of error shown next to each element is at an acceptable level.

Table 4. Results of relationship between organic Mater (OC+ON) and heavy other elements. Bold print indicates correlations higher than 0.5

	TC	**TN**	**OC**	**ON**	**Cu**	**Pb**	**Zn**	**Ni**	**Co**	**Mn**	**Fe**	**As**	**Ca**	**P**	**Mg**	**Al**	**Hg**	**Se**
TC	1.00																	
TN	0.16	1.00																
OC	**0.97**	0.00	1.00															
ON	**0.71**	0.08	**0.65**	1.00														
Cu	**0.54**	**0.59**	0.44	0.24	1.00													
Pb	-0.27	**0.76**	-0.40	-0.50	0.20	1.00												
Zn	-0.20	**0.58**	-0.35	-0.44	**0.63**	**0.68**	1.00											
Ni	-0.31	0.12	-0.32	-0.37	**0.55**	0.09	**0.73**	1.00										
Co	-0.74	0.15	**-0.83**	**-0.69**	0.07	0.49	**0.78**	**0.71**	1.00									
Mn	**-0.52**	**0.59**	**-0.61**	**-0.65**	0.35	**0.80**	**0.89**	**0.65**	**0.84**	1.00								
Fe	**-0.51**	0.48	**-0.63**	**-0.71**	0.12	**0.88**	**0.82**	0.37	**0.81**	**0.88**	1.00							
As	-0.32	**0.78**	-0.43	**-0.55**	0.28	**0.98**	**0.75**	0.26	**0.57**	**0.89**	**0.88**	1.00						
Ca	-0.40	**0.71**	**-0.50**	**-0.61**	0.16	**0.98**	**0.70**	0.21	**0.59**	**0.87**	**0.90**	**0.99**	1.00					
P	-0.24	**0.82**	-0.38	-0.46	0.33	**0.99**	**0.76**	0.22	**0.53**	**0.85**	**0.87**	**0.99**	**0.98**	1.00				
Mg	-0.39	**0.71**	-0.49	**-0.62**	0.36	**0.91**	**0.84**	0.48	**0.69**	**0.96**	**0.89**	**0.97**	**0.96**	**0.95**	1.00			
Al	0.41	**0.65**	0.25	0.01	**0.89**	0.49	**0.81**	0.47	0.28	**0.52**	0.48	**0.53**	**0.43**	**0.58**	**0.57**	1.00		
Hg	-0.10	**0.56**	-0.19	-0.35	-0.13	**0.86**	0.24	-0.42	0.10	0.39	**0.63**	**0.75**	**0.79**	**0.77**	**0.58**	0.20	1.00	
Se	-0.01	**0.83**	-0.13	-0.37	**0.67**	**0.84**	**0.87**	0.47	0.48	**0.85**	**0.75**	**0.90**	**0.84**	**0.91**	**0.92**	**0.81**	**0.52**	1.00

Table 5. Results of relationship between organic Mater (OC+ON) and heavy other elements. Bold print indicates correlations higher than 0.5

	Surface OC+ON	Sub-surface OC+ON
Mo	-0.146	**0.801**
Cu	0.259	**0.829**
Pb	-0.333	0.335
Zn	0.028	0.306
Ni	-0.305	0.459
Co	-0.319	0.127
Mn	-0.292	0.138
Fe	-0.306	0.0685
As	-0.412	0.076
Ca	-0.269	0.412
P	-0.315	0.324
Mg	-0.285	0.469
Al	-0.087	**0.512**
Na	-0.018	0.469
K	-0.207	0.393
Se	-0.320	**0.5849**

Table 6. Descriptive statistics elements

	Count of Sample (N)	Mean	Std. Dev.	Minimum	Maximum
Fe %	18	2.944	2.035	1.342	8.166
Mn (mg/kg)	18	539.811	291.778	169.014	1073.262
Zn (mg/kg)	18	49.951	15.497	30.198	88.752
Hg (mg/kg)	18	187.421	133.665	74.030	517.965
Cr (mg/kg)	18	61.061	22.841	34.960	107.793
A l%	18	1.670	0.483	1.131	2.753
Cu (mg/kg)	18	14.889	4.009	9.564	22.587
Pb (mg/kg)	18	35.590	18.463	14.666	76.459
N i(mg/kg)	18	42.566	7.597	27.605	65.145
As (mg/kg)	18	50.245	59.371	6.711	210.453

Discussion

The metal contaminations in the sediment at the station locations show no considerable differences in heavy metal and grain size between surface and sub-surface sediment. Some local anomalies were observed near the mouth of south side of the Karaada Island area but there were no significant differences between surface and sub-surface values. This should be due different functions of the chemical composition of the rocks and water circulation. This situation coincides with the study that chose the province of Ildır as a reference, considering that there is no residential and industrial area abd this islands is quite far from human influence (Tunca et al. 2018).

Heavy metal rank and some metal concentrates at station 4 were higher than other stations. Many speculations can be made as to why. It may be that a different geological structure was encountered. Or, this area has been exposed to point heavy metal pollution. However, the enrichment factor and the amount of organic matter in the environment do not give us any supporting information about pollution. In future studies, it is recommended to examine the sediment samples and the algae structure together. Because algae are the best biomarkers of bioaccumulation (Cadar et al. 2019, Boutahar et al. 2021). The metal contaminations in sediments of only two stations (sta_1 and sta_9) studied show that slight increases were observed in the heavy metal between surface and sub-surface sediments. However, the increase in Pb, Cu and Mn at station 9 in Figure 4 is much higher than at other stations. In contrast to the heavy metal composition, significant differences in organic matter were observed in the surface sediments in terms of OC contamination across the Gulf. When the factor analysis and metal enrichment factor analysis are compared, it can be said that the increase in organic matter is not compatible with the increase in metal, especially with Cu, Mn and Zn. This is due to the fact that the structure of the Bay in general is very different. It is likely that Cu and Zn have generally entered as aquatic farm nutrient feed. Considering this situation, the metal enrichment in station 9 is not surprising. While samples taken from Gerence Bay and the 2 samples taken from the middle part of Ildır Bay show a serious antropogenic effect, particularly in OC differences, the rise in OC observed at the other stations shows that the antropogenic effect in the bay has begun but it is still at a minimal level. The range of OC concentrations in surface sediments is greater than in subsurface sediments. Nutrient enrichment experiments were carried out in the Gerence Bay, which is an inner gulf located in the Bay of Ildir, and it was determined that the microalgae dynamics in the bay are quite sensitive (Adalioglu et al, 2013). In proportion to the increase in aquaculture activities in the bay, the increase in the amount of OCN observed in this study also predicts a dangerous course for the ecosystem.

Although, there is only one station from the middle and deepest point of Gerence Bay, the area around Ildır and Gerence Bays provides an example of typical different Aegean coasts. Gerence Bay is the only water exchange with the Aegean Sea through the mouth of neighbouring Ildır Bay which also exchanges with the Aegean Sea through the mouth of the north and south side of Karaada Island. Gerence Bay has a maximum depth of 65 m and is connected to Ildır Bay with a depth of 20-40 m. This topography, may not allow for the movement of particulate matter in the sediment to the adjacent bay. The OC concentration measured in Gerence Bay are higher than the OC concentrations measured in Ildır Bay. The results of the analysis carried out show that the environmental kinetics were rather sensitive towards changes at the mouths of Gerence and Ildır Bays. The results of the microplankton bio-assay conducted by Adalıoglu et al. (2013) also support the sensitive structure against anthropogenic pollution in Gerence.

Comparison between the coastal zone stations and the offshore stations shows that the coastal zone stations have higher OC concentrations than the other stations which indicates significant contamination and critical anthropogenic pollution in the coastal zone of Ildır Bay. Although classification changes were not observed in the whole bay, the observation of concentration changes between surface and sub-surface is an important indication of the beginning effects of anthropogenic pollution such as those resulting from insufficient domestic treatment plants and from aquaculture.

Results that were more significant below the surface were obtained from factor analysis. However, the increase in organic matter on the surface and the incompatibilities caused by the interaction of some metal elements with organic matter can be discussed. Many enzyme activities and products of organisms living in marine sediments change depending on changes in environmental conditions (pH, temperature, etc.). Redoxactive metals such as Fe, Mn, Zn are important elements for the organism. The increase of the organism in the ecosystem can produce different intermediates in its biogeochemical cycle.

Although the contaminant levels have not yet reached the eutrophic class for marine sediment, the increasing concentration of organic matter showed at moderate ecological risk for Ildır Bay.

Kucuksezgin et al. (2022) maintained EF between 1-3 in the same region. They also observed TN as 0.34-1.13 mg/g. However, in this study, data between these values could not be obtained at any station. TN values are maximum 0.23 mg/g. The average of the stations (0.08 mg/g) is quite low. A similar situation can be said for metals. For example, the EF value of Mn was found to be 1.64 only in sta 9. It is mostly around 1-1.2. Kucukksezgin et al. (2022) interpreted as an uncontaminated area for Ildır Bay, the change in the process seems to be rapid.

Conclusions

The fuel leaking from the ridge formed in the torso of the "M / V Lady Tuna" on the rocks of İzmir's Çeşme district spread over a wide area and reached the coast of Ildır Bay in 2016. That fuel is leaking into the sea. This study is an also evaluation made before the M / V Lady Tuna ship accident. This study also will provide an opportunity to compare the results of environmental impact assessment and analysis in the future.

As a result, various abiotic factors greatly change the biogeochemical structure of the region. For this reason, this study, which includes a recent study, should be updated, compared and analyzed in order to prevent constructions above the carrying capacity of the region and to provide a sustainable ecosystem.

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Ethical approval

The author declares that this study complies with research and publication ethics.

Data availability statement

A data availability statement should be provided here. An example: The authors declare that data are available from authors upon reasonable request. In case of unavailable data due to conditionals of funding organizations, etc., a clear explanation should be given. The authors declare that data are available from authors upon reasonable request.

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References

Adalıoğlu, S., and Çalışkan, G. (2020). Effect of Nutrient, Light Intensity and Temperature on the Growth Rates and Metabolism of a Stress-Resistant Bacillariophyta – Entomoneis sp. - in Izmir Bay (Aegean Sea). *Mediterranean Marine Science, 21*(1), 1-10. doi:https://doi.org/10.12681/mms.19439.

Adalıoğlu, S., Buyukisik, B., Yasar, D. (2013). Microplankton growth in response to nutrient enrichments in Gerence Bay, Izmir, Western Turkey. *Indian J. Mar. Sci*. 42, 859–867.

Aksu, A. E., Yasar, D., & Uslu, O. (1998). Assessment of marine pollution in Izmir Bay: Heavy metal and organic compound concentrations in surficial sediments. *Translations and Journal of Engineering and Environmental Science*, 22, 387–415.

Arnarson, T., and Keil, R. (2007). Changes in organic matter–mineral interactions for marine sediments with varying oxygen exposure times. *Geochim. Cosmochim. Acta* 71, 3545–3556.

Aure, J., & Dahl, E. (1994). Oxygen, nutrients, carbon and water exchange in the Skagerrak Basin. Continental Shelf

Research, 14(9), 965–977. https://doi.org/10.1016/0278-343(94)90059-0.

Balkis N, Cağatay M.N. (2001) Factors controlling metal distributions in the surface sediments of the Erdek Bay, Sea of Marmara, Turkey, *Environment International*, Volume 27, Issue 1, July 2001, Pages 1-13.

Basaran, K. A., Aksu M., & Egemen Ö. (2006). Ildır koyu"nda (Izmir-Ege Denizi) açık deniz ağ kafeslerde yapılan balık yetistiriciliğinin su kalitesi üzerine etkilerinin izlenmesi. *Tarım Bilimleri Dergisi*. 13 (1) 22-28.

Bhuiyan, M.A.H., Dampare, S.B., Islam, M.A. (2015) Source apportionment and pollution evaluation of heavy metals in water and sediments of Buriganga River, Bangladesh, using multivariate analysis and pollution evaluation indices. *Environ Monit Assess* 187: 4075.

Boutahar L., Espinosa F., Sempere-Valverde J., Selfati, H. Bazairi M. (2021) Trace element bioaccumulation in the seagrass *Cymodocea nodosa* from a polluted coastal lagoon: biomonitoring implications. *Mar. Pollut. Bull*., 166, Article 112209.

Cadar E., Sirbu R., Negreanu P.B., Ionescu A.M., Negreanu P.T. (2019) Heavy metals bioaccumulation capacity on marine algae biomass from Romanian Black Sea Coast, *Rev. De. Chim*., 70 (2019), pp. 3065-3072.

Cobelo-Garcıa, A., and Prego, R. (2003). Heavy metal sedimentary record in a Galician Ria (NW Spain): Background values and recent contamination. *Marine Pollution Bulletin*, 46, 1253–1262.

Duan, Y. (2000) Organic geochemistry of recent marine sediments from the Nansha Sea, China. Org. *Geochem*. 31, 159–167.

El Nemr, A., Khaled, A., & El Sikaily, A. (2006). Distribution and statistical analysis of leachable and total heavy metals in the sediments of the Suez Gulf. *Environmental Monitoring and Assessment*, 118, 89–112.

Garizi, A. Z., Sheikh, V., & Sadoddin, A. (2011). Assessment of seasonal variations of chemical characteristics in surface water using multivariate statistical methods. *Int. J. Environ. Sci. Tech*, *8*(3), 581–592.

Hakanson, L. (1980). Ecological risk index for aquatic pollution control, a sedimentological approach. *Water Research*,14, 975–1001.

Hakanson L. & Jansson M. (1983). Principles of Lake Sedimentology. *Springer*-Verlag, Berlin.

Harnett, H., Devol, A., (2003). Role of strong oxygen-deficient zone in the preservation and degradation of organic matter: a carbon budget for the continental margins of northwest Mexico and Washington State. *Geochim*. *Cosmochim. Acta* 6 (2), 247–264.

Hedges, J.I., Hu, F.S., Devol, A.H., Hartnett, H.E., Tsamakis, E., Keil, R.G. (1999). Sedimentary organic matter preservation: a test for selective degradation under oxic conditions. *Am. J. Sci*. 299, 529–555.

Holmer, M. (1999). The effect of oxygen depletion on anaerobic organic matter degradation in marine sediments. *Estuar. Coast. Shelf Sci.* 48, 383–390.

Keil R.G. and Cowie G.L. (1999). Organic matter preservation through the oxygen-deficient zone of the NE Arabian Sea as discerned by organic carbon: mineral surface area ratios *Mar. Geol.*, 161, pp. 13-22, 10.1016/S0025-3227(99)00052-3.

Kocasoy, G., Mutlu, H.I. and Alagoz, B.A.Z. (2008) Prevention of marine environment pollution at the tourism regions by the application of a simple method for the domestic wastewater. *Desalination.* 226(1-3), 21-37.

Kucuksezgin, F., Pazi, I. & Gonul, L.T. (2022). Environmental impact of fish farming: assessment of metal contamination and sediment geochemistry at three aquaculture areas from the eastern Aegean coast. *Environ Monit Assess* 194, 313 https://doi.org/10.1007/s10661-022-09960-3.

Kwon, Y.T. and Lee, C.W. (1998). Application of multiple ecological risk indices for the evaluation of heavy metal contamination in a coastal dredging area. *Sci. Total Environ*., 214: 203-210.

Larsen B. and Jensen A. (1989). Evaluation of sensitivity of sediment monitoring stations in pollution monitoring. *Marine Pollutions Bull*. 20,556-560.

Lazzari A. De, Rampazzo G., Pavoni B. (2004). Geochemistry of sediments in the Northern and Central Adriatic Sea Estuarine, *Coastal and Shelf Science* 59 429e440.

Magni, P.; De Falco, G.; Como, S. ; Casu,D ; Floris, A. ;Petrov, AN; Castelli, A, Perilli ,A. (2008). Distribution and ecological relevance of fine sediments in organic-enriched lagoons: The case study of the Cabras lagoon (Sardinia, Italy) *Marine Pollution Bulletin* Volume: 56 Issue: 3 Pages: 549-564.

Morillo, J., Usero, J., & Gracia, I. (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, 55, 431–442.

Molvær J, Knutzen J, Magnusson J, Rygg B, Skei J, Sørensen J (1997) Klassifikasjon av miljøkvalitet i fjorder og kystfarvann (Classification of environmental quality in fjords and coastal waters). SFT Guidelines 97:03. TA-1467/1997, 36 pp. (In Norwegian).

Odabası, M., Muezzinoglu, A., & Bozlaker, A. (2002). Ambient concentrations and dry deposition fluxes of trace elements in Izmir, Turkey. *Atmospheric Environment*, 36, 5841–5851.

Pazı I. (2011). Assessment of heavy metal contamination in Candarli Gulf sediment, Eastern Aegean Sea, *Environ. Monit. Assess.*, 174 (2011), pp. 199-208.

Perin G, Bonardi M, Fabris R, Simoncini B, Manente S, Tosi L, Scotto, S. (1997) Heavy metal pollution in central Venice lagoon bottomsediments, evaluation of the metal bioavailability by geochemical speciation procedure. *Environ Technol* 18:593–604.

Pekey, H. (2006). The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. *Marine Pollution Bulletin*, 52, 1197– 1208.

Quality Assurance Pilot Study Selected Methods, 1996. In: Turley, C.M. (Ed.), Handbook of Method Protocols for Quality Assurance Pilot Study of Selected Methods Used in the Mediterranean Targeted Project. Version 2. 34 pp.

Ransom, B., Kim, D., Kastner, M., Wainwright, S. (1998). Organic matter preservation on continental slope, importance of mineralogy and surface area. *Geochim. Cosmochim. Acta* 62 (8), 1329–1345.

Rubio, B., Pye, K., Rae, J. E., & Rey, D. (2001). Sedimentological characteristics, heavy metal distribution and magnetic properties in subtidal sediments, Ria de Pontevedra, NWSpain. *Sedimentology*, 48, 1277–1296.

Simeonov, V., Stanimirova, I., & Tsakovski, S. (2001). Multivariate statistical interpretation of coastal sediment monitoring data. *Fresenius' Journal of Analytical Chemistry*, 370, 719–722.

Santos, I. R., Silva, E. V., Schaefer, C. E. G. R., Albuquerque, M. R., & Campos, L. S. (2005). Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. *Marine Pollution Bulletin*, 50, 185–194.

Tribovillard, N., Desprairies, A., Lallier-Vergès, E., Bertrand, P., Moureau, N., Ramdani, A., Ramanampisoa, L. (1994). Geochemical study of organic-matter rich cycles from the Kimmeridge Clay Formation of Yorkshire (UK), productivity versus anoxia. *Palaeogeogr. Palaeoclimatol. Palaeoecol*. 108, 165–181.

Tunca, E, Aydin, M ,Sahin, UA. (2018). An ecological risk investigation of marine sediment from the northern Mediterranean coasts (Aegean Sea) using multiple methods of pollution determination, *Environmental Science and Pollution Research* V:25 Issue 8: p: 7487-7503 DOI:10.1007/s11356-017-0984-0.

Türk Çulha, S., Karaduman, F.R. (2020). The influence of marine fish farming on water and sediment quality: Ildır Bay (Aegean Sea). *Environ Monit Assess* 192, 528. https://doi.org/10.1007/s10661-020-08487-9.

USEPA (1997). Guidance for assessing chemical contaminant data for use in fish advisories. In: Risk Assessment and Fish Consumption Limits, vol. 2. EPA/8 23/b-97/009, US Environmental Protection Agency, Washington, DC.

Van Der Weijden, C. H. (2002). Pitfalls of normalization of marine geochemical data using a common divisor. *Marine Geology*, 184, 167–187.

Vetö, I., Hetenyi, M., Hamor-Vido, M., Hufnagel, H., Haas, J., (2000). Anaerobic degradation of organic matter controlled by productivity variation in a restricted Late Triassic basin. *Org. Geochem.* 31, 439–452.

Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., Liang R, Gao C., Chen W. (2007). Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Marine Pollution Bulletin*, 54, 974–982.