DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

HISTORICAL TRENDS OF HEAVY METALS IN SEDIMENT FROM İZMİR BAY

by

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İZMİR

HISTORICAL TRENDS OF HEAVY METALS IN SEDIMENT FROM İZMİR BAY

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"HISTORICAL TRENDS OF HEAVY METALS IN SEDIMENT FROM İZMİR BAY"** completed by **FATMA DUYGU GÜLŞEN** under supervision of **PROF. DR AYNUR KONTAŞ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Fatma Duygu GÜLŞEN

HISTORICAL TRENDS OF HEAVY METALS IN SEDIMENT FROM İZMİR BAY

ABSTRACT

Through their bioaccumulation was a serious environmental and ecological problem, assessment of heavy metal contamination in marine sediments have become common and important in recent years. The study area İzmir Bay, one of the greatest natural bays of Mediterranean, was surrounded by a densely populated city. The heavy traffic of the harbor, industrial, domestic and agricultural wastes cause pollution of the bay and the present study mainly aims to determine the origin, distribution and variations with depth of heavy metals in sediments taken from seven regions of İzmir Bay. Sediment core samples were collected on March 2013 during the cruise of R.V.K. Piri Reis, and total metal contents were determined by AAS and ICP-MS techniques after microwave acid digestion. Enrichment factor was evaluated with aluminum normalization, and assessment of metal contamination was made by using contamination factor, geoaccumulation index, TEL-PEL values and Sediment Quality Guidelines criteria. Grain size distribution, total organic matter content of sediment samples and their relationships between the adsorption of heavy metals were also investigated. In order to determine the similarities and differences among the sampling stations and depths along the core in terms of heavy metal concentrations, statistical analyses (ANOVA, PCA Analysis) were performed. It was established that concentrations of metals increased from outer bay towards inner bay. Outer bay (stations 6, 8 and 25) was described as non-polluted, station 11 (for lead and copper) and middle bay (station 22, for mercury, cadmium, copper and tin) was described as moderately polluted. Inner bay was defined as heavily polluted for copper, mercury, lead, tin, cadmium and zinc, and metal pollution seems to decrease compared to past years. The reason of high levels of nickel, chromium, arsenic, selenium and zinc in all stations, was due to lithogenic sources of the region.

Keywords: İzmir Bay, sediment, heavy metals, core

İZMİR KÖRFEZİ SEDİMENTLERİNDE AĞIR METALLERİN ZAMAN İÇİNDEKİ DEĞİŞİMİ

ÖZ

Biyoakümülasyonlarının ciddi bir çevresel ve ekolojik sorun olmasından dolayı, denizel sedimanlarda ağır metal kirliliğinin belirlenmesi son yıllarda yaygın ve önemli bir çalışma haline gelmiştir. Çalışma alanı olan İzmir Körfezi, Akdeniz'in en büyük doğal körfezlerinden biri, yoğun nüfuslu bir şehirle çevrelenmiş olup; limandaki faaliyetlerin sıklığı, endüstriyel, evsel ve tarımsal atıkların körfeze boşaltılması kirliliğe neden olmuştur. Bu çalışmada genel olarak, İzmir Körfezi'nin yedi farklı bölgesinden alınan karot örneklerinde ağır metallerin kaynağı, dağılımları ve derinlikle değişimlerinin araştırılması hedef alınmıştır. Karot örnekleri, Mayıs 2013 tarihinde R.V.K Piri Reis ile çıkılan seferde toplanmış ve ağır metal analizleri mikrodalga çözünürleştirme işleminden sonra AAS ve ICP-MS teknikleriyle tayin edilmiştir. Zenginleşme faktörleri alüminyum normalizasyonu ile ağır metal kirliliğinin belirlenmesi ve sınıflandırılması ise kirlilik faktörü, jeoakümülasyon indeksi, TEL-PEL değerleri ve SQG kriterlerinden yararlanarak yapılmıştır. Ayrıca, sediman örneklerinin tane boyu dağılımları, toplam organik madde içerikleri ve bunların ağır metal adsorpsiyonu ile ilişkileri de araştırılmıştır. Ağır metal konsantrasyonlarının örnekleme istasyonları ve karot derinlikleri arasındaki benzerlik ve farklılıkları belirlemek amacıyla istatistiksel analizler (ANOVA, PCA Analizi) gerçekleştirilmiştir. Metal konsantrasyonlarının dış körfezden iç körfeze doğru arttığı görülmüştür. Dış körfez (istasyon 6, 8 ve 25) kirletilmemiş, istasyon 11 (kurşun ve bakır) ve orta körfez (istasyon 22, cıva, kadmiyum, bakır ve kalay bakımından) orta derecede kirletilmiş olarak tanımlanmıştır. İç körfez bakır, cıva, kurşun, kadmiyum, krom ve çinko metalleri bakımından aşırı kirletilmiş olarak bulunmuş; ağır metal seviyelerinin yüzeye doğru azalma eğiliminde olduğu görülmüştür. Nikel, krom, arsenik, selenyum ve çinko konsantrasyonlarının tüm istasyonlarda yüksek olmasının litojenik kaynaklı olduğu belirlenmiştir.

Anahtar kelimeler: İzmir Körfezi, sediman, ağır metal, karot

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CHAPTER ONE
INTRODUCTION

Rapidly growing population in the world, consequently developing industrialization causes pollution problems and serious increase of this problem. Giving high priority to economic advances rather than protecting environment and natural life especially in developing countries like Turkey, contributes to the pollution problem also. Both ease and cheapness makes the discharging of wastes from coastal regions to the marine environment a very common environmental pollution problem (Yılgör & Avcı, 1997; Doğru, Güven & Erdoğan, 2007). Increasing pollution led to irreparable changes in ecosystem. One of the sources of aquatic pollution is heavy metals. In addition to weathering from rocks, atmospheric and river inputs, since the ancient times when metal ores had been worked, heavy metals enter to the atmosphere, hydrosphere and pedosphere through human activities (Kahvecioğlu, Kartal, Güven & Timur, 2011). The fate of metals that moved to the water is determined by 3 alternatives:

a) They can dissolve and the solubility of metals depends on pH, concentration of components in environment, properties of chelating reagents and reduction potential of the environment (Hahn & Klute, 1990).

b) They can remain in suspense.

c) They can sink to the sediment layer by forming carbonate, sulphur and sulfate compounds and accumulate in sediment layer (Aksoy, 2005).

Sediments represent a natural repository for pollutants additionally being a source for them by reacting with water constantly. In this aspect, sediment layers affect the quality of the water body (Lijklema, 1993). By investigating sediments, contamination levels of water body and historical changes of contamination levels can be determined. In other words sediments are good indicators of pollution history (Kaya, 2007). When concentrations of organic and inorganic materials are excessively high, they must be seen as potential pollutants (Golterman, Sly & Thomas, 1983). Especially heavy metals which are conservative pollutants are not been decomposed and accumulate continuously. They are very important contaminants and their levels must be investigated (Mendil & Uluözlü, 2006). They present a serious threat for human health through food chain since humans are on the top of it (Golterman et al., 1983). These heavy metals, whose toxicity is high, accumulate in human body also. The pollution that caused by these metals around the World is a big and serious problem, so our study is critically important by this reason and also by being the first research about this concept in İzmir Bay.

1.1 Marine Sediments

In aquatic ecosystems, sediments are essential and integral parts because the chemical composition of seawater is principally regulated by biogeochemical processes. Through these processes, dissolved materials are converted into solid forms. Then these solids deposited on the sediment layer and make it very important in the system of material flow between the crust, sea, atmosphere and upper mantle. Sediment can be defined as a layer on the sea floor which is formed by the material that is broken by weathering and erosion and transported to the seas by the wind, water and ice and then precipitate in unconsolidated form on the bottom of the sea. Marine sediments have two basic origins as they are created by the precipitation of dissolved chemicals in situ (authigenic) or they are carried to the ocean in solid form (allochthonous). Authigenic sediments are investigated into two categories that are precipitates of abiogenic means (hydrogeneous) and precipitates of products of biological activities (biogenous). On the other hand, allochthonous sediments are made up from Earth’s crust (lithogenous) and extraterrestrial materials (cosmogenous). And also humans are seen as a source of sediments (anthropogenic) (Libes, 2009).

Sediments play a very important role as they provide habitat and substrate for a wide variety of organisms through interacting with the overlying water continually (Burden, McKelvie, Förstner & Guenther, 2002). They also serve as a significant repository for contaminants that enter the marine environment (Wang, Feng & Ma, 2007). Most of the anthropogenic pollutants and waste materials enter the seas, eventually sink and accumulate in the sediment layer. However, they are not fixed permanently by the sediment and always remain in a cycle with the overlying water achieved by biological and chemical agents (Malins, 1984). Contaminants are precipitated and adsorbed by sediment layer and then released again to the water column continuously. For this reason, sediments are considered to be one of the major sources of pollution in aquatic environments, too (Allen, 1995).

As the contaminants deposited on the bottom and accumulate for ages, sediment cores are used to determine the history of pollution (Hartmann, Quinn, Cairns & King, 2005; Cantwell, King, Burgess & Appleby, 2007). They are great indicators showing the anthropogenic addition of contaminants. Heavy metals are one the most dangerous contaminants because of that they resist to be removed from the environment, and their ability of accumulation in food chain and showing toxic effects (Förtsner & Wittman, 1983). The heavy metal content of sediments results from natural and anthropogenic sources. Rock weathering, soil erosion and dissolution of water-soluble salts are natural sources while agriculture and mining activities and waste water discharges present anthropogenic sources generally (Förtsner & Wittman, 1983).

The sediment characteristics vary considerably in chemical composition, mineralogy, particle size, origin and also in sedimentation rate and geographic distribution. Color, texture and degree of bioturbation are the other factors that show differences (Libes, 2009). The features of sediment depend on the physical, chemical and biological events and this phenomenon explains why the deep layers of the seas are different from each other (Aközcan, 2009). When heavy metals participate into aquatic environment, they undergo a series of physical, chemical and biological processes. The fate and cycling, form, concentration and biologically active fraction of metals in sediments is affected and controlled by various factors (Williamson & Wilcock, 1994). These are sediment texture, composition, adsorption-desorption rates, redox conditions which greatly influence. Also, transport of metals, additional anthropogenic input and bioturbation are the affecting factors (Allen, 1995; Basaham & El-Sayed, 1997).

Monitoring and studying on sediment layer is important in many aspects. For example, benthic organisms have direct contact with sediment, they take up contaminants from it and “bioaccumulation” occurs. When larger animals feed on these contaminated organisms, toxicity increases in food chain and “biomagnification” occurs (Begum, HariKrishna & Khan, 2009). This eventually affects human health as we are on the top of the food chain. Moreover, to protect ecological balance, natural beauties of coastal regions and industrialized harbors and reduce potential health risks, sediments deserve a special consideration.

1.2 Factors Controlling Metal Concentration in Sediment

The first factor that affects heavy metal concentration in sediment is *anthropogenic input of metals*. Increased inputs results in increase in heavy metal contamination in sediment (Luoma, 2000). Metal enrichment is found close to past and present sources of pollution and concentrations drop with distance away from the source of input (Fergusson, 1990; Luoma, 2000). Metal concentrations in sediment are not only controlled by metal inputs but also sediment characteristics affect it seriously. *Sediment texture* is an important one. Fine grained sediment which has particles with diameter <0.063 mm has a high absorption potential of metals because the sediment has a large surface area to ratio, and contain large amounts of interstitial water (Loomb, 2001). In addition to absorption, the concentration, solubility and the mobility of metals depend on grain size (Güven & Akıncı, 2013). The third one is *sediment composition*; in other words the concentration of sediment components especially metal- reactive ones (Luoma, 2000). It is found that the concentration of metal reactive components such as iron and manganese oxides or polar organic matter increases as grain size decreases (Williamson, Lewis, Mills & Vant, 2003). Organic matter amount raises metal concentrations as it adsorbs metals from surrounding environment (Loomb, 2001). Moreover, residues of dead organisms contribute metal adsorption (Fergusson, 1990).

Other important factor that also affects metal transformation is *redox conditions* of sediment (GuoDeLaune & Patrick, 1997; Mansfeldt, 2004).Generally, metals tend to be mobile or dissolve in reducing conditions whereas oxidizing conditions favor metal insolubility. In coastal sediments or other sulfide-rich areas, greater solubility under aerobic conditions for many metals is observed (Pardu & Patrick, 1995). *Adsorption and desorption* conditions are the other significant processes that affect metal concentration. As the salinity increase the release of metals from oxic sediments may occur. This is explained by the high ionic strength of seawater and potential competition for binding sites with Ca and Mg ions (Luoma, 2000). Decreasing oxygen in sediment limits the release of the metals; this can be reduced by readsorption and as Fe- Mn oxides precipitation process. Desorption generates removal of metals while readsorption contributes metal concentration in sediment (Williamson & Wilcock, 1994; Luoma, 2000). The other process that affects metal concentration in sediment is *physical transport*. Coastal environments have low hydrodynamic energy and it cause fine particulates to be trapped. However, in regions that have high hydrodynamic energy fine particulates are mobile and heavy metals are transported with them (Williamson & Wilcock, 1994; Williamson et al., 2003).

Finally, *bioturbation* affects metal concentration. It is the physical mixing and reworking of sediments during the burrowing and feeding activities of benthic organisms (Libes, 2009). Bioturbation significantly affects the physical, chemical and biological features of sediments and has an essential influence on the chemistry of muddy sediments. It also can alter the levels and the speciation of heavy metals in sediments by affecting the sediment stratigraphy. Through bioturbation processes, sediment layer becomes blurred, particle sizes are altered, pore spaces and pH values are changed (Fergusson, 1990).

1.3 Literature Reviews

Heavy metals are one of the most important pollutants because of their persistence in environment and food chain and also high toxicity. Uptaking of heavy metals can cause morphological abnormalities, neurophysiological disorders, genetic alteration of cells and cancer. Moreover, heavy metals affect enzymatic and hormonal activity, growth rate and they increase mortality (Bubb & Lester, 1991). In evaluating the potential health risks and ecological hazard of heavy metals measuring their concentration in sediments plays an important role (Erdoğan, 2009). Therefore, several studies on this concept have been conducted all around the world and in our country also.

For example, Dassenakis et al., investigated Mn, Fe, Cu and Zn concentrations in sediments taken from Euvoikos Gulf, Greece which is a semi-enclosed area receiving polluters from several urban and industrial sources, in 1997. They concluded that the study of sediment cores had indicated the impact of polluting activities on recent surface sediments and they also observed an increase of total metal concentrations at present time compared with previous periods (Dassenakis et al., 2003). In sediment cores taken from Northern Baltic Sea between the years 2008 and 2010 and Vallius determined heavy metal concentrations. His study verified that most harmful metal concentrations had declined over the last two decades. Cu and Cd concentrations remained at elevated levels, As concentrations were at elevated levels but had declined rapidly over the last two decades. Hg levels had declined considerably but remains at harmful levels and the surface concentrations of both Hg and Cd were still too high (Vallius, 2014).

According to literature reviews, several researches about this subject have been conducted in Turkey. In 1989, 3 meter-long sediment core samples from Golden Horn which is a heavily polluted environment were collected. In this study, dating analysis was made by ^{210}Pb isotope technique and metal concentrations were measured with inductively coupled emission spectrometry (ICP). The results demonstrated that the lithophilic elements, Li, K, Rb, Mg, Ca, Ba, Al, La, Ti, V, Mn, Fe, Co and Ni, account for more than 90% of the elemental mass and do not show any change in their concentrations between 1912 and 1987. On the other hand, anthropogenic elements, Mo, Zn, Cr, Cu, Ag, and Cd, account for a small fraction of the elemental mass and their concentrations increase along the core (Tuncel, Tuncer

& Balkas, 2001). In 2000, Aktürk studied in this concept with Black Sea sediments. Generally, Fe and Mn concentration were found as below the average shale Fe and Mn concentrations and they showed a sudden decrease in anoxic conditions thorugh the cores. The highest Pb concentrations were at the top of the cores, Hg concentrations were obtained as below the average shale Hg concentration. Pb, Zn, Cu, Ni and Cr contents showed an increase in the eastern surface sediments (Aktürk, 2000).

The heavy metal content of surface sediments from İzmir Bay is measured by a number of researches. Firstly, Gey and Mordoğan analysed 9 heavy metals (Cu, Mn, Zn, Fe, Pb, Co, Cr, Cd and Ni) in coastal sediments from İzmir inner bay in 1986. They found maximum Cu and Pb levels in Naldöken, maximum Zn, Cr and Cd levels in Denizbostanlısı and maximum Mn, Fe, Co and Ni levels İnciraltı (Gey & Mordoğan, 1988). In another study which is made by collecting surficial sediment samples from 13 different stations from Aegean Sea, total mercury concentrations are measured and the maximum levels are found in Karaburun. They found the Hg levels in between a range of 0.09-3.61 μg/g with a mean value 0.91 μg/g (Balcı, Benli & Küçüksezgin, 1990). Balcı and Türkoğlu determined that the Cr, Cu, Pb and Hg concentrations in inner bay are higher than the other 10 stations of İzmir Bay (Balcı & Türkoğlu, 1993). In another research surfacial sediment samples were collected from 84 stations during whole summer in 1994 and Ag, As, Cd, Cr, Cu, Hg, Mo, P, Pb, Sb, Sn, V and Zn metals were analysed. They established that there was a distinct enrichment in terms of these metals and they commented that inner bay was heavily polluted and it could be a threat for marine organisms (Aksu et al., 1998).

In 1994 and 1995, sediment samples were collected from inner and middle Bay and Homa Lagoon. The heavy metal concentrations were found as 1.60-3.70 μg/g for Cd, 24.10-54.50 μg/g for Pb, 11.00-68.20 μg/g for Zn, 7.50-28.50 μg/g for Cu and 29.00-110.0 μg/g for Ni. In accordance with these values it is stated that the heavy metal content of Homa Lagoon is higher than other parts and this results from shallowness of the sealery, wastewater coming from Gediz River and effect of the inner Bay (Egemen, Sunlu & Kaymakçı, 1998). Atgın et al., collected 50 samples from inner bay, 30 samples from middle bay and 20 samples from outer bay. They measured Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Si, Ti and Zn concentrations. The results showed that Cd, Cr, Cu, Pb and Zn concentrations which are anthropogenic originated metals were high in the Inner Bay (Atgın et al., 2000). Kontaş studied about mercury levels in İzmir Bay sediments. In this research, it is represented that sediments contain high levels of mercury (0.20 and 3.14 nmol/g). The highest values were obtained in the Outer Bay and this is explained by inputs from Gediz River and abandoned mines in Karaburun Peninsula (Kontaş, 2006). Uluturhan et al., (2011) studied temporal and spatial distributions of heavy metals at Homa Lagoon. It is found that sediments were enriched with Cr, Ni and considered as heavily polluted according to the Sediment Quality Guidelines (Uluturhan, Kontaş & Can, 2011).

A considerable number of studies have been carried out to investigate the distribution and monitoring of heavy metals in surface sediments of İzmir Bay. Although there are studies based on the determination of heavy metal concentration in the Bay for 1 year period were present (Demirkurt et al., 1990; Balcı et al., 1994; Küçüksezgin et al., 2001; Küçüksezgin et al., 2002; Güven et al., 2008), long-term, seasonal and periodic data are not available.

CHAPTER TWO
HEAVY METALS IN THE ENVIRONMENT

2.1 Sources and Features

Metals are natural constituents of rocks, soils, sediments and water. The heavy metals are highly electronegative metals and have a density greater than 5 g/cm^3. They are common trace constituents of the earth crust include copper, zinc, lead, mercury, nickel, cobalt and chromium (Förstner, 1989; Stapleton, 2003; Agarwal, 2009). There are different sources of heavy metals in the environment which can be both natural and anthropogenic. The primary natural source of heavy metals is from crustal material that is either weathered on or eroded from Earth's surface or material that is injected to the atmosphere by volcanic activity (Callender, 2005). The natural sources can be well defined in the following classes; disintegration from magmatic rocks, sedimentary rocks, metamorphic rocks, weathering and soil formation, the rock cycle, and the origin of heavy metals from surface and groundwater. The anthropogenic sources can be summarised as metals steaming from industrial production and coming from agricultural and mining activities (Bradl, 2005). Metals have some important features and functions in nature which can be listed as:

- They present the bulk of the composition of earth crust (e.g. Al, Fe, Ti, and Si)
- They can present in four physical phases in natural waters that are solid, gas, colloidal and dissolved (Millero & Pierrot, 2002)
- The reactions of metals in water are affected by their speciation or form and this affects biological uptake (Anderson & Morel, 1982), toxicity (Ferguson & Sunda, 1984) and their solubility (Liu & Milero, 1999)
- They exist in sea water in different chemical forms that are ions, inorganic and organic complexes, and organometallic compound and in different oxidation states.
- Different forms of metals have very different biological and geochemical behaviours and because of this different fates and transport (Steele, Thorpe & Turekian, 2009)
- They are served as micro nutrients (e.g. Fe, Mn, Zn, Mo, Cd, Ni, Ba, Cu, and V)

- They are key participants of redox reactions (e.g. Fe, Mn, Re, V, Mo, U, Ag)
- They carry information about the ocean processes such as mixing, scavenging and pollution history as well
- They provide information to clarify the mechanisms of formation of carbon-rich deposits and petroleum source rocks
- Some of them are toxic to living organisms even at low concentrations (e.g. Pb, Cr, Cd, Hg) (Pedersen, Shimmield & Price, 1992; Calvert & Pedersen, 1993).

Metal ions are supplied to the aquatic environment extensively by riverine input, atmospheric precipitation, hydrothermal venting and human activities. Removal of them happens by adsorption onto sinking particles or incorporation into sinking biologically produced material by active uptake of phytoplankton. According to their vertical profiles these elements can be classified in 4 categories: (Steele et al., 2009)

a) Conservative type: They are present in sea water at relatively high concentrations owing to their low reactivity. Their concentration is in constant proportion to salinity and controlled by physical processes like advection and turbulent mixing and they long mean oceanic residence time (>>10^5 y). e.g. V, Mo, W, Re and Tl

b) Scavenged type: They have strong interactions with particles, short mean oceanic residence time (10^2-10^3 y) and low concentrations. They are removed from sea water by adsorption and transport to the sediment. Their concentrations are rich on the surface water through the rivers and atmospheric dust and low at deep. e.g. Mn, Co, Ga, In, Te, Pb, Bi, Ce

c) Nutrient (recycled) type: Their concentrations are rich at deep because of regeneration of the elements back into solution by bacterial oxidation and low at surface water because of biological uptake. e.g. Fe, Ni, Zn, Ge, Se, Y, Ag, Cd, Ba, La

d) Mixed type: Their distributions are affected by both recycling and scavenging processes, for example copper shows the characteristic surface depletion and deep-sea enrichment, and however its concentration increases almost linearly with depth, indicating the effects of scavenging. e.g. Cu, Fe, Ga, Zr, Ti, La and other rare earths.

The metals must be abundant in nature and they must be readily available as soluble species. In terms of environmental pollution, metals may be classified according to these criteria

- Noncritical (Na, Mg, Fe, K, Ca, Al, Sr, Li, Rb),
- Toxic but very insoluble or very rare (Ti, Hf, Zr, W, Ta, Ga, La, Os, Ir, Ru, Ba, Rh)
- Very toxic and relatively accessible (Be, Co, Ni, Cu, Zn, Sn, Cr, As, Se, Te, Ag, Cd, Hg, Tl, Pb, Sb, Bi) (Wood, 1974)

Metals are conservative pollutants which mean pollutants that are not physically or chemically transformed to nontoxic substances in water. As well as they are not subjected to bacteria attack and they are added to the sea permanently. For this reason heavy metals cause contamination when inputs from human activities causes the increase of concentration of substances in seawater, sediments and finally in organisms compared to natural background values (Clark, 2001). Vernet (1991) emphasized that as the environmental pollution with toxic metals is becoming a global phenomenon, concerns about the potential effects of the metals on human health and ecosystem and therefore the research on fundamental, applied and health aspects of trace metals in the environment are increasing too.

2.2 Heavy Metal Transport

Transport and transformations of the metals usually involve geochemical as well as biological processes and this form the Earth's biogeochemical cycle (Connell, 2005). There are two main pathways for heavy metals to make them incorporated into air-soil-sediment-water and these are transporting by air (atmospheric) and transporting by water (fluvial) (Callender, 2005). There are three microbial processes affecting the transport of metals that are degradation of organic matter to lower-molecular-weight compounds, changes in physicochemical properties of the environment and chemical form of metals by metabolic activities and conversion of inorganic compounds into organometallic compounds by redox reactions (Connell, 2005).

Since the most persistent sediment contaminants are associated with the solid phase, any mobilization of this phase increases contaminant mobility dramatically. Thus, contaminants can be distributed over large areas and increased concentrations in water column can be observed. In less active environments due to deposition and burial of the contaminated sediment, erosion and resuspension eliminate natural recovery (Chien, 2005).

2.3 Most Common Heavy Metals in Aquatic Environments

Metals enter the environment from variety of sources. Erosion and weathering from rocks and soil, smoke from forest fires and aerosols and particulates from the surface of oceans are some of them in marine ecosystems. Principal human activities are mining, agricultural and other operations, domestic effluents and urban storm water runoff, industrial wastes and discharges, agricultural runoff (Connell, 2005). Typical pollutants generated from these activities are lead (Pb), zinc (Zn), chromium (Cr), copper (Cu), cadmium (Cd), mercury (Hg), aluminum (Al), iron (Fe), manganese (Mn), and nickel (Ni) which are considered to be the most abundant metals in sediments. Also heavy metals such as cadmium (Cd), mercury (Hg), lead (Pb), copper (Cu), and zinc (Zn) are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity, and ability to be incorporated into food chains (Förtsner & Wittman, 1983). Today there are new aspects of the pollution problem, such as leading to exposure of the metals to the public through the air, drinking water, and food and consumer products mostly in developing countries.

2.3.1 Aluminum

Aluminum is the third most abundant element of the Earth's crust and it makes up about 8% by weight of the Earth's solid surface (Chen et al., 2011). There exists only one isotope of aluminum (Al_{27}) in nature and it has 6 radioactive isotopes. It is a silvery, ductile metal which is found as in bauxite ore generally. It has an excellent resistance to oxidation (Örnek, 2013). Usually aluminum is combined with other elements such as oxygen, silicon or fluorine and form different compounds because of its reactive properties. However, it can exist in its elemental (Al^0) form in nature (Chen et al., 2011). Aluminum species are at oxidation state (III) and in aqueous solution the simple ion occurs as $Al(H_2O)_6^{3+}$ and this ion dissociates to give other ions such as $Al\ (H_2O)_5OH^{2+}$. Over a wide pH range, species for example, $Al(OH)^{2+}$, $Al(OH)_3$, $Al(OH)_4^-$, $Al_3(OH)_{11}^{2-}$, $Al_6(OH)_{15}^{3+}$ and $Al_8(OH)_{22}^{2+}$ can appear (Krull, 1991).

This metal is used in several industrial areas in many kinds of products. Structural components made up of aluminum are inevitable for aeronautics and space industry. It finds area of usage in transportation and construction industries which require lightness and high strength properties. Through its easy cooling and warming properties it is used in refrigeration industry, its cheapness and prevalence compared to copper, its penetrability and softness make it very commonly used material in a great deal of area (APHA, 1998). Although it is a commonly used metal in many areas, its natural abundance is greater in marine sediments than anthropogenic sources. Therefore, aluminum is often used to normalize trace metal concentrations because of its high natural abundance and minimal anthropogenic contribution and by being a structural element of clays. In other words, aluminum can serve as a measure of clay content of sediment sample (Dassalakis & O'Connor, 1996).

2.3.2 Arsenic

Arsenic is a steel-gray, brittle, crystalline metalloid and has three allotropic forms that yellow, black and gray. The most common oxidation states of As are, -III, 0, III and V. It covalently binds with most nonmetals and metals where elemental As is formed by reduction of arsenic oxides. The most important compounds are As_2O_3 (sulfide), Cu acetarsenite $[3Cu(AsO_2)]_{2,}$.Cu $(CH_3COO)_2]$, Ca arsenate and Pb arsenate. The strong affinity of As for aquatic particles, especially Fe and Mn oxides results its deposition with these metals (Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, 1999). Mobility and bioavailability of As is affected by the chemical forms of As, pH of soil or groundwater, presence of oxides of manganese or iron and clay minerals, redox potential and competing ions and it is more mobile in coarse-grained soils. The primary sources of As are copper and lead ores. By benefiting the toxicity of As, its compounds are widely used in pesticides, herbicides and silvicides. The most common species of As in sediment and water are arsenate As (V) and arsenite As (III). As (III) is the most mobile, soluble therefore toxic specie (Bradl, 2005).

Combustion of coal and disposal of fly ash significantly influences the As discharge to the environment. The other anthropogenic sources can be classified as mining and smelting, pesticide manufacture and use and coal burning and its by products (Bradl, 2005). Ferguson & Gavis (1972) stated that arsenic and its compounds are very toxic and both As (III) and As (V) show high affinities for proteins, lipids and other cellular components, and they accumulate in living tissues. In contrast As seems not to be accumulated in fish, as they can convert it to organic form (Tanner & Clayton, 1990), thus the arsenic which comes from seafood is organic and less toxic. Stapleton, 2003 stated that the ingestion of inorganic arsenic in drinking water brings out several serious health hazards. Taking inorganic arsenic orally in great amounts can be fatal and homicidal. Being subjected to arsenic in small amounts but long period can cause the increase of the cancer risk of bladder, kidney, skin and lung. Also, lesions of the skin, cardiovascular and neurological diseases and problems of reproductive system can be comes out (Arsenic, 2014).

2.3.3 Cadmium

Naturally, cadmium presents mostly in earth crust and it is always found in complex with Zn (Kaya, 2007). It occurs naturally under reducing conditions, in the form of CdS when sulfur is present and a stable solid, $CdCO_3$ at high pH. The most common forms include Cd^{2+}, cadmium cyanide complexes and $Cd(OH)_2$ (Smith et al., 1995).

Nowadays, cadmium is used in nickel-cadmium batteries, ship industry, dye and plastic industry and electronic industry because of its high resistance against corrosion. In addition to these areas, cadmium is used in phosphate fertilizers, detergents and petroleum and its derivatives (Başaran, 2011). Kaya (2007) stated that it is also an inevitable by-product of Zn, Pb and Cu extraction. Through its common use, it brings about significant environmental pollution problems (Kahvecioğlu, Kartal, Güven & Timur, 2011). Cadmium is one of the most toxic pollutants with having teratogenic and carcinogenic effects and it has seriously dangerous influents for marine organisms even at low concentrations (Bebianno & Machado, 1997; Katalay & Parlak, 2004). Cadmium enters to the environment mainly from soil because of its presence in fertilizers and pesticides. And also this metal has a high trend to be adsorbed onto sediment layer (Cadmium, 2014). Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions. Under acidic conditions, Cd form complexes with chloride and sulfate (Evanko & Dzombak, 1997). In sediments, cadmium levels tend to increase with decrease in size and increase in density of sediment. Adsorption of cadmium by sediment increases with pH and decreasing grain size. The release of this metal from sediment is affected by several factors including acidity, redox conditions and complexing agents in water. When its transporting features were studied, it is found less mobile in alkaline conditions (Fergusson, 1990).

Uptake of cadmium mainly happens through food and liver, shellfish, mussel, mushroom and cacao are some examples of these foods. Also, cigarette smoke involves high levels of cadmium. Cadmium is extremely toxic, accumulates in human body and its effects are seen in 20-30 years (Watts, 1997). It causes acute intoxication, lung and prostate cancer, damage in kidneys, osteolysis, anemia, procreation and immune system problems, central nervous system problems, psychological disorders, tooth loss and diminish of smell sensation (Cadmium, 2014).

2.3.4 Chromium

Chromium (Cr) is one of the less common elements in nature and does not occur naturally in elemental form, but only in compounds (Güven, 2008). The most common form of chromium is $FeOCr_2Os_3$ which is a heavy mineral (APHA, 1998). Industrial activities which involve chromium, burning of fossil fuels and wooden products generate six-valence chromium in nature. Cr (VI) is the dominant form of chromium in water bodies if aerobic conditions exist. Major Cr (VI) species include chromate $(CrO_4)^{2-}$ and dichromate $(Cr_2O_7)^{2-}$ which precipitate readily in the presence of metal cations (especially $Ba2^+$, $Pb2^+$, and Ag^+). Güven (2008) stated that this metal was in a cycle that is from rocks to soil, water, air and ecosystem and finally soil again. But approximately 6700 tons of chromium per year leaves that cycle and precipitate and accumulate on the sea, river and lake floors (Kahvecioğlu et al., 2011). Cr (III) is the most dominant form of chromium at low pH (<4). Cr^{3+} forms solution complexes with NH_3, OH^-, Cl^- , F^- , CN^- , SO_4^{2-} , and soluble organic ligands. Cr (VI) is the more toxic form of chromium and is also more mobile (Chrotowski, Durda & Edelman, 1991). Chromium mobility depends on adsorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present. Most of chromium that released into natural waters is particle associated and is ultimately deposited on the sediment (Smith et al., 1995).

Industrially, chromium is used in pesticides and fertilizers (McNeely, Neimanis & Dwyer, 1979). Because of its hardness and high melting point, it is also used for providing roughness to metals and armored vehicle manufacturing.It is used as pigment in dye production, as catalyst and its K_2CrO_7 complex as oxidizing reagent. In addition to these areas, leather industry and textile industry can be counted (Kaya, 2007). It is implied that in Mertz's study (1987) that chromium enters human body via inhalation, eating, drinking and skin contact. The permissible and nontoxic chromium amount is 30–200 μg per day for human. Generally, chromium is destructive for skin, digestive system, cardiovascular system, kidneys and liver and Cr (VI) is carcinogenic and toxic (Kahvecioğlu et al., 2011). Cr (III) is an essential element for human and in case of its deficiency heart diseases, metabolism disorders and diabetes can be seen. On the other hand, when it is excessively taken, skin eruption may occur (Chromium, 2014).

2.3.5 Copper

There are more than 200 kinds of copper minerals in nature, but only 20 of them carry industrial importance as copper ore. Naturally, copper exists in a lot of mineral as sulphur complexes, oxides and carbonates (American Public Health Association, [APHA], 1998). Copper is mined as primary ore product of copper sulfide and copper oxide ores, thus mining activities are the major sources of copper contamination in ground and surface water (Evanko & Dzombak, 1997). The reason of why copper plays a significant role and used in several areas in industry is because it has plenty of different properties. The most important features are high thermal and electrical conductivity, resistance against corrosion and its malleability (Örnek, 2013; Metals handbook, 1978). It is widely used in metal and automotive industries, electric cables, roofing, various alloys, pigments, kitchen equipment, tube production and chemical industry (Örnek, 2013). Therefore, industrial wastewater discharges contribute copper pollution in aquatic environments substantially. In natural waters, copper forms lots of compounds and most known ones are Cu^{2+}, $Cu(OH)_2$ and $CuHCO_3$. In aerobic and sufficiently alkaline systems, the most dominant soluble copper specie is $CuCO_3$ and it forms strong solution complexes with humic acids (Güven, 2008).

Cu^{2+} is the most toxic specie and it is adsorbed by mineral surfaces over a wide range of pH values (Dzombak & Morel, 1990). According to pH values of natural waters copper precipitates on sediment layer. In natural ground water sediments, the range of copper concentration is 16-5000 mg/kg (dry weight) and in marine sediments the range is 2-740 mg/kg (dry weight) (Metals, 2014). Başaran (2011) emphasized that the minor amount of copper in the environment is from natural origin because of the solubility of copper minerals are low.

The effect of copper varies in accordance with the chemistry and size of organisms. While it shows toxic properties for small and simple structure organisms, it is an essential element for bigger ones. For this reason, it is used as funguside and pesticide (Dökmeci, 2005). In case of deficiency of copper some problems are; delay in growing, infection in inhalation system, osteoporosis, anemia, color loss in hair and skin (Copper, 2014). Although it is necessary for humans, the determined limits by WHO are 12 mg/day for women, 10 mg/day for men and 3 mg/day for 6-10 year old children and 2 mg/L for drinking water (World Health Organization, 1996; Habashi, 1997)

2.3.6 Iron

Iron is believed to be the tenth most abundant element in the universe and it is second after aluminum in earth crust and marine sediments (Krull, 1991; Greaney, 2005; Taylor & Macquaker, 2011). It is rarely found in the free elemental form and obtained by extracting from iron ore. It has a wide range of oxidation states (-2 to+6) but most common states are +2 and +3 (Krull, 1991).

The low cost and high strength of this metal makes it indispensable in different sections of industry (Greaney, 2005).Steel is the best known and common alloy of iron. It is an essential metal for automotive, ship industry and buildings as a structural component (Kaya, 2007). The anthropogenic sources of iron are limited when compared to lithogenic sources. In aqueous environments Fe (III) is the form of iron that accumulates (Taylor & Macquaker, 2011). Iron is an essential element almost for all organisms except a few bacteria but the amount of iron shows toxic effects for humans by reacting with peroxides and forming free radicals in the body.

The overtaking of iron causes liver and kidney damages and some compounds of it are suspected carcinogens (Greaney, 2005; Kaya, 2007).

2.3.7 Lead

Lead exists naturally and most commonly with an oxidation state of 0 or II+. The most observed ores are PbS and its oxidized form $PbCO_3$ and $PbSO_4$ (APHA, 1998). Pb (II) is the common and reactive form and forms both mononuclear and polynuclear oxides and hydroxides. In water bodies, a significant fraction of lead remains undissolved and occurs as $PbCO_3$, Pb_2O, $Pb(OH)_2$ and $PbSO_4$ in precipitates. Above pH 6, lead carbonate solids are formed and when high sulfide concentrations are present, PbS is the most stable solid. Fate of lead in soil, include adsorption, is controlled by ion exchange, precipitation and complexation properties. These properties limit the amount of lead transported into surface water or groundwater (Evanko & Dzombak, 1997).

Lead is a soft, heavy and malleable metal and since old ages the use of Pb has been rapidly increasing from anthropogenic sources and lead is used as a geochemical indicator since almost all of Pb is nearly originated from human activities (Kaya, 2007). As it is spead out to the atmosphere in the form of metal or complex it is very toxic and defined as an important pollutant. Watts (1997) showed that lead tends to be adsorbed by water-sediment systems in aquatic environments because of its low mobility. The primary anthropogenic sources of lead contamination are metal smelting and processing, secondary metal production, bullets and battery manufacturing, production of pigments, insecticides and chemicals and lead contaminated wastes (Baş & Demet, 1992; Güven, 2008). Lead and its products are also used in automotive and machine industry, tube and institution material production, batteries and bullet industry and in the form of tetraethyl lead, $(CH_3CH_2)_4Pb$ in petroleum (Kaya, 2007).

Lead is a conservative pollutant that enters living organisms through mixing into air, water, soil and foods and shows highly toxic properties. Some health risks from lead contamination are breakdown on hemoglobin synthesis, anemia, high tension, brain damage, aggressiveness and decrease of learning skills and hyperactivity in children (Kartal, Güven, Kahvecioğlu & Timur, 2004). According to World Health Organization's classification it is second-class carcinogenic (European Commission, 2002).

2.3.8 Manganese

Manganese is a very brittle, whitish-grey metal which is generally found in metamorphic, sedimentary and igneous rocks. There exist more than 100 kinds of Mn minerals containing sulfides, oxides, carbonates, silicates, phosphates, arsenates, tungstates and borates. The most important ones are pyrolusite (MnO_2), rhodochrosite ($MnCO_3$), manganite ($Mn_2O_3 \cdot H_2O$), hausmannite (Mn_3O_4) and rhodonite ($MnSiO_3$). In water and soil, it shows several similarities with Fe (Tunç, 2008). It oxidizes superficially in air and can be exist in oxidation states; I, II, III, IV, VI and VII. And the most stable salts are formed by the oxidation states of II, IV, VI and VI. While the lower oxides such as MnO and Mn_2O_3 shows alkaline properties, the higher ones are acidic. Mn can exist in various oxidation states, its oxides can exist in various crystalline forms and the oxides can form coprecipitates with Fe oxides. Oxides of Mn and Fe shows amphoteric properties with interacting with both anions and cations and redox reactions of Mn are controlled by several physical, chemical and microbial processes. Therefore; mobility, adsorption and other biogeochemical phenomenon of Mn in soil are very complicated. We can say that adsorption increases with increasing pH value and increasing clay content (Bradl, 2005).

The main use of Mn is in metallurgical industry. As it improves strength, toughness and hardness it is the essential ingredient of steel. Moreover, other anthropogenic sources of Mn can be counted as battery, electrical coils, ceramics, matches, glass, dyes, paints production and being used as catalyst (Bradl, 2005). Mn is an essential micronutrient for animals, plants and human. If it exists in excess amounts in human body, it shows toxic behavior. Both its deficiency and rarely its exorbitance bring out serious health problems (Kartal et al., 2004).

2.3.9 Mercury

Naturally, mercury is a rarely existent metal; production of it is expensive and nearly 8000 tons per year around the world. It is usually recovered as a by-product of ore processing (Smith et al., 1995). It is a key element for assessing marine pollution and in most of its compounds it has a high toxicity and tendency to be enriched in natural food chain (Leipe et al., 2013).

Fitzgerald & Lamborg (2003), said that Hg is mobilized naturally through geological and volcanic activities, but Selin (2009) added that the human activities such as coal burning, industry and mining activities has altered mercury cycle and increase its release. Mercury is transported in the atmosphere in three forms: elemental gaseous mercury Hg (0), divalent mercury Hg (II) or particulate mercury Hg (P). Because solubility of divalent and particulate Hg in water is higher than elemental Hg, they present the majority of deposited Hg in the ecosystem (Fitzgerald and Lamborg, 2003; Selin, 2009). It is determined that in freshwater system, estuaries and coastal zones particulate Hg may account for more than 90 % of total Hg (Fitzerald and Mason, 1997; Balcom et al., 2004; Schäfer et al., 2006). After releasing to the environment, mercury usually exists in mercuric (Hg^{2+}), mercurous (Hg_2^{2+}), elemental (Hg^0) or alkyllated form (methyl-ethyl mercury). Alkyllated forms which are soluble in water and volatile in air, is the most toxic forms of mercury (Smith et al., 1995). Stable forms of mercury are; Hg^{2+} under acidic conditions, $HgCl_2$ at normal conditions and $Hg(OH)_2$ above pH 7. Moreover, it binds strongly to sulfide ion, under strongly reducing conditions Hg^0 is stable in the presence of H_2S or HS^-, but HgS precipitates at increasing redox potential (Alloway, 1995).

Industrial sources of Hg contamination are, extracting of metals by amalgamation, burning of fossil fuels, mining and smelting of ores (Cu and Zn), mobile cathode in chloralkali cell for the productions of NaCl and Cl_2 from brine, electrical and measuring apparatus, fungicides, catalysts, pharmaceuticals, dental fillings, scientific instruments, rectifiers, electrodes, mercury vapor lamps, X- Ray tubes (Alloway, 1995; Bradl, 2005).

Mercury is very toxic and carcinogenic and nervous system has a high sensitivity against mercury and its compounds. They are destructive for kidneys and brain. Metallic and methyl mercury mix with blood, reach to brain and accumulates in brain whereas inorganic mercury compounds cannot reach to the brain, accumulate in kidneys and prevent their mechanism. It is observed that mercury destroy lungs and inhalation system when subjected to in a short time period. Moreover, the increase of mercury in human body cause raising in tension, heart attack, damage in eyes, and wound in skin (Ağır metaller, 2014). Uptake of mercury orally at levels of 10-60 mg/kg is mortal for human. Consuming high mercury contaminated food brings tension problems, heart disorders and skin diseases (Mercury, 2014).

2.3.10 Nickel

Nickel is a silvery-white, hard, malleable, ductile, ferromagnetic metal which is the 23rd abundant metal in earth crust. It has five stable isotopes and normally occurs in oxidation states 0 and II. It is not soluble in water and also its I and III oxidation states are not stable in aqueous solutions either. In soils Ni occurs in the form of free ionic form Ni^{2+} or complexed with various organic and inorganic ligands. Ni (II) is stable over a wide range of pH and redox conditions and adsorption of nickel in soils largely depends on pH. The most important nickel ores are pyrhotite and penthlandite which are sulfide ores. In industry nickel is generally used for electroplating, alloy production, batteries, electronic industry, and as catalyst. In addition to these areas, automotive, surgical implants, jewellery, kitchen appliances, coins account for the use of nickel. The main sources of nickel that gives it to the environment are mining, smelting, and fuel oil and coal combustion and sewage sludge. And also petroleum since it contains nickel (Bradl, 2005). Foodstuff contains little amounts of nickel except chocolate and fats which contains it highly. By the consumption of contaminated foods taking nickel increases. Taking nickel is necessary for human on a small scale but dangerous for health when is excess. It can cause blockage in lungs, cancer, skin diseases, asthma and heart disorders (Ağır metaller, 2014).

2.3.11 Selenium

Selenium is a widely dispersed element in nature as being constitute of igneous rocks, volcanic sulfur deposits, hydrothermal deposits and copper ores. It rarely occurs in elemental state or as pure ores and it is found in different oxidation states (-II, II, IV, VI), where Se (4) is the most stable form. In environmental samples, selenium can exist in at least two different ionic forms that are selenite SeO_3^{-2} and selenate SeO_4^{-2} and the concentration and speciation in a sample depends on pH, redox conditions, and the solubility of its salts, the biological interactions and the reaction kinetics (Krull, 1991).

In industry, selenium is used in electronics and photoconductive cells. With its compounds it is also used in chromium plating, glass, ceramics, pigment, rubber, lubricants, pharmaceuticals, and organic substances. This metal is both toxic and an essential nutrient by presenting in an enzyme in the human body (glutathione peroxidase) that protects cells against oxidative threats (Llorente, Gomez & Camara, 1997). The toxicity mainly depends on species. When it is found in high concentrations in food and water, it becomes a cumulative toxic substance while at very low levels it works as an essential trace element. Therefore, selenium determinations at trace levels of environmental samples in a wide variety of matrices have become quite common and important (Krull, 1991).

2.3.12 Tin

Tin is a soft, silvery-white, pliable metal which occurs naturally in both organic and inorganic forms. Tin is ranked 49th in crustal abundance and most important mineral of it is cassiterite (SnO_2). It is not easily oxidized and resists corrosion since it is protected by an oxide film. It occurs in two oxidation states that are II and IV (Bradl, 2005; Tin, 2014). Tin oxides are insoluble and the ore is strongly resistant against weathering, so the amount of tin enters naturally to the soil and natural waters is low (Tin, 2014).

If we take a look at the anthropogenic sources of tin, the primary use of it is coating. It is a good coating agent because of its high resistance against corrosion and it is used in tin-plated steel containers for food preservation, and tin alloys which are needed for automotive aerospace industry. Organotin compounds like mono-, di-, and tributyltin (MBT, DBT, TBT) are used as biocides, stabilizers, catalysts or as antifouling agent in paints for ships. This common use has raised several serious environmental problems. Organotin compounds are toxic and the most toxic form is TBT in aquatic environments. Also they can be methylated and it makes them more bioavailable (Moore, 1991; Newman & Mclntosh, 1991). Organotin compounds can maintain in the environment for long periods of time through their persistent and not easily biodegradable properties. Microorganisms cannot disintegrate organic tin compounds, thus they accumulate on the sea floor, in the bodies of the organisms and food chain (Tin, 2014). Divalent tin salts show more toxicity than tetravalent salts. On the other hand, most of the inorganic compounds are nontoxic because of their low solubility and oral absorption (Cima, 2011). The most toxic and dangerous compound is triethyltin for humans. Through being exposed to tin compounds for several years liver damage, malfunctioning of immune systems, chromosomal damage, brain damage which cause anger, sleeping disorders, forgetfulness and headaches are observed as health effects (Tin, 2014).

2.3.13 Zinc

Zinc is one of the most abundant natural components of the earth's crust and makes up about 75 ppm of it (Emsley, 2001). It never exists in elemental form and obtained by extraction of various ores such as smithsonite, zinc spar or zinc carbonate (Zinc, 2014). Not only in rocks and soil, but also in air, water and biosphere zinc presents. The most common form of it is the sphalerite mineral (ZnS) also known as zinc blende which is found in almost all currently mined zinc deposits

(International Zinc Association, 2011). Zinc usually occurs in the +II oxidation state and forms various compounds with anions, amino acids and organic acids.

The primary industrial area of zinc is using it as a corrosion-resistant coating agent for iron and steel (Smith et al., 1995). The other areas can be summarized as alloys, batteries, fungicide and pigment industry (APHA, 1998). Occurring as soluble compounds at neutral and acidic pH values makes it one of the most mobile heavy metals in groundwater and surface waters. Precipitation comes off in forms of $Zn(OH)_2$, $ZnCO_3$, ZnS or $Zn(CN)_2$ and adsorption by sediments or suspended solids is the primary fate of zinc in aquatic environments (Evanko & Dzombak, 1997).

Zinc is an essential element for plants and animals, but getting of some kinds of it in excessive amounts is toxic for some aquatic organisms. It is an essential element for human also and 10-20 mg per day is the required amount (Zinc, 2014). It shows less toxic and dangerous features than other heavy metals (Örnek, 2013). It is rarely seen that intoxication through zinc and zinc salts but consuming of contaminated food may cause poisoning (R. Tezcan & H. Tezcan, 2007). When excess Zn is taken, apathy and weakening in muscular functions are some of the observed disorders.

CHAPTER THREE
MATERIAL AND METHOD

3.1 Study Area

İzmir Bay is located between latitude $38^0 20^{'}$- $38^0 42^{'}$N and longitude $29^0 25^{'}$-$27^0 10^{'}$ E, at eastern Mediterranean Sea. It is one of the greatest natural bays of Mediterranean with its 200 km^2 area and 11.5 billion m^3 water capacities. İzmir is the third biggest city of Turkey and has the second largest bay. It is one of the most developed and populated cities of Turkey. Topographically, bay is divided into 3 sections namely inner, middle and outer bays (Aksu, Yaşar & Uslu, 1997). Inner bay has a maximum depth of 20 m and represents a limited water exchange with middle bay (Balcı & Türkoğlu, 1993). The depth increases towards middle and outer parts of the bay. The maximum depths of middle and outer bays are 45 and 72 m respectively. Outer bay is 20 km wide and with a 45 km length lies between Karaburun and Foça. Middle and inner bays cover areas that are 24 and 6 km in east-west direction. Yenikale Strait whose depth is 13 m separates inner and middle parts (Aksu, Yaşar & Uslu, 1997). The longest river that falls into the bay is Gediz River. Inner bay is heavily polluted resulting from urban and industrial wastewater discharges. The map of İzmir Bay is given in Figure 3.1 and the coordinates of the stations are given in Table 3.1.

Because of the dense population, dense activity at harbor and industry, inner bay is the place that the pollution is most seen. Continued discharges threaten environment, ecological balance and human health. The most common sources of pollution are domestic and industrial wastewater discharges, atmospheric inputs, agriculture activities, mining, shipping and dredging activities (Atgın et al., 2000). Iron-steel, paper, antifouling dye, cement and beer industry can be counted for the main industrial sources of pollution in İzmir Bay. Güven (2008) emphasized that between 1976 and 1990, partial dredging of the sediments from inner bay was performed in order to remove highly contaminated sediments. The studied area was mainly along the center line of the inner bay and the dredged material was dumped into a natural ditch in outer bay. Almost all of the industrial waste water is discharged into the bay without any treatment. Similarly, domestic wastes reach to the bay from several dump sites around the inner bay. In 2001, as a part of a project handled by İzmir Metropolitan Municipality, the working of Wastewater Treatment Plant of Çiğli has been an important step in preventing and controlling pollution in İzmir Bay. By this project, the creeks that enter the bay were taken under control and waste water is collected and treated by the plant. Still there are some illegal discharges directly or indirectly, and they cannot be prevented (Aksu et al, 1998; Atgin et al., 2000; Cihangir & Küçüksezgin, 2003) but the condition of the bay is getting better day by day.

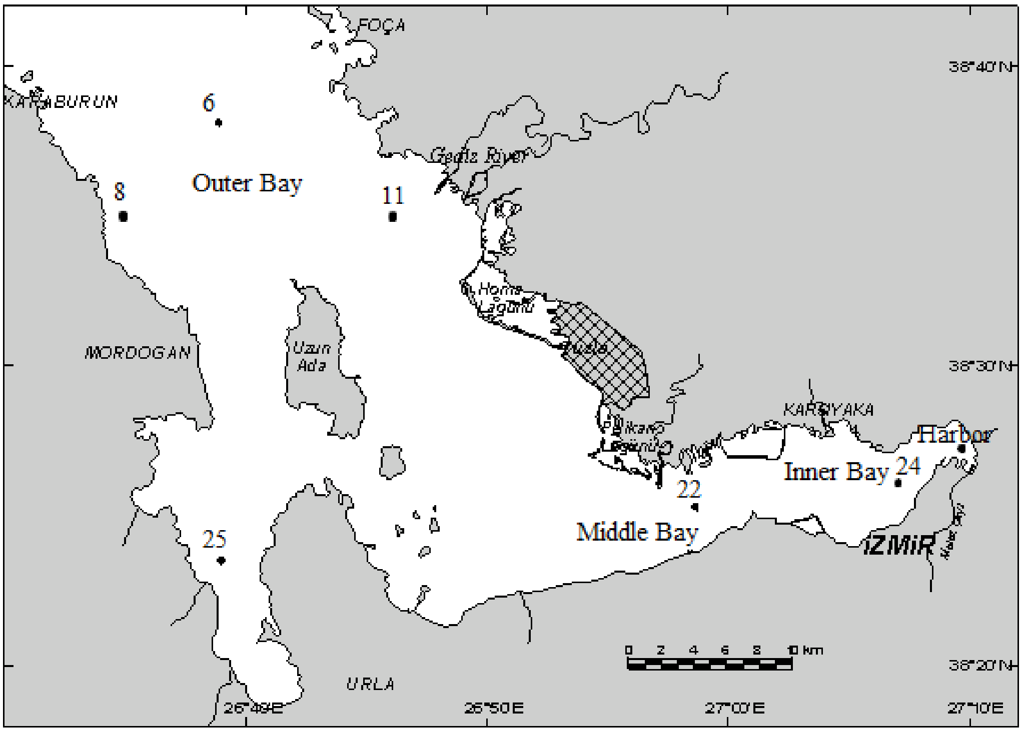

Figure 3.1 Locations of the stations in İzmir Bay

Table 3.1 Coordinates of the stations

Station	***Longitude***	***Latitude***
6	26°38’.89E	38°38’.10N
8	26°34’.99E	38°34’.99N
11	26°46’.09E	38°34’.90N
25	26°39’.00E	38°23’.50N
22	26°58’.60E	38°25’.30N
24	27°04’.68E	38°26’.22N
Harbor	27°09’.65E	38°27’.22N

3.2 Sampling

Sediment samples were collected from 7 stations throughout the İzmir Bay during the cruise of R/V.K Piri Reis (a research boat which belongs to Dokuz Eylul University, Institute of Marine Sciences and Technology) on March 2013. The sampling stations are named as Harbor, stations 24, 25, 22, 11, 8 and 6. Harbor and station 24 locate in the Inner Bay and Harbor is the shallowest point of the Inner Bay. Station 22 is located in the Middle Bay and station 25, 11, 8 and 6 are located in the Outer Bay, and station 11 locates near Gediz River’s mouth. As it can be understood, sampling stations were chosen from different parts of the Bay, according to different water masses, depths and properties. Sediment samples were taken by using a box-core (Figure 3.2). Sediment samples were separated into two portions for different analysis. Wet sediment samples were used for the water content and grain size analysis, while other part was used for chemical analysis. Samples were sliced at 1 cm intervals until the first 20 cm and between 20-30 cm were cut as 2 cm-long (Figure 3.3) for chemical analysis. Then, sediment subsamples were put into plastic bags and stored in deep-freeze at -20 ^{0}C. The subsamples were dried in freeze-dryer and then sieved to pass 63 µm to provide homogenization for the further operations.

Figure 3.2 Sampling with box-core

Figure 3.3 Subsampling of the sediment core

3.3 Water Content

Water content of sediment samples was determined by gravimetric analysis. Wet sediment samples were weighed, dried by freeze drying overnight and weighed again. The freeze dryer used in this study was given in Figure 3.4. The moisture content of samples was calculated by weighing the difference between the weight of wet and dry sediment samples.

Figure 3.4 Freeze-drying of samples

3.4 Organic Matter Content

Schnitzer (1978) said that in all terrestrial and aquatic environments, organic matter in soils and sediments is widely distributed over the Earth's surface. Sediments contain a large variety of organic materials ranging from simple sugars, carbohydrates to the more complex compounds such as proteins, fats, waxes and organic acids. Organic carbon is measured by an approximate relationship with organic matter. In sediments, carbon may be present in three basic forms:

(1) elemental C

(2) organic C

(3) inorganic C.

Organic matter is able to form water-soluble and water insoluble complexes with metal ions and hydrous oxides. It interacts with clay minerals, binds particles together and holds water in sediment. As a result of these characteristics, the determination of total organic carbon is an essential part of monitoring pollutants (Schumacher, 2002).

Total organic matter content (TOM) was measured by dichromate method which involves oxidation of organic carbon to carbon dioxide with a parallel reduction of hexavalent chromium (Cr^{+6}) to trivalent chromium (Cr^{+3}) and a color change from orange to green. The intensity of green color is relevant to the organic matter so organic carbon of the sediment (Hach, 1988).

3.5 Grain Size Analysis

The grains that generate the sea-floor vary in terms of size and shape. Since trace elements tend to be adsorbed onto surfaces of the sediment, their concentrations increase as particle sizes decrease and surface area increase (Daskalakis & O'Connor, 1996). The grain size analysis involves two parts that are sieve and hydrometer analysis. Sieve analysis is used for coarse particles while hydrometer is used for finer particles. The sediment samples were spread on plates and dried. Then by using a small pestle and mortar, samples throughly grinded till all large particle clumps were separated into individual grains. In sieve analysis sieve series were prepared according to their hole sizes; from top to bottom as 4 mm, 2 mm, 1 mm, 0.5 mm, 0.250 mm, 0.125 mm and 0.075 mm. Then sediment samples were poured from the top of the sieve series and sieves were shaken for 10 minutes. After that particles that remain in each sieve were weighed and recorded.

Particles (< 0.075 mm) were determined by hydrometer analysis. In hydrometer method, 50 g sample was dissolved in sodium hexametaphosphate $(NaPO_3)_6$ and waited for 1 day. $(NaPO_3)_6$ is a deflocculating agent, used in the separation of clays into individual particles. Then hydrometer was leaved into the 1000 cm^3 measuring cylinder and measurements were done periodically and recorded. In graphic drawing program two parts of analysis were combined and the grain size distributions were determined.

3.6 Digestion of Samples

For metal analysis, digestion was applied to sediment samples by using microwave acid digestion method. Since it generates much higher temperature and pressure than a traditional hot plate, this method can be applied to a wide variety of samples. As a result of this application, a clear digestate is obtained. $HNO_{3,}$ $HClO_4$, HCl and HF acid mixture was added to all samples and solutions were placed into closed Teflon digestion vessels and digested for 25 minutes. In this study Milestone 1200 Microwave Digestion System was used.

All dried and sieved sediment samples were digested in microwave digestion system (Milestone 1200) with an acid mixture composed of HNO_3-HF-$HClO_4$-HCl (United Nations Environment Programme, [UNEP], 1984; UNEP, 1986). In the process of total decomposition hydrofluoric acid (HF) is used in combination with concentrated oxidizing acids. Using HF has some important advantages:

a) HF is the only acid that completely dissolves the silicate lattices, therefore all associated metals such as Al, Fe, etc., can be released.
b) Analyzing certified reference materials provide us intercomparable data to assess the accuracy.

Strong acid digestion without HF results in incomplete digestion because refractory oxides are not dissolved as well as silicates.

Figure 3.5 Microwave digestion system

3.7 Instrumental Analysis

The realization of significance of even extremely small amounts of heavy metals in the environment has led to increasing demand on the determination of these metals at trace concentrations. In order to measure these levels (parts per million and parts per billion) high sensitivity and selectivity are needed. There are several methods for such analysis and they have different advantages and disadvantages in terms of (i) requirement of sample size (ii) sensitivity and detection limit (iii) sample form (iv) pre-concentration techniques (v) quantitative application (vi) selectivity, interferences and matrix effects (vii) multi element determination (viii) standard preparation and usage (ix) time, space and cost (Tayab, 1991).

In our study, Atomic absorption spectrometry (flame, cold vapor and graphite furnace) and inductively coupled mass spectrometry methods were used. In flame atomic absorption an oxidant gas such as air/acetylene or nitrous-oxide/acetylene is used to dissociate the sample into its atoms. When light from a hollow cathode lamp passes through the cloud of atoms, the atoms absorb the light and this is measured by a detector. Working with FAAS is easy, fast, has high sensitivity, selectivity, and there are relatively less interferences, but it has moderate detection limits, some element limitations and 1-10 elements per determination can be done. Graphite furnace atomic absorption spectrometer (GFAAS) is essentially same with FAAS, except the heating process is achieved by a graphite tube. The temperature is heated up to 3000°C where the maximum temperature is 2600°C (with the N_2O/acetylene flame) in FAAS. The higher atom density and longer residence time in the tube improves detection limits as 1000 times greater than FAAS. It has also the advantage of using small sample size. For the disadvantages, slower analysis time, chemical interferences, element limitations and 1-6 elements per determination can be counted. Mercury analyses were performed using cold vapor- AAS technique.

The other technique is inductively coupled plasma- mass spectrometry. In this technique, an ICP plasma source is used to dissociate the sample into its atoms or ions. In this case, rather than the light emitted, ions themselves are detected, passes into a mass spectrometer and they are separated by mass-to-charge ratio. ICP-MS is a multi-element technique and provides the best detection limits (parts per trillion ranges) for most elements with a very low background. It has also high productivity and wide dynamic range. The limitations of this method are, some method development is required and some spectral interferences (Thermo Elemental, 2001).

To determine heavy metal concentrations, A Varian AA280 FS and AA280 Z atomic absorption spectrometers (AAS) equipped with hollow cathode lamps and inductively coupled plasma mass spectrometer were used. Copper, lead, chromium, zinc, manganese, aluminum and iron were determined by AAS (AA280 FS), flame atomization (air-acetylene flame); while arsenic, nickel, selenium and tin were measured by ICP-MS. The mercury measurements were achieved by cold vapor atomic absorption (VGA-77, Vapor generation accessory) technique; Cd levels were measured by graphite furnace atomic absorption (AA280 Z). By employing standard calibration curves the analytical calculations were done. The validity and accuracy of the method was controlled by with the intercalibration sediment sample (IAEA-433) digested together with samples. The detection limits for heavy metals were given in Table 3.2.

Table 3.2 Detection limits of the elements

Technique	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
Flame AAS (ppm)	0.3	-	-	0.06	0.03	0.06	-	0.02	-	0.1	-	-	0.01
GFAAS (ppb)	-	-	0.1	-	-	-	-	-	-	-	-	-	-
Cold vapor AAS (ppb)							0.05						
ICP-MS (ppb)	-	1	-	-	-	-	-	-	4	-	3	1	-

3.8 Sediment Pollution Assessment

To determine the origin of heavy metals, enrichment factor (EF) and geo-accumulation index (Igeo) were calculated. They are specific indices that are used to assess anthropogenic impact of heavy metals on aquatic environments by providing simple ways to determine the contamination levels. This can be done by defining the ratio of natural concentrations of some resistant elements such as Al, Fe, Li, Rb and Si whose concentrations are not affected anthropogenically (Ravichandran et al., 1995; Daskalakis & O'Connor, 1996).

Commonly, Fe or Al is selected as normalizing elements. Fe has the same geochemical reactions with other heavy metals under oxic and anoxic conditions, and has also more uniform concentration than Al (Tavakoly Sany et al., 2013). However it has high mobility and ability to accumulate in food chain and they decrease its stability (Tavakoly Sany et al., 2013). In our study, Al was selected as normalizing element because this is the structural element of clays, it is almost inactive in marine sediments; and is not affected by anthropogenic contamination and diagenesis process (Rubio et al., 2000). EF is defined as the ratio of the concentrations of measured heavy metals and normalizing element divided by the ratio of background values of the metal and normalizing element (Rule, 1986); and given in equation 3.1.

$$EF = (Cmetal/Cnormalizer)/(Cmetal/Cnormalizer)_{backgroundvalues} \tag{3.1}$$

EF values of 0.5<EF<1.5 indicate that the metal may be completely derived from natural or lithogenic processes. EF >1.5 indicates that a large portion of trace metal was derived from non-natural processes or anthropogenic sources (Zhang et al. 2007). Han et al., (2006) defined the new EF value classification as follows: EF≤2 indicates that metal contamination might be entirely from natural sources, an EF value of 2–5 indicates that a moderate portion of heavy metals originated from an anthropogenic source or non-natural process, an EF of 5–20 indicates that a significant portion are from anthropogenic sources, an EF of 20 to 40 indicates that a high portion of contamination is derived from anthropogenic sources, and an EF>40 indicates an extremely high portion of contamination.

In our study, the EF values were calculated in three ways:

- EF: According to background values (Turekian and Wedepohl, 1961)
- EF_6: According to the deepest layer of the outer bay, station 6
- $EF_{station}$: According to deepest layer of each station

By this way differences in sediment composition between reference area and İzmir Bay could be observed and also enrichments depending on regions and time could be measured.

The geo-accumulation index (Igeo) introduced by Muller (1969) assesses the effect of lithogenic sources and degree of metal pollution and it is calculated as:

$$Igeo = Log_2 (Cn/1.5*Bn) \tag{3.2}$$

Where Cn is measured concentration of heavy metal in sediment, Bn is the geochemical background value (Turekian & Wedepohl, 1961); 1.5 is the background matrix correction factor due to lithogenic effects. The contamination level was defined as :

$$C_f = C_{measued} / C_{background} \tag{3.3}$$

Where, Turekian and Wedepohl's (1961) background values were used

Table 3.3 Classification for geoaccumulation index (Igeo)

Igeo Value	**Class**	**Sediment Quality**
≤0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly polluted to extremely polluted
>6	6	Extremely polluted

Table 3.4 Contamination factor (C_f) and level of contamination (Saha & Hossain, 2011)

Contamination Factor (C_f)	**Contamination level**
$C_f < 1$	Low contamination
$1 \le C_f < 3$	Moderate contamination
$3 \le C_f < 6$	Considerable contamination
$C_f > 6$	Very high contamination

To assess the heavy metal contamination and classify the environmental condition of the sampling sites, there were some criteria used. They are: Threshold effect level (TEL), permissible exposure level (PEL) and Sediment Quality Guidelines (SQG). TEL value referred to the concentration below which adverse biological influences rarely occurred, and PEL value represents the maximum concentration above which adverse effects were expected. TEL-PEL values, background values and SQG criteria were given in Table 3.4.

3.8 Statistical Analysis

The statistical analyses of the relationships between metal concentrations, stations and depths were performed with R 3.1.1 and agricolae package (De Mendiburu, 2014; R Core Team, 2014). Normality tests (Shapiro-Wilk and Anderson-Darling) and homogeneity of variances (Fligner-Killeen and Bartlett), were applied before one-way parametric (or non-parametric) tests. One-Way Analysis of Variance (ANOVA) following the Tukey's HSD test for multiple comparison were applied at significance level of $p<0.05$. Otherwise, One-Way non-parametric Kruskal-Wallis Test was performed ($p<0.05$).

Table 3.4 Criteria for sediment pollution assessment

		Hg	As	Cd	Pb	Cr	Cu	Zn	Mn	Ni	Fe	Al
TEL[a]		0.13	7.4	0.68	30.2	52.3	18.7	124	-	15.9	-	-
EL[a]		0.70	41.6	4.21	112	160	108	271	-	42.8	-	-
SQG [b]	**Non Polluted**	-		-	<40	<25	<25	<90	-	<20	-	-
	Moderately Polluted	-		-	40-60	25-75	25-50	90-200	-	20-50	-	-
	Heavily Polluted	-		>6	>60	>75	>50	>200	-	>50		-
Mediterranean background[c]		**0.34**		**0.10**	**25**	**15**	**15**	**50**	**-**	**-**	**-**	
Background values[d]		**0.40**		**0.30**	**20**	**90**	**45**	**95**	**850**	**68**	**47000**	**84000**

a Long et al., 1995

b Burton, 2002

c UNEP (1978), Whitehead et al. (1985) and MAP (1987)

d Turekian and Wedepohl (1961)

CHAPTER FOUR
RESULTS

4.1 Visual Observations

The visible differences in appearances of the core samples were noted on the sampling day immediately. According to visible differences, the cores were subsampled for grain size analysis.

The core from the outer bay, station 6 was divided into 3 parts. The first part was 10 cm-long and mainly composed of silt and clay. It was light green-brown with no smell, low viscosity and small-broken shell fragments. The second part (10-18 cm), it was brown-grey with medium viscosity and full of unbroken and broken larger shells. The last part (28-40 cm) was green-grey with no smell, medium viscosity and lots of shell fragments.

The other station from outer bay is station 8 and there was a hard ground that sampling could not be done as 30 cm. The first part was the surface part and it was light brown, while the second part involves 10 cm of the core was dark grey.

The core sample from station 11, which is close to Gediz River's mouth, was divided into 3 sections. The first one was 10 cm-long and had a very low viscosity, no smell, no shell fragments and brown-grey color. The second part was between 10 and 21 cm, it was very sticky, dark green-grey colored and had no smell. Also its clay content was higher, viscosity was low and there were no shell fragments. The last part of the core was between 21 and 43 cm, it was very sticky, its clay content was higher, it had no smell or shell fragments as the upper parts.

The other station from outer bay was 25. The length of the total core was 19 cm and 10 cm was used for instrumental analysis. It was divided into two parts and the first one is up to 4 cm, with light brown color, very low viscosity, sand content and shell fragments. The second part was between 4 and 15 cm, dark green-grey and consisted of thin broken shells.

The station from middle bay was 22 and the core was segmented into 3 sections. The first one was up to 3 cm, light brown, stinking and had silt, clay and sand on a small scale. It had low viscosity and broken shell fragments. The other part was between 3 and 21 cm, dark grey, sticky and had a little bit smell and broken shell fragments. The last part was up to 33 cm and it was viscous and stinking.

In inner bay station 24 and harbor were studied. Station 24 was sectioned into 3 parts. The first one was until the fifth cm and light brown. It had a bad smell, low viscosity and shell fragments. The other part was between 5 and 18 cm, it was dark grey, more viscous, more stinking and more clay content. The last part was between 18 and 42 cm, it was viscous and sticky, green-grey and had broken shells.

The final station was harbor and this is the most polluted one. The core sample was divided into 3 sections and the first one was up to 14 cm. It was dark grey and very stinking. It had a low viscosity and many shell fragments. The second part was between 14 and 27 cm, it was dark grey, sticky and had a bad smell and many shell fragments. Finally the last part was between 27 and 49 cm, it was dark green-grey with more clay content and higher viscosity.

4.2 Water Content

Drying of samples could be performed in different methods as oven-drying, air-drying and freeze-drying. In this study freeze-drying method was used and moisture content of sediments was determined. Tanner and Leong, (1995) stated that there is no difference in moisture or metal content results between the methods. Water content of sediments taken from İzmir Bay differs according to different stations by depending on sand, silt and clay contents of the sediment and therefore depending on porosity and permeability to water flow of the sediment. The results are given in Table 4.1.

Table 4.1 Water content of the sediments in İzmir Bay

Stations	Moisture content (%)
6	71.6 ± 2.5
8	71.1 ± 0.8
11	52.9 ± 1.8
25	47.9 ± 1.1
22	51.6 ± 1.2
24	38.5 ± 1.4
Harbor	66.8 ± 1.8

4.3 Grain Size Distribution

Sediment cores from station 6, 8, 25, and harbor were uniform and same charastericties in terms of grain size distribution. Station 6 contains 16.1-27.3 (%) sand content, 41.7-49.7 (%) silt content, and 30.9- 34.2 (%) clay content. Station 8 contains 63.6-68.8 (%) sand, 17.2-22.4(%) silt, and 10.8-14.1 (%) clay content. Station 25 contains 0-2.35 (%) gravel, 5.0-13.6 (%) sand, 54.6-59.1 (%) silt, 27.4-40.5 (%) clay content. The grain size distribution of harbor is 0-0.40 (%) gravel, 0.6-2.35 (%) sand, 79-84.7 (%) silt, and 14.8-19.5 (%) clay. Although the cores were divided into sections according to visual and qualitative observations on the sampling day, the results of the sieve and hydrometer analysis proved empirically that some fragments were the same. The station 11 shows the same distribution up to 21 cm and that is 0.2 (%) sand, 45.5-49.9 (%) silt, and 49.9-54.4 (%) clay and it is silty-clay. The lower part up to 43 cm contains 0.09 (%) sand, 62 (%) silt and 31.9 (%) clay and it is clayey silt. The upper two fragments (0-21 cm) of station 22 shows homogenous properties and contains 1.1-2.6 (%) sand, 57.9-63.5 (%) silt and 33.7-41.1 (%) clay; where the final part (21-33 cm) contains 82.6 (%) silt and 16.7 (%) clay content. Finally the upper fragments of station 24 (0-18 cm) contains 0.2-0.6 (%) gravel, 2-2.93 (%) sand, 78.5-82.9 (%) silt and 14.5-18 (%) clay content and it is categorized as clayey silt. The lower part of the core was between 18 and 42 cm, and the distribution is 1.2 (%) sand, 41.9 (%) silt, and 56.5 (%) clay and this part is categorized as silty-clay.

Table 4.2 Grain size distribution (%) of the sediment core samples

Stations	**Gravel (%)**			**Total**	**Sand (%)**			**Total**	**Silt (%)**			**Total**	**Clay (%)**	
	coarse	**medium**	**fine**		**Coarse**	**Medium**	**fine**		**coarse**	**medium**	**fine**			
6/1 (0-10 cm)	-	-	-	-	7.12	10.95	3.48	21.55	14.77	19.40	13.20	47.37	31.10	Homogenous
6/2 (10-28 cm)	-	-	-	-	4.10	8.20	3.80	16.10	19.10	18.20	12.40	49.70	34.20	
6/3 (28-40 cm)	-	-	0.30	0.30	8.00	14.10	5.10	27.20	15.10	15.80	10.80	41.70	30.90	
8/1 (surface)	-	2.70	0.50	3.20	19.00	29.20	20.60	68.80	5.80	7.80	3.60	17.20	10.85	Homogenous
8/2 (10 cm)	-	-	-	-	13.70	24.40	25.50	63.60	7.60	10.10	4.70	22.40	14.10	
11/1 (0-10 cm)	-	-	-	-	0.04	0.08	0.09	0.21	7.10	25.50	17.30	49.90	49.90	Homogenous
11/2 (10-21 cm)	-	-	-	-	0.05	0.05	0.07	0.17	4.95	22.10	18.40	45.45	54.40	
11/3 (21-43 cm)	-	-	-	-	0.02	0.03	0.04	0.09	38.00	14.10	9.90	62.00	37.90	Different
22/1 (0-3 cm)	-	-	0.16	0.16	0.14	0.26	2.22	2.62	19.30	28.80	15.40	63.50	33.70	Homogenous
22/2 (3-21 cm)	-	-	-	-	0.07	0.10	0.90	1.07	20.60	25.50	11.80	57.90	41.10	
22/3 (21-33 cm)	-	-	0.01	0.01	0.12	0.07	0.56	0.75	34.40	35.40	12.80	82.60	16.70	Different
25/1 (0-4 cm)	-	-	-	-	2.35	5.90	5.40	13.65	23.10	27.40	8.60	59.10	27.40	Homogenous
25/2 (4-19 cm)	-	-	-	-	-	2.80	2.20	5.00	19.80	22.60	12.20	54.60	40.50	
24/1 (0-5 cm)	-	-	0.60	0.60	1.50	0.83	0.60	2.93	45.50	21.70	11.30	78.50	18.00	Homogenous
24/2 (5-18 cm)	-	-	0.15	0.15	1.24	0.50	0.30	2.04	54.00	20.60	8.30	82.90	14.50	
24/3 (18-42 cm)	-	-	0.08	0.08	0.80	0.24	0.15	1.19	4.90	18.50	18.50	41.90	56.50	Different
Harbor/1 (0-14 cm)	-	-	-	-	0.10	0.10	0.42	0.62	57.10	20.70	6.90	84.70	14.80	Homogenous
Harbor/2 (14-27 cm)	-	-	0.40	0.40	0.74	0.13	0.30	1.17	36.10	30.20	12.70	79.00	19.50	
Harbor/3 (27-49 cm)	-	-	0.30	0.30	0.80	0.50	1.05	2.35	46.30	23.10	9.60	79.00	18.30	

4.4 Total Organic Matter Content

The total organic matter content (%) of the stations is given in Table 4.3. In station 6, the organic matter content was found between 0.95-5.6 (%) as the minimum at 14-15 cm and the maximum at 20-22 cm. The mean value was determined as 2.2±0.19 (%). In station 8, it was measured between 1.9-2.8 (%), as the minimum at 6-7 cm and the maximum at 2-3 cm. The mean value of organic matter content was determined as 2.4±0.1 (%). In station 11, the range of organic matter content was determined as 1.7-3.8 (%). The minimum was at 28-30 cm and the maximum was at 1-2 cm. The mean of the values was determined as 2.4±0.09 (%). The results from station 25 were between 4.4 (1-2 cm) and 6.9 (0-1 cm) (%), and the mean was calculated as 5.6±0.27 (%).

In station 22, the minimum value was detected on the surface of the core as 3.2 (%), and the maximum value was detected at 6-7 cm as 5.4 (%). The mean value of the organic matter content was calculated as 3.6±0.09 (%) in the station 22. The results from station 24 showed that the organic matter content varied between 5.2 and 9.2 (%). The minimum concentration was measured at 28-30 cm and the maximum concentration was measured at 20-22 cm. The mean value was determined as 6.8±0.22 (%). Finally in the harbor, the total organic matter content was in a range between 4.4 and 12.5 (%). The minimum concentration was detected at 28-30 cm while the maximum concentration was detected at 7-8 cm. The mean organic matter concentration of harbor was calculated as 7.7±0.46 (%).

The organic matter range of whole İzmir Bay was 1.0-12.5 (%). Total organic matter content increased towards the inner bay. Maximum concentrations were obtained in Harbor and relatively lower concentrations were measured at outer bay. This can be explained that harbor was a highly contaminated area by the industrial and domestic wastes from surrondings.

Table 4.3 Total organic matter (TOM) content of sediments from İzmir Bay

Depth	6	8	11	22	25	24	Harbor
0-1	2,87	2.44	2.76	3.24	6.92	7.01	4.77
1-2	1.47	2.70	3.84	3.56	4.39	6.70	9.21
2-3	1.93	2.78	1.89	3.94	6.19	7.71	6.80
3-4	2.20	2.47	2.14	3.76	5.44	7.18	6.46
4-5	2.16	2.09	2.33	3.02	6.16	6.67	9.23
5-6	1.98	2.23	2.08	3.17	5.42	7.70	7.47
6-7	1.27	1.87	2.42	5.37	4.75	7.92	6.65
7-8	2.16	2.62	2.38	3.45	4.84	8.46	12.54
8-9	1.38	2.19	3.46	3.45	6.61	7.12	11.64
9-10	1.63	2.26	2.32	3.86	5.25	4.47	6.02
10-11	2.04	-	2.46	3.12	-	7.11	5.35
11-12	1.32	-	2.16	3.34	-	7.31	10.01
12-13	2.08	-	3.60	3.98	-	6.98	8.93
13-14	2.38	-	2.29	3.46	-	5.95	8.84
14-15	0.95	-	2.45	3.48	-	6.09	8.46
15-16	2.05	-	2.59	3.92	-	6.60	5.92
16-17	2.01	-	2.24	3.69	-	7.14	8.62
17-18	1.96	-	1.83	3.45	-	6.21	6.52
18-19	3.15	-	2.17	3.15	-	7.56	6.63
19-20	3.77	-	2.09	3.52	-	8.04	5.68
20-22	5.57	-	2.16	3.20	-	9.16	9.45
22-24	1.84	-	2.94	3.31	-	5.80	6.47
24-26	2.31	-	2.30	3.40	-	5.47	5.29
26-28	2.73	-	1.98	3.25	-	5.52	12.16
28-30	2.34	-	1.67	3.24	-	5.21	4.40
Mean	**2.2±0.19**	**2.4±0.1**	**2.4±0.09**	**3.6±0.09**	**5.6±0.27**	**6.8±0.22**	**7.7±0.46**

4.5 Heavy Metal Concentrations

All of the heavy metal concentrations (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn and Zn) were given in Tables 4.4-4.10 and Figures 4.1-4.4. Also variations of metal levels within stations and between stations were statistically evaluated and summarized in Tables 4.11-4.12 and Table 4.13, respectively. Statistically significant results were respresented with group numbers according to one-way ANOVA or Kruskal-Wallis test ($p<0.05$).

4.5.1 Aluminum

Aluminum was 30122 mg/kg at 17-18 cm of station 6 as the minimum value and 65980 mg/kg at 4-5 cm as maximum. The mean value of the station 6 was calculated as 47047±1841 mg/kg. The results of station 8 had shown that the minimum Al concentration was 28011 mg/kg at 3-4 cm, and the maximum concentration was 52441 mg/kg at 2-3 cm with a mean value of 38984±2541 mg/kg. In station 11, the minimum value was found as 50565 mg/kg at 22-24 cm and the maximum value was found as 74083 mg/kg at 3-4 cm. The mean value was 58220±1194 mg/kg. The levels in station 25 were, 20918 mg/kg at 3-4 cm, and 35791 mg/kg at 6-7 cm. The mean value was calculated as 27994±1519 mg/kg. In station 22 the aluminum levels were found 53832 mg/kg at 6-7 cm as minimum, 109413 at 9-10 cm as maximum. The mean concentration was 70142±2645 mg/kg. The results from inner bay station 24 were 52334 mg/kg at 5-6 cm and 119937 mg/kg at 0-1 cm. The mean concentration was 75098±2928 mg/kg. The aluminum levels of harbor were detected between 41959 mg/kg at 14-15 cm and 79733 mg/kg at 28-30 cm. The mean concentration was calculated as 54136±1742 mg/kg.

4.5.2 Arsenic

Arsenic levels in outer bay, station 6, were 22.6 - 54 mg/kg, minimum at 2-3 cm and maximum at 16-17 cm, and mean value was 37.8±2.2 mg/kg. In station 8, they were between 14 (4-5 cm) and 21.4 (7-8 cm) mg/kg with a mean value of 17.5±0.8

mg/kg. In station 11, the minimum value was 22.7 mg/kg at 4-5 cm and 35.1 mg/kg at 0-1 cm, and the mean value was found as 28±0.7 mg/kg. The results of middle bay, station 25, were found between 13.7 mg/kg at 6-7 cm and 27.8 mg/kg at 9-10 cm, and the mean value of the 10 depths was determined as 23.1±1.8 mg/kg. At station 22, the lowest value was determined as 19.3 mg/kg at 3-4 cm, the highest value was determined as 32.9 mg/kg at 9-10 cm, and the mean concentration was determined as 24.8±0.66 mg/kg. In inner bay, station 24, gave the results of arsenic concentration as in the range of 26.4 – 57.5 mg/kg. The minimum value was measured at 4-5 cm, and the maximum value was measured at 19-20 cm. The levels has a mean value of 37.4±1,3 mg/kg. In harbor station, the arsenic levels were determined 28.2 mg/kg as minimum value at 19-20 cm and 39 mg/kg as maximum value at 8-9 cm, with 34.8±0.5 mg/kg mean value.

4.5.3 Cadmium

Cadmium levels were between 0.12 mg/kg at16-17, 24-26 and 28-30 cm and 0.18 mg/kg at 0-1 cm with a mean concentration of 0.13±0.002 mg/kg at station 6. At station 8, the minimum concentration was 0.12 mg/kg at 5-6, 7-8 and 8-9 cm, and the maximum concentration was 0.16 mg/kg at 1-2 cm. The mean concentration was calculated as 0.14±0.005 mg/kg. At station 11, the minimum concentration was measured as 0.10 mg/kg at 8-9 and 17-18 cm and the maximum concentration was 0.17 mg/kg at 5-6 cm, the mean concentration was calculated as 0.13±0.003 mg/kg. At station 25, the minimum concentration was 0.11 mg/kg at 9-10 cm, the maximum concentration was 0.19 mg/kg at 4-5 cm, and the mean concentration was calculated as 0.14±0,007 mg/kg. At station 22, 0.16 mg/kg at 22-24 cm as minimum, 0.33 mg/kg at 7-8 cm were found and mean concentration was calculated as 0.21±0,009 mg/kg. At station 24, the minimum concentration was 0.15 mg/kg at 28-30 cm, the maximum concentration was detected as 0.39 mg/kg at 7-8 cm, and the mean concentration was 0.25±0.015 mg/kg. Finally, the results of harbor were between 0.11 mg/kg at 28-30 cm and 1.24 mg/kg at 9-10 cm. The mean concentration was determined as 0.62±0.008 mg/kg.

4.5.4 Chromium

At station 6, the minimum concentration was determined as 141 mg/kg at 26-28 cm, the maximum concentration was 162 mg/kg at 11-12 cm and the mean concentration was calculated as 151±1.17 mg/kg. At station 8, minimum concentration was found on the surface of the core as 101 mg/kg, the maximum concentration was at 7-8 cm as 144 mg/kg, and the mean concentration of chromium was 135±4 mg/kg. At station 11, the minimum concentration was determined at 8-9 and 28-30 cm as 179 mg/kg, the maximum concentration was detected at 16-17 cm as 217 mg/kg and the mean concentration was calculated as 190±1.7 mg/kg. At station 25, the minimum value was 71 mg/kg at 6-7 cm, the maximum value was 96 mg/kg at 7-8 and 9-10 cm and the mean value was 81±2.8 mg/kg. At station 22, at 6-7 cm 144 mg/kg was detected as minimum, at 9-10 cm 232 mg/kg was detected as maximum and the mean value of this station was 176±3.3 mg/kg. In inner bay, station 24 gave the results that 152 mg/kg at 19-20, 26-28 and 28-30 cm as minimum, 191 mg/kg at 3-4 cm as maximum and 169±2.5 mg/kg as mean concentration. At harbor, 83 mg/kg at 26-28 cm was the lowest value, 424 mg/kg at 10-11 cm was the highest value and 237±21 mg/kg was the mean concentration.

4.5.5 Copper

At station 6, the lowest value was detected at 26-28 cm as 18 mg/kg, the highest value was detected at 4-5 cm as 25.9 mg/kg and the mean concentration was 22.1±0.46 mg/kg. At station 8, the lowest concentration was measured at surface as 13.4 mg/kg, the highest concentration was measured at 2-3 cm as 18.3 mg/kg and the mean concentration was calculated as 15.9±0.50 mg/kg. At station 11, the minimum concentration was 32.4 mg/kg at surface, the maximum concentration was 41.0 mg/kg at 16-17 cm, and the mean concentration was calculated as 35.4±0.36 mg/kg. At station 25, 14.9 mg/kg at surface as minimum, 17.2 mg/kg at 7-8 cm as maximum and mean concentration was calculated as 16.4±0.26 mg/kg. At station 22, the minimum concentration was 26.5 mg/kg at 22-24 cm, the maximum concentration was 35.2 mg/kg at 9-10 cm, and the mean concentration was 30.6±0.47 mg/kg. At station 24, the lowest concentration was 42.2 mg/kg at 20-22 cm, the highest concentration was 53.8 mg/kg at 3-4 cm and the mean concentration was determined as 49.8±0.90 mg/kg. At harbor, the minimum value was 43.5 mg/kg at 28-30 cm, the maximum value was 123 mg/kg at 6-7 cm and the mean concentration was 82.4±4.5 mg/kg.

4.5.6 Iron

At station 6, the results were between 30051 mg/kg (22-24 cm) and 36040 mg/kg (4-5 cm). The mean concentration was calculated as 32542±349 mg/kg. At station 8, the results were detected between 15934 mg/kg at surface and 27022 mg/kg at 7-8 cm, and the mean concentration was 23304±986 mg/kg. At station 11, the minimum concentration was 38709 mg/kg at surface, the maximum concentration was 50475 mg/kg at 16-17 cm, and the mean concentration was 42432±517 mg/kg. The levels at station 25 were between 19773 mg/kg (6-7 cm) and 29256 mg/kg (8-9 cm) and the mean concentration was 24980±1226 mg/kg. At station 22, the lowest value was found as 35446 mg/kg at 6-7 cm, the highest value was 53322 mg/kg at 9-10 cm, and the mean concentration was 38710±716 mg/kg. At station 24, the lowest concentration was detected as 35886 mg/kg at 5-6 cm, the highest concentration was 46207 mg/kg at 19-20 cm, and the mean value was calculated as 42374±578 mg/kg. The results from harbor were between 29639 mg/kg (2-3 cm) and 42033 mg/kg (26-28 cm). The mean concentration was 35074±641 mg/kg.

4.5.7 Lead

Lead levels in station 6, were found between 2.0-18 mg/kg as minimum at 13-14 cm and maximum at 8-9 cm, and with a mean value of 6.4±0.67 mg/kg. In station 8, they were between 0.35 (8-9 cm) and 4.9 (4-5 cm) mg/kg with a mean value of 3.37±0.55 mg/kg. In station 11, the minimum value was 4.0 mg/kg at 28-30 cm and maximum was 16.5 mg/kg at 0-1 cm, and the mean value was 11.0±0.51 mg/kg. The results of station 25 were found between 5.9 mg/kg at 8-9 cm and 10.8 mg/kg at 3-4 cm, and the mean value was determined as 9.0±0.43 mg/kg. Station 22 gave the results of lead concentration as in the range of 7.4-18.4 mg/kg. The minimum value was measured at 20-22 cm, and the maximum value was measured at 9-10 cm. The levels have a mean value of 10.3±0.51 mg/kg. In inner bay, station 24, the concentrations were between 46.9 (4-5 cm) and 81.0 (18-19 cm) mg/kg and the mean concentration was determined as 59.4±1.91 mg/kg. In harbor station, the lead levels were determined as 50.8 mg/kg minimum value at 2-3 cm and 90.5 mg/kg maximum value at 13-14 cm, with 70.8±2.0 mg/kg mean value.

4.5.8 Manganese

At station 6, the minimum concentration was 469 mg/kg at 5-6 cm, the maximum concentration was 707 mg/kg on the surface of the core and the mean concentration was calculated as 506±9.0 mg/kg. At station 8, minimum concentration was detected on the surface as 343 mg/kg, the maximum concentration was found at 1-2 cm as 481 mg/kg, and the mean concentration of manganese was determined as 442±11.7 mg/kg. At station 11, the minimum concentration was detected at 12-13 cm as 397 mg/kg, the maximum concentration was on the surface as 686 mg/kg and the mean concentration was 460±10.4 mg/kg. At station 25, the minimum value was 279 mg/kg at 2-3 and 3-4 cm, the maximum value was 330 mg/kg at surface and the mean value was determined as 288±4.8 mg/kg. At station 22, at 6-7 cm 438 mg/kg was detected as minimum, again on the surface 636 mg/kg was measured as maximum and the mean value of this station was 488±10.1 mg/kg. In inner bay, station 24 gave the results that 461 mg/kg at 2-3 cm as minimum, 688 mg/kg at 26-28 cm as maximum and 548±11.6 mg/kg as mean concentration. At harbor, 358 mg/kg at 11-12 cm was the lowest value, 665 mg/kg at 28-30 cm was the highest value and 438±15.8 mg/kg was the mean concentration.

4.5.9 Mercury

Mercury was found 0.1 mg/kg at 28-30 cm of the station 6 as the minimum value and 0.34 mg/kg at 0-1 and 2-3 cm as maximum. The mean value of station 6 was calculated as 0.20±0.016 mg/kg. The results of station 8 had shown that the minimum mercury concentration was 0.44 mg/kg at 8-9 cm, and the maximum concentration was 4.7 mg/kg at 3-4 cm with a mean value 1.7±0.42 mg/kg. In station 11, the minimum value was found as 0.14 mg/kg on the surface of the core and the maximum value was found as 0.22 mg/kg at 7-8 and 16-17 cm. The mean value was 0.18±0.003 mg/kg. The levels in station 25 were, 0.13 mg/kg at 8-9 cm, and 0.23 mg/kg at 5-6 cm. The mean value was 0.18±0.009 mg/kg. In station 22 the mercury levels were found as 0.17 mg/kg at 15-16 cm as minimum, 0.26 mg/kg at 9-10 cm as maximum. The mean concentration was 0.20±0.004 mg/kg. The results from inner bay station 24 were 0.60 mg/kg at 4-5 cm and 1.4 mg/kg at 16-17. The mean concentration was 0.87±0.038 mg/kg. The mercury levels of harbor were between 0.57 mg/kg at 0-1, 1-2, 2-3 and 5-6 cm and 1.0 mg/kg at 26-28 cm. The mean concentration was calculated as 0.77±0.029 mg/kg.

4.5.10 Nickel

Nickel levels in station 6, were found between 77.6-123 mg/kg as minimum at 0-1 cm and maximum at 15-16 cm, with a mean value of 96.9±2.24 mg/kg. In station 8, they were between 35.3 (0-1 cm) and 52.1 (5-6 cm) mg/kg with a mean value of 46.8±1.56 mg/kg. In station 11, the minimum value was 107 mg/kg at 6-7 cm and maximum was 136 mg/kg at 4-5 cm, and the mean value was found as 118±1.26 mg/kg. The results of station 25 were between 34.4 mg/kg at 0-1 cm and 52.4 mg/kg at 9-10 cm, and the mean value was determined as 43.3±1.99 mg/kg. Station 22 gave the results of nickel concentration as in the range of 97-150 mg/kg. The minimum value was measured at 3-4 cm, and the maximum value was measured at 17-18 cm. The levels have a mean value of 102±1.35 mg/kg. In inner bay, station 24, concentrations were between 94.0 (5-6 cm) and 131 (26-28 cm) mg/kg and the mean concentration was determined as 111±2.04 mg/kg. In harbor station, the nickel levels were determined as 69.4 mg/kg minimum value on the surface of the core and 196 mg/kg maximum value at 6-7 cm, with 85.2±4.84 mg/kg mean value.

4.5.11 Selenium

At station 6, the lowest value was detected at 14-15 cm as 0.69 mg/kg, the highest value was detected at 3-4, 4-5 and 9-10 cm as 2.5 mg/kg and the mean concentration was calculated as 1.7±0.12 mg/kg. At station 8, the lowest concentration was measured at 4-5 cm as 1.4 mg/kg, the highest concentration was measured on the surface as 2.3 mg/kg and the mean concentration was calculated as 1.8±0.083 mg/kg. At station 11, the minimum concentration was 1.5 mg/kg at surface, 4-5 and 9-10 cm, the maximum concentration was 2.0 mg/kg at 2-3, 11-12 and 26-28 cm, and the mean concentration was 1.8±0.030 mg/kg. At station 25, 1.1 mg/kg at 1-2 cm as minimum, 1.9 mg/kg at 6-7 cm as maximum and mean concentration was calculated as 1.5±0.078 mg/kg. At station 22, the minimum concentration was detected as 1.5 mg/kg at 22-24 cm, the maximum concentration was 2.7 mg/kg at 9-10 cm, and the mean concentration was calculated as 1.9±0.056 mg/kg. At station 24, the lowest concentration was 1.2 mg/kg at 3-4 and 24-26 cm, the highest concentration was 2.3 mg/kg on the surface and 7-8 cm and the mean was 1.8±0.066 mg/kg. At harbor, the minimum value was 0.57 mg/kg at 26-28 cm, the maximum value was 2.7 mg/kg at 10-11 cm and the mean concentration was 1.6±0.087 mg/kg.

4.5.12 Tin

At station 6, the results were between 2.9 mg/kg (24-26 cm) and 5.0 mg/kg (3-4 cm) and the mean concentration was calculated as 3.7±0.11 mg/kg. At station 8, the results were obtained between 1.8 mg/kg at surface and 2.8 mg/kg at 3-4 and 5-6 cm, and the mean concentration was 2.4±0.11 mg/kg. At station 11, the minimum concentration was detected as 3.7 mg/kg at 4-5 cm, the maximum concentration was 5.6 mg/kg at 16-17 cm, and the mean concentration was determined as 4.4±0.08 mg/kg. The levels of station 25, were between 2.2 mg/kg (2-3 cm) and 3.1 mg/kg (1-2 cm) and the mean concentration was 2.7±0.088 mg/kg. At station 22, the lowest value was found as 4.0 mg/kg at 3-4 cm, the highest value was found at 7.5 mg/kg at 9-10 cm, and the mean concentration was found as 4.8±0.15 mg/kg. At station 24, the lowest concentration was 6.5 mg/kg at 3-4 cm, the highest concentration was detected as 14.0 mg/kg on the surface, and the mean value was 9.9±0.36 mg/kg. The results of harbor were between 5.7 mg/kg (5-6 and 7-8 cm) and 11.8 mg/kg (20-22 cm). The mean concentration was 8.4±0.38 mg/kg.

4.5.13 Zinc

Zinc levels in station 6, were found between 68.5-88.6 mg/kg as minimum at 26-28 cm and maximum at 4-5 cm, and with a mean value of 77.9±1.04 mg/kg. In station 8, they were between 42.3 (9-10 cm) and 57.6 (4-5 cm) mg/kg with a mean value of 51.7±1.6 mg/kg. In station 11, the minimum value was 93.2 mg/kg at 28-30 cm and the maximum value was 130 mg/kg at 16-17 cm, and the mean value was found as 110±1.5 mg/kg. The results of station 25 were found between 51.1 mg/kg at 8-9 cm and 55.8 mg/kg at 0-1 and 4-5 cm, and the mean value was determined as 54.0±0.51 mg/kg. Station 22 gave the results of zinc concentration as in the range of 99.1-162 mg/kg. The minimum value was measured at 20-22 cm, and the maximum value was measured at 14-15 cm. The levels have a mean value of 122±3.9 mg/kg. In inner bay, station 24, the concentrations were between 104 (28-30 cm) and 276 (3-4 cm) mg/kg and the mean concentration was determined as 170±8.8 mg/kg. In the harbor station, the zinc levels were determined as 155 mg/kg minimum value at 28-30 cm and 481 mg/kg maximum value at 6-7 cm, with 325±19.3 mg/kg mean value.

Table 4.4 Metal concentrations (mg/kg) of station 6 (depths were given in cm)

Depth	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
0-1	55618	24.4	0.18	144	24.5	32440	0.34	708	77.6	12.5	2.2	4.1	83
1-2	59752	23.1	0.13	157	25.6	35056	0.31	526	88.1	12.9	2.3	4.5	86
2-3	58332	22.6	0.13	152	24.4	32922	0.34	484	85.6	10.3	2.3	4.8	82
3-4	54331	25.1	0.13	156	24.9	34415	0.30	516	90.8	11.5	2.5	5.0	83
4-5	65980	24.7	0.13	161	25.9	36040	0.31	512	85.1	11.5	2.5	4.2	89
5-6	48920	24.2	0.14	154	24.8	34951	0.32	479	90.5	10.3	2.3	3.9	85
6-7	48990	26.4	0.13	154	24.6	33799	0.24	491	85.7	9.0	2.0	4.3	84
7-8	52703	26.5	0.13	157	23.7	33250	0.22	469	84.8	8.1	2.1	4.0	80
8-9	56645	28.2	0.13	152	23.1	32813	0.16	487	99.5	18	-	3.6	80
9-10	47263	31.6	0.13	150	23.0	31948	0.19	483	88.4	4.2	2.5	3.7	76
10-11	57406	34.1	0.13	152	22.5	32167	0.19	479	91.6	2.2	2.0	3.0	75
11-12	47195	37.3	0.13	162	22.5	34517	0.19	493	85.7	3.1	1.1	4.0	78
12-13	47999	45.2	0.13	146	20.7	30998	0.16	480	95.7	2.2	1.5	3.2	74
13-14	35102	46.4	0.13	147	19.6	31374	0.19	500	107	2.0	1.0	3.4	73
14-15	37821	40.6	0.13	151	21.6	30954	0.26	485	105	6.3	0.69	3.2	77
15-16	44999	43.9	0.13	162	21.9	34867	0.14	509	123	6.3	2.0	3.8	82
16-17	35296	54.0	0.12	152	20.6	32040	0.13	506	117	4.2	1.2	3.3	75
17-18	30122	53.8	0.13	153	20.3	31577	0.13	517	110	6.0	0.72	3.3	76
18-19	40934	52.9	0.13	152	22.1	33775	0.11	522	105	4.7	1.9	3.6	76
19-20	44286	51.5	0.14	147	21.1	31731	0.14	533	99.3	5.5	1.6	3.4	76
20-22	39058	48.2	0.13	144	19.8	30705	0.11	500	99.2	4.2	1.0	3.1	75
22-24	43089	48.6	0.13	144	18.3	30051	0.13	508	100	4.8	1.6	3.2	71
24-26	38631	44.5	0.12	147	19.9	30299	0.14	489	96.4	4.3	1.5	2.9	70
26-28	34674	43.8	0.13	141	18.0	30249	0.11	491	102	4.3	1.2	3.3	69
28-30	51050	44.0	0.18	144	19.9	30623	0.10	489	105	4.7	1.7	3.5	73

Table 4.5 Metal concentrations (mg/kg) of station 8 (depths were given in cm)

Depth	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
0-1	48655	17.5	0.14	101	13.4	15934	2.8	343	35.3	2.9	2.3	1.8	48
1-2	39406	16.5	0.16	137	16.3	20517	0.94	481	42.9	4.4	1.8	2.7	56
2-3	52441	14.7	0.15	141	18.3	23014	0.77	433	47.2	4.8	2.0	2.5	55
3-4	28011	15.8	0.15	143	17.6	24743	4.7	451	50.3	4.8	1.8	2.8	57
4-5	33116	14.0	0.15	139	15.9	24483	2.0	450	49.0	4.9	1.4	2.6	58
5-6	39740	17.8	0.12	139	16.8	25457	2.2	459	52.1	3.8	1.7	2.8	53
6-7	35212	16.4	0.13	137	16.4	25144	0.73	442	47.8	3.2	1.5	2.2	52
7-8	34002	21.4	0.12	144	16.1	27022	2.0	465	51.6	1.3	2.0	2.7	51
8-9	47087	19.5	0.12	136	15.1	23470	0.44	446	46.9	0.35	1.8	2.2	45
9-10	32170	21.1	0.14	133	13.6	23261	0.45	449	45.1	2.9	1.5	2.2	42

Table 4.6 Metal concentrations (mg/kg) of station 25 (depths were given in cm)

Depth	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
0-1	30640	15.8	0.12	79	14.9	20310	0.20	330	35.6	8.9	1.6	2.9	56
1-2	29776	26.5	0.13	85	17.2	28444	0.18	283	47.4	8.6	1.1	3.1	55
2-3	32811	17.0	0.13	77	15.6	20348	0.20	279	34.4	8.5	1.7	2.2	52
3-4	20918	21.8	0.13	72	16.1	23631	0.18	279	42.4	10.8	1.6	2.6	55
4-5	22328	25.5	0.19	79	16.6	24112	0.19	282	42.4	9.9	1.4	2.5	56
5-6	22783	27.4	0.15	76	17.1	26129	0.23	284	47.5	10.0	1.2	2.6	54
6-7	35791	13.7	0.15	71	15.7	19773	0.20	296	35.5	10.1	1.9	2.7	55
7-8	29506	29.9	0.16	96	17.2	28864	0.14	283	48.4	8.2	1.4	3.0	53
8-9	28669	25.9	0.12	83	17.0	29256	0.13	281	46.8	5.9	1.2	2.5	51
9-10	26727	27.8	0.11	96	17.0	28944	0.14	292	52.4	8.7	1.5	3.0	53

Table 4.7 Metal concentrations (mg/kg) of station 11 (depths were given in cm)

Depth	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
0-1	52813	35.1	0.12	184	32.4	38709	0.14	686	115	16.5	1.5	3.8	112
1-2	55564	26.7	0.12	189	34.7	42645	0.17	454	113	13.1	1.7	4.3	115
2-3	59885	26.6	0.11	193	34.9	42080	0.20	451	119	12.6	2.0	4.5	114
3-4	74083	25.6	0.11	196	35.5	43329	0.18	461	118	12.6	1.8	4.5	115
4-5	51163	22.7	0.16	187	32.6	39303	0.17	435	136	12.8	1.5	3.7	103
5-6	63469	28.9	0.17	185	36.5	45407	0.19	470	112	7.9	1.6	4.7	107
6-7	55170	23.9	0.13	202	33.9	41128	0.17	446	107	10.7	1.7	4.9	109
7-8	57915	24.5	0.14	197	35.3	41275	0.22	439	112	12.5	1.9	4.1	116
8-9	54534	26.1	0.10	179	34.3	41765	0.18	443	120	12.0	1.9	4.5	113
9-10	52402	23.6	0.13	181	34.9	42216	0.19	439	118	14.1	1.5	3.8	107
10-11	59660	25.1	0.13	187	36.7	43237	0.18	452	115	12.8	1.7	4.3	110
11-12	65064	28.7	0.11	196	36.6	44011	0.18	466	120	11.0	2.0	4.7	115
12-13	51449	27.0	0.12	187	35.3	39407	0.17	397	115	10.8	1.8	4.3	107
13-14	56802	29.9	0.15	205	37.5	46684	0.20	468	124	12.1	1.9	5.0	122
14-15	56164	27.8	0.14	188	34.4	42726	0.18	433	119	9.9	1.8	4.4	111
15-16	52256	27.5	0.12	191	37.4	43240	0.17	438	116	9.8	1.7	4.0	113
16-17	68205	34.7	0.15	217	41.0	50475	0.22	516	134	13.3	1.9	5.6	130
17-18	60651	27.9	0.10	193	36.5	41948	0.19	441	117	11.1	1.7	4.2	114
18-19	54770	29.1	0.13	188	36.1	41802	0.20	431	118	9.7	1.7	4.3	117
19-20	57602	29.4	0.11	185	34.2	42701	0.18	469	122	8.8	1.7	4.2	104
20-22	64316	30.0	0.13	191	35.5	43680	0.19	467	122	8.6	1.9	4.3	101
22-24	50565	23.7	0.11	201	33.1	38803	0.18	425	116	11.7	1.6	4.1	105
24-26	64016	29.8	0.11	186	35.6	42816	0.17	467	118	8.7	1.8	4.8	100
26-28	63388	35.0	0.11	188	36.1	42489	0.17	472	122	7.5	2.0	4.2	104
28-30	53600	31.2	0.13	179	34.6	38944	0.15	446	115	4.0	1.7	4.3	93

Table 4.8 Metal concentrations (mg/kg) of station 22 (depths were given in cm)

Depth	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
0-1	56589	23.8	0.16	158	31.9	39108	0.20	636	107	8.3	2.4	5.0	118
1-2	61384	20.6	0.18	185	32.4	36163	0.19	471	114	13.0	1.8	4.9	115
2-3	56212	21.4	0.19	181	32.9	36323	0.21	462	123	14.1	1.8	4.8	114
3-4	64507	19.3	0.20	186	33.1	37650	0.19	462	97	11.8	1.9	4.0	144
4-5	64759	20.2	0.20	178	31.9	36377	0.20	455	103	8.5	1.8	4.1	136
5-6	73063	22.8	0.16	182	31.9	37777	0.20	471	109	9.4	2.3	5.1	117
6-7	53832	22.8	0.21	144	29.1	35446	0.23	438	110	8.3	1.9	4.2	101
7-8	55028	23.6	0.33	176	32.2	37030	0.21	461	112	11.2	2.0	4.4	115
8-9	73705	23.3	0.26	180	32.3	36307	0.23	470	105	11.6	1.8	4.4	116
9-10	109413	32.9	0.31	232	35.2	53322	0.26	622	137	18.4	2.7	7.5	155
10-11	75654	25.7	0.26	186	33.7	40278	0.24	486	120	13.0	2.2	5.8	120
11-12	65216	23.1	0.17	176	30.2	36933	0.19	444	123	10.9	1.8	4.5	156
12-13	69034	22.7	0.22	183	31.1	39583	0.20	494	124	10.2	2.0	4.6	143
13-14	68024	24.3	0.21	156	30.6	39679	0.20	516	128	10.2	2.0	4.5	112
14-15	66667	25.0	0.21	175	30.0	37686	0.18	495	116	8.3	1.7	4.2	162
15-16	62828	26.3	0.22	179	30.3	37428	0.17	465	123	9.0	1.7	4.4	148
16-17	72696	29.8	0.22	182	30.1	38583	0.22	474	115	7.9	1.8	3.8	105
17-18	63584	28.1	0.21	157	30.0	39939	0.20	485	150	8.4	2.0	4.8	107
18-19	70711	25.7	0.20	166	30.8	41906	0.19	519	148	9.7	2.4	5.8	117
19-20	71634	26.2	0.16	171	27.5	38564	0.19	453	123	7.9	1.7	4.7	120
20-22	70081	25.2	0.17	174	27.5	37282	0.18	454	122	7.4	1.7	4.4	99
22-24	72866	27.4	0.16	175	26.5	37206	0.18	468	125	8.3	1.5	4.3	103
24-26	87418	29.6	0.17	172	26.5	37761	0.20	486	133	9.7	1.7	5.0	107
26-28	98516	27.3	0.16	169	27.2	40732	0.19	535	131	11.4	2.0	5.0	109

Table 4.9 Metal concentrations (mg/kg) of station 24 (depths were given in cm)

Depth	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
0-1	119937	31.1	0.23	170	49.4	39578	0.67	507	99.0	50.5	2.3	14.0	154
1-2	94809	32.9	0.24	165	49.4	40056	0.78	513	116	59.6	1.7	8.6	180
2-3	59576	30.5	0.35	172	53.2	36782	0.75	461	116	54.9	2.1	10.9	179
3-4	82331	27.1	0.38	191	53.9	38633	0.78	475	89.5	48.9	1.2	6.5	276
4-5	67954	26.4	0.31	185	49.5	37696	0.60	475	104	46.9	1.6	7.7	271
5-6	52334	30.3	0.25	166	51.6	35886	0.62	505	94.0	49.8	2.0	8.2	160
6-7	77008	33.1	0.24	166	50.8	40809	0.69	497	99.8	49.3	2.0	9.5	163
7-8	70763	37.4	0.39	190	56.7	43966	0.78	518	109	65.6	2.3	9.7	221
8-9	62363	34.9	0.38	183	51.1	41828	0.66	488	111	55.3	2.0	8.5	173
9-10	52798	36.6	0.39	172	53.2	41955	0.73	505	106	63.6	1.9	7.9	171
10-11	72447	38.7	0.24	187	62.0	44013	1.1	536	109	54.1	2.0	9.9	191
11-12	79044	38.0	0.27	187	53.2	42314	0.93	532	116	77.0	1.3	9.3	214
12-13	75678	38.8	0.23	180	50.1	44824	1.1	543	115	71.2	2.1	11.2	159
13-14	75243	37.7	0.20	164	48.9	44661	0.85	551	111	54.3	2.0	9.8	152
14-15	72854	38.6	0.20	169	47.8	44742	0.83	574	119	59.1	2.0	10.5	153
15-16	69527	37.4	0.22	161	48.9	44231	0.87	560	120	56.9	1.7	11.1	153
16-17	87757	37.9	0.25	169	51.5	42484	1.4	573	104	68.4	1.3	10.2	210
17-18	82452	38.4	0.22	162	49.8	42796	1.3	609	120	77.7	1.6	12.2	148
18-19	80199	38.8	0.21	170	48.1	43231	0.95	577	124	81.0	1.6	11.2	145
19-20	53202	57.5	0.21	152	51.7	46207	0.97	589	121	60.3	1.6	13.5	208
20-22	75623	40.3	0.20	162	42.2	45315	0.84	572	120	51.2	1.6	8.9	124
22-24	72351	37.5	0.20	153	43.1	42690	0.87	563	120	64.9	1.8	10.8	131
24-26	65561	42.3	0.16	157	43.9	42856	0.85	627	99.8	56.5	1.2	7.8	122
26-28	87454	48.9	0.18	152	43.2	45839	1.1	688	131	55.3	1.7	10.0	111
28-30	88187	44.9	0.15	152	43.3	45977	0.82	664	120	52.8	1.5	8.4	104

Table 4.10 Metal concentrations (mg/kg) of harbor (depths were given in cm)

Depth	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
0-1	52863	31.1	0.29	168	67.2	30460	0.57	530	69.4	52.5	1.4	5.8	255
1-2	50651	31.4	0.37	171	92.6	30388	0.57	468	85.1	54.5	1.7	6.1	382
2-3	45663	31.3	0.35	166	77.2	29639	0.57	457	71.4	50.8	1.1	5.8	287
3-4	45525	33.8	0.51	205	89.0	31657	0.62	449	77.4	62.9	1.6	6.9	333
4-5	53322	34.7	0.65	232	96.7	34338	0.62	428	84.6	69.4	1.8	7.6	453
5-6	63290	34.1	0.72	221	97.0	33110	0.57	391	74.1	66.7	1.8	5.7	339
6-7	56432	35.1	1.08	331	123	32956	0.60	370	196	83.5	1.7	6.8	481
7-8	57892	36.7	0.80	317	100	33349	0.60	363	75.5	68.7	1.6	5.7	388
8-9	51058	39.0	1.00	413	115	31777	0.70	363	72.1	80.5	1.5	5.9	465
9-10	52743	35.1	1.24	414	113	33561	0.74	384	77.7	81.7	1.6	8.1	458
10-11	48609	38.9	1.68	424	107	34555	0.77	370	89.3	82.2	2.7	10.4	433
11-12	48291	35.6	0.83	367	96.8	34212	0.85	358	85.3	77.7	1.9	9.5	370
12-13	52277	37.6	0.72	297	83.5	35787	0.75	387	79.1	77.4	1.8	8.3	326
13-14	53332	36.5	1.11	331	111	35731	0.76	387	98.8	90.5	2.1	9.2	366
14-15	41959	35.3	0.76	292	80.2	34387	0.78	381	80.1	74.7	1.4	8.7	314
15-16	42032	34.7	0.58	223	70.6	35375	0.85	398	80.3	72.6	1.4	9.9	278
16-17	48876	33.9	0.77	230	73.6	35851	0.84	401	84.3	79.3	1.1	11.0	288
17-18	47879	34.2	0.74	228	70.3	36896	0.90	431	83.8	77.0	1.6	11.7	383
18-19	56135	37.6	0.53	185	66.4	37916	0.89	439	82.7	76.0	1.7	10.3	272
19-20	51134	28.2	0.35	194	69.9	36874	0.97	438	72.4	70.2	1.7	8.5	267
20-22	67176	36.4	0.34	168	62.3	36970	0.90	450	82.1	68.7	1.2	11.8	345
22-24	60225	32.3	0.16	106	54.5	38084	0.93	493	77.3	62.6	1.3	9.4	175
24-26	56935	34.2	0.12	91	49.7	40127	0.99	547	78.6	61.8	0.8	9.0	166
26-28	69389	36.9	0.12	83	48.9	42033	1.0	612	77.2	61.5	0.6	8.5	163
28-30	79733	36.8	0.11	84	43.5	40828	0.89	665	95.9	66.9	1.1	8.9	155

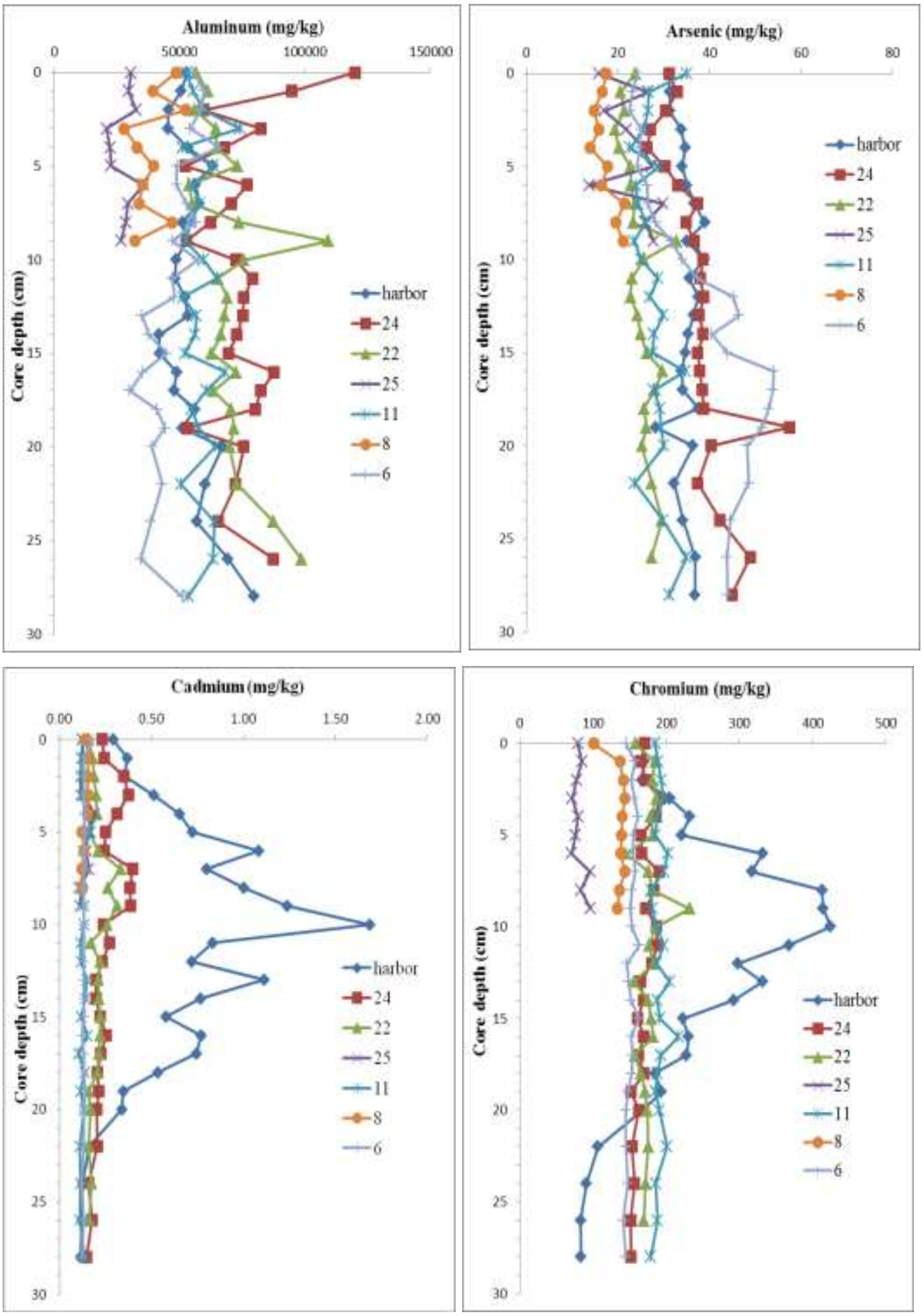

Figure 4.1 Concentrations of Al, As, Cd and Cr in sediment core samples

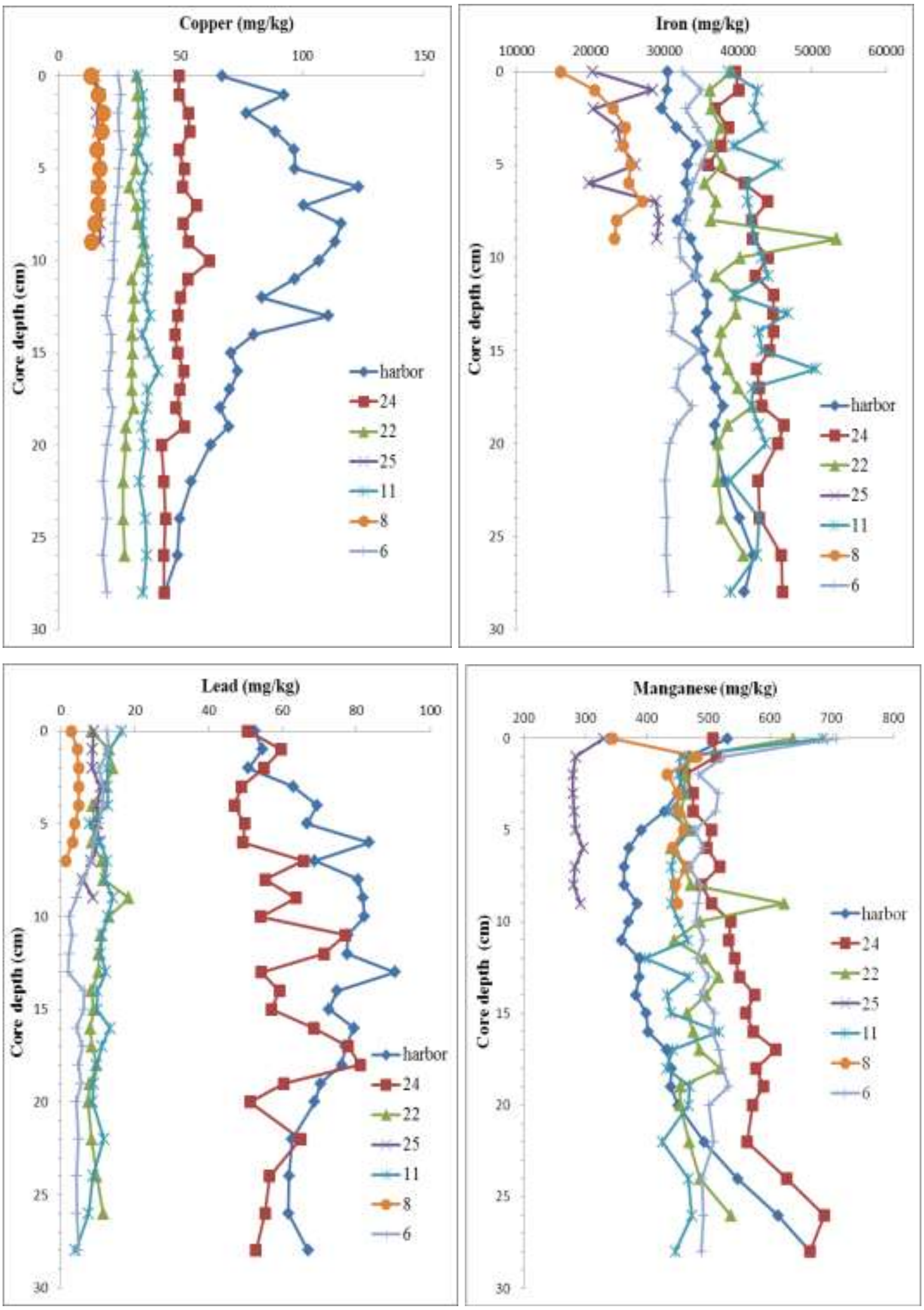

Figure 4.2 Concentrations of Cu,Fe, Pb and Mn in sediment core samples

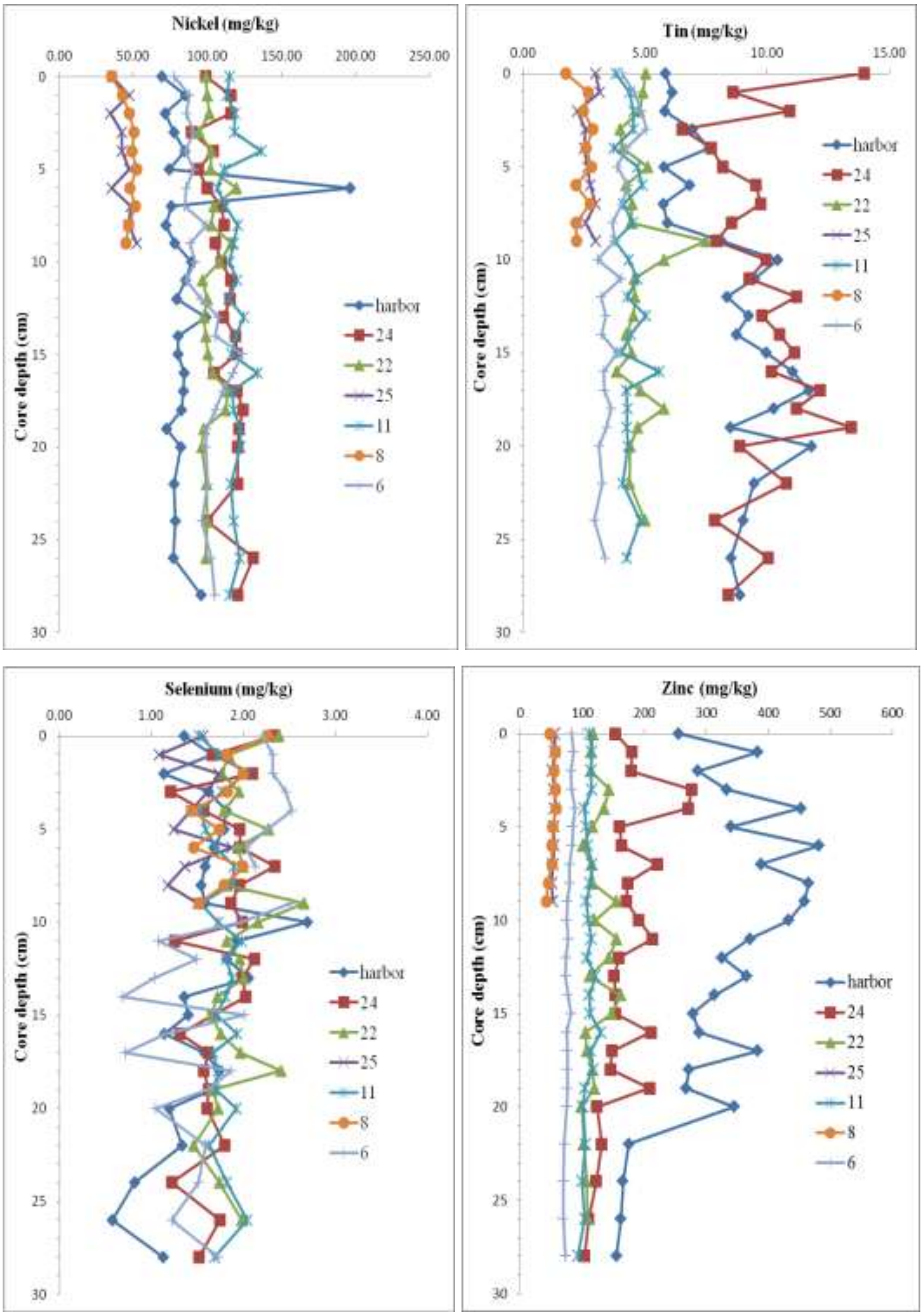

Figure 4.3 Concentrations of Ni, Sn, Se and Zn in sediment core samples

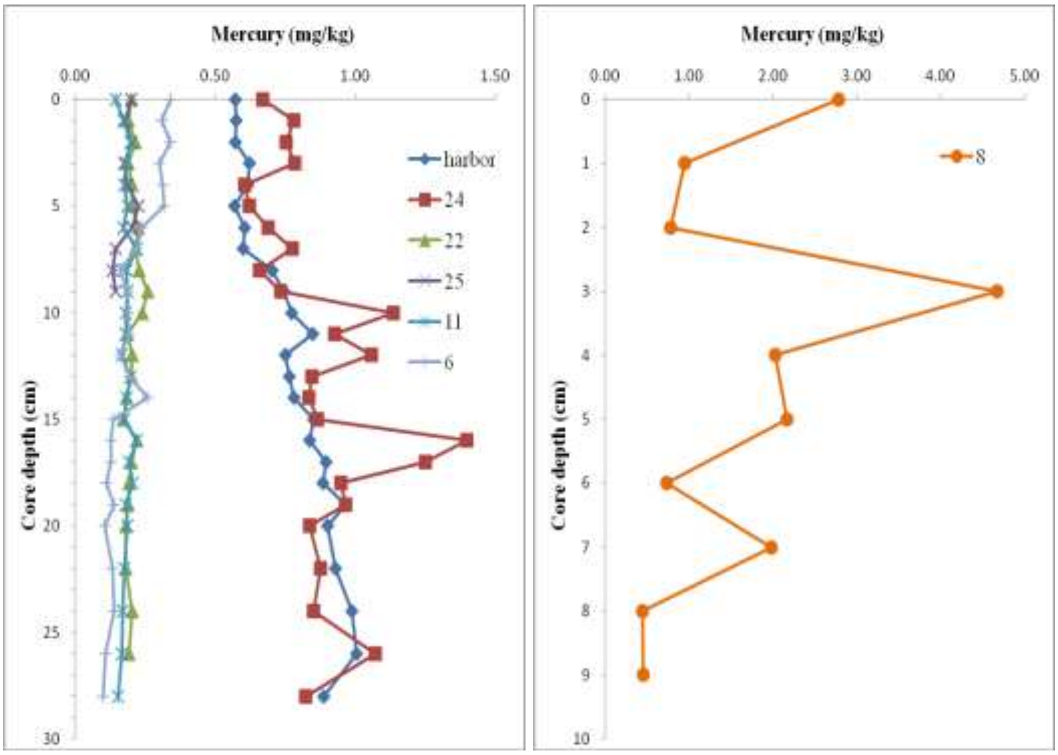

Figure 4.4 Concentrations of Hg in sediment core samples (The right graph represents the concentration of mercury at station 8)

Table 4.11 Statistical analysis ($p<0.05$) for sediment depth variations of heavy metal concentrations at each station (AV: One-Way Analysis of Variance Test; KW: One-Way Non-Parametric Kruskal-Wallis Test; H: Harbor)

	Station	Depth (cm)											
		0-2	**2-4**	**4-6**	**6-8**	**8-10**	**10-12**	**12-14**	**14-16**	**16-18**	**18-20**	**20-24**	**>24**
Hg	6 (KW)	a	a	a	ab	bcd	bc	bc	bc	de	cde	e	e
	8 (AV)	Not significant (p:0.611)											
	11 (AV)	Not significant (p:0.229)											
	22 (AV)	ab	ab	ab	ab	a	ab	ab	b	ab	ab	b	ab
	24 (AV)	bc	bc	c	bc	bc	ab	bc	bc	a	bc	bc	bc
	25 (AV)	Not significant (p:0.215)											
	H (AV)	f	ef	f	ef	def	bcd	cde	abcd	abcd	ab	abc	a
Cd	6 (KW)	Not significant (p:0.272)											
	8 (AV)	Not significant (p:0.114)											
	11 (AV)	Not significant (p:0.35)											
	22 (AV)	Not significant (p:0.07)											
	24 (AV)	bcd	ab	abcd	abc	a	abcd	cd	cd	bcd	cd	cd	d
	25 (AV)	ab	ab	a	ab	b							
	H(AV)	bcd	bcd	abcd	abc	ab	a	abc	abcd	abcd	abcd	cd	d
As	6 (KW)	h	h	g	fg	ef	e	c	d	a	ab	bc	d
	8 (AV)	Not significant (p:0.235)											
	11 (AV)	Not significant (p:0.246)											
	22 (AV)	Not significant (p:0.815)											
	24 (KW)	fg	fg	g	def	ef	bc	c	cde	cd	ab	bc	a
	25 (AV)	Not significant (p:0.713)											
	H(AV)	Not significant (p:0.33)											
Cu	6 (AV)	ab	ab	a	abc	abcd	bcde	ef	cdef	def	cdef	f	f
	8 (AV)	Not significant (p:0.116)											
	11 (AV)	Not significant (p:0.257)											
	22 (AV)	ab	a	ab	ab	a	ab	ab	ab	ab	ab	b	b
	24 (KW)	de	a	abcd	ab	abc	a	cde	def	abcd	bcd	f	ef
	25 (AV)	Not significant (p:0.654)											
	H (AV)	abcde	abcd	abc	ab	a	abc	abc	bcde	cde	cde	de	e
Cr	6 (AV)	Not significant (p:0.056)											
	8 (KW)	b	a	ab	a	b							
	11 (AV)	Not significant (p:0.095)											
	22 (KW)	Not significant (p:0.10)											
	24 (AV)	Not significant (p:0.053)											
	25 (AV)	Not significant (p:0.503)											
	H(AV)	efg	ef	def	abc	a	ab	bcd	cde	def	ef	fg	g
Zn	6 (AV)	ab	abc	a	abcd	bcdef	bcdef	def	abcde	cdef	cdef	ef	f
	8 (AV)	Not significant (p:0.077)											
	11 (AV)	Not significant (p:0.068)											
	22 (KW)	Not significant (p:0.089)											
	24 (KW)	Not significant (p:0.103)											
	25 (AV)	Not significant (p:0.128)											
	H(AV)	ab	ab	a	a	a	a	ab	ab	ab	ab	ab	b
Mn	6 (KW)	Not significant (p:0.188)											
	8 (KW)	Not significant (p:0.912)											
	11 (KW)	Not significant (p:0.703)											
	22 (KW)	Not significant (p:0.339)											
	24 (AV)	cde	e	de	cde	de	bcde	bcd	bc	b	b	bc	a
	25 (KW)	Not significant (p:0.254)											
	H (KW)	ab	bc	de	g	fg	g	ef	ef	d	cd	bc	

Table 4.12 Statistical analysis ($p<0.05$) for sediment depth variations of heavy metal concentrations at each station (AV: One-Way Analysis of Variance Test; KW: One-Way Non-Parametric Kruskal-Wallis Test; H: Harbor)

	Station	**Depth (cm)**											
		0-2	**2-4**	**4-6**	**6-8**	**8-10**	**10-12**	**12-14**	**14-16**	**16-18**	**18-20**	**20-24**	**>24**
Fe	6 (AV)	ab	ab	a	ab	ab	ab	ab	Ab	ab	ab	b	b
	8 (AV)	b	ab	ab	a	ab							
	11 (KW)	Not significant (p:0.801)											
	22 (KW)	Not significant (p:0.466)											
	24 (AV)	bcd	cd	d	abc	abcd	ab	ab	Ab	abc	ab	ab	a
	25 (AV)	Not significant (p:0.566)											
	H (AV)	f	ef	cde	def	def	bcd	bcd	Bcd	bc	b	b	a
Pb	6 (KW)	a	ab	ab	b	cd	ef	f	Bc	d	cd	de	d
	8 (AV)	ab	a	a	ab	b							
	11 (AV)	a	ab	ab	ab	ab	ab	ab	Ab	ab	ab	ab	b
	22 (KW)	Not significant (p:0.123)											
	24 (KW)	Not significant (p:0.305)											
	25 (AV)	Not significant (p:0.411)											
	H (AV)	d	cd	abcd	abc	ab	ab	a	Abc	ab	abcd	abcd	bcd
Se	6 (KW)	ab	a	a	abc	a	cd	d	Cd	d	bcd	d	cd
	8 (AV)	Not significant (p:0.463)											
	11 (AV)	Not significant (p:0.599)											
	22 (AV)	Not significant (p:0.700)											
	24 (AV)	Not significant (p:0.468)											
	25 (AV)	Not significant (p:0.523)											
	H (AV)	abc	abc	ab	abc	abc	a	ab	Abc	bc	abc	bc	c
Sn	6 (AV)	ab	a	abc	abc	bc	bc	bc	Bc	bc	bc	c	c
	8 (AV)	Not significant (p:0.538)											
	11 (AV)	Not significant (p:0.822)											
	22 (KW)	Not significant (p:0.461)											
	24 (AV)	Not significant (p:0.274											
	25 (AV)	Not significant (p:0.111)											
	H (AV)	d	cd	cd	cd	bcd	abc	abcd	Abcd	a	abcd	ab	abcd
Al	6 (AV)	Not significant (p:0.025)											
	8 (AV)	Not significant (p:0.880)											
	11 (AV)	Not significant (p:0.352)											
	22 (KW)	Not significant (p:0.063)											
	24 (AV)	a	ab	b	ab	b	ab	ab	Ab	ab	ab	ab	ab
	25 (AV)	Not significant (p:0.318)											
	H (AV)	abc	bc	abc	abc	abc	bc	abc	C	bc	abc	ab	a
Ni	6 (AV)	b	b	b	b	ab	b	ab	A	a	ab	ab	ab
	8 (AV)	Not significant (p:0.065)											
	11 (KW)	Not significant (p:0.607)											
	22 (AV)	Not significant (p:0.378)											
	24 (AV)	Not significant (p:0.389)											
	25 (AV)	Not significant (p:0.554)											
	H (KW)	Not significant (p:0.629)											

Table 4.13 Statistical analysis ($p<0.05$) for sediment depth variations of heavy metal concentrations at each station (AV: One-Way Analysis of Variance Test; KW: One-Way Non-Parametric Kruskal-Wallis Test)

Metal	**Station 6**	**Station 8**	**Station 11**	**Station 22**	**Station 24**	**Station 25**	**Harbor**
Hg (KW)	c	a	c	b	a	c	a
Cd (KW)	c	c	c	a	b	c	a
As (KW)	a	c	b	d	a	c	a
Cu (KW)	d	e	c	f	b	e	a
Cr (KW)	d	e	b	f	c	a	b
Zn (KW)	d	e	c	f	b	e	a
Mn (KW)	b	c	c	e	a	d	c
Fe (KW)	c	d	a	e	a	d	b
Pb (KW)	e	f	c	g	b	d	a
Se (KW)	b	b	b	a	b	c	c
Sn (KW)	d	e	c	f	a	e	b
Al (KW)	d	e	b	f	a	e	c
Ni (KW)	c	e	a	f	b	e	d

CHAPTER FIVE
DISCUSSION

5.1 Heavy Metal Contamination Assessment

To determine the origin of heavy metals, enrichment factors (EF), geo-accumulation index (Igeo) were calculated. The variations of EF according to Turekian & Wedepohl (1961), EF_{back} with depth were given in Figures 5.1-5.4. Correlations between metal concentrations and total organic matter of whole bay were given Table 5.1.

5.1.1 Station 6

Station 6 is located in the outer bay, and this region is the least influenced area by anthropogenic effects. The aluminum levels were between 30122 and 65980 mg/kg. The arsenic levels were between 22.6-54 mg/kg. Mean As concentrations were measured between TEL-PEL values. The mean EF value according to Turekian and Wedepohl's (1961) background values was calculated as 5.64± 0.60 and this indicates that a significant portion of As comes from anthropogenic sources. However, EF according to concentration from the deepest layer, it was seen that As levels enriched especially in lower 18 cm; and tend to decrease in upper 12 cm. Cadmium, copper, tin and zinc concentrations were measured between 0.12-0.18 mg/kg, 18-26 mg/kg, 2.9-5.0 mg/kg and 69.5-88.6 mg/kg respectively. Almost all EF values of all these metals were lower than 1.5 and all C_f values were smaller than 1. These indicate that metal contents were entirely from natural sources. Cd and Zn mean values were calculated as smaller than TEL values, and Cu mean value was determined smaller than PEL value. Also according to sediment quality guidelines Station 6 was classified as non-polluted for Cd, Cu, Sn and Zn.

Manganese and iron levels were 468-708 mg/kg and 30249-36040 mg/kg respectively. Mercury concentrations were between 0.1-0.34 mg/kg and Hg concentrations were lower than background (0.40 mg/kg) and Mediterranean background values (0.34 mg/kg). EF values according to background indicate that Hg was lithogenic while EF values according to deepest layer of Station 6 indicate that there was enrichment especially in the upper layers. This enrichment was probably due to atmospheric transporting of mercury compounds. All C_f values were smaller than 1, and it can be said that there was an increase in Hg concentration but station was unpolluted according to criteria.

Lead levels were between 2.0-18.2 mg/kg, EF values show that there was enrichment especially in the upper layers and at 17-18 cm. This enrichment was probably due to atmospheric transporting of lead compounds like mercury. Pb concentrations were smaller than TEL value and according to SQG this station is classified as non-polluted in Pb. Chromium concentrations were determined between 141-163 mg/kg and it was greater than the background value, 90 mg/kg. When the EF value was calculated according to the background (3.12±0.12) it was found that chromium has enrichment, however EF_6 value was calculated (1.18±0.04) and it was seen that the high concentration of Cr was lithogenous at this station. Also, Cr shows similarities with other lithogenous elements, Al and Fe. It has a positive correlation with Al (r= 0.38) and strong positive correlation with Fe (r= 0.86).

Tin levels were determined between 2.9-5.0 mg/kg and EF values were smaller than 1.5 except 17-18 cm. This indicates that Sn was greatly originated from lithogenic sources. Selenium and nickel concentrations were detected between 0.68-2.5 mg/kg, 77.6-124 mg/kg respectively. Se has strong positive correlations with Al and Fe. The EF values were 5.1±0.23 and 2.68±0.16 according to backgrounds, respectively. EF_6 values were determined as 1.03±0.06, and 1.06±0.06, and this indicates that Se and Ni was high due to lithogenic sources. But Igeo values of Se indicated moderate pollution especially in upper layers. Geoaccumulation indices were calculated, and small Igeo values indicate that here was an unpolluted to moderately polluted area (except upper 10 cm of Se).

5.1.2 Station 8

Station 8 is located in the outer bay, near Karaburun. Aluminum levels were 28011-52441 mg/kg and these concentrations are lower than the background value (Turekian & Wedepohl, 1961). Arsenic concentrations were detected between 14-21.4 mg/kg and EF values were calculated between 1.81-4.23 and stated high contamination. Also C_f values supported moderate contamination by being between 1 and 3. But according to EF_6 and EF_8 it is indicated that there was not enrichment. Cadmium levels were found between 0.12-0.16 mg/kg it is lower than the TEL, PEL values. C_f values were smaller than 1 and EF_6 value was found smaller than 2 except 3-4 cm. According to Han et al., (2006), Cd was not enriched and this station is unpolluted in Cd. Copper levels were detected between 13.4-18.3 mg/kg, and EF<1.5 except 3-4 cm. According to SQG this station is classified as non-polluted in Cu. Cu show similarity with Fe and Mn and they have positive correlation.

Iron and manganese concentrations were found between 15934-27022 mg/kg and 343-481 mg/kg respectively, and they have strong positive correlation (r= 0.74). The EF<1.5 (except 3-4 cm), there was not an anthropogenic contamination. Chromium and zinc has similar trends, and positive correlation. They were found between 101-144 mg/kg and 42.3-57.6 mg/kg respectively. The mean EF values show that there is an anthropogenic contribution to Cr. However like station 6, EF_6 and EF_8 stated that the high Cr and Zn contents are lithogenous. Like the other metals, Cr and Zn levels increased at 3-4 cm.

Lead, tin and selenium concentration ranges were determined as 0.35-4.9 mg/kg, 1.8-2.8 mg/kg and 1.4-2.3 mg/kg respectively. When EF values were calculated according to Pb background values and the deepest layer of outer bay (station 6), there was not enrichment. The mean EF value of Sn was 0.91±0.095 and this indicates that Sn concentration is originated from lithogenic sources. Enrichment increases at 3-4 cm. The EF value of Se according to backgrounds stated that there was an anthropogenic contamination, EF_6 indicated that it is lithogenic similar to Station 6. Only 0-4 cm shows enrichment and contamination in Se.

Nickel concentration was determined between 35.3-52.1 mg/kg, and it has similar trend with Fe, Cr and Zn. Also it has positive correlation with Zn and strong positive correlation with Mn, Fe and Cu. The low EF value shows that Ni was from lithogenic sources. The Hg levels were detected between 0.44-4.7 mg/kg, the mean of the concentrations was higher than PEL value. According to high mean EF values calculated with all backgrounds, high Igeo and C_f value showed that there was enrichment and serious anthropogenic contamination of Hg. This is because of the closeness of this station with inactive mercury mining site. In a similar study, Türkdoğan (2013) measured mercury concentrations some of them were greater than 50 mg/kg in sediments taken from Karaburun region. . The Igeo values indicate that station 8 was unpolluted to moderately polluted in all metals except Hg.

5.1.3 Station 11

Station 11 is located near the mouth of Gediz River, in the outer bay. In station 11, aluminum concentration was between 50565-74083 mg/kg. Iron and manganese concentrations have similar trends and strong correlations (r= 0.82), except surface layer. Their concentrations were 38709-50475 mg/kg, 397-686 mg/kg respectively. The EF values were lower than 1.5 but Mn was enriched at surface. At 3-4 and 16-17 cm, all of the metals have high concentrations and this can be explained by the high concentration of structural, lithogenous elements, Fe, Al, Mn.

Chromium, nickel, selenium and zinc concentration ranges were found as 179-217 mg/kg, 107-136 mg/kg, 1.5-2.0 mg/kg and 93.2-130 mg/kg respectively. They were higher than the backgrounds and the station was defined as moderately polluted in Zn and heavily polluted in Cr according to SQG. EF_{11} values were determined lower than 1.5, and it can be said that the high concentrations of these metals originated from lithogenic sources and enrichment was not observed.

Copper concentrations were determined as 32.4-41 mg/kg and low EF values (mean: 1.14±0.018) stated that copper was entirely originated from lithogenic sources. However Cu levels were found higher than station 6's levels and enrichment was observed compared to station 6.

Cadmium and tin concentrations were detected between, 0.10-0.17 mg/kg and 3.7-5.6 mg/kg respectively. Low EF values, smaller than 1.5, indicated that Cd and Sn were lithogenic and the station was not polluted. Arsenic concentrations were found between 22.7-35.1 mg/kg and As levels exceeded background and TEL values, and C_f was between 1-3. EF values stated that a moderate portion of this heavy metal comes from non-natural processes. However, according to EF_6, enrichment was not observed along the core. Lead and mercury levels were detected between 4-14.1 mg/kg and 0.14-0.22 mg/kg, respectively. Concentrations of both metals were smaller than backgrounds, C_f and Igeo values indicate non-pollution. According to EF values, enrichment of Pb and Hg were observed.

5.1.4 Station 25

Station 25 is located in the outer bay. The aluminum concentrations were measured between 20918-35791 mg/kg. The arsenic concentrations were measured between 13.7-27.8 mg/kg and the concentrations were higher than background value. The mean EF value according to Turekian and Wedepohl's (1961) was calculated as 5.58±0.59 and this stated that there was an anthropogenic contamination of As. By considering the deepest layer of station 6, EF_6 values showed that As was not enriched. Therefore, it is concluded that As concentrations were high but natural. The cadmium and mercury concentrations were measured between 0.11-0.19 mg/kg and 0.13-0.23 mg/kg respectively. The enrichment factors were calculated and enrichment was observed at 3-4, 4-5 and 5-6 cm. This increase was observed for all measured metals. This station was not polluted according to background, but polluted compared to station 6 in Cd and Hg. Iron and manganese were determined between 19773-29256 mg/kg and 279-330 mg/kg. According to EF values, Fe enrichment was observed (1.65±0.12) especially in 3-4, 4-5 and 5-6 cm.

Copper and zinc concentrations were found between 14.9-17.2 mg/kg and 51.1-55.8 mg/kg respectively. The EF values were not high (means: 1.13±0.07 and 1.75±0.1) and according to C_f values and SQG, this station was classified as non-polluted in Cu and Zn. At 3-4, 4-5 and 5-6 cm, Zn has enrichment and was described as contaminated compared to station 6. Chromium and nickel concentrations have similar trends and strong positive correlations (r= 0.70), and their levels were found between 71-96 mg/kg and 34.4-52.4 mg/kg respectively. When the EF values of these metals were calculated according to background, an anthropogenic contamination was seen, but according to EF_{25} values contamination was not observed.

Selenium was found 1.1-1.9 mg/kg. The EF values indicated anthropogenic contamination, but all of the Se concentrations at İzmir Bay were naturally high according to our experimental results. However, enrichment was observed in Se compared to station 6. Lead and tin levels were found between 5.9-10.8 mg/kg and 2.2-3.1 mg/kg, respectively. The EF values stated that anthropogenic enrichment occurred only at 3-4, 4-5 and 5-6 cm. EF_6 values, C_f values and SQG stated that station 25 showed no enrichment of these metals. But when compared to station 6, enrichment in Pb was clearly observed.

5.1.5 Station 22

Station 22 is located in the middle bay. The structural elements, aluminum, iron and manganese were detected as 53832-109413mg/kg, 36163-53322 mg/kg and 438-636 mg/kg respectively. Mn and Fe had similar trends and strong correlations (r= 0.72) and Al showed similarities with them (r= 0.45 with Mn and r= 0.73 with Fe). Their Igeo values and C_f (< 1) indicated that they were lithogenic and there was no contamination. However at 9-10 and 18-19 cm, maximum metal concentrations were measured. The high concentrations of metals were not due to anthropogenic sources, from lithogenic (high Al, Fe and Mn content). Cadmium and mercury concentrations were found between 0.16-0.33 mg/kg and 0.17-0.26 mg/kg, respectively. EF values according to Turekian and Wedepohl’s stated low contamination. EF_{22} stated that a large portion of trace metal was derived from non-natural processes or anthropogenic sources (Zhang et al. 2007) in upper 18 cm. Also, it was found that Hg<PEL and Cd<TEL at this core.

Chromium concentrations were between 144-232 mg/kg. Cr has positive correlation with Al and strong positive correlation with Mn and Fe and these correlations were due to the rock composition and lithogenic processes. In this station, Cr concentrations were greater than PEL value, and at 2-3 cm EF value was found greater than 1.5. There was an anthropogenic contribution of Cr at only 2-3 cm. Nickel and zinc levels were measured between 97-150 mg/kg and 99.1-162 mg/kg, respectively. According to background, EFs indicated contamination. However, according to EF_{22}, Ni enrichment was observed in upper 7 cm and Zn enrichment was seen in upper 15 cm. Station 22 was classified as moderately polluted in Zn according SQG. Selenium concentrations were measured between 1.5-2.7 mg/kg. The EF, EF_{22} and EF_6 indicated considerable contamination in upper 8 cm.

Arsenic levels were measured between 19.3-32.9 mg/kg. The EF values according to background indicated that a large portion of As came from anthropogenic sources. But, EF_6 stated no enrichment along the core; but contamination was seen supported with C_f values (mean: 1.91±0.05). Lead and tin concentrations were measured between 7.9-18.4 mg/kg and 4.0-7.5 mg/kg, respectively. According to EF and C_f values, enrichment and contamination were not observed in Pb and Sn, and SQG stated that this station was non-polluted for Pb. Copper concentrations were detected between 26.5-35.2 mg/kg, C_f values are smaller than 1. EF values according to deepest layer of station 6, anthropogenic contamination was present. Station 22 was categorized as moderately polluted in Cu according to SQG.

5.1.6 Station 24

Station 24 is located in inner bay which is a heavily polluted area. Aluminum concentration was found between 52334-119937 mg/kg. At some depths, Al levels exceeded background level. Arsenic concentrations were measured between

26.4–57.5 mg/kg and it had a strong correlation with Mn (r= 0.78) and Fe (r= 0.82). Like the outer and middle bays, As levels exceeded the background values in this station. EF values according to background showed enrichment, and moderate contamination. But EF_6 and EF_{24} showed that As levels did not have a significant enrichment. According to the deepest layer of this station, it can be said that As enrichment and contamination was observed at 19-20 cm, but the levels were decreasing towards the surface. Iron and manganese contents were measured between 35886-45977 mg/kg and 461-688 mg/kg and there is a strong positive correlation between them (r= 0.73). Fe and Mn levels were lower than background, but higher than other stations.

Copper levels were measured as 42.2-53.8 mg/kg and anthropogenic enrichment was observed by EF_6 and EF_{24} Additionally, mean concentration of Cu was greater than background and PEL values, and station 24 was classified for Cu as moderately polluted to heavily polluted according SQG and C_f. At 19-20 cm, enrichment was maximum. Chromium levels were detected between 152-191 mg/kg and greater than PEL value. Enrichment factors were calculated with background and deepest layer of station 6 and 24. Results suggested that, an enrichment and anthropogenic contamination occurred according to EF and EF_{24}, but no enrichment and contamination compared to station 6 (EF_6). So we can conclude that, natural Cr content of station 24 was lower than station 6, but enrichment and contamination were due to non-natural processes here. C_f values are between 1 and 3; also SQG stated that station 24 was heavily polluted for Cr. Zinc concentrations were found between 89.5-276 mg/kg, higher than background and classified as moderately polluted according to SQG. Zn enrichments were high in 3-12 cm and decreased towards surface. Nickel concentrations were found between 94-131 mg/kg and higher than the backgrounds and PEL value. EF values stated that the nickel concentration was high but this was due to the high natural nickel content of this station. Enrichment was not observed according to EF_{24} and EF_6. But this station was classified as contaminated in Ni.

Selenium levels were 1.2.-2.3 mg/kg and these levels were higher than the background value (0.6 mg/kg). EF, EF_{24} and EF_6 stated that Se had an anthropogenic enrichment, especially between 2 and 16 cm. Lead levels were 46.9-77.7 mg/kg. High Pb enrichment was observed compared to the outer bay. EF values according to backgrounds and Igeo values indicated moderate pollution for Pb. Mercury and tin concentrations were between 0.60-1.4 mg/kg and 6.5-13.9 mg/kg, respectively. EF and C_f values indicated anthropogenic enrichment and moderate pollution of these metals. Cadmium concentrations were 0.15-0.39 mg/kg. EF, Igeo and C_f values indicated that there was no anthropogenic enrichment, but relatively high EF_{24} and EF_6 values were calculated in 2-10 cm of the core and it decreased towards surface.

5.1.7 Harbor

Harbor is located in inner bay. This station is a polluted area by a very busy harbor activity and dense populated city. Aluminum, iron and manganese were 42032-79733 mg/kg, 29639-42033 mg/kg and 358-665 mg/kg, respectively. These lithogenic elements had strong correlations with each other (Mn-Fe:0.54, Mn-Al:0.64 and Fe-Al:0.58). They were below backgrounds. Arsenic levels were detected between 28.2-39 mg/kg. EF_{harbor}, Igeo and C_f values indicated that there was no anthropogenic enrichment, but high EF values were obtained.

Chromium, copper and zinc levels were determined between 83-425 mg/kg, 43.5-123 mg/kg and 155-481 mg/kg, respectively. EF values according to all backgrounds indicated anthropogenic contamination. The levels of these metals were higher than outer bay, and backgrounds. Enrichment was high especially in between 6-30 cm of the core and the values decreased towards surface. C_f values supported moderate to considerable pollution and according to SQG, harbor was heavily polluted in Cr and Zn, and heavily polluted in Cu. Tin levels were 5.7-11.8 mg/kg. All EF values stated that enrichment and contamination of Sn occurred in harbor. According to C_f values harbor were classified as moderately polluted in Sn. Lead levels were 50.8-83.5 mg/kg, concentrations and enrichment tend to decrease in upper 6 cm. EF_{harbor}, EF_6 and EF indicated enrichment of Pb from anthropogenic sources. C_f, Igeo values and SQG criteria describe harbor as moderately polluted to heavily polluted in Pb.

Mercury, nickel and selenium concentrations were measured between 0.57-1.0 mg/kg, 69.4-197 mg/kg and 0.57-2.1 mg/kg, respectively. EF_{back} indicated an anthropogenic enrichment of these metals, but EF_{harbor} (except Se) and EF_6 (except Hg) values stated there was no enrichment. But, Hg levels showed an anthropogenic enrichment compared to station 6 and according to C_f values, harbor was moderately contaminated in Hg. Cadmium concentrations were between 0.11-1.24 mg/kg. EF, EF_{harbor} and EF_6 showed an anthropogenic enrichment. C_f values were maximum and showed considerable contamination, especially between 6-14 cm, contamination and enrichments decreased towards surface.

Table 5.1 Correlations between metal concentrations (mg/kg) and total organic matter of the whole bay

	Hg	Cd	Ni	As	Cu	Cr	Zn	Mn	Fe	Pb	Se	Sn	Al	TOM
Hg	1													
Cd	0.17	1.00												
Ni	-0.32	-0.03	1.00											
As	-0.06	0.19	0.32	1.00										
Cu	0.19	0.86	0.13	0.28	1.00									
Cr	0.02	0.83	0.30	0.18	0.77	1.00								
Zn	0.17	0.87	0.08	0.25	0.97	0.76	1.00							
Mn	0.09	-0.28	0.48	0.36	-0.07	-0.10	-0.12	1.00						
Fe	-0.17	-0.03	0.78	0.28	0.24	0.27	0.16	0.54	1.00					
Pb	0.36	0.69	0.05	0.38	0.86	0.49	0.82	0.12	0.29	1.00				
Se	-0.02	0.09	0.19	-0.35	-0.01	0.22	-0.03	0.08	0.17	-0.12	1.00			
Sn	0.31	0.45	0.26	0.40	0.64	0.34	0.60	0.35	0.53	0.87	0.03	1.00		
Al	0.00	0.00	0.60	0.08	0.21	0.19	0.17	0.57	0.72	0.31	0.31	0.54	1.00	
TOM	0.27	0.56	-0.14	0.28	0.70	0.30	0.70	-0.10	0.08	0.81	-0.20	0.67	0.16	1.00

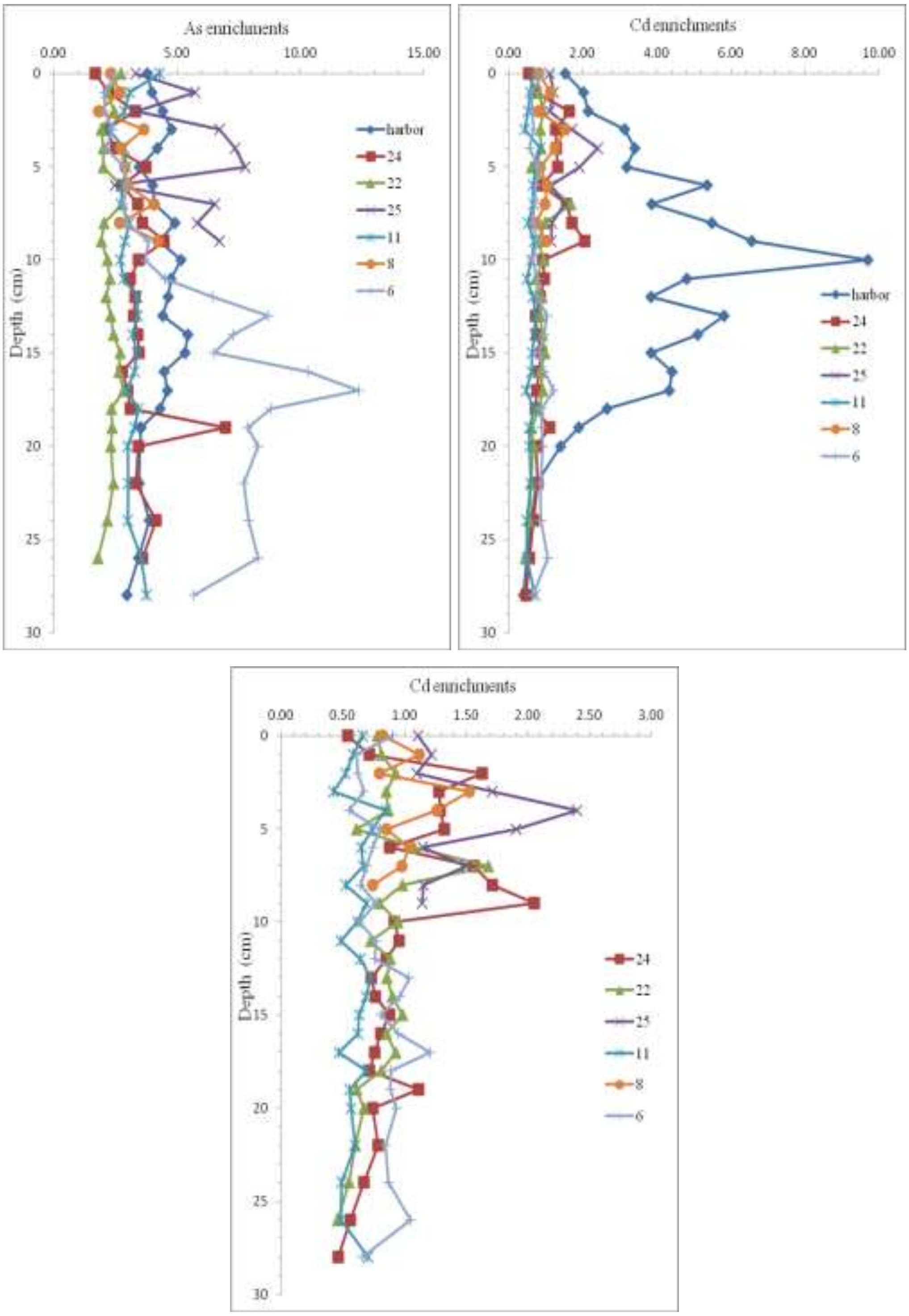

Figure 5.1 EF values (according to Turekian & Wedepohl) of As and Cd (the below graph indicates Cd enrichment values except harbor)

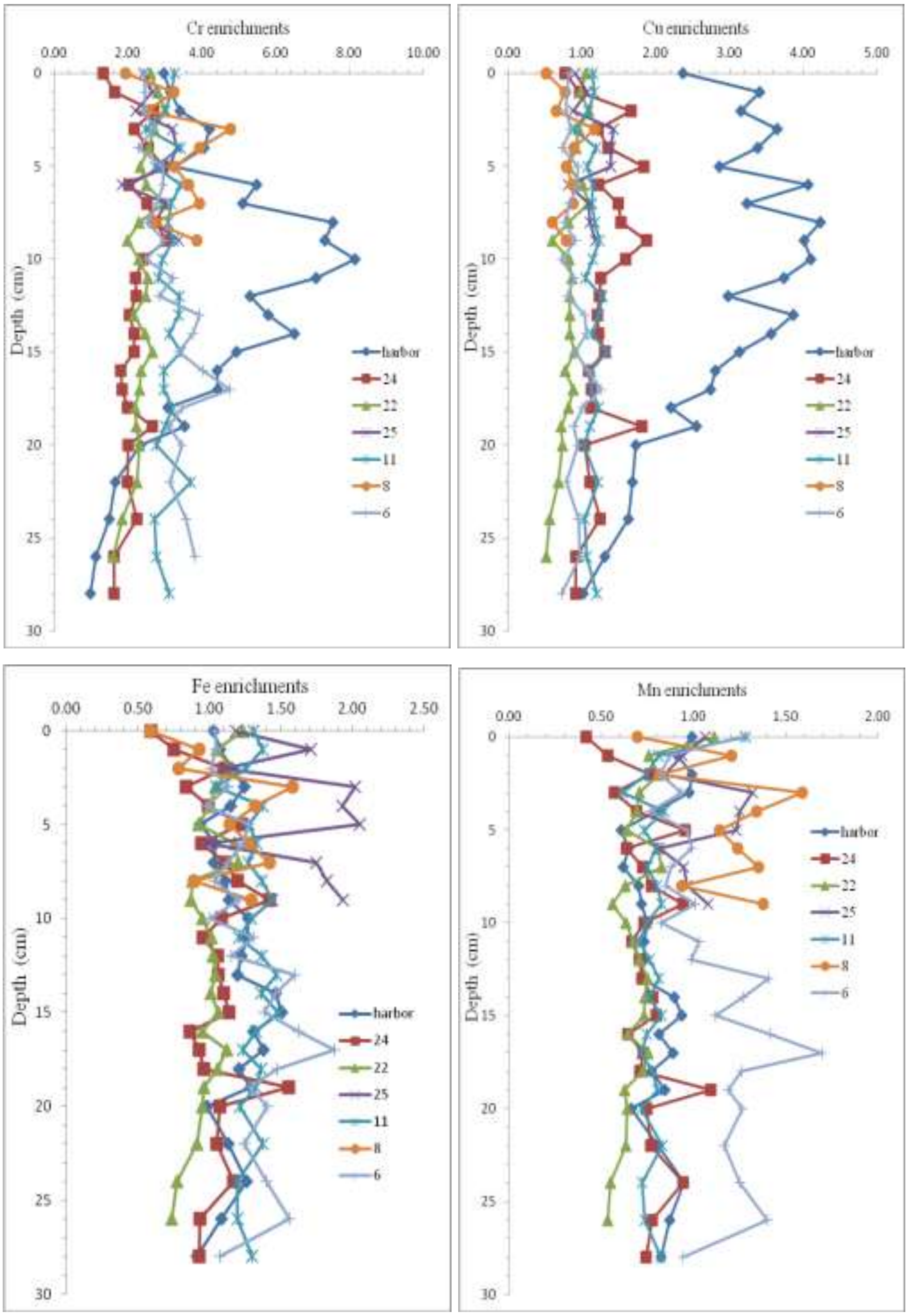

Figure 5.2 EF values (according to Turekian & Wedepohl) of Cr, Cu, Fe and Mn

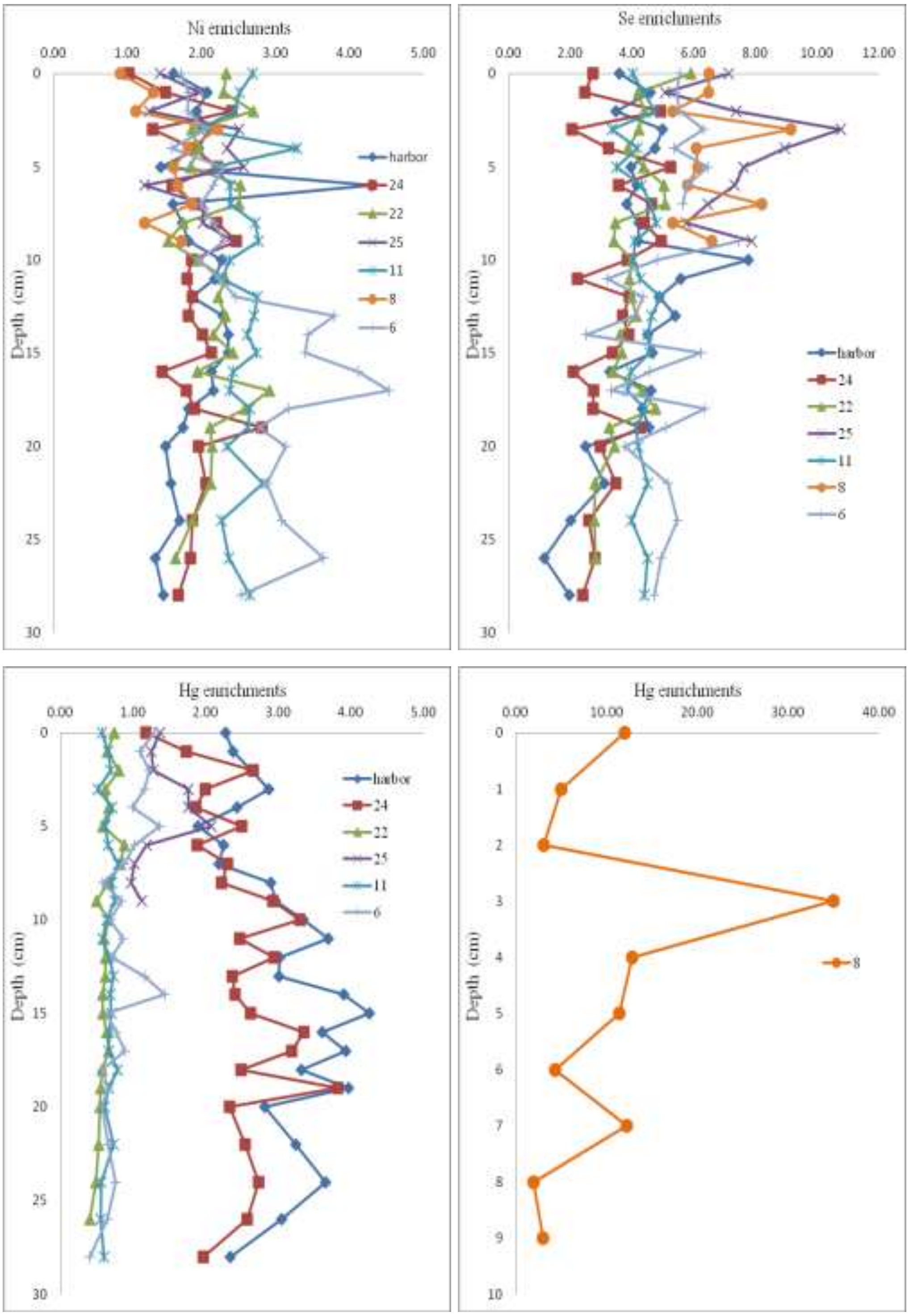

Figure 5.3 EF values (according to Turekian & Wedepohl) of Ni, Se and Hg (the second graph of Hg indicates only enrichment values at station 8)

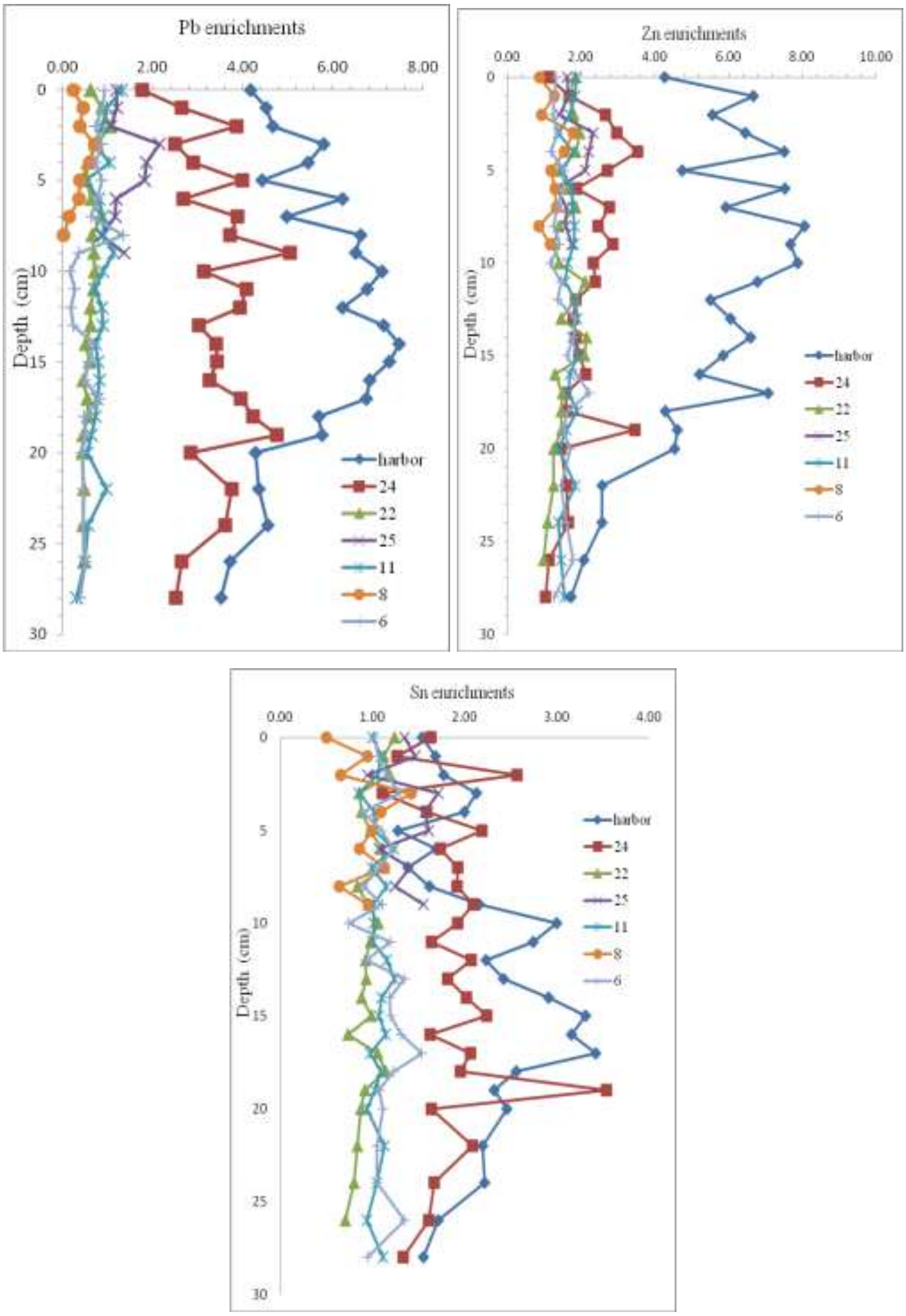

Figure 5.4 EF values (according to Turekian & Wedepohl) of Pb, Zn and Sn

5.2 Evaluation of Statistical Results

Statistical analyses in order to determine the variations of metal concentrations with depth were applied to the data. The results indicate that mercury and copper concentrations varied with depth, within the sediment layers of stations 6, 22, 24 and harbor. Cadmium variations at stations 24, 25 and harbor; arsenic variations at stations 6 and 24; lead variations at stations 6, 8, 11 and harbor with depth were determined. Zinc, tin and selenium variations at stations 6 and harbor; chromium variations at stations 8 and harbor; manganese and aluminum variations at stations 24 and harbor with depth were significant. Additionally, iron concentrations varied with depth at stations 6, 8, 24 and harbor while nickel levels varied with depth only at station 6.

The statistical analyses for the determination of the relationships between variations of metal levels and stations were applied to the data. No significant differences were found among stations 25 and 8 for aluminum, tin, arsenic, nickel, copper, zinc and iron. Lead concentrations differed significantly in all sampling stations. Variations of chromium and manganese levels showed no significant differences among stations 11 and harbor; and 8, 11 and harbor, respectively. No significant variations among stations, except 22 and 11 for As, and station 22 for Hg, were found for As and Hg. Variations of cadmium concentrations among sampling sites were determined. Stations 6, 8,11 and 25 were found as resembling groups whereas station 22 and harbor was another group. Likewise for selenium, 6, 8, 11 and 24 were found as resembling groups and station 25 and harbor were found as another one.

CHAPTER SIX
CONCLUSION

In this study, historical changes of heavy metal concentrations in sediment samples taken from different regions of İzmir Bay were investigated.

Grain size distributions of the sediment core samples were determined. It was found that station 11, 22, 24 and harbor were 97-99.5 % clayey silt, station 6 was 72-84 % clayey silt consisting little amount of sand and station 8 was 63-68 % sand consisting silt and clay. Since grain size distributions were homogenous along core and stations had similar sand, silt and clay contents, it was assumed that there would not be a significant difference in metal adsorption through grain size.

Total organic matter content increased from outer bay to inner bay. Strong correlations were found between TOM and Pb, Sn, Cu, Cd and Zn. Moderate correlations were determined between TOM and Cr. Weak positive correlations were found between TOM and Hg, As and Al.

It was found that concentrations of heavy metals increased from outer bay towards inner bay. To determine the origin and contamination levels of heavy metals, enrichment factor, geo-accumulation index, Threshold effect level and permissible exposure level values and Sediment Quality Guidelines were used. Stations 6, 8 and 25 which are located in the outer bay were identified as non-polluted in terms of many metals. Station 22 which is located in the middle bay was moderately polluted by Hg, Cd, Cu and Sn. Also, station 11, which is the nearest station to the Gediz River was found as moderately polluted for Pb and Cu. Maximum mercury concentrations of whole bay were measured at station 8. The reason of high levels of mercury at station 8 could be explained by the inactive mercury mining site at Karaburun. Also, atmospheric deposition could be one of the reasons that may have contributed to the higher levels of Hg and Pb in İzmir Bay compared to the Mediterranean background values. Relatively high nickel, chromium, arsenic, selenium and zinc concentrations at all stations were due to the lithogenic characteristics of the sediments in the bay.

Station 24 and harbor, in inner bay, were determined as heavily polluted for many metals (Cu, Hg, Pb, Sn, Cd, Cr and Zn). It was seen that the levels of heavy metals with anthropogenic origin were distinctly higher at particular depths of the core and tend to decrease towards the surface in sediment core samples. The metal results from inner bay sediment stated that metal pollution seems to decrease compared to past years. It could be explained by the wastewater treatment plant's working in İzmir since 2001 and by the using of unleaded gasoline since 2004 in Turkey. It is also suggested that the sedimentation rates might be measured at such sediment core studies in order to make more accurate determinations.

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