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DETERMINATION OF LEAD AND CADMIUM BURDEN IN SOME NORTHEAST ATLANTIC AND EASTERN MEDITERRANEAN FISH BY MEANS OF VOLTAMMETRIC METHOD

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Bornova – İZMİR

This study, which has been presented by **Ufuk Çelik** as his **DOCTORATE THESIS** and which is entitled **"Determination of Lead and Cadmium Burden in Some Northeast Atlantic and Eastern Mediterranean Fish by Means of Voltammetric Method"** has been evaluated by us in accordance with the related rules of "E.U. Postgraduate Education and Training Regulations" and "E.U. Institute of Applied and Natural Sciences` Education and Training Directives" and has been found worthdesending and the candidate has been found successful by unanimous/~~majority~~ vote at thesis defence exam on 4th March 2003.

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ABSTRACT

DETERMINATION OF LEAD AND CADMIUM BURDEN IN SOME NORTHEAST ATLANTIC AND EASTERN MEDITERRANEAN FISH BY MEANS OF VOLTAMMETRIC METHOD

ÇELİK, Ufuk

PhD Thesis

Department of Fishing and Processing Technology

Supervisors: Assoc.Prof. Dr. Şükran ÇAKLI

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It is very important to know how much heavy metals are taken by human with seafood consumption. Consumer protection can only be efficient when data on trace elements in fish are available. In this study, lead and cadmium accumulation in edible parts (Fillet, muscle) of common commercial species from Eastern Mediterranean and Northeast Atlantic region were determined by means of voltammetric method.

While it was found as 6.34 ppb in gilthead seabream (*Sparus aurata*) caught from Homa Lagoon as lowest lead concentration, 383 ppb was found as maximum in stripped seabream (*Lithognathus mormyrus*) from Izmir Outer Bay, in all species investigated from Eastern Mediterranean. Highest

cadmium concentration in all samples, which belongs to sharpsnout seabream (*Diplodus puntazzo*) from Izmir Outer Bay, was 14.22 ppb. Mediterranean shad (*Alosa fallax nilotica*), leaping grey mullet (*Liza saliens*), bluefish (*Pomatomus saltator*), brown meagre (*Sciaena umbra*), bonito (*Sarda sarda*), comber (*Serranus cabrilla*), fourspotted megrim (*Lepidorhombus boscii*), sole (*Solea vulgaris*), red pandora (*Dentex machrophtalmus*), annular bream (*Diplodus annularis*), common dentex (*Dentex dentex*), common two-banded seabream (*Diplodus vulgaris*) and thin-lipped grey mullet (*Liza ramada*) has negligible concentrations with the values they gave.

Grey gurnard (*Chelidonichtys gurnardus*) from Tampen region has 80 ppb, which was the highest lead concentration in all analyzed samples from Northeast Atlantic, and it was observed 2.00 ppb in anglerfish (*Lophius piscatorius*) from the north of Shetland Islands as minimum. In this region, whittling (*Melanogrammus aeglefinus*) from Faroe Islands has given top record for cadmium with the value of 2.40 ppb, on the contrary, anglerfish was found under detection limit for it.

All Cd and Pb concentrations observed from species of Eastern Mediterranean and Northeast Atlantic were below the maximum permitted national and international levels.

Keywords: Heavy metal, fish, cadmium, lead, voltammetry.

ÖZET

KUZEYDOĞU ATLANTİK VE DOĞU AKDENİZ`DEKİ BAZI BALIKLARIN KURŞUN VE KADMİYUM YÜKLERİNİN VOLTAMETRİK METOT İLE BELİRLENMESİ

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İnsanların su ürünleri tüketimi ile aldıkları ağır metallerin bilinmesi oldukça önemlidir. Tüketicilerin korunması, sadece balıklarda bulunan ağır metal konsantrasyonları bilindiğinde etkili olabilir. Bu çalışmada, iki Avrupa bölgesi, Kuzeydoğu Atlantik ve Doğu Akdeniz balıklarından ticari olarak kullanılan başlıca türlerin yenebilen kısımlarının (Kas, fileto) kurşun ve kadmiyum birikimleri voltametrik metot ile belirlenmiştir.

Doğu Akdeniz'de incelenen bütün türler içinde en yüksek kurşun konsantrasyonu İzmir Dış Körfezi'nden avlanan mırmır (*Lithognathus mormyrus*) balığında 383 ppb olarak bulunurken, en düşük konsantrasyon ise Homa Dalyanı'ndan avlanan çipura balıklarında (*Sparus aurata*) 6,34 ppb olarak tespit edilmiştir. Tüm türler içinde en yüksek kadmiyum konsantrasyonu ise İzmir Dış Körfezi'nden avlanan sivriburun karagözde (*Diplodus puntazzo*)

14,22 ppb olarak bulunurken tirsi (*Alosa fallax nilotica*), kastros (*Liza saliens*), lüfer (*Pomatomus saltator*), işkine (*Sciaena umbra*), palamut (*Sarda sarda*), asıl hani (*Serranus cabrilla*), cangidez (*Lepidorhombus boscii*), dil (*Solea vulgaris*), patlakgöz mercan (*Dentex machrophtalmus*), ısparoz (*Diplodus annularis*), sinarit (*Dentex dentex*), karagöz (*Diplodus vulgaris*) ve ceran kefal (*Liza ramada*) balıkları ölçüm limitlerinin altında verdikleri değerlerle en düşük konsantrasyonların tespit edildiği balıklar olmuştur.

Kuzeydoğu Atlantik'te ağır metal analizi yapılan tüm türler içinde en yüksek kurşun konsantrasyonu 80,00 ppb olarak Tampen Bölgesi'nden avlanan benekli kırlangıç (*Chelidonichtys gurnardus*) balığında tespit edilirken, en düşük konsantrasyon 2 ppb olarak Shetland Adaları'nın kuzeyinden avlanan fener balığında (*Lophius piscatorius*) görülmüştür. Bölgede ağır metal analizi yapılan tüm türler içinde en yüksek kadmiyum konsantrasyonu 2,40 ppb olarak Faroe Adaları civarından avlanan mezgit balığında (*Melanogrammus aeglefinus*) tespit edilirken, en düşük konsantrasyon Shetland Adaları'nın kuzeyinden ve Faroe Adaları civarından avlanan fener balığında ölçüm limitlerinin altında bulunmuştur.

Doğu Akdeniz ve Kuzeydoğu Atlantik türlerinde tespit edilen bütün Cd ve Pb konsantrasyonları izin verilen maksimum ulusal ve uluslararası düzeylerin altında bulunmuştur.

Anahtar sözcükler: Ağır metal, balık, kadmiyum, kurşun, voltametre.

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INDEX OF ABBREVIATIONS

Abbreviation	Explanation
AAS	Atomic Absorption Spectrophotometer
ASV	Anodic Stripping Voltammetry
DPASV	Differential pulse anodic stripping voltammetry
g	Gram
HMDE	Hanging mercury drop electrode
ICP/MS	Inductively coupled plasma/mass spectrometry
kg	Kilogramm
mg	Milligramm
MT	Metallothionein
Pa	Pascal
ppm	Part per million (ex. mg/kg)
ppb	Part per billion (ex. µg/kg)
ppt	Part per trillion (ex. ng/kg)
USS-ETASS	Ultrasonic slurry sampling electrothermal atomic absorption spectrometry

1. INTRODUCTION

Many elements, which are present in seafood, are essential for human life at low concentration and, however, they can be toxic at high concentrations. Other elements like mercury, cadmium and lead show no known essential function in life and are toxic even at low concentration when ingested over a long period; therefore, many consumers regard any presence of these elements in fish as a hazard to health (Oehlenschläger, 2002). Cause of metallic contamination in food is the substances, which are named as “trace elements”. Trace elements are present at ppm (mg/kg), ppb (µg/kg) or ppt (ng/kg) levels in food. Foods can be contaminated by their raw material, processing and storage steps or the last cooking step in kitchen for consumption. Environmental sources of metals are generally industrial activities, energy power plants, fertilizers, agricultural drugs and earth activities like volcanic explosions.

Lead is a trace element which about is only 0.0018% on earth. It is estimated that half of Pb are used for the production of batteries, quarter of Pb are used for chemicals and the rest are used for cables, alloys and inorganic pigments (Welz and Sperling, 1997). Lead is considered to be a toxic element as a consequence of a variety of biochemical effects. Among these are included neurological problems, haematological effects, renal dysfunction, hypertension and cancer, for which there is evidence for animals but not yet for humans (Munoz-Olivas and Camara,

2001). Fishes are usually at the top of the tropic chain in aquatic ecosystems. The accumulation of lead in fish is dependent on both uptake and elimination rates. It was shown that uptake is dependent on locality, species of fish, sex, age, the specific organs studied and the state of gonodal maturation. Lead occurs in aquatic environments in the form of many species, both inorganic and organic. Speciation analysis is very important because the chemical form of lead determines its solubility in water and consequently its bioavailability, hence toxicity, to organisms (Lobinski and Adams, 1994). While the lead content in deep sea water of the South Pacific amounts to 1-2 ng Pb/L and in Antarctic deep sea water to 0.4 ng/L, which seems to be the natural background level, the lead content of surface water of the central North Atlantic and North Pacific is around 5-50 ng/L (Oehlenschläger, 2002).

The average concentration of cadmium in the earth's crust is only about 0.15 µg/g, making it the sixty-seventh element in abundance. It is widely distributed in the environment because of its use pattern in industry and its natural association with zinc and copper. Cadmium shows no signs of being an essential trace element in biological processes; on the contrary, it is highly toxic to a wide variety of living organisms, including man (Ray, 1994). Cadmium has an extremely long residence time (Over 20 years) in the human body and a significant proportion of the body burden is stored in liver and kidney, and bound to (MTs) metallothioneins. Metallothioneins are still the only biological compounds known to

naturally contain this metal. The synthesis of metallothioneins is induced by the essential elements Cu and Zn in kidney and liver. Cd may replace these metals or share the protein with them. The toxicity of Cd-thioneins then affects the kidney in particular, but can also produce skeletal damage (Osteoporosis). The accumulation of Cd in the kidney increases with age, suggesting that Cd exposure will adversely affect health, particularly in older age groups. However, Cd absorption is higher in children (As in case of Pb) (Munoz-Olivas and Camara, 2001).

Aim of this study is to determine lead and cadmium contents in the edible parts (Muscle, fillet) of commercially used fishes from two European regions, North-East Atlantic and Mediterranean by means voltammetric method. This study is of utmost importance for the estimation of heavy metal intake by people consuming food fish in these areas. Protecting consumers, who are consuming fish, can be efficient only when data on trace elements in fish are available.

2. PREVIOUS STUDIES

An extensive review on the earlier studies about heavy metals and their determination methods in marine organisms is presented below. These studies have been listed according to their publication years.

Harms (1975), determined the contents of the elements manganese, iron, cobalt, nickel, copper, zinc, cadmium, lead and mercury in certain fish species [cod (*Gadus morhua*) and plaice (*Pleuronectes platessa*)] from inshore and offshore waters of the German Bight by using. Atomic Absorption Spectrophotometry (AAS). The results of this study showed that there were comparatively small differences in the prevailing concentrations of the transition metals Mn, Fe, Co, Ni, Cu and Zn between samples of the same species from different areas. Likewise, the levels estimated for plaice did not differ from those estimated for cod.

Fukai and Hynh-Ngoc (1976), investigated the concentration levels of copper, zinc and cadmium in the coastal waters of the North-West Mediterranean. The analyses were performed by anodic stripping voltammetry (ASV) with composite graphite mercury electrodes. Authors stated that the concentrations of Cu, Zn and Cd observed in the coastal waters of the North-West Mediterranean agree fairly with those reported previously.

Roth and Hornung (1977), analyzed samples of water, sediment and fish collected along the Northern part of Mediterranean coast of Israel for cadmium, lead, copper, zinc,

nickel and chromium by atomic absorption spectrophotometry. Authors stated that the obtained values showed no significant heavy metal pollution in the studied area, compared with values found in literature for metal concentrations in other parts of the world.

Stoeppler and Nürnberg (1979) determined Cd, Pb, Hg, Cu, Ni and As in 15 marine species of different tropic levels from the Mediterranean Sea, North Sea and Baltic Sea by using several versions of atomic absorption spectrophotometry and accuracy was checked by differential pulse anodic stripping voltammetry.

Danielson et al. (1981) carried out an investigation about computerized potentiometric stripping analysis for the determination of cadmium, lead, copper and zinc in biological materials. In this study, two types of canned mussels and a bovine liver reference sample have been analysed for Zn, Cd, Pb and Cu by means of computerized potentiometric stripping analysis and atomic absorption spectrometry and authors indicated that since these two kinds of biological samples differ greatly with respect to protein and lipid content, it can be concluded that the potentiometric stripping technique could be used for a great variety of biological samples and food-stuffs.

Stary et al. (1982), investigated uptake and the release of zinc and cadmium in fish (*Poecilia reticulata*). As a result of this study, authors indicated that the uptake of these elements directly from water is relatively low.

Nürnberg (1983) investigated heavy metal speciation in natural waters by voltammetric procedures. The author pointed out the speciation of dissolved heavy metals is of great significance for their interactions with suspended matter and sediments and their uptake by aquatic organisms. In this study, the potentialities for diagnostic measurements and for specific studies on the effects of physicochemical parameters of natural waters on heavy metal species were presented.

Raptis et al. (1983) studied a novel method for the decomposition of organic and biological materials in an oxygen plasma excited at high frequency for elemental analysis. Authors stated that the decomposition method described in this paper stands out for universal applicability.

The effect of the chemical modifiers $(NH_4)_2HPO_4$, $LaCl_3$ and NH_4NO_3, on the determination of lead in a sample of mussel (*Mytilus galloprovincialis*) by using graphite furnace, has been studied by Escriche et al. (1987). For the measurements of absorbance, both the direct and the standard additions methods have been used, as in presence or absence of modifiers. Results of this study showed that, results obtained by direct method, in the presence of 0.5% $(NH_4)_2HPO_4$, and by the standard additions method were similar and it has not been observed any influence from the digestion method, for both digestion procedures led to similar results.

Parlak (1987) studied the separate and together toxic effects of cadmium, iron and lead ions on *Mugil spp*. and *Chasmichtys gulosus* and the results of the experiments showed that the sublethal Cd concentration has no toxic effects to the fish but has became highly toxic together with even very low concentration of Fe ion. In this study, Varian Techtron atomic absorption spectrophotometer with flame technique used for heavy metal analysis.

Concon (1988), stated that, blood lead levels of less than 40µg/100ml have no clinical significance, levels between 40-80µg/100ml may indicate subclinical poisoning and levels greater than 80µg/100ml are usually seen in lead poisoning but this value is mostly applicable to children since older people having greater than this may show no recognizable signs of toxicity, in his declarations about lead toxicity. Author also stated about cadmium toxicity that acute cadmium poisoning from contaminated food or beverages has been reported but possibility of chronic poisoning is greater since it is known that cadmium can accumulate in specific tissues and has a long biological half-life. Author also indicated that the most notable example of chronic poisoning attributed to cadmium is the so-called itai-itai disease reported in Japan.

Cabrera et al. (1991), determined lead in fish by electrothermal atomic absorption spectrometry. The flesh of 32 of the most common species from the coast of the province of

Granada (Spain) was analysed and the concentrations of lead ranged from 15.8 to 303.3 ng g^{-1}.

Parlak et al. (1991) determined Cu, Zn, Mn, Fe, Cd and Hg concentrations in biological samples such as *Unio sp*., *Cyprinus carpio*, *Rutilus rutilus*, *Caspialosa maeotica*, *Chalcalburnus calcoides*, *Blicca björkna*, *Scardinius sp*. ve *Vimba vimba* by using atomic absorption spectrophotometer with graphite furnace.

Sunlu (1994), investigated pollution and some heavy metal concentrations (Cd, Pb, Zn, Cu, Fe) in different organs and tissues of seabass (*Dicentrarchus labrax*), seabream (*Sparus aurata*), thin-lipped grey mullet (*Liza ramada*) and eel fish (*Anguilla anguilla*) collected from Homa Lagoon and the different regions of Aegean Sea by using atomic absorption spectrophotometer (AAS Perkin Elmer 2380). The results of heavy metal analysis showed that Inner Bay of Izmir is very polluted by domestic and industrial sewage, Homa Fisheries Lagoon is less polluted but strongly affected by Gediz River and Inner Bay of Izmir and there is no pollution problem in Karaburun and Cesme.

Antoniou et al. (1996), determined concentrations of lead, cadmium, copper and zinc in 66 samples of mussel (*Mytilus galloprovincialis*) obtained from the gulf of Olympias and Makriyalos Greece by AAS. The results indicated high concentrations of lead while the concentrations of other metals were at acceptable levels.

Chaudhari et al. (1996), reported factors affecting heavy metal toxicity in aquatic organisms. Authors stated that, the toxicity and heavy metal incorporation in aquatic organism is a function of the combine effect of the parameters; water and sediment analysis, parameters influencing metal availability, temperature and oxygen saturation, hardness of water, organic compounds, pH values and salinity.

Cronin et al. (1996) carried out an investigation to determine trace metals (Hg, Pb, Cd, Cu and Zn) in deep sea fish (*Hoplostethus atlanticus*, *Coryphenoides rupestris*, *Macrourus berglas*, *Coryphenoides armatus*) from the North Atlantic by using atomic absorption spectrophotometer. Authors indicated that age and length were highly positively correlated in all cases. In all five species, the Hg concentrations were significantly positively correlated with both age and length. A number of significant positive correlations were found between Cu, Pb, Zn and Cd, particularly in *C. mediterranea*, *C. rupestris* and *H. atlanticus*.

Kargin (1996), determined levels of Cd. Cu, Zn, Pb and Fe seasonally in the liver, spleen, kidney, gill and muscles tissues of stripped mullet (*Mullus barbatus*) and seabream (*Sparus aurata*) from the Iskenderun Gulf, East Mediterranean coast of Turkey by using atomic absorption spectrophotometer. The author stated that metal levels were higher in liver, spleen and kidney compared with the gill and muscle tissues in both species; the levels of all

metals in a given tissue were always higher in stripped mullet than seabream.

Altinel Ataman (1997), investigated lead and cadmium in canned tuna fish by atomic absorption spectrophotometer in his master thesis and stated that obtained concentrations were all below the permissible levels.

Atta et al. (1997) carried out an investigation to examine the effect of cooking on the content of heavy metals in fish (*Tilapia nilotica*) by using atomic absorption spectrophotometer. The results of this study revealed that heavy metal contents in fish parts varied according to concentration in environment and the type of fish tissue and the heavy metal content in all fish parts decreased on steaming and baking.

Nair et al. (1997) determined the concentration levels of Cu, Zn, Mn and Fe in marine fishes from Cochin area, which is one of the major fishing zones along the west coast of India by using a flame atomic absorption spectrophotometer. The authors indicated that the concentration of heavy metals varied from species to species. Cu, Zn, Fe and Mn showed increased levels in the gills and alimentary canal compared to the muscle.

Pip and Stepaniuk (1997) examined cadmium, copper and lead in a catch of fishes from the Nelson River system in Northern Manitoba by IL-151 atomic absorption spectrophotometer. The results of this study showed that, in the Lake Whitefish (*Coregonus clupeaformis*) Cd and Cu concentrations in skeletal

muscle decreased in larger fish. In Northern Pike (*Esox lucius*), Pb concentrations in muscle were inversely correlated with fish weight and fish downstream of the Limestone Dam showed higher copper concentrations than those upstream, reflecting a parallel difference in environmental Cu levels.

Romeo and Ganssia-Barelli (1997), measured peroxidation and peroxidizable lipids in vitro in the gills and digestive gland of the Mediterranean clam *Ruditapes decussatus* incubated with cadmium, copper and mercury. The results of this study showed that cadmium has no effect on the basal peroxidation in the digestive gland and gills of *R. decussatus* until the concentration in the incubation medium reached 500 µg/ml. Basal peroxidation increased with increasing copper concentration in both organisms, whereas simulated peroxidation decreased, particularly in the digessive gland. Mercury caused an increase in basal peroxidation whereas simulated peroxidation did not change.

Canli et al. (1998), determined concentrations of cadmium, lead, copper, chromium and nickel in the gill, liver and muscle of *Cyprinus carpio*, *Barbus capito* and *Chondrostoma regium* caught at 5 stations on the Seyhan river system by using a Perkin Elmer AS 3100 atomic absorption spectrophotometer. The ranges of mean metal concentrations (µg/g d.w.) were found as follows: the range of cadmium concentration was 1.26-6.10, 0.96-4.72 and 0.51-1.67, that of lead was 9.41-44.75, 5.22-37.15 and 2.94-13.73, that of copper was 5.43-58.63, 5.91-201.1 and 3.27-7.35,

that of chromium was 1.72-6.10, 0.23-5.35 and 0.36-1.71 and that of nickel was 6.83-28.03, 3.42-27.05 and 1.62-13.35 in the gill, liver and muscle respectively. The results of this study indicated that the metals present in the river system were taken up by three fishes through food, water and sediment, as all the fish species, regardless of their biological needs, showed high metal concentrations.

Güner et al. (1998) carried out an investigation to determine proximate composition and selected mineral content of commercially important fish species from the Black Sea. Heavy metals were determined by using a GBC model atomic absorption spectrophotometer. The results of heavy metal analyses indicated that when the amounts of these elements were compared with the suggested values, anchovy, garfish and bonito can be considered as good sources of Zn and of Fe and the amounts of Cd, As, Hg, Pb and Ni were all below toxic levels.

Marx and Brunner (1998), investigated cadmium, lead and mercury contents of common shrimp (*Crangon crangon*) from the German mud flats in the North Sea by means of AAS. Authors stated that, mainly due to industrialization, the concentrations of Pb, Cd and Hg in the upper layers of the sediment have risen ten-, seven- and eightfold, respectively, over the last 200 years. Along with this enrichment, heavy metal accumulation in the animals of this habitat has taken place. Adequate measures to protect this ecosystem against further pollution are still disapproved of some

countries bordering the North Sea, e.g. Great Britain. Due to this situation, the Pb, Cd and Hg load of North Sea shrimp from the mud flats used for human consumption is under question.

Senthilnathan et al. (1998), determined metal concentrations in mussel (*Perna viridis*) and oyster (*Crassostrea madrasensis*) from some parts in southeast coast of India by using AAS (Perkin Elmer 373). The results showed that there were definite seasonal variations with an increased metal load during the monsoon period and decreased level during the summer period.

Barlas (1999), measured concentrations of lead, cadmium, copper, cobalt, nickel and manganese in water, sediment and fish samples (*Cyprinus carpio* and *Barbus plebejus*) at the upper Sakarya river basin. The author stated that mean concentrations of lead, cadmium, copper, nickel and manganese differed between water, sediment and fish samples by seasons.

Bat et al. (1999) measured the concentrations of copper, zinc, lead and cadmium in the living tissue of the Mediterranean mussel *Mytilus galloprovincialis* from the Sinop coasts of the Black Sea by AAS to monitor metal pollution in the coastal water. Authors stated that a statistically significant difference in the concentrations of all metals was observed among four sampling stations. However, the levels of the metals found in this study were generally lower than the permitted levels.

Catsiki and Strogyloudi (1999), monitored the concentration of Cu, Cr, Ni, Zn, Fe and Mn during the period 1987-1997 in the

gills and flesh of the demersal *Mullus barbatus* (Stripped mullet) and pelagic *Boops boops* (Bogue) collected from a network of six sampling sites covering the Aegean and Ionian Seas. The effectiveness of the above fish as biomonitors for temporal evolution studies is also investigated. Cu, Ni and Zn seemed to increase with time, while Cr and Fe seemed to decrease. Finally, it is stated that, the determined levels in the studied fish were low and similar to those from other non-polluted Mediterranean areas.

Goldstein and DeWeese (1999), compared trace element (As, Cd, Cr, Cu, Pb, Ni, Se and Zinc) concentrations in tissue of common carp (*Cyprinus carpio*). Cd, Cr, Cu, Ni, Pb and Zn measurements were done by inductively-coupled plasma/mass spectrometry (ICP/MS) and As and Se were analysed with a hydride atomic absorption (AA) generation procedure. The authors of this study indicated that generally trace element concentrations were the greatest in livers while concentrations in whole bodies were greater than those in muscle for Cd, Cu, Ni, Pb and Zn, and concentrations in muscle were similar to whole body for As and Se.

Kalay et al. (1999), determined heavy metal (Cd, Pb, Cu, Cr, Ni, Zn and Fe) concentrations in the muscle, gill and liver of fishes (*Mugil cephalus*, *Mullus barbatus*, *Caranx crysos*) from three stations (Mersin, Karatas and Iskenderun Bay) in the northeast Mediterranean Sea by using a Perkin Elmer AS 3100 flame atomic absorption spectrophotometer. Mean concentrations of

cadmium in the gill, liver and muscle of common grey mullet (*Mugil cephalus*), stripped mullet (*Mullus barbatus*), blue runner (*Caranx crysos*) ranged between 2.19-2.36, 1.29-3.61, 0.86-1.07; 2.25-3.70, 1.63-2.12, 1.03-1.43 and 2.64-3.34, 0.84-5.93, 0.61-1.36 µg/g d.w respectively. Mean concentrations of lead in the gill, liver and muscle of fishes *Mugil cephalus*, *Mullus barbatus*, *Caranx crysos* ranged between 20.17-21.23, 6.13-11.21, 5.44-7.33; 15.61-22.35, 6.10-9.28, 5.34-9.11 and 17.51-20.11, 4.73-15.72, 4.43-7.50 µg/g d.w respectively. Investigators indicated that heavy metal concentrations in the tissues of fishes, regardless of their ecological needs, were considerably high at all stations from the north-east Mediterranean Sea compared to previous studies from other waters and some measures should be taken to prevent the contamination of the marine environment for human and animal health and this may be achieved.

Liao and Jiang (1999) determined Cd, Hg and Pb in several fish samples by ultrasonic slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS). At the end of this study, the influences of the instrument operating conditions and slurry preparation on the ion signals were reported.

Onyenekwe et al. (1999), determined and compared the concentration of heavy metals (Cr, Mn, Fe, Cd, Cu, Zn, Pb and U) in fish samples collected from Lithuania, Berlin (Germany) and Nigeria using ICP-MS. Authors indicated that metal

concentrations influenced by fish type and origin. The results of this study showed that based on origin flesh of sample from Berlin has the least concentration of Cr and Cd. whereas those from Nigeria were least in Mn, Fe, Cu and Zn but highest in Cr. Samples from Lithuania has the highest concentrations of Mn, Fe, Cu and Zn.

Roméo et al. (1999), determined cadmium, copper, zinc and mercury concentrations in pelagic and benthic fishes from the Mauritania coast. Authors stated that the metal concentrations in all the fishes analysed are low except those found for cadmium in the livers of the benthic fishes.

Tao et al. (1999) investigated the uptake of particular lead via the gills of fish (*Carassius auratus*). The results of this study revealed that lead accumulations on the gills increased with increased particulate lead concentrations in the ambient water (Under conditions of constant level of free lead), indicating the bioavailability of lead via the gills.

An investigation was carried out to determine mercury, cadmium and lead content of canned tuna fish by Voegborlo et al. (1999). Mercury concentrations measured by cold vapour atomic absorption spectrophotometry and cadmium and lead concentrations measured by flame atomic absorption spectrophotometry. The results of this study indicated that tuna fish from the Mediterranean coast of Libya have concentrations well below the permissible levels for these toxic metals.

Yaru et al. (1999), determined heavy metals (Cd, Cu, Pb and Zn) in various fish organs (Flesh, kidney and liver) using Zeeman graphite furnace (Cd, Cu, Pb) and flame (Zn) atomic absorption spectroscopy after microwave digestion in non-pressurized, semi-closed vessel. Authors pointed that the method is relatively quick and easy to use for routine analysis of environmental samples, processing up to 100 samples per day.

Zauke et al. (1999) determined the concentrations of Cd, Pb, Hg, Ni, Cu and Zn in liver and muscle tissues of 15 marine fish species collected in the summer of 1994 to assess the significance of metals in biota of the Barents Sea. Authors stated that lead and Ni concentrations were below limits of detection in all tissues, as is Cd in muscle.

Zyadah (1999) determined the accumulation of copper, zinc, cadmium and lead in flesh, gills, liver and gonads of *Tilapia zillii* by atomic absorption spectrometry (AAS). The results of this study showed that the levels of those heavy metals are occasionally higher in females than in males and the flesh accumulated low concentrations of heavy metals in comparison with the other organs.

Zyadah and Chouikhi (1999), studied the accumulation behaviour of copper, zinc, cadmium and lead concentrations in flesh, gills, liver and gonads of three commercial fish *Mullus barbatus*, *Merluccius merliccius* and *Boops boops* (Stripped mullet, hake and bogue) from the Aegean Sea in Turkey. The

authors of this study stated that copper, zinc and lead concentrations in flesh were found low, while in gonads Cd was found high. Liver showed higher concentration of Cu than other fish organs.

Avelar et al. (2000), analysed the seasonal concentrations of some metals of toxicological interest (Cd, Cu, Cr, Pb, Zn) in Ubatuba Bay, northern coast of the State of Sao Paulo, Brazil, using the bivalve *Perna perna* as a biological monitor by flame atomic absorption spectrometry. The results showed higher metal accumulation in July. The values detected for Pb and Cr were relatively high in all seasons, especially in January and July in Ubatuba Bay, with the consequent risk of contamination by mussel ingestion for the local population and for tourists from other regions.

Chiu et al. (2000), carried out an investigation to determine concentrations of Cd, Cr, Cu, Pb and Ni in green-lipped mussels (*Perna viridis*) from three mariculture zones located in the north-east, south and to the west of Hong Kong by using AAS (Varian SpectrAA-20). Authors stated that spatial differences in the metal concentrations in *Perna viridis* from mariculture zones are influenced by two components: metals originating from localised sources – activity or structures associated with the mariculture operations and those originating from a general contamination of coastal waters by discharges of industrial waste effluents.

An investigation was carried out to determine lead in fish samples by slurry sampling electrothermal atomic absorption spectrometry by Huang and Jiang (2000). The analysis results agreed with the reference value. The accuracy was better than 6%. The precision between sample replicates was better than 16% with the USS-ETASS (Ultrasonic Slurry Sampling Electrothermal Atomic Absorption Spectrometry) method.

A method for determination of lead, cadmium, zinc, copper and iron in foods by atomic absorption spectrometry (AAS) after dry ashing at 450 C was collaboratively studied in 16 laboratories (Jorhem, 2000). The author of this study pointed that the method must be considered to give acceptable results for the elements determined (Pb, Cd, Zn, Cu, and Fe).

Jorhem and Engman (2000) performed a collaborative study to determine cadmium, zinc, copper and iron in foods by atomic absorption spectrometry after microwave digestion. At the end of the study, authors stated that there is good agreement between the levels found and the certified means and ranges for the CRMs. There is good agreement between the microwave AAS method and the dry ashing AAS method. There is good agreement between the results from AAS and ICP/ICP-MS after microwave digestion.

Kalay and Canli (2000), investigated, elimination of essential (Cu, Zn) and non-essential (Cd, Pb) metals from tissues of a

freshwater fish *Tilapia zilli*. The results of this study indicated that elimination level changes depending on tissues and metals.

The concentration of heavy metal (Cd, Pb, Ch, Cu, Zn) in seawater and mussel samples collected from the Istanbul Bosphorus by graphite furnace atomic absorption spectrometry was determined by Köklü et al. (2000). The results of this study showed that seawater and mussels have not been heavily contaminated by the toxic elements studied.

Polak-Juszczak (2000), investigated levels and trends of changes in heavy metal concentrations in Baltic fishes. The research results confirm that the heavy metal content in fish tissue depends on the fish species and all concentrations in the upper range found for all species from 1996 onwards were below the EU limits and proposed limits.

Roméo et al. (2000), evaluated heavy metal (Cd, Cu, Zn, Hg) concentrations in four species of bivalve molluscs, the oyster *Crassostrea gigas*, the African mussel *Perna perna*, the clam *Venus verrucosa* and the wedge shell *Donax rugosus* by atomic absorption spectrometry (GBC 904, equipped with GF 3000). Authors stated that the metal body burden in molluscs may reflect the concentrations of metals in seawater and may thus be an indication of water quality along the Mauritanian coast. In this respect, relatively high cadmium concentrations were found in some of the species examined here.

Storelli et al. (2000), determined concentrations of 6 heavy metals (Hg, Pb, Cd, Cr, Zn and Sn) in mussels (*M. galloprovincialis*) collected from 10 locations along a sound formed by two inlets (Mar Piccolo) near the Gulf of Taranto (Ionian Sea, Italy). Authors of this study stated that the concentrations of heavy metals in mussels from the first inlet did not differ greatly from those observed in mussels from second inlet and they were below acceptable levels for consumption.

Tahvonen et al. (2000) investigated the contents of Fe, Cu, Zn, Mn, K, Mg, Ca, Na, As and Cd in gutted Baltic herring, Baltic herring fillets and two commercial ready-to-eat products made from these. The results of this study showed that Baltic herring fillets are good sources of many major and essential elements. Fe, Zn, Mn, Ca and K levels were very high when compared to the recommended daily allowances in the Nordic countries. In addition, the levels of non-essential elements such as Cd and As were typically low. If the bones of Baltic herring are removed, the levels of Ca and Zn decrease significantly.

Wong et al. (2000), determined Cd, Cr, Cu, Ni, Pb and Zn in green-lipped mussels, *Perna viridis*, collected from Tolo Harbour and markets in Hong Kong and Shenzen by using AAS (Varian SpectrAA-20). The results of this study showed that the metal concentrations were below the maximum permissible levels set by the Hong Kong Government.

Campanella et al. (2001) measured the concentrations of Cd, Cr, Pb and Zn in specimens of four marine organisms, the seagrass *Posidonia aceanica* Delile, the brown algae *Padina pavonica* Thivy, and the two gastropod molluscs *Monodonta turbinata* Born, and *Patella caeruela* selected as possible cosmopolitan biomonitors of trace metals in the Mediterranean Area. Cd, Cr, Cu, Pb and Zn analyses were performed by electrothermal atomic absorption spectrometry (ETAAS). Authors stated that *P. oceanica* is located at the base of the food web in the Mediterranean and is probably the main source of metals for many animals grazing on its leaves, while *P. caurela* is a commonly consumed seafood in many Mediterranean countries. Therefore, the investigation of trace metal concentrations in the tissues of these species may provide useful information on the transfer of potentially toxic elements from abiotic compartments (Water, sediments) to higher consumers, including man.

Canli et al. (2001), examined tissues of the sardine (*Sardina pilchardus*) and prawn (*Penaeus japonicus*) for their metal (Cd, Pb, Cr, Ni, Cu, Zn and Fe) loads. Sardines and prawns used in this study were sampled at 3 stations from the northeast Mediterranean Sea and the results indicated that sardines and prawns from this location have high metal concentrations in their tissues, especially in the gill and liver at all stations although there was no significant differences between sampling stations. The results also showed outstanding differences in metal concentrations between the two animals.

An investigation was carried out to determine cadmium, copper, nickel and zinc in fish samples from seven sampling stations of the Roa de Aveiro (Portugal) by Cid et al. (2001). Heavy metal analyses were done by electrothermal atomic absorption spectrometry and the results obtained for all elements were considerably lower than those recommended by specific legislation for these aquatic organisms.

Edwards et al. (2001) determined metal levels in seston and marine fish flesh near industrial and metropolitan centres in South Australia by using anodic stripping voltammetry on the Portable Digital Voltammeter 2000. The authors of this study indicated that seston concentration of pollutant metals are high areas of industrial activity, and that these levels are also reflected in metal content of fish flesh.

Hung et al. (2001), determined trace metals in different species of mollusca, water and sediments from Taiwan coastal area by both graphite atomic absorption spectrophotometry (Hitachi Z-8000) and differential pulse anodic stripping voltammetry (EG & G 384B). The results indicated that trace metal contents in mollusca varied among 30 different species and the environments (Water and sediments) along the Taiwan coast.

Julshamn et al. (2001), determined cadmium, lead, copper and zinc in the soft tissues of blue mussels (*Mytilus edulis*) sampled from four locations along the Hardangerfjord in western Norway. The results showed that the area is still slightly

contaminated with cadmium and lead. However, it is amazing that the fjord system has recovered to such an extent over the last 20 years. With regard to human consumption of blue mussels from the Hardangerfjord, none of the elements analysed should give any cause for concern for consumers, as the European Union is proposing an upper limit of heavy metals in seafood of 1.0 mg kg^{-1} for cadmium and lead.

Kirby et al. (2001), measured, selenium, copper, cadmium and zinc concentrations in mullet (*Mugil cephalus*) from the southern basin of Lake Macquarie, Australia, in 1997 to determine if improved ash-handling practices at an adjacent coal fired power station, implemented in 1995, has significantly lowered trace metal concentrations in mullet tissues.

Kücüksezgin et al. (2001) determined the levels of trace metals and organochlorine residue in red mullet. The concentrations of trace metals found varied with Hg: 16-200µg/kg^{-1}, Cd: 0.57-4.5µg/kg^{-1} and Pb: 40-207µg/kg^{-1} wet weight.

Locatelli and Torsi (2001), proposed new analytical procedures and sample regarding the determination of arsenic, selenium, copper, lead, cadmium, zinc and mercury in matrices involved in food chain as mussel, clams and fishes. The results of this study showed that together with an appropriate sample pre-treatment have shown to be a valid analytical procedure certainly suitable for simultaneous metal determinations in multicomponent complex matrices like mussels, clams and fishes.

Locatelli and Torsi (2001), determined arsenic, selenium, copper, lead, cadmium, zinc and manganese in environmental matrices by differential pulse cathodic (DPCSV) and anodic (DPASV) stripping voltammetry. In conclusion, authors emphasised that, voltammetry together with the standard addition method, is certainly a valid analytical method (Good selectivity and especially, sensitivity) for simultaneously determining elements having very similar peak potentials and consequently, very strong interference problems.

Locatelli et al. (2001a), determined heavy metal (Hg, Cu, Pb, Cd, Zn) concentrations in algae and clams and their possible employment for assessing the seawater quality criteria by using differential pulse anodic stripping voltammetry (DPASV). Authors indicated that the proposed analytical procedures have shown to be sensitive and selective, with good accuracy and precision, suitable for the toxic element determination in complex real samples.

Lohan et al. (2001b), measured the concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in several soft-tissue types of the Antarctic soft-shelled clam, *Laternula elliptica*, by using graphite furnace atomic absorption spectrometry (Perkin Elmer 1100B). The results indicated that *L. elliptica* is a useful long-term biomonitor of heavy metal contamination in Antarctic coastal waters.

An investigation was carried out to measure concentrations of arsenic, cadmium, chromium, copper, lead, mercury, selenium and zinc in coral crab, eel, fish, lobster and sediment samples collected from French Frigate Shoals, North Pasific Ocean by Miao et al. (2001). The results of this study showed that, the concentrations of these metals studied in the sediments and organisms did not vary much among the three Tern Island sites and the reference sites.

Mormede and Davies (2001a) investigated heavy metal (Arsenic, cadmium, copper, lead, mercury and zinc) concentrations in commercial deep-sea fish from the Rockall Trough by various atomic absorption techniques. Researchers indicated that the concentrations in muscle tissues are all well within EU limits for human consumption, the concentrations of cadmium, copper and zinc in fish liver are higher than in muscle tissue and in some cases, particularly cadmium and zinc in *Aphanopus carbo* livers exceed EU limits.

Mormede and Davies (2001b), determined trace elements in deep-water fish from the Rockall Trough by various atomic absorption techniques. The results of this study showed that the concentrations are similar to those previously reported in other species from this area.

Perez et al. (2001) carried out an investigation to determine heavy metals (As, Cd, Pb, Se, Cu and Zn) in the False Mussel, *Mytilopsis domingensis*, from two tropical estuarine lagoons.

Metals of As, Cd, Pb and Se were analysed using a Perkin Elmer Atomic Absorption Spectrophotometer Model 1100B with a HGA-700 graphite furnace and Cu and Zn were analysed with the direct aspiration flame mode. Authors concluded that, the false mussel, Mytilopsis domingensis, showed the potential to bioaccumulate heavy metals, thus becoming a useful biomonitor.

Rashed (2001), determined cadmium and lead in different tissues (Muscle, gill, stomach, intestine, liver, vertebral column and scales) of *Tilapia nilotica* from the High Dam Lake, Aswan (Egypt) to assess the lake water pollution with those toxic metals. The results of this study showed that cadmium and lead concentrations were higher in fish scales and vertebral column than in the other parts of the fish.

An investigation was carried out to present data on the concentrations of heavy metals (Hg, Pb, Cd and Cr) in water, sediments, molluscs, bivalve (*Mytilus galloprovincialis, Tapes decussata*) and fish (*Gobius ophiocephalus*, *Atherina boyeri*, *Blennius pavo*) from the Varano lagoon by *Storelli* and Marcotrigiano (2001). In conclusion, authors indicated that the environment quality appears markedly improved, mainly for what regards the pollution by Hg and Pb. For Cr and Cd the pollution loads in water and sediments have remained similar, while in *M.galloprovincialis*, which is considered one of the best biological markers in defining environment pollution, the levels of these two elements result considerably higher. This observation suggests

the need for an increasing effort in controlling sources of pollution in this area.

Tarley et al. (2001), determined the total concentration of the metals Cu, Fe, Mn, Zn, Sn, Cr and Pb in different brands of sardines canned in soybean oil and tomato sauce, commercialized in Brazil by using flame atomic absorption spectrometer. The authors found that one of the brands presented the highest levels of metals and authors indicated that this can be attributed to differences in the process of canning and sardines quality.

TsuChang et al. (2001) carried out a long-term programme of Asia/Pasific Mussel Watch: Taiwan Regional Studies to determine trace metals (Cu, Zn, Cd, Pb, Ni, As and Sn) in different species of mollusca, water and sediments from Taiwan coastal area. The results of this study indicated that trace metal concentrations in mollusca varied among 30 different species and the environments (Water and sediments) along the Taiwan coast.

Wong et al. (2001) evaluated the levels of six heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in different tissues of three species of cultured marine fishes collected from three fish culture sites in Hong Kong. Authors stated that tissues of all three species contained high concentrations of Zn and Cu, but much lower concentrations of Ni, Pb, Cd and Cr and despite high metal levels in sea water and sediments, concentrations of Cd, Cr and Pb in the edible tissues, including muscle and skin, did not exceed

permissible levels recommended by the Hong Kong Government for human consumption.

YiChun and MengHsien (2001), analysed nine species of most commonly found fishes in the Ann-Ping coastal waters in Taiwan, for Zn, Fe, Cu, Mn and Cd concentration in the muscles, livers and gonads. Authors indicated that the metal concentrations found in this study were similar to the metal levels of the fishes collected from slightly polluted waters all over the world and Taiwan. Therefore, no public health problem would be raised in the consumption of these fishes.

Besada et al. (2002), investigated temporal trends for heavy metals (Cd, Cu, Hg, Pb and Zn) in mussel (*Mytilus galloprovincialis*) from the Galician and Cantabrian areas in Spain, where samples yearly collected from 1991 to 1999 by using Perkin-Elmer 500 spectrophotometer. Authors stated that a decrease of copper levels was detected in Vigo, Pontevedra and Arosa, of mercury in Pontevedra and A Coruňa, of lead in Vigo, Pontevedra, A Coruňa and Bolbao and of zinc in Pontevedra and A Coruňa. However, a cadmium positive trend was registered at Roa de Vigo.

Locatelli and Torsi (2002), determined arsenic, selenium, copper, lead, cadmium and zinc in seawater, sediments, algae and clams by differential pulse cathodic (DPCSV) and anodic (DPASV) stripping voltammetry. Authors highlighted that the greater advantage in using the voltammetric techniques is that a

single instrumental measurement, allows the simultaneous determination of several elements and moreover these techniques are sensitive, selective and very suitable for monitoring heavy metals in complex environmental samples like sea water, sediments, algae and clams.

Burger et al. (2002), reported concentrations of arsenic, cadmium, chromium, copper, lead, manganese, strontium^{88} and mercury in the muscle of 11 species of fish from the Savannah River near the Savannah Near Site. Researchers tested the hypotheses that there are no locational, species or tropic-level differences in contaminant levels and results showed that the levels of most metals were similar to, or lower than, those for the United States generally and the levels of metals in fish from the Savannah River do not appear to pose a health threat to the fish themselves or to higher-order consumers, based on levels known to cause effects.

Hossain (2002) compared heavy metal concentrations (Cd, Pb, Cr, Mn, Ni, Fe, Zn and Cu) of tiger shrimps (*Penaeus monodon*) and spiny lobsters (*Panulirus homarus*) caught from the Bay of Bengal. The results showed that there were seasonal fluctuations in the concentrations and those of Cd, Pb, Cr, Mn and Ni were smaller than those of Fe, Zn and Cu. Author indicated that, the levels of metals in the present study were significantly lower than those of previous studies.

Kavun et al. (2002), investigated concentrations of cadmium, copper, iron, lead, manganese, nickel and zinc in two species of mussel from the Kuril Islands in the North-Western Pacific Ocean by using atomic absorption spectrometry (Hitachi 180-70). Authors indicated that, the concentrations of most elements were low, and these reported levels are believed to reflect background values for pristine locations.

Since 1986 the NOAA National Status and Trends (NS&T) Program Mussel Watch has monitored concentrations of trace chemicals in the coastal United States by sampling mussels, oysters and sediment by O`Connor (2002). The elements and groups of organic compounds monitored were: Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Zn, total PCB, total DDT, total chlordane, total dieldrin, total BT, total LMW, total HMw and total PAH. At the end of the study, author stated that while the purpose of the Mussel Watch Project is to monitor temporal trends in coastal contamination, the data also define concentration distributions and give some indication of when highs are due to nature rather than man. These distributions are a basis that any program can use to judge whether its observed concentrations are at all unusual. However, except for synthetic organic chemicals, PAHs and lead, it should never be assumed that a high concentration is necessarily unnatural and subject to human control. Tissue concentrations in urban areas of two groups of organic chemicals, PAHs and PCBs are in a range that may be causing lysosomal alterations the molluscs.

Rojas de Astudillo (2002), monitored heavy metal concentrations in edible soft tissues of shellfish from Trinidad and Venezuela. Cadmium, copper, lead, nickel and zinc were analysed by flame atomic absorption spectrometry and mercury was determined by cold vapour atomic absorption spectrometry. The results of this study showed that, oysters have a much greater capacity for accumulation of copper and zinc than does green mussel. Concentrations of copper and zinc in oysters at many of the sites in the Gulf of Paria exceed local and international standards, whereas green mussel contained generally acceptable levels for human consumption.

Vincent et al. (2002) conducted a study to determine the effect of cadmium on the bioenergetics of freshwater fish, *Catla catla*. Authors indicated that a concentration-dependent inverse relationship ($p<0.05$) between cadmium concentration and food utilization parameters like food consumption, assimilation metabolism, production, assimilation efficiencies and production efficiencies was observed and heavy metal intoxication was also found to exhibit reduction in biomass.

Yap et al. (2002), correlated total concentrations and speciation of Cd, Cu, Pb and Zn in surface sediment samples with the respective metal measured in the total soft tissue of the green-lipped mussel *Perna viridis*, collected from water of the west coast of Peninsular Malaysia. Heavy metals were determined by using an air acetylene flame atomic absorption spectrophotometer

(Perkin Elmer 4100). The results showed that significant ($P<0.05$) correlations were observed between Cd in *P. viridis* and Cd in the sediment, Cu in *P. viridis* and Cu in the sediment and Pb in *P. viridis* and Pb in the sediment. No significant correlation ($P>0.05$) was found between Zn in *P. viridis* and all the sediment geochemical fractions of Zn and total Zn in the sediment.

Tüzen (2003) determined the concentrations of heavy metals (Pb, Cd, Fe, Cu, Mn and Zn) in fish samples using graphite furnace atomic absorption spectrometry after dry ashing and wet ashing methods. Author assured good accuracy by the analyses of biological reference materials and stated that proposed method is efficient for simple, rapid and reliable determination of some heavy metals in the fish species. Furthermore, it is stated that the concentrations of heavy metals in the fish samples were below those of maximum permitted levels in Turkey.

3. MATERIAL AND METHOD

3.1 Material

3.1.1 Fishes

Fishes from Eastern Mediterranean Sea, collected from local fishermen at 3 stations (Izmir Outer Bay (Table 3.1), Homa Lagoon/Izmir (Table 3.2) and Mersin Bay (Table 3.3)) (Figure 3.1) and fishes from Northeast Atlantic collected onboard the research vessel, “Walter Herwig III” at 4 stations (Figure 3.2) (Tampen (Table 3.4), north of Shetland Islands (Table 3.5), Faroe Islands (Table 3.6) and Copinsay (Table 3.7)).

3.1.2 Chemicals

All solutions were prepared with deionised water obtained from a NANOpure II water purification system (Sybron/Barnstead, Boston, Massachusetts, USA).

Standard cadmium and lead solutions were prepared from a Titrisol concentrate containing 1000mg Cd/l and 1000mg Pb/l (Cd: Merck Nr. 109960, Pb: Merck Nr. 109969, Darmstadt, Germany) with adding 2ml $HClO_4$ (70% w/w, suprapure) and filling up to 1000ml. Working solutions were $HClO_4$ (Suprapure, Merck Nr. 100517) and EDTA (c=0.02 mol/l, Merck Nr. 159294).

CRM No 422 cod muscle from the Commission of the European Communities, Community Bureau of Reference, Luxemburg was used as standard reference material.

Table 3.1. Used fish species obtained from Izmir Bay

No	Scientific Name		Family	English Name
1	*Belone belone*	(L.,1761)	Belonidae	Gav fish
2	*Trachurus trachurus*	(L.,1758)	Carangidae	Horse mackerel
3	*Trachurus mediterraneus*	(S.,1868)	Carangidae	Mediter. horse mac
4	*Spicara smaris*	(L.,1758)	Centracanthidae	Piceral
5	*Sardina pilchardus*	(W.,1792)	Clupeidae	Sardine
6	*Alosa fallax nilotica*	(G.,1809)	Clupeidae	Mediter. shad
7	*Engraulis encrasicholus*	(L.,1758)	Engraulidae	Anchovy
8	*Trisopterus minutus*	(L.,1758)	Gadidae	Poor cod
9	*Merlangius merlangus*	(L.,1758)	Gadidae	Whitting
10	*Merluccius merluccius*	(L.,1758)	Merlucciidae	Hake
11	*Dicentrarchus labrax*	(L.,1758)	Moronidae	Seabass
12	*Liza aurata*	(R.,1810)	Mugilidae	Golden grey mullet
13	*Liza saliens*	(R.,1810)	Mugilidae	Leaping grey mullet
14	*Chelon labrosus*	(R.,1827)	Mugilidae	Ticklip grey mullet
15	*Mullus barbatus*	(L.,1758)	Mullidae	Striped mullet
16	*Mullus surmuletus*	(L.,1758)	Mullidae	Red mullet
17	*Pomatomus saltator*	(L.,1766)	Pomatomidae	Blue fish
18	*Sciaena umbra*	(L.,1758)	Sciaenidae	Brown meagre
19	*Scomber japonicus*	(H.,1782)	Scombridae	Chub mackerel
20	*Sarda sarda*	(B.,1793)	Scombridae	Atlantic bonito
21	*Serranus cabrilla*	(L.,1758)	Serranidae	Comber
22	*Lepidorhombus boscii*	(R.,1810)	Scophthalmidae	Fourspotted Megrim
23	*Solea vulgaris*	(L.,1758)	Soleidae	Sole
24	*Dentex machrophtalmus*	(B.,1791)	Sparidae	Red pandora
25	*Diplodus annularis*	(L.,1758)	Sparidae	Annular bream
26	*Boops boops*	(L.,1758)	Sparidae	Bogue
27	*Sarpa salpa*	(L.,1758)	Sparidae	Salema
28	*Pagellus erythrinus*	(L.,1758)	Sparidae	Common pandora
29	*Dentex dentex*	(L.,1758)	Sparidae	Common dentex
30	*Diplodus sargus*	(L.,1758)	Sparidae	White seabream
31	*Diplodus puntazzo*	(C.,1777)	Sparidae	Sharpsnout seabream
32	*Lithognathus mormyrus*	(L.,1758)	Sparidae	Striped seabream
33	*Oblada melanura*	(L.,1758)	Sparidae	Saddled seabream
34	*Diplodus vulgaris*	(G.,1817)	Sparidae	Two-banded seabream
35	*Spondyliosoma cantharus*	(L.,1758)	Sparidae	Black seabream
36	*Lepidotrigla cavillone*	(L.,1801)	Triglidae	Large scaled gurnard

Table 3.2. Used fish species obtained from Homa Lagoon

No	Scientific Name		Family	English Name
37	*Sparus aurata*	(L.,1758)	Sparidae	Gilthead seabream
38	*Trachurus trachurus*	(L.,1758)	Carangidae	Horse mackerel
39	*Trachinotus ovatus*	(L.,1758)	Carangidae	Derbio
40	*Liza saliens*	(R.,1810)	Mugilidae	Leaping grey mullet
41	*Liza ramada*	(R.,1810)	Mugilidae	Thin-lipped grey mullet
42	*Dentex machrophtalmus*	(B.,1791)	Sparidae	Red pandora

Table 3.3. Used fish species obtained from Mersin Bay

No	Scientific Name		Family	English Name
43	*Trachurus trachurus*	(L.,1758)	Carangidae	Horse mackerel
44	*Caranx crysos*	(M.,1815)	Carangidae	Blue runner
45	*Sardina pilchardus*	(W.,1792)	Clupeidae	Sardine
46	*Mullus barbatus*	(L.,1758)	Mullidae	Striped mullet
47	*Sparus aurata*	(L.,1758)	Sparidae	Gilthead seabream
48	*Boops boops*	(L.,1758)	Sparidae	Bogue
49	*Saurida undosquamis*	(R.,1848)	Synodontidae	Brushtooth lizardfish

Table 3.4. Used fish species obtained from Tampen Region

No	Scientific Name		Family	English Name
50	*Melanogrammus aeglefinus*	(L.,1758)	Gadidae	Haddock
51	*Gadus morhua*	(L.,1758)	Gadidae	Cod
52	*Pollachius virens*	(L.,1758)	Gadidae	Saithe
53	*Molva molva*	(L.,1758)	Lotidae	Ling
54	*Brosme brosme*	(A.,1772)	Lotidae	Tusk
55	*Merluccius merluccius*	(L.,1758)	Merlucciidae	Hake
56	*Microstomus kitt*	(W.,1792)	Pleuronectidae	Lemon sole
57	*Lepidorhombus whiffiagonis*	(W.,1792)	Scophthalmidae	Megrim
58	*Chelidonichthys gurnardus*	(L.,1758)	Triglidae	Grey gurnard
59	*Zeus faber*	(L.,1758)	Zeidae	John dories

Table 3.5. Used fish species obtained from north of Shetland Islands

No	Scientific Name		Family	English Name
60	*Pollachius virens*	(L.,1758)	Gadidae	Saithe
61	*Lophius piscatorius*	(L.,1758)	Lophiidae	Anglerfish
62	*Molva molva*	(L.,1758)	Lotidae	Ling

Table 3.6. Used fish species obtained from Faroe Islands

No	Scientific Name		Family	English Name
63	*Merlangius merlangus*	(L.,1758)	Gadidae	Whitting
64	*Melanogrammus aeglefinus*	(L.,1758)	Gadidae	Haddock
65	*Lophius piscatorius*	(L.,1758)	Lophiidae	Anglerfish

Table 3.7. Used fish species obtained from Copinsay Region

No	Scientific Name		Family	English Name
66	*Scomber scombrus*	(L.,1758)	Scombridae	Mackerel
67	*Melanogrammus aeglefinus*	(L.,1758)	Gadidae	Haddock
68	*Scyliorhinus caniculus*	(L.,1758)	Scyliorhinidae	Small-spotted catshark

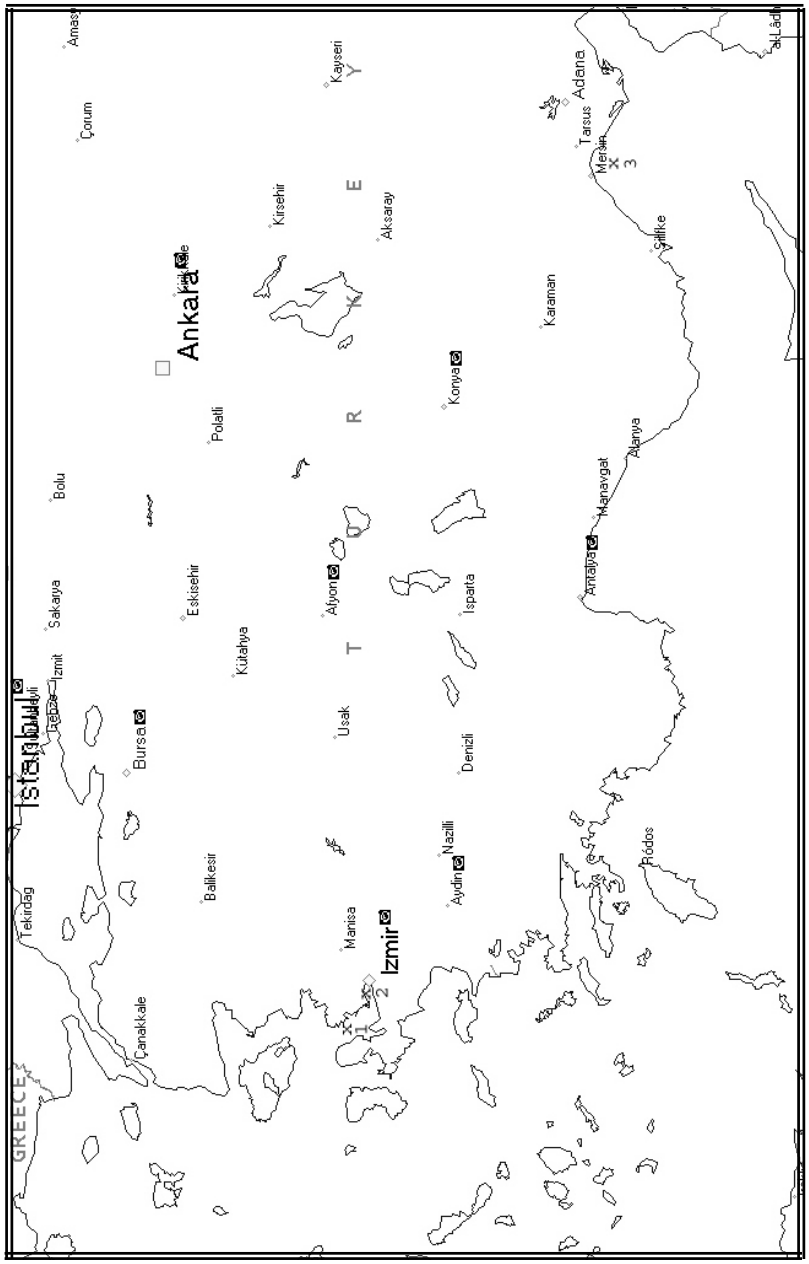

Figure 3.1. Eastern Mediterranean Sea Sampling Locations
(1- Izmir Outer Bay, 2- Homa Lagoon, 3- Mersin Bay)

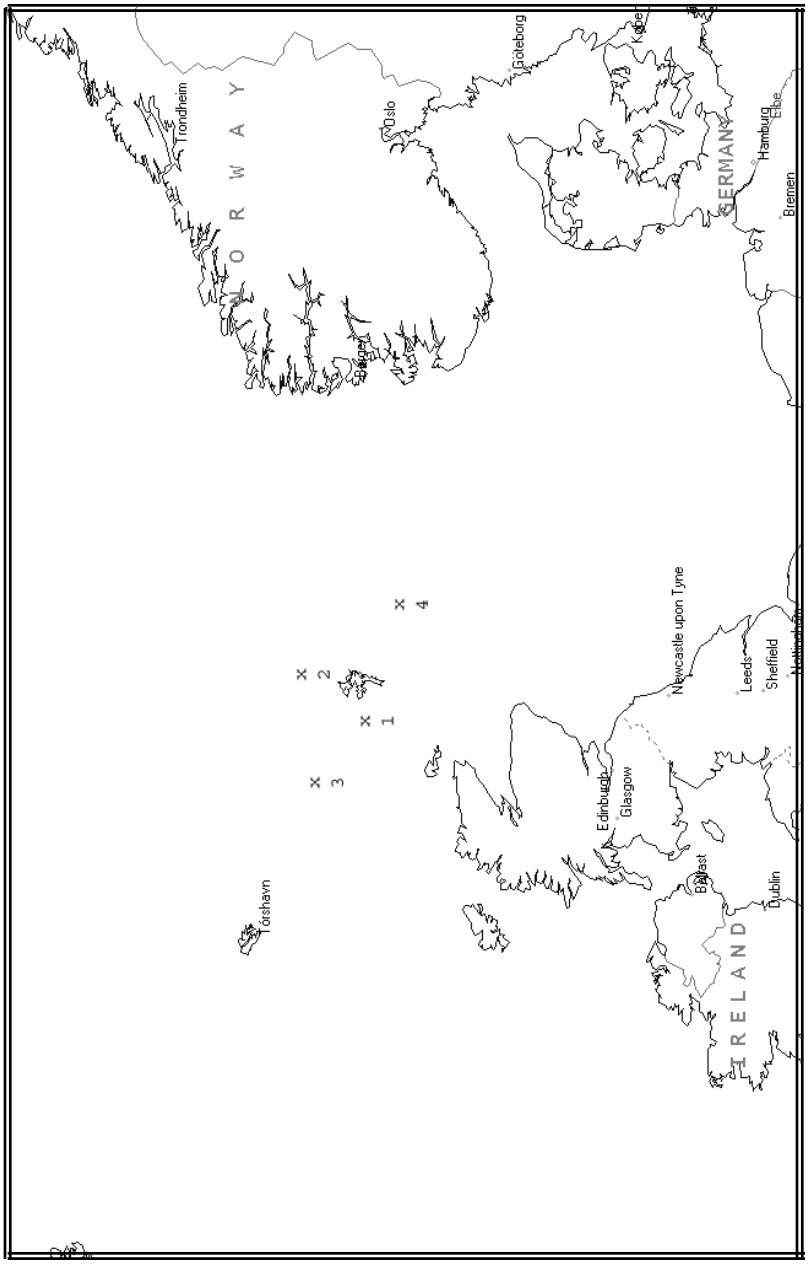

Figure 3.2. Northeast Atlantic Sea Sampling Locations

(1- Tampen, 2- North of Shetland Islands, 3- Faroe Islands, 4- Copinsay)

3.2 Method

Used fish samples hunted from Northeast Atlantic were immediately frozen after hunting and kept in deep freezer till analyzing. Eastern Mediterranean fishes were also frozen in 2 hours after hunting and transferred to Institute of Fishery Technology and Fish Quality of the Federal Research Centre for Fisheries, Germany (Bundesforschungsanstalt für Fischerei, Institut für Fischereitechnik und Fischqualität, Hamburg) and kept in deep freezer until analysing.

3.2.1 Sample preparing

In the sampling step, it is necessary to use glass or titanium knives for sample digestion and to use conditioned teflon or polypropylene bottles. A pre-concentration step (e.g. removal of water by lyophilization) is recommended when the concentration of the analyte is expected to be very low. The digestion is mostly done by wet oxidation. Dry ashing, which was commonly used in the past, is subject to uncontrolled contamination sources. However, modern dry ashing devices like ashing in a microwave activated oxygen plasma at reduced pressure is an excellent alternative to wet digestion, but rather expensive. Many different analytical methods for the determination of cadmium and lead in fish and other seafood have been used.

In this study, the frozen samples were lyophilised in a Finn-Aqua Lyovac GT 2 freeze dryer (Parameters: ambient

temperature 15-25°C, vacuum 5-10 Pa, duration at least 48 h). The lyophilised samples were finally milled in a -ball-mill made from agate (Fritsch, Planetary Ball Mill, puluerisette 5, Idar-Oberstein, Germany) and kept in high-density polyethylene bags at room temperature in an exsiccator until analysis. Approximately 0.4 g lyophilized sample was weighted into Petri-dishes and they were put in a plasma asher chamber for mineralization (Power supply 350-360 W, vacuum 60-90 Pa, oxygen partial pressure 2.0-2.5x10^5 Pa). When decomposition is complete, this can be controlled visually by a change in the sample color from grey/brown/yellow to a bright white and a change in the color of the oxygen plasma from cyan/red to a light blue, the ashed samples are quantitatively transferred into 100 ml volumetric flasks and dissolved in suprapure sulphuric acid (0.2%, w/w) at pH 2. To avoid contamination from the containers, polypropylene vessels (Flask, volumetric flask), high-density polyethylene (HDPE) bottles and all further plastic equipment (Breakers, autosampler cups, spoon, removable tips, tweezers etc.) were used. They were cleaned by soaking into 2% (w/w) nitric acid (Pro analysis grade) for >24 h followed by soaking in de-ionized water for > 24 h. after this cleaning procedure all cleaned vessels and equipment were dried and kept in metal-free containers until use. This avoided metal contamination through room dust.

3.2.2 Equipment

3.2.2.1 Plasma asher (Plasma Prozessor 200-G, Technics Plasma GmbH, München, Germany)

With the necessity of environmental control and analytical monitoring of pollutant species, the low-temperature plasma-oxidation technique has been more extensively applied in recent years to isolate trace constituents from a variety of background matrices.

In the present study, the mineralization of the samples was performed in a closed low temperature microwave oxygen plasma processor equipped with a high performance pump. The parameters were: analyst-selectable power supply 350-360 W, vacuum 60-90 Pa, oxygen partial pressure 2.0-2.5x10^5 Pa and duration of decomposition 144-168 h.

Oehlenschläger (1993a) stated that, the decomposition of biological material is the most time consuming and work intensive step in trace metal analysis. Decomposition is the step with the highest risk of contamination because the samples come into contact with a number of chemicals, decomposition aids and storage materials and it may be defined as the removal of the organic matrix by converting it into suitable gaseous components, which are then volatilized, leaving behind an inorganic residue for element analysis.

A decomposition procedure for trace element analysis ideally involves:

- Complete destruction of all organic components and mineralization of the sample
- Retention of all elements to be determined quantitatively within the organic residue
- Avoiding all possible contamination

Furthermore, choice of the decomposition method should preferably:

- Need only small amounts of ultrapure reagents and chemicals
- Be not dangerous in handling
- Be simple to clean
- Not use $HClO_4$ (Explosion)
- Not use H_2SO_4 (Coprecipitation with insoluble salts)
- Be a closed system
- Work at low temperature
- Use only silica as material for containers
- Have low costs for equipment and consumables
- Be simple in handling

The choice of decomposition method is strongly dependent on the analytical procedure used for the determination of elements in

the decomposed sample. The two most promising methodologies are wet ashing procedures and dry ashing by oxygen plasma.

The decomposition method (Microwave induced oxygen plasma under vacuum) used in present study have the following benefits:

- No contamination, no chemicals used, sample has contact only with oxygen
- Energy and thus temperature can be adjusted according to the matrix to be decomposed
- Approximately 20 samples can be decomposed simultaneously
- Complete destruction of organic matrix
- Best decomposition method for voltammetric determinations
- Reasonable costs during use (Electricity and oxygen)
- A safe process for the analyst (No toxic or hazardous chemicals involved)

The principle of low temperature ashing is to generate in the plasma, through energy of the electrons, free radicals and reactive species, which can degrade organic material at low temperatures. The energy required to initiate and sustain these reactions is supplied by the energy of the electrons, which are capable of decomposing molecular oxygen into atomic oxygen, for

example. Normal dry ashing techniques require thermal energy to break down the molecular oxygen to atomic form, which then initiates oxidation. Since the energy to do this with the low temperature asher is provided through the electrons instead of heat energy, we are able to oxidize materials with atomic oxygen without the usual requirement of heat (IPC Technical Paper, 1973).

Oxidation with excited oxygen is particularly well suited to the determination of trace elements in organic materials. A serious disadvantage is that the low oxygen pressure results in a very slow rate of combustion, so that it may take several hours to burn off one gram of sample, the time depending on the particle size, the conditions, and the nature of the substance. It is difficult to ash completely materials with a high ash content, as the surface layer of ash which is formed at first hinders penetration of the oxygen further into the sample. An important advantage of the technique is that several elements which are normally lost by volatilization during conventional ashing procedures, remain in the residue during low-temperature ashing (As, Cd, Sb, etc.), and another advantage, in common with other simple combustion methods, is that no contamination from metals is to be expected because the temperature never gets very high, the changes of reaction between residue and container are very much reduced, and much better recoveries should be obtained than from high-temperature methods. Many inorganic compounds remain unchanged at these temperatures though salt hydrates will tend to

lose water. If the samples are very carefully, they can even retain their original shape during the combustion (Bock, 1979).

Some of the initial analytical applications of electrodelessly excited gases were described by Gleit and Holland (1962) and much of the early literature deals with the preparation of organic or biomedical samples for trace metal analyses of both stable and radioactive isotopes. Since the early 1960s, the extension of excited plasma to a variety of analytical problems has been achieved.

3.2.2.2 Voltammetry

The classical method for the analysis of heavy metals in biological matrices was the AAS (Atomic Absorption Spectrophotometry). In the 1960s and even more in the 70s and 80s other methods became more popular for the analysis of trace metals e.g. electrochemical methods like polarography is defined as electrochemical method in which a dynamic (Dropping) mercury electrode is used. If the electrode is a static one like the hanging mercury drop (HMDE) and current/voltage curves are recorded the term voltammetry is used.

In this study, DPSAV, Differential Pulse Anodic Stripping Voltammetry, (746 VA Trace Analyzer, Metrohm Ltd., Switzerland) equipped with autosampler (695 VA Autosampler, Metrohm Ltd., Switzerland) was used for the determination of heavy metals. The experimental conditions for the simultaneous determination of

cadmium and lead by differential pulse anodic stripping voltammetry are shown in Table 3.2.

Table 3.2. Experimental conditions for the simultaneous determination of Cd and Pb by differential pulse anodic stripping voltammetry (DPASV). Supporting electrolyte: HMDE (Hanging Mercury Drop Electrode)

Deposition potential	-700 mV
Final potential	-230 mV
Deposition time	300 s
Delay time before potential sweep	10 s
Potential scan rate	13.33 mV/s
Stirring rate	2000 rpm

The accuracy of the determination of cadmium and lead was checked by the reference material CRM No 422 cod muscle from the Commision of the European Communities, Community Bureau of Reference, Luxemburg.

The simplified principle of the voltammetric procedure is: at a microelectrode (e.g. a mercury drop placed in a solution containing trace metals) an electrode process formulated for heavy metal as

occurs (where n*e^- is the number of electrons transferred). In the solution of analyte only a single form of ionic species is found, the oxidized or the reduced type, while the product of electrode process (reduced metal in reduction process and oxidized metal in oxidation process) is formed only during the electrode itself at the electrochemical double layer between electrode and solution *in situ*. The electrode potential E for a given redox reaction is defined and corresponding current I, which is a function of the concentration of the metal in the solution, is measured. If the current/voltage correlation i=f (E) is recorded, a polarogramm or voltammogramm is obtained. Practically the DPSAV, Differential Pulse Anodic Stripping Voltammetry, which is a combination of different pulse polarography and anodic stripping voltammetry, is used for the determination of heavy metals. In this “inverse” technique, the elements in a first step are deposited on the electrode and in a second step stripped off according to their electrochemical potential (Oehlenschläger, 1993b).

4. FINDINGS

Lead and cadmium concentrations of 49 fish species belongs to 19 families from Eastern Mediterranean Sea and 19 fish species belongs to 10 families from Northeast Atlantic determined by using DPSAV, Differential Pulse Anodic Stripping Voltammetry, (746 VA Trace Analyzer, Metrohm Ltd., Switzerland) equipped with autosampler (695 VA Autosampler, Metrohm Ltd., Switzerland) are presented respectively.

4.1 Measurements of Eastern Mediterranean Fish

4.1.1 Fishes from Izmir Outer Bay

4.1.1.1 Lead concentrations

Lead concentrations of Izmir Outer Bay fishes have been shown in Table 4.1 and a sample lead voltammogram has been shown in Figure 4.1.

When Table 4.1 examined, it is seen that the highest lead burden belongs to striped seabream and the lowest lead burden determined in chub mackerel among the 36 species obtained from Izmir Outer Bay. Obtained mean lead values were about 30 ppb. Highest lead concentration belongs to brown meagre as 154.27ppb for first group, striped seabream as 383 ppb for second and 107.88 ppb for third. Lowest values were found in sole as 9.13ppb, salema as 11.22ppb and chub mackerel as 7.88ppb respectively.

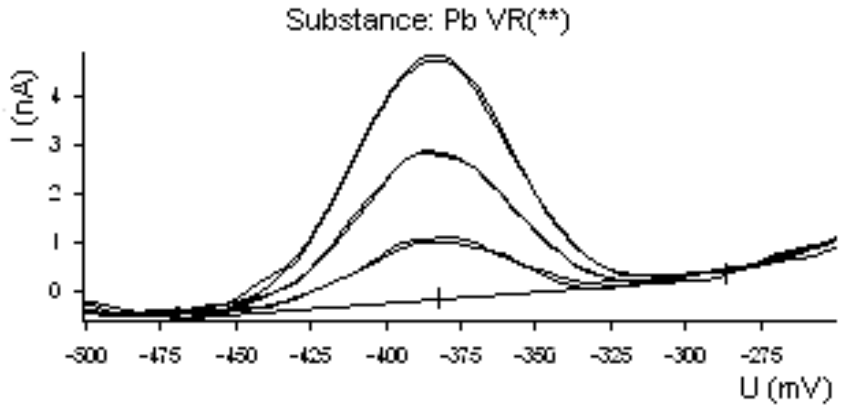

Figure 4.1. Lead voltammogram

Table 4.1. Lead concentrations of Izmir Outer Bay
(ppb Wet Weight, n= sample count)

Species	n	Mean	±	SD	Minimumk	Maximum
Gav fish	5	10.078	±	1.0554	9.1731	11.2698
Horse mackerel	5	23.006	±	2.0684	21.3176	25.5318
Med. Horse mackerel	3	32.399	±	2.5590	28.7266	34.5760
Piceral	5	13.706	±	2.6882	10.8071	16.1165
Sardine	5	45.560	±	6.2449	41.3574	52.7362
Mediterranean shad	3	67.370	±	4.5741	62.0952	70.2467
Anchovy	5	31.439	±	6.3646	27.3919	38.7748
Poor cod	5	14.661	±	0.8938	13.5329	15.7118
Whitting	5	13.544	±	2.0336	11.7429	16.5790
Hake	5	9.542	±	2.6873	7.6416	11.4421
Seabass	3	125.084	±	4.9568	119.8520	129.7100

Table 4.1. Lead concentrations of Izmir Outer Bay (continue)

Species	n	Mean	±	SD	Minimum	Maximum
Golden grey mullet	5	35.926	±	1.9074	34.5774	37.2749
Grey mullet	3	34.819	±	1.3345	33.4704	36.2229
Ticklip grey mullet	3	46.377	±	5.3841	40.7461	51.4748
Striped mullet	5	32.074	±	3.7519	29.4208	34.7268
Red mullet	5	12.544	±	3.2687	9.8506	16.1807
Blue fish	5	12.927	±	1.7696	10.8841	13.9761
Brown meagre	3	154.272	±	4.4671	148.6274	159.2884
Chub mackerel	5	7.877	±	1.4200	6.1635	9.3802
Atlantic bonito	3	107.878	±	2.5110	105.2601	110.6999
Comber	5	15.281	±	1.9004	13.0866	16.3782
Fourspotted megrim	5	23.817	±	0.9022	23.1788	24.4547
Sole	5	9.134	±	3.0366	5.8708	13.2144
Red pandora	5	15.162	±	2.2994	11.9452	17.1057
Annular bream	5	18.542	±	1.0362	17.2591	19.4895
Bogue	5	9.791	±	0.0564	9.7511	9.8308
Salema	5	11.218	±	0.0793	11.1623	11.2744
Common pandora	3	211.693	±	2.0625	210.2346	213.1515
Common dentex	3	57.931	±	2.9586	53.8046	60.8465
White seabream	3	51.157	±	3.7354	46.7707	54.8776
Sharpsnout seabream	3	42.401	±	5.4739	36.8913	47.8383
Striped seabream	3	383.006	±	4.5390	379.7967	386.2158
Saddled seabream	3	89.341	±	4.7486	86.0868	94.7896
Common seabream	3	50.928	±	4.5184	45.8406	55.6871
Black seabream	3	23.927	±	5.0135	18.1386	26.8760
Large scaled gurnard	5	27.884	±	0.3253	27.5680	28.2966

4.1.1.2 Cadmium concentrations

Cadmium concentrations of Izmir Outer Bay fishes have been shown in Table 4.2 and 1 example of cadmium voltammogram has been shown in Figure 4.2.

It can be seen with examining Table 4.2 that among the Izmir Outer Bay fishes, the highest cadmium burden was found in sharpsnout seabream and the lowest was found in mediterranean shad, leaping grey mullet, blue fish, brown meagre, atlantic bonito, comber, fourspotted megrim, sole, red pandora, annular bream, common dentex, common two-banded seabream and thin-lipped grey mullet as under detection limit. In all tables, the values found under detection limit has been given as 0 (zero). The mean concentration was about 1.30 ppb for this region.

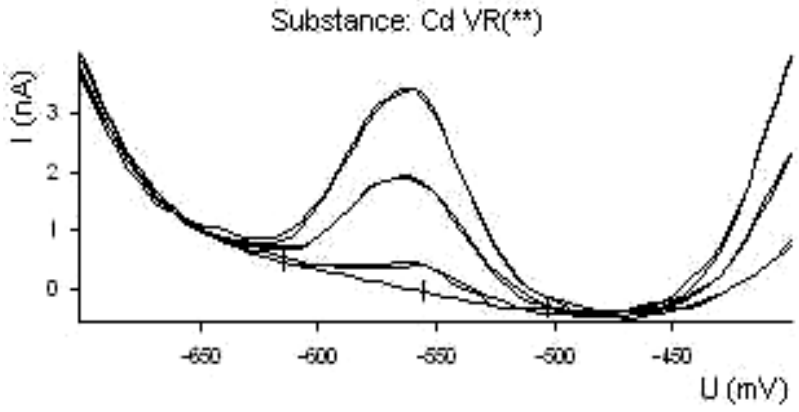

Figure 4.2. Cadmium voltammogram

Table 4.2. Cadmium concentrations of Izmir Outer Bay (ppb w/w)

Species	n	Mean	±	SD	Minimum	Maximum
Gav fish	5	1.1234	±	0.0809	1.0663	1.1806
Horse mackerel	5	2.7123	±	0.2235	2.5543	2.8703
Med. Horse mackerel	3	3.8605	±	0.4044	3.5745	4.1465
Piceral	5	3.6847	±	1.6316	2.5310	4.8384
Sardine	5	1.9825	±	0.7257	1.1869	2.6081
Mediterranean shad	3	0.0000	±	0.0000	0.0000	0.0000
Anchovy	5	5.7713	±	0.9036	5.0319	6.7785
Poor cod	5	2.4288	±	0.4567	1.7742	2.8248
Whitting	5	4.2255	±	1.7697	2.4770	6.0157
Hake	5	2.2116	±	0.2632	2.0255	2.3977
Seabass	3	4.6090	±	1.4269	3.1908	6.0444
Golden grey mullet	5	0.7902	±	0.2731	0.5971	0.9833
Grey mullet	3	0.0000	±	0.0000	0.0000	0.0000
Ticklip grey mullet	3	0.0378	±	0.0536	0.0000	0.0757
Striped mullet	5	2.7828	±	1.1676	1.9572	3.6084
Red mullet	5	1.5404	±	0.3222	1.1802	1.8012
Blue fish	5	0.0000	±	0.0000	0.0000	0.0000
Brown meagre	3	0.0000	±	0.0000	0.0000	0.0000
Chub mackerel	5	1.1962	±	0.1709	1.0494	1.4265
Atlantic bonito	3	0.0000	±	0.0000	0.0000	0.0000
Comber	5	0.0000	±	0.0000	0.0000	0.0000
Fourspotted megrim	5	0.0000	±	0.0000	0.0000	0.0000
Sole	5	0.0000	±	0.0000	0.0000	0.0000
Red pandora	5	0.0000	±	0.0000	0.0000	0.0000
Annular bream	5	0.0000	±	0.0000	0.0000	0.0000
Bogue	5	1.6136	±	0.0862	1.5526	1.6745
Salema	5	1.3413	±	0.6522	0.6727	1.9758

Table 4.2. Cadmium concentrations of Izmir Outer Bay (continue).

Species	n	Mean	±	SD	Minimum	Maximum
Common pandora	3	1.9082	±	0.0888	1.8454	1.9710
Common dentex	3	0.0000	±	0.0000	0.0000	0.0000
White seabream	3	0.5002	±	0.2622	0.3003	0.7971
Sharpsnout seabream	3	14.2201	±	1.0659	13.0816	15.1944
Striped seabream	3	0.0791	±	0.1120	0.0000	0.1583
Saddled seabream	3	0.0249	±	0.0353	0.0000	0.0498
Common seabream	3	0.0000	±	0.0000	0.0000	0.0000
Black seabream	3	0.0127	±	0.0180	0.0000	0.0254
Large scaled gurnard	5	0.8999	±	0.5123	0.4906	1.4744

4.1.2 Fishes from Homa Lagoon

4.1.2.1 Lead concentrations

Lead concentrations of Homa Lagoon fishes have been shown in Table 4.3.

When it is examined, it can be seen that the highest concentration belongs to red pandorra and the lowest concentration belongs to seabream among the six species obtained from Homa Lagoon. Obtained mean lead concentration was about 12 ppb.

Table 4.3. Lead concentrations of Homa Lagoon (ppb ww)

Species	n	Mean	±	SD	Minimum	Maximum
Seabream	5	6.3388	±	0.9044	5.6994	6.9783
Horse mackerel	5	13.4384	±	0.5953	12.7391	14.0442
Derbio	1	8.5075	±	0.4605	8.1819	8.8331
Leaping grey mullet	5	11.7452	±	2.5858	9.4243	14.5324
Thin-lipped grey mullet	5	13.3903	±	3.1651	9.7551	15.5342
Red pandorra	2	17.0398	±	3.3793	14.6503	19.4293

4.1.2.2 Cadmium concentrations

Cadmium concentrations of Homa Lagoon fishes have been shown in Table 4.4.

It is seen in Table 4.4 that the highest cadmium burden was found in red pandorra and the lowest cadmium burden was found in thin-lipped grey mullet among the Homa Lagoon fishes. The mean cadmium values obtained from this region was about 0.6 ppb.

Table 4.4. Cadmium concentrations of Homa Lagoon (ppb w/w)

Species	n	Mean	±	SD	Minimum	Maximum
Seabream	5	0.2660	±	0.5321	0.0000	1.0641
Horse mackerel	5	0.5203	±	0.2245	0.3615	0.6790
Derbio	1	0.4245	±	0.1117	0.3455	0.5035
Leaping grey mullet	5	0.8704	±	0.0105	0.8630	0.8778
Thin-lipped grey mullet	5	0.0000	±	0.0000	0.0000	0.0000
Red pandorra	2	0.9492	±	0.3104	0.7297	1.1687

4.1.3 Fishes from Mersin Bay

4.1.3.1 Lead concentrations

Lead concentrations of Mersin Bay fishes have been shown in Table 4.5.

According to the values shown in Table 4.5, among the 7 species from Mersin Bay, the highest lead concentration was found in sardine and the lowest was found in brushtooth lizardfish. Average lead concentration was about 15 ppb.

Table 4.5. Lead concentrations of Mersin Bay (ppb w/w)

Species	n	Mean	±	SD	Minimum	Maximum
Horse mackerel	5	15.5291	±	1.3846	14.2325	16.9875
Blue runner	5	14.1065	±	0.8306	13.5739	15.0635
Sardine	5	43.3636	±	2.8307	40.4362	46.1680
Striped mullet	5	21.3931	±	3.0713	17.9911	25.6984
Seabream	5	13.3307	±	1.0194	11.9601	14.7276
Bogue	5	14.6709	±	1.0991	13.0573	15.3890
Brushtooth lizardfish	5	7.3803	±	0.9386	6.0811	8.2686

4.1.3.2 Cadmium concentrations

Cadmium concentrations of Mersin Bay fishes have been shown in Table 4.6.

It has been shown in Table 4.6 that highest cadmium burden was found in horse mackereland the lowest was found in blue runner. Average cadmium concentration was about 2 ppb.

Table 4.6. Cadmium concentrations of Mersin Bay (ppb w/w)

Species	n	Mean	±	SD	Minimum	Maximum
Horse mackerel	5	3.5445	±	1.4819	1.8443	4.5619
Blue runner	5	0.9045	±	0.0880	0.8426	0.9671
Sardine	5	2.0460	±	1.5787	1.0843	3.8681
Striped mullet	5	3.3537	±	0.4765	2.8222	3.9235
Seabream	5	1.2141	±	0.2862	0.8590	1.4919
Bogue	5	1.7384	±	0.3131	1.5170	1.9598
Brushtooth lizardfish	5	2.0653	±	1.1588	0.6065	3.0434

4.2 Measurements of Northeast Atlantic Fish

4.2.1 Fishes from Tampen Region

4.2.1.1 Lead concentrations

Lead concentrations of Tampen region fishes have been shown in Table 4.7.

When the Table 4.7 examined, it is shown that among the 10 fish species hunted from Tampen region, the highest lead burden was found in grey gurnard and the lowest was found in cod. Average concentration was about 3.6 ppb.

Table 4.7. Lead concentrations of Tampen Region fishes (ppb w/w)

Species	n	Mean ± SD	Minimum	Maximum
Haddock	5	3.80 ± 0.640	3.00	4.70
Cod	2	2.90 ± 0.043	2.90	2.90
Saithe	6	3.50 ± 0.099	3.40	3.60
Ling	3	3.80 ± 0.139	3.70	3.90
Tusk	3	3.40 ± 0.513	2.70	3.90
Hake	2	3.90 ± 0.407	3.60	4.10
Lemon sole	2	4.30 ± 0.858	3.30	5.30
Megrim	4	3.50 ± 1.910	0.00	7.20
Grey gurnard	3	80.00 ± 0.664	79.00	80.40
John dories	2	3.40 ± 0.689	2.90	3.90

4.2.1.2 Cadmium concentrations

Cadmium concentrations of Tampen region have been shown in Table 4.8.

It has been agreed with the examining of Table 4.8 that the highest cadmium burden was found in lemon sole and the lowest was found in haddock and cod. Average cadmium value of this region was about 1.4 ppb.

Table 4.8. Cadmium concentrations of Tampen Region fishes (ppb w/w)

Species	n	Mean ± SD	Minimum	Maximum
Haddock	5	0.800 ± 0.5425	0.200	1.800
Cod	2	0.800 ± 0.1710	0.700	0.900
Saithe	6	0.900 ± 0.0353	0.900	0.900
Ling	3	1.900 ± 1.0822	1.200	2.700
Tusk	3	1.200 ± 0.6531	0.400	2.300
Hake	2	1.700 ± 1.0144	1.000	2.400
Lemon sole	2	2.900 ± 0.5569	2.000	3.700
Megrim	4	2.100 ± 1.2834	0.000	5.100
Grey gurnard	3	1.500 ± 0.3939	1.000	1.900
John dories	2	1.000 ± 0.7176	0.500	1.500

4.2.2 Fishes from North of Shetland Islands

4.2.2.1 Lead concentrations

Lead concentrations of the fishes hunted from north of Shetland Islands have been shown in Table 4.9.

It has been shown in Table 4.9 that the highest lead burden was found in saithe and the lowest was found in anglerfish among the 3 species from this region. The average lead value was about 3 ppb.

Table 4.9. Lead concentrations of the fishes hunted from north of Shetland Islands (ppb w/w)

Species	n	Mean ± SD	Minimum	Maximum
Saithe	5	4.0 ± 0.760	2.70	5.20
Anglerfish	4	2.0 ± 0.089	1.90	2.10
Ling	3	3.5 ± 1.063	2.10	4.70

4.2.2.2 Cadmium concentrations

Cadmium concentrations of the fishes hunted from north of Shetland Islands have been shown in Table 4.10.

Table 4.10 clarify that the highest value determined from this region belongs to saithe and the lowest belongs to anglerfish. The average cadmium value obtained from this region was about 0.7 ppb.

Table 4.10. Cadmium concentrations of the fishes hunted from north of Shetland Islands (ppb w/w)

Species	n	Mean ± SD	Minimum	Maximum
Saithe	5	1.300 ± 1.4730	0	4.10
Anglerfish	4	0.000 ± 0.0000	0	0.00
Ling	3	0.967 ± 1.0712	0	2.20

4.2.3 Fishes from Faroe Islands

4.2.3.1 Lead concentrations

Lead concentrations of the fishes hunted from around Faroe Islands have been shown in Table 4.11.

It has been shown in Table 4.11 that the highest lead burden belongs to haddock and the lowest belongs to anglerfish among the 3 fish species obtained from around Faroe Islands. The average lead value was about 3.5 ppb.

Table 4.11. Lead concentrations of the fishes hunted from around the Faroe Islands (ppb w/w)

Species	n	Mean ± SD	Minimum	Maximum
Whittling	6	3.80 ± 2.390	1.80	10.70
Haddock	2	3.90 ± 1.336	2.40	6.90
Anglerfish	4	3.00 ± 1.476	0.00	4.80

4.2.3.2 Cadmium concentrations

Cadmium concentrations of the fishes hunted around Faroe Islands have been shown in Table 4.12.

Highest cadmium burden was found in haddock and the lowest was found in anglerfish in this region was shown in Table 4.12. The average cadmium concentration was about 0.9 ppb.

Table 4.12. Cadmium concentrations of the fishes hunted from around the Faroe Islands (ppb w/w)

Species	n	Mean ± SD	Minimum	Maximum
Whittling	6	0.40 ± 0.76	0	2.0
Haddock	2	2.40 ± 2.50	0	7.6
Anglerfish	4	0.00 ± 0.00	0	0.0

4.2.4 Fishes from Copinsay Region

4.2.4.1 Lead concentrations

Lead concentrations of the fishes hunted from Copinsay region have been shown in Table 4.13.

According to the values shown in Table 4.13 the highest lead burden was found in small-spottet catshark and the lowest was found in haddock among the 3 species belong to this region. The average lead value was about 8.7 ppb.

Table 4.13. Lead concentrations of the fishes hunted from Copinsay Region (ppb w/w)

Species	n	Mean	±	SD	Minimum	Maximum
Mackerel	10	5.9	±	1.833	2.40	9.20
Haddock	4	5.3	±	2.067	2.90	8.40
Small-spotted catshark	1	15.0	±	1.677	13.80	16.20

4.2.4.2 Cadmium concentrations

Cadmium concentrations of the fishes hunted from Copinsay region have been shown in Table 4.14.

It has been shown in Table 4.14 that the highest cadmium burden was found in mackerel and haddock and the lowest was found in small-spotted catshark. The average value was about 2.2 ppb.

Table 4.14. Cadmium concentrations of the fishes hunted from Copinsay Region (ppb w/w)

Species	n	Mean	±	SD	Minimum	Maximum
Uskumru	10	2.30	±	1.709	0.0	6.20
Mezgit	4	2.30	±	2.963	0.0	7.10
Kedi baligi	1	2.10	±	0.838	1.5	2.70

4.3 Measurements of Standard Reference Material

Lead and cadmium values of reference material that CRM No 422 cod muscle from the Commission of the European Communities, Community Bureau of Reference have been shown in Table 4.15.

It has been shown in table that average lead concentration was found as 81.425 ppb and average cadmium concentration was found as 17.475 ppb in standard reference material.

Table 4.15. Lead and cadmium concentrations of standard reference material CRM No:422 (ppb dry weight)

CRM No 422 Cod Muscle Meat	Mean ± SD	Minimum	Maximum
Lead	81.425 ± 9.4090	71.9	92.5
Cadmium	17.475 ± 0.7455	16.4	18.1

5. RESULT AND DISCUSSION

5.1 Evaluation of Eastern Mediterranean Fish Measurements

5.1.1 Evaluation of lead measurements

In all samples, highest lead content belongs to striped seabream of Izmir Outer Bay as 383 ppb and the gilthead seabream from Homa Lagoon was given the lowest value as 6.34 ppb. It was detected in samples of Izmir Outer Bay that striped bream has highest concentration of lead as 383 ppb and chub mackerel has the lowest as 8.78 ppb. These values were 43.36 ppb in sardine as maximum and 7.38 in brushtooth lizardfish as minimum for Mersin bay. It was reached 17.04 ppb in red pandorra as top value for Homa Lagoon and gilthead bream has poorest content as 8.34 ppb. Sunlu (1994) reported mean lead contents of fish from Homa Lagoon as 0.64 µg/g (w/w) for gilthead seabream and 0.94 µg/g (w/w) for thin-lipped grey mullet. It was found in Izmir Outer Bay 23.01 ppb as highest concentration and in Homa Lagoon 13.44 ppb as lowest concentration for Horse mackerel, which was the only species belongs all sampling locations of Eastern Mediterranean.

In samples of Sparidae family, which has the most specimens in samples of Izmir Outer Bay, striped bream was given highest value of lead concentration as 383 ppb, and bogue was given the lowest as 9.79 ppb, which reached to value of 14.67 ppb in Mersin Bay. Zyadah and Chouikhi (1999) reported

mean lead concentration of red mullet, hake and bogue from Izmir Bay as 1.4 µg/g (w/w), 0.65 µg/g (w/w) and 0.45 µg/g (w/w), respectively. Lead content of red mullet was found as 126.36 µg/kg (w/w) by Kucuksezgin et al. (2001), which were detected as 32.07 ppb for red mullet and 9.54 ppb for hake in this study. Maximum lead content in three species of Mugilidae family was determined from ticklip grey mullet as 46.38 ppb and minimum from leaping grey mullet as 34.82 ppb.

There are 14 demersal, 13 benthopelagic and 9 pelagic species from Izmir Outer Bay. Highest lead concentration belongs to brown meagre as 154.27ppb for first group, striped seabream as 383 ppb for second and 107.88 ppb for third. Lowest values were found in sole as 9.13ppb, salema as 11.22ppb and chub mackerel as 7.88ppb, respectively.

In the samples of Homa Lagoon, there are 3 pelagic, 2 demersal and 1 benthopelagic species. Top value of lead concentration in pelagic samples belongs to horse mackerel as 13.43 ppb, lowest to derbio as 8.50ppb. It was detected in horse mackerel as 23.01 ppb for Izmir Outer Bay and 15.53 ppb for Mersin Bay.

There are 4 demersal and 3 pelagic species from Mersin Bay. Highest concentration of demersal species was 21.39 ppb for mullet and the lowest concentration was 7.38 ppb for brushtooth lizardfish. Kargin (1996) determined lead concentrations of striped mullet and seabream fishes as 21.5 µg/g

(d/w) and 17.3 µg/g (d/w) respectively that hunted from Iskenderun Bay in September. Lead concentration of seabream was determined as 13.33 ppb in this study. Kalay et al. (1999), determined mean lead concentrations of mullet and blue runner muscle meat as 9.11µg/g (d/w) and 7.50 µg/g (d/w) respectively. In this study, lead concentration of mullet from Izmir Outer Bay determined as 32.07 ppb and lead concentration of blue runner from Mersin Bay determined as 14.11 ppb. Highest concentration of pelagic species belongs to sardine with the value of 43.36 ppb and the lowest belongs to blue runner with the value of 14.11 ppb. It was determined as 45.56 ppb in Izmir Outer Bay for sardine, which has the highest concentration in this region.

5.1.2 Evaluation of cadmium measurements

Highest concentration of all samples was found in sharpsnout seabream as 14.22 ppb and lowests were belong to Mediterranean shad, leaping grey mullet, blue fish, brown meagre, atlantic bonito, comber, fourspotted megrim, sole, red pandorra, annular bream, common dentex, common two-banded seabream and thin-lipped grey mullet with the values that under detection limits.

14.22 ppb was the top value that came from sharpsnout seabream in Izmir Outer Bay, where Mediterranean shad, leaping grey mullet, blue fish, Brown meagre, Atlantic bonito, comber, four

spotted megrim, sole, red pandorra, annular bream, common dentex and common two-banded seabream has the lowest.

In fish of Mersin Bay, cadmium concentration of horse mackerel that observed as greatest was 3.54 ppb and blue runner as lowest was 0.90 ppb. Red pandorra was richest sample with the value of 0.95 in Homa Lagoon where thin-lipped grey mullet has concentration under detection limits. Highest concentration of horse mackerel which was the only common sample of three East Mediterranean areas detected in Mersin Bay was 3.54 ppb and lowest in Homa Lagoon was 0.52 ppb.

Sharpsnout seabream was the species which has the highest cadmium concentration with the value of 14.22 ppb, in the Izmir Outer Bay species of Sparidae family which has the most species among the fishes from this region. Cadmium concentrations determined under detection limits for red pandorra, annular bream, common dentex and common two-banded seabream fishes. Golden grey mullet`s concentration was highest with 0.79 ppb and leaping grey mullet`s was lowest with the values of under detection limits in Mugilidae family which was represented with 3 species in Izmir Outer Bay samples. In demersal species of Izmir Outer Bay, highest content of cadmium was detected in seabass with the value of 4.61 ppb and lowest concentrations was detected from leaping grey mullet, brown meagre, comber, fourspotted megrim and sole with the values of under detection limits. While sharpsnout seabream was giving the highest value as 14.22 ppb among the benthopelagic fishes of

Izmir Outer Bay, Mediterranean shad, red pandorra, annular bream, common dentex and common two-banded seabream has the values under detection limits. Anchovy was the species which has highest concentration as 5.77 ppb and blue fish was the species which has lowest concentration as under detection limits among the pelagic fishes. Kucuksezgin et al. (2001) determined mean cadmium concentrations as 2.49 µg/kg (w/w) in Aegean Sea striped mullet fish. Zyadah and Chouikhi (1999) determined mean cadmium concentrations as 0.35 µg/g wet weight, 0.3 µg/g wet weight, 0.25 µg/g wet weight in flesh of striped mullet, hake and bogue respectively. These values were found as 2.78 ppb, 2.21 ppb and 1.61 ppb in this study respectively.

Among the pelagic species of Homa Lagoon, the greatest concentration of cadmium was 0.52 ppb that found in horse mackerel and lowest concentration was under detection limits. Sunlu (1994) reported in his study mean cadmium concentrations of gilthead seabream and thin-lipped grey mullet which caught from Homa Lagoon as 0.16 µg/g (w/w) and 0.19 µg/g (w/w) respectively. In this study, it was found that seabream from Homa Lagoon contains 0.27 ppb cadmium. Cadmium concentration of horse mackerel was found as 2.71 ppb in Izmir Outer Bay and as 3.54 ppb in Mersin Bay.

Greater cadmium content of demersal fishes hunted from Mersin Bay was 3.35 ppb red mullet and smaller was 1.21 ppb in gilthead seabream. Kargin (1996) determined cadmium

concentrations of striped mullet and seabream fishes as 7.2 µg/g (d/w) and 5.3 µg/g (d/w) respectively that hunted from Iskenderun Bay in September. In this study, while the highest cadmium concentration of striped mullet was found in the Mersin Bay, it was found as 2.78 ppb in Izmir Outer Bay for the same fish species. Kalay et al. (1999) has reported the average cadmium concentrations of striped mullet and blue runner as 1.43 µg/g (d/w) and 1.23 µg/g (d/w) respectively. In this study, the maximum value was 3.54 ppb in horse mackerel and minimum was 0.90 ppb in blue runner among the all pelagic fishes. Regarding of other locations, cadmium concentrations of horse mackerel was 2.71 ppb in Izmir Outer Bay and 0.52 ppb in Homa Lagoon.

5.2 Evaluation of Northeast Atlantic Fish Measurements

5.2.1 Evaluation of lead measurements

While the highest content of lead in all species analysed was found in grey gurnard caught from Tampen area as 80.00 ppb, the lowest was found in anglerfish caught from north of Shetland Islands as 2.00 ppb. In the Gadidae family, which was represented with highest number of individuals, highest concentration was found in haddock from Copinsay with the value of 5.30 ppb and the lowest was found in cod from Tampen as 2.90 ppb. If it would be concerned subject in aspects of fishing areas, highest value in Tampen was 80.00 ppb in grey gurnard; lowest was 2.90 ppb in cod; highest value in north of Shetland

Islands was 4.00 ppb in saithe and lowest value was 2.00 ppb in anglerfish; highest value in around Faroe Islands was 3.90 ppb in haddock and lowest was 3.00 ppb in anglerfish; highest value in Copinsay was 15.00 ppb in small-spotted catshark and lowest was 5.30 ppb in haddock. Haddock, which was the only common species of Tampen, Faroe Islands and Copinsay, has the lead concentrations as 3.80 ppb, 3.90 ppb and 5.30 ppb respectively.

The highest lead concentration was 3.80 ppb in haddock and the lowest was 2.90 ppb in cod which are belonging to the Gadidae family which has the most individuals among the 10 species of 7 family investigated from Tampen area.

There are 8 demersal and 2 benthopelagic species in the samples of Tampen area. In demersal species, highest content was observed in grey gurnard as 80.00 ppb and the lowest was 3.40 ppb in tusk.

Three demersal species belong to three families which was caught from north of Shetland Islands were investigated. In this region, saithe from Gadidae family that represented with greatest number of individuals in all areas, contains 4.00 ppb lead while it was detected as 3.50 ppb in Tampen area. 2.00 ppb lead in anglerfish from Lophiidae family and 3.50 ppb in ling from Lotidae family were detected.

Three demersal species of two families that caught around Faroe Islands were investigated. In this area, haddock and whittling from Gadidae family which was represented with greatest

number of individuals has 3.90 ppb and 3.80 ppb lead respectively. Lead concentration of anglerfish which belongs to Lophiidae family, was determined as 3.00 ppb.

Fishes investigated from Copinsay consisted of three species from three families. Among these fishes, lead concentration was determined as 5.90 ppb in mackerel which is a pelagic species belonging to Scombridae family. In other 2 demersal species, haddock from Gadidae family has 5.30 ppb and small-spotted catshark has 15.00 ppb lead.

5.2.2 Evaluation of cadmium measurements

Among the all species from this area which were analysed for heavy metals, haddock that caught around Faroe Islands has highest content of cadmium as 2.40 ppb and lowest was detected in anglerfish that caught around Faroe Island and north of Shetland Islands with the values under detection limits. Haddock from Copinsay area that belongs to Gadidae family which represented with highest number of individuals has the highest concentration as 2.30 ppb and same family` species whittling from around Faroe Islands has the lowest concentration as 0.40 ppb.

On the base of fishing areas, lemon sole has the highest concentration as 2.90 ppb, cod and haddock has the lowest concentrations as 0.80 ppb in Tampen. In the north of Shetland Islands, the highest value was come from saithe with 1.30 ppb and the lowest was determined from anglerfish as under detection

limits. Haddock and mackerel has maximum content of cadmium as 2.30 ppb and small-spotted catshark has minimum as 2.10 ppb. Determined cadmium concentration for haddock which is the only common species in all samples of Tampen, Faroe Islands and Copinsay, was 0.80 ppb, 2.40 ppb and 2.30 ppb respectively.

Among the all investigated species of Gadidae family from Tampen, the highest concentration was determined as 0.90 ppb in saithe and the lowest as 0.80 ppb in haddock and cod.

Lemon sole has greatest cadmium concentration as 2.90 ppb and haddock has smallest as 0.80 ppb in demersal species of Tampen area samples.

It was determined as 1.30 ppb cadmium for saithe that caught from the north of Shetland Islands which belongs to Gadidae family and was determined as 0.90 ppb cadmium for the same species from Tampen. While it was found as under detection limits for anglerfish which belongs to Lophiidae family, it was found as 0.97 ppb for ling which belongs to Lotidae family.

Cadmium concentrations were determined as 2.40 ppb and 0.40 ppb for haddock and whittling belongs to Gadidae family and caught from around Faroe Islands respectively. It was detected as under detection limits for anglerfish from Lophiidae family.

In Copinsay area samples, while it was determined as 2.30 ppb for mackerel belongs to Scombridae family , it was found as 2.30 ppb for haddock belongs to Gadidae family and 2.10 ppb for small-spotted catshark belongs to Scyliorhinidae family.

Cronin et al. (1996), determined lead concentrations of *C. rupestris*, *M. berglas*, *H. atlanticus*, *C. mediterranea*, *C. labiatus* and *C. armatus* fishes muscle tissues from the North Atlantic as 0-0.06, 0.003-0.04, 0-0.66, 0.07-2.4, 0.31-0.97 and 0.07-0.44 mg/kg wet weight and cadmium concentrations as 0-0.01, 0-0.21, 0-0.01, 0-0.07, 0.01-0.41 and 0.01-0.13 mg/kg wet weight respectively.

5.3 Evaluation of Standard Reference Material Measurements

The accuracy of the concentrations determined in this study was checked by the measuments of the reference material CRM No 422 cod muscle from the Commision of the European Communities, Community Bureau of Reference.

Quevauviller (1995), reported the lead values determined by the commission as 0.085 ± 0.015 µg/g. in this study, mean lead concentration was determined as 81.425 µg/kg. The cadmium concentration was reported as 0.017 ± 0.002 µg/g and it was determined as 17.475 µg/kg in this study. It has been proved accuracy of determined concentrations in this study.

5.4 Evaluation of the Method Used

In this study, the frozen samples were lyophilised and mineralized in a closed low temperature microwave oxygen plasma processor equipped with a high performance pump plasma asher chamber. Than the mineralized samples were dissolved in 0.2% sulphuric acid and lead and cadmium concentrations were determined by DPASV, Differential Pulse Anodic Stripping Voltammetry that is equipped with autosampler

and supported by hanging mercury drop electrode. It was first using for -determination of Cd and Pb in fish- as framed aspects of whole method.

Voltammetry is noticable with its very low detection limits (50 ppt for lead and cadmium). Starting to determine more less heavy metal containing materials at investigations, brought up a necessity of improving new methods that are more sensitive.

Accuracy of voltammetric analysis were also stated by various investigations. Detections by other methods could be checked with measurements performed by voltammetry. Stoeppler and Nurnberg (1979) determined Cd, Pb, Hg, Cu, Ni and As in 15 marine species of different tropic levels from the Mediterranean Sea, North Sea and Baltic Sea by using several versions of atomic absorption spectrophotometry and checked the accuracy by differential pulse anodic stripping voltammetry.

The advantages of Differential Pulse Anodic Stripping Voltammetry (DPASV) are as follows:

- Up to 4 elements can be determined simultaneously
- The equipment is available at a reasonable price compared with other instrumentation
- No clean room or clean benches are necessary (Since operations are carried out in a closed system) and there is no risk to operator. A single electrode filling is sufficient for >5000 determinations

- The consumption of consumables is negligible (No graphit tubes etc.)
- Low risk contamination. The sample comes into contact with only oxygen and sulphuric acid
- The method is of high precision. The current (I) measured is direct proportional to the concentration (C) of the analyte in the solution (I=k*C) (Oehlenschläger, 1993b).

5.5 General Discussion

In this study, 49 fish species belong to 19 family from Eastern Mediterranean and 19 fish species belong to 10 family from Northeast Atlantic were investigated. It could not possible to compare most of these species with the same species from same locations since previous studies about heavy metals covered by mainly a few species from working areas.

Permitted maximum heavy metal levels are 0.1 ppm for cadmium and 1.0 ppm for lead in Turkey, according to Turkish Food Codex (Anonymus, 1997). By regulations which made by Commision of European Union, permissible limit for cadmium is 0.1 mg/kg wet weight for bonito, common two-banded seabream, eel, European anchovy, grey mullet, horse mackerel or scad, louvar or luvar, sardine, sardinops, tuna and wedge sole and 0.05 mg/kg wet weight for all others. Permissible limit was set on lead as 0.4 mg/kg wet weight for bonito, common two-banded seabream, eel, grey mullet, grunt, horse mackerel or scad,

sardine, sardinops, spotted seabass, tuna and wedge sole and 0.2 mg/kg wet weight for all the rest (Byrne, 2002). All detected concentrations in this study were on ppb level and all below the legal limits set by national and international standards. In spite of low levels, some values were found higher than averages. It is considered that, feeding habits, habitat pollution or pollution occurred while they were hunting could be reliable reasons for it.

Although it is not sufficient to decide this only with heavy metal determinations, it is very gladsome and hopeful to detect low metal concentrations. It could be useful that kind of works, which may show, cleaning of our water sources by efficient function of clarification plants with increasing environmental conscious, controlled consumption of natural sources, being performed periodically and followed. From this point of view, with thought of decreasing levels in future, importance of sensitivity of choosen method becomes clearer. Furthermore, another important point on this subject is absence of Food Law in Turkey. A legistation that is unfunctional in practice is not sufficient to perform controls and restrictions for present time. Greatest problem on this issue is sharing of responsibilities and authorities. A lot of institution and foundation and too much people from various professionalities work on this. To solve it, a food law should publish, determination of contemporary controls and restrictions must performed effective in unity of authority by unique institution.

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